NCUT
National Centre for Upgrading Technology
a Canada–Alberta alliance for bitumen and heavy oil research

Dr. Edward (Ted) Little
NCUT Director
CanmetENERGY

It is my distinct pleasure to welcome you to the 5th NCUT Upgrading and Refining Conference 2009. As you may already know, the National Centre for Upgrading Technology is a Canada-Alberta heavy oil and bitumen upgrading research alliance. Formed in 1995, NCUT provides independent upgrading-related research and technical services to industry as well as objective, science-based advice to government policy-makers and regulators.

NCUT is unique in Canada; our staff conducts in-house research projects designed to address issues relevant to industry and governmental, and works with petroleum companies, engineering firms, and technology licensors to solve specific problems encountered in their petroleum processing units. NCUT’s research focuses on the most pressing needs of the downstream energy sector as defined by governments and industry.

NCUT’s VISION

Canadian-derived bitumen and heavy oils command the highest value for Canadians and are produced in the most environmentally sustainable manner.

OUR MISSION

Research and development of innovative upgrading technologies that are implementable at demonstration and commercialization scales and that respond to the needs of the federal/provincial governments and hydrocarbon energy producers. These R&D efforts will focus on:

• upgrading R&D that considers equally, the minimization of emissions and environmental impacts, the effective uptake of new technologies, and the maximization to societal benefits;
• developing the best available upgrading technology for maximum and appropriate usage of the entire heavy oil/bitumen resource;
• enabling alternative technology options for the expansion of markets to include both the US and global energy community;
• providing science-based advice and solutions to industry and government in order to address the presently unacceptable emissions and environmental impacts associated with the processing of heavy oil and bitumen, and;
• upgrading technologies that will make Alberta bitumen the benchmark feedstock for refinery complexes to produce future fuels and petrochemicals at the lowest societal costs.

NCUT’s major areas of expertise are:

• development of a new generation of breakthrough upgrading technologies;
• incremental improvement to existing primary and secondary upgrading technologies;
• development and/or refinement of upgrading technologies leading to improved energy efficiency and environmental performance;
• process improvements and integration that lead to emission reduction in bitumen and heavy oil processing plants;
• testing hydrocracking and hydrotreating catalysts for upgraders, refiners, and catalyst manufacturers; and;
• research on the fundamentals of corrosion and fouling mechanisms in refinery units.

Our scientists and engineers are backed by state-of-the-art process equipment ranging from autoclaves to pilot plant scale, continuous distillation, and slurry hydrocracking/hydrotreating units. A full range of ASTM, CGSB, and API analytical tests of pilot plant and refinery product streams is available. We continually develop and test new analytical protocols, and our services are backed by applied in-house research programs networked to company research centres and universities worldwide.

Doing business with NCUT is straightforward. Companies can interact with us through any one of a variety of approaches that best suits their business needs. Past examples include straight contract for technical services, one-on-one and joint research and development projects, and multi-company research and development consortia. In addition, NCUT has experience directing clients to the funding programs available for doing research and development in Canada.

For those not familiar with NCUT, we are located in Devon, Alberta: in the heart of the Alberta oil patch, just 15 minutes west of the Edmonton International Airport, and at the junction of Highway 19 and Highway 60. Our site is adjacent to the Leduc No. 1 Discovery Well Historical Site and the Canadian Petroleum Interpretative Centre which celebrate the discovery of oil in Alberta.

I look forward to meeting and working with you over the course of this conference, and into the future.

1 Oil Patch Drive, Suite A202, Devon, Alberta, Canada T9G 1A8
Phone: (780) 987-8682 / Fax: (780) 987-5349
E-mail: ncut@nrcan.gc.ca
PROGRAM
**Beverly Hills Ballroom**

**PROGRAM AGENDA**

**Monday, September 14**

**Session 1: Bitumen Upgrading – New Technologies (Day 1)**

<table>
<thead>
<tr>
<th>Time</th>
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<tbody>
<tr>
<td>8:00</td>
<td>Registration and badge pick up</td>
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<tr>
<td>8:30 a.m.</td>
<td>Welcoming remarks</td>
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<td></td>
<td>Parviz Rahimi / Theo de Bruijn, National Centre for Upgrading Technology (NCUT)</td>
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<td></td>
<td><strong>National Centre for Upgrading Technology (NCUT)</strong></td>
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<td></td>
<td>Edward Little, Director</td>
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<td><strong>Natural Resources Canada, Innovative Energy Technology Sector</strong></td>
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<td>Geoff Munro, Chief Scientist and Assistant Deputy Minister</td>
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<td></td>
<td><strong>Alberta Energy Research Institute (AERI)</strong></td>
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<td>Eddy Isaacs, Executive Director</td>
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**SESSION CHAIR: GERALD BRUCE**

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<thead>
<tr>
<th>Time</th>
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<tr>
<td>9:00 a.m.</td>
<td>The Oil Sands Stage – Intermission or Rehearsal?</td>
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<tr>
<td></td>
<td>S. J. (Steve) Kelly</td>
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<td></td>
<td>Purvin &amp; Gertz, Inc.</td>
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<tr>
<td>9:25 a.m.</td>
<td>Bitumen and Heavy Oil Production – Behind the Scenes</td>
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<tr>
<td></td>
<td>Gerald Bruce</td>
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<td>Meg Energy Corp.</td>
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<tr>
<td>9:50 a.m.</td>
<td>Networking Break</td>
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<tr>
<td>10:15 a.m.</td>
<td>I³Q Upgrading at a 1 bbl/d Scale</td>
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<tr>
<td></td>
<td>Wayne Brown</td>
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<td>ETX Systems</td>
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<tr>
<td>10:40 a.m.</td>
<td>Maximizing Heavy Oil Value While Minimizing Environmental Impact with HTL Upgrading of Heavy to Light Oil</td>
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<td>Ed Koshka</td>
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<td></td>
<td>Ivanhoe Energy Inc.</td>
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<tr>
<td>11:05 a.m.</td>
<td>Progress in the Development of the Write Process</td>
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<td>Frank Guffey</td>
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<td>Western Research Institute</td>
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<tr>
<td>11:30 a.m.</td>
<td>Panel Discussion (Presenters 1-5)</td>
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<td>Moderator: Gerald Bruce</td>
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<td>Meg Energy Corp.</td>
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<tr>
<td>12:00 p.m.</td>
<td>Lunch Break (Room 6) – <strong>Session Chair: Edward Little</strong></td>
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<tr>
<td>12:45 p.m.</td>
<td>Luncheon Speaker</td>
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<td></td>
<td>Eddy Isaacs, Alberta Energy Research Institute (AERI)</td>
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<tr>
<td></td>
<td>Shaping the Future – Innovation in Energy and Environment</td>
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</table>
# Beverly Hills Ballroom

## PROGRAM AGENDA

**SESSION CHAIR: WAYNE BROWN**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Presenter</th>
</tr>
</thead>
</table>
| 1:30 p.m. | Upgrading Oil Sands Bitumen with FLUID COKING and FLEXICOKING® Technologies | Paul Kamienski  
ExxonMobil Research and Engineering Company (EMRE) and Syncrude Canada, Ltd. |
| 1:55 p.m. | The Alberta Taciuk Processor (ATP System) for Direct Thermal Processing of Oil Sands, Oil Shales and Heavy | Lucas Rojek  
UMATAC Industrial Processes |
| 2:20 p.m. | Networking Break                                                         |                                                                                               |
| 2:45 p.m. | Breaking Through the Bitumen Upgrading Barriers with the UOP Uniflex™ Process | Daniel Gillis  
UOP LLC |
| 3:10 p.m. | Mobis HRH Process Residue Hydroconversion Using a Recoverable Nano-catalyst | Stefan Romocki  
Mobis Energy Inc. |
| 3:35 p.m. | Upgrading of Bitumen by using Supercritical Water                        | Tomoki Kayukawa  
JGC Corporation |
| 4:00 p.m. | Panel Discussion (Presenters 6-11)                                       | Moderator: Gerald Bruce  
Meg Energy Corp. |
# Beverly Hills Ballroom

## PROGRAM AGENDA

**Tuesday, September 15 - AM**

Session 2: Upgrading – Process Improvement, Catalysis, and Fundamentals (Day 2, AM)

Session 3: Bitumen Transportation, Diluent Requirement, and Processability (Day 2, PM and Day 3)

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<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker/Presenter</th>
</tr>
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<tbody>
<tr>
<td>8:30 a.m.</td>
<td>Field/In Situ Upgrading: Beyond Dilution Limitations For Today and Tomorrow</td>
<td>Pedro Pereira-Almao University of Calgary</td>
</tr>
<tr>
<td>8:55 a.m.</td>
<td>Enhanced E-Bed Bottoms Upgrading Using Latest Catalytic Technology</td>
<td>Hiroshi Toshima Albermarle Corporation</td>
</tr>
<tr>
<td>9:20 a.m.</td>
<td>HDHPLUS®/SHP: Heavy Residue Hydroconversion Technology</td>
<td>Frederic Morel Axens</td>
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<tr>
<td>9:45 a.m.</td>
<td>Networking Break</td>
<td></td>
</tr>
<tr>
<td>10:10 a.m.</td>
<td>Reactivity of Athabasca Residue and of its SARA Fractions during Residue Hydroconversion</td>
<td>Jan Verstraete IFP-Lyon</td>
</tr>
<tr>
<td>10:35 a.m.</td>
<td>Comparison of Thermal Cracking and Hydro-Cracking Yield Distributions</td>
<td>Sim Romero KBC Advanced Technologies, Inc.</td>
</tr>
<tr>
<td>11:00 a.m.</td>
<td>Catalyst Preactivation Using EURECAT TOTSUCAT® CFP Technology</td>
<td>Nilanjan Brahma Eurecat US Inc.</td>
</tr>
<tr>
<td>11:25 a.m.</td>
<td>Panel Discussion (Presenters 12-17)</td>
<td>Moderator: Gerald Bruce Meg Energy Corp.</td>
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<tr>
<td>12:00 p.m.</td>
<td>Lunch Break (Room 6) – <strong>Session Chair: Edward Little</strong></td>
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<tr>
<td>12:45 p.m.</td>
<td>Luncheon Speaker <strong>Neil Edmunds</strong>, Laricina Energy Ltd.</td>
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<td></td>
<td><strong>Innovation and the Future Carbon Footprint of In Situ Oil Sands; A Very Positive Story</strong></td>
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</table>
## PROGRAM AGENDA

**SESSION CHAIR: RANDY SEGATO**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session Topic</th>
<th>Presenter/Company</th>
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</thead>
</table>
| 1:30 p.m. | On the Vapor-Liquid Equilibrium in Hydroprocessing Reactors                  | Jinwen Chen
National Centre for Upgrading Technology (NCUT) |
| 1:55 p.m. | API Gravity and Viscosity of Residues from Conventional and Bitumen-Containing Crude Oils | Warren Ewert
ConocoPhillips Company |
| 2:20 PM | An investigation of problematic solids in oil sands processing – Separation and characterization of organic matter strongly bound to oil sands solids | Thom McCracken
National Research Council of Canada, Institute for Chemical and Environmental Technology NRC/ICPET and V. Bede Technical Associates |
| 2:45 p.m. | Networking Break                                                            |                                                  |
| 3:15 p.m. | Enbridge System: Crude types, transportation and handling systems            | Ashok Anand
Enbridge Corporation |
| 3:40 p.m. | Crude Value Management Through Pipeline Systems                              | Randy Segato
Suncor Energy Marketing Inc. |
| 4:05 p.m. | New Heavy Crude Oil Flow Improver Increases Delivery — Application Scenarios  | Joey Pierce
ConocoPhillips Specialty Products Inc. |
| 4:30 p.m. | Panel Discussion (Presenters 18-24)                                          | Moderator: Gerald Bruce
Meg Energy Corp. |
# Beverly Hills Ballroom

## PROGRAM AGENDA

### Wednesday, September 16

**Session 3: Bitumen Transportation, Diluent Requirement, and Processability**  
(Day 2, PM and Day 3)

<table>
<thead>
<tr>
<th>Time</th>
<th>Topic</th>
<th>Presenter/ Affiliation</th>
</tr>
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<tbody>
<tr>
<td>8:30 a.m.</td>
<td>Processing Canadian High TAN Crudes</td>
<td>Walter Giesbrecht, Flint Hill Resources</td>
</tr>
<tr>
<td>8:55 a.m.</td>
<td>Diluent and Bitumen, An Uneasy Mix Considerations for treating, blending, transportation, marketing and refining</td>
<td>Cameron Todd, Connacher Oil and Gas Limited</td>
</tr>
<tr>
<td>9:20 a.m.</td>
<td>Quality Factors to Consider in Condensate Selection</td>
<td>Bill Lywood, Crude Quality Inc.</td>
</tr>
<tr>
<td>9:45 a.m.</td>
<td>Networking Break</td>
<td></td>
</tr>
<tr>
<td>10:15 a.m.</td>
<td>Diluent Evaluation for Bitumen Pipelining</td>
<td>Parviz Rahimi, National Centre for Upgrading Technology (NCUT)</td>
</tr>
<tr>
<td>10:40 a.m.</td>
<td>Expanded Fluid Based Viscosity Correlation - Diluted Heavy Oil Case Study</td>
<td>Harvey Yarranton, University of Calgary</td>
</tr>
<tr>
<td>11:05 a.m.</td>
<td>Electric Field Induced Instabilities in Free Emulsion Films</td>
<td>Plamen Tchoukov, Schlumberger DBR Technology Center</td>
</tr>
<tr>
<td>11:30 a.m.</td>
<td>Panel Discussion (Presenters 25-30)</td>
<td>Moderator: Gerald Bruce, Meg Energy Corp.</td>
</tr>
<tr>
<td>12:00 p.m.</td>
<td>Lunch Break (Room 6) – <strong>Session Chair: Edward Little</strong></td>
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<tr>
<td>12:45 p.m.</td>
<td>Luncheon Speaker</td>
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</table>

**Bill Keesom**, Jacobs Consultancy and Alberta Energy Institute  
*Life Cycle Assessment of North American and Imported Crudes*
<table>
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<tr>
<th>Time</th>
<th>Session Title</th>
<th>Presenter</th>
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<tbody>
<tr>
<td>1:30</td>
<td>Compositional Analysis of Heavy Crude Oil Fractions by Ultrahigh Resolution FT-ICR Mass Spectrometry</td>
<td>Ryan Rodgers&lt;br&gt;Florida State University</td>
</tr>
<tr>
<td>1:55</td>
<td>Kinetics of Hydrolysis of Emulsified Salts in Canadian Bitumens and Inhibition of Hydrolysis</td>
<td>Murray Gray&lt;br&gt;University of Alberta</td>
</tr>
<tr>
<td>2:20</td>
<td>Networking Break</td>
<td></td>
</tr>
<tr>
<td>2:45</td>
<td>Refinery Corrosion: The Influence of Organic Acid and Sulphur Compound Structure on Global Crude Corrosivity</td>
<td>Heather Dettman&lt;br&gt;CanmetENERGY Devon</td>
</tr>
<tr>
<td>3:10</td>
<td>High Temperature Corrosion Control and Monitoring for Processing Acidic Crudes</td>
<td>Collin Cross&lt;br&gt;Betz/GE Water and Process Technologies</td>
</tr>
<tr>
<td>3:35</td>
<td>Corrosion Inhibitor Development for Slightly Sour Environments with Oxygen Intrusion</td>
<td>Jonathan Wylde&lt;br&gt;Clariant Oil Services, North America</td>
</tr>
<tr>
<td>4:00</td>
<td>Panel Discussion (Presenters 31-36)</td>
<td>Moderator: Gerald Bruce&lt;br&gt;Meg Energy Corp.</td>
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<tr>
<td>4:30</td>
<td>Closing Remarks</td>
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**Beverly Hills Ballroom**

**POSTER SESSIONS**  
September 14–16

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<tr>
<th>Title</th>
<th>Authors</th>
<th>Institution</th>
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<tbody>
<tr>
<td>DuPont™ IsoTherming® Clean Fuel Technology</td>
<td>Ernie Levinski</td>
<td>E. I. DuPont Company</td>
</tr>
<tr>
<td>A Novel Interior Coating for Use in Oil Sands / Hydrotransport</td>
<td>Michael Magerstädt, Judith Weigold, Holger Schmidt, Willi Voss</td>
<td>RO-Plast GmbH</td>
</tr>
<tr>
<td>Athabasca Asphaltene Structures</td>
<td>Heather Dettman, Sara Salmon and David Zinz</td>
<td>CanmetENERGY, Natural Resources Canada</td>
</tr>
<tr>
<td>Advanced HCCI Combustion of oil Sands Diesel Fuel Blends and Second</td>
<td>¹WS Neil, ²V Hosseini, ³C Dumitrescu, ¹WL Chippior, ²R Gieleciak, ³D</td>
<td>¹National Research Council Canada, ²Institute for</td>
</tr>
<tr>
<td>Generation Biofuel</td>
<td>Hager, and ³Craig Fairbridge</td>
<td>³Chemical Process and Environmental Technology, ³CanmetENERGY, Natural Resources Canada</td>
</tr>
<tr>
<td>Microscopy of High Chloride Primary Froth: Refinery Implications of</td>
<td>G. R. D. Elliott, V. A. Muñoz, and R. J. Mikula</td>
<td>CanmetENERGY, Natural Resources Canada</td>
</tr>
<tr>
<td>Naphthenic Acid Removal from HVGO by Alkaline Earth Metal Catalysts</td>
<td>Lianhui Ding, Parviz Rahimi, Randall Hawkins, Sooraj Bhatt, Yu Shi</td>
<td>National Centre for Upgrading Technology (NCUT), CanmetENERGY, Natural Resources Canada</td>
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</tbody>
</table>
# POSTER SESSIONS

**September 14–16**

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**Fouling Mechanisms of Bitumen Containing Unsaturated Hydrocarbons**

Zhiming Fan  
National Centre for Upgrading Technology (NCUT), CanmetENERGY, Natural Resources Canada

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**The Effect of the Composition of Hydrocarbon Streams on Physical Properties and HCCI Combustion Performance**

Rafal Gieleciak  
National Centre for Upgrading Technology (NCUT), CanmetENERGY, Natural Resources Canada

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**Influence of Substituents on Ring-Opening Energetics**

Iain D. Mackie† and Jagannathan Govindhakannan‡  
†National Institute for Nanotechnology, National Research Council Canada  
‡CanmetENERGY, Natural Resources Canada

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**Delayed Coking Studies on Athabasca Bitumen and Cold Lake Heavy Oil**

Jagannathan Govindhakannan and Chandra Khulbe  
National Centre for Upgrading Technology (NCUT), CanmetENERGY, Natural Resources Canada

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**Optimization Bitumen-Based Upgrading and Refining Schemes**

Mugurel Munteanu and Jinwen Chen  
National Centre for Upgrading Technology (NCUT), CanmetENERGY, Natural Resources Canada

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**Synthesis of Functional Mesoporous Materials and their applications for Oil Sands**

Sateesh Mutyala, Parviz Rahimi, Craig Fairbridge*, and Teclemariam Alem  
National Centre for Upgrading Technology (NCUT), CanmetENERGY, Natural Resources Canada  
*CanmetENERGY, Natural Resources Canada
PRESENTATIONS
BIOGRAPHY

S. J. (Steve) Kelly
Purvin & Gertz, Inc.

Steve assumed the role of Calgary office manager for Purvin & Gertz in January 2006, and is a Senior Vice-President of the firm. Since joining Purvin & Gertz in 1996, Steve has been involved in the analysis of regional and global crude oil and petroleum markets. He has assisted numerous crude oil producers in the development of marketing strategies, including projects for a variety of conventional light, heavy and synthetic crude oils. Steve has completed feasibility studies, development projects and independent analysis for a wide range of Purvin & Gertz clients. While on a temporary work assignment in London, he managed the firm’s European market analysis activities. Steve returned to Canada in August 2005.

Steve joined Purvin & Gertz from Shell Canada Limited, where he worked in a variety of manufacturing, operations and optimization roles.

Steve holds B.Eng. and M.Eng. degrees in Chemical Engineering from McMaster University, and an M.B.A from the University of Calgary. He is a registered Professional Engineer in Alberta.

Purvin & Gertz, Inc.
1720 SunLife Plaza
144 - 4th Avenue SW
Calgary, Alberta T2P 3N4 Canada
Phone: +1 403 984 2200
Fax: +1 403 984 2201
Email: sjkelley@purvingertz.com
Website: www.purvingertz.com
The Oil Sands Stage – Intermission or Rehearsal?

Steve Kelly
Purvin & Gertz, Inc.

The development of new oil sands projects slowed significantly in the 2009 economic climate. This has reduced the outlook for oil sands production and upgrading. Is this a pause before new development occurs? Or is this an opportunity for change?

The enormous bitumen resources of Canada’s oil sands are conveniently located next to the largest oil market in the world. But the U.S. market seems to prefer not to use so-called “dirty oil”. What must the oil sands industry do to meet this new challenge?

The paper will show how the outlook for oil sands production has changed, both for bitumen and for synthetic crude oil. It will discuss plans and future needs for petroleum products and refining, as related to oil sands.

The paper will discuss some of the challenges facing the oil sands industry. Issues include the qualities of synthetic crudes and bitumen blends, project costs, natural gas use and environmental considerations.

The paper will present some opportunities for change. These include technologies for new products, new markets and pipelines, and environmental improvements.
The Oil Sands Stage – Intermission or Rehearsal?

Prepared For:
NCUT Upgrading and Refining Conference

Edmonton, Alberta
September 14-16, 2009

Prepared By:
Steven J. Kelly, Senior Vice President
Thomas H. Wise, Vice President
The Oil Sands Stage – Intermission or Rehearsal?
Presentation Outline

- Oil Sands Supply Outlook
- Petroleum Market Trends
- Oil Sands Product Opportunities
- Costs and Value Drivers
- Greenhouse Gas Considerations
Purvin & Gertz and Oil Sands

- **International Energy Consultancy**
  - Private and Independent
- **Firm established in 1947**
  - Headquartered in Houston
  - Maintained office in Calgary since 1973
- **35 years in oil sands (Canada and Venezuela)**
- **Maintain short-term and long-term forecasts**
  - Supply / Demand
  - Pricing
- **Refining and upgrading**
  - Technologies, Costs / Economics
- **Independent Engineer for banks/investors**
  - Initial project reviews and project reports
  - Project monitoring and certification of progress
Western Canada Crude Supply: CAPP Forecast Comparison

- Oil sands forecasts have driven down Canadian crude supply forecasts in recent years
- CAPP “In Construction” case would only complete existing construction projects
The downturn has dramatically changed the outlook for Alberta oil sands projects

- Low projected upgrader returns has shifted focus to developing heavy crude
  - Upgrader deferrals

- Mine / SAGD project delays could slow bitumen growth

- Projected balance for heavy crude supports need for continued development
  - Increased coker capacity
  - Declining traditional sources of heavy crude

- Not all projects are cancelled or deferred; for example:
  - Imperial / Exxon, Kearl Devon, Jackfish II

<table>
<thead>
<tr>
<th>Company</th>
<th>Project Details</th>
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<tbody>
<tr>
<td>Suncor Voyageur</td>
<td>Firebag In-situ delayed</td>
</tr>
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<td></td>
<td>Upgrader delayed</td>
</tr>
<tr>
<td>Shell AOSP Phase II</td>
<td>Mine/upgrader expansion on hold</td>
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<tr>
<td>Shell - Peace River</td>
<td>In-Situ Permit Application withdrawn</td>
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<td>Fort Hills</td>
<td>Mine decision delayed</td>
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<tr>
<td></td>
<td>Upgrader indefinitely shelved</td>
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<td></td>
<td>Merger with Suncor</td>
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<tr>
<td>Long Lake Phase II</td>
<td>In-Situ/upgrader decision delayed</td>
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<tr>
<td>Total Joslyn Creek</td>
<td>Mine delayed</td>
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<td></td>
<td>Upgrader on-hold</td>
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<tr>
<td>Total Northern Lights</td>
<td>Mine/upgrader Permit Application withdrawn</td>
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<tr>
<td>StatoilHydro</td>
<td>Upgrader cancelled</td>
</tr>
<tr>
<td>North West Upgrading</td>
<td>On-hold, pending financing</td>
</tr>
<tr>
<td>BA Energy</td>
<td>In administration, upgrader shelved</td>
</tr>
</tbody>
</table>
Western Canada Crude Supply: CAPP Forecast Comparison

Light Supply

- Light crude includes upgraded synthetic crude
- CAPP did not reduce supply forecast for light crude until 2009

Heavy Supply

- Heavy crude supply forecasts have fallen less than light crude
- Bitumen production forecasts have fallen but so have upgrading forecasts
Issues Facing the Canadian Oil Sands

**Global Factors**
- Economy
- Capital Costs
- Supply / Demand
- Geopolitical factors

**Market Factors**
- Downstream Capacity
- Infrastructure
- SCO Quality
- Diluent Choice

**National / Regional**
- Trade Barriers
- Environmental Regs
- Resource constraints (capital, labour)
- Royalty Issues
World refined product demand growth follows GDP

Annual Change, Million B/D

- 2000-2005 Average: 1.79%
- 2005-2010 Average: 0.22%

2000 2005 2010
Global growth in refined product demand is largely in distillate transportation fuels.
Demand for heavy crude expected to increase with new conversion capacity

- Increased conversion capacity a response to:
  - Wide light / heavy spread
  - Corresponding high coker returns

- However, heavy crude supply tightness projected in Atlantic basin
  - Regional declines
  - Potential shortfalls filled with light sours / fuel oil

- Opportunity for Canadian producers
Refined product specification changes

- Ongoing regulatory improvements
- Low sulphur gasoline & diesel
  - More for heating oil, off-road diesel etc.
- Benzene in gasoline
- Biofuels impact (ethanol & bio-diesel)
- Sulphur in resid fuel oil
  - Local restrictions
  - Marine bunker (may have to switch to diesel, impacting resid supply)
Important regulatory changes are happening which impact long-term demand.

**US: Energy Independence and Security Act**
- Sharp increase in new vehicle efficiency standards
  - Passenger car fleet changes
  - Light-duty truck fleet changes
- Substantial increase in the use of biofuels
  - Corn ethanol to 15 billion gallons by 2015
  - Total renewables target of 36 BGY by 2022, but authority to lower advanced fuels requirements

**Europe: EU climate policy is primary driver**
- Increased vehicle efficiency to lower carbon emissions
- Aggressive targets set for biofuels in gasoline and diesel, but targets have now been scaled back
Upgrading technologies determine product quality and yield as well as costs and environmental footprint

Product quality impacts market and price

Price, yield and cost are major economic drivers
Distillation Comparison
Light Sweet Crude

- Light sweet SCO not fully interchangeable with conventional crudes
- SCO not readily marketable to coking / asphalt refineries
- Distillate and VGO quality considerations
The ideal SCO for the market?

- SCO value is dependent on the ratio of cut fractions
- High VGO quantities tend to be discounted due to processing limits
- High naphtha quantities result in lower refining product yields – potentially lowering value
- Optimal SCO is refinery specific
Distillation Comparison
Bitumen Blends

- DilBit quality close to Maya, but with more naphtha & less distillate
- SynBit quality close to Arab Heavy but with much more VGO & less naphtha
- Western Canadian Select (WCS) is a blend with DilBit, SynBit and conventional heavy crude
- Athabasca and Peace River blends have high acid content
Canadian diluent options

- **Import Condensate**
  - USGC or West Coast

- **Naphtha recycle via Southern Lights P/L**
  - Chicago to Edmonton in late 2010
  - Light Straight Run Naphtha (LSRN)

- **SCO for SynBit**
  - SCO value as a bitumen diluent not likely to be fully recognized until refiners can trust segregation and composition

- **NGL diluents (such as butane and/or LPG mixes)**...
  - USGC NGL values generally at Edmonton plus transportation

- **HotBit**
  - No diluent - rail from Alberta with possible backhaul of condensate

- **Avoid diluent with low conversion upgrading**
Impact of diluent quality on refiners

- Condensate imports & LSRN recycle to be pooled on Southern Lights pipeline
- May be pooled with Canadian C5+ supply
  - Diluent quality could change
- Impact on refinery A and B is different
  - Refinery A offloads LSRN to Refinery B
Sour, heavy SCO expected to increase

- **Lower capital requirements for the upgrader**
  - Refiner assumes the “load” of hydrotreating product to meet specs
  - Refinery cokers need vac. resid

- **Potentially unique processing / transport issues**
  - Olefins, nitrogen, sulfur, gravity
  - Issues with traditional processing, including crude unit
  - Pipeline limitations
Synthetic medium sour crude production

Approaches:

Bitumen → "Black Box" → Medium Sour Synthetic

- Coking Upgrader
- Resid Hydrocracking Upgrader
- New Technology Upgrader

Quality depends on:
- bitumen by-pass
- conversion & product stability

Opportunity???

Capex? Opex? Yield?

- minimize olefins
- minimize nitrogen
Bitumen netback prices down sharply from 2008 peak, but have recovered in recent months.

- **SynBit Basis (MacKay River)**
- **DilBit Basis (Cold Lake Blend)**
- **MSW-WCS**

**Narrow light/heavy differential**
Factors influencing the light / heavy differential

- Global crude production
- Type of crude produced
- Bottoms content of crude
- Demand for light products
  - Conversion equipment availability
- Demand for heavy products
  - Residual fuel oil & asphalt
- Local supply / demand
  - Market outlets
- Applicable discounts

- Residue supply
- Residue demand
- Regional factors
Will higher product price add value?

- **ILLUSTRATIVE** -

### Then
- Wide
- Conversion
- Hydrotreating
- Distillate qualities

### Light – Heavy
- Objectives
- Issues

### Now
- Tight
- Pipeline Specs
- Minimum capital
- Keep vac resid
- Olefins
Gas consumption rising but price is low

**Bitumen versus Gas Price**

- Concerns re. growing gas use for oil sands vs. other clean fuel users
- Gas price for fuel exceeded bitumen price most of the time from 2003 to 2007
  - Now less expensive & forecast to continue
  - Low price will not deter gas use
- Petroleum coke is stockpiled and virtually free, but high cost for combustion equipment & desulphurization
Capital cost indices are declining…

- **Rapid increases in capital cost appear to have abated**
  - Material cost declines
  - Higher labour productivity
  - Lower margins for contractors and vendors
  - Indices based on actual costs

- **“Real” data points for large projects are tricky until projects are built**

- **Additional capital requirements in future for GHG initiatives**
Greenhouse gas / regulatory issues

- **Canadian Plans**
  - Federal/Provincial tensions
    - Alberta has long term reduction targets, initially intensity based
    - Federal government plans long term (2050) limits
  - Carbon Capture and Storage (CCS) is favoured
    - Alberta has geological potential
    - High cost infrastructure
    - May encourage gasification, despite water supply concerns
  - Market mechanisms with costs are uncertain
  - Commitment/ability to harmonization with US?

- **US Plans**
  - Carbon life-cycle regulations (Market Issue)
    - US Energy Bill / Government fleet limitations
    - California Proposal (Low Carbon Fuel Standard)
  - Limits use of fuels derived from non-conventional sources with a carbon life-cycle greater than that of conventional oil
Greenhouse gas emissions along value chain

- **CO₂** from refined product use is more than double **CO₂** from processing energy
  - Higher efficiency product use would reduce fuel demand and need for bitumen, but oil sands supply “push” could displace other crude oil sources
- **CO₂** from processing depends on efficiency and fuel type
  - Heavier fuels like coke or heavy oil would increase **CO₂** emissions
  - Nuclear fuel (where appropriate) would avoid **CO₂**
  - EOR use or sequestration from large point sources may be needed
- Impact of GHG regulations / penalties uncertain

Notes:
1. **CO₂** emissions estimated from fuel gas and power use
2. Refined products assumed = 65% gasoline, 32% diesel, 3% LPG
**CO₂ emissions vary by refinery configuration**

- **Emissions originate from a number of sources**
  - Fuel consumption
  - Carbon burn on FCC unit
  - Hydrogen plant vents

- **Emissions tend to increase with complexity**

- **Full emissions cost (no allowances) a significant “operating cost” addition**

- **Emissions shown on a “downstream” basis**
  - Most recent U.S. bill (HR 2454) includes the refinery emissions as well as emissions from the fuel sold ("upstream" basis)

---

* $35.2/T CO₂ - European Climate Exchange, Phase II, 2008 Average Price

** 100 kb/d crude, includes power generation
Cost of non compliance for GHG reduction

- GHG reduction costs uncertain
- Current GHG costs low
- Potentially high cost
GHG emission mitigation options for upgrading in Alberta

- **Carbon Capture & Storage (CCS)**
  - including Enhanced Oil Recovery (EOR)

- **Cogeneration with gas or syngas**
  - receive credits against coal fired power generation

- **Coke stockpiling (carbon storage)**
  - delayed coking advantage over fluid coking

- **Use natural gas, not coke, as fuel**
  - unless CCS employed

- **Increased efficiency**
  - lower intensity

- **Low conversion processing & less hydrogen use**
  - lower intensity
  - more upgrading & emissions would occur at downstream refineries in Canada and elsewhere

- **Alternate markets for bitumen (blends)**

- **New technology**
Concluding Remarks

- Western Canada development outlook favours bitumen production over conventional upgrading

- Future growth in petroleum products is distillate

- Light / Heavy crude spread to remain narrow as conversion capacity comes on stream
  - Favours new upgrading concepts and technologies
  - Capital cost reductions open opportunities

- Severity of environmental regulations still unclear
  - Will call for creative solutions with effective technologies

Will the players be ready when the curtain rises?
Production and marketability of Oil Sands bitumen blends and synthetic crude oil, crude price differentials, economics of upgrading and diluent issues are analyzed in Purvin & Gertz’ ongoing multi-client service, *Crude Oil & Oil Sands Market Outlook*. 

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BIOGRAPHY

Gerald Bruce
MEG Energy Corp.

Gerald Bruce has spent over twenty-eight years working in the downstream sector of the Canadian oil industry, graduating with a Bachelor of Applied Science Degree in Chemical Engineering from the University Waterloo in 1981.

Gerald has extended his 23 years of refining experience with a large Canadian integrated oil company into the world of heavy oil production, upgrading and refining. Gerald worked for Jacobs Consultancy in Calgary helping a variety of international clients understand the challenges and opportunities in transforming bitumen into value added products, through production, marketing, upgrading and refining of heavy oil.

In 2007, Gerald joined MEG Energy Corp. as Manager, Upgrading. MEG Energy Corp is a privately held junior oil sands company with plans for in excess of 200 kbd SAGD production.

Gerald is on the board of directors for the Canadian Heavy Oil Association and the VP of the Canadian Crude Quality Technical Association (CCQTA).

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ABSTRACT

Bitumen and Heavy Oil Production – Behind the Scenes

Gerald Bruce
MEG Energy Corp.

Development of the vast Alberta oil sands reserves has forecast production levels in excess of 3 million BPD by 2020. This production is poised to make a significant contribution to the security and stability of energy supply for benefit of both North America and global customers as conventional oil supplies decline.

The challenges associated with the successful implementation of development plans include overcoming perception challenges that are now associated with oil sands. The quest for responsible, sustainable and economic development includes the identification; refinement and application of technologies which can help us understand the carbon footprint from “well to wheels”.

Conventional heavy oil, mined bitumen and thermal bitumen production all contribute to the mix of quality feedstocks on their way to finished products. CHOPS, Mining, SAGD CSS and beyond are all part of the landscape.

This presentation provides insight, appreciation and understanding of how oil sands and heavy oil production is evolving to meet the future industry/environmental challenges.
Bitumen and Heavy Oil Production
Behind the Scenes

Presented to:
National Centre for Upgrading Technology (NCUT)
Upgrading and Refining Conference:
September 14-16, 2009 - Edmonton, Alberta, Canada
Our Mission:
To provide an appropriate technical, educational and social forum for those employed in, or associated with, the heavy oil and oil sands industries.

Canadian Heavy Oil Association
500 - 5th Avenue S.W., Suite 400
Calgary, Alberta T2P 3L5
Phone: 403-269-1755
Overview

- History and perspective
  - Heavy oil and bitumen
  - Production methods
    - Mining vs in-situ production

- Growth and Development
  - Production Forecasts
  - Investment Plans

- Moving Forward
  - Sustainability
    - *What does this mean to Alberta heavy oil?*
    - *The role of technology?*

- A new reality……
HEAVY OIL IN ALBERTA
Alberta Crude Oil Reserves

Canada, with 175 billion barrels in oil sands reserves, ranks 2nd only to Saudi Arabia in global oil reserves.
173 billion barrels of proved oil sands reserves remain

- Fort McMurray
- Edmonton
- Calgary
Where Heavy Oil and Oil Sands Are

- Conventional heavy oil
  - Lloydminster

- Mining bitumen near Fort McMurray
  - Deposits close to the surface
    - < 75 m of overburden

- Thermal production of bitumen
  - Deeper deposits
    - > 75 m of overburden
  - In-situ production methods
    - Steam assisted gravity drainage (SAGD)
    - Cyclical Steam Stimulation (CSS)

- Carbonate formations as well
  - Shale oil production techniques
Oil Sands

- Deposits of sand, heavy oil (bitumen)
- 12% bitumen in oil sands
- Surface mining and in-situ production
- 80% of bitumen reserves are too deep to mine
Bitumen

- Bitumen is separated from the sand
- Heavy, sour, viscous hydrocarbon, difficult to process
- Near solid at room temperature
- Challenging chemistry
- Upgrade to Synthetic Crude Oil (SCO) or “dilute and ship”
• Commercial interest dates back to 1906

• Mining “near surface” bitumen
  ➞ Great Canadian Oil Sands (1967)
    ◆ Now Suncor
  ➞ Syncrude (1978)
    ◆ Consortium with 7 partners
      - Imperial, Conoco-Phillips, Petro-Canada, Nexen, Murphy, Mocal Energy, Canadian Oil Sands
    ◆ Albian Sands (2002)
      - Shell(60%), Chevron (20%), Marathon (20%)
    ◆ CNRL (2009)

• Mined bitumen gets upgraded to Synthetic Crude Oil
  ➞ Various types
Mined Bitumen and SCO Production

Alberta mined bitumen production and synthetic crude oil production and price, 1967-2008

- Mined bitumen
- SCO production
- SCO price

Great Canadian Oil Sands (Suncor) start-up
Syncrude start-up
Alberta Oil Sands Project start-up

Source: EUB ST98-2008

SCO = Synthetic Crude Oil
80% of bitumen is too deep to mine
→ Need “in place” production methods

Thermal production methods
→ Cyclical Steam Stimulation (CSS)
  - Cold Lake Blend (1970’s)
→ Steam Assisted Gravity Drainage (SAGD)
  - Diluted bitumen
    - Dilbit (naphtha)
    - Synbit (sweet synthetic crude)

First to market:
→ Cold Lake Blend

Opti/Nexen Long Lake
→ Integrate SAGD and Field upgrading
History – in Situ

Cyclical Steam Stimulation
– Esso Cold Lake

Steam Assisted Gravity Drainage
• Horizontal Well Pairs – Injectors and Producers
• AOSTRA and Roger Butler
Split Between CSS and SAGD

Source: ERCB ST98-2008
Thermal Production

Cyclical Steam and SAGD

500 kbdp

Source: EUB ST98-2008
Bitumen Blend vs Synthetic

Growth Case - Western Canada Oil Sands & Conventional Supply

<table>
<thead>
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<th></th>
<th>Actual</th>
<th>Forecast</th>
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<tr>
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<tr>
<td>2025</td>
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</table>

thousand barrels per day

- June '08 Moderate Growth Forecast
- Bitumen Blend*
- Upgraded Light
- Conventional Heavy
- Conventional Light

* Bitumen Blend includes some volumes of upgraded heavy sour crude oil and bitumen blended with diluent or upgraded crude oil.

Source: CAPP

June 2009 Forecast
Now extends to 2025

4,000 + kBPD total
In Situ vs Mining

Note: Split between in situ and mining

Source: CAPP June 2009 – Growth Case
### Planned Alberta Investment

#### Inventory of Major Alberta Projects

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<tr>
<th>Project Sector</th>
<th># of Projects</th>
<th>Value of All Projects</th>
<th># on Hold</th>
<th>Value of On-Hold Projects</th>
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<td>Biofuels</td>
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<tr>
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<td><strong>Total</strong></td>
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<td><strong>$239,626.2</strong></td>
<td><strong>58</strong></td>
<td><strong>$83,719.7</strong></td>
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</table>

**Source:** Alberta Economic Development

- **Oil Sands**
  > $C136 billion total,
  > $C77 “on hold”

- **TOTAL**
  > $C239 billion
  > $C84 “on hold”
MOVING FORWARD

What a difference a year makes!
Have We Been Here Before?

WTI Price History - 1986 to present

Crude Oil Prices (WTI NYMEX) $US per barrel

Volatility

Aug 2009

Jan 21/09
Price Forecast?

Uncertainty

Price of WTI at Chicago

Source: ERCB ST98 - 2008

Forecast: Variable.... Subject to change
Oil Sands Industry Challenges

- Realities of the current state
  - Oil price decline
  - Financial market turmoil – debt & equity
  - Project Costs remain “misaligned” with current price
    - Project deferral and cancellation

- Ongoing
  - Environmental performance
    - Air, water, and land
    - Public perception of industry

- Balance – energy, environment, economy
  - Demonstrating real improvements

- Positioning for sustainability
• Slow down of the rate of growth
  ➞ More of a sustainability focus

• The “gold rush” is over
  ➞ High cost projects are not viable
  ➞ Adjustment to $40 oil means not all projects will proceed
  ➞ What oil price do you need?

• The industry is doing a lot of “rethinking”
  ➞ Reducing cost, environmental positioning
  ➞ Value adding strategy

• Environmental drivers
  ➞ Greenhouse gases, CO2, water, land
  ➞ Carbon footprint
  ➞ Well to wheels
Industry Attention

- **Sustainability**
  - Land, Water and Air

- **Land**
  - Minimize land use

- **Water Use & Quality**
  - 85-90%+ recycle... zero liquid discharge

- **Air**
  - Manage emissions
  - Anticipate future regulations

- **Advanced technology application**
  - Reservoir, oil/water treatment, steam raising, upgrading, integration
  - Dry tailings, extraction developments
• Improve Production effectiveness through:
  ➔ Enhancements to SAGD
    ♦ Thermal-solvent processes
  ➔ Combustion
    ♦ Toe-to-heal-air injection (THAI)
  ➔ Electrical Heating
  ➔ In-situ upgrading
  ➔ Field upgrading…. Integration with SAGD
    ♦ Reduce/eliminate diluent and make your own fuel
  ➔ Alternate fuels use… Integration

• Goal:
  ➔ Lower cost production
  ➔ Environmental performance
  ➔ Sustainability
The Future

- Long term strategy
  - 40 years+ supply of heavy oil in the ground
- Alberta Oil Sands production volumes will continue to increase
  - Slower pace than initially envisioned
- Dealing with volatility and uncertainty
  - Value added strategy
- The role “technology” will play to improve industry effectiveness
  - Next generation technologies
- Overcoming current oil sands industry perception
  - Demonstrated results
Conclusions

• Fundamentals remain sound for medium to longer term
  ➞ Resource base
  ➞ Canadian industry track record and capability
  ➞ Secure, reliable supplier with good market access

• Serious challenges remain
  ➞ Technical – hard to extract and sensitive to market and input costs
  ➞ Environmental – land, water, emissions (including CO₂)
  ➞ Social – community growth, native population
  ➞ Human resource – maintaining a skilled labor force

• Technology is a key lever

• Security of supply is a strong foundation for major development
Visit the CHOA website for more information

WWW.CHOA.AB.CA
Wayne Brown

ETX Systems

Wayne Brown holds Bachelors (1988), Masters (1991), and PhD (1998) degrees in Chemical Engineering, all from McGill University. Wayne worked for Syncrude Canada at both the Mildred Lake operating facility (1991-94) and at the Edmonton Research Center (1998-99). He worked at McGill University as an Assistant Professor from 1999-2004, where he ran a successful research program. Wayne is listed as principal investigator on a number of patents and patent applications in diverse areas including oil sands processing and biomedical engineering. He is registered as a professional engineer in the province of Alberta, and was a founding member of Envision Technologies Corp., the company under which the IYQ Upgrader was developed. He is responsible for the technical work carried out at ETX Systems, where he holds the position of Chief Technology Officer.

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ABSTRACT

1<sup>1</sup>Q Upgrading at a 1 bbl/d Scale

Wayne Brown

CTO, ETX Systems

All thermal upgrading processes are subjected to the same fundamental chemistry and physics. A serious challenge inhibiting technology development in heavy oil has been how to quantify these underlying processes for such an ill-defined system as oil. Fortunately, research breakthroughs over the past 20 years have provided technology developers with a workable framework through which to understand the intricate relationship between the many chemical and physical processes that drive the end result during the upgrading of heavy oil stocks. In general, it has been established that product yields and qualities are affected by the balance between mass transfer and reaction kinetics. This model is a breakthrough, in that it provides a focus for the development of new upgrading technology.

With these underlying fundamentals, ETX Systems has developed a new upgrading technology, 1<sup>1</sup>Q Upgrading. To displace existing upgrading methods, new technologies must exceed benchmarks with respect to liquid yields, product qualities, and economics. While many concepts have achieved two of these three hurdles, 1<sup>1</sup>Q Upgrading achieves all three: Liquid yields are increased by 6%, while an equivalent increase in hydrogen retention is realized. These benefits are achieved with 30-40% less capital investment, compared to delayed coking. The attributes of the technology result in a decrease in the environmental footprint associated with heavy oil development.

As part of its development plan, ETX Systems has built and operated a pilot plant at a 1 bbl/d scale, based on the 1<sup>1</sup>Q Upgrading concept. Designing a fluidized bed process, complete with circulation of hot solids, is a challenging undertaking, as industry participants will attest. Commissioned in the fall of 2007, the bulk of 2008 was spent resolving numerous challenging technical issues, most of which were related to scale. Having met these challenges, the unit has since achieved the original set of technical objectives of the project, namely providing field support for the original yield and quality claims assigned to the 1<sup>1</sup>Q Upgrading technology. The results, which have been formally vetted by independent third parties have exceeded original expectations. Motivated by these results ETX Systems is continuing along its development path, having embarked on a project aimed at proving commercial operability at a scale of 2,000 bbl/d.

The talk will focus on the challenges faced during the piloting exercise, and the results derived from it. The data clearly demonstrate the advantage of lowering operating temperatures with respect to both yield and quality. Some time will be devoted to introduction of the 1<sup>1</sup>Q Upgrading technology, and the anticipated plans for its development.
The Challenge

- How to meet future energy demands in the face of:
  - Diminishing conventional oil resources
  - Escalating capital costs
  - Unstable oil prices
  - Environmental uncertainties
  - Political uncertainties
  - Challenging capital markets
Role of Technology

- Use technology to:
  - Improve economics
    - Reduce capital
    - Better use of resource
  - Improve environmental footprint
    - Facilitate integration with environmental technologies
    - Better use of resource
The Growing Emphasis on Primary Upgrading

- Primary upgrading converts pitch into distillable liquids

- Primary upgrading benchmark is a century old

- Significant performance gap relative to “ideal coking”

From I.A. Wiehe, “Process Chemistry of Petroleum Macromolecules”
Comparing Primary Upgrading Technology is Simple…

- The technology metrics are:
  - Liquid yield
  - Liquid quality
  - Capacity / Capital

- The winner achieves benefits in some categories, but compromises in none
…but Finding the Winning Concept is Difficult

- Current picture of upgrading science

- How to meet opposing constraints in liquid and vapour phases with a single technology?
IYQ Upgrading Leverages Current Understanding

- Thin films limit liquid severity

- Decoupling of vapour and liquid phase residence times allow constraints of vapour phase to be met without compromising capacity

- Reactor characteristics enable reduction in operating temperature which benefits both yield and quality
Temperature Dictates Fate of Hydrogen

- Final distribution of hydrogen among coking products is significantly affected by reaction temperature

- Positively affects qualities

<table>
<thead>
<tr>
<th>Reaction Temperature</th>
<th>Liquid Products</th>
<th>Gas</th>
<th>Coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C</td>
<td>83%</td>
<td>8%</td>
<td>9%</td>
</tr>
<tr>
<td>470°C</td>
<td>82%</td>
<td>9%</td>
<td>9%</td>
</tr>
<tr>
<td>500°C</td>
<td>79%</td>
<td>13%</td>
<td>8%</td>
</tr>
<tr>
<td>530°C</td>
<td>74%</td>
<td>18%</td>
<td>8%</td>
</tr>
</tbody>
</table>
Demonstration of I^YQ Upgrading at 1 bbl/d

- Objective was to provide additional support for yield and quality claims
- Full coke circulation
Assessing Yield Benefit

- For a given technology, coke production has been shown to be relatively insensitive to temperature.
- Therefore, to assess relative impact of temperature, focus on split between gas and liquid production.
Assessing Yield Benefit (cont’d)

- For once through yields, performance measured based on product produced per quantity of feed consumed
Gas Yields Show Benefits

- Sulfur release indicates excellent data consistency
Coke and Gasoil Yields Consistent with Expectations

- Coke yields relatively insensitive to temperature
- Bulk of yield benefit lies in gasoil
Assessing Quality Benefit

- Primary factor driving quality is hydrogen content
- Hydrogen content of gas is much higher than liquids
- Olefinic character of gas related to severity of treatment
Quality metrics support IYQ Upgrading Claims

- Indications that overcracking dramatically reduced
Hydrogen Losses to Gas Phase Reduced

- Conservative?
Assessing Performance

- Must consider unreacted pitch

![Graph showing the relationship between bed temperature and pitch yield, total liquid yield, and pitch carryover.](image)
Results Support Claims on Once Through Basis

- More liquids produced per amount of pitch reacted
- Liquids are of higher quality
Recycle to Extinction

- Model in good agreement with experimental data

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (Mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model</td>
</tr>
<tr>
<td>Product Liquids</td>
<td>76.1</td>
</tr>
<tr>
<td>Pitch</td>
<td>14.2</td>
</tr>
<tr>
<td>Coke</td>
<td>6.5</td>
</tr>
<tr>
<td>Gas</td>
<td>3.0</td>
</tr>
<tr>
<td>H2S</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Advantage Leveraged Upon Recycle

- Link between once through and recycle to extinction well established

<table>
<thead>
<tr>
<th>Product</th>
<th>Mass Yields (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I^YQ Upgrading</td>
<td>Fluid Coking</td>
</tr>
<tr>
<td>Liquids</td>
<td>66.4</td>
<td>60.8</td>
</tr>
<tr>
<td>HGO</td>
<td>41.6</td>
<td>36.5</td>
</tr>
<tr>
<td>LGO</td>
<td>13.2</td>
<td>11.6</td>
</tr>
<tr>
<td>Naphtha</td>
<td>11.6</td>
<td>12.7</td>
</tr>
<tr>
<td>Coke</td>
<td>25.7</td>
<td>28.3</td>
</tr>
<tr>
<td>Gas</td>
<td>7.9</td>
<td>10.9</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Volume Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquids</td>
</tr>
<tr>
<td>HGO</td>
</tr>
<tr>
<td>LGO</td>
</tr>
<tr>
<td>Naphtha</td>
</tr>
</tbody>
</table>
Commercial Implementation

- Recent commercial projects advertise yields of 80% (vol/vol) from implementation of delayed coking (whole bitumen basis)

- Through lower operating temperatures IYQ Upgrading achieves liquid yields of 90% with:
  - Increased hydrogen retention
  - Lower capital investment

- IYQ performance adds $8 of value per barrel processed
Upgrading without Compromise

- Current results support that IYQ Upgrading can deliver:
  - Improved liquid yields with;
  - Improved product qualities

- Previous studies show a reduction in capital cost of ~30% relative to competing alternatives (Jacobs Consultancy)

- Therefore, IYQ Upgrading can deliver on all three metrics
Beyond the 1 bbl/d Pilot

- ETX Systems has followed a rigorous development path
- Gating process requires third party evaluation at each stage
- Key activity remaining is to prove operability
Proving Operability

- Project involves testing implementation with 2,000 bbl/d reactor feed
- Land purchased in Belle Plaine, SK to support this undertaking
Questions?

Wayne Brown
CTO, ETX Systems
wayne.brown@etxsystems.ca
Edward Koshka
Ivanhoe Energy Inc.

Ed Koshka joined Ivanhoe Energy Inc. as Vice President, Business Development in 2007, responsible for creating partnerships and opportunities for heavy oil production using Ivanhoe’s HTL Upgrading technology. His duties now include leading the development of engineering, infrastructure and marketing initiatives for Ivanhoe’s heavy oil project.

Mr. Koshka has over 20 years of industry related experience. Prior to joining Ivanhoe, Mr. Koshka worked at Synenco Energy where he was responsible for business development, marketing and strategic planning activities. Prior to joining Synenco, Mr. Koshka worked at Purvin & Gertz’s Calgary office, assisting clients in areas of crude oil market assessment, project economic analysis and oil sands strategy development. Mr. Koshka’s industry experience began at Petro-Canada in areas of refining, operations and planning, crude oil marketing and corporate risk management. Mr. Koshka holds a Bachelor degree in Chemical Engineering from the University of Alberta and an MBA from the University of Calgary.

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Fax: 403 237 6865
Email: ekoshka@ivanhoeenergy.com
Website: www.ivanhoe-energy.com
Maximizing Heavy Oil Value While Minimizing Environmental Impact with HTL Upgrading of Heavy to Light Oil

Edward Koshka
Ivanhoe Energy Inc.

Ivanhoe Energy Inc.’s proprietary HTL upgrading technology is designed to cost effectively process heavy oil in the field and produce a stable, significantly upgraded synthetic oil that meets pipeline requirements. By-product energy from the process can be used to generate steam or electricity. In developed markets, HTL improves the economics of heavy oil production by reducing or eliminating the need for natural gas and diluent, and by capturing the majority of the heavy to light oil price differential. In remote areas, integrated HTL production frees otherwise stranded resources. HTL accomplishes all of this at a much smaller scale and at lower per barrel capital costs compared with conventional technologies.

In addition to the foregoing, integrated HTL heavy oil production provides significant environmental benefits, particularly related to greenhouse gas emissions (GHG). This value-add element of HTL integration has taken on significant importance given the dramatic increase in heavy oil production worldwide and the growing pressures related to GHG.

After years of piloting, development and commercial demonstration, the HTL upgrading process is ready for full scale application. This paper provides a description of the HTL Upgrading Process along with its economic benefits to the producer, and a detailed analysis of HTL GHG advantages.
Ivanhoe Energy Integrated Upgrading

Ed Koshka - VP Engineering, Marketing & Infrastructure
FORWARD-LOOKING STATEMENTS

This document includes forward-looking statements, including forward-looking statements within the meaning of the Private Securities Litigation Reform Act of 1995. Forward-looking statements include, but are not limited to, statements concerning Ivanhoe Energy's ability to obtain the financing necessary to pay the balance of the purchase price for the working interest in two oil sand leases acquired from Talisman and financed by Talisman, Ivanhoe Energy's plan to establish integrated HTL heavy-oil projects on Lease 10 in Alberta and Block 20 in Ecuador, the anticipated production capacity of the proposed HTL plants, the anticipated quantities of recoverable barrels of bitumen from lease 10 and heavy oil from Block 20 in Ecuador and other statements which are not historical facts. When use in this document, the words such as "could", "plan", "estimate", "anticipate", "intend", "may", "potential", "should", and similar expressions relating to matters that are not historical facts are forward-looking statements. Although Ivanhoe Energy believes that its expectations reflected in these forward-looking statements are reasonable, such statements involve risks and uncertainties and no assurance can be given that actual results will be consistent with these forward-looking statements. Important factors that could cause actual results to differ from these forward-looking statements include the possibility that the company will be unable to raise financing for the Talisman leases and Block 20 in Ecuador, the potential that the company's projects will experience technological and mechanical problems, new product development will not proceed as planned, the HTL technology to upgrade bitumen and heavy oil may not be commercially viable, samples from the Athabasca bitumen test may not have the product qualities anticipated, market acceptance of the HTL technology may not be as anticipated, Ivanhoe Energy's lack of history in developing commercial HTL opportunities, geological conditions in reservoirs may not result in commercial levels of oil and gas production, the availability of drilling rigs and other support services, uncertainties about the estimates of the reserves, the risk associated with doing business in foreign countries, environmental risks, changes in product prices, our availability to generate cash flow and raise capital as and when required, competition and other risks disclosed in Ivanhoe Energy's Annual Report on Form 10-K files with the U.S. Securities and Exchange Commission on EDGAR and the Canadian Securities Commissions on SEDAR.

