Refinery Modeling

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The Big Black Box
The Big Black Box

Crude A → Crude B

Crude C

Costs

Demand → Profit

Profit
The Big Black Box

Crude B -> Crude A -> Crude C

Costs

Demand

Profit
Hydrotreating

**INPUT:**
- Temperature
- Pressure
- \( H_2/HC \) Ratio
- Sulfur %
- Nitrogen %

**OUTPUT:**
- Sulfur %
- Nitrogen %
- Aromatic %

**MODEL:**
PBR
Hydrotreating

- Removal of sulfur, nitrogen, and aromatics.
- Government regulations are leading to increased sulfur removal requirements.

\[
\text{dibenzothiophene} \xrightarrow{4[H]} \text{biphenyl}
\]
## Typical Processing Conditions

<table>
<thead>
<tr>
<th></th>
<th>Space velocity</th>
<th>H₂/HC</th>
<th>H₂ Pressure (psia)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naptha</td>
<td>1.0-5.0</td>
<td>300</td>
<td>200</td>
<td>290</td>
</tr>
<tr>
<td>Middle Distillate</td>
<td>1.0-4.0</td>
<td>800</td>
<td>400</td>
<td>330</td>
</tr>
<tr>
<td>Light Gas Oil</td>
<td>0.7-1.5</td>
<td>1500</td>
<td>700</td>
<td>425</td>
</tr>
<tr>
<td>Heavy Gas Oil</td>
<td>0.75-2.0</td>
<td>2000</td>
<td>800</td>
<td>355</td>
</tr>
</tbody>
</table>
Hydrocracking

- Cracking is assumed to be insignificant.
  - Therefore, properties such as density and molecular weight are assumed to be constant.
Hydrotreating

• Cracking is assumed to be insignificant.
  – Therefore, properties such as density and molecular weight are assumed to be constant.
Hydrotreating Model

• For MoCo catalyst reaction rates are:
  – $\text{Rate}_s = k_s C_s^2 C_{H2}^{0.75}$
  – $\text{Rate}_n = k_n C_n^{1.4} C_{H2}^{0.6}$
  – $\text{Rate}_{ar} = k_{ar} C_{ar} C_{H2}$

http://www.chem.wwu.edu/dept/facstaff/bussell/research/images/thio-HDS.jpg
Delayed Coking

**INPUT:**
- CCR Pressure

**OUTPUT:**
- Gas Oil
- Coke
- Gas
- Naptha

**MODEL:**
Correlation
Delayed Coking

- Used to process bottoms from the vacuum distillate.
- Breaks down this portion into usable napthas, gas, and gas oil.
Delayed Coking

- Coke Products
  - Shot Coke
  - Sponge Coke
  - Needle Coke
Delayed Coking Model

• Most important parameter is the Conradson Carbon Residue.
  – Coke = 1.6 \times CCR
  – Gas = 7.8 + 0.144 \times CCR
  – Naptha = 11.29 + 0.343 \times CCR
  – Gas oil = 100 – Coke – Gas - Naptha

• This is an estimate from Gary and Handwerk
# Effect of Pressure on Product

<table>
<thead>
<tr>
<th></th>
<th>CCR (wt%)</th>
<th>15 psig</th>
<th>35 psig</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>29</td>
<td>27.2</td>
<td>30.2</td>
</tr>
<tr>
<td>Gas Yield</td>
<td>10.4</td>
<td>9.1</td>
<td>9.9</td>
</tr>
<tr>
<td>Naptha Yield</td>
<td>17.5</td>
<td>12.5</td>
<td>15</td>
</tr>
<tr>
<td>Gas Oil Yield</td>
<td>43.1</td>
<td>51.2</td>
<td>44.9</td>
</tr>
</tbody>
</table>
Delayed Coking Model

• Modified Equations
  – Gas = (7.4 + (.1 x CCR)) + (.8 x (P-15)/20)
  – Naptha = (10.29 + (.2 x CCR)) + (2.5 x (P-15)/20)
  – Coke = (1.5 x CCR) + (3 x (P-15)/20)
  – Gas oil = 100 – Gas – Naptha - Coke
### New Correlation

<table>
<thead>
<tr>
<th></th>
<th>CCR (wt%)</th>
<th>15 psig</th>
<th>35 psig</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>27.2</td>
<td>27.2</td>
<td>30.2</td>
</tr>
<tr>
<td>Gas Yield</td>
<td>9.2</td>
<td>9.1</td>
<td>9.9</td>
</tr>
<tr>
<td>Naptha Yield</td>
<td>13.9</td>
<td>12.5</td>
<td>15</td>
</tr>
<tr>
<td>Gas Oil Yield</td>
<td>49.7</td>
<td>51.2</td>
<td>44.9</td>
</tr>
</tbody>
</table>
**Catalytic Reforming**

**INPUT:**
- Temperature
- Pressure
- % Napthenes
- % Aromatics
- % Paraffins

**OUTPUT:**
- Hydrogen
- LPG
- Reformate

**MODEL:**
- PBR
Catalytic Reforming

FIG. 6.1. Catalytic reforming
Catalytic Reforming

• Simplified reactions and equations from Case Study 108 by Rase

(1) \textit{Napthenes} \leftrightarrow \textit{aromatics} + 3 \times H_2

(2) \textit{Paraffins} \leftrightarrow \textit{napthenes} + H_2

(3) \textit{Hydrocracking \_ of \_ paraffins}

(4) \textit{Hydrocracking \_ of \_ napthenes}
Catalytic Reforming

(1) \[ C_nH_{2n} \leftrightarrow C_nH_{2n-6} + 3H_2 \]

(2) \[ C_nH_{2n+2} \leftrightarrow C_nH_{2n} + H_2 \]

