Refinery Operations Planning

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Refinery Operations Planning

• What is a refinery?
  – Takes crude oil and converts it into gasoline
  – Distills crude into light, medium, and heavy fractions
    • Lightest fractions – gasoline, liquid petroleum gas
    • Medium fractions – kerosene and diesel oil
    • Heavy fractions – gas oils and residuum
Crude oil is heated and passed through a fractionation column. As the oil is heated, different fractions are collected based on their boiling points:

- C_1 to C_4 gases
- 20°C: liquefied petroleum gas
- 70°C: C_5 to C_9 naphtha
- 120°C: C_5 to C_10 petrol (gasoline)
- 170°C: C_10 to C_16 kerosine (paraffin oil)
- 270°C: C_14 to C_20 diesel oils
- 600°C: >C_70 residue

The fractions are then processed for various uses:

- Jet fuel, paraffin for lighting and heating
- Diesel fuels
- Lubricating oils, waxes, polishes
- Fuels for ships, factories and central heating
- Bitumen for roads and roofing

The diagram shows the flow of oil through the column, with arrows indicating the direction of flow and labels for each fraction.
Process that is fed by heavier fractions to produce lighter fractions

Hydrocracker

Reformer

Process used to increase the octane number of light crude fractions
Distillation Column: Process that separates crude oil into fractions according to their boiling point.

Gasoline Blending: Process that blends various streams of gasoline.

Delayed Coking: Process used to produce high value liquid products.
Hydrotreating

Process that uses H₂ to break up sulfur, nitrogen compounds, and aromatics

Isomerization

Process that converts normal, straight chain paraffins to iso-paraffins
Refinery Operations Planning

“Refining is a complex operation that depends upon the human skills of operators, engineers, and planners in combination with cutting edge technology to produce the products that meet the demands of an intensely competitive market.”

Sources: http://www.exxon.mobil.com/UK-English/Operations/UK_OP_Ref_RefOp.asp and http://static.flickr.com/18/24007819_4d67ab2c0b.jpg
Refinery Operations Planning

• Planning groups in a refinery attempt to optimize the refinery’s profits by purchasing specific amounts of different crudes

• Based on:
  – Projected market demands and prices
  – Unit capabilities
  – Planned turnarounds
Refinery Operations Planning
Refinery Operations Planning

• Planning Example
  – Winter
    • high fuel oil demand → more fuel (heating) oil produced
  – Summer
    • lower fuel oil demand → more gasoline produced
Refinery Operations Planning

- LP models use average operating conditions
- Graph shows that average operating conditions may not optimize particular unit (CRU)
Current Models

• Current models operate linearly (LP)
  – Black Box Theory

• PIMS (by Aspentech)
• RPMS (by Honeywell Hi-Spec Solutions)
• GRMPTS (by Haverly)
Black Box Theory
LP Planning

\[ F_{i,\text{out}} = 0.75 \cdot F_{\text{in}} \]

\[ F_{j,\text{out}} = 0.25 \cdot F_{\text{in}} \]

\[ ON_{\text{out}} = 98 \]
Modeling Unit Operations

Operating Variables:
- Temperature
- Pressure
- Flow Rate
- Input Sulfur Weight Percent
Modeling Unit Operations

HDS

Operating Variables:
- Temperature
- Pressure
- Flow Rate
- Input Sulfur Weight Percent

\[ F_{S,\text{out}} = f(T, P, F) \]
General Goal

• To effectively model a refinery’s unit operations in the overall planning model.
• Bangchak refinery in Thailand is used as a case study.
More Specific Goals

• Model Hydrotreaters
• Model Catalytic Reformers
• Model Isomerization
• Tie Unit Operations to GRM
  – Add Operating Costs
• Tie Unit Operations to blending
  – Calculate blending properties
• Integrate Fuel Gas system
• Create Hydrogen balance
Original LP Model

• LP model developed
  – Operates using Black Box theory
• Optimizes purchased crudes and additives
• Evaluates uncertainty and risk
Bangchak Refinery
Bangchak Refinery

- Hydrotreating
  - NPU2
  - NPU3
  - HDS
  - KTU
- Catalytic Reforming
  - CRU2
  - CRU3
- Isomerization
  - ISOU
Bangchak Model
Hydrotreating

• The purpose of hydrotreating is to remove undesired impurities from the stream
  – Sulfur
  – Nitrogen
  – Basic Nitrogen
  – Aromatics
Hydrotreating Reactions

