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 hydroprocessing reactors, catalyst and catalytic process development, kinetics and vapor-liquid phase equilibrium studies of hydroprocessing. Before joining NCUT, Dr. Chen worked on fluid hydrodynamics, 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.

National Centre for Upgrading Technology (NCUT)
1 Oil Patch Drive
Devon, AlbertaT9G 1A8 Canada
Phone: 780 987 8763
Fax: 780 987 5349
Email: Jinwen.Chen@nrcan.gc.ca
Website: http://canmetenergy-canmetenergie.nrcan-rncan.gc.ca

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 hydrotreates 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.

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

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

Natural Resources Canada   Ressources naturelles Canada

AERI
Alberta Energy Research Institute

ALBERTA RESEARCH COUNCIL

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
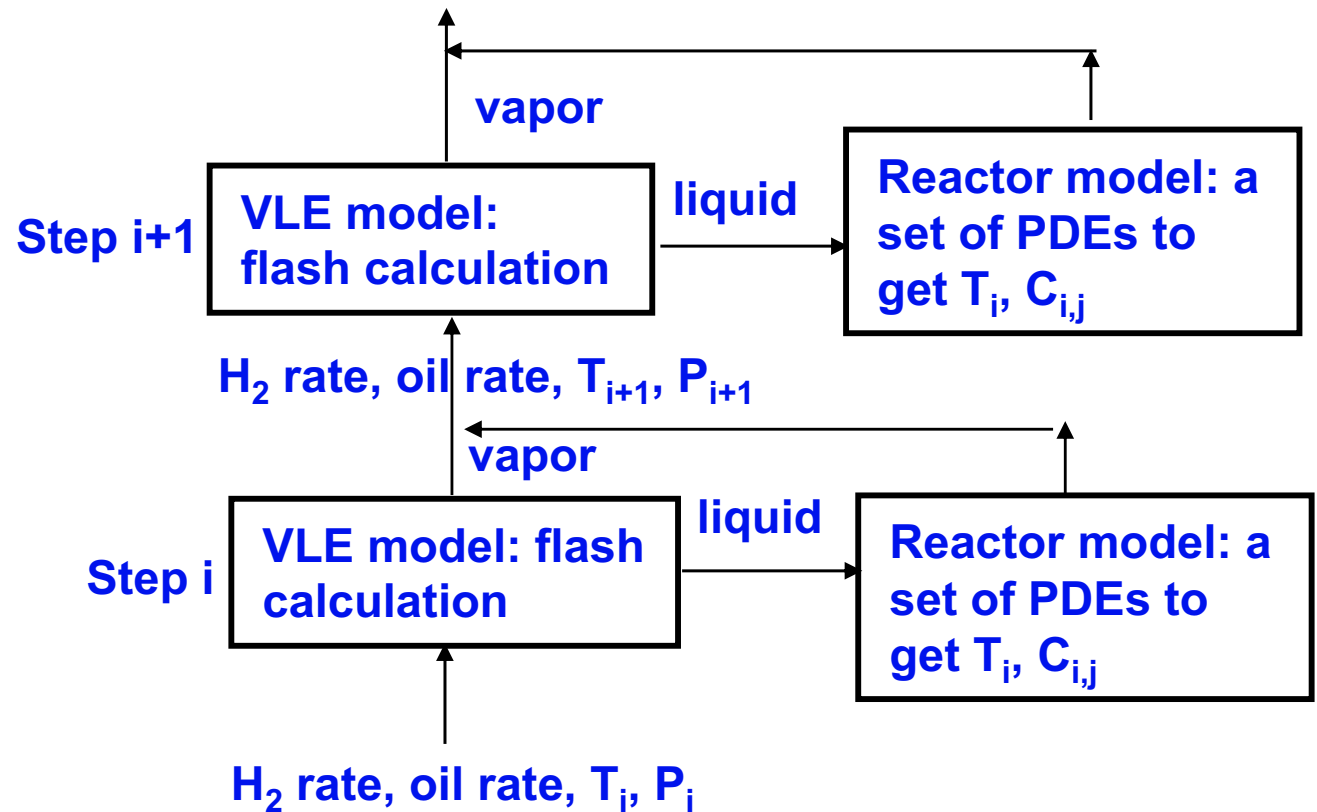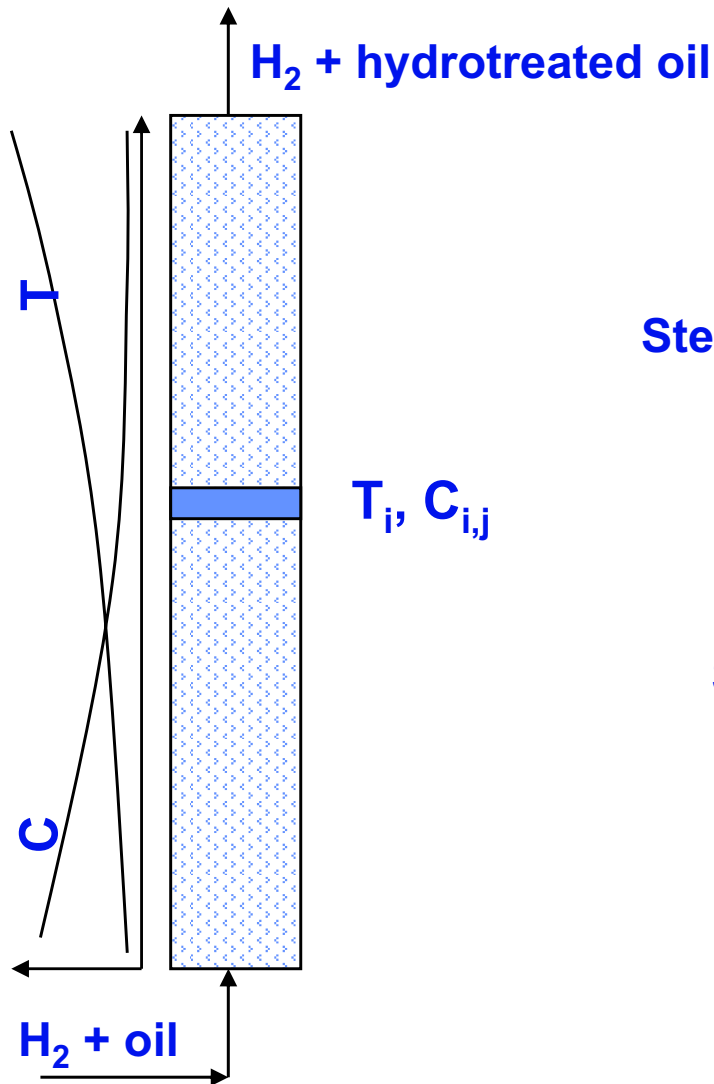
VLE Modeling via EOS

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

$$b = \frac{\Omega_b RT_c}{P_c} \qquad a(T) = \frac{\Omega_a R^2 T_c^2}{P_c} \alpha(T)$$

Mixture

$$b = \sum_{i=1}^{N} y_i b_i$$

$$a = \sum_{i=1}^{N}\sum_{i=1}^{N} y_i y_j a_{ij} \qquad a_{ij} = (a_{ii} a_{jj})^{1/2}(1 - d_{ij})$$

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)