(3) \[ C_nH_{2n+2} + \left( \frac{n-3}{3} \right)H_2 \rightarrow \frac{n}{15}C_1 + \frac{n}{15}C_2 + \frac{n}{15}C_3 + \frac{n}{15}C_4 + \frac{n}{15}C_5 \]

(4) \[ C_nH_{2n} + \frac{n}{3}H_2 \rightarrow \frac{n}{15}C_1 + \frac{n}{15}C_2 + \frac{n}{15}C_3 + \frac{n}{15}C_4 + \frac{n}{15}C_5 \]
Catalytic Reforming

\[ \hat{k}_{p_1} = \exp \left( 23.21 - \frac{34750}{T} \right), \left[ \text{moles} \right] \frac{\text{(hr)(lb_cat.)(atm)}}{(hr)(lb_cat.)(atm)} \]

\[ K_{p_1} = \frac{P_A * P_H^3}{P_N} = \exp \left( 46.15 - \frac{46045}{T} \right), \left[ \text{atm}^3 \right] \]

\[ \hat{k}_{p_2} = \exp \left( 35.98 - \frac{59600}{T} \right), \left[ \text{moles} \right] \frac{\text{(hr)(lb_cat.)(atm)^2}}{(hr)(lb_cat.)(atm)^2} \]

\[ K_{p_2} = \frac{P_P}{P_N * P_H} = \exp \left( \frac{8000}{T} - 7.12 \right), \left[ \text{atm}^{-1} \right] \]

\[ \hat{k}_{p_3} = \hat{k}_{p_4} = \exp \left( 42.97 - \frac{62300}{T} \right), \left[ \text{moles} \right] \frac{\text{(hr)(lb_cat.)}}{(hr)(lb_cat.)} \]
Catalytic Reforming

\[- \dot{r}_1 = \widehat{k}_{P1} \left( P_N - \frac{P_A \cdot P_H^3}{K_{P1}} \right) \]

\[= \text{moles\_napthene\_converted\_to\_aromatics} \]

\[\text{(hr)(lb\_cat.)} \]

\[- \dot{r}_2 = \widehat{k}_{P2} \left( P_N \cdot P_H - \frac{P_P}{K_{P2}} \right) \]

\[= \text{moles\_napthene\_converted\_to\_paraffins} \]

\[\text{(hr)(lb\_cat.)} \]

\[- \dot{r}_3 = \widehat{k}_{P3} \left( \frac{P_P}{P} \right) \]

\[= \text{moles\_paraffins\_converted\_by\_hydrocracking} \]

\[\text{(hr)(lb\_cat.)} \]

\[- \dot{r}_4 = \widehat{k}_{P4} \left( \frac{P_N}{P} \right) \]

\[= \text{moles\_napthenes\_converted\_by\_hydrocracking} \]

\[\text{(hr)(lb\_cat.)} \]
Catalytic Reforming

**Temperature vs. Output Mole %**

- **Parafins (nP)**
- **Napthenes (nN)**
- **Aromatics (nA)**

![Graph showing the relationship between temperature and mole percent for different components in catalytic reforming process.](image-url)
Catalytic Reforming

Pressure vs. Output Mole %

Pressure (atm)

Mole %

- Parafins (nP)
- Napthenes (nN)
- Aromatics (nA)
Xylenes Isomerization

**INPUT:**
Temperature

**OUTPUT:**
Benzene
Toluene
O-Xylene
P-Xylene
Ethyl-Benzene

**MODEL:**
Correlation
Figure 7.32  *Simplified flow diagram of the Shell/UOP process. S: solvent (sulfolane). A: aromatics. NA: non-aromatics.*
Xylenes Isomerization

Paraffins & Napthenes - Blending

Mixed Aromatics – Fractionation

Figure 7.32. Simplified flow diagram of the Shell/UOP process. S: solvent (sulfolane). A: aromatics. NA: non-aromatics.
Xylenes Isomerization

Source: The Oil and Gas Journal

FIG. 2.7 Fractionation of high-purity aromatics
Xylenes Isomerization

C_9+ Aromatics – Blending

Benzene & Toluene – Solvent Quality

Xylenes – Isomerization

FIG. 2.7 Fractionation of high-purity aromatics
Xylenes Isomerization

FIG. 2.11 Xylenes processing complex

Source: Oil & Gas Journal
Xylenes Isomerization

O-Xylene – Chemical Feedstock

P-Xylene – Chemical Feedstock

Mixed Aromatics – Blending
Xylenes Isomerization

- Reaction driven by equilibrium
  \[ m - \text{Xylene} \rightleftharpoons o - \text{Xylene} \rightleftharpoons p - \text{Xylene} \rightleftharpoons \text{EthylBenzene} \]
- Temperature dependence of equilibrium modeled in Kirk-Othmer Encyclopedia of Chemical Technology
Solvent Extraction

**INPUT:**
- Temperature
- S/F Ratio

**OUTPUT:**
- Lube Oil Aromatics

**MODEL:**
Correlation
Solvent Extraction

Aromatics extraction unit using furfural. Flow scheme (Source: Mobil).
Solvent Extraction

Paraffinic Oils - Solvent Dewaxing

Mixed Aromatics – Blending

Figure 7.9  Aromatics extraction unit using furfural. Flow scheme (Source: Mobil).
Solvent Extraction