- Most common non-hydrocarbon by-products:
  - $\text{H}_2\text{S}$
  - $\text{NH}_3$
Hydrotreating PFD
Hydrotreating Model

• Langmuir-Hinshelwood kinetic rate law

• Main operating variables
  – Temperature (600-800°C)
  – Pressure (100-3000 psig)
  – H₂/HC ratio (2000 ft³/bbl)
  – Space Velocity (1.5-9.0)
    • Based on Flow Rate and Volume
Langmuir-Hinshelwood

\[ r = -k \cdot \left[ \frac{C_S \cdot C_{H_2}^{0.45}}{\left(1 + K_{H_2S} \cdot C_{H_2S}\right)^2} \right] \]

\[ k = A \cdot e^{\frac{E}{R \cdot T}} \]

\[ K_{H_2S} = 41769.84 \cdot e^{\frac{2761}{R \cdot T}} \]

Where,
- \( k \) = rate constant
- \( K_{H_2S} \) = adsorption equilibrium constant
- \( A \) = Arrhenius constant
- \( E \) = activation energy
HDS Inputs

- **Variables**
  - Temperature
  - Pressure
  - Flow Rate

- **Data**
  - Sulfur weight percent*
  - $\text{H}_2$/HC ratio (2000 ft$^3$/bbl)
  - Sizing constant (1.8E8)

*Sulfur weight percent is set as a constant due to small effect on percent conversion and specifying too many variables in the overall model causes non-convergence
Excel Model

[Image of an Excel spreadsheet with various calculated values and formulas.]
Catalytic Reforming

• Process used to increase the octane number of light crude fractions
• Converts low-octane naptha into high-octane aromatics
• High octane product is useful for creating premium gasolines
• Hydrogen is the by-product
Catalytic Reforming
Process Flow Diagram
Catalytic Reforming Unit Operating Conditions

- Low pressures (30-40 atm)
- High Temperatures (900-950 °F)
- Feedstock – Heavy naphtha from hydrotreating unit
- Catalyst – Platinum bi-function catalyst on Alumina support
- Continuous process – Catalyst is removed, replaced, and regenerated continuously and online
Catalytic Reforming Model

- **Model Purpose**
  - Predict the output of system through simplified inputs
  - Optimal Operating Parameters = Maximum Yield and Profit

- **Model Method**
  - Differential equations with changeable input parameters

- **Model Challenges**
  - Complicated components (pseudo)
  - Extreme operating conditions
  - Complicated reactions
Catalytic Reforming Model

• Input Parameters
  – Temperature
  – Pressure
  – Volumetric Flowrates
  – Component Composition (Mole %)
    • Napthenes
    • Paraffins
    • Aromatics

• Output Parameters
  – Reformate
  – Hydrogen
  – Liquefied Petroleum Gas
Catalytic Reforming Components

- **Paraffins**
  - Straight chain hydrocarbons
  - Highest H:C ratio

- **Napthenes**
  - Cyclic hydrocarbons
  - Medium H:C ratio

- **Aromatics**
  - Cyclic hydrocarbons
  - Lowest H:C ratio
Catalytic Reforming Reactions

- Dehydrogenation
- Isomerization
- Aromatization
- Hydrocracking
Catalytic Reforming Model

- Simplified Reactions and Equations from Smith (1959)
- Modeled Reactions
  - Dehydrogenation, Cyclization, Aromatization, and Hydrocracking

\[
\begin{align*}
(1) & \text{Napthenes} & \leftrightarrow & \text{aromatics} + 3 \times H_2 \\
(2) & \text{Paraffins} & \leftrightarrow & \text{napthenes} + H_2 \\
(3) & \text{Hydrocracking of paraffins} \\
(4) & \text{Hydrocracking of napthenes}
\end{align*}
\]
Catalytic Reforming Stoichiometry

(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) $C_nH_{2n} + \frac{n}{3}H_2 \rightarrow \frac{n}{15}C_1 + \frac{n}{15}C_2 + \frac{n}{15}C_3 + \frac{n}{15}C_4 + \frac{n}{15}C_5$

Where $n$ is the number of carbon atoms.
Catalytic Reforming
Empirical Kinetic Model