Ivanhoe Energy

NCUT Conference 2009
Outline

• HTL Upgrading Technology Overview
• Ivanhoe Project Development
  – Canada (Tamarack)
  – Ecuador (Pungarayacu)
• Integrated Economics
• GHG Life Cycle Advantages of Field Upgrading
Ivanhoe Energy Snapshot

Tamarack HTL Project
Canada

Pungarayacu HTL Project
Ecuador

Sunwing Energy
China

Additional HTL Opportunities Available Worldwide
The HTL Advantage

- Small scale, field-located, integrated upgrading
- Avoids need for natural gas, diluent, captures differential
- Incremental economics, reduced volatility/risk
  - developed areas: Tamarack
- Frees stranded assets
  - remote areas: Pungarayacu
- Monetize resources in province or country
HTL Technology

- Commercial Biomass: 1989 - ongoing
- Commercial Demo: California 2005 - 2007
- Feedstock Test Facility: Texas 2009
- 20,000 BPD Tamarack / AMEC: Canada

Ivanhoe Energy

NCUT Conference 2009
HTL Technology

- Application of heat at very short residence time
  - improved yields & product quality
  - lower Capex/Opex
  - easy to modularize
  - low minimum scale of 10,000 bpd

- Transport bed of solid inert heat carrier (sand)
- No catalyst, moderate temperature, low pressure
- No hydrogen required
- FCC Analogue
- Broad protection of IP
Simplified Process Flow – HTL Upgrader
Commercial Demonstration Facility (CDF)
FTF at Southwest Research Institute
HTL Feedstock Test Facility - Accomplishments

- Basic construction at Zeton. Construction completed at SwRI.
- Third party contract operation at Southwest Research Institute, SwRI.
- Developed, and operated in accordance with, ISO9001 procedures.
- Run Summary:
  - Hot sand circulation & oil in unit in December 2008.
  - Feed and product, atmospheric and vacuum, distillation successful.
  - Shakedown run on Belridge in January 2009 successful
  - Shakedown run on Athabasca bitumen in February 2009 successful
  - Shakedown run on whole Athabasca bitumen in March 2009 successful with bottoms recycle.
  - Validated pilot plant and CDF yield data. Increased performance proven.
  - On-going testing of feedstocks, operating parameters, and configurations.
Tamarack Project

- Integrated SAGD / HTL Project
- 10 miles NE of Ft. McMurray
- 11 Sections
- 440 MM barrels best estimate
- Top-tier McMurray sands
- Well delineated – 4 wells/section
- 100% Ivanhoe Energy
- Phased 50,000 bpd
Tamarack: Top-Tier Resource

*Strong Analogue to Petro-Canada’s Mackay River*

- net pay
- porosity
- Permeability
- oil saturation
- depth, cap rock
- well productivity
- steam-oil-ratio
Tamarack Phase 1 – 20,000 bpd

• Engineering
  – Upstream Design Basis completed
  – Downstream HTL Basic Engineering Design: Completed July 2009
  – Integrated Capex estimate completed (Q409)
  – Value Improvement Study
  – Resource report completed

• Environmental/Regulatory
  – Application submission June 2010*

• Phase I*
  – First Oil: 4th Qtr 2013
  – First SCO: 2nd Qtr 2014

* Contingent on financing
HTL Engineering Status

• AMEC: Ivanhoe’s Tier 1 Engineering Contractor
  – provides support for FEED, EPCm, feasibility, conceptual

• Tamarack Phase I
  – HTL Basic Engineering Design – Completed
  – Front End Engineering and Design – Q4 2009
  – Updated Capex estimate (+20/-15%) – Q1 2010
Phase 1 HTL/SAGD Capex

- Current estimate based on:
  - 4th quarter 2008 AMEC estimate (top of the market)
  - less 7% adjustment for capital costs declines

- Total initial Capex Phase I: C$ 1,253 MM = C$ 62.6 M / bpd
Production & Economic Assumptions - Tamarack Phase I and II

Economic model assumptions:
• WTI – forward strip (6/4/09)
• Oil to gas price ratio – 10:1
• Diluent premium – 106% of WTI
• Heavy oil differential – 30%
• HTL SCO discount to WTI – 12%
• Capital adjustment – tied to WTI
• Foreign exchange – tied to WTI
## Tamarack – Phased Economics

### Phase I

<table>
<thead>
<tr>
<th>BEFORE TAX ECONOMICS</th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>IRR</td>
<td>%</td>
<td>19.7%</td>
<td></td>
</tr>
<tr>
<td>NPV - 0%</td>
<td>MMC$</td>
<td>$6,596</td>
<td></td>
</tr>
<tr>
<td>NPV - 8%</td>
<td>MMC$</td>
<td>$1,240</td>
<td></td>
</tr>
<tr>
<td>NPV - 10%</td>
<td>MMC$</td>
<td>$811</td>
<td></td>
</tr>
<tr>
<td>Payout</td>
<td>Years</td>
<td>9.62</td>
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<tr>
<td>Maximum Negative Cumulative NCF</td>
<td>MMC$</td>
<td>$(1,273)</td>
<td></td>
</tr>
</tbody>
</table>

**AFTER TAX ECONOMICS**

| IRR | % | 17.5% |  |
| NPV - 10% | MMC$ | 549 |  |

### Phase I & II

<table>
<thead>
<tr>
<th>BEFORE TAX ECONOMICS</th>
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<th></th>
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<tbody>
<tr>
<td>IRR</td>
<td>%</td>
<td>22.0%</td>
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</tr>
<tr>
<td>NPV - 0%</td>
<td>MMC$</td>
<td>$17,490</td>
<td></td>
</tr>
<tr>
<td>NPV - 8%</td>
<td>MMC$</td>
<td>$3,211</td>
<td></td>
</tr>
<tr>
<td>NPV - 10%</td>
<td>MMC$</td>
<td>$2,126</td>
<td></td>
</tr>
<tr>
<td>Payout</td>
<td>Years</td>
<td>10.20</td>
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</tr>
<tr>
<td>Maximum Negative Cumulative NCF</td>
<td>MMC$</td>
<td>$(2,343)</td>
<td></td>
</tr>
</tbody>
</table>

**AFTER TAX ECONOMICS**

| IRR | % | 19.5% |  |
| NPV - 10% | MMC$ | 1,482 |  |
Greenhouse Gas Management
A wells-to-wheels comparison

**Resource Recovery**
- Use NG for steam generation
- Produce, transport & store NG
- Import power

**Pipeline Transportation**
- Ship diluted bitumen to PADD II refinery

**Refinery Processing**
- Recover diluent from dilbit and return to field
- Convert bitumen into end products
- Consume NG for H2 generation
- Operate FGD

**Product End Use**
- Ship products to local network
- Consume products
- Ship coke from PADD II to Far East
- Combust coke for power generation

---

Standalone SAGD
- Use coke and HTL gas for steam generation and HTL process
- Import power
- Ship solids to/from site
- Operate FGD

Ivanhoe Energy

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SAGD Integrated with HTL
- Use coke and HTL gas for steam generation and HTL process
- Import power
- Ship solids to/from site
- Operate FGD

HTL

---

NCUT Conference 2009
HTL Integration reduces Greenhouse Gas-
14.5% advantage on a m³ of bitumen production basis*

*Source: LENEF Consulting (1994) – March 2009
Thank You
BIOGRAPHY

Frank D. Guffey
Western Research Institute

Dr. Guffey received his Ph.D. in chemistry from the University of Wyoming in 1977. He
is a Principal Scientist at Western Research Institute where he has been employed since
it was established in 1983. Dr. Guffey’s research interests include recovery and
processing of unconventional hydrocarbon resources. He is currently WRI’s lead for
development and commercialization of the WRITE Process.

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Progress in the Development of the Write Process

Frank D. Guffey\textsuperscript{1}, Tom Corscadden\textsuperscript{2}, Greg Diduch\textsuperscript{2}, John Fahy\textsuperscript{1}, Devin Worman\textsuperscript{1}, Chris Lowry, and Charles Mones

\textsuperscript{1}Western Research Institute, 3474 North Third Street, Laramie, Wyoming, 82070, USA
\textsuperscript{2}MEG Energy, Corp., 734-7 Avenue SW, Calgary, Albert T2P 3P8 Canada

Western Research Institute (WRI) and MEG Energy Corporation (MEG) have been jointly developing the WRI Thermal Enhancement (WRITE) process as a field deployable upgrader since 2004. Since the initiation of this effort, significant progress has been made toward commercialization of this technology. The WRITE technology has been the subject of previous presentations at earlier NCUT Conferences. These presentations have discussed development efforts conducted using WRI’s 1-bbl/day bench scale unit. Based on the results obtained from the 1-bbl/day testing program, a 5bbl/day WRITE Process pilot plant has been designed, fabricated and is in operation at WRI’s Advanced Technology Center in Laramie, WY.

The 5-bbl/day WRITE Process pilot plant consists of a 5-bbl/day distillate recovery unit (DRU) that is coupled to a continuous coker. The DRU receives the in coming dilbit, strips and recovers the diluent for recycle. The bitumen is then subjected to thermal conversion in the WRITE reactor to produce a pipeline quality overhead. The produced bottoms are then sent to the continuous coker where they are subjected to additional pyrolysis. The pyrolyzate produced by the coker can be blended with the DRU produced overhead to produce a SCO for pipelining to existing refineries.

Studies with the pilot plant, using dilbit produced at MEG’s Christina Lake site, are underway to provide data for scale-up to a demonstration unit. This presentation will introduce and discuss the 5-bbl/day pilot plant and the experimental program that is in progress. Results from the pilot plant will be presented to demonstrate the commercial viability of the technology for producing a pipeline quality product.
PROGRESS IN THE DEVELOPMENT OF THE WRITE PROCESS

Presented to

5th NCUT Conference on Upgrading and Refining
of
Heavy Oil, Bitumen, and Synthetic Crude Oil
September 14, 2006
Edmonton, Alberta
In Memory

• Dr. Lee Brecher, inventor of the WRITE Process, passed away on February 15, 2007.

• His death was a loss to not only WRI and this project, but to the research community as a whole.
A Brief Background…
Western Research Institute

- 1924—A Bureau of Mines laboratory specializing in research and development on heavy oil, tar sands, oil shale and underground coal gasification
- 1970s—A part of the U.S. Department of Energy, the Laramie Energy Technology Center, with lead responsibility for western energy resource development
- 1983—Defederalized and affiliated with the University of Wyoming as the University of Wyoming Research Corporation
- Today—A not-for-profit research and technology development center performing contract research for the federal and state governments and private clients
- January 2007—Completed consolidation of heavy oil research activities into one centralized location
Why is the U.S. Participating in Alberta Oil Sands?

• We have a growing dependence upon foreign sources of energy

• It is unlikely that we will “produce” our way out of this dilemma

• It is even more unlikely that we will “conserve” our way out of this dilemma

• We must develop alternate sources of domestic energy, and

• We must help develop secure sources of imported energy
Energy Policy Act of 2005

• Establishes a Task Force composed of Secretaries of Energy, Interior, Defense and Governors to...

• Coordinate and accelerate the commercial development of strategic unconventional fuels

• Make recommendations regarding a partnership with the Province of Alberta, Canada, relating to the development and production of oil from tar (oil) sands
WRI Activities with Alberta, Canada

- Participated in NCUT’s multi-client study in 1998 & conducted collaborative research on WRITE products in 2002.
- Cosponsoring the Edmonton Heavy Oil Upgrading Conferences
- Had due diligence on the process and the technology performed by AERI consultants in 2003
- Our partner since August 2004 in the development of a field upgrading process
- Holder of options for the Canadian rights to the technology, and
- Owner of site where the process will be piloted
What is the WRITE Process?

A process that can be deployed in oil sands production fields to convert bitumen into a residuum-free heavy oil whose density and viscosity—without diluent addition—exceed pipeline specifications.

The WRITE Process for Pipeline Ready Heavy Oil
Initial WRITE Process Development Effort

• Development effort initiated under the USDOE/WRI Cooperative Agreement as a Jointly Sponsored Research Project (Task 51) – MEG Energy was the cosponsor

• The objectives of task 51 were to:
  – DRU optimization (1-bbl/day DRU)
  – Demonstration of the continuous coker
  – Conceptual design for a 20,000 bbl/day scale up

• Task 51 has been completed
1 bbl/day DRU - Summary

• Mass Balance
  – Feed – 8463 lb (1004 gal)
  – Overhead – 613 lb (613 gal)
  – Bottoms – 3338 lb (357 gal)
  – Gas – 458 lb
  – Closure - 99.8%

• Product splits were 55% overhead, 5% gas and 40% bottoms by weight

• Overhead density was independent of reactor stage
• Overhead density met or exceeded 15 deg API in all BP fractions
• Overhead viscosity met or exceeded 350 cSt in all BP fractions
6-Inch Continuous Coker - Summary

• Preliminary coking kinetics developed
  – Activation energy of 33 kcal/mole

• Maximum throughput limited by design of 6-inch pyrolyzer
  – 40 lb/hour

• Preliminary yield structure defined
  – 46% liquid
  – 40% coke
  – 14% gas
Limitations in the Equipment

• 1-bbl/day unit limited to long residence times (6 – 14 hours)
• Multiple reaction vessels in the 1-bbl/day unit limited data for scale up
• Inability of DRU to supply sufficient bottoms to feed the continuous coker
• Heavy oil entrainment in the continuous coker
• Safe collection the produced coke after it is removed from the reactor
Advancing to a Pilot Plant

Closely or Directly Coupled DRU and Continuous Coker
(Initiated July 2006)

1. Design and fabrication of a 5 bbl/day DRU
   a. Design by Triumph EPCM – Calgary
   b. Fabrication by Silverado Energy Equipment – Red Deer
   c. Delivered to WRI November 2007

2. Design and fabrication of a robust 80 lb/hr (2-inch continuous coker)
   a. Scaled down from initial 6-inch coker
   b. Alleviates feedstock logistics
Completed Placement of the DRU
Pilot Plant Testing

• Both pilot plants require testing individually and as a coupled unit.
• Testing of the DRU was initiated in April 2008 and is ongoing.
• Shake down of the continuous coker was initiated in February 2009 and is complete. Development studies are underway.
Testing Objective

Principal objective is to support design and implementation of a demonstration unit:

– provide sufficient process and analytical data to finalize the scale-up design of the DRU and coker
– narrow the range of possible operating conditions to simplify the design, and
– identify operational and design problems
Secondary Objectives

- Confirm comparability of results between the 1-and 5-bbl/day units
- Establish reliable estimates of bitumen residence time in the DRU reactor
- Establish a complete time/temperature profile in DRU
- Determine the effects of sweep gas flow rate on overhead yield and quality (DRU and coker)
- Determine quality and uses/markets for products and co-products (DRU and coker)
- Identify design and operational deficiencies (DRU and coker)
Operating Pilot Plants

DRU

Continuous Coker
Typical DRU Overhead Production Curve

\[ y = 0.5704x - 386.04 \]

\[ R^2 = 0.9974 \]
## Properties of Overhead Product

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cSt) @ 25°C</td>
<td>9.48 – 12.95</td>
</tr>
<tr>
<td>Specific Gravity (g/cc) @ 60°F</td>
<td>0.9007 – 0.9232</td>
</tr>
<tr>
<td>Density (°API)</td>
<td>25.60 – 21.78</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>84.50 – 84.58</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>11.87 – 12.31</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.05 – 0.10</td>
</tr>
<tr>
<td>Sulfur (wt%)</td>
<td>3.09 – 3.35</td>
</tr>
</tbody>
</table>
# Properties of Bottoms

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cPs) @ 90°F</td>
<td>3240 - 85300</td>
</tr>
<tr>
<td>Specific Gravity (g/cc) @ 60°F</td>
<td>1.0441 - 1.0907</td>
</tr>
<tr>
<td>Density (°API)</td>
<td>4.025 - -1.77</td>
</tr>
<tr>
<td>C₇ Asphaltene (wt%)</td>
<td>18.66 - 32.90</td>
</tr>
<tr>
<td>MCR (wt%)</td>
<td>20.2 - 30.2</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>84.47 - 83.66</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>8.85 - 10.17</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.69 - 0.99</td>
</tr>
<tr>
<td>Sulfur (wt%)</td>
<td>5.48 - 6.19</td>
</tr>
</tbody>
</table>
Summary

• Based on results from the 1-bbl/day DRU, a 5-bbl/day pilot DRU has been designed, fabricated and delivered to WRI.
• The 5-bbl/day DRU is being operated to produce data for scale-up and samples for further study.
• The 2-inch continuous coker has been designed, fabricated and shaken down. Testing has started on this unit.
• The DRU and coker will be directly coupled this fall for testing as a complete unit.
Eddy Isaacs
Alberta Energy Research Institute (AERI)

Eddy Isaacs is the Executive Director of the Alberta Energy Research Institute (AERI) with responsibility for Alberta’s strategic directions and investments in energy innovation areas that include conventional and unconventional oil and gas, coal, petrochemicals, renewable energy and carbon and water management.

He has been instrumental in promoting innovation in energy and environment across Canada and is the co-Chair of the Energy Technology Working Group of the Canadian Council of Energy Ministers.

Eddy holds a Ph.D. from the University of Alberta and a B.Sc. from McGill University. He has over 70 publications and 6 patents in the energy field.

Previously, Eddy served for more than 20 years with the Alberta Research Council (ARC) where he was responsible for ARC’s programs in heavy oil and oil sands. He also served as an adjunct professor in the Department of Chemical and Material Engineering, University of Alberta.

Eddy serves on the Boards of the Petroleum Technology Alliance of Canada (PTAC), Canadian Oil Sands Network for Research and Development (CONRAD) and NRC’s Fuel Cells Innovation Institute and is a Fellow of the Canadian Academy of Engineering.

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Shaping the Future – Innovation in Energy and Environment

Eddy Isaacs, Ph.D., Executive Director
Alberta Energy Research Institute (AERI)

Alberta’s prosperity is closely linked to the sustainable long-term growth of its abundant energy resources including oil, natural gas, oil sands, coal and renewables. Advanced technology is an essential factor enabling the energy sector to create: high skilled, high-income workers; the bulk of Alberta’s revenue and exports and the diversification to valuable products and services. The potential to add such value in the future requires an integrated and balanced approach that minimizes environmental impacts and utilizes Alberta’s energy resources to optimize economic benefits.

This presentation focuses on the emerging technologies and innovations that can be applied to produce and add value to Alberta’s energy resources and products while decreasing impact on greenhouse gas emissions. The strategy is to focus on the innovation needed together with progressive government policies and actions to stimulate next generation technology platforms such as upgrading, gasification, carbon capture and storage and advanced recovery methods thereby ensuring a transition to a lower carbon energy economy.
Shaping the Future - Innovation in Energy and Environment

NCUT 5th Upgrading & Refining Conference: September 14 - 16, 2009

Eddy Isaacs, Executive Director
Alberta Energy Research Institute
(www.aeri.ab.ca)
Government- Industry Collaboration: An Oil Sand Success Story

- AOSTRA was formed in 1974 as the Province’s response to the 1973 oil crisis:
  - Develop technologies that would allow the vast oil sands resources to be exploited at economic rates
  - Fill the gap of declining conventional oil

- AOSTRA invested $80 MM in Underground Test Facility (UTF) – led to SAGD in situ process
  - Industry consortia joined later - shared the risks
  - Over 30 Pilots ~$1 Billion
  - Spawning several less energy intensive variations
  - Trained industry technical experts and today’s management leaders
Benefits from SAGD to Gov’t and Industry

Government Revenue = Royalties + Taxes to 2020

CERI Study (1999)

Revenue to cost

Cost = Government Investment in R&D

SAGD Producing Companies

1989
Numerous Experimental Projects

2009
Encana JACOS PetroCanada
Suncor Connacher Devon
Nexen ConocoPhillips Total

Not an all inclusive list
New 21st Century Crisis?

- Changing global energy landscape
  - Unprecedented growth in energy demand
  - Climate change
  - Energy security
  - Huge investment in infrastructure needed

- Rapid development of the Alberta energy industry
  - Concerns over environmental impacts
  - Increasing GHG emissions
  - Increasing fresh water use
  - Natural gas use
  - Maximizing value of energy products
**Alberta Energy Research Institute (AERI)**
*(transitioned from AOSTRA in 2000)*

- **Mission:**
  - Enhance the development of clean energy resources through research, technology and innovation.

- **Mandate:**
  - Position Alberta for the future in energy
  - Add value to Alberta’s energy resources

- **Strategy:**
  - Invest in technology development projects with industry
  - Partnerships & International collaboration
  - Focus on Technology Platforms such as Advanced Recovery, Upgrading, Gasification and Carbon Capture and Storage (CCS)
# Government Programs and Initiatives

<table>
<thead>
<tr>
<th>Program/Initiative</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Capture and Storage (CCS) Fund – ($2 billion)</td>
<td>Large-scale demonstration plants capable of storing 5 million of CO₂ annually by 2015. Three projects qualified for potential funding – EPCOR Clean Coal, Shell and Enhance Energy.</td>
</tr>
<tr>
<td>Climate Change &amp; Emissions Management Fund (currently at ~$120 million)</td>
<td>Technology fund to offset emissions from large facilities and promote GHG reductions – ‘greening’ of energy system, efficiency, CCS. Expression of interest process underway.</td>
</tr>
<tr>
<td>Innovative Energy Technology Program ($200 million)</td>
<td>Develop new energy supplies from existing oil and natural gas reserves, as well as from in situ bitumen and heavy oil deposits. Over 20 pilot projects underway.</td>
</tr>
<tr>
<td>EcoTrust Fund ($156 million).</td>
<td>Reduce GHG and air emissions of concern. Thirteen projects approved and agreements being negotiated.</td>
</tr>
<tr>
<td>AERI-Industry Programs. ($44 million last year) with similar or greater investment by industry</td>
<td>Technology development and demonstration in 6 strategic areas.</td>
</tr>
<tr>
<td>Bitumen royalty-in-kind.</td>
<td>The government royalty share of bitumen made available to upgrade to higher valued products in the province. Selection of projects underway.</td>
</tr>
</tbody>
</table>
Climate Change & Emissions Management Fund

- Climate Change & Emissions Management Corporation Established
  - Not-for-profit, independent
  - Objective: Fund initiatives that reduce GHG emissions

- Initial Funding Areas
  - Conserving and using energy efficiently ~20%
  - Implementing carbon capture & storage ~ 30%
  - ‘Greening’ energy production ~50%

- Expression-of-Interest due September 30th, 2009
  www.CCEMC.CA
**Research and Technology Development Activities** (Partnership with industry & other government programs)

**Production**
- **Mined Oil Sands**: Reduce water for extraction
  - Dense phase processes
  - Solvent-Water processes
- **In situ extraction**: Reduce Water, Natural Gas and Diluent Requirements
  - Enhancements to SAGD
  - Thermal-solvent processes
  - Heated solvent
  - Combustion
  - Electrical heating
- **Upgrade Bitumen to higher value products**
  - Advanced Upgrading and Gasification Technologies:
- **Unconventional natural gas**
  - Develop economic recovery technologies for Coal Bed Methane, Tight Gas and Shale Gas
- **Coal**
  - Clean Power Generation: IGCC with CO₂ capture
  - Underground Coal Gasification

**Environment**
- **Water recovery from tailings ponds**: Reduce use of tailing ponds
  - Consolidated tailings process: Currently practiced
  - Improved thickening - better flocculants, dry tailings – filter belts,
  - Evaporative/Chemical Drying
  - Paste technology
  - CO₂ for Consolidated Tailings processes
- **Carbon Capture and Storage (CCS)**
  - Pre- post combustion capture technologies
  - Integrated Coal Gasification Combined Cycle (IGCC) with CO₂ capture
  - CO₂ Enhanced Oil Recovery
  - End-to-end Demonstration Plants ($2 B government investment)
Achieving Clean Energy Goals – AERI’s Oil Sands Technology Framework

- New wave - efficient oil sands production technologies
- Next generation upgrading technologies (integration with gasification and CCS)
- Carbon capture & storage
  - Includes CO₂ EOR
- Gasification of pet coke, asphaltenes, coal, biomass
- Combustion of liquid/solid fuels
- Unconventional natural gas
- Nuclear outlook

- Research & technology adaptation costs
- Capacity – human, infrastructure
- Large scale deployment time horizon
- Comparative Life Cycle Analysis
Major R&D Programs Designed to Support Current and Next Generation Technologies

1. Alberta Ingenuity Center for In Situ Energy
   Focus on in situ upgrading technology

2. AERI/ ARC Core Industry Research (AACI) Program
   Energy efficient in situ recovery of heavy oil and oil sands

3. Alberta Ingenuity Center for Oil Sands Innovation
   Focus on non- & less- aqueous oil sands extraction and novel upgrading technologies

4. National Center for Upgrading Technology (NCUT)
   Focus on pilot testing of novel upgrading technologies
**NCUT Piloting Support of AERI’s Hydrocarbon Upgrading Demonstration Program**

Nova NHC and ARORINCLE Technologies produce Olefins and Gasoline from bitumen-derived gas oils

**UOP Slurry Phase Hydrocracking (CANMET technology)** high conversion yields for bitumen and heavy oils

**ETX Crossflow Coking** – superior liquid yields
AERI’s Life Cycle Analysis Project

- Life Cycle Analysis (LCA) was started to understand the impact of oil resources on greenhouse gas (GHG) emissions
- Limitations of prior LCA
  - Simplified, generic model representations
    - Crude production and refinery configurations not well differentiated
- Decision to conduct two independent studies (TIAX LLC and Jacobs Consultancy) to establish the impact of crudes processed in U.S. refineries
  - Well-to-wheel LCA direct emissions only
LCA Comparison TIAx vs. Jacobs - Total GHG Emissions Reformulated Gasoline

- SAGD- Dilbit
  - (SOR = 3; adjusted)
  - No electricity credits

Total GHG Emissions gCO₂e/MJ gasoline
Wide range of emissions for conventional and heavy crude oils in US refineries
- Determined by geological, reservoir, production and transportation factors

Imported and U.S. domestic heavy oil crudes have similar emissions to the oil sands pathways

With some overlap, oil sands pathways generally have 10% higher emissions than conventional crudes

GHG emissions from oil sands crudes are comparable to conventional crudes when potential cogeneration credits are considered
Impact of Technology Advances - SAGD Bitumen (Estimate)

- LCA Studies - SAGD Bitumen
  - Best-in-class SAGD
  - Steam-solvent
  - Next wave technology

Total GHG, g CO₂e/MJ gasoline

Eq. steam-oil ratio
Oil Sand - Technology Options for GHG Reductions

- Increased efficiency of operations
- Reduction in energy intensity of existing processes
- Switching to new generation processes
- Fuel switching
- Carbon capture and storage
Economics of CO$_2$ Capture (Fort McMurray Area)

CO$_2$ Concentration, %
CO$_2$ capture cost, $$/tonne

CO$_2$ supply curve to 2020
SMR + gasification (medium case)

AERI Sponsored ARC Study, 2009
Potential for large storage capacity based on high level screening studies
Storage in Saline Aquifer Studies

- Complementary Initiatives
  - pipeline placement vs. open aquifers vs. reef vs. basal sand

1. **ASAP Phase 1**: Identify best three deep saline aquifer sites; design pilot

2. **Wabamun Phase 1**: Practical application of the geo-storage risk management modelling work

3. **Redwater Phase 1**: Specific site – reservoir delineation and pilot design

4. **Quest Phase 1**: Drill wells and field test

**Saline aquifers provide excellent storage potential - but need better reservoir delineation and injectivity analysis**
$2 Billion CCS Fund
(Kick Start CCS: ‘learning-by-doing’ projects)

- **Enhance / Northwest** - Alberta Carbon Trunk Line to EOR sites in central Alberta. It captures CO$_2$ from the Agrium fertilizer plant and the Northwest upgrader (gasification).

- **EPCOR/ Enbridge** - integrated gasification combined-cycle carbon capture power generation facility, west of Edmonton. Saline formation injection sites

- **Shell Quest** - A fully integrated carbon capture and storage project at the Scotford Upgrader and nearby saline aquifer injection sites.
Promote innovation to ensure sustainable development of Alberta’s vast energy resources (oil sands, carbonates, unconventional gas, coal, pet coke, renewables)

- Sustained investment in targeted research commensurate with benefits
- Risk sharing mechanisms with industry for higher risk and costly demonstration & commercialization of technology
- International collaboration to advance critical technology platforms – gasification, CCS and upgrading

Initiatives focused on CO₂ emissions, water management, enhanced ecology, advanced recovery and upgrading, gasification

Alberta as an international leader in energy and environmental technologies
BIOGRAPHY

Paul W. Kamienski
ExxonMobil Research and Engineering Company (EMRE)

Dr. Kamienski is a Licensing Director with ExxonMobil Research and Engineering Company (EMRE) and is located in Fairfax, Virginia. He is responsible for all technology licensing activities in Europe. Paul is also responsible for licensing EMRE’s heavy feed conversion technology portfolio, which includes EMRE’s FLEXICOKING™ Technology.

Paul received his B.S. in Chemical Engineering from the University of Massachusetts, and his M.S. and PhD from the University of Minnesota. He has 35 years of experience in the petroleum refining industry with expertise in R&D, technology development and application, strategic planning and technology licensing. Paul has an extensive background in heavy feed conversion having conducted research in and managed R&D&E programs in both hydro-conversion and thermal processing. He has a number of patents and published articles in both technical and management journals.

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Email: paul.w.kamienski@exxonmobil.com
Website: www.exxonmobil.com
Upgrading Oil Sands Bitumen with FLUID COKING and FLEXICOKING™ Technologies

*1Paul W. Kamienski, 2Craig McKnight, 1Glen Phillips, *2Boyd Rumball
1ExxonMobil Research and Engineering Company (EMRE)
Syncrude Canada, Ltd
*Presenters

Heavy crudes and oil sands bitumen in Alberta, Canada represent a substantial fraction of worldwide crude reserves, and there has been continuing interest in recovery and upgrading of these hydrocarbon resources into pipelineable crudes or synthetic crudes, which can be further processed into finished transportation fuels. EMRE’s FLUID COKING and FLEXICOKING™ technologies are ideally suited for this difficult upgrading requirement.

FLUID COKING employs a fluidized bed reactor that thermally converts the heavy hydrocarbons into light gases, liquids, and coke, concentrating the metals and much of the sulfur in the coke. Combustion of some of this coke provides the process heat, and the remaining coke is either sold as solid fuel or stored at the resource site for later recovery. FLUID COKING has been used commercially for over 50 yrs to convert a wide variety of heavy feeds, and currently there is more than 400 kBD of operating capacity in North America. Three units and about 300 kBD of this capacity are operated by Syncrude Canada Ltd in northern Alberta. Syncrude’s experience with FLUID COKING for upgrading oil sands bitumen, including their new large 8-3 unit, will be highlighted and key features of FLUID COKING technology will also be discussed.

FLEXICOKING extends FLUID COKING by integrating fluid bed steam (air gasification) of coke to produce a CO / H2 rich fuel gas that when used helps meet fuel and energy requirements of a bitumen recovery and upgrading complex. Light gas and liquid yields are about the same as the FLUID COKING process. Process heat for the thermal conversion and gasification steps is provided by partial combustion of coke. Most of the remaining coke is gasified, and the resulting gas is desulfurized with FLEXSORB™ technology to produce a large volume of clean, lower joule fuel gas. There are currently five FLEXICOKING units operating around the world and a sixth is currently under construction in Greece. There is increasing interest in the FLEXICOKING technology in many parts of the world. Locations with a large demand for clean fuel or electric power, and where natural gas is high priced or not readily available, are especially interested. FLEXICOKING can be particularly attractive for SAGD applications in Alberta, which require very large quantities of energy for both recovery and upgrading. Operating principles of the FLEXICOKING integrated gasification system will be discussed, and will be compared with more expensive oxygen gasification processes.
FLEXICOKING™
Coking and Integrated Steam / Air Gasification

ExxonMobil Research & Engineering Company
Paul Kamienski

Overview

- Heavy Crudes / Tar Sands Upgrading Technologies
- FLUID COKING Technology
- Syncrude Tar Sands Upgrader and 8-1, 8-2, 8-3 FLUID COKING Units
- FLEXICOKING Produces Clean Fuel Gas Instead of Coke
Global Heavy Crude

(Units: billion barrels in place)

- Global total 4-7 trillion barrels in place

Canada (3,700)  USA (165)  Russia (960)
Mexico  Ecuador  Kazakhstan
Colombia  Venezuela (2,200)  Uzbekistan
Trinidad  Nigeria  India
Brazil  Madagascar  Middle East (324)
China (114)  Malaysia  Indonesia

ExxonMobil
Research and Engineering

5th NCUT Upgrading and Refining Conference
Edmonton, Alberta, Canada. September 14-16, 2009
### Heavy Crude Characteristics

<table>
<thead>
<tr>
<th></th>
<th>Athabasca Bitumen</th>
<th>Cold Lake Bitumen</th>
<th>Cold Lake Blend</th>
<th>Syncrude Sweet Blend</th>
<th>West Texas Intermediate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, API</td>
<td>7.9</td>
<td>11.0</td>
<td>23.1</td>
<td>31.8</td>
<td>40.8</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.0151</td>
<td>0.9928</td>
<td>0.915</td>
<td>0.8663</td>
<td>0.8212</td>
</tr>
<tr>
<td>Sulphur, wt%</td>
<td>4.9</td>
<td>4.6</td>
<td>3.5</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>4000</td>
<td>3740</td>
<td>3230</td>
<td>630</td>
<td>800</td>
</tr>
<tr>
<td>CCR, wt%</td>
<td>13.4</td>
<td>12.9</td>
<td>11.0</td>
<td>0.0</td>
<td>1.08</td>
</tr>
<tr>
<td>Vanadium, ppmw</td>
<td>222</td>
<td>182</td>
<td>152</td>
<td>&lt;0.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Nickel, ppmw</td>
<td>87</td>
<td>65</td>
<td>57</td>
<td>&lt;0.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Asphaltene, wt%</td>
<td>17.5</td>
<td>16.0</td>
<td>13.4</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>TAN</td>
<td>3</td>
<td>1</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt, lb/1000 bbl</td>
<td>40</td>
<td>20</td>
<td>15-20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Gerald W. Bruce -Jacobs Consultancy-
Presented at the 4th Conference on the Upgrading and Refining of Heavy Oil, Bitumen, and Synthetic Crude Oil
Edmonton, Alberta, Canada September 25-27, 2006
Tar Sands Extraction Approaches

Mining:

SAGD:

### Tar Sands Extraction Approaches

#### Mining:

- **Projects – Operating**
  - **Bitumen Capacity Barrels/day**
    - Canadian Natural Resources mining/upgrading: 135,000
    - ConocoPhillips Surmont Insitu Ph 1: 25,000
    - Devon Jackfish Insitu Ph 1: 30,000
    - Encana Christina Lake Ph 1A-1B: 18,000
    - Jacobs Pilot Insitu: 7,000
    - MEG Energy Pilot: 3,000
    - Nexen Long Lake Insitu Upgrader Phase 1: 70,000
    - Petro Canada MacKay River Insitu: 30,000
    - Petrobank in situ pilot: 2,000
    - Shell Muskeg River Mine: 155,000
    - Suncor Base Plant mining/insitu/upgrading: 350,000
    - Syncrude mining/upgrading: 350,000
    - **Total:** 1,175,000

#### SAGD:

#### Remaining Established Crude Bitumen Reserves

<table>
<thead>
<tr>
<th></th>
<th>Billion Barrels</th>
<th>Billion m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineable:</td>
<td>31.2</td>
<td>4.96</td>
</tr>
<tr>
<td>In Situ:</td>
<td>141.5</td>
<td>22.49</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>172.7</strong></td>
<td><strong>27.45</strong></td>
</tr>
</tbody>
</table>

#### Projects – Under Construction

<table>
<thead>
<tr>
<th>Projects</th>
<th>Status</th>
<th>Est. Start Up Production</th>
<th>Bitumen Capacity Barrels/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devon Jackfish Insitu Ph. 2</td>
<td>Construction</td>
<td>2011</td>
<td>35,000</td>
</tr>
<tr>
<td>Encana Christina Lk. Insitu Ph. 1C</td>
<td>Construction</td>
<td>2010</td>
<td>40,000</td>
</tr>
<tr>
<td>Imperial Keari Phases 1-3</td>
<td>Construction</td>
<td>2012-2015</td>
<td>300,000</td>
</tr>
<tr>
<td>MEG Energy Christina Lk. Insitu Ph. 2A</td>
<td>Construction</td>
<td>2009</td>
<td>22,000</td>
</tr>
<tr>
<td>Shell Exp 1 (Jackpine Mine Ph. 1A/IRM facilities)</td>
<td>Construction</td>
<td>2010</td>
<td>100,000</td>
</tr>
<tr>
<td>Statoil Hydro Leismer Demon Insitu</td>
<td>Construction</td>
<td>2009</td>
<td>10,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>507,000</strong></td>
</tr>
</tbody>
</table>
What Does It Take to Get a Barrel of SCO from Tar Sands?

- Mining: 4.3 tonne Material
- Extraction: 2.0 tonne Oil Sand (1.29 barrel bitumen)
- 1.16 barrel Bitumen
- OR ~ 10-15 Nm3 Natural Gas
- OR FLEXI
- OR DLK/FLK

1 barrel SCO (Synthetic Crude Oil)
FLUID COKING Technology

- Developed by ExxonMobil Research and Engineering Company (EMRE) as an Extension of FCC Fluid Solids Technology
  - Heavy feed injected into fluidized coke bed with feed rings / nozzles
  - Partial combustion of coke in heater and coke circulation provides heat for reaction
  - Scrubber preheats feed, separates coke fines, and sets recycle cut point
  - Liquid products split in downstream fractionators
  - Coke pneumatically convey and stored in silos for fuel coke market
FLUID/FLEXICOKING vs. Delayed Coking

**FLUID COKING/FLEXICOKING**

- Liquid Product Yields Slightly Higher Than in Delayed Coking
- Continuous Process
  - Staffing requirements low
  - Steady state operations
  - Avoids process & equipment thermal cycles
- Handles Virtually Any Pumppable Hydrocarbon Feed
- Coke Has Multiple Roles
  - Heat transfer medium
  - Low value coke supplies process heat
  - Low value coke produces low cost gas for refinery fuel (FLEXICOKING)

**DELAYED COKING (DLK)**

- Liquid Product Quality Higher Than Fluid Bed Coker
- Cyclic Process
  - Staffing requirements high
  - Short drum cycles (12-18 hours)
  - Fractionator performance from "unsteady operations"
  - Drum stressing from temperature cycles
- High CCR Feeds Can Coke Furnace
  - More frequent spalling/decoking
  - Feed "dilution," derating thru-put
- Coke Is Only a Reaction Product
  - High cost fuel gas supplies process heat
**FLUID/FLEXICOKING vs. Delayed Coking**

**FLUID COKING/FLEXICOKING**

- **Coke Product**
  - FLUID COKING produces less than Delayed Coking
  - FLEXICOKING produces only ~1 wt%FF coke at 30% higher capital cost (Estimate: $4800/Bbl Feed/SD)

- **Utilities**
  - Little or no fuel gas use
  - High net steam generation

- **Environmental**
  - FLUID COKING offgas scrubbed to meet sulfur emissions
  - FLEXICOKING coke gas desulfurized to make low sulfur fuel for refinery use

**DELAYED COKING (DLK)**

- **Coke Product**
  - Produces significant amount of coke
  - Different kinds of coke (shot vs. sponge) depending on properties of feedstock

- **Utilities**
  - Large amount of fuel gas use for furnace
  - Almost zero net steam generation

- **Environmental**
  - Open coke piles becoming problematic
  - Require low sulfur fuel gas to meet sulfur emission limits
FLUID COOKING:  
A Proven Commercial Technology

- First Commercial Application in Billings, Montana in 1954  
  Over 50 years Ago  
  - Over 350 Cumulative Years of Operating Experience  
- Significant Improvements in Capacity, Reliability and Run Length  
- Currently 7 Operating Units Process >420 kb/D of Heavy Feeds

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>LOCATION</th>
<th>CURRENT FEED RATE, kb/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>ExxonMobil</td>
<td>Montana</td>
<td>10</td>
</tr>
<tr>
<td>Valero</td>
<td>Delaware</td>
<td>52</td>
</tr>
<tr>
<td>Imperial Oil</td>
<td>Canada</td>
<td>21</td>
</tr>
<tr>
<td>Valero</td>
<td>California</td>
<td>28</td>
</tr>
<tr>
<td>Syncrude 8-1</td>
<td>Canada</td>
<td>110</td>
</tr>
<tr>
<td>Syncrude 8-2</td>
<td>Canada</td>
<td>110</td>
</tr>
<tr>
<td>Syncrude 8-3</td>
<td>Canada</td>
<td>95</td>
</tr>
</tbody>
</table>

New Large Syncrude Unit Started Up in 2006
Syncrude Upgrader

- Located in Fort McMurray, Alberta
Syncrude Upgrade

• Ownership:

  - Imperial Oil Resources 25%
  - Conoco-Phillips Oil Sand Partnership II 9.03%
  - Mocal Energy Limited 5%
  - Murphy Oil Company Ltd. 5%
  - Nexen Oil Sands Partnership 7.23%
  - Petro-Canada Oil and Gas 12%

• Size: Design of 129 million barrels per year
  - Produces High Quality Synthetic Crude (33 API)
  - Transported to market via Pembina Syncrude Pipeline
Syncrude Operating Commercially 31 Years!

1978
- Diluted Bitumen
- Atmospheric Bottoms
- FLUID COKERS (2)
- All Distillates
- HYDROTREATERS (4)
- Synthetic Crude Oil

2009
- Diluted Bitumen
- Atmospheric Bottoms
- FLUID COKERS (3)
- All Distillates
- HYDROTREATERS (6)
- Syncrude Sweet Premium

ExxonMobil Research and Engineering
Syncrude

5th NCUT Upgrading and Refining Conference
Edmonton, Alberta, Canada. September 14-16, 2009
### Bitumen Achieve Significant Quality Improvement

#### Table: Properties of Bitumen

<table>
<thead>
<tr>
<th></th>
<th>Athabasca Bitumen</th>
<th>Cold Lake Bitumen</th>
<th>Cold Lake Blend</th>
<th>Syncrude Sweet Blend</th>
<th>West Texas Intermediate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, API</td>
<td>7.9</td>
<td>11.0</td>
<td>23.1</td>
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<tr>
<td>Specific gravity</td>
<td>1.0151</td>
<td>0.9928</td>
<td>0.915</td>
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<tr>
<td>Sulphur, wt%</td>
<td>4.9</td>
<td>4.6</td>
<td>3.5</td>
<td>0.1</td>
<td>0.3</td>
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<tr>
<td>Nitrogen, ppm</td>
<td>4000</td>
<td>3740</td>
<td>3230</td>
<td>630</td>
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<td>CCR, wt%</td>
<td>13.4</td>
<td>12.9</td>
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<td>Vanadium, ppmw</td>
<td>222</td>
<td>182</td>
<td>152</td>
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<td>Nickel, ppmw</td>
<td>87</td>
<td>65</td>
<td>57</td>
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<td>Asphaltenes, wt%</td>
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<td>TAN</td>
<td>3</td>
<td>1</td>
<td>0.8</td>
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<tr>
<td>Salt, lb/1000 bbl</td>
<td>40</td>
<td>20</td>
<td>15-20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FLEXICOKING:
Coke Gasified in Integrated Steam Air Gasifier

- Produces Clean CO/H₂ Fuel Gas Product Instead of Coke
- FLEXSORB® Hindered Amine Reduces H₂S to Low Level → Low SOₓ
- Nitrogen Diluent Reduces BTU Content, But → Low NOₓ
- FLEXIGAS Burned in Refinery or Third Party Furnaces / Boilers

Diagram:

- Reactor
- Heater
- Gasifier
- Scrubber
- Cold Coke
- Hot Coke
- Coke Withdrawal
- Steam
- Air Blower
- Sour Water
- Direct Contact Cooler
- Tertiary Cyclones
- Fines Recovery
- Coke Fines
- TO FLEXSORB Gas Treating
- FLEXIGAS Clean Fuel
- FLEXIGAS Users:
  - Pipestill Furnaces
  - Hydrogen Plant Furnaces
  - Reformer Furnaces
  - Steam Superheaters
  - Waste Heat Boilers
  - Power Plant Boilers
  - Third Party Consumers
FLEXICOKING Produces a Significant Quantity of Valuable Clean Fuel Gas

GAS: 23 mtons/hr
LIQUIDS: 122 mtons/hr

FEED: 208 mtons/hr
(31 kb/D)

COKE: 3. mtons/hr

FLEXIGAS

Composition, mol%  Metric  English
CO/H₂  40
N₂  48
Other  12
Total  100

Rates  Metric  English
Coke Gassified, mtons / hr  60
Flexigas, mtons / hr  351
Heating Value, kj / kg (BTU / SCF)  4,800  128
Heat Rate, MW (th) (MBTU / hr)  460  158

FLEXIGAS Users:
- Pipestill Furnaces
- Hydrogen Plant Furnaces
- Refomer Furnaces
- Steam Superheaters
- Waste Heat Boilers
- Power Plant Boilers
- Third Party Consumers
FLEXICOKING
Operating Commercially for 30 Years

- TOA Oil - First Commercial Unit S/U in 1976, Expanded in 2002
- Currently 5 Units Operating With a Total Capacity of ~200 kb/D
- New Unit for Hellenic Petroleum in Greece
  - Currently under construction at Elefsina Refinery site

<table>
<thead>
<tr>
<th>COMPANY</th>
<th>LOCATION</th>
<th>FEED RATE, kb/D</th>
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</thead>
<tbody>
<tr>
<td>TOA Oil</td>
<td>Japan</td>
<td>27</td>
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<tr>
<td>PDVSA</td>
<td>Venezuela</td>
<td>65</td>
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<tr>
<td>Shell</td>
<td>California</td>
<td>22</td>
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<tr>
<td>ExxonMobil</td>
<td>Netherlands</td>
<td>42</td>
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<tr>
<td>ExxonMobil</td>
<td>Texas</td>
<td>42</td>
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<tr>
<td>Hellenic</td>
<td>Greece</td>
<td>21</td>
</tr>
</tbody>
</table>

5th NCUT Upgrading and Refining Conference
Edmonton, Alberta, Canada. September 14-16, 2009
FLEXICOKING Unit – ExxonMobil Rotterdam

- Started Up in 1986
- Currently 42 kb/D
- Gasifier in Center (green)
- Coke Silos on Left
- Heater and Reactor / Scrubber on Right
Rotterdam Refinery Fuel Gas Grid

Rotterdam Site

Steam Drivers

LJG Grid

Steam Generation

Furnaces

Flare

Flare

FLEXICOKER

Sales Gas Treating

Co Generation

Refinery Power Consumers

Power Grid

EuroGen

Gas Terra

Power former

WSP

Air Products

Air Liquid

HJNG Grid

LPG Vaporizer

Offgas

HNJG

RHJG

UHJG Untreated

UHJG Treated

LJG

Hydrogen

Steam

Min Possible Flow

Electric Power

ExxonMobil

Research and Engineering

5th NCUT Upgrading and Refining Conference
Edmonton, Alberta, Canada. September 14-16, 2009

20
TOA Oil FLEXICOKING Unit, Japan

**FLEXICOKING Unit**
- Started up in 1976 (21 kb/SD)
- Current Capacity: 27 kb/SD
- Fluid Solids Vessels:
  - Gasifier on Left,
  - Heater in Center
  - Reactor on Right
- Earthquake-Proof Structure

**FLEXIGAS Users:**
- Refinery Furnaces 50%
- Power Plant Boilers 50%
Keihin Refinery Participates in Wholesale Electricity Business

- Operation Began in 2003 in Co-operation with Other Electric Power Company
- LCG is Supplied as Fuel for Steam-Generating Boiler
- Steam is Used for Power Generation and also by Refineries
- Stable Supply of Electricity and Steam

**Diagram:**

- TOA OIL Keihin Refinery
- Genex (Power-Generating Plant)

**Products:**
- Frac. L/E
- R
- H
- G

**Frac. L/E:**
- Vacuum Residue Fraction
- Low Calorie Gas (LCG)
- High Calorie Gas (C1, C2)
- FCC HCG Gas
- LPG (C3, C4)

**Refinery furnaces:**
- Air & Steam

**Genex (Power-Generating Plant):**
- Steam Boiler
- Waste Heat Boiler
- Gas Turbine: ~80 MW
- Steam Turbine: ~190 MW
- Total: ~270 MW

**Gas Turbine:**
- ~80 MW

**Steam Turbine:**
- ~190 MW

**Total:**
- ~270 MW
Summary

- Significant Oil Sands Reserves in Western Canada
  - Remote location and requires significant upgrade for downstream processing
- FLUID COKING Commercially Proven Heavy Feed Upgrading Technology
  - Continuous Fluid Bed Process similar to FCC, heat of reaction provided by partial coke and coke circulation
  - Produces similar products to other coking processes
- Syncrude summary points messages
  - Includes three large Fluid Coking units
  - Produces high quality pipelineable synthetic crude
  - Recent start up of new 8-3 unit significantly added to processing capability
- FLEXICOKING Offers Another Option for Oil Sands Upgrading
  - Produces large quantity of clean fuel gas product instead of coke
  - Fuel gas can be used to meet energy requirements of complex
    - Mine or SAGD resources recovery
    - Upgrade furnaces and boilers or power production
Lucas Rojek
UMATAC Industrial Processes, Division of AECOM Canada

Lucas Rojek is a process engineer at UMATAC Industrial Processes where his work focuses on the recovery and quality of the oil and gas products extracted using UMATAC’s Alberta Taciuk Process (ATP) technology. Lucas is involved in all phases of development, design, and commissioning of ATP facilities for oil shales and oil sands processing. He has experience with bench scale and pilot plant evaluations, conceptual design and feasibility studies, and the process design and development of commercial facilities.

UMATAC is a division of AECOM, a leading global provider of design, engineering, and technical and management services to major infrastructure projects worldwide. The UMATAC division is focused on the development and commercial application of the Alberta Taciuk Process (ATP) technology.

*speaker note: UMATAC is pronounced “you-ma-tack”

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Email: Lucas.Rojek@aecom.com
Website: www.aecom.com
The Alberta Taciuk Processor (ATP System) for Direct Thermal Processing of Oil Sands, Oil Shales and Heavy Oil

Steven Odut and Lucas Rojek
UMATAC Industrial Processes

The Alberta Taciuk Processor offers a compelling technology for the extraction and primary upgrading of bitumen and heavy oils. Mineable oil sands are directly processed to pipelineable, low viscosity crude oil without the need for tailings ponds. This presentation will provide an overview of the ATP System and key milestones achieved during 34 years of research and development of the technology by UMATAC Industrial Processes. Attention will be given to major scale up achievements of the past 10 years and processability of the oil products.

The ATP process is based on thermal cracking of the hydrocarbons using a solid heat carrier (e.g. sand) in an innovative rotating process vessel. The ATP was invented to improve oil recovery, reduce water consumption and eliminate the need for tailings ponds necessary in the water based oil sand extraction process. The ATP also generates much of its own fuel, minimizing the need to import valuable supplies of natural gas.

These characteristics have made the technology attractive for a number of applications which have been demonstrated at various scales. UMATAC maintains test facilities in Calgary which include a 5 t/h portable ATP unit. Over 15,000 tons of various grades of oil sands feeds have been processed using this unit, capable of roughly 60 bbl/day. Heavy oil upgrading and other applications have also been demonstrated on this scale.

Since 1988, the ATP technology has been adapted to the processing of oil shales in Australia and in China. Current oil shale units are constructed at sizes of 250 t/h, with a 500 t/h unit being developed. For oil sand applications, similar size machines would have capacities of roughly 400 and 800 t/h due to the higher density of oil sand compared to oil shale. The synthetic crude oil production of these units corresponds roughly to 5,500 bbl/d and 11,000 bbl/d per unit. Elevated environmental concerns and recent Alberta Government legislation about water consumption, phased elimination of tailings ponds and residual bitumen in the tailings disposal areas has served to focus attention on improved environmental performance. ATP System provides a viable technology to meet these challenges.
UMATAC Industrial Processes

Overview:
- Based in Calgary, Canada
- Engineering Offices
- Pilot Plant Facility, Laboratory
- Field Technical Services

UMATAC Offers:
- Oil Shale Project Engineering
- Alberta Taciuk Process (ATP) Technology
- Oil Sand, Oil Shale, and Heavy Oil Evaluations
- Specialist Process and Mechanical Engineering
Comparison of Major Processing Steps

Alberta Taciuk Process (ATP) Technology – Application to Oil Sands, Oil Shales, and Heavy Oils

Mineral Oil Sands Plants
Comparison of Major Processing Steps
ATP Processor - Schematic

The ATP Processor
Stuart Australia Plant - 250 t/h ATP Processor Unit
Flow Scheme – ATP System and Related Facilities
ATP Technology Development – 34 Years of Experience

1978 to 1994 Oil Sand Piloting
- over 15,000 t, various grades
- over 8,000 h & 500 start ups
- Joint Industry Task Force

Developing Commercial Plant Concepts and Cost Estimates

1986 to 1991 Australia Oil Shale Piloting and Engineering
First Steps Towards Stuart Oil Shale Demonstration Plant

Preheat Zone Fouling During Oil Sands Piloting, 1982
ATP Mobile Plant – Hazardous Waste Facility

ATP Processor at a Superfund Clean up Site in Michigan

10 t/h unit was used from 1989-1995
ATP Technology Development – 34 Years of Experience

1996 to 2004
Stuart, Australia, 250 tph ATP Demonstration Plant
Constructed in 1999 and Operated Until 2004

ATP Processor and Hydrocarbon Recovery Plant - Australia
ATP Technology Development – 34 Years of Experience

1999 to 2009
Major ATP60 Pilot Plant Test Operations and Commercial Studies for Oil Shales Deposits in:
- USA
- Jordan
- Estonia
- Australia
- China

2009
ATP Facility Currently Under Construction in China
Feasibility Study for ATP Plant Located in Jordan

ATP Processor Erection in China September 2008
Fushun, China, Construction Photos

ATP Processor Scale-up 1977 to 2010

1977 Pilot Plant 5 t/h, Shell 2.8 m dia. x 6.7 m long, 3.1 dia. Tyre

1989 Waste Treatment Plant 10 t/h, Shell 3.7 m dia. x 15 m long, 4.3 dia. Tyre

1991 ATP60 Pilot Plant 5 t/h, Shell 3.1 m dia. x 9.3 m long, 3.7 m dia. Tyre

1999 Stuart Demonstration Plant 211 t/h, Shell 8.3 m dia. x 65 m long, 11.1 m dia. Tyre

2008 Fushun Commercial Plant 230 t/h, Shell 8.4 m dia. x 63 m long, 11.1 m dia. Tyre

2010 Jordan ATP Scale-Up 500 t/h, Shell 11.5 m dia. x 76 m long, 15.5 m dia. Tyre
ATP Technology – Advantages for Oil Sands and Heavy Oil

ATP System Achieves High Yield
- Yield consistent with low, medium, and high grade oil sands.
- Process not sensitive to connate water chemistry, bitumen conditioning, and clays.

Oil Products are Low Viscosity, Bottomed, and Hydrotreatable
- Pumpable without requiring diluent or upgrading

ATP System Produces Dry Tailings
- Direct disposal of tailings as backfill in mine (no tailings ponds)
ATP Technology – Advantages for Oil Sands and Heavy Oil

Low natural gas and water requirements
- By-product coke used as primary fuel source (no coke piles).
- Off gas is available as fuel to balance of plant
- ATP water use limited to controlling tailings moisture and process cooling

ATP System Scalable & Versatile
- Satellite or central facility options
- Can be constructed in increments and oil products pipelined to a regional upgrader.

Cost Effective
- ATP System capital and operating costs are favourable compared to existing HWE systems.
# Athabasca Oil Sand – Liquid Products Compared

<table>
<thead>
<tr>
<th></th>
<th>Bitumen</th>
<th>Fluid Coker TLP</th>
<th>ATP TLP, typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity</td>
<td>8.0</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>S, wt%</td>
<td>4.9</td>
<td>3.5</td>
<td>3.3</td>
</tr>
<tr>
<td>N, wt%</td>
<td>0.4</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>IBP-204°C</td>
<td>1.6</td>
<td>21.5</td>
<td>23</td>
</tr>
<tr>
<td>204-343°C</td>
<td>13.8</td>
<td>32.7</td>
<td>33</td>
</tr>
<tr>
<td>343-525°C</td>
<td>37.5</td>
<td>45.8</td>
<td>44</td>
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<tr>
<td>525+°C</td>
<td>47.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HYCAL H2, SCF/BBL</td>
<td></td>
<td>886</td>
<td>900-950</td>
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</tbody>
</table>

Not pumpable without diluent or upgrading

Pumpable, low viscosity, thermally cracked, bottomed. Hydroprocessing can control stability, S, N

Source: 1982 ATP Test Program
Oil Sands Yield vs. Grade

[Graph showing the relationship between wt% Bitumen in Oil Sand and Yield - wt% of Bitumen in Feed.]
Secondary Upgrading Experience

Oil sands
Gulf & CANMET testing

Stabilization of total liquid product with partial heteroatom removal possible in single stage of hydrotreating

Removal of heteroatoms to WMSCO requires separate heavy and light oil hydroprocessing

ATP naphtha highly cracked, required staged temperature profile in reactors to prevent oligermization

Oil Shale
NCUT studies, Licensor studies, Stuart Operation

Heteroatom Challenge:
- Jordan S (>8% S, all fractions)
- Estonia O (>5% O, high in phenols)
- China N (>1.0% N, ammonia)
- Australia ~ 0.4% S, 0.9% N

Stuart plant produced Certified Jet Fuel using 3 stage hydro-treating with standard industrial catalysts
Stuart Demonstration Plant - Hydrotreating

Shale Oil: Diesel & Naphtha

Hydrotreated Fuel
- < 1 ppm S
- < 4 ppm N

Upgrading Facility
Current Major Activities

Jordan, Al Lajjun ATP Project Feasibility Study
- ATP System & Processor Engineering
- Two 500 t/h capacity ATP trains, 15,000 bbl/d SCO (hydrotreated)
- Reserves estimate, logistics, oil upgrading, power plant, and environmental studies

China, Fushun ATP Project
- ATP Processor fabrication and construction underway
- Detail engineering and plant construction in progress – commissioning Fall 2009

Ongoing Opportunities and Investigations
- Oil sands (oil and water wet), oil shales, heavy oil pyrolysis
ATP60 Processor – UMATAC Pilot Plant

ATP60 Processor at UMATAC pilot plant site in Calgary, Alberta
Summary

Developed for Oil Sands

✓ Fundamental ATP advantages: thermal processing to a pumpable distillate with dry tailings
✓ High recoveries independent of feed characteristics
✓ Extensive piloting experience

Proven in Oil Shale

✓ Scale-up methodology & new construction methods successful
✓ Processor mechanical design proven to be robust
✓ Learnings / advances incorporated into new designs

Ready for future opportunities

✓ Oil sands (oil and water wet), oil shales, heavy oil pyrolysis.
✓ Scalable for diverse applications
Acknowledgements

UMATAC and its staff take this opportunity to thank many members of AOSTRA and ADOE for their assistance in completion of UMATAC’s activities from 1977 through 1995. Without the financial support received from the Alberta Oil Sands Technology and Research Authority, the ATP Technology developed and described in this paper would not have been possible.
UMATAC Industrial Processes

UMATAC appreciates this opportunity to present the ATP Technology as it has been developed in the last 34 years. UMATAC is of the opinion that, based on our earlier oil sands test program successes, the ATP Technology could provide an efficient means of overcoming some of the concerns being raised with regard to expansion of the current oil sands industry.
### ATP Technology Development – 34 Years of Experience

<table>
<thead>
<tr>
<th>Year</th>
<th>Event Description</th>
<th>Year</th>
<th>Event Description</th>
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<tbody>
<tr>
<td>1975</td>
<td>UMATAC Inception</td>
<td>1993</td>
<td>Treatability Testing of Oil Sands and Shales from Numerous Locations</td>
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<tr>
<td>1977</td>
<td>AOSTRA Agreement</td>
<td>1994</td>
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<td>1978</td>
<td>First ATP Pilot Plant Built</td>
<td>1995</td>
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<td>1979</td>
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<td>1996</td>
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<td>1980</td>
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<td>1997</td>
<td></td>
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<td>1981</td>
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<td>1998</td>
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<td>1982</td>
<td>Oil Sand Pilot Studies and</td>
<td>1999</td>
<td>Stuart Stage I Oil Shale Demonstration in Australia - First Major Scale-up</td>
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<tr>
<td>1983</td>
<td>Developing Commercial Plant</td>
<td>2000</td>
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<td>1985</td>
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<td>1986</td>
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<td>2003</td>
<td>USA, Jordanian, Estonian, and Chinese Oil Shale Pilot Testing and Studies</td>
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<td>1987</td>
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<td>2004</td>
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<td>1988</td>
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<td>2005</td>
<td>Commercial ATP Plant Design &amp; Construction in China</td>
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<td>1989</td>
<td>Australia Oil Shale Pilot Studies</td>
<td>2006</td>
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<td>2007</td>
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<td>1991</td>
<td>ATP60 Pilot Plant Built,</td>
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<td>Oil Sand Pilot Studies, and</td>
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<td>1993</td>
<td>10 t/h Commercial</td>
<td>2010</td>
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<tr>
<td>1994</td>
<td>Hazardous Waste Clean-up Plant Constructed</td>
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ATP Technology Development – 34 Years of Experience

First ATP Pilot Plant Construction – 1977
(William Taciuk on Left)
ATP Technology – Stuart Demonstration Plant Summary

ATP Processor

- Scale-up (75:1) methodology was successful.
- Achieved process design throughput and oil yield.
- Operated at 200% of design water load.
- Mechanical design proven to be robust.
- Availability of ATP Processor was high.