- Furfural Extraction – Averaged K Values
  - Benzene from Cyclohexane
  - Benzene from Iso-octane
  - 1,6-diphenylhexane from Docosane
- Temperature (°R) dependence of K correlated from this

\[
E = K \times \frac{S}{F} \quad \text{\%Extracted} = 1 - \frac{1}{\sum_{n=0}^{N} E^n}
\]

\[
K = T^2(-2E5) + 0.0259 \times T - 7.371
\]
Solvent Extraction

- Correlations developed from Institut Français du Pétrole data

\[
\text{Raffinate Yield}\% = \left( \frac{S}{F} \right) \times (-0.0426) + 0.9318
\]

\[
\text{Raffinate S.G.} = \left( \frac{S}{F} \right)^2 \times 0.0004 - \left( \frac{S}{F} \right) \times (0.0073) + 0.9229
\]
Solvent Extraction

Mole or Yield % vs. Temperature

Temperature (°R)

Mole or Yield %

- Extract - Paraffins (nP)
- Raffinate - Paraffins (nP)
- Extract - Napthenes (nN) + Aromatics (nA)
- Raffinate - Napthenes (nN) + Aromatics (nA)
- Extract - % Yield
Visbreaker

**INPUT:**
*Temperature*

**OUTPUT:**
*Gas*
*Gasoline*
*Gas Oil*
*Residue*

**MODEL:**
PFR
Visbreaking

Diagram:
- Feed
- Preheating
- Furnace (485°C, 3 bar)
- Cyclone Separator
- Fractionation
  - Gas + gasoline
  - Gas oil
  - Residue
Visbreaking

- Carbon chains cracking into smaller chains of varying carbon numbers
Visbreaking

- $S_i$ forms all components with carbons less than $i-1$

$$
\begin{align*}
S_i & \rightarrow S_{i-2} + O_2 \\
& \rightarrow S_{i-3} + O_3 \\
& \rightarrow S_{i-j} + O_j \\
& \rightarrow S_2 + O_{i-2} \\
& \rightarrow S_1 + O_{i-1}
\end{align*}
$$
Visbreaking

- $S_i$ forms all components with carbons less than $i-1$
- $S_i$ is formed from all components with carbons greater than $i+1$

\[
\begin{align*}
O_{n-i} & \quad \leftrightarrow \quad S_n \\
O_{n-1-i} & \quad \leftrightarrow \quad S_{n-1} \\
O_{k-i} & \quad \leftrightarrow \quad S_k \\
O_3 & \quad \leftrightarrow \quad S_{i+3} \\
O_2 & \quad \leftrightarrow \quad S_{i+2} \\
S_{i-2} & \quad + \quad O_2 \\
S_{i-3} & \quad + \quad O_3 \\
S_{i-j} & \quad + \quad O_j \\
S_2 & \quad + \quad O_{i-2} \\
S_1 & \quad + \quad O_{i-1}
\end{align*}
\]
Visbreaking

- First order kinetics with molar concentrations

\[ rs_i = \sum_{k=i+2}^{n} K_{k,i} Cs_k - Cs_i \sum_{j=1}^{i-2} K_{i,j} \]

\[ ro_i = \sum_{j=i+1}^{n} K_{j,j-i} Cs_j \]

\[ \frac{dCs_i}{dz} = \frac{1}{4} \pi \phi^2 \frac{\rho}{F} rs_i \]

\[ \frac{dCo_i}{dz} = \frac{1}{4} \pi \phi^2 \frac{\rho}{F} ro_i \]
Visbreaking

- Rate Constant dependent on molecular weight

\[ K_{i,j} = A_{i,j} e^{-B_{i,j}/RT} \]

\[ B_{i,j} = b_0 + b_1 \cdot PM_i + b_2 \cdot PM_j \]

\[ A_{i,j} = \left( a_0 + a_1 \cdot PM_i + a_2 \cdot [PM_i]^2 \right) e^{\frac{1}{2} \left( \frac{PM_j - PM_i}{a_4} \right)^2 \frac{1}{a_3}} \]

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.51E+12</td>
<td>42894</td>
</tr>
<tr>
<td>1.90E+08</td>
<td>-4.5</td>
</tr>
<tr>
<td>2.06E+06</td>
<td>3</td>
</tr>
<tr>
<td>146.95</td>
<td></td>
</tr>
<tr>
<td>11.35</td>
<td></td>
</tr>
</tbody>
</table>
Visbreaking

• Model inputs
  – Temperature and mass flow rate

• Model Product form
  – Weight percents
  – Components are lumped into 4 categories
    • Gas: C1-C4
    • Gasoline: C5-C10
    • Gas Oil: C11-C21
    • Residue: C22-C45
Isomerization

**INPUT:**
*Temperature*
*H₂/HC Ratio*

**OUTPUT:**
*Hydrocarbons*
*C₄-C₆*

**MODEL:**
PFR
Isomerization
Isomerization

- Main reactants: n-Butane, n-Pentane, n-Hexane
- Typically catalyzed-gas phase reaction
- Low temperature favors isomer formation
- Seven rate laws
  - Only one of n-Pentanes isomers forms
Isomerization

- n-Butane
  \[ r_{n-C4} = -K_1 \cdot \frac{P_{n-C4}}{P_{H_2}} + K_2 \cdot \frac{P_{iso-C4}}{P_{H_2}} \]

- n-Pentane
  \[ r_{n-C5} = -K_2 \cdot \left( \frac{C_{n-C5}}{[H_2]} \right)^{0.125} - 0.0000197 \cdot t \left[ K_{eq} \cdot C_{n-C5} - (K_{eq} + 1) \cdot C_{i-C5} \right] \]

- n-Hexane
  \[ r_i = - \left( \sum_{j=1}^{5} K_{j,i} \right) \cdot C_i + \sum_{j=1}^{5} K_{i,j} C_j \]
Isomerization

- Model inputs
  - Temperature, mass flow rate, and $\text{H}_2/$HC ratio
- Model Product form
  - Weight percents of the individual isomers
Hydrocracking