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

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

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

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

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

\[-\tilde{r}_1 = \tilde{k}_{p_1} \left( P_N - \frac{P_A * P_H^3}{K_{p_1}} \right) \Rightarrow \frac{\text{moles}_\text{napthene}_\text{converted}_\text{to}_\text{aromatics}}{(hr)(lb\_cat.)} \]

\[-\tilde{r}_2 = \tilde{k}_{p_2} \left( P_N * P_H - \frac{P_P}{K_{p_2}} \right) \Rightarrow \frac{\text{moles}_\text{napthene}_\text{converted}_\text{to}_\text{paraffins}}{(hr)(lb\_cat.)} \]

\[-\tilde{r}_3 = \tilde{k}_{p_3} \left( \frac{P_P}{P} \right) \Rightarrow \frac{\text{moles}_\text{paraffins}_\text{converted}_\text{by}_\text{hydrocracking}}{(hr)(lb\_cat.)} \]

\[-\tilde{r}_4 = \tilde{k}_{p_4} \left( \frac{P_N}{P} \right) \Rightarrow \frac{\text{moles}_\text{napthenes}_\text{converted}_\text{by}_\text{hydrocracking}}{(hr)(lb\_cat.)} \]
## Excel Model

### Partial Flowrates

<table>
<thead>
<tr>
<th>#</th>
<th>W (lb cat.)</th>
<th>V (vol %)</th>
<th>VPAR (vol %)</th>
<th>L (ft)</th>
<th>T (Torr)</th>
<th>T (°C)</th>
<th>F (lb/h)</th>
<th>T (lb/h)</th>
<th>F (lb/h)</th>
<th>T (lb/h)</th>
<th>F (lb/h)</th>
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<td>78.8475365</td>
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<td>61.741631</td>
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<td>17.417594</td>
<td>78.8475365</td>
<td>61.741631</td>
</tr>
</tbody>
</table>

### Additional Details

- **Input Calculations Output Results Ranges**

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NOTE: This Excel model is designed to simulate the partial flowrates in a catalytic reforming process. The table above shows the input parameters and output results, including VPAR, V (vol %), L (ft), T (Torr), T (°C), F (lb/h), and T (lb/h).
# Excel Model

## Rate of Reaction

| Time (s) | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | W | X | Y | Z |
| 0       | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1       | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

## Rate Constants

| Time (s) | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | W | X | Y | Z |
| 0       | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1       | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

## Equilibrium Constants

| Time (s) | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | W | X | Y | Z |
| 0       | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1       | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
GAMS Model
Catalytic Reforming Model Results

- Increased Temperature Dependence
  - Endothermic reactions
  - Increase rate constant
  - Increase equilibrium constant
  - Increase concentration of aromatics
Catalytic Reforming Model Results

- Decreased Pressure Dependence
  - Increase overall reaction rate for hydrocracking
  - Increases concentration of aromatics
Isomerization

- Gas-phase catalyzed reaction
- Transforms a molecule into a different isomer
- Transforms straight chained isomers into branched isomers
- Increases octane rating of gasoline
Isomerization Unit

- 2 types of catalysts most commonly used
  - Platinum/chlorinated alumina
  - Platinum/zeolite
Isomerization Unit

• Feeds
  – Butanes
  – Pentanes
  – Hexanes
  – Small amounts Benzene
  – Make-up Hydrogen

• Products
  – Branched alkanes
Isomerization Unit

- Feed to isomerization
- H₂ make up to isomerization
- H₂ recycle from stabilization to isomerization
- Fuel gas to stabilization
- H₂ recycle from deisohexanizer to stabilization
- Isomerate from deisohexanizer
Isomerization

Diagram showing a process flow with labeled components such as Reactors, Dryer, Stabilizer, Make-up Hydrogen, Recycle Gas, Gas to Scrubbing and Fuel, Deisohexanizer, and Isomerate.
Isomerization Model

• Goal
  – To create a model that determines the products of the isomerization unit

• Model inputs
  – Temperature (range depends on catalyst used)
  – Mass flow rate
  – H₂/HC ratio (typical values 0.1-4)
  – Feed stream concentrations

• Model outputs
  – Product weight percents
Isomerization Model

• Modeling
  – Determine feed partial pressures
  – N-Butane kinetic model
  – N-Pentane kinetic model
  – N-Hexane kinetic model
Isomerization – Partial Pressures

• Antoine Equation
  – $\log_{10} P_o = A - B/(T+C)$
  – $T =$ temperature in ºC
  – $P_o =$ vapor pressure in mmHg

• Partial Pressure
  – Used to determine mole fraction each component
Isomerization – N-Butane Model

• Bursian (1972)

\[ r_{nC4} = -K_1 \frac{P_{nC4}}{P_{H2}} + K_2 \frac{P_{iC4}}{P_{H2}} \]

\[ K = A e^{\frac{-E}{RT}} \]