Oil Recovery & Upgrading

- Vapour scrubber design and scale-up proven.
- Hydrotreating – industrial catalysts were adequate - high nitrogen removal achieved, unit worked as designed.
ATP Technology – Recent Process Developments

Scale-up

✓ 75 : 1 Stuart and China
✓ 2 : 1 Jordan design

Larger Capacity Plants Developed In Increments to Reduce Risk

Increased Thermal Performance

✓ ATP spent solids (heat recovery from 400 to 150°C).
✓ ATP flue gas (heat recovery from 365 to 150°C).

New Waste Heat Recovery options result in 15% Lower Fuel Consumption for ATP in China
ATP Technology – Recent Mechanical Developments

Mechanical Scale-up and Support Tyres

✓ mechanical reliability proven at Stuart Demonstration Plant
✓ new fabrication technique proved at FMG plant in China: segmented transport, field welding and machining technique for 11.1 m dia. Tyres – reduces fabrication and transport restrictions.

Scale-up Obstacle Removed For Larger Units
Single Piece (top) vs. Segmented (bottom) Tyre Transport – both 11.1 m Diameter
On-Site Tyre Welding & Machining – FMG China

Weld Preparation

On-Site Machining by Self Leveling Machines (SLM)
Oil Sands Yield vs. Grade

Oil Sands Feed - ATP Processor Yield

- C3- Gas
- Gross Coke
- C4+ Liquid

Yield - wt% of Bitumen in Feed

wt% Bitumen in Oil Sand

7 8 9 10 11 12 13 14

0 10 20 30 40 50 60 70 80 90 100
Daniel Gillis

UOP, LLC

Dan Gillis is the Business Manager, Heavy Oil in the Refining Business Group at UOP, LLC. Dan is accountable for the Product Line Management and Technology Sales coordination of UOP’s current and emerging Heavy Oil technologies, including the commercialization of UOP’s Uniflex Process. At UOP, Dan has had roles in Technology Sales Support, predominately Heavy Oil, and more recently management of Engineering and Sales Support functions for Clean Fuels, Heavy Oil, and Gas Processing technologies. He joined UOP in 1995 after working in the Refining and Oil Sands Industries in operations and process engineering, followed by project and business development roles. Dan is a 1977 engineering graduate of the University of Saskatchewan, Canada.

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Email: Dan.Gillis@UOP.com
Website: www.UOP.com
Breaking Though the Bitumen Upgrading Barriers with the UOP Uniflex™ Process

Daniel Gillis
UOP LLC

Bitumen upgrading has never before been challenged as it is today. Justification in today’s environment to install conversion and hydroprocessing facilities, whether at the production site or self supporting upgrading plants, is difficult due to the high capital investment requirements, expected modest rates of return, and unclear future product prices. Further challenging justification of these projects is that the yields from conventional processes such as coking and ebullated bed hydrocracking are much lower than desired. Consequently, to justify upgrading there is a need for processes that can maximize conversion and selectively produce transportation boiling range products, especially distillates. Not only is there a technical challenge to provide a reliable high-conversion technology, there is a commercial financing challenge, due to the risk averseness of the investment community in what is perceived as “new” technology.

UOP has responded to this market situation with the UOP Uniflex Process, a commercially based, high-conversion residue upgrading process that selectively converts residues from both conventional crude oils and bitumen to transportation fuels, especially distillates, and high quality synthetic crude oil.

This presentation will explain the technology features, commercialization background, and how this technology meets the challenges of significantly improving the profitability of upgrading while managing the technical and commercial concerns when applying new technologies. Also discussed are recent advances being developed by UOP under the AERI Hydrocarbon Upgrading Demonstration Program, including catalyst, engineering design and residue byproduct utilization. UOP’s latest flow scheme options, especially for applications with existing residue upgrading technologies, are presented.
Breaking Through the Bitumen Upgrading Barriers with the UOP Uniflex™ Process

Dan Gillis
UOP LLC

2009 Canadian Refining and Upgrading Conference
September 14-16th, 2009
Edmonton, Alberta

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Bitumen Upgrading Challenges

- Product Yields and Qualities
- Byproduct Disposal
- Expansion of Existing Assets
- Return on Investment
- Project Financing
Strong Incentive for High Conversion Technologies

Source: 2008 FACTS Global Energy
High Conversion Technology Barriers

- Technical Issues
- Commercialization Status
- Costs
- Technology Support
- Risk Management
UOP Uniflex Process

- Contains elements of proven processes
  - Commercialized CANMET Hydrocracking Process
  - UOP Unionfining™ and Unicracking™ Processes

- Up flow high temperature and pressure reactor
- Hydrogen and proprietary dispersed phase catalyst added to the feed
- Results in high conversion to desired products

Uniflex Process has a 26 vol% yield advantage!
CANMET Hydrocracking Process Background

- Supported by 25 years of R&D
- Technology owned by Natural Resources Canada
- Commercially proven high conversion on a wide range of feedstocks
- UOP acquired exclusive licensing rights in 2007

Petro-Canada Montreal Unit

- 15 years of operation
- Achieved 95% conversion
- Processed many vacuum residues
- Also processed VGO, Visbroken Vacuum Residue, FCC Slurry Oil
- Long term operational learning curve
- 97%+ availability
Product Yields Drive Economic Advantages

Uniflex Process focus is on medium to high conversion with high process reliability!
UOP is Advancing the Technology

- Best Practices from CANMET Experiences
- Advanced Pilot Plants
- New Catalysts
- Flow Scheme and Equipment Improvements
- Pitch Product Options
Alberta Energy Research Institute (AERI)

- Energy technology arm of the Alberta Government
- Partners with industry to develop technologies of strategic importance

Hydrocarbon Upgrading Demonstration Program (HUPD)

- Phase 1: Screened over 100 technologies for upgrading bitumen
- Phase 2: UOP Uniflex Process was selected for further development and demonstration
- AERI providing financial support

AERI support is helping to enable technology advances
Petro-Canada Montreal Unit Yields

Product Yields, vol% vs Vacuum Residue Conversion, wt%

- Diesel
- VGO
- Naphtha
UOP Pilot Plant Yields Match Petro-Canada Montreal Unit Yields
Key Equipment designed to assure Product Stability and avoid Equipment Fouling
UOP Uniflex Process
with Heavy Vacuum Gas Oil Recycle

- Makeup $\text{H}_2$
- Uniflex Reactor
- Recycle Gas Heater
- Feed
- Catalyst
- HVGO Recycle
- Feed Heater

- Hot Separator
- Cold Separator
- Cold Flash Drum
- Hot Flash Drum

- Flash Gas
  - $\text{C}_4^-$
  - Naphtha
  - Diesel
  - Vacuum Fractionator
  - LVGO
  - HVGO
  - Pitch

- Recycle
- Gas Heater
- Fractionator Heater
Poly-aromatics ideal for reducing mesophase by improving asphaltene solubility.
Significant improvement in VGO quality to downstream FCC and Hydrocracking
End uses include:
- Cement kilns
- Fluidized bed boilers
- Conventional boilers
- Gasification
- Delayed coking
- Solvent deasphalting

Can be handled in:
- Liquid form for nearby uses
- Solidified for transportation to distant markets

UOP can assist customers for all applications
UOP Uniflex Process Creates Additional Opportunities

- Heavier Crude Processing
- FCC Slurry Oil Conversion
- Hydroprocessing Integration
- Synergies with other Residue Processes
  - Solvent Deasphalting
  - Delayed Coking
  - Residue Hydrotreating
Several integration options are possible
Best flow scheme depends on product objectives
Project specific issues need to be considered

Integration can reduce Costs
Benefits are Project Specific
**Fractionation Approach has Implications**

- Yields are impacted by both process conversion and fractionation approach.
- Maximizing conversion and product recovery can lead to equipment reliability issues.
- Uniflex Process has addressed these issues with:
  - Flow scheme and equipment designs that manage product stability and fouling issues.
  - Advanced separation systems to maximize product recoveries.

---

**Pitch Yield versus Conversion**

- Conventional Fractionation
- Specialized Fractionation Equipment
- Solvent Extraction Potential
- Light Solvent
- Heavy Solvent

*Yields are impacted by both process conversion and fractionation approach.*

---

**Product Separation Approach Impacts Profitability and Process Reliability**

- Feed → Uniflex Process → Products
- Residue → Advanced Separation Systems → Pitch
- Recycle

*NCUT Pilot Plant*
Uniflex Process Integration with Coking

**Yields**

<table>
<thead>
<tr>
<th>Conversion, wt %</th>
<th>Liquid Yields, vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC only</td>
<td>65</td>
</tr>
<tr>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>90</td>
<td>95</td>
</tr>
<tr>
<td>95</td>
<td>105</td>
</tr>
</tbody>
</table>

**Margins**

<table>
<thead>
<tr>
<th>Conversion, wt %</th>
<th>Margin, $/bbl VR</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC only</td>
<td>10</td>
</tr>
<tr>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>85</td>
<td>20</td>
</tr>
<tr>
<td>90</td>
<td>25</td>
</tr>
<tr>
<td>95</td>
<td>30</td>
</tr>
</tbody>
</table>

- Conventional residue byproduct
- Yields much less sensitive to Uniflex Process conversion
- High margins even at low Uniflex Process conversion

Very high margins can be sustained based on combining proven technologies
UOP Uniflex Process Breaks Through the High Conversion Selection Barriers

- Best Practices from CANMET Hydrocracking
- Continuous Development facilitated by AERI
- High Conversion and Upgrading Margins
- Design assures High Reliability
- Meets Investors Expectations

UOP Uniflex Process Will Maximize Your Upgrader’s Profitability
Q&A
BIOGRAPHY

Stefan Romocki
Mobis Energy Inc.

Stefan Romocki is the president of Mobis Energy, a company taking a different approach to bottom of the barrel upgrading, using recoverable nano catalysts. Stefan graduated from the Rotman Commerce program at University of Toronto with a specialization in Economics. He has been working in technical sales and business development in the heavy oil industry for over a decade, with a focus in heavy oil upgrading. He is co-chair of the facilities and upgrading technical committee of the Canadian Heavy Oil Association and was recently recognized for entrepreneurship as a “Leader of Tomorrow” in Calgary Business magazine.

George Rhodey
Mobis Energy Inc.

George Rhodey is the Director, Bitumen and Heavy Oil Projects for Mobis Energy. Mr. Rhodey has BASc. and MASc. Degrees in Chemical Engineering from the University of Waterloo, Waterloo Ontario. He is a member of APPEGA, the Canadian Heavy Oil Association. His experience includes participation in development and implemented of a major NGL strategy for PetroCanada including an MTBE plant, ICG, centralized fractionation, and a development proposal to build a petrochemical complex using upgrader off gas as feedstock. Through his 40 years of experience, Mr. Rhodey has worked in the petrochemical and oil refining sectors in roles ranging from operating, marketing, and business development.

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Calgary, AB T2G 0W3 Canada
Stefan Romocki
Phone: 403 617 8356
Fax: 403 290 4742
Email: sromocki@mobisenergy.com
George Rhodey
Phone: 403 290 4675
Email: grhodey@mobisenergy.com
Website: www.mobisenergy.com
Mobis HRH Process
Residue Hydroconversion Using a Recoverable Nano-catalyst

Stefan Romocki and George Rhodey
Mobis Energy Inc.

Conventional hydroconversion of residue has been achieved through high pressure, capital intensive processes with significant operating costs associated with maintaining catalyst activity. Despite the usefulness of heterogeneous catalysts in numerous refining processes, their potential for hydroconversion of heavy feeds with high levels of sulfur, nitrogen, resins, asphaltenes and metals is limited.

This paper will introduce a Pseudo-homogeneous Catalyst (PHC) developed for the specific chemistry of heavy hydrocarbon feeds. The term pseudo-homogeneous reflects the fact that an active catalyst is formed in the reaction system, consisting of particles having a size 2-9nm and properties close to those of a colloid solution at both room and reaction temperature.

Residue processing using a high performance pseudo-homogeneous catalyst system results in improved cracking and hydrogenation performance at lower process severity. The (PHC) system in the Heavy Residue Hydroconversion (HRH) process achieves up to 95% residue conversion at pressure below 7.3 MPa, reaction temperatures between 400 - 460 °C, with feed space velocity between 1.0-2.0 h⁻¹; making (PHC) catalyst systems well suited for deep conversion of hydrocarbon residues.

The sustainability profile of the HRH process is improved as residue conversion to liquids and process on-stream time are maximized, while up to 95% catalyst is recovered and regenerated within the process.

Pilot plant results from hydroconversion of Athabasca vacuum bottoms using a pseudo-homogeneous catalyst system are discussed.

Application of the HRH process in oilsands and refinery operations are discussed with comparative yields and economics.
Mobis HRH Process
Residue Hydroconversion Using a Recoverable Nano-catalyst

NCUT Upgrading & Refining Conference 2009
September 14-16
Agenda

- Background
- Physical and Chemical Basis of the HRH nano-catalyst
- Process Flow Description
- Pilot Plant Data
- Conceptual Yields with HRH
- HRH Projects & Facilities
Who is Mobis Energy?

- Private Canadian Technology Licensing Company
- North American Licensor of the Heavy Residue Hydroconversion
- Focus on Bringing Successful Process Innovation to New Markets
Current Conversion Practices

- Heavy Residue Processing Options;
  - Historical
    - Coking, Residue Hydrocracking and De-asphaltene
  - New Developments
    - Gasification
    - Reservoir Reactor Through Carbon Burn (THAI, CAPRI)

- Most Difficult to Process Molecules are Separated from Lighter, more Valuable Components

- Viability of Hydroprocessing Dependent upon Feedstock (Metals, S, N, Asphaltenes, ...)

MOBiS ENERGY INC.
Limitations of Conventional Residue Processing

Hydrogen Addition;
- High Investment Cost
- High Operating Costs
- Conversion Limitations
- Catalyst Deactivation

Carbon Rejection;
- Low Liquid Product Yields
- Low Product Quality
- Solid By-product Disposal Issues
Performance Limitations with Conventional Supported Catalysts

- Catalyst Deactivation Through Feed Metal Precipitation and Coking

- Conversion of >525°C Residual Oil Limited by Product Stability (Increased Sedimentation)

- High Gas yield as Conversion is Increased
Conventional Upgrading Processes do not Provide an Economically Effective Solution for Conversion of Residual Oil into Lighter more Valuable Products
Something Innovative... The Mobis HRH Process

- Dispersed Nanocatalyst
- Up to 95% Residue Conversion
- Online Catalyst Regeneration
- High Selectivity to Distillates
- Hydrocracking at Hydrotreating Pressure
The Chemistry which Drives Conversion Reactions Takes Place on a Molecular Level
Catalyst Geometry

- **Size Matters!**
  - The Geometry of a Supported Catalyst Limits Access to Reactive Surface Area
  - High Molecular Mass Feed Components Require a Catalyst to be Engineered with Larger Pore Size to Maintain Activity
  - Catalyst Surface Area is Reduced as Pore Size is Increased, Thereby Reducing the Effective Potential of a Catalyst
Ultra-Dispersed Nano-catalyst Tailored for Effective Residual Oil Conversion

• Unsupported Catalyst Structure Tailored from the Atomic Level
• Molecule Sizes 2-9nm Ensure Maximum Reactive Surface Area
• Catalyst Geometry Provides Effective Contact for Conversion of Asphaltenes and Resins

4 nm MoS² Nanocrystal (1)
Asphaltene Molecule (2)

(2) Proposed Molecular Structure of Asphaltene, INTEVEP S.A. Tech. Rept., 1992
Online Catalyst Regeneration

- Substantially Lower Operating Costs Catalyst is Recovered and Reused
- Reduced Environmental Footprint Approaches Zero Solid Waste
- Constant Catalyst Activity with Unconstrained Time On-Steam
- Eliminates Disposal Liabilities Associated with Spent Catalyst and Coke Handling
HRH – Colloid Chemistry

Mycelium Safety Layer

Asphaltenes

RRR 1-10 nm

Colloid

(NH₄)₆Mo₇O₂₄.4H₂O

H₂O

NH₃

MoO₃ + H₂S = MoS₂

3-5 nm

MoS₂ + H₂ + R• = RH

Asphaltene Radicals

R•

200-600 nm

H₂

MoO₃

MoS₂

H₂S

(Route)
Benefits of Improved Molecular Efficiency

• Up to 95% Conversion with Product Stability

• Hydrocracking at Hydrotreating Pressure (1000 psig range)

• Low Gas yield with Selectivity of Conversion to Liquids

• Fewer Process By-products

• Enhanced Throughput – Low Residence Time

• Simple Reactor Design

• Lower Capital, Operating and Maintenance Costs
## Upgrading Athabasca Residue

### Feedstock Properties

<table>
<thead>
<tr>
<th></th>
<th>HRH Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>3.5</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>4.54</td>
</tr>
<tr>
<td>Nitrogen, wt%</td>
<td>1.00</td>
</tr>
<tr>
<td>Asphaltenes + Resin, wt%</td>
<td>40.4</td>
</tr>
<tr>
<td>Nickel + Vanadium, ppm</td>
<td>349</td>
</tr>
</tbody>
</table>
Upgrading Athabasca Residue

HRH Product Properties 73 vol. % Conversion

<table>
<thead>
<tr>
<th></th>
<th>Wt%</th>
<th>°API</th>
<th>S</th>
<th>N</th>
<th>Ni+V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>10.48</td>
<td>58.41</td>
<td>0.69</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td>40.1</td>
<td>26.76</td>
<td>1.7</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>Gas Oil</td>
<td>18.2</td>
<td>17.07</td>
<td>2.12</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>Product C5</td>
<td>10.48</td>
<td>18.2</td>
<td>1.66</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>10.48</td>
<td>18.2</td>
<td>1.66</td>
<td>0.39</td>
<td>Trace</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Residence Time</th>
<th>Reactor Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>41 minutes</td>
<td>460°C</td>
</tr>
</tbody>
</table>

Operating Conditions
Single Pass Conversion;

- 73% volume
- 63% Desulfurization
- 60% Denitrogenation
- Total elimination of feed metals
HRH Product Composition Compared to Delayed Coking and EB Hydrocracking

Assumes Athabasca Vacuum Residue as Feed
Mobis HRH - Block Flow Diagram
## Canadian Upgrader Yields – 200MBPD Feed

<table>
<thead>
<tr>
<th></th>
<th>DELAYED COKER with Gasifier</th>
<th>EBUGULATED BED with Gasifier</th>
<th>HRH 95% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Gas MMBTU/Hr</td>
<td>1925</td>
<td>0</td>
<td>-6790</td>
</tr>
<tr>
<td>H2 SCF/B Feed</td>
<td>1243</td>
<td>1933</td>
<td>2083</td>
</tr>
<tr>
<td>Synthetic Crude</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>API</td>
<td>36.7</td>
<td>33.4</td>
<td>32.7</td>
</tr>
<tr>
<td>Wt % Sulphur</td>
<td>0.06</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Naphtha MBPD</td>
<td>42.9</td>
<td>21.0</td>
<td>17.8</td>
</tr>
<tr>
<td>Distillate MBPD</td>
<td>76.7</td>
<td>85.9</td>
<td>100.0</td>
</tr>
<tr>
<td>VGO MBPD</td>
<td>56.2</td>
<td>83.4</td>
<td>97.6</td>
</tr>
<tr>
<td>Total MBPD</td>
<td>175.8</td>
<td>190.3</td>
<td>215.4</td>
</tr>
<tr>
<td>% Feed</td>
<td>87.9</td>
<td>95.2</td>
<td>107.7</td>
</tr>
</tbody>
</table>
Effect of Volume on Upgrader Economics

![Graph](https://example.com/graph.png)

- Base Graph Courtesy Strategy West Inc. Volume Expansion Effect Estimated by MOBIS
## Refinery Yields – 200MBPD Feed

<table>
<thead>
<tr>
<th></th>
<th>CATCRACKING + COKER</th>
<th>CATCRACKING + HRH</th>
<th>HYDROCRACKING + HRH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂ SCF/B Feed</strong></td>
<td>430</td>
<td>730</td>
<td>890</td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline MBPD</td>
<td>89.8</td>
<td>101.5</td>
<td>63.7</td>
</tr>
<tr>
<td>Middle Distillates MBPD</td>
<td>69.2</td>
<td>92.7</td>
<td>78.4</td>
</tr>
<tr>
<td>Resid /Asphalt MBPD</td>
<td>35.0</td>
<td>1.1</td>
<td>52.5</td>
</tr>
<tr>
<td>Petchem MBPD</td>
<td>5.4</td>
<td>9.2</td>
<td>4.3</td>
</tr>
<tr>
<td><strong>Sub Total</strong></td>
<td>199.4</td>
<td>204.5</td>
<td>198.90</td>
</tr>
<tr>
<td><strong>% Feed</strong></td>
<td>99.7</td>
<td>102.3</td>
<td>99.5</td>
</tr>
<tr>
<td><strong>Residue Coke Tonnes/day</strong></td>
<td>1770</td>
<td>1770</td>
<td>0</td>
</tr>
<tr>
<td><strong>Sulphur Tonnes/day</strong></td>
<td>205</td>
<td>220</td>
<td>318</td>
</tr>
</tbody>
</table>

**Increase in Motor Fuel Yield**  
- CATCRACKING: 22.1%  
- HYDROCRACKING: 43.3%
HRH Projects & Facilities

- 180,000 BPD Heavy Oil Refinery – Basic Design Complete
- 200 BPD Demonstration Plant
- Pilot Plants from 0.5 LPD to 2 BPD
Conclusion – Benefits of the HRH process Using a Recoverable Nano-catalyst

- Any Residue can be Upgraded to 29 – 34°API SCO or refined oil products
- High Liquid Yield with Distillate Selectivity
- Hydrocracking at Mild Pressure (1000 Psig)
- Catalyst Recovered, Remanufactured and Re-used within the Process
- Time On-stream Unconstrained by Catalyst
- Enhanced Throughput -- Low Residence Time
- Approaches Zero Solid Waste
- Piloted, Demonstrated with First Commercial Project Underway
Thank You!

For additional details please contact:

Stefan Romocki
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Tel:(403) 617-8356

George Rhodey
grhodey@mobisenergy.com
Tel: (403) 290-4675
BIOGRAPHY

Tomoki Kayukawa
JGC Corporation

<Education>

- **April 2002 - March 2004**
  Master Degree in Mechanical Engineering (Energy Conversion System) of Kyoto University. Studied “Characteristic of Auto-ignition of Unsteady Gaseous Fuel Jet”

<Professional Experiences>

- **April 2004 - Present**
  Research and Development Division, JGC Corporation.

- **June 2004 – August 2008**
  Development of process for synthesis gas purification in IGCC plant by catalytic conversion technology to eliminate COS, HCN, and other impurities.

- **November 2004 - September 2005**
  Study on heavy oil upgrading process in terms of thermal and hydrotreating technologies.

- **October 2005 - March 2006**
  Study on a technology for CO₂ removal from natural gas in terms of absorbent technology under high operating pressure.

- **February 2006 – Present**
  Upgrading of ultra-heavy crude oil by thermal cracking with supercritical water.

- **September 2008 – August 2009 (Dispatched to NCUT)**
  Quantification of Reactive Naphthenic Acids in HVGO.

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E-mail: kayukawa.tomoki@jgc.co.jp
Upgrading of Bitumen by using Supercritical Water

Tomoki Kayukawa
JGC Corporation

Upgrading of heavy oil by supercritical water (SCW) is simple and unique process to produce pipeline-transportable oil from high-viscous bitumen, because it utilizes water and requires neither hydrogen nor catalysts. Pre-heated bitumen and water are introduced to vertical reactor with flows of counter current at the condition of supercritical point of water. Bitumen is allowed to crack thermally to obtain upgraded oil, so-called synthetic crude oil (SCO) and pitch, from the top and the bottom of the reactor, respectively. Bench scale test (the capacity is 0.15BPD) demonstrated that Canadian oil sands bitumen can be converted to 80vol% of SCO and 20vol% of pitch. API gravity and kinetic viscosity of thus obtained SCO satisfied Canadian pipeline specifications, and the pitch also satisfied the boiler fuel specification in terms of kinetic viscosity. In this paper, characteristics and advantages of thermal cracking by SCW are overviewed from technical and economical standpoints.
Upgrading of Bitumen by using Supercritical Water

Tomoki Kayukawa
JGC Corporation
World’s Proven Reserves

Billion bbl

North America
South America
Africa
Europe
Middle East
Asia
Russia

Bitumen (Vis. >10,000CP)
Light & Middle Crudes (API 22° ~ 31°)
Heavy & Ex. Heavy Crudes (API < 22°)

Source: Nexant Report

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Transportation of Ex. Heavy Oil and Bitumen

Dilution

Well → Diluent → Dilution → Pipeline transportation → Dil-Bit → Refinery

Full Upgrading

Well → Upgrader (Thermal & Hydro cracking) → Pipeline transportation → Sweet SCO → Refinery

- Low availability of diluent
- Soaring diluent price
- Complex scheme
- Large-scale upgrader
Conventional Bitumen Upgrading Process

Extraction & Froth Treatment Plant

Diluted Bitumen → Diluent

Diluent Recovery Unit

Diluent → Virgin LGO

Vacuum Distillation Unit

AR → Hydrocracker Unit

Bottom → H2

Vacuum HGO

Coker Unit

H2

Hydrocracker Unit

Naphtha HTU

LGO HTU

HGO HTU

Sour Gas

Sweet Gas To Utilities

Sulfur

Amine & Sulfur Plant

Sour Gas

Sweet Gas

Sweet SCO

Coke

(Oil & Gas Journal / April 23, 2001)

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Partial Upgrading by using Supercritical Water

Dilution

Well → Dilution → Diluent → Pipeline transportation → Dil-Bit → Refinery

Full Upgrading

Well → Upgrader (Thermal & Hydro cracking) → Pipeline transportation → Sweet SCO → Refinery

- Low availability of diluent
- Soaring diluent price

Partial Upgrading by using Supercritical Water (SCW)

Well → Partial Upgrader → Pipeline transportation → Sour SCO → Refinery

- Simple scheme
- Small-scale upgrader
- No diluent
Integration of SAGD and SCW Cracking

SAGD*

Boiler Facility

Bitumen Recovery Facilities

High Press. Steam

Oil Sands Reserves (underground)

Upgrader

Supercritical Water Cracking Facilities

Residue (Liquid)

Hot Water

Bitumen (API 8.5°)

Drain

Sour SCO (API 19~25°)

- No hydrogen
- No natural gas
- No catalyst
- Small quantities of by-products

* Steam Assisted Gravity Drainage

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What is Supercritical Water?

Water at a temperature and under a pressure above its critical point

SCW has physical properties between liquid and gas

Press. | Liquid (Water) | Critical Pressure (22.1 Mpa) | Critical Temperature (374°C) |
--- | --- | --- | --- |
Solid (Ice) | Gas (Vapor) | SCW | |

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas</th>
<th>SC Fluid</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>1</td>
<td>100~1,000</td>
<td>1000</td>
</tr>
<tr>
<td>Viscosity (mPa·s)</td>
<td>0.01</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Diffusion Coefficient (m²/s)</td>
<td>10⁻⁵</td>
<td>10⁻⁷~10⁻⁸</td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>Thermal Conductivity (mW/mK)</td>
<td>5~30</td>
<td>20~150</td>
<td>50~200</td>
</tr>
</tbody>
</table>
### Roles of Supercritical Water

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water @20°C</td>
<td>81.1</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>25.8</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7</td>
</tr>
<tr>
<td>Propanol</td>
<td>20.3</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>8.93</td>
</tr>
<tr>
<td>THF</td>
<td>7.58</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.81</td>
</tr>
<tr>
<td>Diethylether</td>
<td>4.33</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.38</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.27</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.92</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.88</td>
</tr>
</tbody>
</table>

**Dielectric Constant $\varepsilon$ [-] of Water**

SCW has characteristics of non-polar solvent.

SCW has a low dielectric constant somewhere in the range of 2 to 10.

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Direct Observation of Reaction and Extraction Phenomena

Injection of samples

Setup

Monitoring & Recording

✓ Temperature change
✓ Pressure change
✓ Phase change

✓ Temp. range: ≤ 430 °C (Heating rate: ~ 3 °C/min)
✓ Press. range: ≤ 30 MPa

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Results of Direct Observation

Roles of Supercritical Water

1. Thermal Cracking of VR
2. Extracting Distillate and VGO
3. Inhibiting polymerization of asphaltene (coking)
Test Apparatuses & Test Results
### Feedstock Properties

#### Bitumen (produced by SAGD)

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (@15°C)</td>
<td>g/cc</td>
<td>1.012</td>
</tr>
<tr>
<td>API</td>
<td>°</td>
<td>8.3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>wt%</td>
<td>5.15</td>
</tr>
<tr>
<td>CCR</td>
<td>wt%</td>
<td>13.8</td>
</tr>
<tr>
<td>Viscosity (@40°C)</td>
<td>cSt</td>
<td>17,000</td>
</tr>
<tr>
<td>Metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>wtppm</td>
<td>75</td>
</tr>
<tr>
<td>Vanadium</td>
<td>wtppm</td>
<td>194</td>
</tr>
<tr>
<td>Distillation (SimDis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-360°C</td>
<td>wt%</td>
<td>17</td>
</tr>
<tr>
<td>360-540°C</td>
<td>wt%</td>
<td>33</td>
</tr>
<tr>
<td>540°C+</td>
<td>wt%</td>
<td>50</td>
</tr>
</tbody>
</table>
Schematic Diagram of Test Unit

Bitumen

Design Temp.: 480°C
Design Press.: 30MPa
Capacity: 0.15BPD
Material: SUS316

Vertical Reactor Vessel

Water

Pump

Heater

Condenser

Back Pressure Regulating Valve

Flow Meter

Light Products

Water

Heavy Residual Products

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Light Products (75.7 vol%)

<table>
<thead>
<tr>
<th></th>
<th>API</th>
<th>°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>22.9</td>
</tr>
<tr>
<td>Viscosity@10°C</td>
<td>cSt</td>
<td>26.0</td>
</tr>
<tr>
<td>Distillation Characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~360°C</td>
<td>wt%</td>
<td>57</td>
</tr>
<tr>
<td>360-540°C</td>
<td>wt%</td>
<td>39</td>
</tr>
<tr>
<td>540°C+</td>
<td>wt%</td>
<td>4</td>
</tr>
</tbody>
</table>

Heavy Residual Products (25.2 vol%)

<table>
<thead>
<tr>
<th></th>
<th>API</th>
<th>°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-6.5</td>
</tr>
<tr>
<td>Viscosity@310°C</td>
<td>cSt</td>
<td>17.5</td>
</tr>
<tr>
<td>Distillation Characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~360°C</td>
<td>wt%</td>
<td>5</td>
</tr>
<tr>
<td>360-540°C</td>
<td>wt%</td>
<td>27</td>
</tr>
<tr>
<td>540°C+</td>
<td>wt%</td>
<td>68</td>
</tr>
</tbody>
</table>
*1 Feedstock for Delayed Coker is VR from Bitumen. Products include Coker products and straight run Distillate & Naphtha.
Summary of Reaction Tests

- Bitumen was successfully cracked by using SCW
  - 60% of VR was converted to Distillate & VGO.

- SCW cracking system involves the functions of reaction and extraction. SCW worked as a solvent for the separation of light and heavy residual products.

- The kinematic viscosity and density of light products satisfied the Canadian pipeline specifications.

- The heavy residual products satisfied the boiler fuel specifications in terms of kinematic viscosity.
Economic Evaluations
**Economic Efficiency vs. Residence time**

- **CAPEX** includes on-site facilities, utility facilities, power plant, off-site facilities and owner cost.

---

- **Capacity:** 30,000BPD of Bitumen (8°API)

---

- **IRR [\%]**
  - **Base x 3:** 6.6
  - **Base:** 10.0
  - **Base x 0.5:** 8.1

---

- **Economic Efficiency vs. Residence time**

  - **High Press. Equipment:** 54%
  - **Water Recycle:** 15%
  - **Others:** 3%
  - **Reactor:** 27%
**Economic Comparison**

### D. Coker-based plant

- **Bitumen** 30KBD, 8° API
- **SCO** 24KBD, 21° API
- **Naphtha**
  - **HDS**
- **CDU**
- **VDU**
- **D. Coker** 15KBD
- **Coke** 990 tpd

(*) D. Coking and Vis Breaking tests were conducted by PARC.

### SCW Cracking-based plant

- **Bitumen** 30KBD, 8° API
- **SCW Cracking** 30KBD
- **SCO** 24KBD, 21° API
- **Pitch** 6KBD

### Visbreaker-based plant

- **Bitumen** 30KBD, 8° API
- **Visbreaker** 30KBD
- **SCO** 30KBD, 11° API

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### Results of Economic Comparison

<table>
<thead>
<tr>
<th>Relative Index of CAPEX and Net Margin</th>
<th>SCW Cracking</th>
<th>Coker (30KBD)</th>
<th>Coker (60KBD)</th>
<th>Visbreaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPEX</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Net Margin</td>
<td>100</td>
<td>75</td>
<td>75</td>
<td>100</td>
</tr>
</tbody>
</table>

| IRR [%] | 10.0 | 5.5 | 8.5 | 8.3 |

- **Capacity**: 30,000BPD of Bitumen (8°API)
- **CAPEX** includes on-site facilities, utility facilities, power plant, off-site facilities and owner cost.
- In the case of Coker (60KBD) above, its CAPEX is estimated at half of that of whole plant.
Summary of Economic Evaluations

- SCO value of SCW cracking was higher than other thermal operations because of lower density and higher liquid yield.
- Pitch from SCW is more valuable than solid coke, as Pitch is usable as boiler fuel oil for SAGD Boiler.
- Lower capital cost due to simple process
- Lower plant complexity without crude distillation columns and hydro-finishing process
- Lower operating cost without consumption of hydrogen and catalyst

Economic efficiency of SCW cracking-based plant has proved to be higher than that of D. Coker- or Visbreaker-based plant
### SCW

#### Simple, Clean, minimal Waste

<table>
<thead>
<tr>
<th></th>
<th>SCW (30KBD)</th>
<th>D. Coker (30KBD)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Foot Print</strong> (excl. Tank Yard)</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td><strong>Solid Waste</strong> (By-Product)</td>
<td><img src="image3.png" alt="Sulfur" /> 1</td>
<td><img src="image4.png" alt="Sulfur" /> 12.5</td>
</tr>
<tr>
<td><strong>Energy Consumption</strong> (API 8° → 21°)</td>
<td><img src="image5.png" alt="Energy" /> 1</td>
<td><img src="image6.png" alt="Energy" /> 1.4</td>
</tr>
</tbody>
</table>

1. SCW: Simple, Clean, minimal Waste
2. D. Coker: Detailed Coker with Tank Yard.
~Acknowledgment ~

JGC Corporation owes JOGMEC (Japan Oil, Gas and Metals National Corporation) a great deal for this research.
“Energy”, “Environment”, “Engineering” for the quality of human life

Thank you for your kind attention!!

Tomoki Kayukawa
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Dr. Pedro Pereira-Almao

University of Calgary

Dr. Pereira-Almao received his PhD in Heterogeneous Catalysis from L'Université de Poitiers, France, in 1980; was Associate Professor with the Department of Chemical Engineering, at the Universidad de Los Andes, Venezuela from 1980 until 1987 and a visiting professor and postdoctoral fellowship at the University of California Berkeley-Lawrence Berkeley National Laboratory from 1987 through 1990. He worked for Venezuela’s national oil company (PDVSA) for 14 years, specializing in upgrading and heavy oils processing. In 2003, he was recruited by the University of Calgary as an Alberta Ingenuity Scholar and professor for the Schulich School of Engineering and is a cross-posted professor of Science and Engineering. Dr. Pereira-Almao is the author of more than 70 peer reviewed published articles with more than 20 invited international conferences, and 10 original patents. Fluent in Spanish (originally from Venezuela), English and French, he is currently Director of the Alberta Ingenuity Centre for In Situ Energy focusing research on mechanisms for in reservoir bitumen and heavy oils upgrading.

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ABSTRACT

Field/In Situ Upgrading: Beyond Dilution Limitations
For Today and Tomorrow

Pedro Pereira Alma
Catalysis for Bitumen Upgrading and Hydrogen Production
Schulich School of Engineering, University of Calgary

Ultra dispersed, sub micronic or nano sized catalysts and adsorbents (UDCAs) are an emerging technology with potential for generating breakthroughs for the oil industry. The navigability of these particles within liquid media makes their applicability extremely versatile. They can be sent either to reactors, pipelines, porous media and virtually everywhere dense liquids can permeate.

In principle, sub-micronic particles have higher intrinsic catalytic/adsorptive activity and a higher number of active sites exposed without the pore restrictions typical of conventional catalysts/adsorbents. UDCAs effectively contact heavy molecules within the reaction media, thereby increasing the percentage converted into cleaner, lighter molecules.

Our research group is addressing chemical and engineering challenges for the application of UDCAs to bitumen and heavy oil upgrading for both upstream and downstream processes. It has designed setups for reproducible, stable and reliable UDCAs preparation that will simplify the manufacturing process to enable unattended operation. Examples from our UDCAs reactivity database will be presented with specific emphasis on in-situ upgrading.

Research on reliable methods to assess the nature of the catalyst active species is underway in our group with particular emphasis on the interaction of these particles with the molecular environment of heavy oils. Findings will be presented on analytical advances related to identification of reaction pathways as well as on the dynamics of UDCAs agglomeration with temperature up to reaction conditions.

Due to the absence of pore plugging, UDCAs would keep site activity for much longer periods of time than conventional catalysts. Thus recycling UD-Cats to the reaction zone should be implemented to secure this advantage. This presentation will also focus on fluid dynamics simulation as a tool to produce original inexpensive methods for UDCAs separation, redispersion-reactivation and recycling.
Field/In Situ Upgrading: Beyond Dilution Limitations

For Today and Tomorrow

Dr. Pedro Pereira Almoo

Catalysts
Bitumen Upgrading and Hydrogen Production
On dilution

• Dilution may become unsustainable in the mid/short term
  1. Availability of light oils and naphtha decreasing
  2. Construction and maintenance of long distance diluent ducts expensive, environmentally risky
  3. Extreme acidity of some heavy oils is not solved by dilution and there is no magic chemistry thus far for it
  4. Heavy oils-light oils/Diluent blends stability may be an issue in some cases
Field/In Situ Upgrading: the solution? or a trouble to solve the troubles?

- Need to break the downscaling economical barriers
- Need to be simple yet sufficiently autonomous
- Need to be integrated to the HO exploitation, preferably bringing enhancements to it
Some facts

• Many medium/small HO reservoirs exploitations have no economical solution to overcome dilution
• Most HO reservoirs are richer in water than bitumen
• HOs richer in Vacuum Gas Oil than bitumen, the latter are richer in residue than HOs
• Acidity is typically higher in VGO than in residue
• Upgrading has focused on residues
An interesting feature

Acidity, API gravity and Sulphur Distribution of a Heavy Oil

S (wt%): TAN (mg KOH/g fraction)

API gravity

Distill. Fraction (C)

- Sulphur wt%
- Total Acid Number (TAN) mg KOH/g fraction
- API gravity
Until now

• Upgrading solutions have not considered transformation of VGO
• Most upgrading technologies are adaptations from refinery environments
• Refineries are mostly placed on industrialized areas with abundance of utilities and services
• Refineries have wide variety of transporting options and access to disposition alternatives
Rethinking heavy oils/bitumen upgrading (Field/In Situ)

- Field Upgrading should not tackle a large residue conversion [solids, stability of blends (asphaltenes)]
- Bitumen & low water-heavy oil reservoirs more suitable for in situ upgrading
- F/ISU processes should ensure stability of light products to secure pipeline acceptance (olefins)
- Should efficiently handle energy (heat)
  - Catalytic processing a good option for low energy requirements, but not conventional catalysts!
  - Heat Integrate with oil extraction activities
Challenges and Achievements

Field Upgraded oil

In Situ Upgraded oil

Surface upgrading

Bitumen/Heavy oils

WTI

0.3-3 hours

1-2 days

430-500°C

200-1800 psi

32-30 API

10-8 API

R_t T P
The Potential... For Hydroprocessing

Typical hydroprocessing behaviour of a vacuum residue for Venezuelan extra-heavy oil using a bimodal catalytic formulation

Catalyst: Ultradispersed transition metal sulphides and a coarse carbonaceous macroporous solid fraction (P. Pereira et al, Heavy Oils International Seminars, Petrobras-Cenpes, 2002)
Applying Catalytic Steam Processing to Athabasca VGO

The Potential... for Aquaprocessing

- Steam VHSV = 1 hr⁻¹
- Thermal Cracking
- Aquaprocessing
- Fixed bed cat, Deactivates fast
The Potential of Nanocatalysts for Heavy Oil Upgrading

‘bring the catalyst to the molecules not of the molecules to the catalyst’

Dispersed $\rightarrow$ Ultradispersed $\rightarrow$ Nanocatalysts
By simple geometrical calculations, assuming non porous particles

Assuming non porous particles with an initial diameter of 30 nm, the surface area ‘available’ varies little until the agglomerated particles have an approximate 90-100 nm diameter.

The smaller the initial particle diameter the higher the surface area but it declines faster due to agglomeration.

Since a distribution of particles diameter is always present therefore there is a distribution of surface area.
Controlled Synthesis of Nanocatalysts

The Potential… For Innovation

- Oxides Hydroxides
- Sulfides Sulfoxides
- Carbides Nitrides
- Reduced Metal
- Reverse Micelles
- Nano particles
- Liquid Crystals
- Direct Micelles
- Emulsions

Closer to large scale application
Unlocking the Potential of Nanocatalysts…

- So far, up-scaled demonstrations have not produced transformative results: No upgrading process based on ultradispersed catalysts have been commercialized.
- UD cats imply lower metallic contents to manufacture and, if the catalyst is recycled then there are even further reductions in purchased volumes.
- UD cats do not require ceramic or other massive supports that typically constitute 80+ % by weight, in conventional catalysts and involve significant manufacturing activity.

Thus, catalyst manufacturers have few business drivers to actively pursue ultra dispersed catalysts.
Chemical and Engineering Challenges for the Adoption of Nanocatalysts for Upgrading

1. Designing setups for reproducible, stable and reliable UD cats preparation and delivery
2. Building a nanocatalysts reactivity database
3. Identification of the nature and effective size of the catalyst active species
4. Control transport & fluid dynamics of nano-catalyst regarding navigability, un/desirable settling, reliable separation and recycling
5. Assessment of Nanocatalysts stability in terms of activity: The recycling advantage. But how to prove it at low cost?
Unlocking the Potential: Chemical and Engineering Challenges

Designing setups for reproducible, stable and reliable UD cats preparation both at lab scale and for industrial application

Simplifying manufacturing process to enable field test demonstrations and unattended operation
Unlocking The Potential: Chemical And Engineering Challenges

UD-cats reactivity database

Ni-W series

Co-Mo series

Toluene conversion rate (mol.g cat⁻¹.h⁻¹) x 10⁵

Ni/(W+Ni) atomic ratio

400 C

350 C

300 C

Toluene conversion rate (mol.g cat⁻¹.h⁻¹) x 10³

Co/(Co+Mo) atomic ratio

400 C

350 C

300 C
Scanning electron microscope images of particles produced in VR at 523 K (A) and HR at 498 K (B)
Case 1 (100% W, $C_{P0} = 1.1 \text{ mol/m}^3$)

Experiments

Modeling

$D_E = 3.5 \times 10^{-9} \text{ m}^2/\text{s}$
Critical Particle Size For Deposition Of Catalytic Particles (Moo$_3$) In Athabasca Bitumen

\[ \rho_p = 4500 \text{ kg/m}^3 \]
\[ D_E = 1 \times 10^{-9} \text{ m}^2/\text{s} \]
\[ C_0 = 100 \text{ mol/m}^3 \]
\[ Q_0 = 112.65 \text{ ml/min} \]
\[ L = 1.4 \text{ m} \]
\[ D = 1.75 \text{ in} \]

~ 250 nm
The Life Cycle Of A Nano Catalyst In The Oil Sands Porous Media

Reduced gravity, viscosity and contaminants → Upgraded Oil

Recovery

On-line catalyst preparation

Catalyst Recycle

Catalyst incorporation specific of EOR

Catalyst Fluid Dynamics Modeling for In-situ Conditions

PRODUCER

REACTIVITY @ INSITU CONDITIONS (Rec. process)
AKNOWLEDGEMENTS

• GRADUATED
  – MSc. ALEJANDRO VASQUEZ
  – MSc. JOHN THOMPSON
  – PhD HERBERT LORIA
  – MSc. GUSTAVO TRUJILLO
BIOGRAPHY

Hiroshi Toshima
Albemarle Corporation

Hiro Toshima worked for ExxonMobil Japan for 17 years and joined Albemarle Corporation (ex. Akzo Nobel) in 2004. Hiro’s specialty spreads wide range of process and catalyst developments in the petroleum refining industry. He is now in charge of Resid Hydroprocessing technologies, and is involved in the technology and business developments. He resides in the Netherlands with his family to work in the Amsterdam marketing headquarter.

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ABSTRACT

ENHANCED E-BED BOTTOMS UPGRADING
USING LATEST CATALYTIC TECHNOLOGY

H. Toshima, S. Mayo, Z. Sedlacek, T. Hughes, and M. de Wind
Albemarle Corporation

The heavy-oil upgrading impacts very much on the refinery profitability with the possible parameters of crude and product prices, conversion, yields, volume swell, and quality of the products. The Ebullated-bed process is one of the solutions for the effective primary upgrading with the heavy oils. Albemarle commercialized several E-bed catalysts since the 1970’s for the bottoms upgrading in low sediment and high hydrogenation operations.

The E-bed plant operation is focused on maximizing the VR conversion and throughput while keeping a certain product specification. However, frequently conversion increase is limited by the fouling problem caused primarily by the sediment in the product. Albemarle has tackled this tough subject through thoroughly characterizing the asphaltenes and sediments for in-depth understanding of oil chemistry and compatibility. With such deeper understanding, Albemarle succeeded in developing the improved E-bed catalytic technologies to extremely reduce the sedimentation in the products. The latest development involves both the patented catalyst-staging technology and the improved single catalyst application. Those technologies can achieve extremely low sediment and/or a higher HDS and CCR removal for greater bottom upgrading.

The author will present the oil chemistry and its based catalytic technology developed for the improved E-bed process performance.
Enhanced E-bed Bottoms Upgrading Using Latest Catalytic Technology

5th NCUT Upgrading and Refining Conference 2009

Business Drivers for Bottoms Upgrading

- Increasing Sour and Heavier Crudes
- Growing Unconventional Crudes
- Changing Product Demands
  - Dieselization
  - Lower Fuel Oil Demand
- Growing Imbalance of Fuel Oil Demand and VR Production
- Economic Incentives
- MARPOL Annex VI Revision
Increasing E-Bed Capacity

- **EBR (Ebullated-Bed Resid) process capacity has been extensively increased since the mid 1980’s**
- **Canada has the biggest EBR capacity**
Albemarle’s Vision for Heavy Oil Upgrading

• **Albemarle will be the leader in emerging heavy oil fuels technologies**
  - Leverage cutting-edge catalytic technologies for Oil Sands Bitumen upgrading in Canada
    - EBR and FBR Catalytic Technologies for Primary Upgrading
    - STARS™ and Nebula® Catalytic Technologies for Secondary Upgrading
EBR Fouling Mechanism

- Fouling in EBR units is predominantly caused by formation of a mesophase (asphaltene aggregate)
  - Foulants: Ash=5-20wt%, H/C=0.62-0.75, fa=0.84-0.94, MW=500-2,500, WAX molecular stacking parameters d_{002}/L_{c002}=3.5Å/60Å

- Controlling this mesophase formation is key

Polarized-light Microscopy (micron order)  SEM (sub-micron)  WAX (angstrom)
(a) Asphaltene in Product  (b) Foulant  (c) Foulant  (d) Molecular Stacking Model
Asphaltene Management

- Perform detailed characterization of the asphaltene molecules in the reactor
- Incorporate molecular structures into a database for catalytic design to reduce asphaltene and sediment
Albemarle’s EBR Catalyst Portfolio

Commercially Proven Sediment Reduction Technology
Value of Sediment Reduction Technology

- Higher Conversion and/or More Barrels
  - Higher conversion by up to 10 vol%
  - Margin increase by $10 – 20 million p.a. (@30kbd)

- Replacing Diluent by More VR-intake

- Extended Cycle Length

- Reduced Heat-Exchanger and Towers Cleaning Cost

- Reduced CAR (Catalyst Addition Rate)
Latest EBR Needs and Catalyst Development

- Recent industry operations favor higher CCR and Sulfur removal as well as improved sediment reduction.

- Albemarle has been developing new EBR catalyst technologies for higher HDCCR and HDS while further improving HDM and sediment reduction capacity.
  - **The first target is even lower sediment formation in severe operations with heavier and higher metals feedstocks.**
  - **The second target is higher HDCCR and HDS with constant low sediment formation.**
Catalyst Testing and Modeling
- Testing with streamlined pilot capacity
- Activity and stability
- Pore plugging
- Accessibility and stability
- Reactor kinetic model

Feed Characterization
- Feed source, diluent
- Distillation
- Contaminants (S, N, CCR, Ni, V, Na, Fe, Ca, Si, As)
- SARA composition
- MW distribution

Catalyst Design
- Component/molecule focus
- Pore architecture
- Surface activity
- Accessibility and stability

Process Conditions
- Process objectives
- P, T, scf/bbl, lhsv, recycles, CAR
- Catalytic/Thermal ratio
- Spent catalyst properties
Catalyst Development Protocol

**Feed Characterization**
- Distillation
- Contaminants
- SARA composition
- MW distribution

**Catalyst Design and Testing**
- Focus on specific components/molecules for performance selectivity
- Pore architecture and surface activity
- Testing with streamlined capacity
- Pore plugging, deactivation and accessibility
- Reactor kinetic modeling

- Distillation
- Contaminants
- SARA composition
- MW distribution

**Different VR-feeds**

- log (molecular size)
- Fraction

**Catalyst Effective. Factor 0.6**

- V-deposition in Extrudate
- Catalyst Effective. Factor 0.6
Development Approach

- **Sediment Reduction**
  - More focus on Asphaltene diffusion and reaction
  - Controlled hydrogenation for better oil compatibility

- **CCR and Sulfur Removal**
  - HDCCR and HDS improvements target primarily on Aromatics and Resin components
New Catalyst Development

- **KF 1316 for Lowest Sediment Formation**
Improved Oil Compatibility

- HDS (HDCCCR) and sediment reduction is a trade-off
- State-of-the-art pore architecture in KF 1312 and KF 1316 results in better performance selectivity
Summary of New Developments

- **KF 1312 – Strong Sediment Control Catalyst**
  - Improved HDAsp and sediment reduction
  - Valuable tool for heavy and high metals crudes, higher conversion-barrels, and longer cycle length
  - Proven successful commercial track record

- **KF 1316 – New Generation Sediment Control Catalyst**
  - Custom designed pore architecture and surface activity
  - Further enhanced HDAsp for lowest sediment formation
  - Extremely robust tool for processing much heavier and higher metals crudes in high severity operations
    - Higher conversion-barrels
    - Longer cycle length
    - Robustness for crude slate changes
Conclusions

- Canada is a leading country in commercial EBR upgrading
- Albemarle’s cutting-edge catalyst technologies help leverage Canadian Oil Sands Bitumen upgrading
- Albemarle has continuously developed a variety of improved EBR catalyst technologies
  - KF 1312 – Strong Tool for Sediment Control
  - KF 1316 – New Generation Sediment Control Catalyst
  - New Generation HDCCCR/HDS Catalyst – Will be emerged soon
- Albemarle is able to tailor EBR catalysts for customer specific needs utilizing our state-of-the-art catalyst design strategies
Frédéric Morel

Axens

Frédéric Morel is working at Axens in the Technology Department as Product Line Manager for VGO and Resid Conversion. He was formerly Manager of Axens Hydroprocessing and Conversion Technical Services. He has 30 years of experience in oil refining, having worked previously with IFP Lyon Development Center as Research Engineer, as Project Leader of Distillates and Residues Hydroprocessing and as Development Department Manager. He holds a degree in Chemical Engineering from Ecole Supérieure de Chimie Industrielle de Lyon and a Graduate Degree from Institut d'Administration des Entreprises.

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“HDHPLUS®/SHP: Heavy Residue Hydroconversion Technology”

Frederic Morel
Axens

Integration of HDHPLUS® vacuum residue slurry technology with Sequential Hydro-Processing (SHP) of primary hydrocracked products was demonstrated within the Axens, IFP and Intevep / PDVSA Alliance. The integrated process allows achieving almost full conversion of heavy and refractory residues into valuable ultra high quality and ultra low sulphur transportation fuels with a yield in excess of 100 vol%.

HDHPLUS®/SHP technologies have gone through extensive bench unit validation procedures in view of the 50,000 BPSD commercial plant at the refinery of Puerto La Cruz (RPLC), Venezuela, to be started up in 2012.

The presentation reviews:

- the HDHPLUS 10 B/D process demo unit operation, at INTEVEP, used to support the industrial projects and for the production of effluent for the downstream SHP processing,

- the SHP 0.3 B/D bench unit operations, at IFP’s Lyon, France research center and the final product yields and qualities obtained.

The test results effectively demonstrate the expected RPLC deep conversion commercial unit performances and fully secure its design basis.

The presentation also describes the industrial deep conversion RPLC project status.
HDHPLUS® / SHP:
A technological option for deep conversion of heavy and extra-heavy crude oil

G. Rivas, C. Canelon (PDVSA / Intevep)
F. Morel (Axens)
H. Dulot, A. Quignard (IFP)

5th NCUT Upgrading and Refining Conference
14-16 September 2009, Edmonton, Canada
• HDHPLUS®/SHP technology

• RPLC deep conversion project

• HDHPLUS® pilot test run

• SHP pilot test runs (EU & US market oriented)
HDHPLUS®/SHP process overview

- Seamless SHP integration
- HQ marketable products
- Resid-free sweet product
HDHPLUS® catalyst

- Soluble in vacuum residue
- Very low concentrations needed
- Based on thiomolybdate chemistry fundamentals
- Fully scalable formulation
HDHPLUS® performance

- Total Pressure (bar): 170 - 200
- \( \text{H}_2 \) Partial Pressure (bar): 125 - 150
- Reaction Temperature (°C): 440 - 470
- Space Velocity LHSV (h\(^{-1}\)): 0.4 - 0.7
- Treating-gas/Feed Ratio (N\(\text{v}/\text{v}\)): 600 - 700

Conversión vs. Temperatura

VR conversion (wt\%) vs. Temperature

- P-310 Zuata
- P-310 Merey-Mesa
- P-340 Coctel
- P-340 Merey-Mesa
- P-340 Athabasca
- P-340 Zuata

HDHPLUS®/SHP - 5\textsuperscript{th} NCUT Upgrading and Refining Conference 2009
Slurry hydrocracking reactor testing

- 0.3 BPD Plant (Venezuela) 12000 Hours
- 3 BPD Plant (Germany) 3000 Hours
- 10 BPD Plant (Venezuela) 5000 Hours
- 150 BPD Plant (Germany) 7200 Hours

Cold reactor modeling

- Small scale (0.3, 0.6 and 1.2 m Diam.)
- Commercial size model (2.5 m Diam.)
• HDHPLUS®/SHP technology

• RPLC deep conversion project

• HDHPLUS® pilot test run

• SHP pilot test runs (EU & US market oriented)
RPLC deep conversion project challenge

Current situation:
1.2 MBD - 22-28 °API (CRP, ELP, PLC)
0.6 MBD - 8 °API (Jose upgraders)
• Decrease API diet to 21°API
• Increase Xtra Heavy Oil processing to 170 KBD
• Increase distillate output to 180 KBD
RPLC deep conversion project

• Refining scheme
  • Crude: 170 MBD 16 °API Merey + 40 MBD 40 °API SB
  • HDHPLUS®: 50 KBD VR
  • SHP: 100 KBD HDHPLUS® product + SR VGO

• Project schedule
  • June 2009: Construction start-up
  • Fall 2012: Project start-up
RPLC deep conversion project schedule

- **PDP**
- **FEED**
- **DETAILED ENGINEERING**
- **PROCUREMENT**
- **CONSTRUCTION**
- **PURCHASE ORDERS**
- **RX ON SITE CONST**
- **Startup**
Deep conversion EU market oriented
Maxi Diesel, Cetane > 51, high quality VGO
Deep conversion US market oriented
Cetane > 45, VGO to FCC

SR AGO/VGO

≈20%

H₂

LPG

LN
HN
Jet
AGO

AD

VGO to FCC

HDH PLUS

VR

H₂

flakes

500°C -

500°C +

≈80%

HPHT sep

SHP
• HDHPLUS®/SHP technology

• RPLC deep conversion project

• HDHPLUS® pilot test run

• SHP pilot test runs (EU & US market oriented)
HDHPLUS® pilot test run

- Simulate RPLC industrial project design for HDHPLUS® section
- Achieve >80 wt% conversion on 500°C+ VR
- Test for performance with Merey-Mesa as reference feedstock (820 H)
HDHPLUS® pilot process scheme

PDVSA INTEVEP pilot plant unit: 10 B/D
### VR Feed analysis & material balance

#### MERÉY- MESA (53/47) VR  P340 FEED

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity</td>
<td>5.0</td>
</tr>
<tr>
<td>Viscosity @ 212°F (cSt)</td>
<td>19000</td>
</tr>
<tr>
<td>Asphaltene (IP-143) (%wt)</td>
<td>19.3</td>
</tr>
<tr>
<td>Microcarbon (%wt)</td>
<td>21.7</td>
</tr>
<tr>
<td>Total Nitrogen (%wt)</td>
<td>0.76</td>
</tr>
<tr>
<td>Sulfur (%wt)</td>
<td>3.28</td>
</tr>
<tr>
<td>Carbon (%wt)</td>
<td>84.3</td>
</tr>
<tr>
<td>Hydrogen (%wt)</td>
<td>11.06</td>
</tr>
<tr>
<td>Vanadium (wppm)</td>
<td>432</td>
</tr>
<tr>
<td>Nickel (wppm)</td>
<td>104</td>
</tr>
</tbody>
</table>

#### HDHPLUS Products Yield (%wt)

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>13.5</td>
</tr>
<tr>
<td>Mid distillates</td>
<td>22.5</td>
</tr>
<tr>
<td>VGO</td>
<td>43.1</td>
</tr>
<tr>
<td><strong>Distillates</strong></td>
<td><strong>79.1</strong></td>
</tr>
<tr>
<td>C1-C4</td>
<td>5.4</td>
</tr>
<tr>
<td>C5+</td>
<td>0.3</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.9</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Gas</strong></td>
<td><strong>7.7</strong></td>
</tr>
<tr>
<td><strong>Flakes</strong></td>
<td><strong>13.2</strong></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

(includes H₂ consumption)
• HDHPLUS®/SHP technology

• RPLC deep conversion project

• HDHPLUS® pilot test run

• SHP pilot test runs (EU & US market oriented)
2 SHP pilot test runs performed in IFP

• Feed = blend of HDHPLUS® 500°C- product + SR VGO at two different ratio

• Simulate SHP section for RPLC industrial project design
  • maxi distillate and maxi cetane >51, EU market type

• Simulate SHP section for ELP type project design
  • cetane >45, Mild HCK resid to FCC, US market type,

• Validate product quality & yields

• Validate HDHPLUS®/SHP integration
**IFP pilot plant unit:**
- 2 x 1L reactor, upflow, isothermal
- Interstage sampling
- 2 gas analyses
- N\textsubscript{2} Stripper

![Diagram of IFP pilot plant unit]

**Feed**

\[ \text{Cold water} \rightarrow \text{H}_{2}\text{S+NH}_{3}+\text{N}_{2} + \text{C1-C6} \]

\[ \text{Liquid effluent} \]

**R1** Pretreat.\ cat.

**R2** HCK cat.

**HP** sep

**LP** sep

**Stripper**
IFP pilot plant unit:
- 1 x 1L reactor, upflow, isothermal
- gas analyses
- N₂ Stripper
### Example of SHP material balances

<table>
<thead>
<tr>
<th></th>
<th>Feed EU Market (RPLC)</th>
<th>HDT/HCK EU Market (1)</th>
<th>Feed US Market</th>
<th>HDT US Market (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁-C₄+H₂S+NH₃</td>
<td>wt %</td>
<td>2.4</td>
<td>4.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Naphtha</td>
<td>wt %</td>
<td>21.8</td>
<td>5.6</td>
<td>7.9</td>
</tr>
<tr>
<td>Jet</td>
<td>wt %</td>
<td>37.3</td>
<td>11.3</td>
<td>13.6</td>
</tr>
<tr>
<td>Diesel</td>
<td>wt %</td>
<td>28.9</td>
<td>18.4</td>
<td>22.2</td>
</tr>
<tr>
<td>VGO</td>
<td>wt %</td>
<td>64.6</td>
<td>8.0</td>
<td>64.7</td>
</tr>
<tr>
<td>Total Liquid</td>
<td>wt %</td>
<td>100</td>
<td>96.0</td>
<td>96.9</td>
</tr>
<tr>
<td>Net VGO Conv</td>
<td>wt%</td>
<td>84</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

*Example of SHP material balances (1) Yields include H₂ consumption*
SHP product quality for EU type market

- Naphtha: extra low N & S content, very high Naphthene (60-70%) content, excellent reforming feedstock
- Jet A1: excellent smoke point > 25 mm, low freezing point < -47°C
- ULS Diesel: < 10 ppm S, Cetane N° > 55, excellent Cold Flow properties (CP < -20°C)
- Extra high quality VGO: %H > 14.5%, no aromatics nor resins, extra low S & N content
- High VI (100-120) Dewaxed VGO suitable for lubes
SHP product quality for US type market

- Naphtha: high Naphthene content (40-45%), excellent reforming feedstock after HDT (N & S compounds removal)
- Jet A1: very good smoke point > 20 mm, low freezing point < -47°C
- Diesel: Cetane N° > 43, excellent Cold Flow properties
- VGO excellent feedstock for FCC: %H ≈ 13%, high saturate content (> 60%), low S & N content,
Highlights

• Full validation of integrated HDHPLUS®/SHP technologies before RPLC 50 kBPSD start-up in 2012

• HDHPLUS®/SHP pilot test runs demonstrated expected RPLC commercial unit performances

• Full conversion of refractory residues into ultra high quality fuels with > 100% liquid yield:
  • in a maxi mid-distillates & high Cetane EU configuration
  • or USA market oriented using a FCC unit
BIOGRAPHY

Jan Verstraete
IFP-Lyon

Jan Verstraete is a Senior Research Engineer at the Industrial Development Center of the French Petroleum Institute (IFP). He holds a M.S. degree in Chemical Engineering from the University of Ghent (Belgium) and a Ph.D. from the same university, where he studied the kinetic modeling of catalytic reforming under the supervision of Prof. dr. Gilbert Froment.