**INPUT:**
- °API
- $K_w$
- $H_2/BBL$

**OUTPUT:**
- Naptha
- Light
- Heavy
- $C_3$ Up
- i-Butane
- n-Butane
- Gas Oil

**MODEL:**
Correlation
Hydrocracking

- Convert higher boiling point petroleum fractions into lighter fuel products
Hydrocracking

- **Complementary Reactions**
  - Cracking reactions
    - Provides olefins for hydrogenation
      \[ R-C-C-C-R + \text{heat} \rightarrow R-C=C + C-R \]
  - Hydrogenation reactions
    - Provides heat for cracking
      \[ R-C=C + H_2 \rightarrow R-C-C + \text{heat} \]
**Hydrocracking**

- **Feedstocks**: Heavy distillate stocks, aromatics, cycle oils, and coker oils
- **Catalysts**: zeolites
- **Operating conditions**:

<table>
<thead>
<tr>
<th></th>
<th>Residuum</th>
<th>Distillate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Consumption (SCFB)</td>
<td>1200-1600</td>
<td>1000-2400</td>
</tr>
<tr>
<td>LHSV (hr⁻¹)</td>
<td>0.2-1</td>
<td>0.5-10</td>
</tr>
<tr>
<td>Temperature (°F)</td>
<td>750 -800</td>
<td>500-900</td>
</tr>
<tr>
<td>Pressure (psi)</td>
<td>2000-3000</td>
<td>500-3000</td>
</tr>
</tbody>
</table>
Hydrocracking Model Development

• Correlated data from “Oil and Gas Journal” W.L. Nelson
• Graphical correlated data was made continuous for hydrogen feed rate, Kw and API of the feed
• 3 inputs
• 5 outputs
Hydrocracking Model

Approximate relationship between the yields of $(C_5-180^\circ)$ and $(180^\circ-400^\circ F)$ hydrocrackates

Fig. 1
Hydrocracking Model

\[ y = 0.84165e^{0.00096x} \]
\[ R^2 = 0.99872 \]

\[ y = 0.91507e^{0.00099x} \]
\[ R^2 = 0.99903 \]

\[ y = 1.03077e^{0.00102x} \]
\[ R^2 = 0.99873 \]

\[ y = 1.17542e^{0.00105x} \]
\[ R^2 = 0.99820 \]

\[ y = 1.35330e^{0.00110x} \]
\[ R^2 = 0.99840 \]

\[ y = 1.48461e^{0.00120x} \]
\[ R^2 = 0.99873 \]

\[ y = 1.6485e^{0.00129x} \]
\[ R^2 = 0.99907 \]

\[ y = 1.80073e^{0.00143x} \]
\[ R^2 = 0.99873 \]

\[ y = 3.40926e^{0.00157x} \]
\[ R^2 = 0.99855 \]

\[ y = 2.67927e^{0.00193x} \]
\[ R^2 = 0.99871 \]

\[ y = 2.20169e^{0.00147x} \]
\[ R^2 = 0.99876 \]

\[ y = 1.80073e^{0.00143x} \]
\[ R^2 = 0.99873 \]

\[ y = 1.6485e^{0.00129x} \]
\[ R^2 = 0.99907 \]

\[ y = 1.48461e^{0.00129x} \]
\[ R^2 = 0.99873 \]

\[ y = 1.35330e^{0.00110x} \]
\[ R^2 = 0.99873 \]

\[ y = 1.17542e^{0.00105x} \]
\[ R^2 = 0.99873 \]

\[ y = 1.03077e^{0.00102x} \]
\[ R^2 = 0.99873 \]

\[ y = 0.91507e^{0.00099x} \]
\[ R^2 = 0.99873 \]

\[ y = 0.84165e^{0.00096x} \]
\[ R^2 = 0.99872 \]
Hydrocracking Model

A Constant

\[ y = 1.852 \times 10^{-5}x^4 - 1.206 \times 10^{-3}x^3 + 2.920 \times 10^{-2}x^2 - 2.531 \times 10^{-1}x + 1.546 \times 10^0 \]
\[ R^2 = 9.992 \times 10^{-1} \]

B Constant

\[ y = 6.024 \times 10^{-11}x^6 - 6.539 \times 10^{-9}x^5 + 2.738 \times 10^{-7}x^4 - 5.600 \times 10^{-6}x^3 + 5.935 \times 10^{-5}x^2 - 2.996 \times 10^{-4}x + 1.509 \times 10^{-3} \]
\[ R^2 = 9.982 \times 10^{-1} \]
## Hydrocracking Model

