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On the Vapor-Liquid Equilibrium in Hydroprocessing Reactors

Jinwen Chen, Mugurel Munteanu and Hena Farooqi
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During petroleum distillates hydrotreating (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

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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

\[ \text{H}_2 + \text{hydrotreated oil} \]

Step \( i \):
- VLE model: flash calculation
  - \( \text{H}_2 \) rate, \( \text{oil rate, } T_i, P_i \)

Step \( i+1 \):
- VLE model: flash calculation
  - \( \text{H}_2 \) rate, \( \text{oil rate, } T_{i+1}, P_{i+1} \)

Reactor model: a set of PDEs to get \( T_i, C_{i,j} \)

\[ \text{vapor} \rightarrow \text{liquid} \]

\[ \text{vapor} \rightarrow \text{liquid} \]
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, \( V_{\text{small}} \) and \( V_{\text{large}} \) are liquid and vapor mole volume, respectively.

\[
b = \frac{\Omega_b RT_c}{P_c}
\]

\[
a(T) = \frac{\Omega_a R^2 T_c^2}{P_c} \alpha(T)
\]

Mixture

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

\[
a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij}
\]

\[
a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - d_{ij})
\]

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

<table>
<thead>
<tr>
<th></th>
<th>Middle Distillates</th>
<th></th>
<th>Heavy Distillates</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed 1 (LCO)</td>
<td>Feed 2 (white oil)</td>
<td>Feed 3 (LCO + white oil 50-50)</td>
<td>Feed 1 (heavy gas oil)</td>
</tr>
<tr>
<td>Density (15.6°C), g/mL (ASTM D4052)</td>
<td>0.9360</td>
<td>0.8152</td>
<td>0.8714</td>
<td>0.9609</td>
</tr>
<tr>
<td>Saturates (wt%)</td>
<td>15.9</td>
<td>98.9</td>
<td>61.0</td>
<td>30.9</td>
</tr>
<tr>
<td>Aromatics (wt%)</td>
<td>83.9</td>
<td>1.1</td>
<td>39.0</td>
<td>61.2</td>
</tr>
<tr>
<td>Polars (wt%)</td>
<td>0.2</td>
<td></td>
<td></td>
<td>7.9</td>
</tr>
<tr>
<td>SimDis, °C (ASTM D2887)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>128.4</td>
<td>210.5</td>
<td>148.0</td>
<td>201.8</td>
</tr>
<tr>
<td>10wt%</td>
<td>225.0</td>
<td>237.5</td>
<td>233.0</td>
<td>292.6</td>
</tr>
<tr>
<td>30wt%</td>
<td>255.3</td>
<td>256.5</td>
<td>255.0</td>
<td>350.2</td>
</tr>
<tr>
<td>50wt%</td>
<td>288.5</td>
<td>272.5</td>
<td>277.0</td>
<td>386.4</td>
</tr>
<tr>
<td>70wt%</td>
<td>326.4</td>
<td>312.5</td>
<td>318.5</td>
<td>445.4</td>
</tr>
<tr>
<td>90wt%</td>
<td>373.9</td>
<td>395.0</td>
<td>381.0</td>
<td>529.6</td>
</tr>
<tr>
<td>FBP</td>
<td>430.8</td>
<td>490.0</td>
<td>483.5</td>
<td>702.6</td>
</tr>
</tbody>
</table>
Experimental Observations

**Middle Distillates**

**Heavy Distillates**

![Graph showing Wt% Oil in Vapor vs. Temperature for Middle and Heavy Distillates at different pressures.](image-url)
Experimental Observations