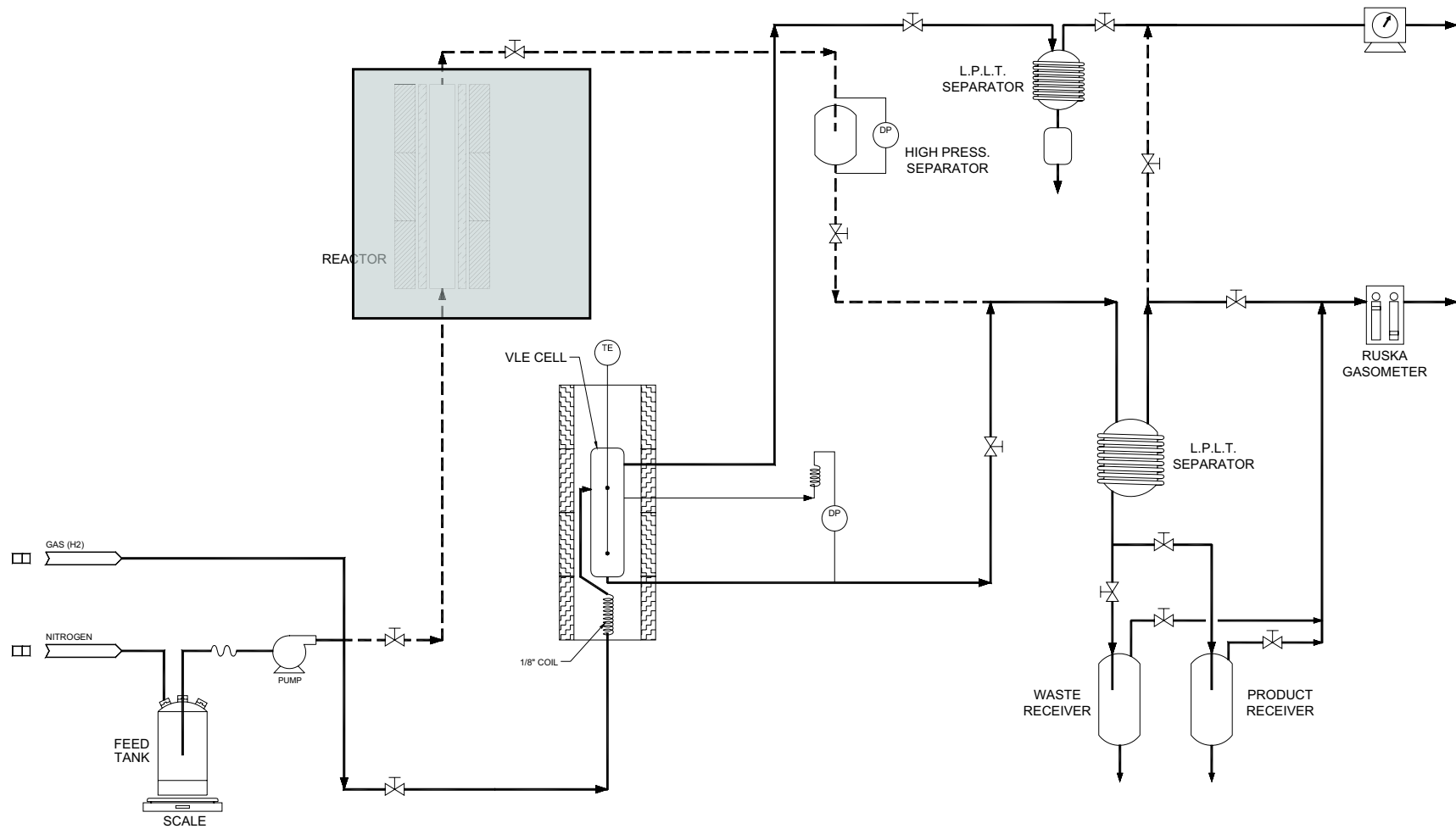   Temperature: 350 – 430°C

   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

	Middle Distillates			Heavy Distillates	
	Feed 1 (LCO)	Feed 2 (white oil)	Feed 3 (LCO + white oil 50-50)	Feed 1 (heavy gas oil)	Feed 2 (heavy gas oil)
Density (15.6°C), g/mL (ASTM D4052)	0.9360	0.8152	0.8714	0.9609	0.8709
Saturates (wt%)	15.9	98.9	61.0	30.9	69.7
Aromatics (wt%)	83.9	1.1	39.0	61.2	26.1
Polars (wt%)	0.2			7.9	4.2
SimDis, °C (ASTM D2887)					
IBP	128.4	210.5	148.0	201.8	180.2
10wt%	225.0	237.5	233.0	292.6	253.4
30wt%	255.3	256.5	255.0	350.2	324.8
50wt%	288.5	272.5	277.0	386.4	391.2
70wt%	326.4	312.5	318.5	445.4	441.4
90wt%	373.9	395.0	381.0	529.6	505.4
FBP	430.8	490.0	483.5	702.6	589.8

Experimental Observations

Middle Distillates — chart: Wt% Oil in Vapor vs Temperature, °C; P = 70 bar; Feed 1, Feed 2, Feed 3