He joined the IFP-Lyon research center in 1994, where he worked on the kinetic and process modeling of various refining processes, amongst which are catalytic reforming, gas oil hydrotreating and Fluid Catalytic Cracking. In 1999, he became FCC R&D program manager, a position where he is in charge of directing the FCC research team and planning the R&D program pertaining to IFP’s activity in the field of FCC. Concurrently, he continued his basic research through the supervision of several PhD. theses. From 2004 onwards, he has been involved in the R&D process development on fixed-bed hydrotreating of residue feeds and leading the R&D process development on ebullated-bed hydrocracking of residue feeds.

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ABSTRACT

Reactivity of Athabasca Residue and of Its SARA Fractions during Residue Hydroconversion

P. Danial-Fortain\textsuperscript{a}, T. Gauthier\textsuperscript{a}, I. Merdrignac\textsuperscript{a}, J. Verstraete\textsuperscript{a}, H. Budzinski\textsuperscript{b}

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\textsuperscript{b} ISM-LPTC, UMR CNRS 5255, Université Bordeaux 1

Due to a declining market for residual fuel oil and an increasing demand for middle distillates and motor fuels, residue conversion processes are becoming increasingly more important. At the same time, the conventional crude oil resources slowly decline and are being replaced by non-conventional extra-heavy crude oils and tar sand bitumen. Hence, more and heavier residue fractions need to be upgraded to lighter fractions. Among the various processes, ebullated-bed hydroconversion is a commercially proven technology that has the unique feature of deeply converting heavy feedstocks with high amounts of impurities, while operating with a long cycle time and maximizing liquid yields. Indeed, this process allows to convert atmospheric or vacuum residues under severe temperature (up to 440 °C) and liquid hourly space velocity (LHSV) conditions (in the range of 0.15 to 0.5 h\textsuperscript{-1}). In these conditions, a 540°C+ conversion of up to 80 wt\% can be reached. However, only little knowledge is available regarding the mechanisms involved in the process.

At IFP-Lyon, a large-scale ebullated-bed bench unit is used to study residue hydroconversion and investigate the impact of operating conditions and feed properties on yields and product qualities. The bench unit consists of an arrangement of two ebullated-bed reactors of 2.2 liters in series, operating at high pressure (150-200 bars) and high temperature (400-440°C). Hydrogen is added to the feed in order to keep a high hydrogen partial pressure and favor the catalytic hydroconversion reactions. Hydroconversion runs were also conducted in a small-scale batch reactor using a 300 mL autoclave. In a typical test, the reactor was charged with 50 g of feedstock and 0.45 g of crushed equilibrium industrial NiMo catalyst, pressurized with hydrogen in excess and quickly heated at the reaction temperature.

In this paper, we first discuss the conversion of Athabasca SAGD vacuum residue in the large-scale pilot plant and in the small scale batch reactor. The effect of operating temperature and space velocity is investigated. To better understand the conversion mechanisms and reactivities, it was decided to study the reactivity of the Athabasca SAGD SARA (Saturates, Aromatics, Resins and Asphaltenes) fractions separately. Hence, it was necessary to recover each of the SARA families at a preparative scale (approximately 1 kg). These fractions were recovered separately in a 60 L deasphalting batch reactor by means of a dedicated protocol that is based on several liquid-liquid separations operated in series with a n-paraffinic solvent. Three different families have been obtained, called Asphalt C7, Resins C3 and DARO C3. They are respectively
ABSTRACT

enriched in C7-asphaltenes, resins, and saturates and aromatics. The Athabasca SAGD feed, the different families and the SARA fractions have been extensively analyzed in terms of standard petroleum analyses, SARA fractionation, Elemental Analysis (EA), Size Exclusion Chromatography (SEC), and 13C NMR.

Hydroconversion experiments have been performed at different severities in the batch unit, varying reaction temperature and reaction time on Athabasca Vacuum Residue and on the various families (DARO C3, Resins C3 and Asphalt C7). The results on the Athabasca Vacuum Residue obtained in the small scale batch reactor were compared to those obtained with the continuous large-scale bench unit. Similar trends are observed. The results obtained with the different Athabasca fractions clearly show that reactivity of Athabasca is related to the SARA fraction of the residue. Since, from one residue to another, the main differences in composition are related to SARA composition, our study suggests that, based on SARA composition of residue, it is possible to estimate the reactivity of a given residue with respect to conversion.
Reactivity of Athabasca Residue and of Its SARA Fractions during Residue Hydroconversion

P. Danial-Fortain, T. Gauthier, I. Merdrignac, J. Verstraete, H. Budzinski

IFP–Lyon, France
University Bordeaux 1, France
Outline

- Introduction
- Feedstock characterization
- Production of fractions with different SARA compositions
- Hydroconversion experiments
- Conclusions
Asphaltenes

- Petroleum residues contain several thousand of species of varying composition, structure and polarity.
- Asphaltenes are the most polar compounds of the residue and precipitate in the presence of light apolar solvents.

Many challenges are linked to asphaltenes

- Reactivity of large asphaltene structures/aggregates
- Catalyst deactivation
- Sediment formation and stability of the conversion effluents
Challenges of Residue Upgrading

Upgrading approaches

- Removal of asphaltenes
  - Solvent DeAsphalting
  - Coking

- Conversion of asphaltenes
  - High temperature
  - High hydrogen partial pressure
  - Hydrogenation catalyst with a low acidic support

Operating challenges in hydroconversion

- Reaction exothermicity
- Metals deposit on catalyst
- Stability of converted effluents
Objectives of this R&D Study

■ Objectives
  ■ Study the effects of feed composition on reactivity
  ■ Provide a better understanding of the hydroconversion reaction mechanisms

■ Strategy
  ■ Characterize several feedstocks and their SARA fractions in terms of molecular size distribution, elemental analysis, NMR, ...
  ■ Prepare feeds with different SARA compositions
    Separation of residue by polarity in SARA fractions at a preparative scale (kg) by means of consecutive deasphalting steps
  ■ Carry out hydroconversion experiments in a batch reactor of the initial residue of the various fractions of the residue
Outline

- Introduction
- Feedstock characterization
- Production of fractions with different SARA compositions
- Hydroconversion experiments
- Conclusions
Analytical procedure for feeds, SARA fractions and effluents

Feedstocks
- Naphtha (IBP-220°C)
- Gas Oil (220-375°C)
- VGO (375-520°C)
- VR (520°C+)

Effluents
- Detailed composition
  - Mass spectrometry
  - Chromatography
  - SEC
  - MW
  - 13C NMR
  - Elemental analysis
    - C, CH, CH₂, CH₃
    - Cq,sub, Cq,cond
    - C, H, S, N, O, Ni, V

Liquid
- Density
- Viscosity
- SimDist
- Elemental analysis
  - C, H, S, N, O, Ni, V

Gas
- Chromatography
- Detailed composition
- Gas
- Gas Chromatography

Preparative Distillation
- Detailed composition
- Gas Chromatography

SAR Liquid Chromatography
- Detailed Composition
  - Sat
  - Aro
  - Res

Detailed composition
- Gas
- Gas Chromatography

SARA Liquid Chromatography
- Detailed Composition
  - Sat
  - Aro
  - Res
  - Asp
Analytical Characterization

- **Molecular size distribution, average molecular weight**
  - Size Exclusion Chromatography *(Waters 150CV+ with RI detector)*
    - Molecular Weight (eq. PS) confirmed with SEC - MS coupling *(APCI ionization source)*

- **Chemical structure of asphaltenes**
  - Elemental analysis *(C, H, N, O, S)*
  - $^{13}$C NMR *(Spin Echo Technique + Attached Proton Test)*
    - aliphatic carbon *(CH$_3$, CH$_2$, CH, C$_q$)*
    - aromatic carbon *(CH, C$_q$,sub, C$_q$,cond)*
    - substitution index
    - condensation index: peri-condensed and cata-condensed rings
$^{13}$C NMR Terminology

Classification of the carbon atoms

**46 Total saturated carbon**
- 2 Quaternary carbon
- 5 CH carbon
- 26 CH$_2$ carbon
- 13 CH$_3$ carbon

**54 Total aromatic carbon**
- 38 Quaternary carbon
- 22 Fused quat. carbon
- 16 Substituted quat. carbon
- 16 CH carbon
## Properties of VR feedstocks

<table>
<thead>
<tr>
<th>Feed</th>
<th>Athabasca</th>
<th>Ural</th>
<th>Duri</th>
<th>Arabian Light</th>
</tr>
</thead>
<tbody>
<tr>
<td>d 4,15</td>
<td>1.044</td>
<td>1.003</td>
<td>0.964</td>
<td>1.022</td>
</tr>
<tr>
<td>Viscosity (cSt)</td>
<td>14563</td>
<td>540</td>
<td>396</td>
<td>964</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>82.68</td>
<td>85.00</td>
<td>86.24</td>
<td>84.22</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>9.86</td>
<td>10.60</td>
<td>11.39</td>
<td>11.34</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>6275</td>
<td>5800</td>
<td>5934</td>
<td>4011</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>5.74</td>
<td>2.72</td>
<td>0.58</td>
<td>4.22</td>
</tr>
<tr>
<td>Ni + V (ppm)</td>
<td>431</td>
<td>220</td>
<td>76</td>
<td>125</td>
</tr>
<tr>
<td>Saturates (wt%)</td>
<td>6.8</td>
<td>11.7</td>
<td>21.0</td>
<td>11.6</td>
</tr>
<tr>
<td>Aromatics (wt%)</td>
<td>31.2</td>
<td>46.1</td>
<td>28.6</td>
<td>48.6</td>
</tr>
<tr>
<td>Resins (wt%)</td>
<td>42.1</td>
<td>36.1</td>
<td>36.8</td>
<td>31.3</td>
</tr>
<tr>
<td>Asphaltenes (wt%)</td>
<td>14.1</td>
<td>4.6</td>
<td>5.7</td>
<td>7.7</td>
</tr>
<tr>
<td>MW by SEC (g/mol in eq. PS)</td>
<td>5778</td>
<td>2689</td>
<td>4931</td>
<td>2966</td>
</tr>
</tbody>
</table>

- **Differences in chemical composition**
- **Differences in SARA distribution**
## Properties of SARA fractions

### Example of the resins

<table>
<thead>
<tr>
<th>Feed resins</th>
<th>Athabasca</th>
<th>Ural</th>
<th>Duri</th>
<th>Arabian Light</th>
</tr>
</thead>
<tbody>
<tr>
<td>13C NMR (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caro total</td>
<td>36.90</td>
<td>37.20</td>
<td>33.70</td>
<td>41.00</td>
</tr>
<tr>
<td>CH</td>
<td>29.27</td>
<td>33.87</td>
<td>29.67</td>
<td>31.71</td>
</tr>
<tr>
<td>C_q</td>
<td>70.73</td>
<td>66.13</td>
<td>70.33</td>
<td>68.29</td>
</tr>
<tr>
<td>C_qsub</td>
<td>39.30</td>
<td>35.75</td>
<td>34.42</td>
<td>37.80</td>
</tr>
<tr>
<td>C_qcond</td>
<td>31.44</td>
<td>30.38</td>
<td>35.91</td>
<td>30.24</td>
</tr>
<tr>
<td>Cali total</td>
<td>63.10</td>
<td>62.80</td>
<td>66.30</td>
<td>59.00</td>
</tr>
<tr>
<td>CH_3</td>
<td>20.13</td>
<td>18.15</td>
<td>13.57</td>
<td>22.20</td>
</tr>
<tr>
<td>CH_2</td>
<td>59.59</td>
<td>65.29</td>
<td>72.85</td>
<td>58.31</td>
</tr>
<tr>
<td>CH</td>
<td>18.38</td>
<td>16.56</td>
<td>13.57</td>
<td>19.49</td>
</tr>
<tr>
<td>MW by SEC (g/mol in eq. PS)</td>
<td>4695</td>
<td>2676</td>
<td>5628</td>
<td>3609</td>
</tr>
</tbody>
</table>

- Similar SAR average hydrocarbon structure
- Average MW in the same range
Feedstocks properties

Conclusions

- SAR fractions
  - Represent 85 to 95 wt% of the residue
  - Exhibit similar structures, *whatever the geochemical origin*

- Asphaltenes
  - Present differences in size

  *Feed reactivity ↔ SAR distribution*

- Selected feedstock: Athabasca VR
  - Industrial interest
  - High content of resins and asphaltenes
Outline

- Introduction
- Feedstock characterization
- Production of fractions with different SARA compositions
- Hydroconversion experiments
- Conclusions
SDA batch unit
SDA batch unit
SDA batch unit
Athabasca VR fractionation at a preparative scale

- Dedicated protocol
  - Successive liquid-liquid extractions
  - Polarity separation

Results: SARA composition

<table>
<thead>
<tr>
<th>Athabasca VR</th>
<th>S (wt%)</th>
<th>A (wt%)</th>
<th>R (wt%)</th>
<th>As (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7</td>
<td>31</td>
<td>48</td>
<td>14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>n-C7 deasphalting</th>
<th>Asphalt C7</th>
<th>DAO C7</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 steps 220 °C</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>1 step 220 °C</td>
<td>1</td>
<td>41</td>
</tr>
<tr>
<td>4 steps 220 °C</td>
<td>42</td>
<td>50</td>
</tr>
<tr>
<td>2 steps 220 °C</td>
<td>57</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>n-C3 deresining</th>
<th>Resins C3</th>
<th>DARO C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 steps 60 °C</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>3 steps 60 °C</td>
<td>28</td>
<td>58</td>
</tr>
<tr>
<td>3 steps 60 °C</td>
<td>72</td>
<td>22</td>
</tr>
<tr>
<td>3 steps 60 °C</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Outline

■ Introduction

■ Feedstock characterization

■ Production of fractions with different SARA compositions

■ Hydroconversion experiments

■ Conclusions
Experimental protocol

- **Autoclave batch unit (300 mL)**

  - **Feedstock**: 50.0 g
  - **395 °C < T°C < 420 °C**
  - **Reaction time = 2 h**
  - **Initial H₂ pressure = 150 bar**
  - **Catalyst**
    - With crushed spent NiMo/Al₂O₃ catalyst: 0.45 g
    - Without catalyst: at 395 °C

  ![](diagram.png)

  - **Solubilization**
  - **Filtration step**
  - **Toluene removal by distillation at 150 °C**

  ![](diagram.png)

**Product analysis**

<table>
<thead>
<tr>
<th></th>
<th>IBP-150</th>
<th>150 °C+</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₄,₁₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S, Ni, V</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Reactivity results
Residue X520 °C+ conversion

- Continuous increase of conversion with temperature
- Slight increase of residue conversion without catalyst

Reactivity results

Hydrogen consumption (a) and Gas production (b)

- Lower hydrogen consumption without catalyst
- Hydrogen consumption related to
  - Liquid hydrogenation
  - HDS, HDN, HDM

- Gas yield
  - Continuous increase with residue conversion
  - Low catalyst effect on gas formation
Reactivity results
Product yield selectivity

- VGO (375-520 °C) = intermediate product
Reactivity results
Product yield selectivity

- VGO (375-520 °C) = intermediate product
- Cracking reaction mechanisms probably not affected by the presence of a catalyst
Outline

- Introduction
- Feedstock characterization
- Production of fractions with different SARA compositions
- Hydroconversion experiments
- Conclusions
Conclusions

- **Overall analytical data of feeds**
  - in terms of SARA distribution and chemical analyses are different from one feed to another
  - BUT chemical structure of SAR fractions are similar and asphaltenes present specific aggregation properties

  Feed reactivity $\leftrightarrow$ SAR distribution

- **Hydroconversion experiments**
  - Cracking reactions thermally initiated
  - Catalyst impacts conversion levels
  - Catalyst probably does not affect cracking reaction mechanisms
  - Proposed conversion mechanism
    - VR $\rightarrow$ lighter products (VGO, Gas Oil, Naphtha, Gas)
    - VGO = intermediate $\rightarrow$ lighter cuts
Reactivity of Athabasca Residue and of Its SARA Fractions during Residue Hydroconversion

P. Danial-Fortain, T. Gauthier, I. Merdrignac, J. Verstraete, H. Budzinski

IFP–Lyon, France
University Bordeaux 1, France
BIOGRAPHY

Sim Romero
KBC Advanced Technologies, Inc.

Sim Romero, Principal Consultant for KBC Advanced Technologies, Inc., has over 30 years experience in Heavy Oil Processing, and he is a specialist in Delayed Coking. Mr. Romero has worked in the area of delayed coking for several major oil companies (ConocoPhillips, BP Oil, ARCO, ExxonMobil and Valero), where he directed numerous expansion and optimization programs. As the Delayed Coking Technical Manager at Bechtel, he oversaw the construction of four grass roots delayed coker units. Mr. Romero’s expertise ranges from heavy oil thermal kinetic model development to startup, trouble shooting and general operations of delayed coker units.

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Fax: +1 281 616 0900
Email: sromero@kbcat.com
Website: www.kbcat.com
Comparison of Thermal Cracking and Hydro-Cracking Yield Distributions

Sim Romero and Scott Sayles
KBC Advanced Technologies, Inc.

Bitumen upgrading is challenging. In the current economic climate operators of upgraders are faced with obtaining the maximum performance from existing equipment. The existing equipment is typically operating at the upper end of the design envelope and performance is pushed to the limits of the constraining equipment. The typical major constraint is the primary upgrader processes, coking or hydrocracking. Funding for new equipment to remove the constraints is difficult to obtain at the current time and economic conditions. However, by understanding of the fundamental kinetics in thermal cracking and hydrocracking provides insights into the operational changes that can be made to optimize unit performance.

This paper will briefly review the yield distribution differences between thermal cracking and hydrocackering. The goal is to compare yields, product quality distributions and the elemental balances. Once these basic components to the unit operation are understood, the opportunities to increase production and improve performance can be analyzed quantitatively within the existing unit equipment limits.
Comparison of Thermal Cracking and Hydro-Cracking Yield Distributions

Sim Romero  
Principle Consultant

Scott Sayles  
VP Process Consulting Americas
Contents

- Introduction
- Kinetics in thermal cracking and hydrocracker
- Yields comparison
- Carbon and hydrogen balance
- Sulfur and nitrogen balance
- Product stream summary comparison
- Conclusions
Introduction

• Goals is to obtain the maximum performance from existing equipment.

• Existing equipment is typically:
  – Operating at the upper end of the design envelope
  – Performance is pushed to the limits of the constraining equipment.
  – Typical major constraints are the primary upgrader processes:
    ▪ coking or hydrocracking.
  – Funding for new equipment to remove the constraints is difficult to obtain at the current time and economic conditions.

• Understanding of the fundamental kinetics in thermal cracking and hydrocracking provides insights into the operational changes that can be made to optimize unit performance.
Generic Coker

- Delayed Coker Reactions Consist of Cracking and Polymerization
KBC Kinetic Model: RDS-SIM

- Design Screen from DC-SIM
KBC Kinetic Model: RDS-SIM

- Design Screen from RDS-SIM
Kinetics

• Conversion
  – Both coking and hydrocracking use thermal cracking to convert residua
  – Hydrocracking injects hydrogen which short circuits the polymerization or condensation reactions – hydrogen approach
  – Delayed Coking allows polymerization or condensation – a carbon rejection approach
Kinetics: Hetero-Atom Removal

- Downflow Desulfurization Example
  - Oil and gas residence times
  - Catalyst activity varies with time

- Catalyst deactivation increases due to feed contaminants
- HDS is a function of catalyst activity
**Yield Comparison: Basis**

- **Feedstock**
  - Typical Athabasca Bitumen
  - SAGD produced
  - Diluent Removed
  - Bitumen is cut first in a Vacuum Unit

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>Bitumen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Method</td>
<td></td>
<td>SAGD</td>
</tr>
<tr>
<td>% Diluent in Blend</td>
<td>v%</td>
<td>0</td>
</tr>
<tr>
<td>w%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>API</td>
<td>w%</td>
<td>9.0</td>
</tr>
<tr>
<td>Elemental Analysis, Dry</td>
<td>w%</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>w%</td>
<td>84.1</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>4.6</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Metals</td>
<td>wppm</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>wppm</td>
<td>60</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>170</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>Oxygen</td>
<td>w%</td>
<td>0.8</td>
</tr>
<tr>
<td>Total</td>
<td>w%</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Yield Comparison: Basis

- Assumed a unit feed from a Vacuum Unit
  - 1,020°F residue cut point

<table>
<thead>
<tr>
<th></th>
<th>Whole Bitumen</th>
<th>Gas Oil</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol%</td>
<td>100.00%</td>
<td>47.72%</td>
<td>52.28%</td>
</tr>
<tr>
<td>API</td>
<td>9.00</td>
<td>16.37</td>
<td>2.88</td>
</tr>
<tr>
<td>UOP K</td>
<td>11.33</td>
<td>11.40</td>
<td>11.27</td>
</tr>
<tr>
<td>MW</td>
<td>527</td>
<td>384</td>
<td>763</td>
</tr>
<tr>
<td>C/H wt</td>
<td>8.70</td>
<td>8.02</td>
<td>9.26</td>
</tr>
<tr>
<td>Sulfur Wt%</td>
<td>4.60%</td>
<td>3.45%</td>
<td>5.55%</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>4,000</td>
<td>2,299</td>
<td>4,756</td>
</tr>
<tr>
<td>MCC wt%</td>
<td>14.5%</td>
<td>1.1%</td>
<td>25.7%</td>
</tr>
<tr>
<td>Metals, ppm</td>
<td>530</td>
<td>207.75</td>
<td>776</td>
</tr>
</tbody>
</table>

- Operations
  - 100 KBPD
  - Coker + Equipment to make same sulfur as Hydrocracker
  - Ebullated Bed Hydrocracker + H2 plant
Yield Comparison: Basis

• Coking
  – Severe Thermal Conversion
  – Coker Drum in multiple pairs (i.e. 100,000 BPD unit will have 6 drums or 3 modules)
  – Target a 4 to 5 year run length with slowdowns for heater cleaning

• Hydrocracking
  – Moderate Conversion
  – Ebullated Bed, three reactors
  – Catalyst Addition
  – Target a three year run length
Yield Comparison: Comparison

A mass comparison shows the yields are very similar.
Sulfur Balance

- In the Delayed Coker, sulfur mostly reports to the coke and H2S
- Liquid products have ~25% of the total sulfur

- In the Hydrocracker, sulfur mostly reports to H2S for obvious reasons
- Products have very little sulfur - liquid products (C5 to 1000°F) have ~5% of the total sulfur
Nitrogen Balance

• Nitrogen mostly reports to the coke because nitrogen is concentrated in the asphaltenes
• Relatively small amounts of NH3 because there is no hydrotreating or free hydrogen reactions
• Nitrogen content is higher in the liquid products (approximately twice the hydrocracker)

Nitrogen mostly reports to the residual bottoms product. Nitrogen is concentrated in the asphaltenes and are difficult to hydrotreat.
• Nitrogen removal in the form of NH3 is significant in the hydrocracker
• Liquid products have far less nitrogen
Carbon and Hydrogen

• The Delayed Coker is a carbon rejection process
• Liquid products are still rich in carbon and are generally aromatic

• The Hydrocracker is a hydrogen in process but the carbon is still rejected to the heavy residual stream
• Carbon rejection (1000°F plus stream) is a function of conversion and catalyst life
• The Delayed Coker is a carbon rejection process with a high concentration of carbon leaving with the coke
• The hydrocracker injects hydrogen into the balance and both saturates the residual bottoms and removes sulfur and nitrogen from the liquid products
Yield Comparison Summary

- The hydrocracker yields are much less aromatic and have been hydrotreated.
- Coker products have reduced sulfur and nitrogen levels with the coke receiving a large potion of the contaminates - despite the lack of hydrogen and active removal of sulfur and nitrogen.

<table>
<thead>
<tr>
<th>Liquid Products</th>
<th>Delayed Coker</th>
<th>Hydrocracker</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>API Gravity</td>
<td>Wt% Sulfur</td>
</tr>
<tr>
<td>Naphtha(c5 - 400ºF)</td>
<td>62.5</td>
<td>0.5%</td>
</tr>
<tr>
<td>LCGO(400-650ºF)</td>
<td>28.3</td>
<td>2.1%</td>
</tr>
<tr>
<td>HCGO(650ºF plus)</td>
<td>13.5</td>
<td>3.7%</td>
</tr>
<tr>
<td>1000ºF plus residual</td>
<td>N/A</td>
<td>8.8%</td>
</tr>
</tbody>
</table>
Conclusions

- Delayed Coking and Hydrocracking are not competing processes
  - Most heavy oil streams must undergo multiple steps to produce finished products
  - The economics favor a multi-step process
  - Capitalize on the strengths of both processes
Conclusions

• Other issues can play in the analysis and economics
  – Conversion in the hydrotreater
  – Availability of hydrogen
  – Coke disposal – market value
  – Product margins (diesel vs. gasoline market)

• Selection of the process needed for a given refinery configuration is site specific and KBC can help.
Questions?
Nilanjan Brahma

EURECAT USA

Nilanjan has close to 20 years of experience in development and technical support involving hydroprocessing catalysts and catalyst sulfiding and preactivation. Nilanjan is currently the Business Manager for EURECAT’s global Nickel Sulfur Guard services that are utilized in trace sulfur removal from reformer and ISOM feeds. In addition to this there remains a strong involvement with R&D.

Prior to joining Eurecat France in 1992, Nilanjan worked in the hydroprocessing catalyst development group at AkzoNobel (now ALBEMARLE) in Amsterdam (NL). He holds a PhD from the University of Utrecht (The Netherlands) in heterogeneous catalysis and is co-author of numerous articles and patents in the field of catalyst regeneration and preconditioning.

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E-Mail: nbrahma@eurecat.com
ABSTRACT

CATALYST PREACTION USING EURECAT TOTSUCAT® CFP TECHNOLOGY

Randy Alexander, Jim Robinson, and Nilanjan Brahma
EURECAT US Inc. Houston TX

Activation of catalysts in commercial hydroprocessing units is typically done by injecting a sulfur containing compound such as DMDS, DMS, DMSO, or TBPS54 during the startup phase, or in some cases using sour gas or using the sulfur present in the feedstock. When sulfur containing chemicals are concerned, this will require a setup for injecting these into the reactor system and may raise potential HSE issues related to handling these hazardous chemicals. After the activation phase is complete, the catalyst is typically allowed to stabilize for 3-5 days on virgin feed prior to the introduction of cracked feed stocks. Introducing cracked stocks too early can cause irreversible catalyst activity loss due to excessive coke and gum formation.

EURECAT has developed a patented technology that allows the start up of a hydrotreating unit WITHOUT the introduction of the sulfur containing chemicals mentioned above. This ex-situ process, called TOTSUCAT®, ensures complete activation and sulfiding of the catalyst prior to loading in the reactor.

When TOTSUCAT is applied, the following benefits are generally observed:

- The formation of sour water is eliminated; as a rule of thumb, the quantity of sour water formed during startup with in-situ sulfiding is roughly equivalent to 10wt% of the catalyst as loaded.

- Potential exotherms are prevented: the highly exothermic sulfiding reactions have already taken place ex- situ prior to loading.

- Minimal H₂S partial pressure: in the initial phase of a TOTSUCAT startup, an equilibrium will be established when hydrogen is passed over the catalyst bed. In recycle mode, this quantity of H₂S will never exceed a few hundred ppms. This protects sulfur-sensitive catalysts downstream such as reformer and isomerization catalyst. In addition, there is not a need to sample the gas stream during startup, eliminating a potential H₂S exposure hazard for the operators.

- No additional hydrogen is needed: since the catalyst is preactivated and sulfided, no additional hydrogen will be needed to complete the sulfiding process. This lightens the duty on the hydrogen make-up compressor in the s/u phase. As a rule of thumb a quantity of hydrogen comparable to about 1wt% of the catalyst weight is consumed during in-situ sulfiding, or about 2scf/lb of catalyst.
ABSTRACT

TOTSUCAT is often applied in cases where the unit has temperature limitations that prevent a complete and thorough activation of the catalyst.

TOTSUCAT CFP is an enhanced treatment that combines the benefits of preactivation with the ability to start up a unit with cracked stocks. TOTSUCAT CFP eliminates the requirement to delay the introduction of cracked feeds for 3-5 days after startup. The CFP treatment reduces the acidity of the catalyst, making it suitable for the early introduction of cracked stocks. This may be essential when considering the potential use of TOTSUCAT on catalysts applied in the Resid hydrocracking application field.

TOTSUCAT CFP has been commercially applied in numerous North American refineries.
Catalyst Preactivation Using EURECAT TOTSUCAT Technology

Nilanjan Brahma
EURECAT US Inc.
Sulfiding of Hydrotreating Catalysts

Temperature

H₂ + Sulfiding Agent

Oxide catalyst
Polymolybdate structure
Mo₇O₂₄⁶⁻

Sulfided catalyst
Lamellar structure
MoS₂ slabs

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CoMo Catalyst
Active Phase Structure

«CoMoS»

S
Mo
Co

0.615 nm
(0002)

Alumina
NiMo Catalyst Active Phase Structure

Morphology of an activated Ni-Mo-S / Au Structure (STM Picture)

Courtesy of (Haldor Topsoe)

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STM Images of Co-Mo-S / Au

Co-Mo-S Nanocrystal  MoS$_2$  MoS$_2$ + Co

Courtesy of (Haldor Topsoe)

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Sulfur Vacancies

When exposed to $\text{H}_2$ atoms, $\text{MoS}_2$ forms two S vacancies.

Courtesy of (Haldor Topsoe)
Sulfiding of Hydroprocessing Catalysts

Chemical Reactions
(for every sulfiding agent and method)

\[
\begin{align*}
\text{MoO}_3 &+ 2 \text{H}_2\text{S} + \text{H}_2 \rightarrow \text{MoS}_2 + 3 \text{H}_2\text{O} \\
\text{WO}_3 &+ 2 \text{H}_2\text{S} + \text{H}_2 \rightarrow \text{WS}_2 + 3 \text{H}_2\text{O} \\
9 \text{CoO} &+ 8 \text{H}_2\text{S} + \text{H}_2 \rightarrow \text{Co}_9\text{S}_8 + 9 \text{H}_2\text{O} \\
3 \text{NiO} &+ 2 \text{H}_2\text{S} + \text{H}_2 \rightarrow \text{Ni}_3\text{S}_2 + 3 \text{H}_2\text{O}
\end{align*}
\]

Sour Water Produced: Approximately 10 wt% of catalyst weight
Hydrogen Consumption: Approximately 1 wt% of catalyst weight
What is Totsucat®?

Totsucat = Totally Sulfided Catalyst

The catalyst is preactivated, not just “presulfided”.
Totsucat Processes

- Proprietary patented processes
- All available active metal sites are sulfided
- Homogeneous sulfiding
- Customized solutions available
Typical Totsucat Applications

- Any Critical Path Unit – the cost of unit downtime typically outweighs the cost of Totsucat preactivation by a significant margin.
- Any Unit that cannot achieve adequate temperatures required for sulfiding – insufficiently sulfided catalysts cannot perform as designed.
- Any Unit upstream of an H₂S sensitive unit such as a Reformer or Isom Unit.
- Any Unit that can benefit from starting up with Cracked Feeds.
Totsucat Benefits

- Load-and-Go reactor startups
- No exotherms
- Minimal sour water formation
- No additional $H_2$ needed at startup
- Negligible amounts of $H_2S$ released
- No odors
- No handling of sulfiding chemicals
- Catalyst performance is maximized
- Upset conditions will not damage the catalyst
Startup with In-Situ Sulfiding
Liquid phase with SR Feed

Temperature (°F)

- DMDS
- Cracked feed
- H₂S breakthrough
- Stop DMDS
- Secondary Sulfiding

- SR Feed + DMDS at 175-300°F
- Monitor H₂S at outlet
- Sulfide at 600-660°F
- Sulfiding 3 days of SR feed
- completed in 15-24 hrs

Drying step

SR Feed

H₂S breakthrough

Secondary Sulfiding

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• September 14-16, 2009
Totsucat G Startup
Liquid phase with SR Feed

Temperature (°F)

<table>
<thead>
<tr>
<th>Temperature</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>575</td>
</tr>
<tr>
<td></td>
<td>750</td>
</tr>
</tbody>
</table>

- **Straight Runfeed**
- **SR Feed introduction at low T (175-300°F)**
- Go to Start of Run Temp in only 6-10 hours
- SR Feed for 3-4 Days
- Progressively switch to cracked feed
- **Advantages:** Simple startup procedure.
- No risk of event which could damage the catalyst

- **Cracked feed**

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Totsucat G Applications

- Primarily for Type I Catalysts used in Light End Applications – Naphtha, Gasoline Post-treat, Pygas, Tail Gas, H₂ Plant
- Applied commercially to:
  - Albemarle – KF-841, KF-647
  - ART - AT-724G, AT-535, HOP-473K
  - Axens - HR-426, HR-845, HR-806, TG-107
  - Criterion - DN-200, DN-3310, C-424
  - Haldor Topsoe - TK-527, TK-431, TK-437
- Normally supplied as non-passivated
- Also used in:
  - Petrochem Units
  - Lube Units

- September 14-16, 2009
- 5th NCUT Upgrading and Refining Conference, Fantasyland Hotel, Edmonton AB
Totsucat D Applications

- Distillate Hydrotreaters - ULSD
- For some of the latest generation Type II catalysts
  - STARS KF-757
  - ART CDXi
  - Topsoe BRIM
- Process being evaluated for some other catalyst types
Totsucat HC/Totsucat N Applications

- For Hydrocracking and Hydrocracker Pretreat Catalysts
- Totsucat HC for Hydrocracking catalysts
  - Successfully tested on HC-26 by UOP
- Totsucat N for Type II Hycrocracker Pre-treat (HCPT) catalysts
  - Albemarle KF-848 STARS
  - ART NDXi
Totsucat E (formerly Sulficat® E)

- Majority of active metal sites are sulfided
- Sulfur in the feed completes the sulfiding process during a four hour finishing step at startup.
- For units with Sufficient Sulfur in the Feed (S > 0.5%) and capable of reaching >600°F (315°C)
- Passivation is available for loading under air
Totsucat E Applications

- FCC Feed Hydrotreaters, Diesel Units, VGO Units, Resid Units
- Applied commercially to:
  - Criterion - DN-3551, DC-2551, MaxTrap, RN-412, C-411, and DN-200
  - ART – AT-575, HOP-492K, HOP-608
  - Albemarle – KF-841, KF-901, KF-647
  - Haldor Topsoe – TK-551, TK-525, TK-559
  - Axens – HR-538, HR-438

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Totsucat E for Fixed Bed VGO Units

- Totsucat E was successfully used to preactivate 1.6 million pounds (725 MT) for 2 different VGO Units.
- In-situ sulfiding of these units would have required 48-72 hours and produced approximately 20,000 gallons (75,000 liters) of sour water.
- With preactivation, the unit was online in 12 hours with less than 50 gallons (190 liters) of water removed from the separator.
For Totsucat E - Introduce feed at 80°C; at least 75% of normal rate; recycle back to feed line; WETTING PHASE

For DMDS - Introduce feed at 120°C; WETTING PHASE

INITIAL SULFIDING 12h @ 220°C

SECOND STAGE SULFIDING 6h @ 320°C

Totsucat E vs DMDS: 48 hrs

Time Gain

Liquid Heat Up rate @ 17°C/hr S content
S >> 0.5 wt%

Gas Phase Heat up Rate @ 4°C/hr

Activation Complete

Time [h]
Totsucat Properties

- Sulfides are sensitive to oxidation by air
- Product is classified in all cases as: Self-heating Solid (Class 4.2, UN 3190, Packaging Group II or III)
- Two types of formulations depending on the application type or customer preference:
  - Oil Passivation – Allows for loading under air
  - Non-passivated – Requires inert loading
- Treated catalyst is packaged in bins or metal drums with metalized liners

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Issue of Cracked Feed

Cracked Feeds contain olefins, di-olefins, and other polynuclear aromatics (PNA) that form gums and tars when exposed to hyper-active sites on freshly sulfided catalysts.
Issue of Cracked Feed

Gums and tars formed during startup are readily deposited on the catalyst surface.

These deposits will block the catalyst pores and active sites, leading to a permanent loss of catalyst activity.
Issue of Cracked Feed

To avoid this problem, catalyst manufacturers recommend a break-in period of at least three days using only straight run feed at startup.

By running only straight run feed, a small amount of coke will form on the catalyst surface, gradually reducing the hyperactivity of the catalyst.

Coke Molecule
Issue of Cracked Feed

Delaying the introduction of cracked feeds can have significant costs:

- Lost profits from processing cracked and heavy feeds.
- May need to purchase additional straight run feed for startup.
- Storage costs for a sufficient quantity of straight run feed required at startup.
- Storage costs for cracked feeds that must be held for processing later.
Solution: Totsucat CFP

- CFP = Cracked Feed Protection
- In addition to Totsucat preactivation, Totsucat CFP has carbon carefully deposited on the catalyst surface which moderates the hyper-active sites.
- Catalytic acidity is also reduced.
Totsucat CFP Benefits

- Totsucat CFP allows direct introduction of cracked feeds at 175-450°F
- Provides normal cycle lengths without waiting 3-4 days before adding cracked feeds
- No additional SR required
- No storage of cracked feeds during startup
Case Study – NHT with Totsucat CFP

Naphtha Hydrotreater

Feed: 20% Coker Naphtha/80% Straight Run

Feed Rate: 35,000 BPD

Catalyst Type: NiMo

Catalyst Quantity: 53,000 pounds
Case Study – NHT with Totsucat CFP

- **Run 1** – In-situ Sulfiding with 3 Day Break In – Catalyst A, Sock loaded
- **Run 2** – Totsucat CFP Preactivation – Startup with 20% cracked feed – Catalyst A, Dense loaded
- **Run 3** – Totsucat CFP Preactivation – Startup with 20% cracked feed – Catalyst B, Sock loaded

Note - Unit is heat limited due to fouling.
Case Study – NHT with Totsucat CFP

Reactor Temperature

WABT - In-situ with Break In
WABT - Totsucat CFP Run 1
WABT - Totsucat CFP Run 2

• September 14-16, 2009
• 5th NCUT Upgrading and Refining Conference, Fantasyland Hotel, Edmonton AB
• September 14-16, 2009
Case Study – NHT with Totsucat CFP

ΔT – Inlet to Bottom

- Inlet to Bottom ΔT - In-Situ with Break In
- Inlet to Bottom ΔT - Totsucat CFP Run 1
- Inlet to Bottom ΔT - Totsucat CFP Run 2

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Case Study – NHT with Totsucat CFP

Coker Naphtha Feed Rate

- Coker Naphtha - In-situ with Break In
- Coker Naphtha - Totsucat CFP Run 1
- Coker Naphtha - Totsucat CFP Run 2

Days on Oil

Coker Naphtha Feed (CBPD)

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Progressive Introduction of Cracked Feed

Introduce cracked feed at 175-450°F
Heat up at 35°F/h up to 475°F
After 475°F Heat up at 20°F/h up to SOR.

Advantages: Safe fast start-up; Additional 3 to 4 days of cracked feed processed; No need for SR or Cracked Feed storage
Totsucat Commercial Experience

Over 300 Totsucat Projects Completed at EUS totaling 16+ million pounds of catalyst (June 2009)

- **FCC Naphtha HDS**
  Various hydrotreating catalysts
- **VGO HDS Unit**
  Unit with over 1.6 million pounds of catalyst started up in 12 hrs
- **Selective Hydrogenation (chemical application)**
  NiMo catalysts
- **Selective Hydrogenation of Pyrolysis Gasoline**
  CoMo catalysts
- **Coker Naphtha Hydrotreater**
  Totsucat CFP on NiMo catalyst – on fifth cycle with Totsucat CFP
- **Wax Hydrofinishing**
  NiW catalysts
- **Tail Gas Units** – Totsucat provides the easiest method for starting a Tail Gas Unit

5th NCUT Upgrading and Refining Conference, Fantasyland Hotel, Edmonton AB  September 14-16, 2009
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*5th NCUT Upgrading and Refining Conference, Fantasyland Hotel, Edmonton AB • September 14-16, 2009*
• Totsucat CFP – Cracked Feed Protection
ISSUE OF CRACKED FEED INTRODUCTION

- A period of 2-3 days is usually recommended before cracked stocks introduction. This is for letting the catalyst gently coke at SOR conditions with an olefin/di-olefin free feed.
- A specific Totsucat product can address this problem: Totsucat CFP (Cracked Feed Protection). It contains already some carbon deposited on catalyst surface.
- Then cracked feed may be directly introduced at low temperature, with a slow heat-up phase to SOR temperature (Direct introduction of cracked feed at SOR temperature is not recommended).
**TOTSUCAT CFP : START-UP GUIDELINES**

**TOTSUCAT CFP START-UP: cracked feed intro at low T**

- Temperature (°C)
- Direct cracked feed introduction at 80-120°C,
- Heat up at 20°C/h up to 250°C,
- Heat up at 10°C/h up to SOR.
- Advantages: safe start-up, very quick (3 to 4 days are saved), no need of SR feed storage
Evidence that Totsucat CFP protects the catalyst

Coke and gums formation is related to the interaction between acidic sites and unsaturated molecules.

How to prove that Totsucat CFP decreases acidity?
Use of a ortho-xylene Isomerization test

The more acidic the catalyst, the higher the Isomerization rate
Validation of the o-xylene isomerization testing for characterizing acidity

Increase of the isomerization rate – in line with increase of the acidity of the catalyst

NiMo
Totsucat G
Low acidity alumina

CoMo1
Totsucat G
Standard alumina
Medium acidity

CoMo2
Totsucat G
Standard alumina
High acidity

O-xylene isomerization test is sensitive to the acidity of different known catalysts

Eurecat – Totsucat CFP
Evidence that Totsucat CFP protects the catalyst

- CFP treatment lowers the acidity of the catalyst → less coke and gum formation
BIOGRAPHY

Neil Edmunds
Laricina Energy Ltd.

Neil Edmunds is currently Vice President, Enhanced Oil Recovery (EOR) for Laricina Energy Ltd. in Calgary. Mr. Edmunds brings a background of over 31 years in the oil and oil sands industry focused primarily on thermal recovery of bitumen. Prior to his current position with Laricina, Mr. Edmunds was Reservoir Engineering Specialist with EnCana Corp. from 2000 to 2005 where he provided reservoir and operations direction for the Foster Creek SAGD and Vapex pilots, researched new recovery technologies and provided expert testimony on gas over bitumen issues before regulatory hearings. Formerly, Mr. Edmunds was Manager, Enhanced Oil Recovery for CS Resources Limited, responsible for the Senlac thermal project and later Vice President, Recovery Technologies focused on enhanced recovery research. As Principal of Clearwater Engineering he provided consulting services in thermal recovery and developed reservoir simulation software. Prior to that, Mr. Edmunds was Process Development Coordinator at the Underground Test Facility (UTF) for Alberta Oil Sands Technology and Research Authority (AOSTRA), and was previously Senior Reservoir Engineer with Vikor Resources Ltd. and AOSTRA.

Mr. Edmunds holds a Bachelor of Science in Mechanical Engineering (Gold Medal) from the University of Alberta. He is a member of the Canadian Heavy Oil Association, Petroleum Society of the CIM and Association of Professional Engineers, Geologists and Geophysicists of Alberta. In 2008 he was appointed Adjunct Associate Professor with the Schulich School of Engineering, University of Calgary.

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Innovation and the Future Carbon Footprint of In Situ Oil Sands; A Very Positive Story

Neil Edmunds
Laricina Energy Ltd.

In situ oil sands is an emerging energy subsector where innovative recovery technology is providing an opportunity for both more cost effective resource recovery, and a reduced carbon footprint. Laricina Energy Ltd is a leading in situ recovery innovator, with an emphasis on solvent applications. Laricina has operated cold solvent tests in the emerging carbonate bitumen play, and is advancing a commercial demonstration project of its proprietary solvent-cyclic-SAGD application. Recent work on life-cycle carbon emissions shows that solvent can transform the carbon footprint of Canadian in situ oil sands, to match that of the average imported crude into the United States. In situ innovation in oil sands offers a good news story, meeting a balance in energy security, environment and the economy for Alberta, Canada and North America.
This Laricina Energy Ltd. (the “Company”) Presentation is confidential and should not be distributed to any person other than attendees to whom this Presentation was initially presented to by the Company. Some of the statements contained in this Presentation may be forward-looking statements. Forward-looking statements may include, but are not limited to, statements concerning estimates of exploitable original-bitumen-in-place, predicted recovery factors, steam-to-oil ratios and well production rates, estimated recoverable resources, expected regulatory filing, review and approval dates, construction and start-up timelines and schedules, company project potential production volumes as well as comparisons to other projects, statements relating to the continued overall advancement of the Company’s projects, comparisons of recoverable resources to other oil sands projects, estimated relative supply costs, potential cost reductions, recovery and production increases resulting from the application of new technology and recovery schemes, estimates of carbon sequestration capacity, costs for carbon capture and sequestration and possible implementation schedule for carbon capture and sequestration processes or related emissions mitigation or reduction scheme and other statements which are not historical facts. You are cautioned not to place undue reliance on any forward-looking statements as there can be no assurance that the plans, intentions or expectations upon which they are based will occur. By their nature forward-looking statements involve numerous assumptions, known and unknown risks and uncertainties, both generally and specific, that contribute to the possibility that the predictions, forecasts, projections and other forward-looking statements will not occur. Although the Company believes that the expectations represented by such forward-looking statements are reasonable, there can be no assurance that such expectations will prove to be correct and, accordingly that actual results will be consistent with the forward-looking statements. Some of the risks and other factors that could cause results to differ materially from those expressed in the forward-looking statements contained in this Presentation include, but are not limited to geological conditions relating to the Company’s properties, the impact of regulatory changes especially as such relate to royalties, taxation and environmental changes, the impact of technology on operations and processes and the performance of new technology expected to be applied or utilized by the Company; labour shortages; supply and demand metrics for oil and natural gas; the impact of pipeline capacity, upgrading capacity and refinery demand; general economic business and market conditions and such other risks and uncertainties described from time to time in the reports and filings made with security regulatory authorities, contained in other disclosure documents or otherwise provided by the Company. Furthermore the forward-looking statements contained in this Presentation are made as of the date hereof. Unless required by law the Company does not undertake any obligation to update publicly or to revise any of the included forward-looking statements, whether as a result of new information, future events or otherwise. The forward-looking statements contained in this Presentation are expressly qualified by this advisory and disclaimer.
Outline

• Why the oil sands?
• *In Situ* oil sands in Alberta
• Environmental impacts: land, water & air
  – with respect to local sustainability
  – relative to international norms
  – compared to our existing options
• Lower impacts by better (still) technology
  – the coming solvent revolution
  – reductions in all impact intensities
The energy challenge

- At current levels of consumption, the present world oil reserves would be depleted in 40 years.
- At current levels of demand growth, the reserve life would be 27 years.
- The potential for demand growth from developing nations is very large.
Why are we in this business?

Source: Based on IEA World Energy Outlook 2007/ConocoPhillips

Natural decline forecast at 8% rate

Observed decline forecast at 4.5% rate requires substantial investment
The future of oil sands is *in situ*

- Canada’s bitumen resource of 1.7 trillion bbls retains enormous potential for reserve growth.
- *In situ* oil sands supply potential is 85% of 174 billion bbls of Alberta’s oil sands reserves or ~150 billion bbls.
- Ultimate reserves are ~50% higher (315 billion bbls) via advanced *in situ* recovery technology.
Laricina: Leader in the future of oil sands development

- One of 3 emerging *in situ* oil sands companies with > 4 billion bbls of net recoverable bitumen
- High quality resource, with scale and proximity to infrastructure
- Clear path to 350,000+ net barrels per day production potential
- Well advanced, resource focused development of innovative SAGD processes, solvent recovery and carbon sequestration
- Leading the recovery of bitumen from carbonate reservoirs
Alberta *in situ* bitumen technology

- New plants will primarily use Steam-Assisted Gravity Drainage (SAGD)
- **SAGD:**
  - descendant of steamflood technology developed in California in the ’50’s and 60’s
  - technology home grown in Alberta
  - applicable to “bitumen”, i.e. immobile oil
  - uses horizontal wells; minimal surface disturbance
  - *significantly more efficient* (lower impacts) than conventional steamflood/CSS processes
SAGD well configuration

- SAGD uses pairs of horizontal wells, drilled from surface.
- Steam is injected in the top well and oil produced from the bottom.
- A typical pair of SAGD well-heads drains an area of 8 ha (20 acres) in 5-10 years.

Source: EnCana Corporation
Environmental impacts of *in situ* recovery

- **Land**
  - intensity of disturbance
  - reclamation cycle

- **Water**
  - source volumes
  - recycling
  - disposal

- **Air**
  - \( \text{CO}_2 \)
  - \( S_{ox}, N_{ox} \)

*What are the impacts in terms of:*

- Local environmental sustainability
- “International norms”
  - the oil industry
  - other industry
- The Alberta regulatory environment
Land (Habitat) impacts

• About 10% of the greater oil sands regional area has economically viable reserves
• SAGD well sites, facilities, and roads disturb about 15% of the area under active development
  – ultimate impact ~1.5% over the region
  – not all at once!
SAGD land use intensity

- A SAGD well pair produces 500-2000 bopd from a 1-hectare (2.5 acre) clearing
- Land areas required to produce the same amount of energy as 500 bopd:
  - from California-style thermal recovery:
    - 20 hectares (50 acres)
  - from wind turbines:
    - 50 x 1.5 MW turbines, plus power lines
  - from Iowa corn to ethanol:
    - 750 hectares (1900 acres)
Land use intensity

- The total designated oil sands areas in Alberta contain 140,800 km² \( (375 \text{ km})^2 \)
- Potentially 5 million bpd of *in situ* recovery:
  - would require a total of about 10,000 ha in use, equivalent to 100 km² (10x10 km)
  - less than 0.1% of the area would be under active development at any one time
Foster Creek, Alberta (SAGD)
Duri, Indonesia (conventional steam)
Kern River, California
Belridge, California
Land impact mitigations

• A typical clearing-to-reclamation cycle is likely to be ~20 years
• Local residents are consulted with regard to special places; *in situ* siting is flexible
• Extensive flora & fauna studies are mandatory
• Timely reclamation is mandatory
• No soil contamination is permitted
  – *In situ* piping systems have to contain steam and are constructed to very high standards
• Shared land use (e.g. roads/ROW’s) with conventional oil & gas, forestry, power transmission
SAGD water consumption

- Water for new steam projects in Alberta is sourced from deep, brackish (non-potable) aquifers
- Produced water is 80-95% recycled
- e.g.:
  - SOR=3 & 80% recycle:
    - 0.6 bbl of (brackish) makeup / bbl of oil
  - SOR=2 & 90% recycle:
    - 0.2 bbl of (brackish) makeup / bbl of oil
### Volume of water used to produce things

<table>
<thead>
<tr>
<th>Product</th>
<th>Average virtual water content (m³/ton)</th>
</tr>
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<tbody>
<tr>
<td>Beef</td>
<td>15,500</td>
</tr>
<tr>
<td>Rice</td>
<td>2291</td>
</tr>
<tr>
<td>Wheat</td>
<td>1334</td>
</tr>
<tr>
<td>Corn</td>
<td>909</td>
</tr>
<tr>
<td>SAGD Bitumen</td>
<td>0.6</td>
</tr>
</tbody>
</table>

http://www.waterfootprint.org/Reports/ResearchData/Appendix%20XV.xls
SAGD water consumption

• Compared to local rainfall:
  – e.g. rainfall of 40 cm/year over 1 Twp. (93 km$^2$) project area
  – averages to 640,000 bbls of water per day (bwpd)
• Expected typical/maximum SAGD project demand over the same area would be
  ~50,000 bwpd (100,000 bopd/township)
  – *no surface or potable water is used for steam*
Waste water disposal

- All non-recycled waste water is injected into deep formations (below the oil sands)
- Generally the injected water is of higher quality than the receiving formation
- ‘Zero’ water is discharged at the surface

Suncor, camp operator fined $400,000 for dumping waste into Athabasca River
- Calgary Herald, April 2, 2009
Life Cycle GHG Emissions for Gasoline – Max Cogen Credit

Include Cogen Credit

Total GHG, g CO2e / MJ Gasoline

- Conventional Crudes
- Thermal
- Mining

*other feeds: IC4 for Alky; diluent

*Cogen credit based on export of natural gas based power that offsets 80% coal based Alberta grid power
CO₂: “3 times” what, exactly?

Life Cycle GHG Emissions from Petroleum Products for Various Crudes

Canadian Light
Brent Blend
Arab Light
Canadian In Situ (SOR 1.5)
Nigerian Excravos
Mexican
Canadian Mined
Canadian In Situ (SOR 3.0)
Venezuelan Partial Upgrader
California In Situ

Light/Sweet 150
Advanced In Situ 225
In Situ 450
Consumer 2750

Source: T.J. McCann & Associates & IOSA

CO₂: “3 times” what, exactly?
AERI LCA - Conclusions

• A wide range of GHG emissions for crude oils in North American refineries
• Imported and U.S. domestic heavy oil crudes have similar emissions to the oil sands pathways
• With some overlap, oil sands pathways generally have 10% higher emissions than conventional crudes
• GHG emissions from oil sands crudes are comparable to conventional crudes when potential cogeneration credits are considered
Canadian oil sands and the world

Another inconvenient truth...

China
4.34 billion tons CO²

US coal
1.9 billion tons CO²

Oil sands
5.3 million tons CO²
Reducing energy use

• More efficient use of energy reduces CO\textsubscript{2} generation proportionately:
  – Innovations in reservoir recovery will reduce energy requirements (lower Steam/Oil ratios):
    • Solvent additives to SAGD
    • Cold solvent processes
    • Variants of above
  – Facility synergies between projects
  – Cogeneration
Steamflood carbon intensity vs. steam/oil ratio

- Duri, Sumatra
- Midway-Sunset
- Kern River
- S. Belridge
- Cold Lake
- Primrose (horizontal)
- Foster Creek (SAGD)

New solvent technology
Improved performance through innovation

• Optimized reservoir exploitation
  – Optimize how steam is utilized
  – Solvent assisted processes
  – Cold solvent applications in the carbonates

• Drilling and completion operations
  – Reduce well costs and number of well pairs over life of project

• Facility engineering and construction
  – Build a template that can be repeated

• Laricina’s goal is to reduce breakeven WTI oil price from $70 to less than $50

A culture of innovation: Passive Heat Assisted Recovery Methods (PHARM), patent pending
The solvent opportunity

- Higher recovery factor
  - lower residual oil saturation
- Reduced SOR:
  - lower startup capital
  - leverage steam capital going forward
  - reduced emissions, water demand
- No new hardware or applications required to implement
- Accelerated production
Solvents – lowering the viscosity

1500 kPa

Mixture Viscosity (mPa-s) vs Temperature (°C)

- Propane
- Butane
- Pentane
- Bitumen
Solvent mechanisms

Steam Front

Steam+Solvent Front

depleted low-temp zone

Temperature

Oil Sat.