Middle Distillates

Heavy Distillates

T = 350°C

T = 390°C

Pressure, atm

Pressure, bar

Wt% Oil in Vapor

Feed 1

Feed 2

Feed 3

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.
Fitting Experimental Data with Flash Model

| 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           |

Sulphur components

dibenzothiophene
4-methyl dibenzothiophene
2-methyl dibenzothiophene
3-methyl dibenzothiophene
4-ethyl dibenzothiophene
4,6-dimethyl dibenzothiophene
2,4-dimethyl dibenzothiophene
1,4,6-trimethyl dibenzothiophene
2,4,8-trimethyl dibenzothiophene
2,4,7-trimethyl dibenzothiophene
1,4,6-trimethyl dibenzothiophene
3,4,7-trimethyl dibenzothiophene
1,3,7-trimethyl dibenzothiophene

H2 + Feed

SimDis

0.5 113.8
1 141.1
2 170.1
3 188.6
4 202.8
5 211
6 214.8
94 386.9
95 391
96 394.8
97 401
98 408.1
99 420
99.5 431.9

Pseudo-components

S Speciation
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

Cut 8 → SimDis, MW and Density Measurement

......

Correlations of MW~BP, Sg~BP
Pseudo Components – MW & Density

Middle Distillates

MW correlation with boiling point (BP)

Heavy Distillates

Sg correlation with boiling point (BP)
Estimation of Interaction Coefficients

- Composition
- Density
- Molecular Weight
- Boiling Point
- T and P

Yield and composition of vapor phase

Flash Calculation (EOF)

\( d_{iH} \) between \( H_2 \) and hydrocarbon

Measured yield and composition of vapor phase

Measured yield and composition of liquid phase

\( d_{iH} \) 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>Heavy distillates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>Feed 1</td>
<td>Feed 1</td>
</tr>
<tr>
<td>0.1865</td>
<td>0.5712</td>
</tr>
<tr>
<td>0.00388</td>
<td>0.004713</td>
</tr>
<tr>
<td>Feed 2</td>
<td>Feed 2</td>
</tr>
<tr>
<td>0.386</td>
<td>0.2977</td>
</tr>
<tr>
<td>0.00226</td>
<td>0.002956</td>
</tr>
<tr>
<td>Feed 3</td>
<td></td>
</tr>
<tr>
<td>0.285</td>
<td></td>
</tr>
<tr>
<td>0.00302</td>
<td></td>
</tr>
</tbody>
</table>

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

For Middle distillates:

\[ a = 0.3852 - 0.00241 \times C_{Aromatics\%} \]
\[ b = 0.002245 + 1.96 \times 10^{-5} \times C_{Aromatics\%} \]

For Heavy distillates:

\[ a = 0.0943 + 0.009779 \times C_{Aromatics\%} \]
\[ b = 0.00165 + 5.0196 \times 10^{-5} \times C_{Aromatics\%} \]
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: \( d_{ij} = 0.1765 + 0.00298 \times \text{BP} \)

#### Middle distillates Feed 1

<table>
<thead>
<tr>
<th>Compounds</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>
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<td>3,7-DMDBT</td>
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<td>340.7</td>
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<tr>
<td>1,8-DMDBT</td>
<td>212.32</td>
<td>341.7</td>
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<tr>
<td>1,4-DMDBT</td>
<td>212.32</td>
<td>342.1</td>
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<tr>
<td>1,6-DMDBT</td>
<td>212.32</td>
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<td>3,4-DMDBT</td>
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<td>343.8</td>
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<tr>
<td>4-E-6-MDBT</td>
<td>226.36</td>
<td>344.5</td>
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<td>212.32</td>
<td>345</td>
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<td>345.8</td>
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<td>346.6</td>
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<td>2,4,8-TMDBT</td>
<td>226.36</td>
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<td>2,4,7-TMDBT</td>
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<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>Light hydrocarbon content in vent gas – Feed 1 GC data</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4+Other HCs (%)</td>
</tr>
<tr>
<td>Temp (C)</td>
</tr>
<tr>
<td>350.0 360.0 370.0 380.0 390.0 400.0 410.0 420.0 430.0</td>
</tr>
<tr>
<td>&gt; 0.5%</td>
</tr>
</tbody>
</table>

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.
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Thank you!