Heavy Distillates — chart: Wt% Oil in Vapor vs Temperature (°C); P = 90 bar; Feed 1, Feed 2
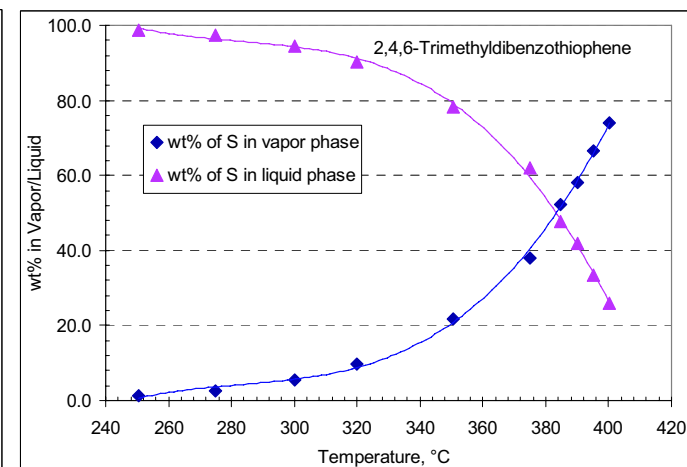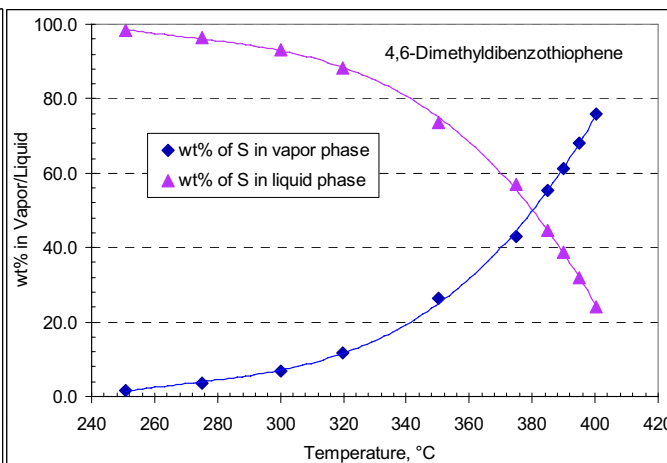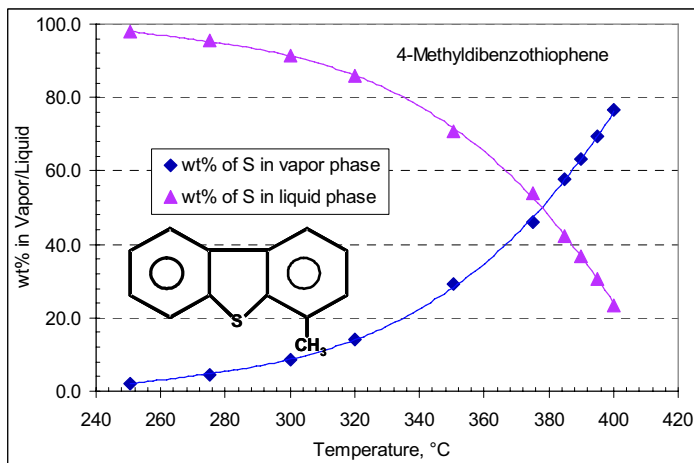
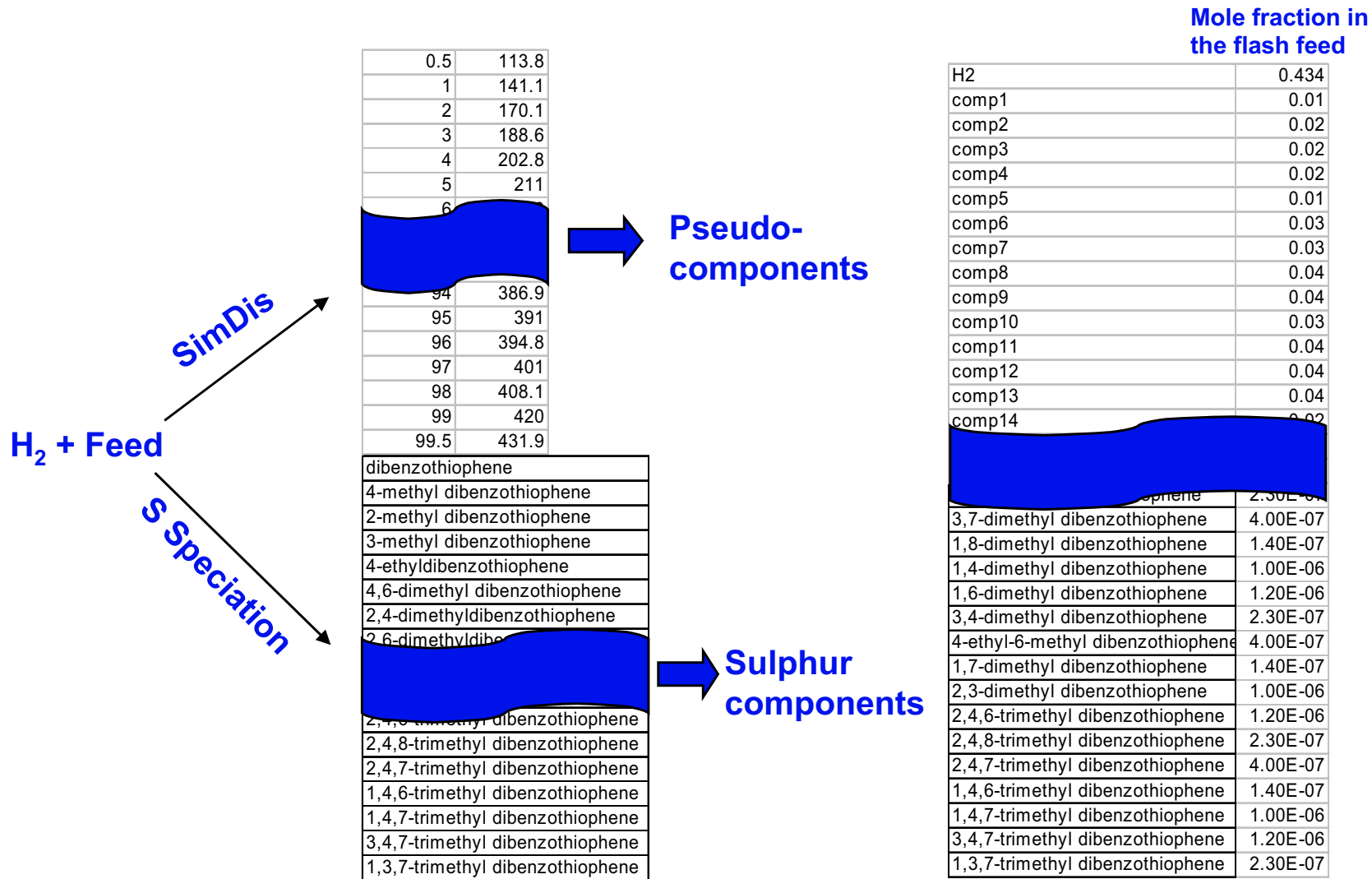# Experimental Observations

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
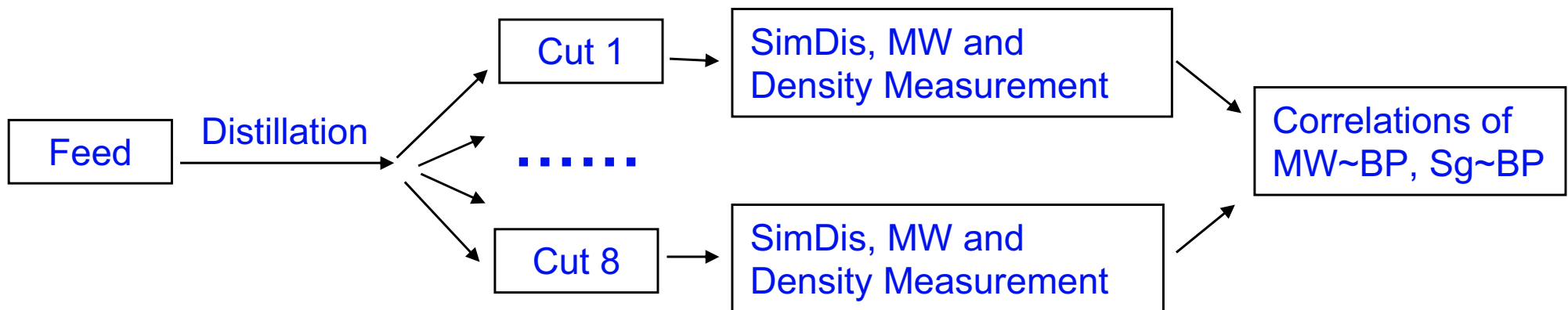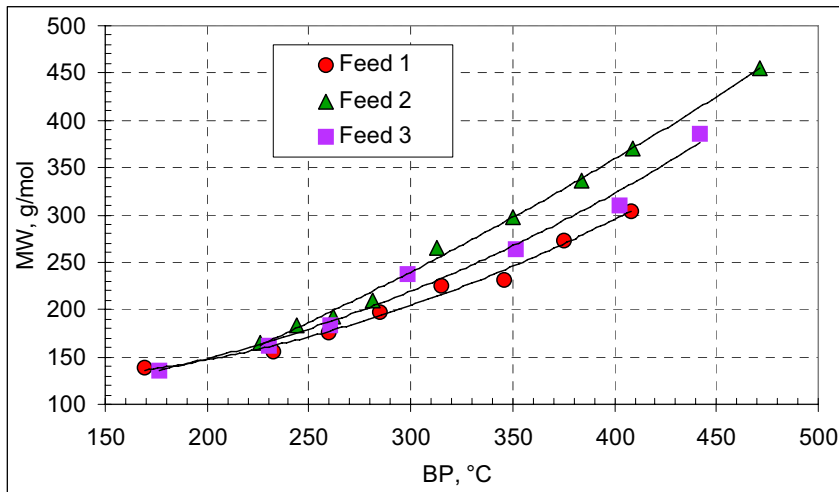
Fitting Experimental Data with Flash Model

H₂ + Feed

SimDis

S Speciation

0.5	113.8
1	141.1
2	170.1
3	188.6
4	202.8
5	211
6	
94	386.9
95	391
96	394.8
97	401
98	408.1
99	420
99.5	431.9

➡ **Pseudo-components**

dibenzothiophene
4-methyl dibenzothiophene
2-methyl dibenzothiophene
3-methyl dibenzothiophene
4-ethyldibenzothiophene
4,6-dimethyl dibenzothiophene
2,4-dimethyldibenzothiophene
2,6-dimethyldibenzothiophene
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

➡ **Sulphur components**

Mole fraction in the flash feed

H2	0.434
comp1	0.01
comp2	0.02
comp3	0.02
comp4	0.02
comp5	0.01
comp6	0.03
comp7	0.03
comp8	0.04
comp9	0.04
comp10	0.03
comp11	0.04
comp12	0.04
comp13	0.04
comp14	0.02