<table>
<thead>
<tr>
<th>N-Butane</th>
<th>E (J/mol)</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>58615.2</td>
<td>3973362</td>
</tr>
<tr>
<td>K2</td>
<td>66988.8</td>
<td>25296143</td>
</tr>
</tbody>
</table>
Isomerization - N-Pentane Model

- Aleksandrov (1976)

\[ K_{eq} = e^{\frac{1861 - 1.299}{R}} \]

<table>
<thead>
<tr>
<th>n-pentane</th>
<th>E (kcal/mol)</th>
<th>E (J/mol)</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>10.1</td>
<td>42.2887</td>
<td>4023.872</td>
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<tr>
<td>K2</td>
<td>119.5</td>
<td>500.3465</td>
<td>7331.974</td>
</tr>
</tbody>
</table>

\[ r_{nC5} = -[K_2\left(\frac{C_{nC5}}{H_2}\right)^{0.125} \cdot -0.0000197t][K_{eq}C_{nC5} - (K_{eq} + 1)C_{iC5}] \]
Isomerization - N-Hexane Model

- Cheng-Lie (1991)

\[
\frac{dC_i}{dt} = -\left( \sum_{j=1}^{5} K_{j,i} \right) \cdot C_i + \sum_{j=1}^{5} K_{i,j} C_j
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
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<tbody>
<tr>
<td>n-Hexane</td>
<td>1</td>
</tr>
<tr>
<td>3-MP</td>
<td>2</td>
</tr>
<tr>
<td>2-MP</td>
<td>3</td>
</tr>
<tr>
<td>2,3-DMB</td>
<td>4</td>
</tr>
<tr>
<td>2,2-DMB</td>
<td>5</td>
</tr>
</tbody>
</table>
Isomerization Model

• Rate equations solved using finite integration
• Output - concentrations of various isomers in product stream
### Isomerization Model - Excel

#### Inputs

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>Inlet Mass Flow Rate</th>
<th>Pressure (atm)</th>
<th>Volume (l)</th>
<th>Octane</th>
<th>Time (sec)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4800000</td>
<td>16500</td>
<td>28.6050487</td>
<td>71745.30822</td>
<td>81.69866</td>
<td>300</td>
<td>5</td>
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</tbody>
</table>

#### Feed Components

<table>
<thead>
<tr>
<th>Component</th>
<th>wt%</th>
<th>MW</th>
<th>moles</th>
<th>mole fraction</th>
<th>Concentration (g)</th>
<th>Partial Pressure (atm)</th>
<th>Feed Values</th>
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<tbody>
<tr>
<td>n-C4</td>
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<td>50.08</td>
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<td>0.060</td>
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<tr>
<td>n-Pentane</td>
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<td>0.195934</td>
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<td>0.116</td>
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<td>0.042857</td>
<td>0.11610</td>
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<tr>
<td>Dimethyl-2,2-Butane</td>
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<td>65.18</td>
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<td>0.000</td>
<td>0.00000</td>
<td>0.000001</td>
<td>0.00000</td>
</tr>
<tr>
<td>i-C8</td>
<td>0.0</td>
<td>118.80</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00000</td>
<td>0.000001</td>
<td>0.00000</td>
</tr>
<tr>
<td>2-Methyl-2-Cyclohexane</td>
<td>2.8</td>
<td>94.16</td>
<td>0.064</td>
<td>0.006</td>
<td>0.06420</td>
<td>0.004193</td>
<td>0.00641</td>
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<tr>
<td>Cyclohexane</td>
<td>0.4</td>
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<td>0.002</td>
<td>0.01810</td>
<td>0.000109</td>
<td>0.00181</td>
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<tr>
<td>Benzene</td>
<td>1.9</td>
<td>78.11</td>
<td>0.008</td>
<td>0.001</td>
<td>0.00800</td>
<td>0.000013</td>
<td>0.00080</td>
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<tr>
<td>Sum</td>
<td>100</td>
<td>6135.298</td>
<td>1.000</td>
<td>1.000</td>
<td>1.00000</td>
<td>1.000000</td>
<td>1.00000</td>
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</tbody>
</table>

#### Conversion Processes Table 6.5

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Concentrations</th>
<th>Change in Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>15</td>
<td>0.00653948</td>
<td>0.000417</td>
</tr>
<tr>
<td>30</td>
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</tr>
<tr>
<td>120</td>
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</tbody>
</table>