Oil Mobility
After the first year, SC-SAGD is really a steam-enhanced solvent process, rather than solvent added to steam.
• EnCana SAP Process
  – 1 year steam (ceiling rise)
  – Add butane with a slight decrease in steam
  – Produce for 2-4 years at 40% higher rates
  – Circulate dry gas to recover remaining solvents

Sustained 40% increase in rate
Cold solvent production test

- Follow-up cold solvent test was executed in winter 2009
  - 10 times larger than 2008 test
  - Produced bitumen at steady rates for 6-8 weeks
- Main objective of the test was to gather production fluid data, compositions, and pressure data, to improve predictive capability of numerical models
- Findings consistent with 2008 test
  - Extremely high reservoir permeability, both vertical and horizontal
    - Better than the “best” of the McMurray
  - Connectivity between the ‘C’ and ‘D’ zones
  - Bitumen was mobilized and produced
- Data from 2009 test will outline scope for further solvent-based projects at Saleski
Conclusions

• Going forward, most new oil sands development in Alberta will be *in situ* projects
• Environmental impacts from *in situ* projects will be environmentally responsible w.r.t.:
  – absolute/cumulative local impacts
  – an exacting regulatory environment
  – international norms & intensities
Conclusions

• Carbon dioxide emissions from Alberta *in situ* oil sands development will exceed the life-cycle emissions due to conventional crude sources, by at most 10%

• SAGD (steam) technology is about to get a big boost from solvent additives, cutting emissions by as much as half

• *In situ* plants make natural cogeneration hosts, and by replacing coal-fired power, would render *in situ* bitumen carbon-equivalent to any source of crude
Oil Sands in the Environment
BIOGRAPHY

Jinwen Chen
National Centre for Upgrading Technology (NCUT)

Dr. Jinwen Chen is a research scientist and the process modeling section head at the National Centre for Upgrading Technology (NCUT), CanmetENERGY. Dr. Chen joined NCUT in 1999. His research area and expertise at NCUT include process modeling and simulation of bitumen and heavy oil upgrading and petroleum refining, CFD modeling and simulation of hydrotreating reactors, catalyst and catalytic process development, kinetics and vapor-liquid phase equilibrium studies of hydrotreating. Before joining NCUT, Dr. Chen worked on fluid hydraulics, and modeling and simulation of multiphase reactors in Washington University in St. Louis and in University of Calgary. He has authored/co-authored over 60 papers published in scientific journals and many industrial client reports. He has been actively involved in organizing many international conferences, symposiums and workshops. He received his B. Sc., M. Sc. and Ph. D. in Chemical Engineering from Tianjin University.

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ABSTRACT

On the Vapor-Liquid Equilibrium in Hydroprocessing Reactors

Jinwen Chen, Mugurel Munteanu and Hena Farooqi
National Centre for Upgrading Technology, CanmetENERGY Devon

During petroleum distillates hydroprocessing (hydrotreating and hydrocracking), the feedstock and hydrogen pass through trickle-bed catalytic reactors at high temperatures and pressures with relatively large hydrogen flow. These conditions result in partial vaporization of oil and partial dissolving of hydrogen in liquid to form a vapor-liquid equilibrium (VLE) system with both vapor and liquid phases containing oil and hydrogen, which might result in significant changes in flow rates, physical properties, and chemical compositions of both phases, and thus in flow dynamics, mass and heat transfer, and reaction kinetics. This paper presents the experimental observations of VLE behaviors in distillates hydrotreaters with different types of feedstocks under various operating conditions. Furthermore the prediction of VLE and the analysis of its effects on distillates hydrotreaters of both pilot plant and commercial scale are discussed in detail.
On the Vapor-Liquid Equilibrium in Hydroprocessing Reactors

Jinwen Chen, Mugurel Munteanu, and Hena Farooqi
National Centre for Upgrading Technology (NCUT)
Canmet ENERGY, Natural Resources Canada

For presentation at
5th NCUT Upgrading and Refining Conference

Edmonton, Alberta, Canada
September 14-16, 2009
Background

• Distillates hydrotreating/mild hydrocracking are important processes in bitumen upgrading and petroleum refining.

• In a distillates hydrotreater (T: 350 – 450°C; P: 50-120 atm), hydrogen and hydrocarbons are present in both vapor and liquid phases to form a vapor-liquid equilibrium (VLE) system.

• There are complex interactions between chemical reactions, mass and heat transfers, and VLE. VLE changes flow hydrodynamics and the concentrations of the reacting components in each phase, affecting mass and heat transfers, reaction kinetics and catalyst performance.

• It is important to understand the VLE behavior in a distillates hydrotreater and to obtain the quantitative information on distribution and composition of the two phases for accurate reaction kinetics and process modeling.

• VLE study can provide such understanding and information. So far very limited studies have been reported on this subject to the complexity of the problem.
VLE in Reactor Modeling

VLE model: flash calculation

Step i

H₂ rate, oil rate, Tᵢ, Pᵢ

VLE model: flash calculation

Step i+1

H₂ rate, oil rate, Tᵢ₊₁, Pᵢ₊₁

Reactor model: a set of PDEs to get Tᵢ, Cᵢ,j

VLE model: flash calculation

Reactor model: a set of PDEs to get Tᵢ, Cᵢ,j

H₂ + oil

H₂ + hydrotreated oil

Tᵢ, Cᵢ,j

T
VLE Modeling via EOS

Under certain T and P, a fixed system can be in vapor phase, liquid phase, or vapor-liquid phase equilibrium. If the system is VLE, using flush calculation can determine the relative amount and composition of each phase.

Flash calculation:

\[ M_{i,f} = M_v y_{i,v} + M_L x_{i,l} \]

Use equation of state (EOS) to get \( M_{i,f}, M_v, M_l, y_{i,v}, x_{i,l} \):

\[ P = \frac{RT}{V - b} - \frac{a(T)}{V^2 + 2bV - b^2} \]

Peng-Robinson Equation, \( V_{small} \) and \( V_{large} \) are liquid and vapor mole volume, respectively

\[ b = \frac{\Omega_b R T_c}{P_c} \]
\[ a(T) = \frac{\Omega_a R^2 T_c^2}{P_c} \alpha(T) \]

\[ b = \sum_{i=1}^{N} y_i b_i \]

Mixture

\[ a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij} \]
\[ a_{ij} = \left( a_{ii} a_{jj} \right)^{1/2} (1 - d_{ij}) \]

\( d_{ij} \): Interaction coefficient, must be known in order to use EOS
VLE Experimental Studies

Flash experiments were performed in a continuous flow VLE unit

1) Middle distillates hydrotreating system:
   - 3 different feeds (Light cycle oil (LCO), white oil, LCO+ white oil)
   - Temperature: 250 – 400°C
   - Pressure: 50 – 100 bar
   - Gas/oil ratio: 1000 NL/kg

2) Heavy distillates hydrotreating system:
   - 2 different feeds (heavy gas oils)
   - Temperature: 350 – 430°C
   - Pressure: 70 – 110 bar
   - Gas/oil ratio: 800 NL/kg

SimDis data to determine pseudo-components
Sulphur speciation to determine individual sulphur compounds
The Experimental Setup
# Feedstocks Properties

<table>
<thead>
<tr>
<th></th>
<th>Middle Distillates</th>
<th>Heavy Distillates</th>
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<tbody>
<tr>
<td></td>
<td>Feed 1 (LCO)</td>
<td>Feed 2 (white oil)</td>
</tr>
<tr>
<td>Density (15.6°C), g/mL (ASTM D4052)</td>
<td>0.9360</td>
<td>0.8152</td>
</tr>
<tr>
<td>Saturates (wt%)</td>
<td>15.9</td>
<td>98.9</td>
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<tr>
<td>Aromatics (wt%)</td>
<td>83.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Polars (wt%)</td>
<td>0.2</td>
<td></td>
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<tr>
<td>SimDis, °C (ASTM D2887)</td>
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<td></td>
</tr>
<tr>
<td>IBP</td>
<td>128.4</td>
<td>210.5</td>
</tr>
<tr>
<td>10wt%</td>
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<tr>
<td>FBP</td>
<td>430.8</td>
<td>490.0</td>
</tr>
</tbody>
</table>
Experimental Observations

Middle Distillates

Heavy Distillates

Wt% Oil in Vapor vs Temperature (°C)

- Feed 1
- Feed 2
- Feed 3

P = 70 bar

Wt% Oil in Vapor vs Temperature (°C)

- Feed 1
- Feed 2

P = 90 bar
Experimental Observations

Middle Distillates

<table>
<thead>
<tr>
<th>Pressure, atm</th>
<th>Wt% Oil in Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 350°C</td>
<td></td>
</tr>
</tbody>
</table>

Feed 1: ▲
Feed 2: ●
Feed 3: ▲

Heavy Distillates

<table>
<thead>
<tr>
<th>Pressure, bar</th>
<th>Wt% Oil in Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 390°C</td>
<td></td>
</tr>
</tbody>
</table>

Feed 1: ○
Feed 2: ▲

T = 390°C

Middle Distillates

<table>
<thead>
<tr>
<th>Pressure, atm</th>
<th>Wt% Oil in Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 350°C</td>
<td></td>
</tr>
</tbody>
</table>

Feed 1: ▲
Feed 2: ●
Feed 3: ▲

Heavy Distillates

<table>
<thead>
<tr>
<th>Pressure, bar</th>
<th>Wt% Oil in Vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 390°C</td>
<td></td>
</tr>
</tbody>
</table>

Feed 1: ○
Feed 2: ▲
Experimental Observations

Distribution of individual sulphur compounds in vapor and liquid phases

Sulphur speciation: HP6890 - GC, atomic emission detector (AED), sulphur channel 181 nm, 60 m silica capillary column. Total of 26 dibenzotipophenic compounds.

4-Methyldibenzothiophene (4-MDBT), 4,6-Dimethyldibenzothiophene (4,6-DMDBT) and 2,4,6-Trimethyldibenzothiophene (2,4,6-TMDBT) are three typical refractory sulphur compounds in middle distillates. They are the most difficult ones to remove by hydrotreating.

![Graphs showing distribution of sulphur compounds in vapor and liquid phases at different temperatures.](image)
# Fitting Experimental Data with Flash Model

## Pseudo-components

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.434</td>
</tr>
<tr>
<td>comp1</td>
<td>0.01</td>
</tr>
<tr>
<td>comp2</td>
<td>0.02</td>
</tr>
<tr>
<td>comp3</td>
<td>0.02</td>
</tr>
<tr>
<td>comp4</td>
<td>0.02</td>
</tr>
<tr>
<td>comp5</td>
<td>0.01</td>
</tr>
<tr>
<td>comp6</td>
<td>0.03</td>
</tr>
<tr>
<td>comp7</td>
<td>0.03</td>
</tr>
<tr>
<td>comp8</td>
<td>0.04</td>
</tr>
<tr>
<td>comp9</td>
<td>0.04</td>
</tr>
<tr>
<td>comp10</td>
<td>0.03</td>
</tr>
<tr>
<td>comp11</td>
<td>0.04</td>
</tr>
<tr>
<td>comp12</td>
<td>0.04</td>
</tr>
<tr>
<td>comp13</td>
<td>0.04</td>
</tr>
<tr>
<td>comp14</td>
<td>0.04</td>
</tr>
</tbody>
</table>

## Sulphur components

- Dibenzothiophene
- 4-methyl dibenzothiophene
- 2-methyl dibenzothiophene
- 3-methyl dibenzothiophene
- 4-ethyl dibenzothiophene
- 4,6-dimethyl dibenzothiophene
- 2,4-dimethyl dibenzothiophene
- 2,6-dimethyl dibenzothiophene
- 2,4,6-trimethyl dibenzothiophene
- 2,4,8-trimethyl dibenzothiophene
- 2,4,7-trimethyl dibenzothiophene
- 1,4,6-trimethyl dibenzothiophene
- 1,4,7-trimethyl dibenzothiophene
- 3,4,7-trimethyl dibenzothiophene
- 1,3,7-trimethyl dibenzothiophene

## Mole fraction in the flash feed

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,7-dimethyl dibenzothiophene</td>
<td>4.00E-07</td>
</tr>
<tr>
<td>1,8-dimethyl dibenzothiophene</td>
<td>1.40E-07</td>
</tr>
<tr>
<td>1,4-dimethyl dibenzothiophene</td>
<td>1.00E-06</td>
</tr>
<tr>
<td>1,6-dimethyl dibenzothiophene</td>
<td>1.20E-06</td>
</tr>
<tr>
<td>3,4-dimethyl dibenzothiophene</td>
<td>2.30E-07</td>
</tr>
<tr>
<td>4-ethyl-6-methyl dibenzothiophene</td>
<td>4.00E-07</td>
</tr>
<tr>
<td>1,7-dimethyl dibenzothiophene</td>
<td>1.40E-07</td>
</tr>
<tr>
<td>2,3-dimethyl dibenzothiophene</td>
<td>1.00E-06</td>
</tr>
<tr>
<td>2,4,6-trimethyl dibenzothiophene</td>
<td>1.20E-06</td>
</tr>
<tr>
<td>2,4,8-trimethyl dibenzothiophene</td>
<td>2.30E-07</td>
</tr>
<tr>
<td>2,4,7-trimethyl dibenzothiophene</td>
<td>4.00E-07</td>
</tr>
<tr>
<td>1,4,6-trimethyl dibenzothiophene</td>
<td>1.40E-07</td>
</tr>
<tr>
<td>1,4,7-trimethyl dibenzothiophene</td>
<td>1.00E-06</td>
</tr>
<tr>
<td>3,4,7-trimethyl dibenzothiophene</td>
<td>1.20E-06</td>
</tr>
<tr>
<td>1,3,7-trimethyl dibenzothiophene</td>
<td>2.30E-07</td>
</tr>
</tbody>
</table>
Minimum information required for flash calculation: density, molecular weight, boiling point of each component.

Pseudo-component:
Pseudo Components - MW & Density

Middle Distillates

MW correlation with boiling point (BP)

Heavy Distillates

MW correlation with boiling point (BP)

Sg correlation with boiling point (BP)
Estimation of Interaction Coefficients

$d_{iH}$ is obtained for each $H_2$-hydrocarbon pair and correlated with hydrocarbon properties.
Results - Interaction Coefficients

Assume $d_{ih} = a + b \times Bp_i$, $Bp_i$ is the boiling point (in °C) of pseudo-component $i$

<table>
<thead>
<tr>
<th>Middle distillates</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed 1</td>
<td>0.1865</td>
<td>0.00388</td>
</tr>
<tr>
<td>Feed 2</td>
<td>0.386</td>
<td>0.00226</td>
</tr>
<tr>
<td>Feed 3</td>
<td>0.285</td>
<td>0.00302</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heavy distillates</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed 1</td>
<td>0.5712</td>
<td>0.004713</td>
</tr>
<tr>
<td>Feed 2</td>
<td>0.2977</td>
<td>0.002956</td>
</tr>
</tbody>
</table>

$a$ and $b$ are further correlated to aromatics content in the feed:

<table>
<thead>
<tr>
<th>Middle distillates</th>
<th>a = 0.3852 - 0.00241$\times C_{Aromatics%}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b = 0.002245 + 1.96 \times 10^{-5} \times C_{Aromatics%}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heavy distillates</th>
<th>$a = 0.0943 + 0.009779 \times C_{Aromatics%}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b = 0.00165 + 5.0196 \times 10^{-5} \times C_{Aromatics%}$</td>
</tr>
</tbody>
</table>
Flash Calculation vs. Experimental Data

**Middle distillates**

- **Wt% of oil in vapor with T**
  - Graph showing experimental and calculated data for Feed 1.
  - Temperature range from 240 to 420 °C.

- **Wt% of oil in vapor with P**
  - Graph showing experimental and calculated data for Feed 1.
  - Pressure range from 5000 to 11000 kPa.

- **SimDis of vapor and liquid**
  - Graph showing comparison of liquid and vapor experimental and calculated data by Run05.
  - Pressure range from 0 to 500 kPa.
Flash Calculation vs. Experimental Data

Middle distillates

Wt% of oil in vapor with T

Wt% of oil in vapor with P

SimDis of vapor and liquid
Flash Calculation vs. Experimental Data

Middle distillates

Wt% of oil in vapor with T

Wt% of oil in vapor with P

SimDis of vapor and liquid
Flash Calculation vs. Experimental Data

Individual sulphur compounds: $d_{ij} = 0.1765 + 0.00298*BP$

Middle distillates Feed 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>BP, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBT</td>
<td>184.26</td>
<td>332.5</td>
</tr>
<tr>
<td>4-MDBT</td>
<td>198.28</td>
<td>321.26</td>
</tr>
<tr>
<td>2-MDBT</td>
<td>198.28</td>
<td>327.3</td>
</tr>
<tr>
<td>3-MDBT</td>
<td>198.28</td>
<td>328.4</td>
</tr>
<tr>
<td>4-EDBT</td>
<td>212.32</td>
<td>335.4</td>
</tr>
<tr>
<td>4,6-DMDBT</td>
<td>212.32</td>
<td>366</td>
</tr>
<tr>
<td>2,4-DMDBT</td>
<td>212.32</td>
<td>336.2</td>
</tr>
<tr>
<td>2,6-DMDBT</td>
<td>212.32</td>
<td>337.2</td>
</tr>
<tr>
<td>3,6-DMDBT</td>
<td>212.32</td>
<td>338.1</td>
</tr>
<tr>
<td>2-EDBT</td>
<td>212.32</td>
<td>337.8</td>
</tr>
<tr>
<td>2,8-DMDBT</td>
<td>212.32</td>
<td>339.2</td>
</tr>
<tr>
<td>2,7-DMDBT</td>
<td>212.32</td>
<td>340.1</td>
</tr>
<tr>
<td>3,7-DMDBT</td>
<td>212.32</td>
<td>340.7</td>
</tr>
<tr>
<td>1,8-DMDBT</td>
<td>212.32</td>
<td>341.7</td>
</tr>
<tr>
<td>1,4-DMDBT</td>
<td>212.32</td>
<td>342.1</td>
</tr>
<tr>
<td>1,6-DMDBT</td>
<td>212.32</td>
<td>342.5</td>
</tr>
<tr>
<td>3,4-DMDBT</td>
<td>212.32</td>
<td>343.8</td>
</tr>
<tr>
<td>4-E-6-MDBT</td>
<td>226.36</td>
<td>344.5</td>
</tr>
<tr>
<td>1,7-DMDBT</td>
<td>212.32</td>
<td>345</td>
</tr>
<tr>
<td>2,3-DMDBT</td>
<td>212.32</td>
<td>345.8</td>
</tr>
<tr>
<td>2,4,6-TMDBT</td>
<td>226.36</td>
<td>346.6</td>
</tr>
<tr>
<td>2,4,8-TMDBT</td>
<td>226.36</td>
<td>348</td>
</tr>
<tr>
<td>2,4,7-TMDBT</td>
<td>226.36</td>
<td>349.1</td>
</tr>
<tr>
<td>1,4,6-TMDBT</td>
<td>226.36</td>
<td>353.3</td>
</tr>
<tr>
<td>1,4,7-TMDBT</td>
<td>226.36</td>
<td>353.9</td>
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<tr>
<td>3,4,7-TMDBT</td>
<td>226.36</td>
<td>356.1</td>
</tr>
<tr>
<td>1,3,7-TMDBT</td>
<td>226.36</td>
<td>356.2</td>
</tr>
</tbody>
</table>
Flash Calculation vs. Experimental Data

Heavy distillates

Wt% of oil in vapor with T

Wt% of oil in vapor with P

SimDis of vapor and liquid
Flash Calculation vs. Experimental Data

Heavy distillates

Wt% of oil in vapor with T

Wt% of oil in vapor with P

SimDis of vapor and liquid
VLE Experiments at High Temperature (400ºC above)

Light hydrocarbon content in vent gas – Feed 1 GC data

<table>
<thead>
<tr>
<th></th>
<th>CH4+Other HC's (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>&gt; 0.5%</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

Feedback 1 T&B 350°C T&B 430°C

SimDis Data

Clearly thermal cracking becomes significant when temperature is above 400ºC, which cannot be simply accounted for in VLE flash calculation. Therefore, the data points above 400ºC were not included in the interaction coefficients evaluation.

Further investigation is underway.
Conclusions

1) Comparative VLE experiments were conducted with hydrogen and petroleum middle and heavy distillates under typical hydroprocessing conditions.

2) The relative amount of oil in the vapour phase significantly increased with the increase in temperature and decrease in pressure.

3) The volatilities of these distillates are related to the aromatics contents.

4) The interaction coefficients between hydrogen and hydrocarbon pseudo-components were evaluated by fitting flash calculations to the experimental data. These interaction coefficients linearly increased with the increase in boiling point.

5) The parameters a and b correlating the interaction coefficients with boiling point were further correlated to the aromatics contents in the feed. These correlations are expected to reasonably simulate flashing of any type of feedstock, provided that its SimDis, density, molecular weight distributions with boiling point and aromatics contents are known.

6) Substantial thermal cracking occurred at high temperature (400°C above) with the heavy distillates, which cannot be accounted for in the flash calculation program.
Acknowledgement

Partial funding for NCUT has been provided by the Canadian Program on Energy Research and Development (PERD), the Alberta Research Council (ARC), and the Alberta Energy Research Institute (AERI). The authors are grateful to staff of the NCUT analytical lab and pilot plant for their help and support in conducting the analyses and VLE experiments.
Thank you!
BIOGRAPHY

Warren M. Ewert
ConocoPhillips

Warren Ewert is a Fellow in the Heavy Oil Division of ConocoPhillips’ R&D organization, based at the Bartlesville Technology Center. Warren joined Phillips Petroleum R&D in Bartlesville in 1979 and has 30 years of experience in chemical and refining pilot plant scale process development and commercialization, including the Chevron Phillips Chemical selective ethylene-to-hexene-1 process that won the 2005 Kirkpatrick Chemical Engineering Achievement Award and the ConocoPhillips S Zorb Sulfur Removal Technology. He has B.S. and M.S. degrees in chemical engineering from Kansas State University and an M.S. degree in chemistry from Oklahoma State University. Warren is a registered professional engineer in the state of Oklahoma and is a member of the National and Oklahoma Societies of Professional Engineers, the American Institute of Chemical Engineers, and the American Chemical Society. He and his wife, Joleen, have been married for 29 years and have four daughters, ages 23, 20, 18, and 13.

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Email: Warren.Ewert@ConocoPhillips.com
Website: www.conocophillips.com
API Gravity and Viscosity of Residues from Conventional and Bitumen-Containing Crude Oils

Warren M. Ewert and Chris Lewis
ConocoPhillips Company, Research and Development

API gravity and viscosity are two key properties of atmospheric and vacuum residues that refiners must consider when replacing conventional crude oils with bitumen-containing crudes. Crude oil assays are commonly used to estimate residue yields and properties, but results from different laboratories can vary significantly. This presentation will demonstrate that high-temperature simulated distillation analysis of the assay residues provides a convenient way to reconcile data from multiple samples and different sources. It will also show that this methodology allows comparisons between different types of crude oil residues to be made on a consistent cut point temperature basis.
API Gravity and Viscosity of Residues from Conventional and Bitumen-Containing Crude Oils

Warren Ewert and Chris Lewis
Research & Development, Bartlesville, OK

Presented at the 5th NCUT Upgrading and Refining Conference 2009, Edmonton, Alberta, Canada. September 14-16, 2009
Residue Yields and Properties are Important to Refiners

Atmospheric Tower

Desalted Whole Crude

~660°F+

Atmospheric Resid

Vacuum Tower

~1000°F+

To Asphalt Sales or Coker

Vacuum Resid
Resid Density and Viscosity Issues

- Resid density and viscosity are important for designing and operating refinery transfer line systems
- Vacuum resid viscosity is a key performance characteristic of asphalt
- Vacuum resid density (API gravity) is an important characterization parameter for predicting coker performance
- Resid cut point is an important operating parameter, impacting yield and vacuum tower and coker design
- Refinery crude slate changes potentially impact resid properties and yields
- Reported resid properties differ from assay to assay for the same crude, creating a potential dilemma for refiners
Refiners use laboratory-scale Crude Oil Assays to determine the yields and properties of various boiling point fractions.
Crude Oil Assay - Source for Resid Information

Yields and Properties of Atmospheric and Vacuum Residues from Crude Oil Assay are used to for Refinery Modeling and Design.
Resid Viscosity Can Be Linearized as a Function of Temperature Using the Method Outlined in ASTM D 341

\[
\log(\log(\text{Vis}(\text{cSt}) + 0.7)) = C_0 + C_1 \log(T(\text{oR}))
\]

- Bitumen Vac Resid
- Synbit Vac Resid
- Dilsynbit Vac Resid
- Dilbit Vac Resid
- Refinery Sour Vac Resid
- West Texas Sour Vac Resid
- Refinery Sweet Vac Resid
- Synbit Atm Resid
- West Texas Sour Atm Resid

Modified Viscosity:
- 0.1 = 17 cSt
- 0.3 = 98 cSt
- 0.5 = 1,452 cSt
- 0.7 = 102,770 cSt
Variability in Vacuum Resid Yields and Properties from Different Assays - Which Values are “Correct”?

<table>
<thead>
<tr>
<th>Reported Resid Cut Point (°F)</th>
<th>Vac Resid Yield - Wt % of Whole Crude</th>
<th>Vac Resid API Gravity @ 60ºF</th>
<th>Vac Resid Viscosity @ 210ºF (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1022</td>
<td>20.1</td>
<td>7.3</td>
<td>1145</td>
</tr>
<tr>
<td>1050</td>
<td>24.9</td>
<td>9.3</td>
<td>609</td>
</tr>
<tr>
<td>1050</td>
<td>24.3</td>
<td>9.0</td>
<td>818</td>
</tr>
<tr>
<td>1050</td>
<td>24.9</td>
<td>9.6</td>
<td>589</td>
</tr>
<tr>
<td>1100</td>
<td>17.7</td>
<td>7.0</td>
<td>1888</td>
</tr>
<tr>
<td>1100</td>
<td>14.9</td>
<td>6.9</td>
<td>2576</td>
</tr>
<tr>
<td>1100</td>
<td>14.9</td>
<td>6.2</td>
<td>6098</td>
</tr>
</tbody>
</table>

Resid yield, gravity, and viscosity do not correlate well with reported cut point. 
(r² values for linear correlations with cut point temperature = 0.39 to 0.58)
Vacuum Residue API Gravity and Modified Viscosity are Well-Correlated with Yield

Modified Viscosity = -0.0105 * Wt% Yld + 0.7079
R² = 0.9085

API = 0.2893 * Wt% Yld + 2.0445
R² = 0.9287
Can High-Temperature Simulated Distillation of Resids Provide a Representative Cut-Point Temperature for Property Correlation?
Can High-Temperature Simulated Distillation of Resids Provide a Representative Cut-Point Temperature for Property Correlation?
T(10 wt%) Temperature from High-Temperature SimDist Correlates Well with Dilsynbit Resid Modified Viscosity

SimDist T @ Various Wt% Off Values (ºF)

Log(Log(Viscosity @ 250ºF (cSt) + 0.7))

- 0.5 wt%
- 1 wt%
- 5 wt%
- 10 wt%
- 15 wt%
- 20 wt%
- 25 wt%

R² values:
- 0.674
- 0.803
- 0.968
- 0.992
- 0.997
- 0.998
- 0.995

R² = 0.985
R² = 0.992
R² = 0.997
R² = 0.998
R² = 0.999
R² = 0.992
R² = 0.995

ConocoPhillips
T(10 wt%) Temperature from High-Temperature SimDist Correlates Well with Dilsynbit Resid API Gravity

![Graph showing correlation between T(10 wt%) temperature and API gravity for different wt% values.](image)

Key:
- **0.5 wt%**
- **1 wt%**
- **5 wt%**
- **10 wt%**
- **15 wt%**
- **20 wt%**
- **25 wt%**

**R² values:**
- 0.972
- 0.980
- 0.987
- 0.953
- 0.804
- 0.686

**SimDist T @ Various Wt% Off Values (°F)**

**API Gravity @ 60°F**
Modified Viscosity @ 250°F for Resids from Conventional and Bitumen-Containing Crudes vs. T(10 wt%) HT SimDist Temperature

Log(Log(Vis(cSt)+0.7))

- Bitumen Resid
- Synbit Resid
- Dilsynbit Resid
- Dilbit Resid
- Refinery Sour Resid
- West Texas Sour Resid
- Refinery Sweet Resid

Modified Viscosity
- 0.1 = 17 cSt
- 0.2 = 38 cSt
- 0.3 = 98 cSt
- 0.4 = 324 cSt
- 0.5 = 1,452 cSt
- 0.6 = 9,573 cSt

High-Temp SimDist T(10 wt%) Temperature (°F)
API Gravity @ 60ºF for Resids from Conventional and Bitumen-Containing Crudes vs. T(10 wt%) HT SimDist Temperature

[Graph showing the relationship between API Gravity @ 60ºF and High-Temp SimDist T(10 wt%) Temperature (ºF) for various types of residuum.]

- Bitumen Resid
- Synbit Resid
- Dilsynbit Resid
- Dilbit Resid
- Refinery Sour Resid
- West Texas Sour Resid
- Refinery Sweet Resid
Modeling Resid Density and Viscosity

• Resid viscosity can be predicted as a function of sample temperature and cut point using the T(10 wt%) temperature from high-temp SimDist

\[
\log(\log(\text{Vis}(cSt) + 0.7)) = C_0 + C_1 \times \log(T(\text{o}R)) + C_2 \times T(10\text{wt%})
\]

• Resid density (API gravity) can be predicted as a function of cut point

\[
\text{API} = C_0 + C_1 \times T(10\text{wt%})
\]
“What If” Scenario #1

- A refiner running West Texas Sour crude wants to convert to Canadian dilsynbit. If the current vacuum tower bottoms cut point, represented by a HT SimDist T(10%) temperature of 975ºF, is maintained, what changes might the refiner expect in resid properties?
Resid Modified Viscosity @ 250°F vs. T(10 wt%) HT SimDist Temperature

Case 1: WTS to Dilsynbit Crude Change at Constant Cut Point

Viscosity @ 250°F increases by a factor of 10.

Modified Viscosity
0.1 = 17 cSt
0.2 = 38 cSt
0.3 = 98 cSt
0.4 = 324 cSt
0.5 = 1,452 cSt
0.6 = 9,573 cSt

Log(Vis(cSt)+0.7)
Resid API Gravity @ 60°F
vs. T(10 wt%) HT SimDist Temperature

Case 1: WTS to Dilsynbit Crude Change at Constant Cut Point

API gravity decrease predicts lower coker liquid yields.

7.4°API

3.9°API

Dilsynbit Resid
West Texas Sour Resid
“What If” Scenario #2

• A refiner running a conventional sour crude slate wants to replace it with Canadian synbit. If the current vacuum tower bottoms cut point is represented by a HT SimDist T(10%) temperature of 1000°F, how much might the vacuum tower cut point temperature have to be dropped to maintain a constant viscosity at 250°F for asphalt sales?
Case 2: Sour to Synbit Crude Change at Constant Viscosity

Synbit vac resid cut point may have to be dropped ~70°F to maintain constant viscosity.

Modified Viscosity
0.1 = 17 cSt
0.2 = 38 cSt
0.3 = 98 cSt
0.4 = 324 cSt
0.5 = 1,452 cSt
0.6 = 9,573 cSt
Conclusions

• Data from crude oil assays, supplemented with high-temperature SimDist data, can be used to predict key resid properties.

• Assay-to-assay differences in reported resid properties can be explained by cut point temperature variations.

• The impact of crude changes on resid gravity and viscosity can be modeled so that the refiner can:
  ▪ Revamp transfer systems to deal with changes in density and viscosity.
  ▪ Predict changes in coker yields.
  ▪ Change vac tower cut points to hit a target viscosity.
BIOGRAPHY

Thomas W. McCracken

National Research Council / Institute for Chemical Process and Environmental Technology
NRC / ICPET

EDUCATION:

M.A.Sc. (Chemical Engineering), University of Toronto, Canada
B.A.Sc (Chemical Engineering), University of Toronto, Canada

EXPERIENCE:

Extensive experience in oil sands processing application including development of feed injection systems for coker reactors and development of novel bitumen extraction and upgrading processes. Has published more than 65 scientific articles, written 35 reports and presented the results of his work at over 50 scientific meetings. Also is inventor as co-author of 10 process and equipment patents. Now leading and coordinating oilsands R&D research for significant projects at NRC in collaboration with other government departments, academia and industry partners.

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Website: www.nrc-cnrc.gc.ca
AN INVESTIGATION OF PROBLEMATIC SOLIDS IN OIL SANDS PROCESSING - SEPARATION AND CHARACTERIZATION OF ORGANIC MATTER STRONGLY BOUND TO OIL SANDS SOLIDS

T.W. McCracken, J.R. Woods, J. Kung, D.Fu, D. Kingston, L. S. Kotlyar, and B.D. Sparks

National Research Council of Canada, Institute for Chemical and Environmental Technology

1V. Bede Technical Associates

In Athabasca oilsands certain solids fractions are associated with strongly bound organic matter insoluble in common organic solvents for bitumen such as toluene. This material is known as toluene insoluble organic matter or TIOM. Presence of TIOM increases oil wettability of solids and this may adversely affect the release of bitumen from the oilsands. The finest oil-wettable particles remain with the oil phase after bitumen separation. Some of this solid material is therefore carried over from the coking operation to downstream operations where it can be involved in fouling of those process units.

In this work, supercritical fluid extraction with methanol was used to remove TIOM from oilsands after extraction of bitumen by toluene. After removal from the solids the methanol extract (ME) is soluble in toluene. This allows for a detailed analysis of the ME by several advanced and complementary analytical techniques. The results are compared to similar data for the corresponding parent bitumen fractions prepared using a modified HPLC SARA separation technique.

Number average molecular weights for the ME are close to those for resins separated from bitumen. The number of alkyl substituents on aromatic ring systems and the lengths of paraffinic straight chains for resins and ME samples were found to be similar. Only minor differences exist between ME and the resins in terms of H/C atomic ratios and aromaticities. As indicated by the higher hetero atom contribution, the methanol extracts are more polar than the resin and asphaltene fractions. This may explain the apparent selective adsorption of this fraction, particularly through the predominant pyrrole and pyridine species.
AN INVESTIGATION OF PROBLEMATIC SOLIDS IN OIL SANDS PROCESSING - SEPARATION AND CHARACTERIZATION OF ORGANIC MATTER STRONGLY BOUND TO OIL SANDS SOLIDS

T.W. McCracken¹, J.R. Woods¹, J. Kung¹, D. Fu¹, D. Kingston¹, L. S. Kotlyar¹, B.D. Sparks²

¹ National Research Council of Canada, Institute for Chemical Process and Environmental Technology
² V. Bede Technical Associates

Presentation to 5th NCUT Upgrading and Refining Conference 2009
Edmonton, September 14-16, 2009
In Athabasca oil sands, certain solids fractions are associated with strongly bound organic matter insoluble in common organic solvents for bitumen such as toluene (resulting in toluene insoluble material or TIOM).

Presence of TIOM increases oil wettability of solids and affects the release of bitumen from the oilsands.

The finest oil wettable particles remain with the oil phase after bitumen separation -- Some of this solid material is carried over from the coking operation to downstream operations where it may contribute to fouling of process units.
Research Objectives

To gain insight into chemical composition of TIOM:

- Use of supercritical fluid extraction with methanol to separate TIOM from bitumen free oil sands solids.
- Fractionation of bitumen from corresponding oil sands using high performance liquid chromatography (HPLC).
- Use of complimentary advanced analytical techniques for comparative analysis of TIOM and bitumen fractions.
Supercritical fluid extraction (SCFE) of Solids

- After removal from the solids the methanol extract was soluble in toluene
- This facilitated characterization and allowed direct comparison with fractions from the corresponding parent bitumen.

High performance liquid chromatography (HPLC) of Bitumen

After asphaltene removal, fractionated bitumen into:
- Saturates
- Aromatics
- Three resin fractions (R1; R2; R3)
After bitumen had been exhaustively extracted with toluene, oilsand solids were subjected to SFE with methanol.

Extracted bitumen was separated into asphaltenes (asp) and maltenes.

Application of HPLC to maltenes yields saturates (sat) aromatics (ar) and resins fractions.

The resin component is divided into three fractions (R1, R2 and R3) based on increasing polarity (Fuel 2004, 83, 1907-1914).
SFE Methodology

- Supercritical methanol was delivered at a flowrate of 5 mL/min to a 50 mL extraction cell containing 50 grams of dried soxhlet extracted oilsand. The solvent was preheated to 250°C.
- The extraction cell temperature was also set at 250°C and system pressure was controlled to a constant 2000 psi by manually closing and opening a heated restrictor valve. The extract was collected into a 1 litre conical flask set in an ice bath for a total of 100 minutes.
**Molecular weights:**
GPC

**Elemental analysis:**
C,H,N,S with LECO analyzer

**Nitrogen and sulfur types:**
X-ray photo electron spectroscopy

**Carbon and proton types:**
$^{13}$C NMR, $^{1}$H NMR

**Average structural parameters:**
Calculated based on elemental analysis, MW and NMR results.
Structural parameters comparison

- Parameters indicated similarities between the methanol extract and resins included:
  - Cn ar (number of aromatic carbon atoms in molecule)
  - Cn alfa (number of alkyl substituents on aromatic ring system)
  - L (length of paraffinic straight chains)
- Compared to resins, methanol extracts exhibited a lower degree of aromatic ring condensation (K).
Average structural parameters
(Fuel 1982, 61, 402-410)

Calculations based on molecular weights, elemental analysis, $^{13}$C NMR and $^1$H NMR.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cn ar</td>
<td>Number of aromatic carbon atoms in average single molecule</td>
</tr>
<tr>
<td>Cn alfa</td>
<td>Number of alkyl substituents on aromatic ring system in an average single molecule</td>
</tr>
<tr>
<td>K</td>
<td>Degree of condensation of aromatic ring system</td>
</tr>
<tr>
<td>L</td>
<td>Average paraffinic straight chains. Estimated from the ratios of the $^{13}$C NMR resonances at 29.7ppm and 14.2ppm.</td>
</tr>
</tbody>
</table>
Results

- Molecular weight of methanol extract (ME) and bitumen fractions
Results

- *Nitrogen in methanol extract (ME) and bitumen fractions*
Results

- **Sulfur in methanol extract (ME) and bitumen fractions**
Results

- **Nitrogen and sulfur types in bitumen fractions and methanol extracts**

<table>
<thead>
<tr>
<th>Species</th>
<th>Species distribution in sample (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resin (R3)</td>
</tr>
<tr>
<td>N Pyrrole</td>
<td>81.0</td>
</tr>
<tr>
<td>Pyridine</td>
<td>19.0</td>
</tr>
<tr>
<td>S Thiophenic</td>
<td>74.0</td>
</tr>
<tr>
<td>Sulphide</td>
<td>26.0</td>
</tr>
<tr>
<td>Sulphoxide</td>
<td>bdl</td>
</tr>
<tr>
<td>Sulphone</td>
<td>bdl</td>
</tr>
</tbody>
</table>

*bdl = below detection limit*
While pyrrole was always the primary nitrogen species, pyridine groups were also present in each case; the greatest contributions from pyridine species occurred in the ME samples.

In every case the sulphur species were predominantly thiophenic with some contribution from sulphides.

The sulphoxide and sulphone species occurred in only some of the asphaltene fractions from the parent bitumens; the highest concentrations of this species were found in the ME samples.

Concurrently with this observation the thiophenic sulfur contents in the methanol extracts are lower than those for the corresponding fractions from bitumen.
Results

- **Atomic H/C ratios for methanol extract (ME) and bitumen fractions**

![Bar chart showing H/C ratios for various fractions](image)
Results

- $^{13}$C NMR aromaticity of methanol extract (ME) and bitumen fractions

![Graph showing 13C NMR aromaticities for different fractions.]
Results

- *Number of aromatic carbon atoms in molecule (Cn ar)*

![Bar chart showing Cn ar values for different categories: sat, ar, R1, R2, R3, Asp, ME. The chart indicates a significant increase in Cn ar for the Asp category compared to the others.]
Results

- *Degree of condensation of aromatic ring system (K)*
Results

- **Number of alkyl substituents on aromatic ring system (Cn alfa)**

![Bar Chart]

- x-axis: sat, ar, R1, R2, R3, Asp, ME
- y-axis: Cn alfa
- Values: 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20
• **Length of paraffinic straight chain substituents (L)**

![Bar chart showing the length of paraffinic straight chain substituents (L) for different categories: sat, ar, R1, R2, R3, Asp, ME.](chart.png)
Results

- **Fraction of carbon associated with oxygen (fo)**

\[
\begin{array}{c|c|c|c|c|c}
& 50-70 & 145-160 & 160-190 \\
\hline
R3 & \text{Aliphatic C-OH, C-OR} & \text{Aromatic C-OH, C-OR} & \text{COOH, COOR, acid, ester} \\
\end{array}
\]
Conclusions

• Contributions of elemental nitrogen and carbon associated with oxygen for the methanol extract are higher than those measured for the resin and especially the asphaltene fractions from bitumen.

• In all cases -- nitrogen species were predominantly pyrrolic. Pyrolle rich organic matter is known to undergo oxidative polymerisation to form the adhesive material with high propensity to fouling.

• Owing to its polar nature, TIOM may be responsible for increased interaction with bulk bitumen leading to associated difficulties with oil release and/or fouling during conventional water-based separation processes.

• Both elemental sulfur content and the contribution of thiophenic sulfur in the methanol extract samples is lower than those in the bitumen components.
Conclusions

- Molecular weights for methanol extracts from bitumen free oilsands solids are close to those for resin fractions, and much lower than those for asphaltenes.
- Only minor differences exist between methanol extract and the resins in terms of H/C atomic ratios and aromaticities.
- Number of aromatic carbon atoms in molecule, number and chain lengths of alkyl substituents on aromatic rings were among parameters pointing to similarities between the methanol extract and resins.
- Degree of condensation of aromatic ring systems for the ME samples are much lower than the values for the corresponding resin fraction.
- Both elemental sulfur content and the contribution of thiophenic sulfur in the methanol extract samples is lower than those in the bitumen components.
Acknowledgements

• CONRAD (Canadian Oil sands Network for R&D) support for project, especially for Syncrude Research contributions and feedback throughout the project

• Financial support and collaboration under NRCan programs supporting oil sands development, including PERD 1.1.3 Program-Petroleum Conversion for Cleaner Air and ecoETI (Federal government – ecoAction funding)
Questions?

Thank-you...
BIOGRAPHY

Ashok Anand
Enbridge Pipelines Inc.

Ashok was born in Kenya and graduated with a degree in chemical engineering from University of Toronto. He has worked 16 years in various technical and managerial capacities in the petroleum refining industry, mainly with Imperial Oil and Suncor Energy companies. He moved to the pipelining of crude and petroleum products and is presently Senior Manager of Petroleum Quality with Enbridge Pipelines Inc where he has worked for 10 years.

Ashok has been married for over 34 years and has two children who are also married and has two grand children. He enjoys traveling and is very passionate about hockey and cricket.

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Email: ashok.anand@enbridge.com
Website: www.enbridge.com
Enbridge System: Crude types, transportation and handling systems

Ashok Anand
Enbridge Pipelines Inc.

Crude supply from the Canadian Western Sediment Basin is expected to grow by about 2.1 million barrels per day by 2015. This increased supply will bring with it a growth in the new types of commodities or will add to volumes of existing commodities on the Enbridge system which handles a very diverse crude slate including conventional heavy, synthetic heavy, heavy high tan, heavy low resid, medium, light sour, heavy sour, light sweet, light sweet synthetic, condensate and olefinic. They range anywhere from 19 API to 40 API and 0.1% sulfur to 4.7% sulfur. Enbridge’s infrastructure plans include expansion of regional pipelines to bring increased crude supplies to the mainline; expanding mainline capacity to existing markets; and providing pipeline access to new markets. The pipelines will be supplemented by providing merchant storage terminals in some key locations. Inclusive in the infrastructure expansions are plans to maintain the quality of the various crude types through judicious sequencing and tank bottoms crossings. The presentation will discuss in some detail the infrastructure expansion plans, crude types and quality assurance program.
Enbridge System: Crude Types, Transportation and Handling Systems

Ashok Anand
Senior Manager, Petroleum Quality
September 2009
Certain information provided in this presentation constitutes forward-looking statements. The words "anticipate", "expect", "project" and similar expressions are intended to identify such forward-looking statements. Although Enbridge believes that these statements are based on information and assumptions which are current, reasonable and complete, these statements are necessarily subject to a variety of risks and uncertainties pertaining to operating performance, regulatory parameters, economic conditions and commodity prices. You can find a discussion of those risks and uncertainties in our SEC filings. While Enbridge makes these forward-looking statements in good faith, should one or more of these risks or uncertainties materialize, or should underlying assumptions prove incorrect, actual results may vary significantly from those expected. Enbridge assumes no obligation to publicly update or revise any forward looking statements made herein or otherwise, whether as a result of new information, future events or otherwise.
Enbridge Infrastructure Overview
WCSB Supply Production Growth vs. Pipeline Capacity

2006 CAPP Forecast

New Pipeline 1

New Pipeline 2

New Pipeline 3

Southern Access

Current Unutilized Export Capacity

Enbridge Market Unconstrained Case
Incremental Disposition Summary

Need to Accommodate 2.1 Million BPD incremental basin production by 2015

Export

300-500

25

50

250

750

125

750

125

250

250-450

100

75

100

50
Infrastructure Requirement

- Regional Pipeline Development
- Mainline Expansions
- New Market Access Pipelines
- Terminaling
Alberta Oilsands Regional Pipeline Development

- Athabasca Pipeline Expansion & Cheecham Terminal
  - Terminal In-Service Late 2006
- Waupisoo Pipeline
  - 30” diameter, 390 km.’s,
    350 KBPD initial capacity
- In service mid 2008

Cheecham Terminal
Waupisoo Pipeline
- PetroCanada/UTS (Forthills)
- Total/Deer Creek (Joslyn)
- PetroCanada (MacKay River)
- ConocoPhillips/Total (Surmont)
- EnCana (Christina Lake)
- Synenco (Northern Lights)
- Imperial (Kearl)
- Husky (Sunrise)
- EnCana (Borealis)
- Opti-Nexen (Long Lake)
- Suncor

Athabasca Pipeline
Access Pipeline
Waupisoo Pipeline
- Synenco (Northern Lights)
- Imperial (Kearl)
- Husky (Sunrise)
- EnCana (Borealis)
- Opti-Nexen (Long Lake)
- Suncor

PetroCanada/UTS (Forthills)
Total/Deer Creek (Joslyn)
PetroCanada (MacKay River)
ConocoPhillips/Total (Surmont)
EnCana (Christina Lake)
Mainline Expansion –
Southern Access Expansion

- 400 kbdp Edmonton to Chicago
- Under construction, in-service Q1, 2009
- New 42” Pipe from Superior, Wisconsin to Chicago, 456 miles
Mainline Expansion – Southern Access Extension

- 400 kbpd Chicago to Patoka
- Under construction, in-service Q1, 2009
- 36” diameter, 178 miles
Mainline Expansions
- Alberta Clipper

- New 36” diameter line, Hardisty to Superior, 1,000 miles
- 400 kbpd additional capacity into Chicago
- in-service late 2010
Mainline Expansion
Southern Lights Diluent Supply

- 180 kbpd diluent capacity
- Contract pipeline
- In service 2010
- Fully supported by industry
- Under Construction
New Market Access

   II : 100 kbdp, US $215 MM, 2011


5. PADD I Pipeline : 300 kbdp, US $1.4 B, 2010 - 12
Terminaling Footprint & Hotspots

Existing Storage

Active Development

Terminaling Footprint & Hotspots

<table>
<thead>
<tr>
<th>Location</th>
<th>Upstream</th>
<th>Downstream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing (mil. bbls)</td>
<td>4.0</td>
<td>12.5</td>
</tr>
<tr>
<td>Under Development</td>
<td>16.0</td>
<td>14.3</td>
</tr>
</tbody>
</table>
# Enbridge Commodity Types
(Enbridge.com & crudemonitor.ca)

<table>
<thead>
<tr>
<th>Commodity Type</th>
<th>API</th>
<th>%S</th>
<th>MCR</th>
<th>TAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy</td>
<td>19-21</td>
<td>2.6-4.5</td>
<td>8.5-11.3</td>
<td>0.5-1.05</td>
</tr>
<tr>
<td>Heavy Hi Tan</td>
<td>19-21</td>
<td>3.0-4.5</td>
<td>7.5-10</td>
<td>1.4-3.5</td>
</tr>
<tr>
<td>Heavy Lo Resid</td>
<td>20</td>
<td>3.0</td>
<td>&lt;1.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Medium</td>
<td>30-35</td>
<td>2.5</td>
<td>6.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Sour</td>
<td>30-35</td>
<td>1.1-1.8</td>
<td>4.0-6.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Sweet</td>
<td>40</td>
<td>&lt;0.5</td>
<td>2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Lt Sweet Synthetic</td>
<td>30-35</td>
<td>0.1-0.25</td>
<td>&lt;0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Condensate</td>
<td>60</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Olefinic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NGL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refined Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Quality Management of Commodities in Enbridge Batched Pipeline

- Enbridge controls quality of delivered crude in the following ways.
  - In the Pipe: Manage Interface - number, type, size, cut
    - Line Splits: Like Commodities in segregated lines
    - Line Rates: Turbulent flow to minimize interface sizes
    - Batch Sizes: Minimum 60KB, Multiples batch trains
    - Batch Sequence: Based on least contamination risk
    - Batch Cuts (Interfaces): Mid point
  - In the Tank
    - Tank Bottoms Crossing
    - Tank Selection/Terminal Piping/Service Change
## CRUDE TYPE MATRIX - THE QUALITY PROCESS

<table>
<thead>
<tr>
<th></th>
<th>Heavy -TAN</th>
<th>Heavy</th>
<th>Medium</th>
<th>Sour</th>
<th>Sweet</th>
<th>Synthetic</th>
<th>Condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy -TAN</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Heavy</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Medium</td>
<td>7</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Sour</td>
<td>7</td>
<td>6</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Sweet</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Synthetic</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Condensate</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

The above numbers rank the order (as a guideline) that should be followed when changing from crude types.

**One** being first choice. **Seven** being the last choice.

When making sequence decisions between crudes of the same type (Heavy-Heavy), reference the crude prices for best choice.
Line Rates at Turbulent flow - size

Turbulent Flow

Laminar Flow

Notice the increased size of the mixing area from the Turbulent to Laminar flow.
In The Tank

- **Tank Selection** - This is important to determine the amount of contamination created from station piping. This may increase or decrease depending on the location of the tank and the amount of common piping. Most sensitive crude types closest to manifold.

- **Tank Bottoms Crossing** - The procedure for this is outlined in the Service Levels (Table 5). Outlines how each commodity is treated through tankage at every location from receipt to delivery.

- **Tank Service Change** - Follows a rigid procedure to minimize contamination.

- **Tank Cleaning** - Can cause a product to be delivered with a high S&W which can cause refinery problems. Procedure in place to monitor and restrict high S&W
Special Procedures

- High Tan (Total Acid Number >1.0) commodities have dedicated tanks or flush batch (destined to same facility) is required if routed through a regular heavy tank.
- Cracked products contain olefins desired by very few refineries. Cracked products require both front and back buffers that are sized to contain the cracked crude interfaces. The whole train (buffers and crude) moves into the same refinery.
ITS Quality Metrics

• Reward/penalty based on meeting or exceeding targets set over 5 years (2005-2009). Targets negotiated based on baseline data on main lines only – to Sarnia & Chicago
• Targets set on formula which includes
  – Absolute change + constant x std dev at delivery
• Quality metrics parameters – receipt to delivery
  – Heavy: sulphur, MCR, TAN
  – Light Synthetic: sulphur, density
  – Refined products: diesel flash, uLSD sulphur pick-up
• Light Targets tighten by 50% and Heavy targets tighten by 30%
• Performance has been excellent – 23 out of 28 targets in 2007 were in bonus situation indicating the gains in quality of crude being delivered
• Connecting pipelines benefiting
Summary

- Increased crude production of 2.1M barrels/day expected by 2015
- Growth expected in new and existing crude types – some challenging
- Enbridge infrastructure being expanded to connect increased supply sources to existing & new markets
- ITS Quality metrics benefiting connecting pipelines
- Quality metrics principles/practices extended to all expanded infrastructure
Randy Segato
Suncor Energy Inc.

Randy Segato has a diversified background with 22 years of experience covering Refining and Upgrader operations, as well as Products and Crude Oil Trading. He is a champion of crude quality within Suncor and is active within CAPP, CCQTA and the COQG, chairing several industry panels. Randy maintains a position as crude quality specialist at Suncor Energy Marketing Inc.

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5th NCUT Upgrading and Refining Conference 2009
September 14-16, 2009
Edmonton, Alberta, Canada

ABSTRACT

Crude Oil Value Management Through North American Pipeline Delivered Systems

Randy Segato
Suncor Energy Marketing Inc.

Suncor produces synthetic crude from its operations in Fort McMurray for destinations across North America. Injected and delivered crude quality varies due to pipeline and terminal system logistics which implies changes in valuation. Refinery Planners/Engineers and Crude Traders are tasked to maximize profitability while minimizing risk within this varying world of crude classifications, new commodity developments, batch interfaces, shared tank bottoms and sampling limitations. In order to manage this continuously changing landscape, Suncor’s integrated oil flow operations will be reviewed with focus on best practices in Crude Oil Quality management from source to refineries.
Crude Value Management
Through Pipeline Systems

5th NCUT Upgrading and Refining Conference
September 15, 2009
Edmonton, Alberta, Canada

Randy Segato
Crude Value Management … is the process to acknowledge, measure, and act on system variances that affect crude quality.

A crude’s Refining Value is derived from the delivered crude quality vs alternatives.

Fundamental changes to crude quality dynamically alter crude value and thus shift crude price differentials.
Considerations of Pipeline Delivered Networks

Benefits of a Disciplined Crude Value Management Program
  - Principles of Crude Quality
    - For Producers
    - For Refiners

Objectives

to obtain appreciation of crude quality variances on Refining Value.
we will touch on some best practices in obtaining and managing crude quality data.
Crude Value Management

It seems so simple!

Buy Here!

We've been doing this for years so what's the problem?

Deliver Here!
New Crudes are entering the market faster. New Pipelines and logistics continue to come on stream.

US and Canadian growth imply expanded crude quality valuation because of more options available.
Commodity Classes ie. “rules and regs”

- **Batch system** (Enbridge, KM)
  - Nominal 10 km³ batches maintain unique quality from injection to delivery

- **Basket approach** (line 9, Capline, Keystone (ACS))
  - Like crude grades managed by pipeline as a like commodity, delivery of crude grade not specifically guaranteed to be single crude quality

- **Pooled feeder streams** (MSW, CRW, SLE, SHE)
  - Feeder streams equalized across month into delivered tank but injected batches vary and are rarely “just the average”

Fluid Flow Realities alter quality as batch moves down pipelines

- **Flow Regime**
  - Expect turbulent flow to minimize interface but sometimes operate in laminar flow, or even start/stop; can changes over time; sometimes line service switches

- **Interfaces**
  - Similar gravity, similar viscosity makes interface difficult to detect; large pipelines can have 25%+ contamination based on one interface; best practice would have interfaces governed based on a known predictable “batch cut matrix” outlining accepted cuts between grades

- **Tank Logistics**
  - Breakout tankage change in service; can have like grade in one tank; can have dissimilar crudes share tank bottoms; rarely have full grade mixing in a tank but is possible
### Table 5
Commodity Segregation through Tankage

<table>
<thead>
<tr>
<th>Transport Commodity</th>
<th>Crude Quality Category</th>
<th>Edmonton</th>
<th>Hardisty</th>
<th>Kerrobert</th>
<th>Regina</th>
<th>Clearbrook</th>
<th>Superior</th>
<th>Griffith</th>
<th>Stockbridge</th>
<th>Sarnia</th>
<th>Westover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate Blend (CRW)</td>
<td>Condensate</td>
<td>Note 2</td>
<td></td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0,F&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0,F&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0,F&lt;/sup&gt;</td>
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<td></td>
<td>B/B&quot;&lt;sup&gt;0,F&lt;/sup&gt;</td>
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</tr>
<tr>
<td>BP Condensate Blend (ACB)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R/B</td>
<td>B/B&quot;&lt;sup&gt;0,F&lt;/sup&gt;</td>
<td></td>
<td></td>
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<tr>
<td>Suncor A (OSA)</td>
<td>Light Synthetic</td>
<td>R/S</td>
<td>R/S</td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Suncor C (OSC)</td>
<td></td>
<td>R/B</td>
<td>R/B</td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Syncrude (SYN)</td>
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<td>R/S</td>
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<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/S</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Premium Albian Synthetic (PAS)</td>
<td></td>
<td>R/S</td>
<td></td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/S</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Shell Synthetic Light (SSX)</td>
<td></td>
<td>R/S</td>
<td></td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/S</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Husky Synthetic Blend (HSS)</td>
<td></td>
<td>R/S</td>
<td></td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/S</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>BP Sweet Synthetic Blend (BSS)</td>
<td></td>
<td>R/S</td>
<td></td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/S</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Long Lake Light Synthetic Blend (PSC)</td>
<td></td>
<td>R/S</td>
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<td>R/S</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Newgrade Synthetic Blend (NSA)</td>
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<td></td>
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<td></td>
<td>R/B</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<td>Newgrade Synthetic Blend (NSB)</td>
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<td>R/B</td>
<td>B/C</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Mixed Blend Sweet (SW)</td>
<td></td>
<td>Note 2</td>
<td></td>
<td></td>
<td>R/S</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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</tr>
<tr>
<td>Long Lake Sweet Blend (PSW)</td>
<td></td>
<td>R/S</td>
<td></td>
<td></td>
<td>B/C</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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</tr>
<tr>
<td>Kerrobert Light (SW)</td>
<td></td>
<td>Note 5</td>
<td></td>
<td></td>
<td>R/S</td>
<td>B/C</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>EDMONTON LIGHT SOUR (SLE)</td>
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<tr>
<td>Long Lake Sour Blend (PSO)</td>
<td></td>
<td>R/S</td>
<td></td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>Moose Jaw Tops (MJT)</td>
<td></td>
<td>R/S</td>
<td></td>
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<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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</tr>
<tr>
<td>Light Sour Blend (LSB)</td>
<td></td>
<td>R/S</td>
<td></td>
<td></td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
<td>High Sulfur Sour (SHE)</td>
<td></td>
<td>Note 2</td>
<td></td>
<td></td>
<td>B/C</td>
<td>B/C</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardesty Sour (SO)</td>
<td></td>
<td>Note 5</td>
<td></td>
<td></td>
<td>B/C</td>
<td>B/C</td>
<td>B/B&quot;&lt;sup&gt;0&lt;/sup&gt;</td>
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</tr>
</tbody>
</table>

As a first option, a commodity will cross bottoms with the same commodity. Second, third, and fourth choices (commodity group) are noted in superscript in preferential order.