...phene	2.30E-07
3,7-dimethyl dibenzothiophene	4.00E-07
1,8-dimethyl dibenzothiophene	1.40E-07
1,4-dimethyl dibenzothiophene	1.00E-06
1,6-dimethyl dibenzothiophene	1.20E-06
3,4-dimethyl dibenzothiophene	2.30E-07
4-ethyl-6-methyl dibenzothiophene	4.00E-07
1,7-dimethyl dibenzothiophene	1.40E-07
2,3-dimethyl dibenzothiophene	1.00E-06
2,4,6-trimethyl dibenzothiophene	1.20E-06
2,4,8-trimethyl dibenzothiophene	2.30E-07
2,4,7-trimethyl dibenzothiophene	4.00E-07
1,4,6-trimethyl dibenzothiophene	1.40E-07
1,4,7-trimethyl dibenzothiophene	1.00E-06
3,4,7-trimethyl dibenzothiophene	1.20E-06
1,3,7-trimethyl dibenzothiophene	2.30E-07

Physical Properties of Components

Minimum information required for flash calculation: density, molecular weight, boiling point of each component.
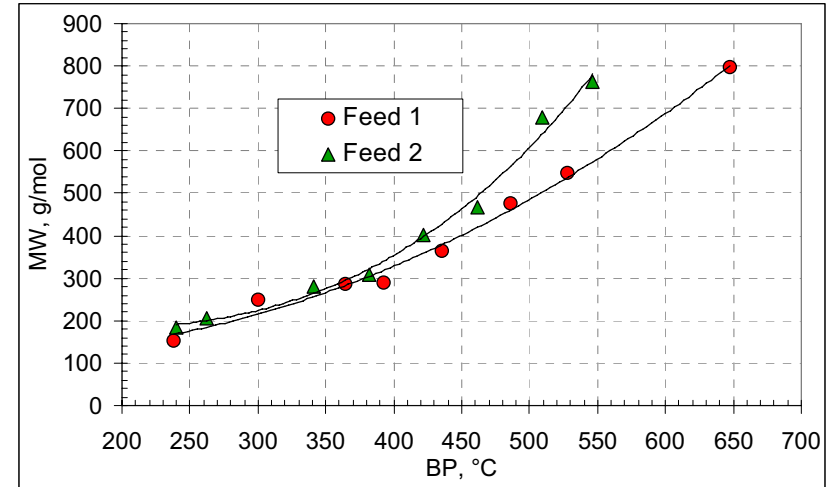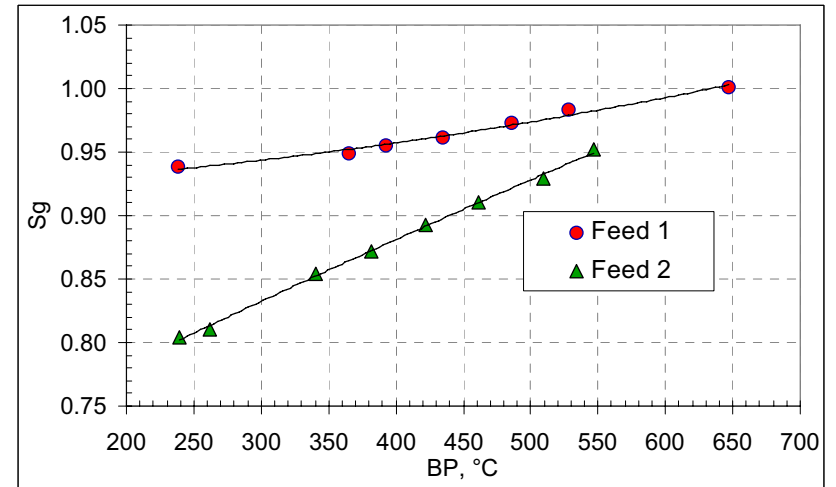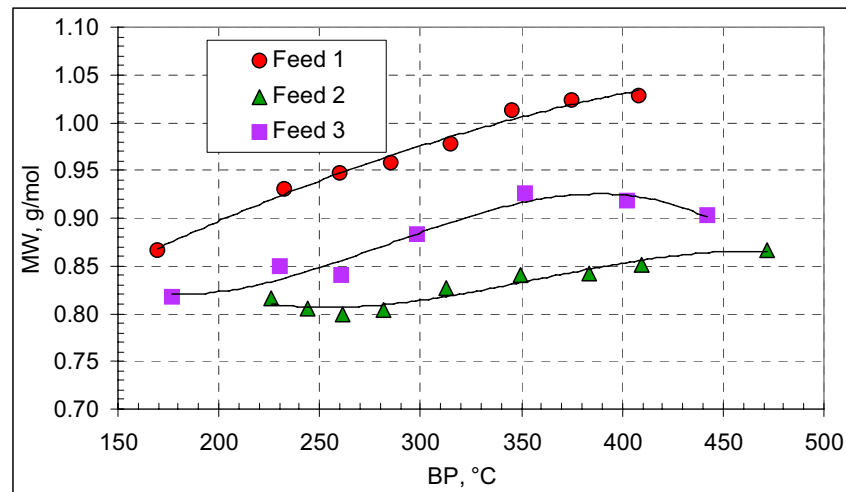
Pseudo-component:

```
Feed --Distillation--> Cut 1 --> [SimDis, MW and Density Measurement] --> [Correlations of MW~BP, Sg~BP]
              ......
          --> Cut 8 --> [SimDis, MW and Density Measurement] -->
```

Pseudo Components – MW & Density

Middle Distillates

MW correlation with boiling point (BP)

Heavy Distillates

Sg correlation with boiling point (BP)

Estimation of Interaction Coefficients
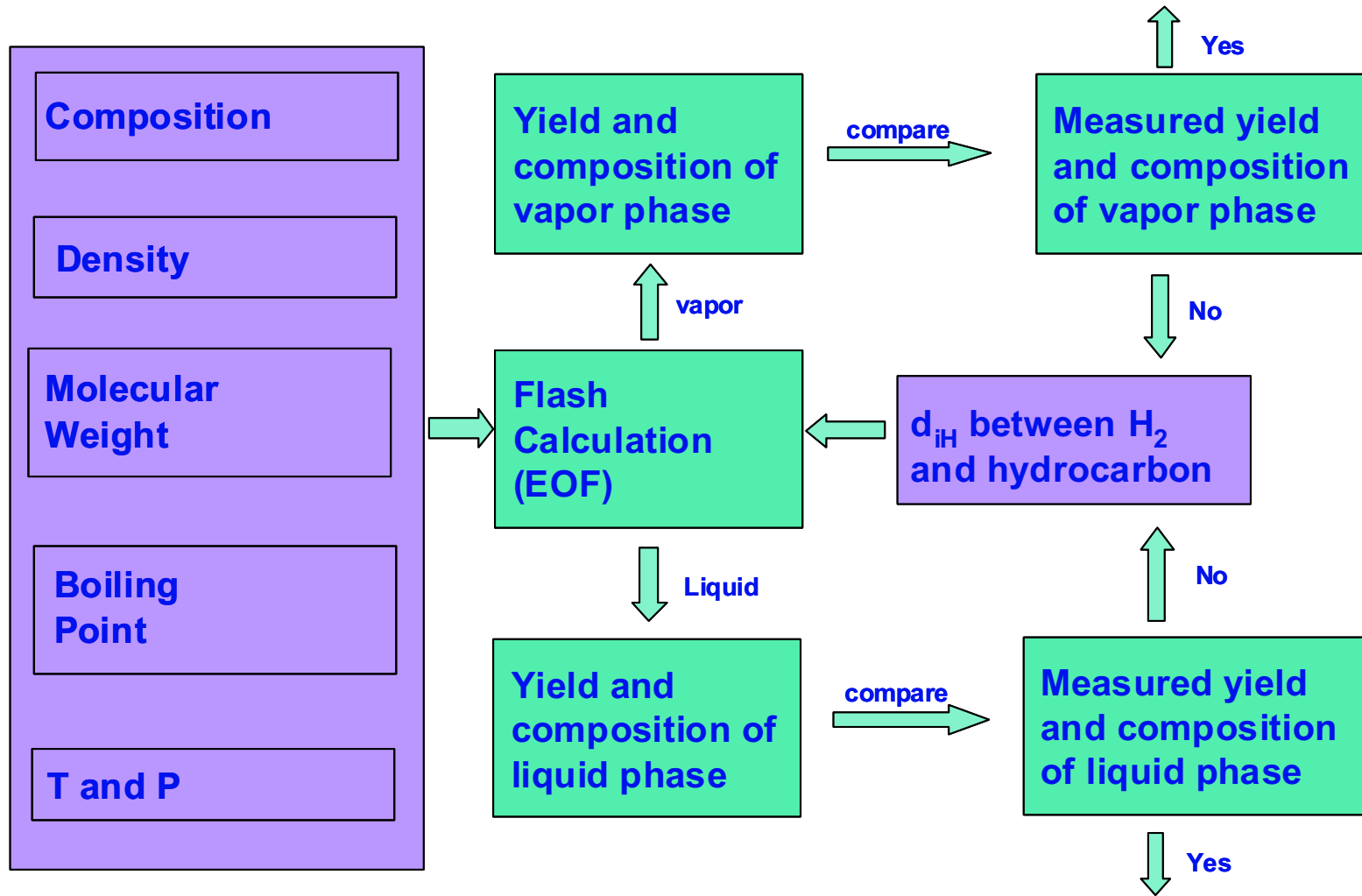
d_{iH} is obtained for each H_2- hydrocarbon pair and correlated with hydrocarbon properties