### Vol% of light naptha

<table>
<thead>
<tr>
<th>Hydrogen Rate (SCFB)</th>
<th>7.5</th>
<th>10</th>
<th>12.5</th>
<th>15</th>
<th>17.5</th>
<th>20</th>
<th>22.5</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_w = 12.1 )</td>
<td>9.25</td>
<td>11</td>
<td>13</td>
<td>16</td>
<td>21</td>
<td>30</td>
<td>45</td>
<td>80</td>
</tr>
<tr>
<td>diff. from ( K_w = 10.9 )</td>
<td>0.75</td>
<td>1</td>
<td>1</td>
<td>1.25</td>
<td>1.75</td>
<td>2.5</td>
<td>5</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>8.11%</td>
<td>9.09%</td>
<td>7.69%</td>
<td>7.81%</td>
<td>8.33%</td>
<td>8.33%</td>
<td>11.11%</td>
<td>9.38%</td>
</tr>
<tr>
<td>1500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_w = 12.1 )</td>
<td>3.4</td>
<td>4</td>
<td>4.8</td>
<td>5.8</td>
<td>7.3</td>
<td>9.1</td>
<td>11.25</td>
<td>14.25</td>
</tr>
<tr>
<td>diff. from ( K_w = 10.9 )</td>
<td>0.35</td>
<td>0.45</td>
<td>0.5</td>
<td>0.55</td>
<td>0.7</td>
<td>1</td>
<td>1.5</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>10.29%</td>
<td>11.25%</td>
<td>10.42%</td>
<td>9.48%</td>
<td>9.59%</td>
<td>10.99%</td>
<td>13.33%</td>
<td>12.28%</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_w = 12.1 )</td>
<td>1.4</td>
<td>1.55</td>
<td>1.7</td>
<td>2</td>
<td>2.3</td>
<td>2.8</td>
<td>3.4</td>
<td>4.2</td>
</tr>
<tr>
<td>diff. from ( K_w = 10.9 )</td>
<td>0.1</td>
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<td>0.2</td>
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<tr>
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<td>7.14%</td>
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<td>11.76%</td>
<td>10.00%</td>
<td>10.87%</td>
<td>10.71%</td>
<td>10.29%</td>
<td>9.52%</td>
</tr>
</tbody>
</table>
Hydrocracking Model

\[ y = -0.7691x + 11.739 \]
\[ R^2 = 0.9916 \]

Approximate relationship between the yields of \((C_5 - 180^\circ)\) and \((180^\circ - 400^\circ F)\) hydrocrackates

Fig. 1
Hydrocracking Equations

\[ vol\% p_1 = (1.00833K_w - 0.00833)Ae^{B\cdot H} \]
\[ vol\% p_2 = (\ -0.7691 \cdot K_w + 11.739)(vol\% p_1) \]
\[ vol\% p_3 = 0.337(vol\% p_1) \]
\[ vol\% p_4 = 0.186(vol\% p_1) \]
\[ vol\% p_5 = 1 + 0.09(vol\% p_1) \]
### Hydrocracking Model

<table>
<thead>
<tr>
<th>°API</th>
<th>Hydrogen (SCFB)</th>
<th>$K_w$</th>
<th>vol% $p_1$</th>
<th>vol% $p_2$</th>
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<td>15</td>
<td>2500</td>
<td>12.1</td>
<td>16.4</td>
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<tr>
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<td>40.5</td>
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<td>750</td>
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<td>3.5</td>
<td>10.0</td>
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<td>1250</td>
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<td>16.3</td>
<td>54.7</td>
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<tr>
<td>actual</td>
<td></td>
<td></td>
<td>13.0</td>
<td>43.0</td>
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</tbody>
</table>

°API: °API, Hydrogen: SCFB, $K_w$: Kw, vol% $p_1$: vol% $p_1$, vol% $p_2$: vol% $p_2$.
Solvent Dewaxing

INPUT:
Composition Temperature

OUTPUT:
Wax Lube Oil

MODEL:
Correlation
Solvent Dewaxing

- Separate high pour point waxes from lubricating oils
Solvent Dewaxing

• Feedstocks
  – Distillate and residual stocks – heavy gas oils
  – Solvents – Ketones (MEK) and Propane

• Operating conditions
  – Solvent to oil ratio 1:1 to 4:1
  – Desired pour point of product
Dewaxing Model Development

• Correlation from “Energy and Fuels” Krishna et. al.
• 3 experimentally determined parameters
• 3 inputs
• 2 outputs

\[ PPT = A0 \log(100 / PC) + A1 / CL + A2 \]

\[ OilYield(\text{wt\%}) = \frac{(100 - PC(\text{feed}))}{(100 - PC(\text{product}))} \]
## Dewaxing Model Error

<table>
<thead>
<tr>
<th>°C</th>
<th>BC2</th>
<th>NC6</th>
<th>NC7</th>
<th>NC8</th>
<th>NC9</th>
<th>NC10</th>
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<tr>
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<td>400-425</td>
<td>425-450</td>
<td>450-475</td>
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<tr>
<td>wax wt%</td>
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<td>44.88</td>
<td>47.28</td>
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<td>31.00</td>
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<td>39</td>
<td>45</td>
<td>48</td>
<td>51</td>
<td>57</td>
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<td>44.0</td>
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<td>3.5%</td>
<td>1.9%</td>
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<table>
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<th>dewaxing model</th>
<th>Desired PPT= 10</th>
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<td>PPT high</td>
<td>10.01 10.50 10.23 10.18 10.35 10.19</td>
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<td>wax wt% low</td>
<td>0.368 0.819 0.608 0.336 0.202 0.133</td>
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<tr>
<td>wax wt% high</td>
<td>0.369 0.931 0.643 0.352 0.220 0.139</td>
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<td>yield high</td>
<td>0.5340 0.5564 0.5306 0.5177 0.5139 0.5302</td>
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<tr>
<td>error %</td>
<td>0.001% 0.112% 0.036% 0.016% 0.019% 0.006%</td>
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</table>
**Alkylation**

**INPUT:**
- Iso-butane
- Butylene / Propylene
- Reaction time

**OUTPUT:**
- Propane
- Butane
- Alkylate

**MODEL:**
Correlation
Alkylation PFD

Exxon-Mobil Autorefrigiration \( \text{H}_2\text{SO}_4 \) alkylation

Alkylation

\[
\begin{align*}
\text{isobutylene} & \quad \text{isobutane} & \quad 2,2,4\text{-trimethylpentane} \\
\text{propylene} & \quad \text{isobutane} & \quad 2,2\text{-dimethylpentane}
\end{align*}
\]

*Lots of side reactions*
Alkylation

\[ F = \frac{I_E (I/O)_F}{100(SV)_O} \]