**Commodity Group Codes** — **A**-Heavy, **B**-Heavy High Tan, **C**-Cracked, **D**-Medium, **E**-High Sour, **F**-Sweet, **G**-Light Synthetic, **H**-Condensate, **I**-Light Sour, **J**-Heavy Synthetic
### Table 5 Continued
**Commodity Segregation through Tankage**

#### Tank Service Legend

<table>
<thead>
<tr>
<th>Service</th>
<th>Receipt</th>
<th>Breakout</th>
<th>Tank Service Definitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segregated</td>
<td>R/S</td>
<td>B/S</td>
<td>Crude streams that does not share tankage with other crude streams.</td>
</tr>
<tr>
<td>Share Common Bottoms</td>
<td>R/B</td>
<td>B/B</td>
<td>Crude streams that can share tank bottoms with other crude types.</td>
</tr>
<tr>
<td>Commingled</td>
<td>R/C</td>
<td>B/C</td>
<td>Crude components that share tankage with other like-crude components to form single commingled streams e.g. SW, SLE, SHE, SO, CRW, LSB, M. Crude streams that can be commingled with a given commodity are noted in superscript in preferential order.</td>
</tr>
<tr>
<td>No Tankage Requirement</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### General Notes

1. Above tankage references Enbridge facilities only.
2. The CRW, SW, SLE, SHE, LSB and M commodities are blended from their individual components and are combined on receipt and segregated receipt service is provided for these streams.
3. OCC, PBS and CCA require buffering.
4. SHE and SO will be commingled as required at breakout locations. Once commingled, they are treated as a single commodity and may cross bottoms with compatible sours.
5. US and Foreign crude is received at Clearbrook, Mokena, Griffith, and Lewiston on the Enbridge system. US sweet crude will cross bottoms with commodity group “F”. US Sour crude will cross bottoms with commodity groups, in the order of E, D, and I. US medium crude will move through the system the same as Midaile. US heavy crude streams are segregated through the system the same as heavy streams.
6. Natural Gas Liquids, Gasoline, and Distillate do not utilize Enbridge tankage and are therefore not included in this table.
Let’s not forget that there is also exposure to quality changes due to Intra-Terminal manifold lineups and configuration.
Overall,

Crude Value Management requires a detailed understanding on the complete crude logistic system
...from creation of the Crude Commodity
...through to delivery into refinery tanks.

Pipelines function given the assets they have and the mix of commodities they carry. However, these will change over time and shippers must always be knowledgeable of current practice.

*Refiners expect the pipeline systems to be predictable and steady.*
Overview of Pipeline Delivered Network (USA/CAN)

Benefits of a Disciplined Crude Quality Management Program
  - Principles of Crude Quality
    - For Producers
    - For Refiners
Crude Value Management

For Refiners, crude selection is based on relative price differentials (diffs) between grades, which are based on relative crude quality differences.

Without appropriate crude quality assessment for planning models (Linear Programs/LP), higher basis risk ensues…

you could guess right? 😊
you could guess wrong? 😅
but why guess?

Managing Crude Value proactively should be a core refinery business process.
Quality within a commodity class, is still quite variability in quality and thus value (typically perceived as small relative quality changes but in fact can be significant).

Quality across commodity class is often considered as “contamination” and results from pipeline interfaces and/or tank mixing. (typically perceived as large relative quality changes).
Benefits from improved (=accurate) Crude Quality Management

- Improved realization of producer value
  
  If Refinery buyers consider “worst case” yields, value is lost by Producers and Refiner
  
  - Poor choice by Refiner in determining (incorrect) sub optimal case for relative crude marginal value understanding with hurdle rate to enter Refinery higher than it should be
  
  - Crude parity point moves to next available Tier/location typically at lower netbacks to producer

*It is recommended to model actual landed quality for most LP’s seeking profit maximization in monthly planning processes.*

*Alternatively, and during new crude introductions, It is acceptable to model blends of crudes to represent delivered qualities but must be based on real crude contaminations expected and expected landed qualities.*

*Use of injected crude quality representation adds large errors (positive or negative) to crude valuation for most customers.*
Crude Value Management

Benefits from improved (=accurate) Crude Quality Management

- Understand your customer
  - Refineries inevitably establish prices based on crude quality fundamentals
  - Refiners continue evolving Linear Programming (LP) models requiring more sophisticated/accurate crude Assay data
Let’s consider a real world example

LSB injected at Cromer delivered to Suncor Sarnia Refinery.

– Source Monitoring
– Refinery Landed Monitoring
Crude Value Management

Let’s consider a real world example

LSB injected at Cromer delivered to Suncor Sarnia Refinery.

- Source Monitoring options:
  - Arrange your own samples (difficult)
  - Utilize Canadian Association of Petroleum Producers (CAPP) support for industry crude quality at source

Next slides via CrudeMonitor Inc (thanks Bill)
Crude Value Management

CrudeMonitor.ca

“bringing the crude oil industry together with data”

Welcome to CrudeMonitor.ca!

Statistical Reports

The 2001-2005 results for the Heavy Crude Quality Monitoring program have been summarized and statistically tested and reported. The results of the statistical review are available through the following selections.

Summary properties sheets are available for light streams and heavy streams.

Data sources
Crude Value Management

### Heavy Crude Quality Testing Project -- Typical Crude Properties

<table>
<thead>
<tr>
<th>Crude</th>
<th>Sulphur (wt%)</th>
<th>API Gravity</th>
<th>Nickel (mg/L)</th>
<th>Vanadium (mg/L)</th>
<th>MCR (mass%)</th>
<th>TotalC4's (vol%)</th>
<th>TotalC5's (vol%)</th>
<th>Distillation Profile (% off at oC)</th>
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<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10%</td>
</tr>
<tr>
<td><strong>Light Sour Blend</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.15</td>
<td>36.2</td>
<td>5.73</td>
<td>9.82</td>
<td>2.99</td>
<td>2.12</td>
<td>3.29</td>
<td>95</td>
</tr>
<tr>
<td>Upper</td>
<td>1.50</td>
<td>38.6</td>
<td>10.16</td>
<td>18.94</td>
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<td>2.78</td>
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<tr>
<td>Lower</td>
<td>0.81</td>
<td>33.8</td>
<td>1.30</td>
<td>0.70</td>
<td>1.86</td>
<td>1.45</td>
<td>2.39</td>
<td>81</td>
</tr>
</tbody>
</table>

Some simply use the typical data.

This however is only numerically average data over time and does not lead to acceptable level of detail for refining.
More data is available on trends which is valuable insight into longer term trends and key for producers, strategists etc.

Though an upgrade vs simply averages, interpretation of trend is difficult.
Available trends for key properties help establish source changes

This historical data is best suited for trends over months.
Sidebar: Let’s leave LSB for a moment …

Seasonal changes can be seen clearly with this source data.

Q? how many assay representations would you consider for this crude?
Crude Value Management

Example of LSB @ Cromer data
This data is very good at providing trends in SOURCE data.

It has sufficient frequency for longer term trends.

It does not necessarily translate to changes in delivered quality.
Best Practices at Refineries

Monitor all crudes for landed quality

1. Custody Transfer Based Qualities with Pipelines
   Density/Sulfur….per batch (from composite sample)
   (part of existing Refinery and P/L accounting data)

2. Key Bulk Qualities to identify need for detailed assay change
   MCR/HTSD….frequency of 8-12 batches/month (from composite sample)
   (2 – 5 k$/month)

3. Full assay of landed quality for use in LP
   Full Assay of Landed Crude….frequency of 5-12 grades/year (from composite sample)
   (12 – 20 k$/assay)
With this increased frequency of data, we can see and eliminate outliers caused by poor sampling, poor lab analysis or outright exceptions.

Changes in landed crude quality starting in 2008 also show change in variance.

This variance now is wider than historical. The “system” surrounding LSB movements is changed.

NOTE SHOWN IN SOURCE DATA.
MCR is simple cheap accurate test used to track resid content.

Very beneficial for indications of type of contamination

(especially in systems with resid free synthetics which have MCR<0.2)
HTSD (ie D2887) is vital for yield understanding and thus the key value parameter to be monitored.

HTSD provides improved Crude Value understanding.

Best Practice would be to do 3-6 HTSD per crude run per year.

Software Tools (such as H/CAMS) are available to take HTSD, Density, Sulfur and do a “flash assay update” to a base assay. This provides 90% of the accuracy update vs a full assay update at a fraction of the cost.
a 15% change in naphtha content for the same crude!!!
A full assay should be done “when the quality has fundamentally changed”. This is self-guided by each Refinery but should be based on multiple quality variances.

Assay complexity dictated by LP model need (or Unit monitoring needs).

Use changes in these qualities to trigger new assay needs for LP.

Density
Sulfur
MCR
HTSD
Crude Value Management

In Summary

To maximize value retention to Producers and also value maximization for Refiners.....

- Understand the Logistics affecting Crude Quality
- Track Source Crude Quality for long term trends
- Have a disciplined system to track landed refinery crude quality at a higher frequency
- Monitor continuously to keep pace with changing quality.

Thank you!
BIOGRAPHY

Joey D. Pierce
ConocoPhillips Speciality Products Inc.

Joey Pierce holds a Bachelor of Science in Chemistry from Southwestern Oklahoma State University and a Master of Science in Physical Chemistry from the University of Texas at Austin. He began his career with Phillips Petroleum Company working in the Specialty Chemicals Division. Since then, Joey has been in commercial development, plant operations, lab management, sales and sales management and refinery economics and planning. In 2004, Joey transferred to ConocoPhillips Specialty Products Inc. (CSPI) as Director, Marketing. In that position, he worked to define and understand the global heavy oil market. In 2008, Joey moved into his current role of Director, Sales, Heavy Oil Flow Improvement. He has published several papers, written technical articles on flow improvers and their uses and presented at major conferences and associational meetings.

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Website: www.conocophillips.com
New Heavy Crude Oil Flow Improver Increases Delivery – Application Scenarios

Ray Johnston, Joey Pierce, Peter Lauzon
ConocoPhillips Specialty Products Inc.

For more than 25 years, Flow Improvers (also known as drag reducing agents) have been used to increase fluid flow in hydrocarbon pipeline systems. The existing technology is effective in refined products, light, (and to a limited extent) medium crude oils. This paper discusses the breakthrough in flow improver technology that allows treatment of heavy crude oil slates. Case studies of flow improver treatment of heavy oils in various pipeline systems will be discussed and factors influencing commercial success will be highlighted.
New Heavy Crude Oil Flow Improver
Increases Delivery – Application Scenarios

5th NCUT Upgrading and Refining Conference 2009

Ray Johnston
Peter Lauzon
Joey Pierce

ConocoPhillips Specialty Products Inc.
Drag Reduction Mechanism

- Laminar Sublayer
- Buffer Region
- Turbulent Core

with DRA

Diminished turbulent bursts
DRA’s (Traditional)

- Low viscosity
- High Turbulence
- **Excellent performance**

Light/Moderate Crude Oil

- High viscosity
- Low turbulence
- **Poor or no performance**

Heavy Crude Oil
The Key to Performance:

Interaction between the DRA polymer and the crude oil

<table>
<thead>
<tr>
<th>Crude Oil Sample</th>
<th>LiquidPower™ Flow Improver Compatibility</th>
<th>ExtremePower™ Flow Improver Compatibility</th>
<th>API Gravity</th>
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<tr>
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<tr>
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<td>Merey</td>
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<tr>
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<tr>
<td>Petrozuata</td>
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</table>
Scenario 1:

Increasing Delivery of Produced Heavy Crude Oil
Apiay – El Porvenir Pipeline

16-inch, 120 km, 91,000 barrel linefill

Batching 2 crude oils:
Apiay ("light", 21 °API)
Castilla blend ("heavy", 18 °API)

~35% “light” / 65% “heavy”

Base Capacity: 94,000 BPD avg.
LP™ 300 Flow Improver:
103,000 BPD
(in Apiay batches only)

Apiay-El Porvenir pipeline samples were evaluated for interaction in the lab.

<table>
<thead>
<tr>
<th>Crude Oil Sample</th>
<th>LiquidPower™ Flow Improver Compatibility</th>
<th>ExtremePower™ Flow Improver Compatibility</th>
<th>API Gravity</th>
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<tr>
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<td>None</td>
<td>High</td>
<td>9.1</td>
</tr>
</tbody>
</table>
Pipeline Regime Profile

With Castilla blend

- Reynolds Number
- Pipeline Viscosity (cSt)

- turbulent
- transition
- laminar

- 45°C
- 29°C

- Apiay pump station
- Monterrey pump station
Pipeline Model – Capacity Trend with Batch Cycle

Basis: 70K BBLS Castilla blend → 31K BBLS Apiay →

- Baseline: 94,000 BPD avg.
- 75 ppm ExtremePower™ FI: 118,000 BPD avg.

Start pumping Castilla → Start pumping Apiay

Barrels pumped
### Field Test Results

**October 2007**

**Performance exceeded model**

**Achieved 26 - 32% throughput over baseline operation**

<table>
<thead>
<tr>
<th>Pipeline System Condition</th>
<th>Baseline (Thousands of BPD)</th>
<th>ExtremePower™ DRA Dosage (ppm,)</th>
<th>LP™ 300 DRA Dosage (ppm,)</th>
<th>Model (Thousands of BPD)</th>
<th>Result (Thousands of BPD)</th>
<th>Percent Flow Increase</th>
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<tr>
<td>Test Pipeline Operations – ExtremePower™ injected into Castilla Blend</td>
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<td>107</td>
<td>110.4</td>
<td>21.0</td>
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<tr>
<td>Normal Pipeline Operation – ExtremePower™ injected into each crude</td>
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<td></td>
<td></td>
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<tr>
<td>65% Castilla Blend/35 % Apiay</td>
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<td>ExtremePower™ injection in each crude</td>
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<td>118.0</td>
<td>121.0</td>
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<td>Normal Pipeline Operation – ExtremePower™ injected into Castilla, LP™ 300 injected into Apiay</td>
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<td>LP™ 300 in Apiay</td>
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</table>
Scenario 2:

Increasing Heavy Crude Oil Delivery via Dilution to Optimum Viscosity tied with Drag Reduction
Transition Pipeline Hydraulics

Frictional Pressure Drop

Reynolds Number

Increasing flow

Constant viscosity

Laminar

Turbulent
Transition Pipeline Hydraulics

Frictional Pressure Drop vs. Reynolds Number

- Laminar
- Turbulent
- Drag Reduction

Constant viscosity

Increasing flow

"Laminar extension"
Example Pipeline: Throughput Versus Viscosity

Pipeline Capacity (BPD)

Crude Oil Viscosity (cst)

10” diameter
50 miles
1400 MAOP
Example Pipeline: Throughput Versus Viscosity

![Graph showing the relationship between Pipeline Capacity (BPD) and Crude Oil Viscosity (cst). The graph includes two lines, one for untreated and one for DRA treated oil, with annotations indicating a 10” diameter, 50 miles, and 1400 MAOP.]
Impact of Diluents on Viscosity

WCS Crude Oil

- WTI 41 °API
- Naphtha 54 °API

Viscosity (centistokes) vs. Dilution Level (Volume %)
Example Pipeline: Dilution Effects on Flow Capacity

WCS crude oil diluted with WTI crude

DRA treated

38,500 BPD

47,300 BPD

10" diameter
50 miles
1400 MAOP
Example Pipeline: Dilution Effects on Net Throughput

WCS crude oil diluted with WTI crude

Net Heavy Oil Throughput (BPD)

- DRA treated
- 34,800 BPD
- 39,500 BPD

Net WCS volumes increased

Dilution Level (% volume)

- 10" diameter
- 50 miles
- 1400 MAOP
Summary

**New DRA developed for heavy crude oil**
- Strong interaction with heavy crude oil (<23 °API)
- Performance in transition flow ($N_{RE} 2100+$)

**Successful field trials for production flow increase**
- Demonstrated 20 to 30% flow increase during test
- 50 ppm with ~25% flow increase in application

**Combine ExtremePower™ Flow Improver with further dilution to an optimized viscosity**
- Utilizes drag reduction in transition flow
- Increases NET heavy crude oil throughput capacity
Acknowledgements

CSPI would like to thank Ecopetrol and Delrio for partnering with us on the flow improver test and allowing CSPI to share the results of the test with the participants of the 2008 International Pipeline Conference.

CSPI would like to thank ConocoPhillips Pipe Line Co. for the numerous field tests and ongoing application to provide valuable data of heavy crude oil and transition flow performance.
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BIOGRAPHY

Walter Giesbrecht
Flint Hills Resources

Walt Giesbrecht has 35 years experience in Corrosion, Materials and Inspection activities. He is currently a Principal Engineer – Corrosion and Materials, with the Refinery Technical Section of Flint Hills Resources LP at the Pine Bend Refinery, where he provides technical support to refinery operations. Walt also travels extensively to most Flint Hills locations where he provides technical support. He also supports Koch HC Partnership B.V in Rotterdam. Walt joined Flint Hills Resources in 1995 and prior to moving to Minnesota, he worked in Indiana, Nova Scotia, Ontario and Alberta and filled several positions including Inspection Supervisor.

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Rosemount, Montana 55068 USA
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Email: walt.giesbrecht@fhr.com
Website: www.fhr.com
ABSTRACT

Processing Canadian High TAN, High Sulfur Crudes

Walter G. Giesbrecht
Flint Hill Resources

A detailed review at what it takes to process Canadian high TAN, high sulfur, heavy crudes. Understanding how these crudes may potentially impact the processes and what are the 2nd, 3rd and even 4th order effects of these crudes. The paper will include what one can expect from when the crudes arrives at your location; to the effect these crudes will have through the complete refinery including the impact on the back end waste water treatment plants.

Please contact Walter Giesbrecht at Flint Hill Resources to request a copy of the presentation. Coordinates are contained on Mr. Giesbrecht’s biography on the preceding page.
BIOGRAPHY

Cameron Todd

Connacher Oil and Gas Company Limited

Cameron Todd is currently Vice President Refining and Marketing for Connacher Oil and Gas Limited. Cameron is responsible for downstream operations including operation of the company’s 10,000 BPD heavy oil refinery in Great Falls, Montana, the blending and sale of bitumen production from the company’s 10,000 BPD Great Divide SAGD project, located south of Ft McMurray, Alberta, the procurement and transportation of diluent and the marketing of the company’s conventional oil and gas production.

Cameron has worked for over 29 years in the oil and gas industry, and has held various executive, management, operational and engineering positions with companies in Alberta, the US and Argentina. Cam’s first experience with diluent and heavy oil, goes back to 1984 when he worked on development of Amoco’s Elk Point project and later on the company’s Primrose project. He is the author of a number of papers and studies on heavy oil, bitumen, upgrading, diluent and transportation.

Cameron graduated from the University of Calgary in 1980 with a BSc in Mechanical Engineering. He lives in Calgary, is married and has four children.

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Email: ctodd@Connacheroil.com
Diluent and Bitumen, An Uneasy Mix  
Considerations for treating, blending, transportation, marketing and refining  

Cameron M. Todd  
Connacher Oil and Gas Limited

Condensates and gasolines are commonly used to dilute heavier and more viscous crude oils in order to improve field processing, transportability in pipelines and acceptability in markets and refineries. The large amount of heavy oil and bitumen currently produced in Canada and projected for the future has resulted in a large demand for such diluent, and attractive prices have resulted. Consequently a wide range of diluent sources, quality and components are finding their way into the Canadian diluent supply stream, with attendant concerns arising regarding diluent performance and impact upon resulting blended crude oil. The cost of diluent is one of the largest controllable expenses associated with most bitumen production projects. This paper assesses a number of the issues associated with the use of diluent as a blending agent with Canadian bitumen. Issues to be considered include market factors such as supply, demand, price and infrastructure, operational processing and blending issues, diluent quality and component variability, and downstream issues including refinery processing and yields.
Diluent and Bitumen – An Uneasy Mix

A Presentation by Cameron Todd, VP Refining and Marketing
to the 5th NCUT Upgrading and Refining Conference

September 2009

Keeping our ducks in a row
Forward Looking Information and Advisories

This presentation contains forward looking information including expectations of future production and bitumen production goals including the anticipated timing associated therewith, the role of diluent in bitumen operations, estimates of supply of natural gas condensates, future diluent requirements, density equalizations and what constitutes the best diluent for use in blending with bitumen including associated economics. Forward looking information is based on management’s expectations regarding future growth and take into account expectations regarding operating costs, average realized oil and natural gas prices, average throughput, costs of purchased feedstock, steam:oil ratios, results of operation, production, future capital and other expenditures (including the amount, nature and sources of funding thereof), plans for and results of drilling activity, environmental matters, business prospects and opportunities, future royalty rates, commodity prices and foreign exchange rates and future economic conditions and involves significant known and unknown risks and uncertainties, which could cause actual results to differ materially from those anticipated. These risks include, but are not limited to: the risks associated with the oil and gas industry (e.g., operational risks in development, exploration and production; delays or changes in plans with respect to exploration or development projects or capital expenditures; actual steam:oil ratios being different than what was anticipated; the uncertainty of reserve and resource estimates; the uncertainty of estimates and projections relating to production, costs and expenses, and health, safety and environmental risks), the risk of commodity price and foreign exchange rate fluctuations, risks related to future royalty rate changes and risks and uncertainties associated with securing and maintaining the necessary regulatory approvals and financing to proceed with the continued expansion of the Great Divide Project at Algar and other regions and expansion of the company’s conventional and refinery operations. In addition, the current financial crisis has resulted in severe economic uncertainty and resulting illiquidity in credit and capital markets which increases the risk that actual results will vary from forward looking expectations and these variations may be material. These risks and uncertainties are described in detail in Connacher’s Annual Information Form for the year ended December 31, 2008, which is available at www.sedar.com. Certain assumptions relating to reserves and resources and the future net revenue associated therewith are contained in Connacher’s Annual Information Form. Certain assumptions relating to estimated future operating margins and netbacks are included in the notes to slides 16 and 38. The Corporation assumes no obligation to update or revise the forward-looking information to reflect new events or circumstances, except as required by law. All references to barrels of oil equivalent (boe) are calculated on the basis of 6 Mcf : 1 bbl (unless otherwise indicated). This conversion ratio is based on an energy equivalency conversion method primarily applicable at the burner tip and does not represent a value equivalency at the wellhead. Boes may be misleading, particularly if used in isolation.

This paper represents solely the opinions and conclusions of the author which may not agree with those of Connacher
Uneasy Mix Outline

- Introduction
- Diluent - what is it good for?
- Will there be enough diluent?
- Where does diluent come from?
- What about quality – Does it matter what we mix with our bitumen?
- How much does it cost – is it economic?
- What diluent is best?
- Conclusions
Who is Connacher?

- **Small integrated oil sands producer/developer**
  - Great Divide Project (Athabasca)
    - 10,000 BPD SAGD
    - Currently 8,000 BPD bitumen production
  - Algar Project
    - 10,000 BPD SAGD
    - Under construction, 2010 startup

- **Fully integrated company**
  - SAGD oil sands production
  - Natural gas production
  - Refinery – 10,000 BPD Great Falls, Montana
  - Diluent producer

- **Great Divide**
  - Treat bitumen with diluent
  - Purchase diluent
    - Refinery naphtha
    - Condensate
  - Truck dilbit to market
  - Rail and truck transport
  - Pursuing pipeline connection
What is the Role of Diluent in Heavy Oil/Bitumen Operations?

- Dilute heavy oil / bitumen to:
  - Reduce viscosity
  - Reduce TAN (Total Acid Number)
  - Reduce sulphur / heavy metals
  - Reduce density
- Aid in de-watering and treating
- Removal of non-hydrocarbon solids (clay and fines)
- Extraction and upgrading (froth treatment, asphaltene removal)
- Future - next generation solvent SAGD
- Historically the dilution function has largely been a volume function (i.e.. volumetric dilution)
- Increasingly chemistry has been of interest / concern
Treating Challenges for the SAGD Operator

- SAGD Operations produce tight emulsions
- Primarily oil-in-water
- But also water –in-oil (simultaneously)
  - Also micro-emulsion
- Tight emulsions (high interfacial tension)
  - Steam injected at high temperature and pressure “collapses” into water drawing in bitumen and forming emulsions in-situ
  - Additional shearing occurs in reservoir, flow through liner slots, downhole pumps and during pressure reduction at surface
  - Emulsions are very stable
  - Emulsifying agents may include clays, dissolved silica and other minerals as well as complex components in bitumen

Figure 9a – Top layer O/W emulsions of batch 2 (B2S2). Circles are oil droplets in water
Bitumen and Water Treating Challenges

- Water separation is very difficult, must be <.5% BSW
  - Very tight emulsions are formed
  - Athabasca bitumen heavier than water, but close to water density
  - Heating changes density but difference not enough unless very hot
  - Tiny difference in electric potential (zeta)
  - Add diluent to “lighten” the crude, improve separation
  - Modify pH and add demulsifiers
- Diluent and chemicals must work together
- High water recycle (95%) means no oil residue is allowed
  - Water in oil emulsion/micro-emulsion is a problem
- Solids build-up in treater can be a problem
  - Sand and clay in most operations, not at Connacher
  - Possibly due to precipitation of asphaltene film in water-in-oil emulsion
- Light ends of diluent flash off in sales tanks (diluent losses and VRU loading)
Will there be enough diluent?

- Alberta ran out of sufficient natural gas condensate to meet local demand for diluent long ago
  - Natural gas condensate is in decline
  - Bitumen production is steadily increasing
  - Every 100,000 bpd of bitumen produced will require 35-40,000 bpd of additional diluent (excluding upgraded bitumen and synthetic diluent)
  - We now rely on imported diluent to balance the supply
  - US and offshore diluent supply is increasing and sufficient
    - Southern Lights will bring diluent in 2010 (up to 180,000 bpd)
  - Diluent recycle may be an efficient solution

- Since diluent is broadly defined as hydrocarbon liquid between 600 to 800 kg/m3 density (API 45 to 105°) a wide range of diluents is used
  - Natural gas plant condensate
  - Refinery naphtha’s and light gasoline blend stocks
  - Other blended hydrocarbons

- Many transportation means are used to supply diluent
  - Pipeline, truck, rail, ship
  - Transportation and storage logistics are challenging
Diluent – Where does it come from?

- Diluent is a light hydrocarbon with density between 600-800 kg/m3
- Natural gas condensate comes from processing natural gas, much from Alberta production, collected from gas plants and shipped by pipeline, truck and rail
- Natural gas condensate is also produced with LNG, then is shipped to N. America by tanker
- Condensate produced from solution gas plants is “richer” and contains small amounts of heavier components
- Refinery straight run gasoline, light and heavy naphtha’s and distillates are produced by distilling crude oils at refineries. They may contain more aromatic components which are generally desirable blending agents. US refineries have excess capacity for export.
- Reformulated or alkylated gasoline blending stocks are generally expensive but may be used as diluent when gasoline is in short supply
- Cracked refinery or upgrader products such as cracked gasoline, distillates or coker products may be “under-saturated” and less stable. They may contain olefins and other components which may work as diluents but be less desirable to refiners downstream
- Light crude oils may fall into acceptable density range for blending but may cause concern with asphaltene precipitation and are not desirable as diluent
- LPG’s in small amounts may be blended with heavier hydrocarbons (such as light oils) with the blended product used as diluent. For most heavy producers this is not desirable. Light ends flash off and may cause asphaltene precipitation.
Natural Gas Plant Condensate

- Condensate comes from natural gas which in its natural reservoir state is in a gaseous form
- Condenses out of gas with reduction in pressure and/or temperature
- Separated at gas plants and fractionation facilities primarily by chilling
- Gas is primarily methane with progressively smaller amounts of C2, C3 and heavier components
- Condensate is mostly C5 with lesser amounts of heavier components; mostly simple straight chain paraffins
- Historically condensates have required additional processing to make useful products
  - Petrochemicals
  - Gasoline (too low octane number)
- Today diluent is easier (no processing) and higher value
• Refinery condensates/naphthas are distilled from crude oil
  – In natural state in the reservoir they are liquid
  – Separated between distillation “cut points”
  – They are a complex mix of liquid hydrocarbons which can include dozens or hundreds of different molecules
  – Can include non-naturally occurring cracked hydrocarbons
  – Aromatics, cyclo-hydrocarbons
  – Compatibility
Diluent Quality Considerations

- Broad range of diluent sources, broad specifications and premium diluent prices create potpourri of diluent characteristics

- Great incentive to make diluent for volumetric purposes and little control over chemistry

- Blending economics may result in undesirable blend stock such as LPG’s, light oils, cracked products and some upgraded products

- Suppliers to general “pool” will not be familiar with end customer (producer) needs

- Concerns with contaminants and solids

Solids found in diluent strainer prior to treating train
Diluent Blending Economics 101

Diluent Volume

- Assume we blend to 930 kg/m³ density (API 20.7) to make pipeline specs
- Assume we start with 8 API (1014 kg/m³) Athabasca bitumen and 65 API condensate (720 kg/m³)
- Blend ratio is % bitumen in the blend
- Required ratio is 71.4% bitumen and 28.6% condensate
- If we use 86 API condensate (650 kg/m³) then the required diluent is less (77% bitumen and 23% condensate)
Diluent Blending Economics 101

Diluent Cost

• Not all of the cost of diluent purchased is a loss. Diluent blended increases the volume of blend crude sold. It is however sold at a lower price.

• Net cost of diluent used is a function of price paid for diluent (premium over light sweet crude) and the price received for blended heavy crude (discount from light sweet crude)

• Net Cost per barrel bitumen = volume of diluent times (price of diluent minus price of dilbit)

• If diluent premium is $5/bbl and heavy oil discount is $20/bbl (assuming a $70/bbl WTI price) and blend ratio is 71% bitumen to 29% diluent as in previous example then net diluent cost is .29/.71*($75-$50) or $10.21/bbl bitumen

• For the same condensate price using lighter diluent with the ratio 77% bitumen to 23% diluent the net cost is $7.46/bbl

• Pipeline equalization will recover some compensation (approximately $.75/bbl) but economics lean to lighter diluent (lighter gravity diluent is better!)
Density Equalization - Explained

- The market basis for density equalization currently stands at 750.0 kg/m³.
- Anything of a higher density will receive additional value and anything of a lower density will be penalized.
- Using June as the equalization basis, we can therefore calculate that:
  - a condensate with a density of 700.0 kg/m³ will be valued at C$3.50 more than the market basis
  - a condensate with a density of 800.0 kg/m³ will be penalized by C$3.50
So what is the best diluent?

- The best diluent is no diluent – less is more
- Every operation is unique – one size does not fit all
  - Special needs may require special diluents
- Light diluents allow reduced diluent blending volume
- Minimize light components to reduce diluent losses and precipitation risks (no c3 or c4 at all!)
- Aromatics increase blending compatibility and reduce precipitation risks
- Oils and heavy components offer little value and increased risk of solids precipitation – should be restricted from diluent pool
- Cracked components, benzene and contaminants may be of significant concern to refiner customers, should be segregated
Conclusions from a SAGD Producer’s Perspective

- Diluent is a scarce commodity; must be imported to ensure sufficient supply

- Diluent is the highest single cost a SAGD operator faces – minimizing diluent use is a high priority

- Challenging bitumen treating problems require careful assessment and analysis of bitumen and diluent chemistry – consider the “system" not just the pipeline requirements

- Diluent is not just a volumetric component, other physical and chemical properties are critical

- Diluent quality issues are a key concern in optimizing and ensuring stable operations

- Special needs may require segregated supplies, on-site diluent treating, recycle and dedicated transportation
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www.connacheroil.com
Acknowledgements and Resources

I have relied on a number of individuals and organizations with a great deal of expertise on the subjects presented here most of which have far greater experience in the area than myself. I appreciate the work they have done and would refer you to them. In addition I would like to acknowledge a number of the pictures included herein from Dr. Chandra Angle and Canmet Energy.

- Dr. Declan Livesey – Connacher Oil and Gas

- Canmet, Dr. Hassan Hamza, Dr. Chandra Angle, Dr. Tadek Dabros

- Canadian Crude Quality Technical Association (CCQTA) Andre Lemieux

- CAPP Crude Quality working group

- Purvin and Gertz, Tom Wise, Steve Kelly

- Consortium for Asphaltene and Emulsion Research, Dr. Harvey Yarranton

- Canadian Crude Oil and Condensate Shippers, Equalization Steering Committee
BIOGRAPHY

Bill Lywood

Crude Quality Inc.

Bill Lywood is president of Crude Quality Inc, an Alberta based company focused on crude quality related issues pertaining to the upstream, midstream and downstream sectors of the industry. Among Crude Quality’s many projects is the flagship crudemonitor.ca website where detailed quality information on western Canadian crude streams is available through the sponsorship of the Canadian Association of Petroleum Producers (CAPP) and the Small Explorers and Producers Association of Canada (SEPAC). Previously, Bill partnered in another consulting firm dealing with issues related to refinery processing impacts caused by crude contamination and quality variability. Bill holds a Bachelor of Applied Science degree from the University of Waterloo and is an avid saltwater and freshwater fly fisherman.

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Phone: 780 991 9900
Email: lywood@crudequality.com
Website: www.crudequality.com
Quality Factors to Consider in Condensate Selection

Bill Lywood
Crude Quality Inc.

There are a host of factors to consider when evaluating condensates as a diluent for bitumen and/or heavy crude production blending. Apart from the commercial issues, the impact of condensate quality remains a key consideration in the evaluation. Condensate quality traditionally includes the obvious parameters of density and viscosity, however valuation decisions could be improved through the expansion of quality definitions and understanding.

This presentation is meant to provide expanded insight into condensate quality parameters of importance in the selection of a diluent grade product. In addition to a review of pipeline and industry specifications, this presentation will provide additional information relating to general properties, bitumen – condensate compatibility, sampling and quality testing requirements, and available information sources related to condensate quality.
Quality Factors to Consider in Condensate Selection

5th NCUT Upgrading and Refining Conference
September 16, 2009
Edmonton, Alberta, Canada

W.G. (Bill) Lywood
Crude Quality Inc.
Quality Factors to Consider in Condensate Selection

- Two principal quality groupings in the selection of condensate

  - Characteristics that are required for the functional use of condensate as a diluent

  - Characteristics that present POTENTIAL and REAL benefits and risks in the blended dilbit
Quality Factors to Consider in Condensate Selection

- Characteristics that are required for the functional use of condensate as a diluent
- Pipeline specifications for density and viscosity
  - Density (API gravity)
    - Density blending models for dilbit available
      - Need to take into account shrinkage factors (three step dilution)
  - Viscosity
    - Viscosity blending models for dilbit available
Quality Factors to Consider in Condensate Selection

Characteristics that present POTENTIAL and REAL benefits and risks in the blended dilbit

Much longer list of characteristics, including:

- Physical properties
  - RVP, sediment, BS&W

- Chemical properties
  - Aromatics (BTEX), olefins, benzene, sulphur compounds, additives/contaminants, compatibility/stability, organic chlorides, mercury, oxygenates
Quality Factors to Consider in Condensate Selection

Physical properties

- **RVP (Reid Vapour Pressure)**
  - High concentrations of “small” molecules increases RVP, potentially beyond dilbit pipeline specifications
  - Generally balanced off against density

- **Sediment**
  - Sedimentation, deposition in low flow zones and tankage
  - No benefits, only liabilities → MAX limits

- **BS&W**
  - Traditional, “non-oil” measurement
  - Important in crude accounting, no benefits → MAX limits
Quality Factors to Consider in Condensate Selection

Chemical Properties

- Olefins
  - Native only at miniscule levels in WCSB production
  - Consumes $\text{H}_2$ and can form gums/deposits in refineries
  - No benefits, valuation & operational liability $\rightarrow$ MAX limit

- Aromatics
  - Sum of vol% Benzene, Toluene, Ethylbenzene, Xylenes
  - Normally present at 2 – 10 vol% in WCSB condensates
  - Positively stabilizes condensate – bitumen blends
  - Real benefits, limited liability $\rightarrow$ MIN limit
Quality Factors to Consider in Condensate Selection

Chemical Properties (cont ...)

- Benzene (component of BTEX)
  - Negative valuation implications in mogas
    - Negatives shared with Me-cycloC5, nC6, cycloC6
    - Negatives not generally shared with TEX portion of BTEX
  - → MAX limit

- Oxygenates
  - Not naturally present, sources include biodiesel (FAME), reformulated mogas, chemical production, methanol
  - Some pipeline rules & regs prohibit oxygenates
  - No benefit, value and operational liability → MAX limit
Quality Factors to Consider in Condensate Selection

- Crude Compatibility
  - CAPP studies conducted at NCUT
    - Bluesky, Wabasca, Athabasca, McMurray, Coldwater, conventional heavy have identical stability numbers (+/-)
    - Use $I_N = 38$ and $S_{BN} = 114$ ($P = 3.0$) *FOR BASE BITUMENS*, not blended dilbit
  - Using Wiehe formulas, other references & healthy dose of conservatism, recommended
    - $P \geq 2.0$ – green light, no anticipated compatibility issues
    - $2.0 \leq P \leq 1.4$ – amber light, OK but increasing risk
    - $P \leq 1.4$ – red light, may still be OK, but risks appreciable
Quality Factors to Consider in Condensate Selection

- Crude Compatibility (cont ...)
- Example blending limit tables

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Solubility (SBN)</th>
<th>Insolubility (IN)</th>
<th>P-Value (SBN/IN)</th>
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<tbody>
<tr>
<td>Athabasca Bitumen</td>
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<td>30</td>
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</table>
Quality Factors to Consider in Condensate Selection

Test Methods

- When evaluating condensates, or when establishing specifications, one MUST specify the test method.
- Test methods should be representative of the stream being evaluated.
- Test methods must be widely available at reasonable costs.
- ASTM methods provide interlab comparisons.
Quality Factors to Consider in Condensate Selection

Looking Forward

- Industry, in co-operation with regulated pipeline, is establishing specifications for **ALL** condensate feeders “at the gate” to the blended (CRW) pool
  - Will require ongoing feeder quality testing program and mitigation procedures
  - Will require routine panel review of parameters & limits

- Crudemonitor.ca has been operating a distinct section for CRW condensate since 1Q2008
Quality Factors to Consider in Condensate Selection

Thank you for your attendance and your attention

Questions ??

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Parviz Rahimi
National Centre for Upgrading Technology (NCUT)

Parviz Rahimi obtained his PhD in Chemistry from the University of Alberta in 1980 and joined Natural Resources Canada in 1981. Currently he is working as senior research scientist in the primary upgrading division of the National Centre for Upgrading Technology (NCUT) in Alberta, Canada.

His expertise in bitumen chemistry extends beyond molecular characterization into upgrading processes including field upgrading. He has extensive knowledge of partial upgrading either using thermal conversion such as visbreaking or partial deasphalting for the purpose of reducing the required diluent for pipeline transportation. He has established an expert team to address the stability and compatibility issues related to partially upgraded bitumen and heavy oils as well as during production and upgrading. His recently research activities include fouling and corrosion related to bitumen processing. He has established networking research into understanding bitumen/heavy oil processing with Universities, Government departments and private research organizations as well as major oil companies.

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Diluent Evaluation for Bitumen Pipelining

Parviz Rahimi, Simon Cooper, Teclemariam Alem
National Centre for Upgrading Technology (NCUT)

Oil sands crudes are expected to represent more than 75% of the crude produced in Western Canada. The bitumen are too viscous and must be diluted with a lighter hydrocarbon stream to meet the specifications required for shipping in pipelines, i.e., viscosity 350cSt (11°C) and gravity 19 °API, etc. Thermal processing could reduce the viscosity of the bitumen crudes and thus require less diluent but produces less stable fuels. It is expected that there will be a shortage of local diluent for pipeline transportation of bitumen which leads to demand for imported and recycled diluents. Compatibility and stability characteristics when blending diluents and crudes are important issues in the pipeline transportation.

The objectives of this work are:

• Investigation of the compatibility and stability of virgin and cracked bitumen in natural diluents and synthetic diluents

• Diluents ranking for asphaltenes stability in virgin bitumen, cracked bitumen

Four heavy oils and bitumens where used in this study – Athabasca bitumen (AB), cracked Athabasca bitumen, heavy oil B, and a light crude C were chosen to investigate their compatibility and stability characteristics with two different diluents, i.e. natural gas condensate (NGC), oil sands derived liquid (Synthetic).

Following oil compatibility model developed by Irwin Wiehe, the insolubility number and solubility blending number of different crudes, diluents and their blends were investigated. Using an optical method it was shown that the stability of different heavy oils can be accurately determined and ranked by observing flocculation of asphaltenes. Similarly the strength of different diluents including natural gas condensates and synthetic diluents for keeping asphaltenes soluble in the oil matrix were evaluated and ranked. It was shown while synthetic diluents are better solvents than NGC for bitumen, when bitumen is processed the order of the solvent strength is reversed. The reason for this behavior will be discussed.
Diluent Evaluation for Pipelining

Parviz Rahimi, Zhiming Fan, Simon Cooper, Teclemariam Alem, National Centre for Upgrading Technology (NCUT) and
Irwin Wiehe
Soluble Solutions

For presentation at
5th NCUT Upgrading and Refining Conference 2009

Edmonton, Alberta
September 14-16, 2009
Outline

- Background
- Objectives
- Bitumen – solvent Compatibility
- Asphaltenes stability in different solvent
- Conclusions
Background

- Bitumen production is increasing:
  - Current: 1.5 MMBD
  - 2015: 3.0 MMBD
  - 2030: 5.0 MMBD
Heavy oils in western Canada are characterized by:

- High viscosity >100,000 cP
- High gravity 7-15 °API
- High asphaltenes 17 wt% (C₅)
- High aromaticity 0.33

Pipeline Specifications

- Viscosity 350 cSt @ 11°C
- Gravity 19 °API
Pipeline Transportation - Issues

• Heavy oils/bitumens are too viscous and require diluent for pipeline transportation

• Thermal processing will reduce viscosity (less diluent required) but produces less stable fuel

• Shortage of local diluent for pipeline transportation of bitumen leads to demand for imported and recycled diluent

• Compatibility between diluents and bitumens/heavy oils is an important issue that should be addressed
Objectives

• Investigate the compatibility and stability of virgin and cracked bitumen in:
  - Natural diluents
  - Synthetic diluents

• Diluents ranking for asphaltenes stability in virgin bitumen, cracked bitumen
Feedstocks

- **Oils:**
  - Athabasca Bitumen (AB)
  - Cracked AB (bottoms)
  - Bitumen B
  - Light crude (C)

- **Diluents:**
  - Natural Gas Condensate (NGC) - Dilbit
  - Oil Sands-derived liquid - Synbit
  - N-alkanes
Properties of Diluents

- Natural Gas Condensate (NGC) - Dilbit
- Oil sand-derived liquid - Synbit

<table>
<thead>
<tr>
<th></th>
<th>Naphthenes (wt%)</th>
<th>Paraffins (wt%)</th>
<th>Aromatics (wt%)</th>
<th>Carbon #</th>
<th>NGC</th>
<th>Syn</th>
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<td>35.0</td>
<td>4</td>
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<td>3.67</td>
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<td>29.1</td>
<td>33.9</td>
<td>5</td>
<td>38.9</td>
<td>11.1</td>
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## Properties of the Oils

- Athabasca Bitumen (AB)
- Cracked AB (bottoms)
- Bitumen B
- Light crude (C)

<table>
<thead>
<tr>
<th></th>
<th>AB</th>
<th>Cracked AB</th>
<th>Bitumen B</th>
<th>Light Crude</th>
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<td>53.2</td>
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<td>Polars</td>
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<td>18.1</td>
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<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>17.4</td>
<td>100</td>
</tr>
</tbody>
</table>
Bitumen - Diluent Compatibility
Asphaltenes Stability - Optical Method

- ASTM D- 7157
- ASTM D- 6703
- ASTM D- 7060
- ASTM D- 7061
Compatibility Model

Developed by Irwin Wiehe to determine crude incompatibility that causes fouling and coking

\[ I_N = \frac{TE}{1 - \frac{V_H}{25d}} \]

\[ S_{BN} = I_N \left(1 + \frac{V_H}{5}\right) \]

- \( S_{BN} \) – Solubility Blending Number – a measure of the oil solvency for asphaltenes
- \( I_N \) – Insolubility Number – a measure of asphaltene solubility
- \( d \) - Density

For compatible blends: \( S_{BN} > I_N \)
Laboratory Test
Based on Toluene - Heptane Scale

• TE – minimum vol% of toluene in test liquid (toluene/n-heptane mixture) to keep asphaltenes in solution at a concentration of two grams of oil and 10mL of test liquid

• $V_H$ – the maximum volume of heptane that can be blended with 5mL of oil without precipitating asphaltenes.
Solubility Parameters

\[ I_N = \frac{TE}{1 - \frac{V_H}{25d}} \]

\[ S_{BN} = I_N \left(1 + \frac{V_H}{5}\right) \]

For compatible blends: \( S_{BN} > I_N \)
Compatibility Model

Predicted solubility numbers for blends

\[ S_{BN_{\text{blend}}} = \frac{V_A S_{BN(A)} + V_B S_{BN(B)}}{V_A + V_B} \]
Compatibility of Synthetic Diluent with Athabasca Feed

<table>
<thead>
<tr>
<th>Volume of Synthetic</th>
<th>Volume AB Feed</th>
<th>$S_{BN_{mix}}$</th>
<th>P-Value ($S_{BN}/I_N$)</th>
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## Compatibility of NGC with Athabasca Feed

<table>
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<th>Volume NGC</th>
<th>Volume AB Feed</th>
<th>SBN&lt;sub&gt;mix&lt;/sub&gt;</th>
<th>P-Value (S&lt;sub&gt;BN&lt;/sub&gt;/I&lt;sub&gt;N&lt;/sub&gt;)</th>
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<td>70</td>
<td>30</td>
<td>29.3</td>
<td>1.03</td>
</tr>
</tbody>
</table>

### Key Results
- **NGC**
  - Solubility ($S_{BN}$): 5.2
  - Insolubility ($I_N$): 0
  - Non-solvent oil

- **AB Feed**
  - Solubility ($S_{BN}$): 85.5
  - Insolubility ($I_N$): 28.3
### Compatibility of Synthetic Diluent with Cracked AB Feed

<table>
<thead>
<tr>
<th></th>
<th>Solubility ($S_{BN}$)</th>
<th>Insolubility ($I_N$)</th>
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<th>Volume C-Feed</th>
<th>$SBN_{mix}$</th>
<th>P-Value ($S_{BN}/I_N$)</th>
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<tbody>
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<td>1.22</td>
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<td>88.8</td>
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<td>20</td>
<td>80</td>
<td>84.7</td>
<td>1.02</td>
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## Compatibility of NGC with Cracked AB Feed

<table>
<thead>
<tr>
<th></th>
<th>Solubility ($S_{BN}$)</th>
<th>Insolubility ($I_N$)</th>
<th>P-Value ($S_{BN}/I_N$)</th>
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<tbody>
<tr>
<td>NGC</td>
<td>5.2</td>
<td>0</td>
<td>Non-solvent oil</td>
</tr>
<tr>
<td>Cracked Feed</td>
<td>101.12</td>
<td>82.88</td>
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<tr>
<td>Volume NGC</td>
<td></td>
<td>Volume C-Feed</td>
<td>$S_{BN_{mix}}$</td>
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<tr>
<td>0</td>
<td></td>
<td>100</td>
<td>101.1</td>
</tr>
<tr>
<td>5</td>
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<td>95</td>
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<td>10</td>
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<td>15</td>
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<td>86.7</td>
</tr>
</tbody>
</table>

Alberta Energy Research Institute

Natural Resources Canada

Ressources naturelles Canada

Alberta Research Council
Condensate Requirement

Vol% condensate

Solubility numbers

Visbroken

Bitumen
Asphaltenes Stability in Different Solvents
Equipment - Turbiscan AGS

- The Turbiscan AGS is a fully automated near-infra red (880nm) optical scanner
- Capable of fully scanning a sample once a minute with scans at 40µm intervals
- Temperature Control
Turbiscan AGS

Simultaneous Transmission (T%) and Backscatter (BS%) Profile
Sample Preparation

- **Basic sample preparation modified from ASTM D7061**
  - 10g Oil + 90g Toluene (1:9)
  - magnetic stir 1-3hr
  - 4mL Oil/Toluene + 46mL precipitant
  - shake for 6s and immediately add 20mL of solution to vial
  - Insert vial for immediate scanning
Turbiscan Data Output

Cracked Bitumen / Heptane

heptane & ahs (25C-8m1d)_1 - [File created by Turbisoft-AGS Version 1.1 English]  (01/08/07 16:50:30)

Transmission - No zoom

Backscattering - No zoom

Temperature - No zoom

Control point

Set point
Interpretation of Data

- Profile changes are due to changes in the localized concentration of particles and changes in the average particle size.

- Separability number (Eqn. 1) (ASTM D7061) can be calculated from data as a measure of stability.

\[
\text{Separability number} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - X_T)^2}{n - 1}} \quad (1)
\]

where:
- \(X_i\) = average transmittance for each 60 s,
- \(X_T\) = average of \(X_i\) \(X_T = X_1 + X_2 \ldots + X_{16}/16\), and
- \(n\) = the set of replicate measurements (16 in the method).
Output Data Manipulation with Turbisoft

- Average percent Transmission values for each scan can be obtained and plotted versus time
N-alkanes with Cracked AB (1:9)
Comparison of oil stability (n-C₇)

Transmission Percent vs. Time

- Cracked AB
- Bitumen B
- AB
Stabilization of Cracked AB by Maltenes

M/C = 0/1  SN = 11.3
M/C = 0.5/1  SN = 9.2
M/C = 1/1  SN = 6.8
Separability vs Asphaltene Content

- Virgin Oils with higher amounts of asphaltenes are more stable than processed oils
- Light oils with low asphaltenes are unstable

<table>
<thead>
<tr>
<th>Oil</th>
<th>C5 Insoluble (wt. %)</th>
<th>Separability Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>18.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Bitumen B</td>
<td>17.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Cracked AB</td>
<td>10.5</td>
<td>11.4</td>
</tr>
<tr>
<td>Crude A</td>
<td>1.2</td>
<td>8.2*</td>
</tr>
</tbody>
</table>

* Light oil - oil/toluene=1:1
Conclusions

Compatibility data:
• Oil sands-derived liquids are better solvent for bitumen than NGC
• With cracked feed lower volume of both Synthetic solvent and NGC result in incompatibility

Stability data:
• Using an automated Turbiscan it is possible to compare and rank stability of oils and diluents
• Asphaltenes stability studies showed:
  - For cracked feed NGC is a better solvent than oil sands-derived solvent
  - For Athabasca bitumen oil sands-derived solvent is better than NGC
Acknowledgements

This work was supported by:

NCUT: PERD and AERI
BIOGRAPHY

Harvey Yarranton
University of Calgary

Harvey Yarranton is a Professor of Chemical and Petroleum Engineering at the University of Calgary. He received his B.Sc. (1985) and Ph.D. (1997) degrees in Chemical Engineering from the University of Alberta. Between degrees, he worked for Dome Petroleum Ltd. and Amoco Canada Ltd. in reservoir, production and operations engineering. His research interests are the phase behavior and properties of heavy oils and solvents, the fundamentals and treatment of water-in-oil emulsions, and oil sands extraction and froth treatment. He is the director of the Consortium for Asphaltenes and Emulsions Research and his group has contributed over 70 journal and conference papers in the area.

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Expanded Fluid Based Viscosity Correlation - Diluted Heavy Oil Case Study

H.W. Yarranton, M.A. Satyro, F. Schoeggl Author
Department of Chemical and Petroleum Engineering, University of Calgary

In previous work (Yarranton and Satyo, 2009), the viscosity of pure hydrocarbons was correlated using a simple function based on the fluid density. The correlation has three adjustable parameters, a compressed state density, \( \rho_s \), an empirical parameter, \( c_3 \), that scales the viscosity response to fluid expansion, and another empirical parameter, \( c_3 \), used to enhance the model performance at pressures above 10 MPa. The only inputs to the correlation are the fluid density, the low pressure gas viscosity, and the pressure. The correlation was developed based on measured densities from the NIST database. The correlation has also been refit to use the densities predicted from the Advanced Peng-Robinson equation of state. The utility of the correlation is illustrated for pure hydrocarbons including n-alkanes, branched alkanes, alkenes, cyclics, and aromatics as well as binary mixtures of pure hydrocarbons. A case study is presented on the viscosity of a heavy oil diluted with solvent. The method provides a single framework for the calculation of liquid and vapour viscosities, is simple to implement, and is very fast computationally making it ideal for incorporation into process and reservoir simulators.

Expanded Fluid Based Viscosity Correlation
Diluted Heavy Oil Case Study

September 2009

Harvey W. Yarranton, Marco A. Satyro
Department of Chemical and Petroleum Engineering
University of Calgary
Is Heavy Oil Viscosity Different?

What is this fluid?

Viscosity changes almost 3 orders of magnitude.

Possibly double log behavior.
Is Heavy Oil Viscosity Different?

![Graph of viscosity vs. temperature for saturated liquid propane](image)

**SATURATED LIQUID PROPANE**
Is Heavy Oil Viscosity Different?

Base correlation on expansion of fluid from near solid condition?

Looks like a liquid approaching a solid or glass phase transition.
Fluidity is related to the expansion of a fluid from a compressed state (Hildebrand).

\[
\frac{1}{\mu} = B \frac{V - V_o}{V_o}
\]

Adapting this concept:

\[
\frac{1}{\mu} = f \left[ \exp \left( \frac{\rho_s^*}{\rho} \right)^n - 1 \right] - 1
\]

\[
\mu - \mu_G = f \left[ \frac{1}{\exp \left( \frac{\rho_s^*}{\rho} \right)^n - 1} - 1 \right] = f(\beta)
\]

- \(\mu\) = viscosity
- \(\mu_G\) = low pressure gas viscosity
- \(\rho_s^*\) = compressed state density
- \(\rho\) = density
- \(n\) = fitted exponent

as \(\rho \to \rho_s^*, \mu \to \infty\)

as \(\rho \to 0, \mu \to \mu_G\)
Methodology

Fitted n-alkane, branched alkane, alkene, aromatic, cyclic, and some complex aromatics
   - 39 pure components
   - data from NIST

Correlated tuning parameters to physical properties.

Tested on binary mixtures of pure hydrocarbons.
   - 39 mixtures
   - data from Chevalier et al.

Tested on viscosity standards.
   - data from website

Applied to 3 heavy oils as function of temperature and solvent dilution.

Refitted model for EoS densities.
Viscosity Correlation

After fitting to NIST data base:

\[ \mu - \mu_G = f(\beta) = c_1 \left( \exp \{ c_2 \beta \} - 1 \right) \]

\[ \beta = \frac{1}{\exp \left( \left( \frac{\rho_s^*}{\rho} \right)^n - 1 \right) - 1} \]

Fixed Parameters:
\[ c_1 = 0.165 \]
\[ n = 0.65 \]

Tuning Parameters
\[ \rho_s^* - \text{compressed state density} \]
\[ c_2 - \text{decay of viscosity with fluid expansion} \]
\[ c_3 - \text{pressure function, significant for } >10\text{MPa} \]

Also requires estimate of \( \mu_G \)
Fitting

saturated n-propane (data from NIST)

Adjust $\rho_s^\circ$ and $c_2$ to fit saturation data.

liquid/supercritical n-propane

Adjust $c_3$ to fit high pressure data
Compressed State Density, $\rho_s^\circ$

$\rho_s^\circ$ approximately 10% > triple point density
Not accurate enough to use in correlations
Parameter $c_2$ – Viscosity Decay

For most components:

$$c_2 = 0.241 \mu_{25}^{0.13}$$

For complex aromatics:

$$c_2 = 0.20 \mu_{25}^{0.115}$$

$c_2$ correlated well to viscosity at 25°C
Parameter $c_3$ – Pressure Adjustment

$c_3 = 1.68 \times 10^{-8} M^{0.5}$ 1/kPa

$c_3$ correlated approximately to molar mass
Model Performance

Two parameter tuning: \( \rho_s^\circ \) and \( c_3 \) to fit data. Average absolute relative deviation less than 5% except for methane (16%). Deviation is within scatter of data.
Binary Mixtures

Mixing rules:

\[ \rho_{s,\text{mix}} = \sum_{i=1}^{m} \phi_i \rho_{s,i} \]
\[ c_{2,\text{mix}} = \sum_{i=1}^{m} \phi_i c_{2,i} \]
\[ c_{3,\text{mix}} = \frac{1}{\sum_{i=1}^{m} \phi_i / c_{3,i}} \]

Ideal:

\[ \ln(\mu_{\text{mix}}) = \sum_{i=1}^{m} \phi_i \ln(\mu_{i}) \]

hexane and hexadecane

Binary Mixtures

$n$-decane and toluene

Heavy Oil Case Study
Methodology

Data Collection:
Heavy Oil A: density and viscosity at $25^\circ < T < 175^\circ C$ and $P < 10$ MPa
Multicomponent Solvent: density and viscosity at same range of $T$ and $P$

Model Fitting:
Using measured densities, find $\rho_s^o$, $c_2$ and $c_3$ that fit viscosities for each of heavy oil data and solvent

Model Prediction:
Use mixing rules to predict viscosity of mixtures of heavy oil and solvent
Heavy Oil Case Study
Heavy Oil Data

Density

Viscosity

Heavy Oil A fitted with correlation.

\[ \rho_s^o = 1068 \text{ kg/m}^3, \quad c_2 = 0.539, \quad \text{and} \quad c_3 = 0.2 \times 10^{-6} \text{ kPa}^{-1} \]
Multicomponent Solvent fitted with correlation.

\[ \rho_s^\circ = 895 \text{ kg/m}^3, \; c_2 = 0.23, \text{ and } c_3 = 0.2 \times 10^{-6} \text{ kPa}^{-1} \]
Heavy Oil Case Study
Dilution with Solvent

Heavy Oil A + Solvent at 2.5 MPa

Heavy Oil A/Solvent mixtures predicted using mixing rules.
Two More Heavy Oil Examples

Heavy Oil B + n-Decane at 1 atm

Barrufet and Setiadarma,
Fluid Phase Equil. 2003, 213, 65-79

Cold Lake Bitumen + Toluene at 1 atm


Heavy Oil/Solvent mixtures predicted with correlation.
To Do List

Refit for EoS densities (simulator applications)

Extend to live oils

Test on more heavy oils – correlate parameters?
  - more data required please…

Test on more conventional oils
  - more data required please…

Extend to heteroatom-containing species
Acknowledgements

Mr. Florian Schoeggl
Mr. Hamed Motahhari

The Consortium – Asphaltenes & Emulsions Sponsors:
Viscosity Standards


HC = mixed hydrocarbons,
MO = mineral oil,
SBO = synthetic base oil,
HCP = hydrocarbon polymer
Plamen Tchoukov
CanmetENERGY, Natural Resources Canada

Dr. Tchoukov has a Masters Degree in Physics with specialization in Spectroscopy from Sofia University, Bulgaria. He did his PhD in the research group of Professor Exerowa at the Institute of Physical Chemistry, Bulgarian Academy of Sciences. The focus of his PhD research was the investigation of self-assembled amphiphilic structures in confined geometry of thin liquid films. Following his PhD defence in 2006, he worked as a research associate in the same institute. During that period Plamen also worked as short term visiting researcher at Max Plank Institute of Colloids and Interfaces (2007), Institute of Catalysis and Surface Chemistry of Polish Academy of Sciences (2006) and the University of Delaware (1998).