Results - Interaction Coefficients

Assume $d_{iH} = a + b*Bp_i$, Bp_i is the boiling point (**in °C**) of pseudo-component i

Middle distillates

	a	b
Feed 1	0.1865	0.00388
Feed 2	0.386	0.00226
Feed 3	0.285	0.00302

Heavy distillates

	a	b
Feed 1	0.5712	0.004713
Feed 2	0.2977	0.002956

a and b are further correlated to aromatics content in the feed:

Middle distillates

$$a = 0.3852 - 0.00241 \times C_{Aromatics\%}$$

$$b = 0.002245 + 1.96 \times 10^{-5} \times C_{Aromatics\%}$$

Heavy distillates

$$a = 0.0943 + 0.009779 \times C_{Aromatics\%}$$

$$b = 0.00165 + 5.01.96 \times 10^{-5} \times C_{Aromatic\%}$$

Flash Calculation vs. Experimental Data
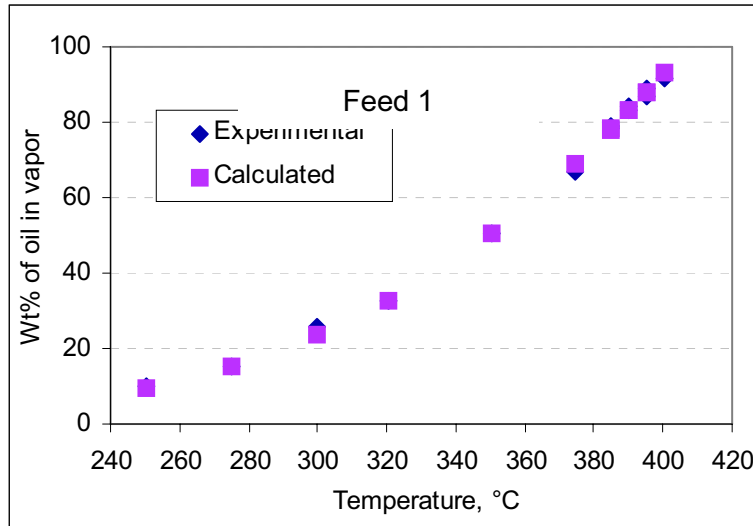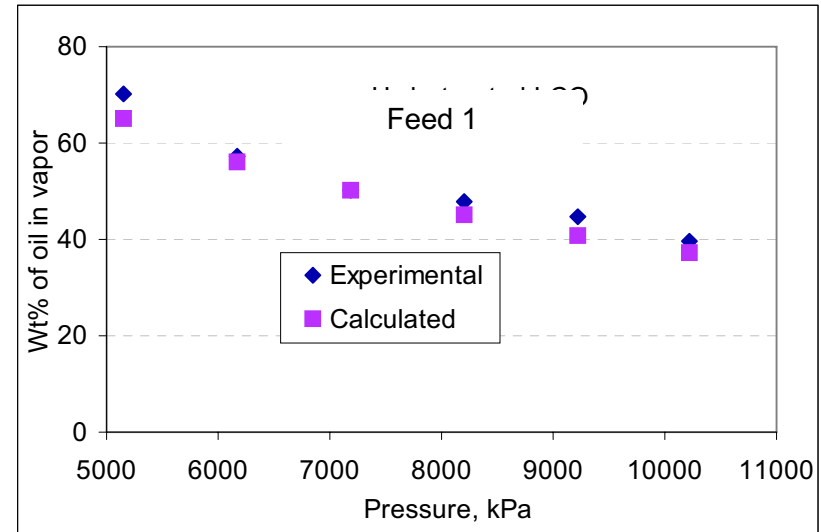
Middle distillates

Wt% of oil in vapor with T

Wt% of oil in vapor with P
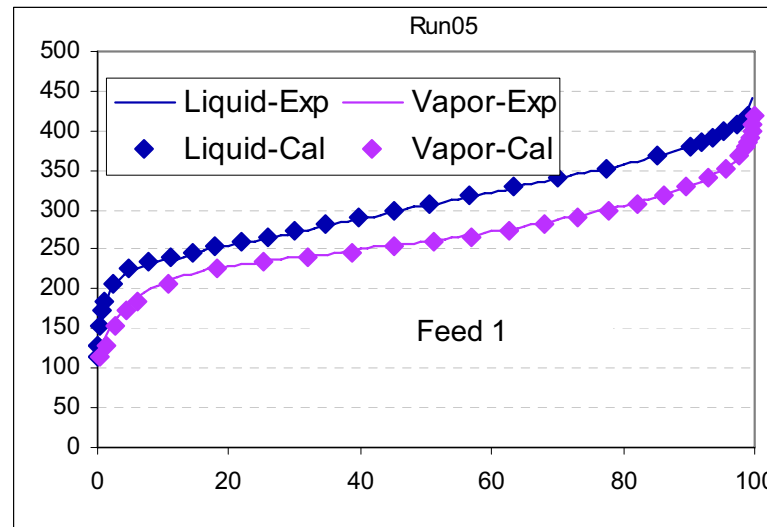
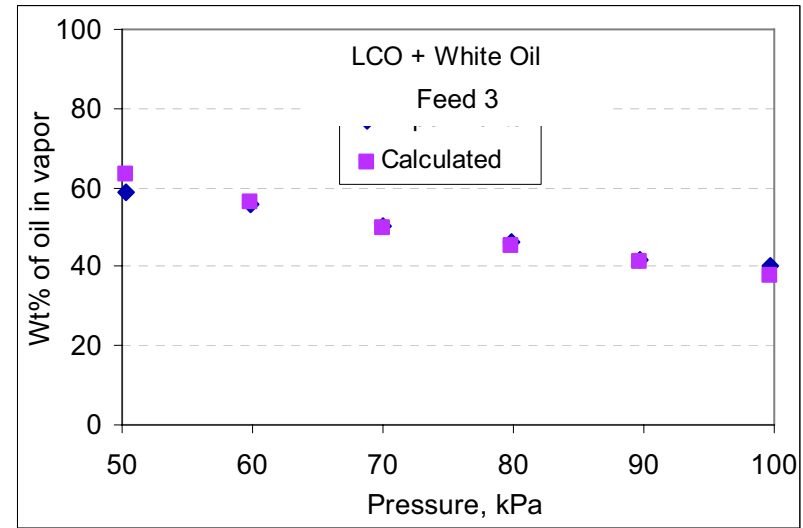**SimDis of vapor and liquid**
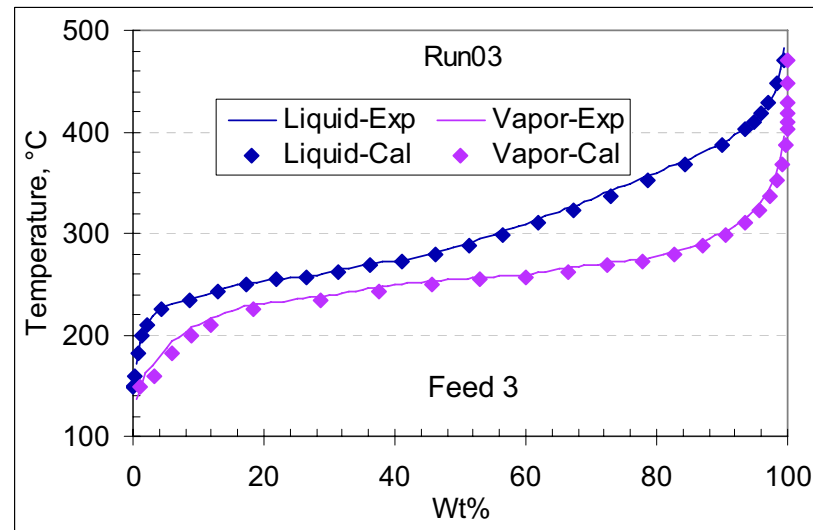
Flash Calculation vs. Experimental Data