\((I/O)_F\) = volumetric isobutane/olefin ratio in feed

\(I_E\) = isobutane in reactor effluent, liquid volume %

\((SV)_O\) = olefin space velocity, v/hr/v

\(F\) = Factor defined by A.V. Mrstik

“Progress in Petroleum Technology” AV Mrstik et al. ACS Publications

Figure 7. Sulfuric Acid Alkylate Octanes, ASTM Research (CRC-F-1)
Polymerization

**INPUT:**
- Iso-butane
- Butylene / Propylene

**OUTPUT:**
- Gasoline
- Diesel

**MODEL:** Correlation
Polymerization

- Converts Propylenes and butylenes into saturated carbon chains
- 1\textsuperscript{st} used Catalytic Solid Phosphoric Acid (SPA) on silica fell out of popularity in 1960s.
- Now experimenting with Zeolites.

\[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{C} = \text{C} - \text{C} & \quad + \quad \text{C} = \text{C} - \text{C} \\
\rightarrow & \quad \text{C} - \text{C} - \text{C} = \text{C} - \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} = \text{C} - \text{C} & \quad + \quad \text{C} = \text{C} - \text{C} \\
\rightarrow & \quad \text{C} - \text{C} - \text{C} = \text{C} - \text{C} \\
\end{align*}
\]

- Polymerization reaction is highly exothermic and temperature is controlled either by injecting cold propane quench or by generating steam.
- Propane is also recycled to help control temperature

CO School of Mines http://jechura.com/ChEN409/11%20Alkylation.pdf
http://www.personal.psu.edu/users/w/y/wyg100/fsc432/Lecture%202015.htm
Zeolite Polymerization

- Converts propylenes and butylenes into saturated carbon chains by means of zeolite catalysis (ZSM-5)

Figure 1. ZSM-5 Catalyst.
Zeolite Polymerization

- Converts propylenes and butylenes into saturated carbon chains by means of zeolite catalysis (ZSM-5)
Zeolite Polymerization

- Converts propylenes and butylenes into saturated carbon chains by means of zeolite catalysis (ZSM-5)

<table>
<thead>
<tr>
<th></th>
<th>Specific Gravity</th>
<th>Octane</th>
<th>RON</th>
<th>MON</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.73</td>
<td>92</td>
<td>79</td>
<td></td>
</tr>
</tbody>
</table>

[Tabak, 1986]
Zeolite Polymerization

**Charge**
- 17wt.% Propylene
- 10.7 wt.% Propane
- 36.1 wt.% 1-butene
- 27.2 wt.% isobutane

**Temperature** = 550K

**Total Pressure** = 5430 kPa

**Propylene partial pressure** = 7~3470kPa.
*Depending on desired chain length*
**Zeolite Polymerization**

**Charge**
- 17wt.% Propylene
- 10.7 wt.% Propane
- 36.1 wt.% 1-butene
- 27.2 wt.% isobutane

**Temperature** = 550K

**Total Pressure** = 5430 kPa

Propylene partial pressure = 7~3470kPa.
*Depending on desired chain length*

![Graph showing average carbon number vs. propylene partial pressure]
**Polymerization**  vs  **Alkylation**

- **Polymerization**
  - PBR-gas phase
  - Solid catalysis
  - Produce either diesel or gasoline range chains
  - Typical octane number = 92 (RON)

- **Alkylation**
  - CSTR- liquid phase
  - Liquid catalysis
  - Requires very vigorous agitation
  - Typically .1 lb\textsubscript{m} acid consumed per gallon product
  - ++Typical octane number = 96 (RON)
Deasphalting

**INPUT:**
- %Heavies
- Temperature
- Pressure

**OUTPUT:**
- %Heavies
- Lube oil

**MODEL:**
Correlation
Propane Deasphalting - PFD

Typical Propane Deasphalting

Propane Deasphalting

Types


Both remove greater than 99% asphalt
Sub Critical Propane Deasphalting

Hildebrand solubility

$$\delta = \left( \frac{\Delta H - R_g T}{V} \right)^{\frac{1}{2}}$$

$\delta$ = Solubility Parameter [J/mol]
$\Delta H$ = Heat of vaporization [J/mol]
$R_g$ = Universal gas Constant [8.314J/mol/K]
$T$ = Temperature [K]
$V$ = molar volume [L/mol]
Super Critical Propane Deasphalting

Models typically break down near the critical point. Including Redlick-Kwong, Soave-Redlick-Kwong and Perturbed-Hard-Chain (PHC). Therefore correlations have to be used.

Typically operate at
T=400K
Pressure=55 bar
Ratio= 4:1 propane to oil mixture

Catalytic Cracking

**INPUT:**
- $K_w$
- Temperature

**OUTPUT:**
- Gas Oil
- Gasoline
- LPG
- Dry Gas
- Coke

**MODEL:** PFR
Fluidized Catalytic Cracking

- Pretreated feedstock is fed into the bottom of the riser tube where it meets very hot regenerated catalyst.