Since 2008, Plamen has been a postdoctoral fellow within the research group of Dr. Dabros at CanmetENERGY, Devon. In collaboration with Dr. Czarnecki they are studying the stability of single water in oil emulsion films in order to gain better understanding of underlying stabilization mechanisms of emulsions that occur in the oil sands industry. As a part of this project, a new Thin Liquid Film Apparatus was built at CanmetENERGY. This instrument allows for simultaneous measurements of surface forces, film thickness, and electrical parameters of thin films (e.g. critical voltage of rupture, film capacitance and dielectric constant).

Dr. Tchoukov is the author of ten articles, one review article, one book chapter, and more than twenty five contributions at scientific conferences.

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Website: www.canmetenergy.nrcan.gc.ca
ABSTRACT

Electric Field Induced Instabilities in Free Emulsion Films

Farshid Mostowfi, Plamen Tchoukov, Nikolay Panchev, Tadeusz Dabros, and Jan Czarnecki

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Natural Resources Canada, 1 Oil Patch Drive, Devon, Alberta, T9G 1A8, Canada
Champion Technologies, Inc. Houston, Texas, 77545, USA
Department of Chemical and Materials Engineering, University of Alberta, Edmonton, T6G 2G6, Canada

The mechanism of electric field induced breakdown of free emulsion films is studied. Once electric polarization was applied across a water/oil/water film, instability patterns were observed on the plane of the film and recorded using a CCD camera. The polarization was applied in the form of step functions at various potentials using a potentiostat. The characteristic length-scales of the instabilities were measured by analyzing each image right after application of the electric field. Furthermore, using linear stability analysis the theoretical dominant wavelengths were calculated taking into account contributions of stabilizing disjoining pressure and de-stabilizing electric field. Good agreement between measured and calculated values of the dominant wavelength was evident.

The films were formed in a thin film apparatus (Sheludko-Exerowa cell) modified such that the oil film separated two aqueous phase compartments, each in contact with a platinum electrode. This modification allows measurements of disjoining pressure while applying electric field to the film. The films were formed from a solution of a block copolymer Tegopren (Degussa, Germany) in decane.

Electric field induced breakdown of thin films has various applications such as electrostatic de-emulsification/desalination of crude oil and emulsion stability measurements. Various mechanisms have been proposed as the underlying phenomenon driving the electric field induced breakdown of thin films such as electroporation and dielectric breakdown. While pore nucleation is a known mechanism for breakdown of bilayer lipid membranes, rupture mechanism of thicker films with substantial solvent core such as those observed in petroleum industry is not well understood yet. Furthermore, dielectric strength of typical hydrocarbons is an order of magnitude higher than those observed here, which makes the dielectric breakdown model an unlikely mechanism for rupture of the film. In this study, we show telltale sign of growth of electric field induced instabilities in emulsion films leading to their rupture.
Electric Field Induced Instabilities in Free Emulsion Films

Farshid Mostowfi\textsuperscript{a}, Plamen Tchoukov\textsuperscript{b}, Nikolay Panchev\textsuperscript{c}, Tadeusz Dabros\textsuperscript{b}, and Jan Czarnecki\textsuperscript{d}

\textsuperscript{a}Schlumberger-DBR Technology Center, \textsuperscript{b}Natural Resources Canada, \textsuperscript{c}Champion Technologies, and \textsuperscript{d}Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, CANADA
Motivation

• Electrocoalescence of emulsion droplets
  – Separation of water from oil
  – De-salting of crude oil

• Measurement of stability of emulsions and emulsion films using electric field
  – Gaining better understanding of emulsion stabilization
  – De-emulsifier screening


Background

- Repulsive disjoining pressure stabilizes a thin film
- Applying an electric field causes a compressive force on the film
- The film ruptures beyond a certain electric field
Possible Mechanisms

• Electric field induced pore nucleation (electroporation)
  – Formation of temporary holes inside the film (BLM)

• Dielectric breakdown
  – Growth of conduction path through oil beyond a critical electric field

• Electrohydrodynamic instability
  – Growth of instabilities induced by electric field

Schaffer et al., *Nature*, 2000, 403, 874
Experimental Setup
Electric Field Induced Instabilities

Bitumen 25 wt. % in toluene – Ramp potential

![Image of electric field induced instabilities](image-url)
Electric Field Induced Instabilities

Tegopren 0.52 wt. % in decane - 600mV step function
Electric Field Induced Instabilities

- (a) 0 mV
- (b) 400 mV
- (c) 500 mV
- (d) 600 mV

Graph showing probability against wavelength (μm).
Dominant Wavelength

![Graph showing the relationship between wavelength and applied potential.]
Governing Equations

\[ \frac{\partial}{\partial t} h(x,t) = -\frac{\partial}{\partial t} j = C \frac{\partial^2}{\partial x^2} P[h(x,t)] \]

\[ P(x,t) = p_0 - \gamma \frac{\partial^2 h}{\partial x^2} + \Pi + \frac{1}{2} \varepsilon E^2 \]

\[ h(x,t) = h_0 + \delta \cos(kx)e^{\omega t} \]

Linear Stability Theory

Growth rate:
\[ \omega = C \left( -\gamma k^4 + 2 \left( \frac{d\Pi}{dh} \right)_{h_0} k^2 + 2 \varepsilon \frac{U^2}{h_0^3} k^2 \right) \]

Fastest growing wave number
\[ k_{\text{max}} = \left[ \frac{1}{\gamma} \left( \frac{d\Pi}{dh} + \frac{\varepsilon U^2}{\gamma h_0^3} \right) \right]^{1/2} \]

Critical wavenumber
\[ k_{\text{crit}} = \left[ \frac{2}{\gamma} \left( \frac{d\Pi}{dh} + \frac{\varepsilon U^2}{h_0^3} \right) \right]^{1/2} \]
Characterization of the Film

<table>
<thead>
<tr>
<th>Concentration (wt. %)</th>
<th>Eq. Thickness (nm)</th>
<th>Interfacial Tension (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>72</td>
<td>3.2</td>
</tr>
<tr>
<td>0.058</td>
<td>57</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Fastest Growing Wavelength

\[ \lambda_{\text{max}}(\mu\text{m}) \]

\[ \lambda_{\text{max}} = \frac{2\pi}{k_{\text{max}}} \]

Applied Potential (V)

- %0.058 Exp data
- %0.058 Theory
- %0.52 Exp data
- %0.52 Theory
Growth Rate

For Tegopren 0.058 wt % in decane

\[ \omega = C \left( -\gamma k^4 + 2 \left( \frac{d\Pi}{dh} \right)_{h_0} k^2 + 2 \varepsilon \frac{U^2}{h_0^3} k^2 \right) \]
Concluding Remarks

• Electric field induced instabilities were observed in water-in-oil emulsion films
• The wavelength of the instabilities were in reasonable agreement with those calculated from the linear instability model
• Electrohydrodynamic instability could be considered as the underlying mechanism in electric field induced breakdown of emulsion films
BIOGRAPHY

Bill Keesom
Jacobs Consultancy

Bill is a group manager in the Jacobs Consultancy office based in Chicago. While at Jacobs he developed bitumen upgrading configuration processing schemes for clients in Alberta. Prior to coming to Jacobs, Bill worked for nearly 29 years at UOP where he helped clients around the world choose the best technology routes for meeting economic and environmental goals when converting crude oil and intermediates into more valuable products. He has dabbled in bio-processing. Bill holds a Masters in Management from Northwestern University, a Masters of Science in Chemical Engineering from the University of California, Berkeley and a Bachelor of Science in Chemistry from Indiana University.

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Life Cycle Assessment of North American and Imported Crudes

Bill Keesom
Jacobs Consultancy and Alberta Energy Research Institute

California has recently introduced a Low Carbon Fuel Standard (LCFS), with the stated objective of reducing the carbon intensity of its transportation fuels by 10 percent by 2020. It shall apply to all refiners, blenders, producers and importers of transportation fuels and shall be measured on a full fuels cycle basis.

A broader adoption of LCFS currently being considered in the United States may have significant implications regarding how the Canadian oil sector responds to the challenge of producing and upgrading heavy oil and bitumen in an environmentally responsible way. The LCFS standard creates the potential to significantly burden Canadian heavy oil and bitumen, while encouraging crude oil production in other parts of the world that have less stringent environmental regulations.

Key shortcomings of existing life cycle analyses include the use of outdated information, inaccurate model representations, incomplete well-to-wheels analysis, excessive aggregation, differing boundary conditions, and insufficient consideration of GHG mitigation potential.

The Alberta Energy Research Institute commissioned Jacobs Consultancy to carry out a rigorous life cycle assessment of various North American and imported crudes in order to address these shortcomings. The study provides a realistic comparison of the well-to-wheels carbon footprint associated with Canadian bitumen and heavy crudes versus other prevalent crudes. The study also identifies GHG mitigation options. This paper provides an overview of the study results as well as planned next steps.
Impact of Low Carbon Fuel Standards and Other GHG Regulations on Oil Sands

5th NCUT Upgrading and Refining Conference
September 14-16, 2009
Edmonton, Alberta
Three Messages

- GHG emissions reduction in its many forms will affect you
- Significant uncertainties exist
- Short term focus should be on
  - Improved efficiency
  - Technology development
Agenda

- GHG regulations and carbon pricing
- Oil Sands LCA emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Cogeneration
  - Carbon capture
  - Path forward
- Wrap-Up
California, Washington, Canada, Europe leading the way

Final legislation will likely include a combination of
- Energy conservation and efficiency
- Fuel switching
- Renewable fuels and alternate energy mandates
- Emissions caps and carbon taxes (less common)
- Low Carbon Fuel Standard (LCFS)
- Carbon capture ready and other directives

Indicative GHG Timeline

- 2008: Transition & Planning
- 2012-13: Trading & Implementation
- 2020 (first targets met): Continued Reduction
- 2050: Transition & Planning
Carbon Pricing Uncertainty

**CO2 Equivalent Prices in ACESA Main Cases**

- Prices range from 40 to 190/MT in 2030
- Depends on:
  - Entry rate and price of low/no Carbon technologies
  - Availability of international agreements and trading of C offsets

**Source** – EIA Report: Energy Market and Economic Impacts of H.R. 2454, the American Clean Energy and Security Act of 2009 – Figure 5 and data
Agenda

- GHG regulations and carbon pricing
- Oil Sands LCA emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Cogeneration
  - Carbon capture
  - Path forward
- Wrap-Up
Low Carbon Fuel Standard Reduces Carbon Intensity of Refined Products

- 10% reduction in carbon intensity by 2020
- Targets transport fuels
- May penalize heavy crudes
- Based on well-to-wheels life cycle analysis of GHG emissions

**California LCFS**

Compliance Schedule from 2010 to 2020
For Gasoline or Gasoline Substitutes

10% Reduction
Impact on Oil Sands Area

- Potential limit on refining of SCO and bitumen
- US may restrict import
- Classified as high carbon intensity (CI) material
Carbon Intensity Determined by Well-to-Wheels Life Cycle Assessment

Incorporate results from rigorous engineering analysis into GREET*
Use ISO 14040 Methodology

Crude & Bitumen Production
- Specific crudes evaluated
- Public & Jacobs data
- Rigorous modeling

Upgrading and Refining
- Reflect crude and product variations
- Jacobs experience
- Rigorous modeling

*GREET: Greenhouse gases, Regulated Emissions, and Energy use in Transportation
Life Cycle GHG Emissions for Gasoline

Source: Life Cycle Assessment Comparison of North American and Imported Crudes, July 2009, prepared by Jacobs for AERI
Life Cycle GHG Emissions for Gasoline

Source: Life Cycle Assessment Comparison of North American and Imported Crudes, July 2009, prepared by Jacobs for AERI
Life Cycle GHG Emissions for Gasoline

Co-products
Crude Oil Production
Venting and Flaring
Upgrading
Other Feeds*
Transport
Fuel Cycle
Refining
Delivery
Carbon in Fuel

Source: Life Cycle Assessment Comparison of North American and Imported Crudes, July 2009, prepared by Jacobs for AERI
Observations from LCA Work

- Rigorous Life Cycle analysis required
- GHG burden for Oil Sands smaller than shown in previous studies
- GHG emissions of Oil Sands and some conventional crudes overlap
- Oil Sands GHG mitigation may offer Alberta advantage over US locations

Source: Life Cycle Assessment Comparison of North American and Imported Crudes, July 2009, prepared by Jacobs for AERI

http://eipa.alberta.ca/home/lifecycle.aspx
Agenda

- GHG regulations and carbon pricing
- Oil Sands LCA emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Cogeneration
  - Carbon capture
  - Path forward
- Wrap-Up
Start with Ideal SAGD Heat Cycle™

- Ideal SAGD Heat Cycle identifies minimum energy consumption for a given reservoir
- Benchmark and capture fuel savings using the Ideal SAGD Heat Cycle as a guide
Identify Gaps in Actual SAGD Operation

- Actual SAGD facilities are less efficient
  - Reservoir operation
  - Glycol system
  - Heat loss from stack
  - Water management
  - Poor heat recovery
SAGD Energy Optimization
Comparison of Ideal vs. Typical

- Losses for the Ideal case mostly to earth
- Losses for typical case are 60% higher vs. ideal
- Expect practical savings of 10-20% achievable by reducing gaps
Agenda

- GHG regulations and carbon pricing
- Oil Sands LCA emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Cogeneration
  - Carbon capture
  - Path forward
- Wrap-Up
Breakdown of CO₂ Reduction Potential*

*Sample; actual results vary by facility
Agenda

- GHG regulations and carbon pricing
- Oil Sands LCA Emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Cogeneration
  - Carbon capture
  - Path forward
- Wrap-Up
Base Oil Sands LCA GHG Emissions

Cogen Reduces Life Cycle GHG Emissions

Include 50% Cogen Credit vs. Coal Based Grid

Total GHG, g CO2e / MJ Gasoline

- SAGD Sco - Ckr
- SAGD Sco - Eb-Bed
- SAGD Bitumen
- SAGD DilBit
- Mining Sco - Ckr
- Mining Bitumen

Source: Life Cycle Assessment Comparison of North American and Imported Crudes, July 2009, prepared by Jacobs for AERI

*Other feeds: iC4 for Alky; diluent

+Cogen credit based on export of natural gas based power that offsets 80% coal based Alberta grid power
Agenda

- GHG regulations and pricing
- Oil Sands LCA Emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Cogeneration
  - Carbon capture
  - Path forward
- Wrap-Up
**CO₂ Capture Options**

- Capture CO₂ from existing concentrated, high pressure sources
  - H₂ Plant
  - Gasification
- More difficult and costly to capture from dilute sources
- Capture costs range from $70 to $150+ per ton

**Typical CO₂ Concentrations**

- Process Heater
- Oxy-Combustion
- Gasifier
- H₂ Plant Process Side
Agenda

- GHG regulations and pricing
- Oil Sands LCA Emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Cogeneration
  - Carbon capture
  - Path forward
- Wrap-Up
Oil Sands GHG Abatement Roadmap

- Identify Oil Sands CO$_2$ Mitigation Roadmap
- Address Oil Sands production, upgrading, & refining
- Develop CO$_2$ abatement curve with cost vs. impact
- Energy & efficiency, CO$_2$ avoidance, and CCS
- Identify high-priority technologies to be developed
- Identify unique Alberta oil sands mitigation potential
- Prioritize projects, analyze & implement

Identify Oil Sands CO$_2$ Mitigation Roadmap

- $$/MT \text{ CO}_2$
- Cost
- MT/D CO$_2$
- Projects with positive economic return
Agenda

- GHG regulations and pricing
- Oil Sands LCA Emissions
- GHG mitigation
  - SAGD
  - Upgrading/Refining
  - Fuel Switching
  - Carbon capture
  - Path forward
- Wrap-Up
Meeting California LCFS Targets Will be a Challenge

- **Gasoline**: options to meet 2020 target
  - Blend more ethanol especially E85
    - Not ethanol from Midwest
    - Low CI Ethanol
    - Cellulosic
    - Adv Renewable Ethanol
  - More electric and advanced technology vehicles

CA currently has 25 MM light duty vehicles And consumes 15.8 bil gal/yr of CA RFG

Source: Proposed Regulation to Implement the Low Carbon Fuel Standard Volume II, March 5, 2009
Horses to Water...

- LCFS and other GHG regulations may lead to replacement of petroleum based transportation fuels
- Regulatory control on fuel suppliers
- No controls over fuel users
- Will consumers use new fuels and will there be enough new vehicles to use the new fuels?
Wrap-Up

- GHG regulations are here or will be here soon
- Expect changes in transportation fuel mix
- Modern efficient, low GHG facilities are needed
- Energy efficiency, fuel switching, cogen, CCS will be part of the solution
- Potential for Alberta advantage exists through high efficiency and deployment of new technology
Next Steps

- Identify unique Alberta oil sands GHG mitigation opportunities
- Focus on primary pathways covering production, upgrading, and refining
- Develop CO$_2$ abatement curves with cost vs. percent CO$_2$ capture for full spectrum of options
- Identify high-priority technologies to be developed or commercialized that have significant impact on abatement
- Reevaluate oil sands life cycle GHG emissions after abatement
Thank You
Ryan P. Rodgers
National High Magnetic Field Lab, Florida State University

Ryan P. Rodgers, born in Pensacola, Florida on September 7, 1972, received a B.S. in chemistry from the University of Florida in 1995, and Ph.D. in analytical chemistry from Florida State University in 1999. Following a postdoctoral appointment in aerosol mass spectrometry at Oak Ridge National Laboratory, he joined the Ion Cyclotron Resonance Program at the National High Magnetic Field Laboratory as an Assistant Scholar-Scientist and a courtesy faculty member of the Department of Chemistry and Biochemistry at Florida State University. His current position as Director of Environmental and Petrochemical Applications, Ion Cyclotron Resonance Program sees him directing environmental, petrochemical and forensic applications of FT-ICR mass spectrometry at NHMFL.

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Compositional Analysis of Heavy Crude Oil Fractions by Ultrahigh Resolution FT-ICR Mass Spectrometry

Amy M. McKenna\textsuperscript{a}, Ryan P. Rodgers\textsuperscript{a, b} and Alan G. Marshall\textsuperscript{a,b}\textsuperscript{*}

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1800 East Paul Dirac Dr., Tallahassee, FL 32310-4005

The ultrahigh mass resolving power and mass accuracy of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) allow for the assignment of chemical formulas to each peak in the mass spectrum. Consequently, it is especially useful for complex petroleum mixtures such as heavy and unconventional crude oil (Athabasca bitumen). As the global oil supply of light, sweet crudes is depleted, the need for characterization of heavy, high sulfur crudes is crucial for development optimization and future upgrading procedure development. Because of the high abundance of sulfur in bitumen and heavy crudes, detailed compositional characterization is necessary to help develop removal strategies in the refinery. Here, we provide detailed characterization of middle distillate fractions of Athabasca bitumen to define the structural evolution of polycyclic aromatics that may also contain N, O, and/or S atoms as a function of boiling point. We then analyze higher distillate fractions and vacuum resid to prove that the structural distribution in petroleum is continuous. The fundamental differences in solution-phase behavior between asphaltene and maltene fractions will be discussed, namely, the self-associative properties of asphaltenes that form nanoaggregates at low concentration. A collection of mass spectral and molecular diffusion techniques indicate that asphaltene monomers are < 2000 Da. Bulk property measurements indicate that asphaltenes are more aromatic and contain higher heteroatom content (nitrogen, sulfur, oxygen, nickel and vanadium) than maltenes. Here, we present a systematic argument for the structural evolution of polyaromatic hydrocarbons and define the boundary in compositional between asphaltene and maltenes which suggests that asphaltenes and maltenes share the same carbon number space. Furthermore, we extend that characterization to vanadyl porphyrins and demonstrate their quantitation by electrospray and atmospheric pressure photoionization FT-ICR MS.

Supported by NSF Division of Materials Research through DMR-0654118 and the State of Florida.

\textbf{Keywords:} APPI, petroleum, Fourier Transform, Ion Cyclotron Resonance, ICR, FT-ICR, FTMS
The Composition of Heavy Crude Oil

Ryan P. Rodgers, Amy M. McKenna, Alan G. Marshall
National High Magnetic Field Laboratory
Florida State University

5th NCUT Upgrading and Refining Conference 2009
Vacuum Bottom Residue (593+ °C) from Middle Eastern Heavy Crude Positive Ion APPI FT-ICR MS at 9.4 Tesla

30,377 peaks > 6σ (400 < m/z < 1300) 86 peaks/nominal mass
m/Δm_{50%} = 800,000 at m/z 800

40 mDa Zoom Inset
Absorption Mode

10 mDa Zoom Inset
Absorption Mode

[\text{M}_{63}H_{100}S_{2}^{13C_{1}}]^{•+0.4ppm}
[\text{M}_{64}H_{101}S_{2}]^{•+0.2ppm}
[\text{M}_{66}H_{96}S_{1}^{13C_{1}}]^{•+0.2ppm}

1054.93
1054.92
1054.93

[\text{M}_{74}H_{121}S_{1}^{13C_{1}}]^{•+0.2ppm}
[\text{M}_{75}H_{122}S_{1}]^{•-0.1ppm}
[\text{M}_{72}H_{126}S_{2}]^{•-0.1ppm}

Time (s)
Magnitude Mode FT-ICR Mass Spectrum
Molecular Composition of Maltenes and Asphaltenes

Hypothesis:

• Boduszynski’s “Continuity Model”:
  Petroleum composition is a continuum in carbon number, aromaticity and boiling point.

• Asphaltenes are not abnormally high in molecular weight
The Continuity Concept of Petroleum Composition

Mieczyslaw M. Boduszynski
Klaus H. Algelt

PAH → 1 (N,S,O) ~2-3 fewer #C

1 → 2 (N,S,O) ~2-3 fewer #C

Altgelt, K.H. and M.M. Boduszynski, Composition and Analysis of Heavy Petroleum Fractions, Dekker, NY, 1994
Middle Eastern Heavy Crude Oil Distillation Series
Positive-Ion APPI FT-ICR MS at 9.4 Tesla

191 – 315 °C
315 – 371 °C
371 – 510 °C
510 – 538 °C
538 – 593 °C
593+ °C

m/z

200  400  600  800  1000  1200
Middle Eastern Heavy Crude Distillation Series
Positive Ion APPI FT-ICR MS at 9.4 Tesla

Hydrocarbon Class

Carbon Number

Relative Abundance (% total)

60 40 20 0

0 20 40 60 80 100

191 – 315 °C

315 - 371 °C

371 - 510 °C

510 – 538 °C

538 - 593 °C

593+ °C

DBE

Carbon Number

Relative Abundance (%)
Positive-Ion APPI FT-ICR MS 9.4 T

Whole Crude

593+ °C Bottoms

Relative Abundance (% total)
Combined S$_1$ Class Normalized Middle Eastern Heavy Crude Distillation Series

Increasing Boiling Point

Relative Abundance (% total)

Maltene
H/C $\sim$1.25 - 2
$S_1$ Class

DBE degeneracy is limited at low m/z and low DBE to stable aromatic PASH structures
Where’s the “Magic”? 

371 – 482 °C

PASH “Magic” Numbers

DBE degeneracy is limited at low m/z and low DBE to stable aromatic PASH structures. In other words, cycloalkanes are a must…
The Greatest Irony...

The seeds of compositional diversity and the subsequent evolution of the continuum of petroleum structural complexity are planted in the lightest, least complex distillate fractions... Unbelievably, we think the answer lies where it is and has been, most analytically accessible...
The Asphaltene Problem

- Insoluble in $n$-paraffin solvents
- Self-aggregate in solution (ppm - ppb)
- High-boiling, highly polar
- Heavy crudes = high asphaltene content
Asphaltenes: What We Know

1. MW = 700-800 Da
   - MS: FI/MS, ESI, APPI, APCI, 2D/LD-MS
   - Diffusion: Fluorescence Depolarization, Taylor Dispersion, NMR

2. Molecular Size = 10 Å (~6-7 Fused Rings)
   - Direct Imaging: HRTEM, STM

3. Contain 50-55% aromatic carbon
   - 40-45% saturated carbon
   - $^{13}$C NMR

4. H/C ratio ~ 1.045
   - Elemental Analysis
Middle Eastern Heavy Crude Asphaltene
APPI LTQ-MS
Crude Oil (APPI)

Zoom mass inset of single nominal mass (m/z = 553)

Asphaltene (APPI)

Shift to lower mass defect (increase in aromaticity and heteroatom content)

Petroporphyrin
19 DBE N₄OV
~ 140 peaks / nominal mass

Mass Isolated Segment from Broadband Mass Spectrum
Positive Ion ESI LTQ-MS
Iso 1800 (50 Da Window) CID

Large Neutral Mass Loss

Small Neutral Mass Loss
Isolation of m/z 625 at 35
Sum all plots

SEC Fraction F
Basic N₁ Class

Relative Abundance (% total)
Positive-Ion ESI LTQ-MS
Middle Eastern Heavy Crude Asphaltene

400-4000 m/z
Iso 1800 Da (50 Da window)
40 V Source Fragmentation
0 NCE

400-4000 m/z
Iso 1800 Da (50 Da window)
40 V Source Fragmentation
200 NCE
Probing the molecular weight distributions of non-boiling petroleum fractions by Ag$^+$ electrospray ionization mass spectrometry

Stilianos G. Roussis* and Richard Proulx

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Received 1 September 2003; Revised 2 June 2004; Accepted 7 June 2004

This work explores the possibility of Ag$^+$ electrospray ionization mass spectrometry (ESI-MS) to determine the molecular weight distributions of non-boiling petroleum fractions. Information about the molecular weight distributions is needed for fundamental studies on the nature of heavy crude oils and bitumens and for the development of novel recovery and processing methods. The method does not depend on thermal processes for the introduction of the fractions into the gas phase of the mass spectrometer, which is a considerable advantage over most other ionization methods. The Ag$^+$ electrospray mass spectra of the fractions analyzed by using a toluene/methanol/cyclohexane (60:28:12%) solvent system display bimodal distributions in the ranges m/z 300 to ~3000 and m/z 3000 to ~20 000. The abundances of the high molecular weight peak distributions can be reduced by in-source collisional activation experiments. Comparisons with the results obtained for model heteroatom-containing compounds (molecular weight <600 Da) and high molecular weight polystyrene standards (up to one million Da) indicate that the majority of the structures in the saturate, naphthenoaromatic and polar aromatic fractions, and a significant portion of the asphaltenes, are small molecules. However, a considerable portion of the asphaltenes and some portion of the other fractions contain high molecular weight structures bound by covalent or strong non-covalent bonds. The results obtained by the Ag$^+$ ESI method in this study for the saturate, aromatic, and polar fractions in a bitumen are in qualitative agreement with published molecular weight average results obtained for Cold Lake bitumen fractions analyzed by conventional gel permeation chromatography and field desorption mass spectrometry. Further work is needed to study the nature of the bonds and the interactions of the molecules in the asphaltene fractions by Ag$^+$ ESI-MS. Copyright © 2004 John Wiley & Sons, Ltd.
Maltene Ag⁺ ESI TOF-MS

100V Focus

120V Focus
Asphaltene Ag⁺ ESI TOF-MS 0.5 mg/mL

Monomer

Aggregate
Asphaltene Ag⁺ ESI TOF-MS 0.5 mg/mL

120V Focus

Signal magnitude (au)

Monomer

Aggregate

m/z
Asphaltene Ag⁺ ESI TOF-MS 0.5 mg/mL
160V Focus

Monomer

Aggregate
Asphaltene Ag⁺ ESI TOF-MS 0.05 mg/mL no ACID

m/z ~ 6800 = octamer
Monomer ~ 850 Da

ESI process is gentle and results in no fragmentation as evident by the detection of noncovalent Ag⁺ species.

Monomer 200 < m/z < 2000
Center of Distribution ~ 850 Da
Asphaltene Ag⁺ ESI TOF-MS 0.05 mg/mL
100V Focus

Aggregate

Monomer
Asphaltene Ag⁺ ESI TOF-MS 0.05 mg/mL
150V Focus RF 0.15Vpp

Aggregate

Monomer

6000 au

m/z

0 10000 20000 30000

6000 au

0 10000 20000 30000

m/z
Middle Eastern Heavy Crude Asphaltene
APPI LTQ-MS

Low Molecular Weight Species pose a “problem”
Positive-Ion APPI LTQ-MS
Distillable Asphaltenes (538 - 593°C)

Molecular Weight of Parent Distillate

- 100 ug/mL
- 250 ug/mL
- 500 ug/mL
Positive Ion APPI FT-ICR MS 9.4 Tesla

Parent Distillate

Distillable Asphaltenes
Positive-Ion APPI FT-ICR MS at 9.4 Tesla

$S_1$ Class

**Parent Distillate**

**Distillable Asphaltenes**

Relative Abundance (% total)

Carbon Number
S₁ Series

- Parent Distillate
- Distillable Asphaltenes

DBE

Carbon Number

(538 - 593°C)

DNT
BP ~ 520°C
Positive Ion ESI FT-ICR MS
9.4 Tesla

Parent Distillate

Distillable Asphaltenes
Middle Eastern Heavy Crude Asphaltene
APPI LTQ-MS
Middle Eastern Heavy Crude Positive-Ion APPI 9.4 Tesla

593+ °C

Asphaltene

Maltene

S₂ Class

DBE

S₃ Class

Relative Abundance (% total)

Carbon Number

PAH Planar limit
Composite Plots of Asphaltene and Maltene Fractions
Middle Eastern Heavy Crude

Asphaltene Space

Maltene Space

Relative Abundance (% total)

Carbon Number

DBE

S_1

S_2
Composite Plot of Asphaltene and Maltene Fraction
Middle Eastern Heavy Crude

Asphaltenes vs. Maltenes

- Solubility
- Alkylation
- H/C Ratio
Asphaltenes …

1. NOT high abnormally MW (95% below 2 kDa)

2. Share carbon number space with maltenes

3. Exist in DBE space _above_ maltenes but _below_ planar limit

4. FT-ICR MS results agree with bulk property, NMR, etc.
Acknowledgements

Paul B. Glaser
GE Global Research
United States - India - China - Germany

Lynda Donald
Ken Standing

The Marshall Research Group

NHMFL/FSU Research Funded by
The National Science Foundation
NSF Award # DMR 0654118
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Department of Chemical Engineering, University of Alberta

Dr. Murray Gray has been with the University of Alberta since 1983. He has held a number of senior academic positions at the U of A, including Chair of the Department of Chemical Engineering and Dean of Graduate Studies and Research. He is currently Director of the Imperial Oil – Alberta Ingenuity Centre for Oil Sands Innovation. With over 22 years of experience in kinetics and reaction engineering, Gray has focused on bitumen and heavy oil upgrading and bioprocessing. His achievements have been recognized by the CSChE Syncrude Innovation Award (1996), the Syncrude/NSERC Industrial Research Chair in Advanced Upgrading of Bitumen (2000), the Industrial Practice Award of the CSChE (2003), and the Frank Spragins Technical Award from APEGGA (2007). In 2005 he was elected a Fellow of the Canadian Academy of Engineering. In 2006 he was awarded a Canada Research Chair and an NSERC Industrial Research Chair in Oil Sands Upgrading. He has served the national and international engineering and science communities in many roles, including president of the Canadian Society for Chemical Engineering and the Chemical Institute of Canada.

Gray obtained his Ph.D. in Chemical Engineering from the California Institute of Technology in 1984. He also holds a M. Eng. degree in Chemical Engineering from the University of Calgary (1980) and a B.Sc. in Chemical Engineering (with honours) from the University of Toronto (1978).

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Kinetics of Hydrolysis of Emulsified Salts in Canadian Bitumens and Inhibition of Hydrolysis

Murray R. Gray¹, Harmeet Kaur¹, and Paul E. Eaton²

¹Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada
²Champion Technologies, Fresno TX

Salt contamination is a growing problem with heavy oils and diluted bitumens, due to difficulty of desalting these materials. As the crude oil is heated in the presence of steam, the chloride can be released from the salts, giving corrosion and fouling of refinery equipment. The rate of reaction of the salts, and the rate of release of the chloride, depends on a number of physical and chemical factors, including the concentration of mineral solids, naphthenic acids, and the size and composition of the salt crystals. To understand the factors causing HCl release in refinery units, hydrolysis of chloride salts was investigated in model oil and heavy crude oil blends by contacting with flowing steam at 100°C to 350°C. The decomposition of brine salts was highly influenced by the components of the crude oil medium. Pure CaCl₂·2H₂O was highly reactive in actual crudes due to the presence of naphthenic acids. Chemical inhibitor formulations, based on alkaline earth elements such as magnesium, were successful in reducing both the extent and the initial rate of hydrolysis, thereby offering potential protection of refinery equipment.

Keywords: Hydrolysis, Salts, Naphthenic acids, Inhibitors
KINETICS OF HYDROLYSIS OF EMULSIFIED SALTS IN CANADIAN BITUMENS AND INHIBITION OF HYDROLYSIS

Murray R Gray¹, Harmeet Kaur¹ and Paul E Eaton²

1. Dept of Chemical and Materials Engineering, University of Alberta
2. Champion Technologies, Houston, Texas
Summary

- Salt hydrolysis in upgraders and refineries
- Past studies of hydrolysis
- Methodology
- Factors that accelerate and inhibit hydrolysis
- Kinetics of hydrolysis reactions
How do salts react in refinery processes?

- Salts in crude oil react with steam:
  \[ \text{NaCl} + \text{H}_2\text{O} = \text{NaOH} + \text{HCl} \]
  \[ \text{CaCl}_2(s) + \text{H}_2\text{O}(g) = \text{CaOHCl}(s) + \text{HCl}(g) \]
  \[ \text{MgCl}_2(s) + \text{H}_2\text{O}(g) = \text{Mg(OH)Cl}(s) + \text{HCl}(g) \]

- Extent and rate of reaction varies as:
  \[ \text{Mg}(40\text{-}49\%) > \text{Ca} >> \text{Na} (<1\%) \]
Problem Areas in Refinery Crude Units

Salts Contained in Crude Charge: NaCl, CaCl₂, MgCl₂

Hydrolysis Occurs 150°C-350°C

HCl Formation, Fouling, Overhead Corrosion

To Vacuum Tower

Un-reacted Chlorides @ 300°C
Hydrolysis in Upgrading Processes

Data from Syncrude Canada Ltd for Chlorine balances on process units (Diluent Recovery Unit through to Fluid Coking Unit)
Effect of Crude Oil Impurities

### Decomposition of CaCl$_2$ \( .2\)H$_2$O

**Cumulative Chloride evolved in overhead condensate (\% Initial)**

<table>
<thead>
<tr>
<th>Nature of salts</th>
<th>No additive</th>
<th>With naphthenic acid (1 wt%, 36 meq/L)</th>
<th>With Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid Salts</strong></td>
<td>0.14</td>
<td>2.02</td>
<td>-----</td>
</tr>
<tr>
<td><strong>Emulsified Salts</strong></td>
<td>2.59</td>
<td>-----</td>
<td>5.87</td>
</tr>
</tbody>
</table>
Issues with Chloride Hydrolysis

- Corrosion /reduced life of refinery equipment
- Salt fouling in columns leading to plugging
- Contamination of downstream processes
- Premature shutdown and significant safety issues.
Crude Oil Desalting
Paraffinic froth treatment

- Emulsions stabilized by asphaltenes and fine particles
- Add n-alkane rich solvent to give flocculation of asphaltenes with water droplets and fine clays
- Yields clean, dry bitumen
- Yield penalty from asphaltene removal
Are these solutions effective?

- Desalting of heavy oils removes only 90-95% salts.
  - small difference in density makes this process less effective
  - presence of solids and stable water in oil emulsions further retard the effectiveness of the operation
  - inoperable for with high solids bitumen from mining

- Paraffinic froth treatment reduces the yield of bitumen

- Addition of bases tends to cause deposits and fouling
Hydrolysis Procedure

- **Oil media**
  - Model Oil - Paraflex
  - Husky - Cold Lake Lloydminster blend, chloride content-76ppmw
  - Western Canada Select with chloride content of 53ppmw

- **Method**
  - Salt mixture added as a 10% solution in water.
  - Nitrogen sparged at 300 std ml/min to maintain positive pressure.
  - Steam supplied at the rate of 2 ml/min (liquid basis).

Non-Isothermal Hydrolysis-10ml of condensate samples collected at 50°C intervals between 100°C-300°C, at 320°C and 350°C.

Isothermal Hydrolysis-15ml of condensate samples collected at 250°C.
Hydrolysis apparatus

- Nitrogen
- Steam
- Heated Flask
- Product Cooler
- First Trap
- Second Trap
- Third Trap
- Condensate Samples
- Water
- Thermocouple
- Oil Heater
- Mantle

- Heater
- Metering Pump
Hydrolysis in Bitumen Blends

Oil + Mixed Brine Salts
Hydrolysis to 350° C
[Kaur, 2008]

• Model oil
• Husky Cold Lake + Lloydminster blend
• WCS = Western Canada Select

![Graph showing chloride release vs. total salt concentration for Husky, WCS, and Model oil blends.](image)
Factors causing abnormal behaviour

- Acids can accelerate release of Cl
- "Natural inhibitors" can delay release
Profile of Chloride hydrolysis during rising temperature test

Oil + Mixed Brine Salts
Hydrolysis to 350° C
Contribution of individual chloride salts

![Graph showing cumulative Cl release for different salts](image)

**Pure Salts**

Stepwise temperature increase from 150-350°C
Images from SEM analysis of solids from CaCl₂ hydrolysis

WCS with added calcium chloride, steamed at 150-350°C

**Initial Solids**

**Solids after experimental run**
Possible role of Naphthenic Acids

- **Suggested Reaction Equation:**
  - $\text{CaCl}_2.2\text{H}_2\text{O} (s) + 2\text{NapH} (l) \rightleftharpoons \text{Ca (Nap)}_2 (l) + 2\text{HCl} (g)$
  - $\Delta G$ is positive, but continuous stripping of HCl (g) drives reaction

- **Objective:**
  - Determine quantity of CaCl$_2$.2H$_2$O needed to consume naphthenic acids
  - Is % hydrolysis reduced when salt is in excess?
Naphthenic acid accelerates Cl release

WCS, TAN = 0.86 mg KOH/g oil, steamed at 150-350°C
What are Inhibitors?

- Natural or added agents that reduce HCl release from the hydrolysis of chloride salts at elevated temperatures.
- Addition of divalent inhibitor provides reactive metal bases in the oil to react with the HCl, forming stable salts like metal-hydroxychloride.

Example for Mg:

\[
\begin{align*}
Mg(OH)_2 (s) + HCl (g) &= Mg(OH)Cl (s) + H_2O(g) \\
Mg(OH)_2 + 2NapH &= Mg(Nap)_2 + 2H_2O \\
Mg(OH)_2 + 2HCl &= MeCl_2 + 2H_2O
\end{align*}
\]
Effectiveness of inhibitors with increasing temperature

WCS with 576 ppm of mixed salts
Inhibitors added at 1:1 to salts
Effectiveness of Inhibitors in WCS with pure CaCl₂·2H₂O under isothermal conditions at 250°C
## Kinetics of Cl release

<table>
<thead>
<tr>
<th>Condition</th>
<th>Initial Rate Constant (k, min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>4.31 \times 10^{-03}</td>
</tr>
<tr>
<td>Calcium Overbase</td>
<td>1.01 \times 10^{-05}</td>
</tr>
<tr>
<td>Ca(OH)(_2) Slurry</td>
<td>9.05 \times 10^{-05}</td>
</tr>
<tr>
<td>Inhibitor A</td>
<td>1.02 \times 10^{-05}</td>
</tr>
<tr>
<td>Inhibitor B</td>
<td>2.03 \times 10^{-05}</td>
</tr>
</tbody>
</table>

WCS with NaCl -87.5% and MgCl\(_2\).6H\(_2\)O -12.5%

Apparent first-order kinetics at 250°C
Effectiveness of inhibitors under isothermal conditions at 250°C

<table>
<thead>
<tr>
<th>Additives</th>
<th>Overall Recovery (% Initial)</th>
<th>Time for 50% recovery</th>
<th>Overall Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>1.23± 0.12</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Calcium Overbase</td>
<td>1.04</td>
<td>44</td>
<td>23</td>
</tr>
<tr>
<td>Calcium Hydroxide Slurry</td>
<td>1.00</td>
<td>46</td>
<td>26</td>
</tr>
<tr>
<td>Inhibitor A</td>
<td>0.13</td>
<td>44</td>
<td>90</td>
</tr>
<tr>
<td>Inhibitor B</td>
<td>0.12</td>
<td>17</td>
<td>91</td>
</tr>
</tbody>
</table>

WCS with NaCl + MgCl₂ mixture added
## Effect of inhibitor dosage

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Inhibitor: Salt (mass)</th>
<th>Cl release (% Initial)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inhibitor A</strong></td>
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<tr>
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<td></td>
<td>0.5:1</td>
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</tr>
</tbody>
</table>

*Mixed Salts (NaCl -87.5% and MgCl₂·6H₂O -12.5%) in WCS at 250°C*
Physical interactions of Inhibitors with NaCl + MgCl₂

Base Case

Calcium Hydroxide Slurry Inhibitor

Average

Ca/Na-0.029
Ca/Cl-0.015

Average

Ca/Na-0.18
Ca/Cl-0.096
Conclusions

- Hydrolysis strongly influenced by impurities in crude oils
  - Naphthenic acids
  - Clays
  - Natural inhibitors
- Naphthenic acid component increases hydrolysis from CaCl$_2$.2 H$_2$O
- Added inhibitors associate with salt crystals to reduce extent and rate of HCl release.
Acknowledgements

- Funded by Champion Technologies and Natural Sciences & Engineering Research Council (NSERC)
- Tuyet Le
- Yissella Londono
- Fausto Marelli
- Lisa Boddez
- Alvin Kim
BIOGRAPHY

Heather Dettman
CanmetENERGY

Dr. Heather Dettman received her PhD in Biochemistry from the University of Alberta and held an NSERC Postdoctoral Fellowship at Yale University. In 1990, she joined the Energy, Mines and Resources, now Natural Resources Canada where she began work on developing quantitative nuclear magnetic resonance techniques to describe the chemical changes that occur during heavy oil and bitumen upgrading. Since then, she has developed expertise in characterization of heavy oil and bitumen and has used the knowledge to target specific research objectives to understand the cracking of hydrocarbons in petroleum under thermal conditions, corrosivity of organic acids and sulphur species under refinery conditions, the applicability of biotechnologies to bitumen and heavy oil upgrading, and modeling of diesel fuel combustion. She is currently the Manager of the Bioprocessing Program at CanmetENERGY in Devon.

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Refinery Corrosion: The Influence of Organic Acid and Sulphur Compound Structure on Global Crude Corrosivity

Heather D. Dettman\textsuperscript{1}, Nana Li\textsuperscript{1}, and Jingli Luo\textsuperscript{2}

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\textsuperscript{2}Department of Chemical & Materials Engineering, University of Alberta, Edmonton, Alberta, Canada, T6G 2G6

Since 1920, certain crude oils world-wide have been found to be corrosive in refineries. At temperatures between 220 and 400\degree C, organic acid and sulphur-containing species are known to be involved. Organic acids, usually referred to as naphthenic acids and described as cycloalkane ring(s) with an attached aliphatic chain having a terminal carboxylic acid group, have been implicated. Elemental sulphur, mercaptan, sulfide and polysulphide species convert to hydrogen sulphide which attacks metal. However, neither total sulphur contents measured by elemental analyses nor total acid contents measured by total acid number (TAN) have been found to correlate well with corrosivity.

A fundamental study of the relationships of molecular structures of organic acid and sulphur compounds to refinery corrosivity has been performed. To understand acid species, the corrosivity of homologous series of organic acids in white oil with respect to temperature and vacuum have been assessed in a test unit that simulates corrosion found in vacuum distillation towers. To understand the corrosion behaviour of sulfur species, two steps were needed. Firstly, thermal decomposition of model sulfur compounds dissolved in white oil was assessed with respect to temperature and residence time in a batch autoclave. The results revealed that the rates of sulfur conversion to hydrogen sulfide were different for different compounds depending on the types of carbon-sulfur bonds present in the molecule. Secondly, the corrosivities of model oil mixtures containing specific organic acid and sulphur compounds in white oil were measured. The type and content of sulfur compound determined whether the presence of the sulfur compound: 1) reduced organic acid corrosion rates by forming a protective film; 2) enhanced organic acid corrosion rates by regenerating the acid species; or, 3) had no influence on organic acid corrosion rates. Corrosivities of global crudes including Athabasca bitumen were measured in the same corrosion test unit. The results for the different crudes will be discussed in terms of their contents of different types of organic acid and sulfur species.
Refinery Corrosion: The Influence of Organic Acid and Sulfur Compound Structure on Global Crude Corrosivity

Heather D. Dettman, Nana Li and D. Wickramasinghe (NRCan)
J. Luo (U. of Alberta)

5th NCUT Upgrading and Refining Conference 2009
Edmonton, Alberta
September 14 - 16, 2009
Mechanisms of Refinery Corrosion

- Refinery corrosion occurs at temperatures between 220°C and 400°C
  - Organic acids in gas oil reach their boiling points and condense on metal surfaces, eventually causing pits
  - Sulfides decompose to form H₂S, causing general corrosion
- Acids and hydrogen sulfide work together:
  
  \[
  \begin{align*}
  \text{Fe} + 2\text{RCOOH} & \rightarrow \text{Fe}(\text{RCOO})_2 + \text{H}_2 \\
  \text{Fe} + \text{H}_2\text{S} & \rightarrow \text{FeS} + \text{H}_2 \\
  \text{Fe}(\text{RCOO})_2 + \text{H}_2\text{S} & \rightarrow \text{FeS} + 2\text{RCOOH}
  \end{align*}
  \]
Corrosivity, TAN, and Sulfur

- Corrosivity does not always correlate with total acid number (TAN) (Derungs, 1956; Messer 2004)
  - Are organic acid molecular species in some oils “less active” that those in other oils?
  - Does high sulfide content result in iron sulfide film that protects the plant metallurgy?
  - Another reason?
- This project was conducted to improve the understanding of the contributions of specific structural features of organic acids and sulfur compounds to corrosivity at refinery temperatures
Corrosion Test Unit

Simulates corrosion in vacuum distillation unit

Features:
1. Volume: 250 mL
2. Charge: Any crude or refinery feed blend
3. No. of coupons: 4
4. Operates under vacuum throughout the temperature range

Coupon locations in vapor phase where vapor condenses on metal surface

Coupon location in liquid
Corrosion Unit Commissioning

- Commissioning runs were performed using:
  - White oil (bp 227-512°C)
    - Used to test the mass balance for the unit; obtained > 99% retention of material over 48 hours at atmospheric equivalent temperature (AET) of 350°C (300°C and 225 Torr)
    - Used as the carrier oil for organic acid (model and crude oil-derived) mixtures
  - Commercial naphthenic acids mixture (bp 180-540°C)
Corrosion Unit Performance

Tests performed using 1018 carbon steel coupons either immersed in liquid phase of commercial naphthenic acids in white oil or suspended in vapor phase with varying TAN and atmospheric equivalent temperatures.

Corrosion rates in vapor phase increase with TAN and temperature while corrosion rates in liquid increase with TAN (due to increased acid concentration at the coupon locations).
Global Crudes

<table>
<thead>
<tr>
<th>Global Crude</th>
<th>Density (g/mL)</th>
<th>Content (wt%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
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<tr>
<td>ATHB</td>
<td>1.0100</td>
<td>83.07</td>
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<tr>
<td>Asia1</td>
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<tr>
<td>ME1</td>
<td>0.9964</td>
<td>83.33</td>
</tr>
</tbody>
</table>

Notes

1. Geographical sources: Athabasca (ATHB), Asia, South America (SA), and Middle East (ME)
2. Crudes were topped at 204°C (if -204°C fraction present) before corrosion testing except ME1 which was an atmospheric residue (+343°C)
3. Corrosion tests were performed using 1018 carbon steel coupons at an atmospheric equivalent temperature (AET) of 300°C (250°C and 225 Torr)
Corrosion Rates of Carbon Steel Coupons by Global Crudes

TAN (mg KOH/g)                               5.00  3.39  0.55  0.60  2.70  0.29

Crude Sources
CMNA – Commercial naphthenic acids in white oil
ATHB – Athabasca
Asia – Asia
SA – South America
ME – Middle East

Corrosivity does NOT correlate with TAN for oils from different sources! Why?
Model Organic Acids

- Model organic acid were chosen to represent the different group of acid species. For example:

- **Aliphatic acids with a straight chain:**
  \[ \text{CH}_3\text{(CH}_2\text{)}_3\text{CH}_2\text{OH} \quad \text{CH}_3\text{(CH}_2\text{)}_{15}\text{CH}_2\text{OH} \]

- **Aromatic acids with single aromatic ring**

- **Cycloparaffinic acids with single cycloalkane ring**

- **Other acids with multiple rings:**

- Corrosion tests of each model organic acid dissolved in white oil (TAN = 5mg KOH/g) were performed
Corrosivity by Acid Molecular Weight

Corrosion rates of carbon steel coupons immersed in model oils consisting of organic acid compounds in white oil (TAN = 5.0mg KOH/g) at an AET of 300°C
Corrosion rates of carbon steel coupons either immersed in the model oil (●) or suspended in vapor phase (▲) at an AET of 300°C (TAN = 5.0mg KOH/g)
Conclusions for Corrosion due to Organic Acids

- For model oil mixtures with the same TAN (5.0mg KOH/g), different corrosion rates were obtained.

- As molecular weight and number of rings increased, corrosivity decreased.

- Boiling point of the model organic acid determined a threshold temperature for vapor phase corrosion where acid vapors condensed on the coupons.
HTSD of Isolated Petroleum Organic Acids

Organic Acids (OA)
CMNA – Commercial naphthenic acids
ATHB – Athabasca
Asia – Asia
SA – South America
ME – Middle East

High temperature simulated distillation results of CMNA and organic acids extracted from Global crude oils

AET of Corrosion Test
Corrosion Rates of Global Crudes

TAN (mg KOH/g)                          5.00       3.39       0.55       0.60        2.70       0.29

Crude Sources
CM – Commercial naphthenic acids in white oil
ATHB – Athabasca
Asia – Asia
SA – South America
ME – Middle East

- Boiling point distribution (and structure) explain the relatively high corrosivity of CMNA in both liquid and vapor phases
- Differences between the boiling point distributions of the organic acids from these global crudes do not explain corrosivity differences
  - For these crudes, corrosivity differences are not explained by size (or structure)
What about Sulfur?

- Sulfur compounds $R\text{-}S\text{-}R$ lead to $H_2S +$ by-products through Thermal Cracking, resulting in FeS.

- Model sulfur compounds were chosen to represent the different C-S bonds found in petroleum. For example:

  - Octyl sulfide
  - Dibenzothiophene

- Thermal decomposition studies of nine sulfur compounds dissolved in white oil (1 wt% sulfur) were performed.
Sulfur Identification In Liquid

GC-SCD plot of liquid before and after thermal treatment of octyl sulfide
At temperatures as low as 200°C, within 2 hours - CH₂-S- bonds (sulfides) crack and form H₂S
H₂S Effects on Corrosivity of Organic Acids under Refinery Conditions

Influence of presence (1wt% S) or absence of sulfur compounds on the corrosion rates of commercial naphthenic acids (CMNA) in white oil (TAN = 5.0mg KOH/g) for carbon steel coupons at AET of 300°C
Conclusions for Influence of Sulfur Species on Corrosivity of Organic Acids

- $\text{H}_2\text{S}$ formation from thermolysis of sulfur species depends on their molecular structures: sulfur in ring structures (i.e. thiophenic) are most stable while those in chains (sulfides) are least stable.

- Organic acid corrosivity can be inhibited, enhanced, or not affected by the presence of sulfur compounds, depending both on the content and “$\text{H}_2\text{S}$-generating ability” of the sulfur compounds.
Identification of Sulfidic Corrosion Influences

- Replace the oil matrix with a sulfur-free medium i.e. white oil
  - Organic acids isolated from each of the Global crudes were dissolved in white oil at TAN values similar or slightly lower than those of the original crude oils tested
  - If the oil matrix has no influence on corrosion, the corrosion rates of the white oil mixtures should be the same as that of the original oil
  - If the oil matrix influences corrosion, the corrosion rates of the white oil mixtures could be either greater or lesser than those of the original oil
**Possible Sulfidic Corrosion Influences**

**Mechanism**

1) \( Fe + H_2S \rightarrow FeS + H_2 \)
   - High \( H_2S \) generation
   - Inhibited corrosion due to significant film formation

2) \( Fe(RCOO)_2 + H_2S \rightarrow FeS + 2RCOOH \)
   - Low \( H_2S \) generation
   - Enhanced corrosion with little film formation

3) \( Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2 \)
   - No \( H_2S \) present so corrosion only depends on organic acids (structure and size)

**Corrosion Rate Expected**

1) Extracted organic acids in white oil will have higher rates than the original oil – no film protection

2) Extracted organic acids in white oil will have lower rates than the original oil – no acid regeneration

3) Extracted organic acids in white oil will have the same rates as the original oil – no matrix effect
Sulfidic Corrosion Influences on Corrosion Rates of Global Crudes

<table>
<thead>
<tr>
<th>TAN (mg KOH/g)</th>
<th>5.00</th>
<th>3.39</th>
<th>0.55</th>
<th>0.60</th>
<th>2.70</th>
<th>0.29</th>
</tr>
</thead>
<tbody>
<tr>
<td>S content (wt%)</td>
<td>0.00</td>
<td>4.77</td>
<td>0.59</td>
<td>0.94</td>
<td>3.76</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Corrosion Rate Difference* (mm/y)

1) Film protection
2) No matrix effect
3) Acid regeneration (or only sulfidic corrosion occurs)

* Corrosion rate difference (Isolated organic acids in white oil – Original oil)
Conclusions

- TAN values of crude oils are not reliable for predicting the corrosivity of crude oils
- Contributions from sulfidic corrosion must be included:
  - Total sulfur content is not reliable for predicting sulfidic corrosion contributions
  - Both rates and total amount of hydrogen sulfide formed under prior/present thermal conditions (in the field or refinery) will be important for understanding the influence of sulfidic corrosion
- “High shear” locations will prevent sulfidic film formation/protection
Funding Acknowledgements

- Alberta Science and Research Authority (COURSE/Alberta Energy Research Institute [AERI])
- Canadian Association of Petroleum Producers (CAPP)
- Natural Resources Canada through partial funding by the Canadian Program for Energy Research and Development
Collin W. Cross
Betz GE Water and Process Technologies

Collin Cross received his Ph.D. in Physical Chemistry from the University of Oklahoma in 1994. During this time he pursued studies of the computational physics of Liquid Crystals. Following this he accepted a postdoctoral fellowship with the Keck Center for Computational Structural Biology in Houston. In 1996 Collin joined Betz/GE Water and Process Technologies as an Analytical Chemist. Since that time he has occupied various roles in R&D, and the Enabling Technologies groups. All of these roles have revolved around supporting process chemicals. Collin now occupies a position in the Technical Marketing organization. His areas of responsibility are for Corrosion Control, Antifouling and Fuel Additives.

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High Temperature Corrosion Control and Monitoring for Processing Acidic Crudes

Collin W. Cross
Betz/GE Water and Process Technologies

As the importance of heavy crudes and bitumen laden feedstock continues to increase, challenges also continue to increase regarding the ability to process them in a reliable and economical way. Unfortunately, estimations of the possible problems involved with processing these crudes are often fraught with uncertainty. Rules of thumb, experiential based strategies and reactionary tactics have dominated the industry in its approach to managing the associated risks. Due to the complexities involved with these estimations, many refiners adopt a conservative stance regarding the rate at which they utilize discounted crudes, or depend upon capital-intensive upgrades to equipment.

In order to gain the most benefit from heavy feedstock, new strategies and tactics based on data-driven decisions, are needed. By better understanding the interactions between a particular feed and a particular crude unit, it is possible to more accurately estimate the feasibility of successfully processing more challenging feeds. Additionally, the refiner is able to deploy a host of proactive measures allowing him to do so more confidently and reliably.

Better understandings of the complexities of the feeds corrosion potential, as well as the likelihood for this potential to manifest itself in a given crude unit, have been developed recently. Techniques based on these experiences will be discussed which are allowing many refineries to run more aggressive feed slates at higher levels.
High Temperature Corrosion Control and Monitoring for Processing Acidic Crudes

Dr. Collin Cross

Naphthenic Acid Crude Impacts

- Processing HAC
  - Meets Product Requirements
  - Availability
  - Handling & Storage
  - Energy
  - Desalter
  - Define Product Issue
  - Product Issues Solvable
  - Define Issue
  - API
  - Slop
  - Flotation Treatment
  - Waste Treatment
  - Water Discharge
  - Process HAC

- Crude Unit Corrosion
- Vacuum Unit Corrosion
- Overhead Corrosion
- Condenser Corrosion
- High Temperature Corrosion
- Appropriate Metallurgy
- Effective Monitoring
- Don't Process HAC
- Corrosion Control
- Cost
- Process HAC
• Process Management Tool
• Designed to Maximize Refiner:

– Operational Flexibility
– Safety
– Environmental Protection
– Reliability
– Profitability
A Complex Process

Naphthenic Acid Corrosion

- Temperature
- Sheer Stress
- Sulfur
- Acid Characterization & Concentration
- Thermodynamics
- Metallurgy

MPY
Atmospheric Column Nap Acid Corrosion

Crude Tanks
Slop Tanks

START

To Sat. Gas Plant

Lt. Nap.

Hvy. Nap.