Middle distillates
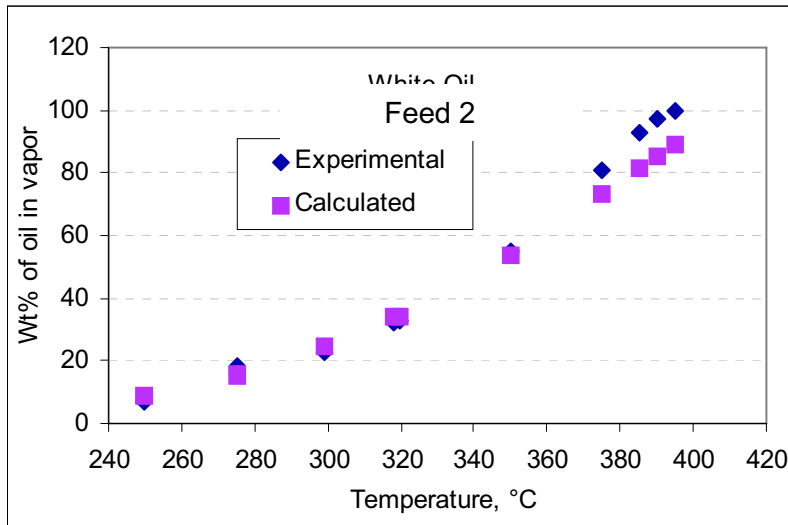
Wt% of oil in vapor with T
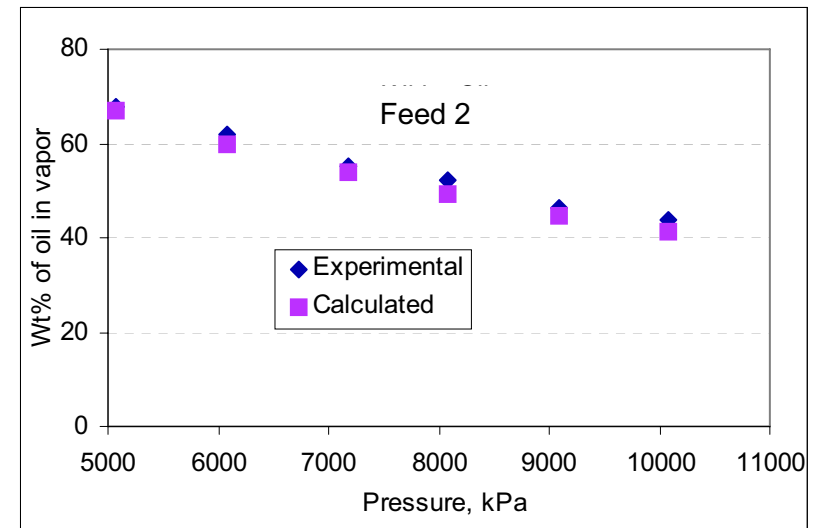
Wt% of oil in vapor with P
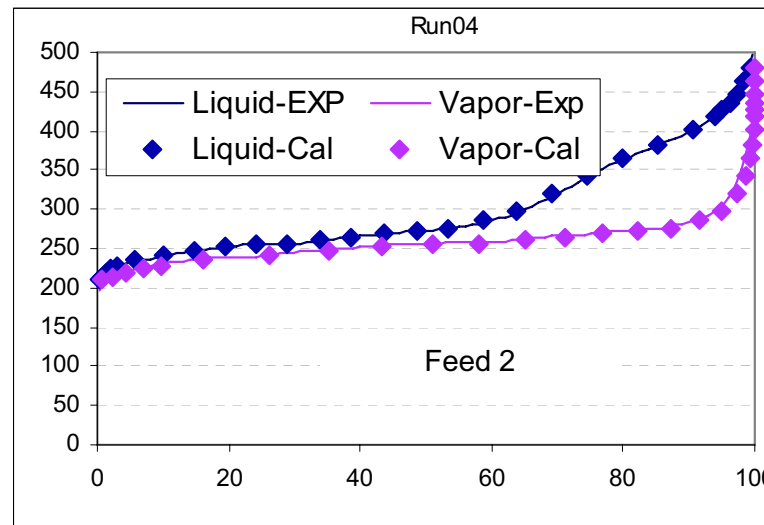
SimDis of vapor and liquid
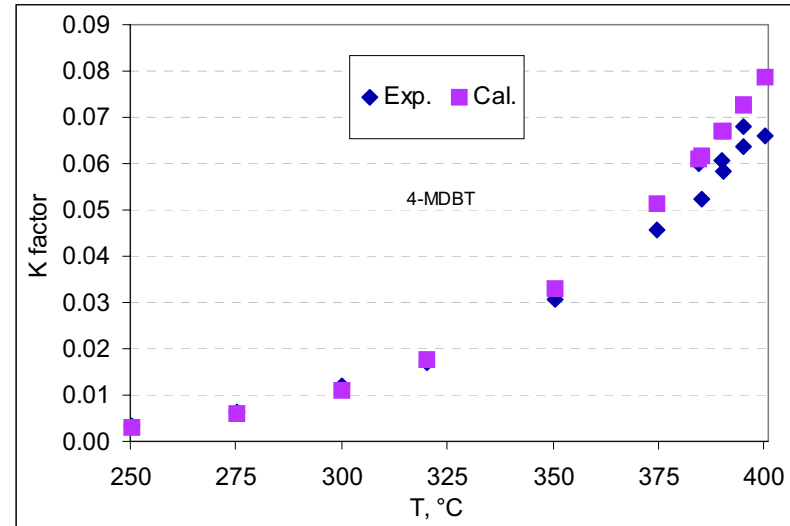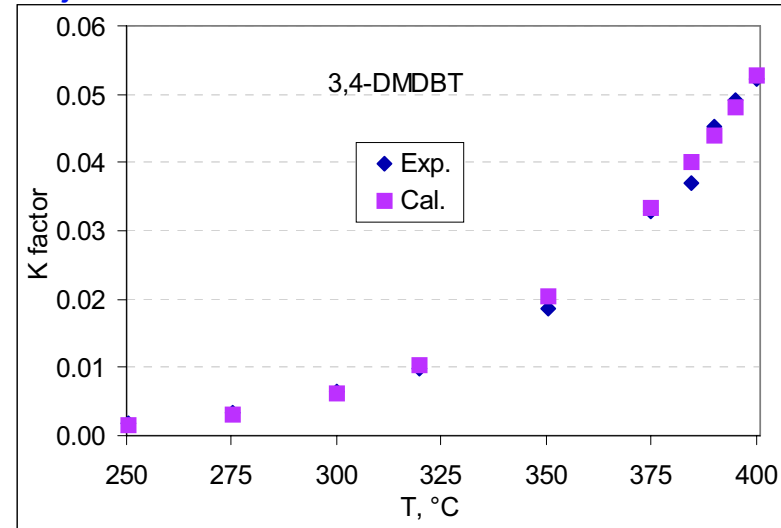
Flash Calculation vs. Experimental Data