- The feed vaporizes and is cracked as it passes up the riser.

http://www.uyseg.org/catalysis/petrol/petrol2.htm
Fluidized Catalytic Cracking

- Different yields of products will occur depending on:
  - **Temperature**
  - **Inlet Feed Properties**

- Top of the riser, the catalyst separates from the mixture and is steam stripped

- The final product exits the top of the reactor

http://www.uyseg.org/catalysis/petrol/petrol2.htm
Fluidized Catalytic Cracking

- One product from catalytic cracking is "coke" or carbon that forms on the surface of the catalyst.
- To reactivate catalyst, it must be regenerated.

http://www.uyseg.org/catalysis/petrol/petrol2.htm
Fluidized Catalytic Cracking

- Catalysis is **regenerated** by entering a combustion chamber and mixed with superheated air.
- Energy released from regenerating the catalysis is then coupled with the inlet feed at the bottom of the riser.
  - *Cracking*

http://www.uyseg.org/catalysis/petrol/petrol2.htm
Fluidized Catalytic Cracking

\[ r_A = -\left( k_{A-B} + k_{A-C} + k_{A-D} + k_{A-E} \right) y_A^2 \Phi \]

A = gas oil
B = gasoline
C = LPG
D = dry gas
E = coke

Fluidized Catalytic Cracking

\[ r_B = (k_{A-B} y_A^2 - k_{B-C} y_B - k_{B-D} y_B - k_{B-E} y_B) \phi \]

A = gas oil
B = gasoline
C = LPG
D = dry gas
E = coke

Fluidized Catalytic Cracking

\[ r_C = (k_{A-C} y_A^2 + k_{B-C} y_B - k_{C-D} y_C) \Phi \]

A = gas oil
B = gasoline
C = LPG
D = dry gas
E = coke

Fluidized Catalytic Cracking

\[ \Phi = e^{-k_d t_c} \]

- A = gas oil
- B = gasoline
- C = LPG
- D = dry gas
- E = coke

Fluidized Catalytic Cracking

- 8 kinetic constants
- One catalyst deactivation
- Gas Oil considered as a second order reaction


\[ \Phi = e^{-k_d t_c} \]
**Fluidized Catalytic Cracking**

- **Assumptions**
  - One-dimensional tubular reactor
    - No radial and axial dispersion
  - Cracking only takes place in the riser
  - Dispersion/Adsorption inside catalyst is negligible
  - Coke deposited does not affect the fluid flow
Fluidized Catalytic Cracking

• Change
  – Temperature
  – Inlet Feed

Mass Balance:

\[ \frac{dy_i}{dz} = \frac{1}{WHSV} \left( \frac{\rho_L}{\rho_C} \right) \times r_i \]

<table>
<thead>
<tr>
<th>Kinetic Parameters for each Feedstock at 500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>k_d</td>
</tr>
<tr>
<td>k_ab</td>
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<tr>
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<td>k_ad</td>
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<td>k_e</td>
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<tr>
<td>k_be</td>
</tr>
<tr>
<td>k bd</td>
</tr>
<tr>
<td>k_be</td>
</tr>
<tr>
<td>k_cd</td>
</tr>
</tbody>
</table>
Fluidized Catalytic Cracking

- Change
  - Temperature
  - Inlet Feed

**TEMPERATURE:**
480, 500, 520 ºC

Mass Balance:

\[
\frac{dy_i}{dz} = \frac{1}{\text{WHSV}} \left( \frac{\rho_L}{\rho_C} \right) * r_i
\]

<table>
<thead>
<tr>
<th>Kinetic Parameters for each Feedstock at 500 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>(k_a)</td>
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<tr>
<td>(k_{ab})</td>
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<td>(k_{ae})</td>
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<td>(k_{bd})</td>
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<td>(k_{be})</td>
</tr>
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<td>(k_{cd})</td>
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</tbody>
</table>
Fluidized Catalytic Cracking

- Constant C/O Ratio of 5
- Varying space velocity (WHSV)
  - 6 – 48 h⁻¹
- Gas Oil Conversion ~ 70 %
- Gasoline ~ 50%
- LPG ~ 12 %
- Constant C/O Ratio of 5
- Varying space velocity (WHSV) /square4 6 – 48 h
- Gas Oil Conversion ~ 70%
- Gasoline ~ 50%
- LPG ~ 12%

Fluidized Catalytic Cracking

<table>
<thead>
<tr>
<th></th>
<th>% YIELD</th>
<th>%</th>
<th>C_A</th>
<th>C_B</th>
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<th>C_D</th>
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### Fluidized Catalytic Cracking

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<th>SUM</th>
<th>%</th>
<th>C_A</th>
<th>C_B</th>
<th>C_C</th>
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Blending

INPUT:
35 streams

OUTPUT:
Gasoline
   Regular
   Premium
LPG
Coke
Lube Oil
Wax
Asphalt
Blending

• Final products are created by blending streams from refinery units
• 35 streams from 13 units are blended
• 30 streams are used in gasoline
• 5 streams are other products
  – Propane gas, lube oil, asphalt, wax, and coke
Blending Indexes

- Most properties do not blend linearly
- Empirical blending indexes are used to linearize the blending behavior

\[ BI_{mix} = \sum_{i} x_i BI_i \]

Where \( BI \) is the Blending Index
\( x_i \) is the volume fraction of component \( i \)
Blending Indexes

Reid Vapor Pressure

\[ \text{VPBI} = (RVP)^{1.25} \]

Viscosity Index

\[ BI_v = \frac{\log_{10} \nu}{3 + \log_{10} \nu} \]

Pour Point

\[ BI_p = T_p \left( \frac{1}{0.08} \right) \]

Cloud Point

\[ BI_{CL} = T_{CL} \left( \frac{1}{0.05} \right) \]

Flash Point

\[ \log_{10} BI_F = -6.1188 + \frac{2414}{T_F - 42.6} \]

Aniline Point

\[ BI_{AP} = 1.124[\exp(0.00657AP)] \]
Gasoline Blending

• Specifications:
  – Octane (normal 87, premium 91)
  – Reid Vapor Pressure (EPA mandated)
  – Maximum additive amounts

• Inputs:
  – Market conditions (Price, Demand)
  – Incoming streams from refinery units

• Objective: Maximize Profit
Gasoline Blending

• Vapor pressure blending can be improved by using thermodynamically based methods