Kerosene

Diesel

Lt. Gas Oil

Hvy Gas Oil

Steam

To Vacuum Unit
Vacuum Unit Nap Acid Corrosion

Crude Atm. Frac. Bottoms

START

1

2

3

4

Steam

Oil/Water Sep.

Lt. Gas Oil

Hvy Gas Oil

Lube Unit

FCC Unit

Vacuum Resid

Coker, FCCU, Asphalt Blending

Vacuum Unit Nap Acid Corrosion

Crude Atm. Frac. Bottoms

START

1

2

3

4

Steam

Oil/Water Sep.

Lt. Gas Oil

Hvy Gas Oil

Lube Unit

FCC Unit

Vacuum Resid

Coker, FCCU, Asphalt Blending
Solution For Processing Naphthenic Acid Crude

- **Crude Inputs**
  - NAN & TAN
  - Fingerprint & Corrosion
  - Characterization Sulfur etc.

- **Asset Inputs**
  - Flow, Pipe Size, Velocity, Temperature, Pipe Configuration and Spatial Relationship, Pipe Geometry, Impingement Factor, Metallurgy

**Predator Assessment Output**
- Highlight critical impact areas
- Identification of specific priority points within critical impact area
- Monitoring requirements/schedule, location & sensor type
- Analysis requirements/schedule & location
- Chemical injection requirements /chemistry & application
- Baseline conditions & entitlement (expected gain)
- Develop program controls /Data Interpretation / training / documentation & improvements
Technologies

Predict - Determine the impact before it occurs

Monitor - Measure the asset condition and the rate of change

Control - Implement corrective actions to maintain the asset integrity and optimize process efficiencies
Total Acid Number vs. Nap. Acid Number
Predict

**TAN Vs. NAN**

**TAN VS NAN**

- **Crude Charge**
  - 1.34 mg/g Vs. 0.93 mg/g

- **AGO**
  - 1.95 mg/g Vs 1.09 mg/g

- **Diesel**
  - 1.74 mg/g Vs 0.96 mg/g

- **Kerosene**
  - 0.75 mg/g Vs. 0.35 mg/g

- **Vacuum Resid**
  - 0.89 mg/g Vs 0.12 mg/g

- **Heavy Gas Oil**
  - 1.74 mg/g Vs 1.54 mg/g

- **Light Gas Oil**
  - 1.95 mg/g Vs 1.09 mg/g

**TAN**
- Organic & inorganic acids
- Esters
- Phenolic compounds
- Lactones
- Resins
- Salts of weak acids (soaps)
- Basic salts of polyacidic bases
- Salts of heavy metals
- Additives--i.e.. inhibitors & detergents
Predict

Crude Oil Assessment

Crude A

Crude B

Crude C
Sulfide Inhibiting Effect

Corrosion of CS and SS at TAN = 5.0

<table>
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<tr>
<th></th>
<th>CS</th>
<th>CS + H₂S</th>
<th>SS</th>
<th>SS + H₂S</th>
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<tbody>
<tr>
<td><strong>500 °F</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>600 °F</strong></td>
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</table>
Predict  **Predator Assessment**

- Tools to develop strategies for processing opportunity crude
  - Opportunity Crude Oils
  - Monitoring Program
  - Chemical injection Points
  - Operating parameters
- Establishes
  - Base line conditions
  - Opportunity Improvement
  - KPI
  - Criteria for success
  - Plans for continuous improvement
Impingement Factor & Velocity

- Pumps
- Downstream of Welds and orifice plates
- Pipe Bends Especially with Thermocouple Points
- Control Valves

Thermocouple
Thermodynamics

High Turbulence --- Column Internals

- Packed Sections
- Bed
- Internals

- Support Beams

- Total Trapout Trays

- Undertray Condensation

- Tray Bubbling Areas

2 Phase Flow
Condensation
Vaporization
Refinery piping configuration obtained during Predator Assessment

Pipeline configuration simplified in terms of components and geometry

Corrosion models developed for individual components

- Corrosion potential
- RCM placement
- Chemical injection locations

Priority Assessment

Predict
Monitor

Fully Integrated Suite Covers Sensor Gaps

- RCM
- Hi Temp UT
- PCOM
- Hydrogen Diffusion
- Odometer
- PCOM Plus
- Probes / Coupons
- Speedometer

Local (more sensitivity)

Global (less sensitivity)

Fe / Ni Ratios
Predator™ Resistance Corrosion Monitor

- High temperature capability > 950 F
- Able to install without shutdown
- Calculates wall thickness by measuring the electrical resistance and comparing to the initial baseline
- Fully automated operation

- Measures 2% change in wall thickness with 6-Sigma accuracy
- Patented technology designed to eliminate electronic noise
- Optimum Coverage 1 Square Meter
RCM Terms

RCM Response or output → Voltage measured between adjacent pins
Monitor

Sample Thickness Report

Plotting Threshold

Remaining Wall

Sample RCM Report

Wall < 320 mils
Start Date: 2/3/2005
Stop Date: 6/14/2005

Time Interval

Monitor

Sample Thickness Report

Plotting Threshold

Remaining Wall

Sample RCM Report

Wall < 320 mils
Start Date: 2/3/2005
Stop Date: 6/14/2005

Time Interval
Monitor

RCM Corrosion Rate Report

- Each channel corresponds to unique real estate on pipe surface.
- Exception Reporting → Only channels above a threshold are plotted.

Sample RCM Report

Corrosion Rate > 5 MPY
Start Date: 2/3/2005
Stop Date: 6/14/2005
~ One year data from the RCM indicates a maximum wall loss of 11 mil, a maximum corrosion rate of 11 mpy and 29+ years remaining service life.
Monitor

Baseline Performance

Corrosion Tower Shell

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</tr>
</tbody>
</table>

21.4 mpy represents nominal 2.4% wall loss and indicates 17+ years remaining.
Control

- Blending
- Phosphate Ester “Best in Class”
- Non Phosphorous - Phosphorous efficacy without the fouling or catalyst poisoning
- New patent pending molecules
Effect of Inhibitor Type on Corrosion Rate

Conditions:
VEN LVGO, 600 F, 1018CS
100 ppm active

Untreated Corrosion Rate
Control

ER Probe
Data Predator
61N

HVGO Corrosion

Patented Predator
61N
Started

Date

3-Jan 17-Jan 3-Feb 17-Feb 2-Mar 11-Mar 25-Mar 30-Apr 20-May 12-Jun 6-Jul

HVGO

Case History

ER Probe Data Predator 61N

5th NCUT Upgrading and Refining Conference 2009
Control Case History Predator 6tN1401

Atmos Tower

1.50
1.53

Diesel

2.23
2.40

AGO

Atmos Bottoms

2.10
2.44

Vacuum Tower

2.20
2.65

LVGO PA

1.96
2.47

HVGO

0.24
1.00

VTB

NAN

TAN
AG0 Stream Corrosion - Previous Competitive Phosphorous Program

Control

Case History 6N1401

3 Week Rolling Average
Control

Case History DM20074

AGO Stream Corrosion - Current DM20074

Corrosion

3 Week Rolling Average
Predator Program Recommendations

- Chemical Injection
- Metals Analysis
- UT Readings
- RCM
- Hydrosteele
- Corrosion Probes
Delivers

- Safety
- Environmental Protection
- Reliability
- Operational Flexibility
- Profitability
BIOGRAPHY

Jonathan Wylde
Clariant Oil Services, North America

Wylde graduated with a BSc (Hons) in Geology from the University of Bristol in 1999 and went to complete his PhD in 2002, also at the University of Bristol. His PhD was on the mechanisms of growth and inhibition of mineral scale on surfaces. Wylde joined Clariant Oil Services in 2002 where initially he worked in the scale team of the R&D Center in Aberdeen, UK. He went on to hold several account manager roles over the next 4 years managing the production chemistry on several major North Sea assets. In March 2007 Wylde relocated to Houston, Texas as the technical manager for North America. Recently Wylde became the Business Manager for Clariant Oil Services Canada based in Calgary, Alberta.

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Corrosion Inhibitor Development for Slightly Sour Environments with Oxygen Intrusion

Hongbin Wang, Jonathan Wylde and John Li
Clariant Oil Services, North America

This paper contains the results of a case history where oxygen contamination took place in a slightly sour system. Details are also given on the laboratory testing results and development of corrosion inhibitors for such an environment.

The ingress of oxygen had been occasionally reported in the slightly sour water injection system through the vapor space in storage tanks and process system, through pump seals and electrical cable to aquifer wells. As a consequence, severe localized corrosion (> 500 mpy) developed on the corrosion coupons when oxygen intrusion was recorded during the exposure period. As a stronger oxidant than H₂CO₃, oxygen greatly aggravated the corrosion attack by directly participating in the cathodic reaction, generally under full or partial diffusion control. This serves to create a more acidic local environment through reaction with FeS solids generating elemental sulfur in the H₂S containing system. However, to the author’s knowledge, few publications have systematically addressed the effect of O₂ in the inhibition of carbon steel in the slightly sour system, particularly on the initiation and propagation of localized attack.

In this paper, the effect of oxygen on the inhibition of slightly sour corrosion was studied by using bubble testing cells with continuous H₂S/CO₂ mixture gas sparging and occasional O₂ intrusion of a period of 2-4 hours in the total 7-day long test. The corrosion attack was quantified by linear polarization resistance (LPR) measurements and weight loss corrosion coupons.

Significant findings include the magnitude of localized attacks at different O₂ concentrations and intrusion periods without and with the presence of corrosion inhibitors.
Corrosion Inhibitor Development for Slightly Sour Environments with Oxygen Intrusion

5th NCUT Upgrading and Refining Conference 2009
Presentation Overview

- Introduction to the Case History
- Overview of Oxygen Corrosion
- Experimental Data
- Application of Lab Tests to the Field
CASE HISTORY INTRODUCTION AND BACKGROUND
Introduction

- Large water injection system

- Processes 500,000 bbl (80,000 m³) of water per day in about 3,000 injector wells

- Injection water comes from two sources which represent two production zones

- Except for the water injection tubing and casing, the transmission pipelines were cement lined

- One of the KPIs for this system was to maintain the integrity of the downhole injection tubular in order to minimise system downtime and maximise injection
General Corrosion Relevant Conditions

- Low temperature (22 to 60°C)
- High pH (6.8 to 7.0)
- Low CO₂ content
- Trace amount of dissolved H₂S from upstream or possible inline SRB colonies
- FeS deposits, complicated by other scale types and oil excursions
- Long distance from chemical injection points to the injectors (consumption of chemicals along the transportation lines)
- Low flow rate as one moves further downstream into the distribution system
- Occasional O₂ intrusion through tanks, source wells, and pumps, etc
System Flow Schematic
Oxygen Intrusion

- The risk of localized corrosion cannot be underestimated for the injectors. Possible localized corrosion mechanisms are:
  - $O_2$ corrosion
  - Underdeposit corrosion
  - Microbiologically influenced corrosion (MIC)

- $O_2$ intrusion has been occasionally identified, particularly before the installation of gas blankets on the tanks at the aquifer plant. Severe $O_2$ ingress had also occurred before via the aquifer wells. When $O_2$ intrusion took place, the localized corrosion rate was measured at hundreds of mpy.

- As oxygen contamination is intermittent, its ingress is usually not easily detected in a timely manner
Field Corrosion Rate Summary

![Corrosion Rate Graph](image)

Corrosion Rates (mpy)

MPY

0 20 40 60 80 100 120

INTRODUCTION AND OVERVIEW OF OXYGEN CORROSION
General Point

- Oxygen dissolved in water is one of the primary causes of corrosion in the oil field. When oxygen is present, the most common types of corrosion include pitting corrosion and uniform corrosion.

- Oxygen is a strong oxidant and reacts quickly with metal. The maximum amount of oxygen in water is only 8 ppm, so the mass transport of oxygen is the rate limiting step in oxygenated non-acidic environments. Controlling the rate of oxygen transport (often by controlling flow velocity) is thus critical to corrosion control.

- $O_2$ corrosion products include iron oxides, including $\text{FeO(OH)}$ - goethite, $\text{Fe}_2\text{O}_3$ - hematite, $\text{Fe}_3\text{O}_4$ - magnetite, and $\text{FeO(OH)}$ - ferrous hydroxide.
**UNIFORM CORROSION OR GENERAL CORROSION/ATTACK**

Uniformly over the exposed surface without appreciable localization of attack.

Metal itself is metallurgically and compositionally uniform

Uniform corrosive environment/geometry

Perhaps the least insidious type of corrosion — since the rate is predictable.
Relevant Types of Corrosion

LOCALIZED CORROSION
- PITTING CORROSION

Deep, narrow corrosive attack which often causes rapid penetration of the metal.
Particularly the case for SS, aluminum, etc

Failure of local passive film or protective films

Non-uniformity of steel microstructure

A local cell is set up between the interior of the pit and external surface

Pitting corrosion usually occurs in stages: initiation, propagation, termination, and re-initiation.
Types of Corrosion

LOCALIZED CORROSION
- Pitting Corrosion

NACE classification:
- Low pitting: 0-5 mpy
- Moderate pitting: 5-8 mpy
- High pitting: 8-15 mpy
- Severe pitting: >15 mpy

Characterized by the pit density, pit depth, pit size, maximum penetration rate, etc... [ASTM G46]
Oxygen Corrosion Theory

- The presence of oxygen accelerates the cathodic reactions that cause corrosion, for example:

\[
\begin{align*}
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O \text{ (oxygen reduction in acidic solution)} \\
\frac{1}{2}O_2 + H_2O + 2e^- & \rightarrow 2OH^- \text{ (oxygen reduction in neutral or basic solution)} \\
2H^+ + 2e^- & \rightarrow H_2 \text{ (hydrogen evolution from acidic solution)} \\
2H_2O + 2e^- & \rightarrow H_2 + 2OH^- \text{ (hydrogen evolution from neutral water)}
\end{align*}
\]
## Quantification of Oxygen Influence

<table>
<thead>
<tr>
<th>CR (mpy)</th>
<th>O₂ concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Temp /F</td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>0.5</td>
</tr>
<tr>
<td>113</td>
<td>0.6</td>
</tr>
<tr>
<td>122</td>
<td>0.7</td>
</tr>
<tr>
<td>131</td>
<td>0.7</td>
</tr>
<tr>
<td>140</td>
<td>0.8</td>
</tr>
<tr>
<td>149</td>
<td>0.9</td>
</tr>
<tr>
<td>158</td>
<td>1.0</td>
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<tr>
<td>167</td>
<td>1.1</td>
</tr>
<tr>
<td>176</td>
<td>1.1</td>
</tr>
<tr>
<td>185</td>
<td>1.2</td>
</tr>
</tbody>
</table>
**Other Oxygen Intrusion Effects**

- Corrosion inhibitor and corrosion rate:
  - Almost all CI deployed are designed for deployment in an oxygen free system. The presence of oxygen will not be inhibited by many programs.

- Many other production chemicals are degraded by oxygen – e.g. THPS biocide

![Figure 1 – THPS Chemical Structure](image)

- FeO, FeOH$_{(2-3)}$, FeOOH scales will form as Fe is oxidized with intrusion which can itself lead to an UDC and exacerbated MIC risk.
Mitigating Oxygen Effects

- Chemically this is possible but operationally challenging due to very high injection rates and a relatively low residency time, either specialist CI or injection of oxygen scavenger

- Best way is to ensure no physical intrusion of oxygen occurs in vessels, pipes, tanks etc.
EXPERIMENTAL DATA
Test Equipment
# Test Conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>130</td>
<td>°F</td>
</tr>
<tr>
<td>$P_{\text{total}}$</td>
<td>14.5</td>
<td>psi</td>
</tr>
<tr>
<td>Gas composition</td>
<td>$\text{CO}_2/\text{H}_2\text{S}/\text{N}_2, % = 20.4/0.02/79.6$</td>
<td></td>
</tr>
<tr>
<td>Brine</td>
<td>Field brine obtained at Aquifer Plant</td>
<td></td>
</tr>
<tr>
<td>Water cut</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>Weight loss corrosion coupon</td>
<td>Carbon Steel C1018</td>
<td></td>
</tr>
<tr>
<td>Stirrer</td>
<td>300</td>
<td>rpm</td>
</tr>
<tr>
<td>Surface area of corrosion coupon</td>
<td>7.6</td>
<td>cm$^2$</td>
</tr>
<tr>
<td>Chemical Dosage</td>
<td>Blank and 15</td>
<td>ppm</td>
</tr>
<tr>
<td>$O_2$ intrusion (500 ppb at eqm)</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Test Duration</td>
<td>7</td>
<td>Days</td>
</tr>
</tbody>
</table>
## Test Matrix

<table>
<thead>
<tr>
<th>Test</th>
<th>Water</th>
<th>Oxygen Intrusion</th>
<th>Chemical</th>
<th>Dosage (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Field Brine</td>
<td>No</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Field Brine</td>
<td>No</td>
<td>Product A</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Field Brine</td>
<td>No</td>
<td>Product A</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Field Brine</td>
<td>Yes</td>
<td>Product A</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Field Brine</td>
<td>Yes</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Field Brine</td>
<td>No</td>
<td>Product B</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>Field Brine</td>
<td>No</td>
<td>Product C</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>Field Brine</td>
<td>Yes</td>
<td>Product B</td>
<td>15</td>
</tr>
</tbody>
</table>

- **Product A**: Imidazoline / CBQ1
- **Product B**: Imidazoline / CBQ2
- **Product C**: Imidazoline / CDA
Testing Results – General CR

Weight Loss Corrosion Rate

![Image of corrosion test setup]

Chemicals

- BLANK - O2
- Product A 15 ppm
- Product B 15 ppm
- Product C 15 ppm
- Product A 30 ppm
- Product B 15 ppm - O2
- Product A 15 ppm - O2

Corrosion Rate (mpy)
Coupon Appearance

In order to study the impact of oxygen intrusion on overall corrosion, 5% O₂ (95% N₂) gas was introduced into the Cell 4 after a 2-day exposure in CO₂-H₂S corrosive environment.

\[ 3FeS + 2O_2 \rightarrow Fe_3O_4 + 3S \]
Coupon Appearance

**Front**
- Blank
- 15 ppm Product A
- 15 ppm Product A + O₂

**Back**
- Blank

Area attacked by O₂
## Pitting Rates

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Maximum Penetration Rate /mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field brine, 0 ppm</td>
<td></td>
</tr>
<tr>
<td>Coupon #00</td>
<td>23.1</td>
</tr>
<tr>
<td>Coupon #01</td>
<td>25.7</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>24.4</strong></td>
</tr>
<tr>
<td>15 ppm <strong>Product A</strong></td>
<td></td>
</tr>
<tr>
<td>Coupon #26</td>
<td>7.7</td>
</tr>
<tr>
<td>Coupon #27</td>
<td>7.7</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>7.7</strong></td>
</tr>
<tr>
<td>30 ppm <strong>Product A</strong></td>
<td></td>
</tr>
<tr>
<td>Coupon #24</td>
<td>7.7</td>
</tr>
<tr>
<td>Coupon #25</td>
<td>7.7</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>7.7</strong></td>
</tr>
<tr>
<td>15 ppm <strong>Product A</strong> O₂ intrusion</td>
<td></td>
</tr>
<tr>
<td>Coupon #28</td>
<td>12.4</td>
</tr>
<tr>
<td>Coupon #29</td>
<td>12.4</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>12.4</strong></td>
</tr>
<tr>
<td>Field brine 0 ppm + O₂</td>
<td></td>
</tr>
<tr>
<td>Coupon #00</td>
<td>45.7</td>
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<tr>
<td>Coupon #01</td>
<td>48.2</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>47.0</strong></td>
</tr>
<tr>
<td>15 ppm <strong>Product B</strong></td>
<td></td>
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<tr>
<td>Coupon #26</td>
<td>5.1</td>
</tr>
<tr>
<td>Coupon #27</td>
<td>7.7</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>6.4</strong></td>
</tr>
<tr>
<td>15 ppm <strong>Product C</strong></td>
<td></td>
</tr>
<tr>
<td>Coupon #24</td>
<td>2.6</td>
</tr>
<tr>
<td>Coupon #25</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>2.6</strong></td>
</tr>
<tr>
<td>15 ppm <strong>Product B</strong> O₂ intrusion</td>
<td></td>
</tr>
<tr>
<td>Coupon #28</td>
<td>15.4</td>
</tr>
<tr>
<td>Coupon #29</td>
<td>25.7</td>
</tr>
<tr>
<td><strong>Average corrosion rate</strong></td>
<td><strong>20.5</strong></td>
</tr>
</tbody>
</table>
LPR Rates

- CI greatly reduced the corrosion rate
- Addition of O₂ increased CR and Product A was far superior in presence of O₂
- Some protection offered by CI when O₂ present but showed most organic inhibitors are not capable of fully protecting a system when O₂ is present
- O₂ may also present any protective inorganic films from forming (e.g. FeS)
Conclusions and Field Recommendations

- WL coupons and LPR testing suggested a generally low corrosive environment if there is steady state operation – attributed to ↓[corrosive species] and trace H₂S
- FeS formed quickly in the H₂S-CO₂ env. Confirming field observations
- O₂ intrusion had a major impact on corrosion inhibitor performance
  - Turned blackened water into pale white
  - WL coupons showed a doubling in CR; supported by the LPR results
- Surface morphology showed moderate surface CR without inhibition that was greatly aggravated in the presence of O₂
- It is crucial to take more effort to keep the system O₂ free and continue the inhibitor program
- A further recommendation was to install an online O₂ analyzer to better detect excursions so to implement a more robust O₂ scavenging and inhibition program
Acknowledgements

The authors would like to thanks Clariant Oil Services for allowing us to present this information and NCUT for the kind invitation to attend and present at this conference.
DuPont® IsoTherming® Clean Fuel Technology

Ernie Levinski, E. I. DuPont Company

**Figure 1: IsoTherming® Clean Fuel Technology**

- **DuPont IsoTherming** combines proprietary technologies to convert heavy feedstock into high-quality gasoline.
- **Clean Fuel** technology involves an oxidative to hydrothermal conversion process.
- **Figure 2: Flow Diagram**

**Lower Product Inversion**

Lower product losses are achieved by operating the process to reduce coke deposition and increase yield. The figure shows a simplified flow diagram of the process.

**Reduced Equipment/Plant Turnover Times**

The delivery time from heavy fuel oil to gasoline is reduced from 25 to 4 years.

**Reduced Light Ends/Gas**

The lower temperature across the IsoTherming® reactor allows for the removal of low-boiling-point hydrocarbons, improving gasoline quality.

**Increased Output Capacities**

A monochromatic reactor configuration is shown, with the IsoTherming® reactor pressure vessel, heat exchanger, and other ancillary equipment.

**Figure 3: Downstream Configuration**

The IsoTherming® reactor is followed by a downstream configuration, including a separator, cooler, and final distillation column.

**Figure 4: Downstream Configuration**

- **DuPont IsoTherming®** is a versatile technology that can be applied to a variety of feedstocks, including heavy fuel oils.
- **The IsoTherming® process** involves a unique combination of chemical and thermal refining technologies to achieve high-quality gasoline.
- **Environmental Benefits**

This technology reduces emissions and improves fuel quality, making it a key component in DuPont’s commitment to sustainability.

**References**


**Figure 5: Flow Diagram**

The flow diagram illustrates the key components of the IsoTherming® process, including the reactor, heat exchanger, and downstream equipment.

**Figure 6: Flow Diagram**

- **DuPont IsoTherming®** technology offers a range of benefits, including lower emissions, improved fuel quality, and reduced equipment turnover times.
- **The IsoTherming® process** is modular and can be tailored to specific feedstock and product specifications.

**Figure 7: Flow Diagram**

- **DuPont IsoTherming®** technology is designed to convert heavy feedstocks into high-quality gasoline, offering a sustainable solution for the refining industry.
- **The IsoTherming® process** is scalable and can be integrated into existing refinery infrastructure.

**Figure 8: Flow Diagram**

- **DuPont IsoTherming®** technology is a key component in DuPont’s efforts to reduce emissions and improve fuel quality.
- **The IsoTherming® process** is designed to be environmentally friendly and economically viable.

**Figure 9: Flow Diagram**

- **DuPont IsoTherming®** technology offers a range of benefits, including reduced emissions, improved fuel quality, and lower equipment turnover times.
- **The IsoTherming® process** is modular and can be tailored to specific feedstock and product specifications.

**Figure 10: Flow Diagram**

- **DuPont IsoTherming®** technology is designed to convert heavy feedstocks into high-quality gasoline, offering a sustainable solution for the refining industry.
- **The IsoTherming® process** is scalable and can be integrated into existing refinery infrastructure.

**Figure 11: Flow Diagram**

- **DuPont IsoTherming®** technology is a key component in DuPont’s efforts to reduce emissions and improve fuel quality.
- **The IsoTherming® process** is designed to be environmentally friendly and economically viable.
A Novel Interior Coating for Use in Oil Sands / Hydrotransport

Technology Background

Unique properties of RoPathfan:
- Very high tear propagation and abrasion resistance.
- Excellent chemical resistance.
- Very high hydrodynamic resistance.
- Abrasion, wear resistant - filled, and fast quality grades.
- Extremely low and high temperature resistant grades.

Technology Background

Unique properties of RoPathfan:
- Very high tear propagation and abrasion resistance.
- Osmosis by abrasion to materials.
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- Excellent chemical resistance.
- Very high hydrodynamic resistance.
- Abrasion, wear resistant - filled, and fast quality grades.
- Extremely low and high temperature resistant grades.

Technology Background

Unique properties of RoPathfan:
- Very high tear propagation and abrasion resistance.
- Osmosis by abrasion to materials.
- Excellent chemical resistance.
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ABSTRACT
Molecular characterization of oil components is important for understanding and modeling petroleum behavior during production and refining processes. For those components with boiling point (bp) >254°C, gas chromatography (GC) can be used to separate species before analysis. For asphaltene (bp >254°C) GC cannot be used but gel permeation chromatography (GPC) has proven useful. Deitman et al. Energy & Fuels, 2003, 19:1390-1404. Analyses of Athabasca asphaltenes GPC fractions reveal that the asphaltenes consist of two species: “crunchy” (graphitic in appearance) and “oily”, with molecular weights from 400 to 2000 g/mole measured by low resolution mass spectrometry. Work has continued to separate the asphaltenes by polarity. Firstly, Athabasca asphaltenes were subfractionated into four parts based on differential solubility in pentane and centrifugation (Nakayama et al. Ind. Eng. Chem. Res. 1995, 34, 947-972). Secondly, adsorption chromatography was used to isolate acidic species from the asphaltenes. The four “polarity” fractions and acid species were characterized including elemental and metal content and Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) carbon type analyses. Their elution profiles by GPC were also compared.

PENTANE ASPHALTENES SUBFRACTIONATED BY “SIZE”
Gas Permeation Chromatography (GPC) was used to separate Athabasca pentane asphaltenes (PA) by “size” into sub-fractions. First to elute (A to B below), are crunchy in texture, the later to elute (C to H below) are oily in texture.

Crunchy and Oily Asphaltenes Have Different Characteristics:
1. Metals Analyses

Pentane Asphaltenes GPC Fractions

2. Coaxial Microscopy:
Oily asphaltenes (Fraction E) show areas with relatively strong yellow fluorescence and the groundmass with lower fluorescence. The situations are due to changes in solvent evaporation rate. The excitation wavelength range was 450-460 nm with a barrier filter of 515 nm. Crunchy asphaltenes (Fraction A) do not fluoresce under these conditions.

3. Molecular Weights by Negative Ion, Electrospray ionization, Linear Trap Quadrupole Mass Spectrometry (LTI) ESI LTQ MS and Vapor Pressure Osmometry:

PENTANE ASPHALTENES SUBFRACTIONATION BY “POLARITY”
1. Solubility and Centrifugation:
Pentane asphaltenes were dissolved in methylene chloride and gradually precipitated by increasing proportions of pentane; the precipitates were isolated by centrifugation (Nakayama et al. Ind. Eng. Chem. Res. 1995, 34, 947-972). the last fraction being supernatant (SN)

2. Adsorption of Acidic Species:
The ion exchange Sphadex AAE 25 (Medaas et al. SPE 5th International Symposium on Oilfield Scale, SPE90340, Aberdeen, UK) was used to separate acidic species from the pentane asphaltenes or whole asphaltenes. The acidic fraction were treated with pentane 40:1 ratio to precipitate the asphaltenes present.

ACKNOWLEDGMENTS
Financial support: Partial funding by the Canadian Program for Energy Research and Development (PERD), the Alberta Research Council and the Alberta Energy Research Institute.

CONCLUSIONS
Athabasca bitumen asphaltenes consist of two distinct types of species: “crunchy” and “oily”.

Crunchy asphaltenes:
- Are the major species of pentane asphaltenes (i.e. 58 wt% and have the highest metal contents.
- Have monomer size ranges from 400 to 1900 g/mole and do not aggregate (by mass spectrometry) and do not fluoresce.

Oily asphaltenes:
- Are the minor species of pentane asphaltenes (i.e. 42 wt%) and have the lowest metal contents.
- Have monomer size ranges from 400 to 2600 g/mole.

Tend to aggregate (by MS); VP0 measures the size of dimers.
- Do not fluoresce.

Were the least polar, having the lowest aromatic carbon, sulphur, nitrogen, and metal contents.
- Are predominantly non-acidic.

Oily asphaltene carbon type structure:
- Aromatic bridge (1) Aromatic alkyl (2)
- Alkenyl (3)
- Alkyl (4)
- Alkane (5)

CARBON TYPE CONTENTS OF ASPHALTENE SUBLATION:

Molecular structures shown above are illustrative of the information obtained from NMR carbon type analyses. Structures were drawn based on fitting the following parameters:
- Aromatic carbon content
- Sulfuric carbon content
- Chain length
- Nitrogen content
- Aromatic cluster size
- Carbon type carbon to aromatic carbon ratio
- Aromatic carbon to aliphatic carbon ratio

Example of and average chain length calculation:

Carbon type carbon composition is shown in the following graph:

Aromatic Bridge (1) Aromatic alkyl (2)
Alkenyl (3) Alkyl (4) Alkane (5)

OILY ASPHALTENES:
- Sulfuric carbon content
- Chain length
- Nitrogen content
- Aromatic cluster size
- Carbon type carbon to aromatic carbon ratio
- Aromatic carbon to aliphatic carbon ratio

Example of and average chain length calculation:

Carbon type contents of asphaltene subfractions:

Blending light and heavy oil:

Carbon type carbon composition is shown in the following graph:

Aromatic Bridge (1) Aromatic alkyl (2)
Alkenyl (3) Alkyl (4) Alkane (5)
Advanced HCCI Combustion of Oil Sands Diesel Fuel Blends and Second Generation Biofuel

W. Stuart Nell, Vahid Hosseini, Cosmin Dumitrescu, Wallace L. Chipper, Rafael Gielecki, Darcy Hager, and Craig Fairbridge

1 National Research Council Canada, Institute for Chemical Process and Environmental Technology, 2 Natural Resources Canada, CAMEX Energy Technology Centre, Devon

Background

**Compression ignition (diesel) combustion**
- High pressure, high-temperature

**Premixed ignition (gasoline) combustion**
- Lower temperature, lower pressure

**Homogeneous Charge Compression Ignition (HCCI)**
- Low emission, high efficiency

**HCCI Combustion**
- HCCI combustion involves the autoignition of a homogeneous highly diluted air/mixture such that the engine produces near-zero NOx and soot emissions and high fuel conversion efficiency.
- There is no direct method to control HCCI combustion timing, usually HC and CO emissions are high and the power is limited.
- Conventional fuel rating parameters (octane and cetane number) are not suitable for predicting HCCI combustion characteristics.

**Objectives**
- Understanding the relationship between HCCI combustion characteristics and fuel chemistry is important.
- The focus is on fuels with dual-stage autoignition characteristics, especially oil sands derived diesel fuels.

**Experimental Engine – Cooperative Fuels Research**

**Results**

Fuels for HCCI
- Three upgrading methods were applied to the minimally processed oil sands derived diesel fuel (OS-CN37) to achieve higher cetane (CN) fuels: hydrotreating, blending with cetane improver and blending with supercetane (CN) renewable diesel.
- Similar CN changes resulted from each upgrading method, the chemical compositions of the resultant fuels were different. Fuels include:
  - Minimally processed oil sands derived diesel (OS-CN37): CN 58.
  - Two upgraded fuels with hydrotreating at 260°C (OS-CN39) and CN of 41 (OS-CN41).
  - Two fuels produced by blending the base oil sands fuel (OS-CN37) with commercial cetane improver (UltraHyCetate). The resultant cetane numbers were: CN40 (OS-CN40) and CN41 (OS-CN41).

**Fuels Analyses**
- Severe hydrotreating of OS-CN41 decreased boiling range considerably. 5% and 10% supercetane blends increased.

**In order to isolate effects fuel chemistry from other initial and operating conditions effects, the engine was operated in a series of fixed speed-load conditions in which all initial conditions were similar and construction timings were kept constant.**

**Conclusions**
- HCCI autoignition characteristics are coupled strongly with fuel chemistry.
- Conventional fuel rating parameters (octane and cetane number) are not adequate for predicting HCCI combustion quality.
- Hydroprocessing substantially improves HCCI combustion fuel conversion efficiency and reduces emissions.
- HC emissions are highly dependent on the fuel chemistry while CO emissions are primarily a function of dilution.
Microscopy of High Chloride Primary Froth: Refinery Implications of Non-mixing Emulsified Water

G. R. D. Elliott, V. A. Muñoz, and R. J. Mikula

CanmetENERGY Research & Development, Natural Resources Canada, Devon, Alberta, T9G 1A8, CANADA

Abstract: The water chemistry of oil sand ores depends upon the geological formation in which the original oil was intruded. Prehistoric marine environments typically have significantly higher chloride contents than oil sand ores from eskeruate or fluvial locations. Since most of the water used to extract bitumen from the oil sands is recycled, any dissolved ions contributed from the water may accumulate. Chloride is of particular concern because it can affect the refinery operations (corrosion). During the water-based extraction process, a bitumen concentrate known as primary froth is produced with a distribution of emulsified water. The larger emulsion droplets are removed with the recycled process water, while the smaller emulsion droplets reflect a water chemistry of the original geological deposition. As the oilsands mixing operation moves from a low chloride ore to a higher chloride ore, the impact of the new water chemistry on the refinery due to the ore is expected to only change gradually as the high chloride from the one ore is mixed with the large volumes of recycle water. This study shows that the water originated from the ore, containing high chloride concentration, does not mix well with the process water and remains in form of small droplets (<10 µm). Therefore, the chloride is carried over with the bitumen phase. This means that the impact on the upgrading and refinery due to chloride) can be immediate, rather than gradually occurring over a number of years as it would be predicted if the water in the ore and the recycled water were a well mixed system. A method was developed to measure the size of the droplets and chloride concentration in a froth stream using a combination of cryo-scanning electron microscopy and elemental mapping by x-ray spectroscopy analysis.

**Table 2:** Cation and Anion concentrations in the ore water samples and the solubility limits in the ore.

<table>
<thead>
<tr>
<th>Cation Concentration (mg/L)</th>
<th>Anion Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>K</td>
</tr>
<tr>
<td>ORE A</td>
<td>25</td>
</tr>
<tr>
<td>ORE B</td>
<td>14</td>
</tr>
<tr>
<td>ORE C</td>
<td>5</td>
</tr>
</tbody>
</table>

**Figure 1:** A: Location of the Athabasca oil sand and B) process map showing the flow of the oil sand to the upgrading and finally to the refinery where Cl loading is immediate.

**Figure 2:** Diagram depicting the steps in processing oil sand ore. A) Oil sand ore before hot water in an average oil sand ore. Water in the ore separation; B) primary froth produced during a mixture of connate water and pour extraction; and C) bitumen product to be sent to hot water. Connate water remains unaltered during the extraction processes and represents the original water chemistry.

**Figure 3:** Distribution of elements found in oil sand ore. A) Oil sand ore before hot water in an average oil sand ore. Water in the ore separation; B) primary froth produced during a mixture of connate water and pour extraction; and C) bitumen product to be sent to hot water. Connate water remains unaltered during the extraction processes and represents the original water chemistry.

**Figure 4:** Bulk Chloride distributions in the froth were investigated by A) X-ray fluorescence (XRF) for the oil phase and B) ion chromatography (IC) for the water phase. These results show a non-linear relationship between water content and total Cl in the froth. The smaller water droplets represent the original connate water chemistry and have a higher Cl content present as inorganic salts. The larger water droplets with a lower Cl content were diluted and removed by mixing with extraction water. However, no relationship existed with Cl content in the ore from low to high as shown in both A & B where ORE C had the highest Cl content in soluble ions test but had the lowest Cl content in the emulsified water. Water samples below 5% gave variable results due to sample volume dilution for IC analysis. Further analyses by direct cryo-scanning electron microscopy was required to measure Cl content in small water droplets (1-10 µm).

**Figure 5:** A): Type 1 precipitate morphology found in sublimed primary froth emulsified water droplets. Type 1 is composed of a single composite clay and fines and type 2 is a diffusive network of clays and fines. Scale bar, 20 µm. B): X-ray spectrum from type 1. C): X-ray spectrum from the type 2.

**Figure 6:** Scanning electron image of a fractured, sublimed primary froth emulsion of water droplets in an x-ray spectroscopy element map. A) Scanning electron image of a fractured primary froth sample showing the precipitates from the sublimed water droplets. B) X-ray spectroscopy element map showing the distribution of chlorine, potassium (blue) and background carbon (green). Scale bar, 10 µm.

**Figure 7:** Scanning electron image of the high chloride froth emulsion showing a distribution of water droplets and corresponding x-ray elemental spectrum. Scale bar, 100 µm.

**Figure 8:** C): Type 1 and 2 precipitate morphology and x-ray spectrum. A): Two precipitate morphologies found in sublimed primary froth emulsified water droplets. Type 1 is composed of a single composite clay and fines and type 2 is a diffusive network of clays and fines. Scale bar, 20 µm. B): X-ray spectrum from type 1. C): X-ray spectrum from the type 2.

**Figure 9:** Scanning electron images of a high chloride froth samples that were spikied with: A) 300 ppm of NaHCO3 and B) 300 ppm of NaCl. Scale bar, 100 µm. Open stars indicate mixing only occurred in droplets larger than 1 µm.

**Table 3:** X-ray elemental analysis (weight%) of small water droplet (<10 µm) precipitates from froth samples that were spikied with 300 ppm of NaHCO3 (Fig 8A), 300 ppm of NaCl (Fig 8B), and a low chloride ore, and high chloride ore (Fig 7).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>NaHCO3</th>
<th>NaCl</th>
<th>Low Cl Ore</th>
<th>High Cl Ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>0.99</td>
<td>1.22</td>
<td>0.11</td>
<td>0.07</td>
<td>1.91</td>
<td>0.73</td>
<td>0.56</td>
<td>0.22</td>
<td>0.17</td>
<td>0.23</td>
<td>0.04</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>0.17</td>
<td>0.15</td>
<td>0.26</td>
<td>0.07</td>
<td>1.75</td>
<td>0.02</td>
<td>0.27</td>
<td>0.06</td>
<td>0.29</td>
<td>0.07</td>
<td>0.1</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>1.91</td>
<td>0.56</td>
<td>0.22</td>
<td>0.17</td>
<td>0.23</td>
<td>0.04</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Future Work: More observations need to be conducted on a high Cl ore to help differentiate the relatively small total Cl contents, the method of transport of high Cl through the di-bite, and how these small water droplets are stabilized preventing mixing with extraction water. One hypothesis is that particular clays and fines are stabilizing the small water droplets preventing them from coalescing, which requires further treatment to prevent corrosion of pipes.
Naphthenic Acid Removal from HVGO by Alkaline Earth Metal Catalysts

Lianhui Ding, Parviz Rahimi, Randall Hawkins, Soora Bhatt, Yu Shi
NCUT, ConmetENERGY, Natural Resources Canada

Introduction

- Naphthenic acid (NA) contaminants are organic acids in crudes with general formula: \( \text{RC(=O)CH}_{2}\text{R} \) + \( \text{COOH} \).
- Negative effects:
  - Corrosion in refineries (distillation, transfer lines, heat exchangers, etc).
  - Stable emulsion (oil and water separation difficult).
  - Lower value of oil in market.
- Typical chemical structures

Composition of spent catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CaO</th>
<th>CaCO3</th>
<th>MgO</th>
<th>ZnO</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-230A</td>
<td>41.4</td>
<td>52.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO-300A</td>
<td>54.7</td>
<td>45.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO-380H</td>
<td>56.1</td>
<td>43.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO-380H</td>
<td>72.0</td>
<td>23.2</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO-300A</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO3-30A</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO-300A</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NanoCaO-300A</td>
<td>86.5</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaOH2-300A</td>
<td>94.2</td>
<td>5.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaO-300A</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Effect of Ca compounds and particle sizes

<table>
<thead>
<tr>
<th>Particle size</th>
<th>CaO</th>
<th>Ca(OH)2</th>
<th>CaCO3</th>
<th>Nano-sized Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAV reduction, %</td>
<td>24.2</td>
<td>27.1</td>
<td>24.6</td>
<td>49.2</td>
</tr>
<tr>
<td>CCE, %.</td>
<td>0.010</td>
<td>0.012</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
- Ca\(^{2+}\) cation probably plays more important role.
- External surface and efficiency that NAC molecules access to active sites.

TAV, liquid yields and conversion after reaction

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>TAN (mg KOH/g oil)</th>
<th>Liquid yield, wt%</th>
<th>NA conversion, %</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-200A</td>
<td>4.116</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO-300A</td>
<td>3.704, 99.8</td>
<td>7.8</td>
<td>0.16</td>
<td>0.60</td>
</tr>
<tr>
<td>MgO-300A</td>
<td>3.507, 99.2</td>
<td>14.8</td>
<td>0.04</td>
<td>0.37</td>
</tr>
<tr>
<td>BaO-300A</td>
<td>3.767, 99.3</td>
<td>20.9</td>
<td>0.20</td>
<td>0.99</td>
</tr>
<tr>
<td>ZnO-300A</td>
<td>3.767, 99.9</td>
<td>8.5</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>Ca(OH)2-300A</td>
<td>3.103, 100.0</td>
<td>24.8</td>
<td>0.01</td>
<td>0.19</td>
</tr>
<tr>
<td>Ca(OH)2-300A</td>
<td>2.584, 97.6</td>
<td>35.3</td>
<td>0.02</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Main properties of liquid oil products

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>N</th>
<th>TAN (mg KOH/g oil)</th>
<th>Metal, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>After reaction</td>
<td>HCl washed</td>
<td>After reaction, centrifuged</td>
<td>HCl washed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HVO Feed</td>
<td>85.44</td>
<td>10.87</td>
<td>3.42</td>
<td>0.26</td>
<td>4.116</td>
<td>13.1 (Ca) 0.0 (Mg) 0.5 (Zn) 0.1 (Ba)</td>
</tr>
<tr>
<td>CaO-300A</td>
<td>85.17</td>
<td>11.58</td>
<td>3.23</td>
<td>0.34</td>
<td>3.367</td>
<td>11.44</td>
</tr>
<tr>
<td>ZnO-300A</td>
<td>85.14</td>
<td>11.56</td>
<td>3.33</td>
<td>0.24</td>
<td>2.502</td>
<td>3.482</td>
</tr>
<tr>
<td>Ca(OH)2-300A</td>
<td>85.11</td>
<td>11.56</td>
<td>1.05</td>
<td>0.16</td>
<td>3.301</td>
<td>3.389</td>
</tr>
<tr>
<td>BaO-300A</td>
<td>85.76</td>
<td>11.48</td>
<td>1.57</td>
<td>0.18</td>
<td>0.910</td>
<td>0.459</td>
</tr>
</tbody>
</table>

Performance evaluation:

- 300 mL autoclave
- Catalysts MgO, CaO, BaO, ZnO, CaCO3, Ca(OH)2
- Feed: HVGO
- Reaction conditions:
  - Temperature: 250-300°C
  - Pressure: (H2) Atmosphere-32.8MPa
  - Oil/catalyst weight ratio: 10:1
- Time: 60 min
- Stir speed: ~600 rpm

Conclusions:

- Using CaO as catalyst, some CaO is converted to Ca(OH)2 and CaCO3, and the conversion increases with NA removal.
- No extra crystalline phases are observed using CaCO3, ZnO, and MgO.
- The BaO is completely converted to Ba(OH)2 during this reaction.
- Compared with thermal cracking (no catalyst), NA removal is considerably increased. The difference becomes more pronounced at higher temperatures. The catalysts did not enhance cracking of the oil.
- With CaO, more H2 and less CO2 are produced than without catalysts and when other catalysts (MgO, BaO, and ZnO) are used. High pressures impede hydrogen production and oil cracking. With MgO and ZnO, NA removal proceeds mainly via catalytic decarboxylation, and no crystalline phase changes occurred after reaction.
- With CaO, multiple pathways (catalytic decarboxylation, neutralization, and thermal cracking) are responsible for the NA conversion. Ca(OH)2 an CaCO3 were identified in spent catalysts.
- With BaO, NA conversion occurs mainly through neutralization. All Ba is converted to Ba(OH)2 during the reaction.
Fouling Mechanisms of Bitumen Containing Unsaturated Hydrocarbons

1Z. Fan, 1P. Rahimi, 1T. Alem and 2A. Eisenhaver
1NCUT, CarmentENERGY, Natural Resources Canada, Devon, AB, Canada
2Nalco Canada Company, Fort McMurray, AB, Canada

Background
- Cracked naphtha as a solvent in the froth treatment process, the resulting bitumen contains olefins and di-olefins, which cause fouling in different processing units:
  - Condensed deposits: locations of high temperatures;
  - Gums: areas of lower temperatures;
  - Mixture of the above deposits in preheat exchangers;
  - For hydrocracker beds, mostly polymers formed from oxygen exposure in intermediate tankage
- Fouling mechanisms are complex, and may be different at different environments.

Fouling Rates of CGO at Different Surface Temperatures
- At low temperature (<250°C), fouling rate caused by chemical reactions is very low.
- At the temperature ca. ~300°C, the polymerization of olefins and di-olefins lead to an observed high fouling rates.
- At the temperature ca. ~400°C, the bonds formed by polymerization of olefins and di-olefins could be broken faster than they are formed, and caused an observed lower fouling rate.

Concluding Remarks
- The bench scale fouling tests indicate that fouling rates of CGO followed a bimodal distribution as a function of temp. As the surface temp. increased up to 300°C, the fouling rate increased. Further increase of temp. resulted in a decline of the fouling rate, and then an increase again at temp. above 400°C. The phenomena are consistent with the industrial observations, i.e., different kinds of deposits were noticed at different temperature location.
- At the temp. of 270°C, the highest degree values of CGO decline, but viscosity, molecular weight, density increase with the times. These suggest that polymerization of unsaturated hydrocarbons in CGO was taking place, and led to the formation of fouling precursors.

Objectives
- Investigate the fouling mechanisms of CGO by using a bench scale hot liquid process simulator (HLPS) Alcor units, and autoclave treatment.
- Mitigate the fouling problems for the bitumen crudes containing olefins and di-olefins.

Autoclave treatment
- CGO was treated at the temperature of 270°C, under either inert atmosphere up to over 20 days.
- Analyze olefin and diolefin contents (bromine and diene value, respectively), viscosity, molecular weight, density, at different reaction times.

Concluding Remarks
- Based on the fouling rate observation, either minimize the residence time or the concentration of conjugated olefins in the temperature range of greatest polymerization rate could mitigate the fouling problems, but increase the operation temperature above the range of the greatest fouling rate also could mitigate the fouling problems caused by polymerization of olefins and diolefins. This concept was verified in the industrial practice by韦克(2003).
- More detailed fouling mechanisms of CGO still need further investigations, and large scale lab or commercial tests are encouraged.

Experimental Apparatus
- Alcor hot liquid process simulator
- Pressure: 300-900psi
- Tube diameter: ~0.3 cm
- Flow rate: ~1 ml/min

CGO properties change with the time at 270°C
- Br value changes with the time;
- Diene value changes with the time;
- Viscosity changes with the time;
- Molecular weight changes with the time

On-Going Work
- CGO treated under other temperatures (i.e., 350 and 400°C) is on-going.
- A fiber fouling probe is under design and to be put into autoclave to test the fouling at different surface temperatures.
- Different fouling depositions are going to be collected at different surface temperature and characterized with GCMS, TGA, ATR-IR, element analysis, etc.
- More detailed CGO fouling mechanisms will be provided.
The effect of the composition of hydrocarbon streams on physical properties and HCCI combustion performance

Rafael Gieleciej 1, Craig Fairbridge 2, Darcy Hager 2, Bruce Bunting 2, Thomas Gallant 4 and Ken Mitchell 5

1National Centre for Upgrading Technology, 2CanmetENERGY Natural Resources Canada, 3Oak Ridge National Laboratory, 4Pacific Northwest National Laboratory, 5Shell Canada Limited

**Introduction**

New engine combustion technologies such as Homogeneous Charge Compression Ignition (HCCI) are receiving considerable attention for their ability to significantly reduce nitrogen oxides emissions. Since it is not obvious which fuel chemical or physical properties are responsible for processes occurring during advanced combustion, we describe an **Q(2d)RPR approach** which looks at the sample as a whole. This method can predict physicochemical and combustion properties of hydrocarbon streams directly from GCxGC (Comprehensive Two-Dimensional Gas Chromatography) chromatograms. Seventeen samples used in our experiments were all derived from Canadian oil sands crude and represent a variety of processing options and blending.

The GCxGC maps describe the composition of tested samples, and were treated as compositional descriptors of such fuels. The enormous amount of data generated in this way could not be easily processed by classical statistical methods. We used PLS (Partial Least Squares) calibration method to correlate GCxGC chromatograms with chemical/physical (i.e. cetane number, density, viscosity) or engine properties taken from combustion experiments. The results show that models are robust and statistically reliable. The investigation of the coefficients calculated by the PLS procedure gives information which confirms how different regions of the chromatogram contribute, positively and negatively, to the value of the properties responsible for selected HCCI fuel properties.

**Methodology**

**GCxGC**: Comprehensive two-dimensional gas chromatography is a hyphenated technique in which two different chromatographic separation mechanisms are in series and greatly improves the result of component separation and identification. The system contains a jet-cool modulator between the two chromatographic columns with different selectivity, and all the effluents out of the second column enter the detector.

**HCCI**: Homogeneous Charge Compression Ignition is a form of internal combustion in which homogenous fuel and air mixture is compressed to the point of auto-ignition. Ignition occurs in many places simultaneously. A major advantage of HCCI combustion is its fuel-flexibility, fuels economy, low levels of NOx emissions and particulate matter (PM).

**PLS**: Partial Least Squares is a generalization of multiple linear regression (MLR) but unlike MLR, it can analyze data with strong collinear (correlated), noisy, and numerous X-variables and model the relationship between X and Y.

The linear PLS model finds new variables, a latent variables (X-scores). These scores are linear combination of the original variables and they have following properties: they are good predictors of Y, they are few in number and they are orthogonal.

**Samples characteristics**

- 17 samples (100%) derived from Canadian oil sands crude
- Half of the streams upgraded by coking and half by hydrotreating
- All streams are nominated of diesel boiling point range
- All hydro sulfur levels below 15 ppm (except one)
- All have middle chemistry

**Physicochemical and Engine Properties**

- Cetane number, n-paraffins, iso-paraffins, mono-cycloparaffins, poly-cycloparaffins, mono-iso-paraffins, poly-iso-paraffins, Olefins, 70-150, 30, density, viscosity, carbon, hydrogen
- Smoke (PC ppm), CO (ppm), NOx (ppm), COV (IL), MF50, CAD-90, eMHC, NL, TR, GPC, etc

**Quantitative Two-Dimensional Retention Property Relationship (Q(2d)RPR)**

**Results**

**Conclusion**

- **2D-3C** is an emerging analytical technique which separates compounds in fuels. This allows analysis by identifying individual compounds, grouping compounds by chemistry and boiling points and performing statistical analysis by testing the chromatograms as compositional descriptors of fuels
- **Q(2d)RPR technique allows correlations to be developed between the 2D-GC data and fuel chemical / physical properties and engine performance data (quantitative 2D retention property relationship)**

Reasons of chromatograms were shown to correlate, positively and negatively, to the values of fuel properties (cetane number, viscosity) and to HCCI research engine performance (MF50, %TRHR)

This technique provided good correlations for some properties indicating that it is worthy of further study.
Influence of Substituents on Ring-opening Energetics

Iain D. Mackie† and Jagannathan Govindha kanna†
†National Institute for Nanotechnology, National Research Council Canada, Edmonton, AB. ‡NCUT, CanmetENERGY, Natural Resources Canada, Devon, AB.

Abstract

The effect of an electron donating or withdrawing group (EDG or EWD) on the gas-phase ring contraction mechanism of a cyclohexane-derived cation has been studied using density functional theory.

The barrier to rearrangement of the parent cyclohexane cation (1) was previously calculated to be 7.7 kcal/mol which is in excellent agreement to experiment (7.4 ± 1 kcal/mol).

We find in this work that addition of an EWG (CH₃) 2 raises the average barrier to contraction, relative to the parent, while an EDG (CF₃) 3 lowers the average barrier.

Calculated barrier heights range from 4.3 – 23.3 kcal/mol for 2 and 0.8 – 14.0 kcal/mol for 3.

Key points

- Ring contraction barriers for 2 are significantly larger than those for 1 and 3.
- Why? For 2, most likely reactions start from a tertiary carbonation with final product formed via secondary intermediates. However, for 1 and 3, the reaction starts with a secondary cation and heads downhill in energy to a tertiary product.
- Ring contraction barrier for 3 lower than for 1.
- Why? The presence of delocalizing interactions from the CF₃ group, carry over stabilize intermediates and transition states. For example, in 3 there is a favorable interaction of 0.78 kcal/mol from NBO analysis between CF₃ lone-pair and carbon charge center. Similar interactions are evident in many other CF₃-intermediates.

Parent cation contraction

We found that B3LYP/3-21G+Gd(2p) is capable of replicating the expensive, high-level QCISD(T) structures, energies and kinetics.

CF₃ substituent

Relative energies (kcal/mol)

0.0  0.0  0.0  0.0  0.0
-2.2 -2.2 -2.2 -2.2 -2.2
+1.7 +1.7 +1.7 +1.7 +1.7
+6.1 +6.1 +6.1 +6.1 +6.1
+11.3 +11.3 +11.3 +11.3 +11.3
+14.6 +14.6 +14.6 +14.6 +14.6
+16.0 +16.0 +16.0 +16.0 +16.0
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Acknowledgements

We thank the Program of Energy Research & Development for funding, and the Centre for Integrated Nanoscale (CEN) at the University of Alberta and WestGrid for computing resources.
Delayed Coking Studies on Athabasca Bitumen and Cold Lake Heavy Oil

Jagannathan Govindhakannan and Chandra Khupe
NCUT, CanmetENERGY, Natural Resources Canada

Objectives
- Quantify delayed coking product yields
- Investigate the effect of operating pressure and feed rates on product yield and quality
- Investigate the effect of pressure on conversion of sulfur and nitrogen

Feedstock Properties
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<th>Athabasca Bitumen</th>
<th>Cold Lake Heavy Oil</th>
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<tr>
<td>Hydrogen</td>
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<td>Sulfur</td>
<td>%</td>
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<tr>
<td>Nitrogen</td>
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<tr>
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<tr>
<td>Naphtha (IBP-177°C)</td>
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<td>Gas Oil (260-316°C)</td>
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| Coke Properties – Athabasca Bitumen
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<tr>
<td>Sulfur</td>
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<tr>
<td>Nitrogen</td>
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Conclusions
- Experimental results indicate that the yield of liquid products decreases and the yields of coke and gases increase as the operating pressure increases.
- Sulfur and nitrogen conversions increase with increasing pressure.
- The yield and quality of delayed coking products were not affected by the variation in feed rates within the range studied.
- The observed trend supports the general observation that feed rate changes do not significantly affect the yield and quality of delayed coking products because the residual liquid and coke trapped in the coker drum result for a duration that approaches infinity as compared to the residence time of the feedstock in the coker.
OPTIMIZATION BITUMEN – BASED UPGRADING AND REFINING SCHEMES

Muçurel Munteanu, Jinwen Chen
National Centre for Upgrading Technology, CanmetENERGY, Devon, Alberta

Project Objectives
- Model and simulate the whole refining scheme with Canadian bitumen as feedstock under different process configurations, operation conditions and product structures.
- Optimize the economic benefit, product quality and energy consumption under different configurational and operational scenarios.
- Propose optimal refining schemes and process conditions/options according to different existing refinery configurations and objectives.
- Provide guidelines and quantitative information for upgrading and refining process design and retrofitting.
- Identify the critical steps in upgrading process and provide debottlenecking solution recommendations.

Benefits
Exploitation of the results generated from the simulations would lead to significant improvement in process performance and operations and in reducing the capital cost for building new upgraders and refineries. The simulations results will also provide valuable information for increasing the bitumen marketability, reducing GHG emissions and other related environmental impacts from the bitumen upgrading and refining industry.

Hysys Simulator
SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL MESOPOROUS MATERIALS AND THEIR APPLICATIONS FOR OIL SANDS
Sateesh Mutyala, Parviz Rahimi, Craig Fairbridge and Teclemariam Alem
National Centre for Upgrading Technology, CanmetENERGY, Devon, AB, Canada

ABSTRACT
- The synthesis and characterization of functional hybrid mesoporous materials are described. These materials were characterized by SEM/TEM and FT-IR.
- Thiol modified mesoporous materials displayed higher activity for adsorption of metals (i.e., Pd).
- Alkyl or aryl sulfonic acid-functionalized mesoporous silicas were synthesized in one step approach with in situ oxidation of thiol groups to the sulfonic acid groups.
- The resulting solid acid materials were tested for their catalytic performance in the esterification of naphthenic acids model compounds (i.e., Cyclohexane carboxylic acids) with methanol to produce corresponding methyl esters.

Preparation of functional mesoporous SBA-15

Synthesis of functionalized mesoporous silicates

Methylation of NAs – Conventional methods

Esterification catalysts

CONCLUSIONS
- Synthesized functional mesoporous materials
- Functional materials displayed higher activity for adsorption of heavy metals
- Identified well dispersed palladium nanoparticles in mesoporous materials
- Obtained high product yields for Naphthenic acids model compounds and isolated NAs by sulfonicacid functionalized catalyst.
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**List of Participants – by Company**
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ACKNOWLEDGEMENTS

The organizing committee of the 5th NCUT Upgrading and Refining Conference 2009 would like to thank the following staff for their exceptional efforts and contributions:

Administrative Assistance:   KJ Meharg
                              Chantal Roy
                              Deanna Lizotte

Graphics:                   Erick Barba
                              Stephen Kieser

IT Support:                 Scott McIntyre
                              Alfred Mo

The committee also would like to thank the management of the CanmetENERGY at the Devon Research Centre for their support and contributions during conference preparations throughout the last year.