Middle distillates
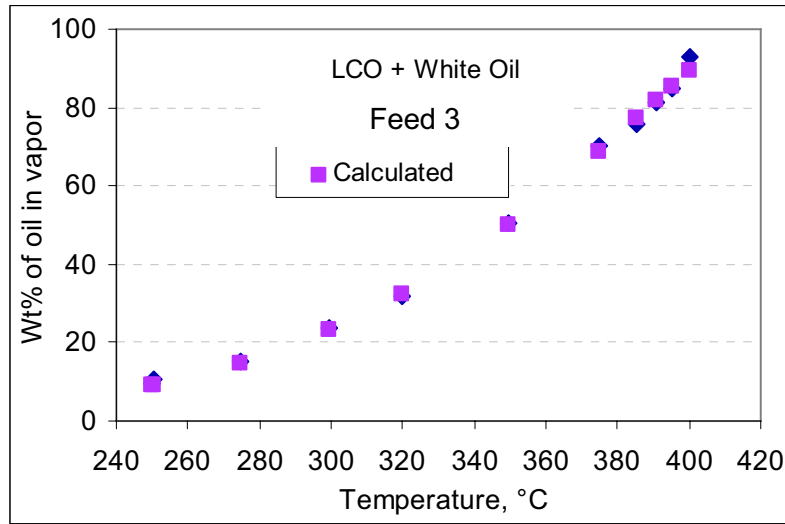
Wt% of oil in vapor with T

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

	MW	BP, °C
DBT	184.26	332.5
4-MDBT	198.28	321.26
2-MDBT	198.28	327.3
3-MDBT	198.28	328.4
4-EDBT	212.32	335.4
4,6-DMDBT	212.32	366
2,4-DMDBT	212.32	336.2
2,6-DMDBT	212.32	337.2
3,6-DMDBT	212.32	338.1
2-EDBT	212.32	337.8
2,8-DMDBT	212.32	339.2
2,7-DMDBT	212.32	340.1
3,7-DMDBT	212.32	340.7
1,8-DMDBT	212.32	341.7
1,4-DMDBT	212.32	342.1
1,6-DMDBT	212.32	342.5
3,4-DMDBT	212.32	343.8
4-E-6-MDBT	226.36	344.5
1,7-DMDBT	212.32	345
2,3-DMDBT	212.32	345.8
2,4,6-TMDBT	226.36	346.6
2,4,8-TMDBT	226.36	348
2,4,7-TMDBT	226.36	349.1
1,4,6-TMDBT	226.36	353.3
1,4,7-TMDBT	226.36	353.9
3,4,7-TMDBT	226.36	356.1
1,3,7-TMDBT	226.36	356.2

Flash Calculation vs. Experimental Data
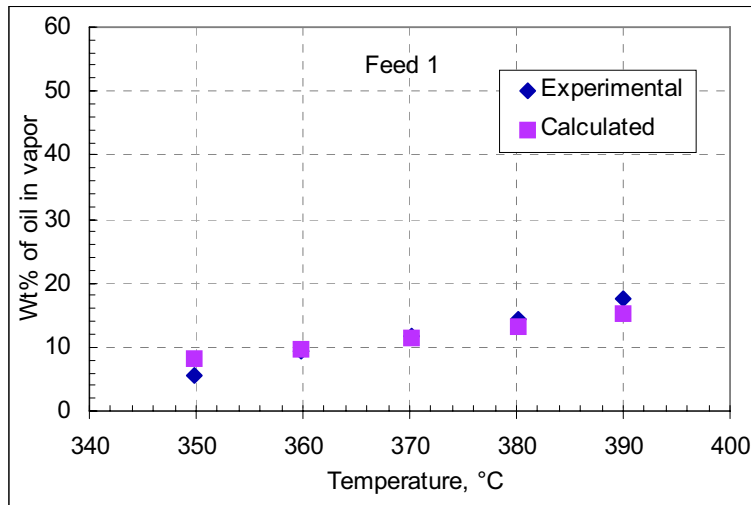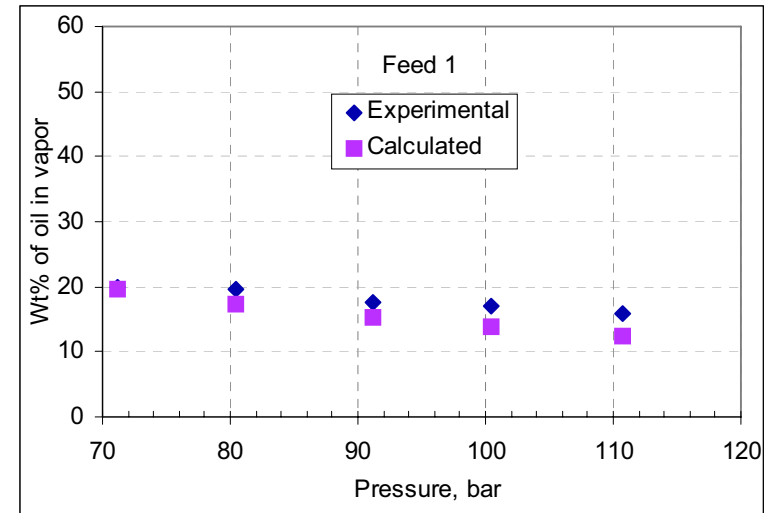
Heavy distillates

Wt% of oil in vapor with T

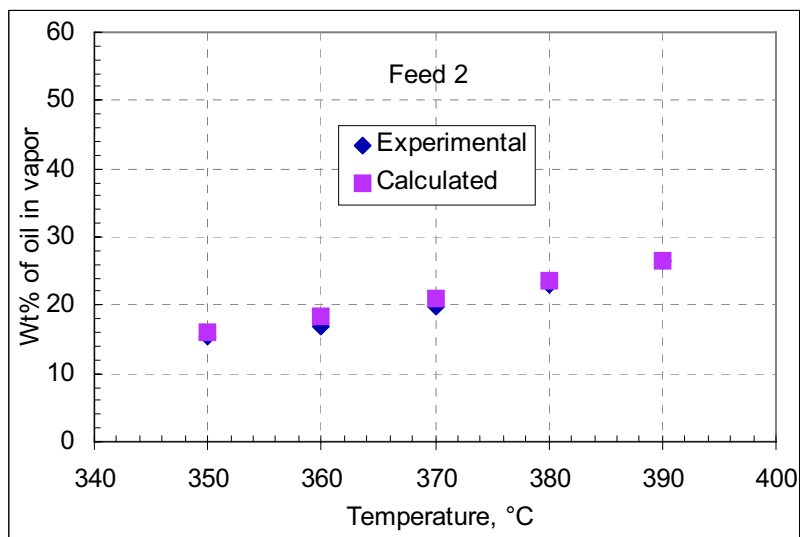**Wt% of oil in vapor with P**
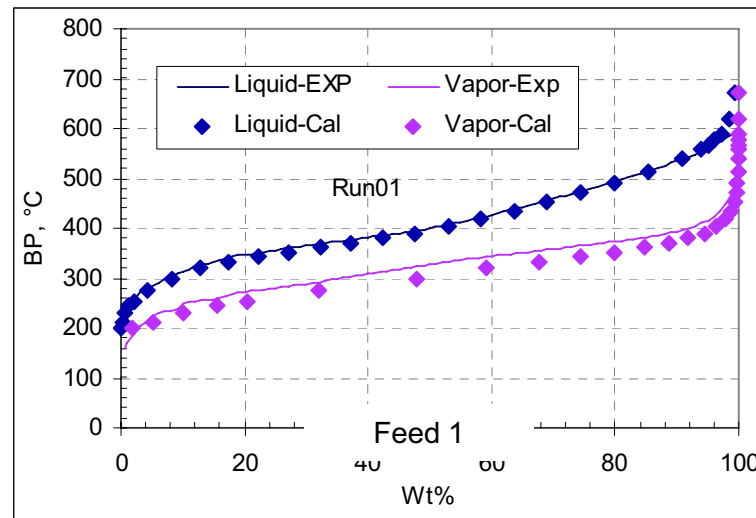
SimDis of vapor and liquid