• Raoult's Law

\[ P = \sum x_i \cdot P_i^* \]
Blending

• Other possible products
  – Fuel oils
  – Lube oils
  – Diesel fuel

• Blending requires data for aniline point, pour point, cloud point, flash point, and diesel index
Refinery Planning

- Addresses the planning of short-term crude oil purchasing and processing
- Does not address risk or uncertainty
- Determine purchasing schedule to meet:
  - Specification (Octane, n-Butane, etc.)
  - Demand with HIGHEST profit

- Decision Variables:
  - Crude oil purchase
  - Processing variables
    - Temperatures, Pressures, Blending mixtures
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Refinery Planning

- **Max Profit**


\[
= \sum_{t\in T} \sum_{c\in C_p} MANU_{c,t} \ast cp_{c,t} - \sum_{t\in T} \sum_{c\in C_o} AC_{c,t} \ast co_{c,t} - \sum_{t\in T} \sum_{c\in C_p} AL_{c,t} \ast cl_{c,t}
\]
Refinery Planning

• Max Profit

Pongsakdi, Arkadej, et. al, “Financial risk….”, Int. J. Production Economics, accepted 20 April 2005

**Product Sales**

\[
\sum_{t \in T} \sum_{c \in C_p} MANU_{c,t} \times cp_{c,t} - \sum_{t \in T} \sum_{c \in C_o} AC_{c,t} \times co_{c,t} - \sum_{t \in T} \sum_{c \in C_p} AL_{c,t} \times cl_{c,t}
\]

Amount of product produced in that time period *multiplied* by unit sale price of product c
Refinery Planning

• Max Profit


**Product Sales** = \[ \sum_{t \in T} \sum_{c \in C_p} MANU_{c,t} \cdot cp_{c,t} \]

**Crude Oil Costs** = \[ \sum_{t \in T} \sum_{c \in C_o} AC_{c,t} \cdot co_{c,t} - \sum_{t \in T} \sum_{c \in C_p} AL_{c,t} \cdot cl_{c,t} \]

- Amount of product produced in that time period *multiplied* by unit sale price of product c
- Amount of crude oil refined in that time period *multiplied* by unit purchase price of crude oil
Refinery Planning

• Max Profit


\[
\text{Product Sales} = \sum_{t \in T} \sum_{c \in C_p} \text{MANU}_{c,t} \ast cp_{c,t} \\
\text{Crude Oil Costs} = \sum_{t \in T} \sum_{c \in C_o} \text{AC}_{c,t} \ast co_{c,t} \\
\text{Discounted Expense} = \sum_{t \in T} \sum_{c \in C_p} \text{AL}_{c,t} \ast cl_{c,t}
\]

- Amount of product produced in that time period *multiplied* by unit sale price of product c
- Amount of crude oil refined in that time period *multiplied* by unit purchase price of crude oil
- Amount of product volume that cannot satisfy demand *multiplied* by discounted price
Modeling

• A Visual Basic macro in Excel was used to help Solver find the optimal crude selection
A Visual Basic macro in Excel was used to help Solver find the optimal crude selection.

```vba
Dim i, j, k As Integer
Dim BestCrude(1 To 3) As Long
Dim MaxProfitSoFar As Double
Dim SolverError As Integer
Dim n As Integer
Dim rowNumber As Long

MaxProfitSoFar = -100000 'Initialize the max profit
rowNumber = 1

For i = 4 To 12 Step 1
    For j = 4 To 14 Step 1
        For k = 4 To 16 Step 1
            rowNumber = rowNumber + 1
            Range("U84").Select
            ActiveCell.FormulaR1C1 = "+" & i & "+dc"
            Range("U85").Select
            ActiveCell.FormulaR1C1 = "+" & j & "+dc"
            Range("U86").Select
            ActiveCell.FormulaR1C1 = "+" & k & "+dc"

            SolverError = SolverSolve(True)
            If SolverError > 3 Then
                For n = 50 To 89 Step 1
                    Range("C" & n) = 0.5
                    Range("H" & n) = 0.5
                Next n
            End If

            Range("H112").Select
            If ActiveCell.Value > MaxProfitSoFar Then
                MaxProfitSoFar = ActiveCell.Value
                BestCrudes(1) = i
                BestCrudes(2) = j
                BestCrudes(3) = k
            Range("V97").Value = "+" & BestCrude(1) & "+dc"
            Range("V98").Value = "+" & BestCrude(2) & "+dc"
            Range("V99").Value = "+" & BestCrude(3) & "+dc"
            Range("V100").Select
            ActiveCell.Value = MaxProfitSoFar
        End If
    Next k
Next j
Next i
```
Model Inputs

• Inputs:
  – Crude A: $71.88 / barrel (Australia)
  – Crude B: $72.00 / barrel (Kazakhstan)
  – Crude C: $71.20 / barrel (Saudi Arabia)
  – Regular Gasoline:
    • $2.75 / gal ($2.12)
    • Demand: 310,000 bbl/month
  – Premium Gasoline:
    • $3.00 / gal ($2.31)
    • Demand: 124,000 bbl/month

Energy Information Administration, U.S. Department of Energy
http://www.eia.doe.gov/oil_gas/petroleum/info_glance/petroleum.html
Model Results

• Outputs:
  – Maximum Profit: $21 per barrel
  – Crude Selection:
    • Crude A: 150,000 bbl/month
    • Crude B: 150,000 bbl/month
    • Crude C: 300,000 bbl/month
  – Demand exactly met
Future Work

• Include storage of crude and products
• Include risk and uncertainty
• Demand changing over time
• Wider variety of products: diesel, solvents, fuel oils, lube oils, etc.
Questions?