Flash Calculation vs. Experimental Data

Heavy distillates

Wt% of oil in vapor with T

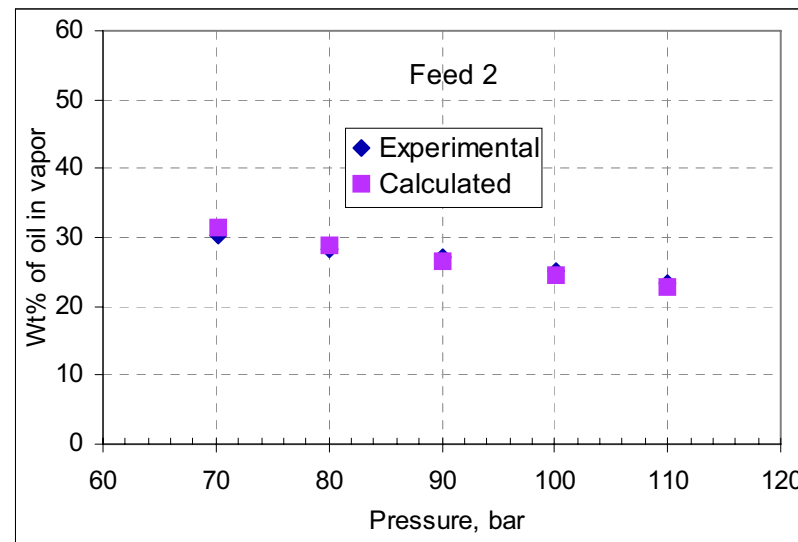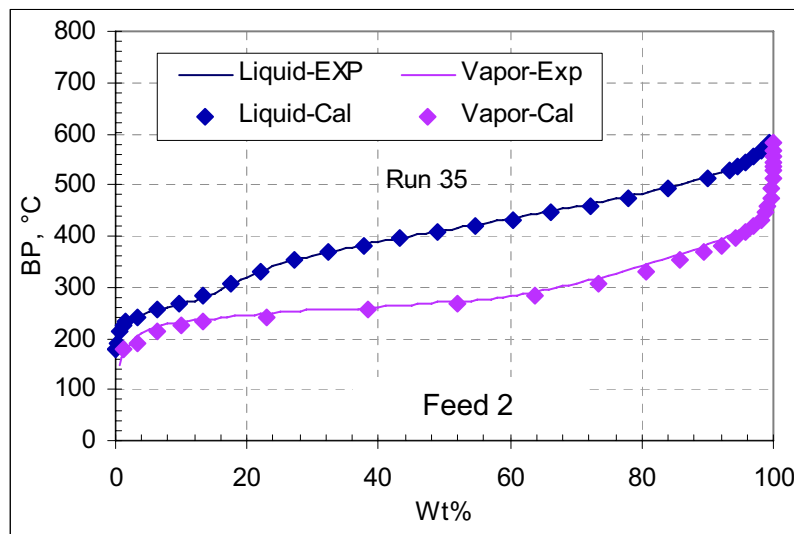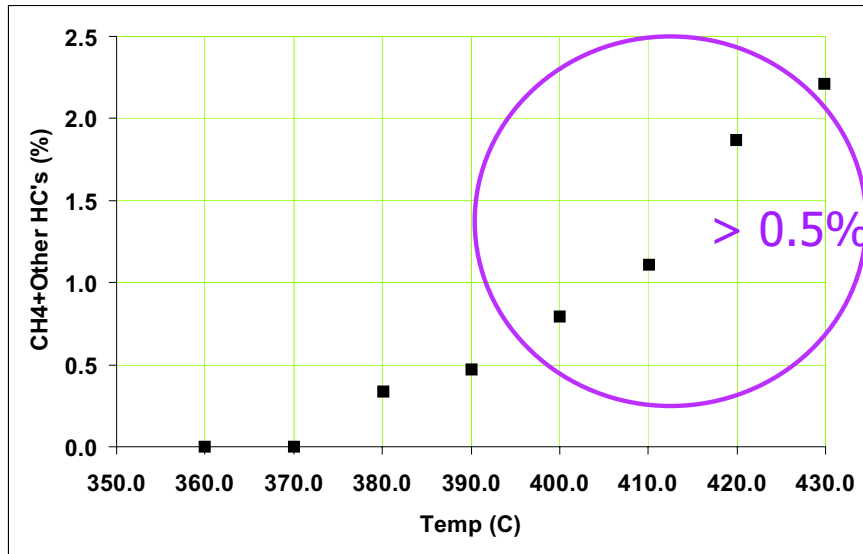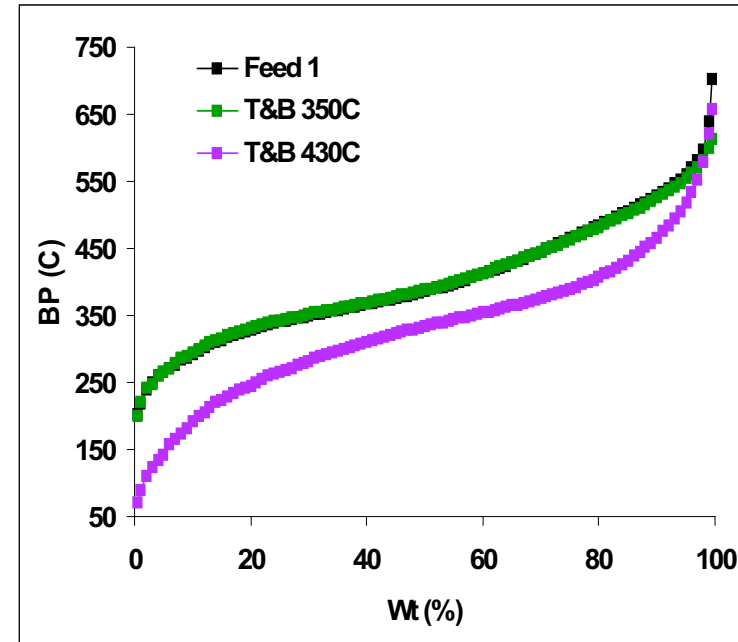**Wt% of oil in vapor with P**

SimDis of vapor and liquid

VLE Experiments at High Temperature (400ºC above)

Light hydrocarbon content in vent gas – Feed 1 GC data

SimDis Data

Feed 1	0.9609
Blend of vapor and liquid phases (350°C)	0.9603
Blend of vapor and liquid phases (430°C)	0.9478

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

Natural Resources
Canada   Ressources naturelles
Canada

AERI
Alberta Energy
Research Institute

ALBERTA
RESEARCH
COUNCIL

Thank you!