#### Product Values

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Mol Fraction</th>
<th>Mass (g)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C4</td>
<td>0.00653948</td>
<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>i-C4</td>
<td>0.00653948</td>
<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>Isopentane</td>
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<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>n-Pentane</td>
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<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>Cyclopentane</td>
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<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>Dimethyl-2,2-Butane</td>
<td>0.00653948</td>
<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>2,3-Dimethyl-Butane</td>
<td>0.00653948</td>
<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>2-Methyl-2-Pentane</td>
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<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>3-Methyl-Butane</td>
<td>0.00653948</td>
<td>0.000417</td>
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</tr>
<tr>
<td>i-C8</td>
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<td>0.000417</td>
<td>0.00653948</td>
</tr>
<tr>
<td>2-Methyl-2-Cyclohexane</td>
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<td>0.000417</td>
<td>0.00653948</td>
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<tr>
<td>Cyclohexane</td>
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<td>Benzene</td>
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<td>0.000417</td>
<td>0.00653948</td>
</tr>
</tbody>
</table>
Isomerization Model Results

- **Temperature Increase**
  - Pt/Chlorinated Alumina 120-180°C
  - Pt/Zeolite 250-270°C
Isomerization Model Results

• $\text{H}_2/\text{HC}$ Ratio increase
  – Range 0.1-4

![Octane # vs. H2/HC graph](image-url)
Modeling Unit Operations

- Excel
  - Excel is not used for overall model due to the problem being too complex for Excel’s Solver
- CPLEX
  - CPLEX is a MIP mathematical optimization program
- GAMS
  - User interface for CPLEX
Option #1 (NLP)

- Model each unit in Excel
- Transfer to GAMS (NLP)
- Add NLP directly into GAMS model
Option #1 (NLP)

• Problems
  – Non-linearities in overall model create difficulty to determine global optimum
  – Added one unit (HDS)
    • Overall model converged
    • GRM changed (because operating costs were added)
    • Recommendations remained the same
  – Added second unit (NPU2)
    • Overall model did not converge

• Did Not Use
Linearization of a Non-Linear Problem

• For example, a CSTR has the following equations:

\[
X = \frac{V \cdot (-r_A)}{F_{A0}}
\]

\[
-r_A = k \cdot C_A^{0.5} \cdot C_B^2
\]

\[
k = k_0 \cdot e^{-\frac{E}{R \cdot T}}
\]

• X can be shown as a function of the input variables:

\[
X = f(T, C_{A0}, C_{B0})
\]
Linearization of a Non-Linear Problem

• To linearize, discretize the input variables
  – Where Z is a binary variable

\[
X = \sum_{(T, C_{A0}, C_{B0})} Z(T, C_{A0}, C_{B0}) \cdot f(T, C_{A0}, C_{B0})
\]

\[
\sum_{(T, C_{A0}, C_{B0})} Z(T, C_{A0}, C_{B0}) = 1
\]

\[
X = \frac{V \cdot (-r_A)}{F_{A0}} \quad -r_A = k \cdot C_A^{0.5} \cdot C_B^2 \quad k = k_0 \cdot e^{-\frac{E}{R \cdot T}}
\]
Non-Linearities in Unit Operations

• CSTR

\[ X = \frac{V \cdot (-r_A)}{F_{A0}} \quad -r_A = k \cdot C_A^{0.5} \cdot C_B^2 \quad k = k_0 \cdot e^{\frac{-E}{R \cdot T}} \]

• Catalytic Reformer

\[ \hat{k}_{p2} = \exp\left(35.98 - \frac{59600}{T}\right) \quad \hat{k}_{p3} = \hat{k}_{p4} = \exp\left(42.97 - \frac{62300}{T}\right) \quad \hat{k}_{p1} = \exp\left(23.21 - \frac{34750}{T}\right) \]

\[ K_{p2} = \frac{P_p}{P_N \cdot P_H} \quad K_{p1} = \frac{P_A \cdot P_H^3}{P_N} \]

\[ -\hat{r}_1 = \hat{k}_{p1} \left( P_N - \frac{P_A \cdot P_H^3}{K_{p1}} \right) \]

\[ -\hat{r}_2 = \hat{k}_{p2} \left( P_N \cdot P_H - \frac{P_p}{K_{p2}} \right) \]

\[ -\hat{r}_3 = \hat{k}_{p3} \left( \frac{P_p}{P} \right) \quad -\hat{r}_4 = \hat{k}_{p4} \left( \frac{P_N}{P} \right) \]
Option #2 (MIP)

- Take Excel model
- Write MIP utilizing table of possible variables
- Add MIP directly into GAMS model
Option #2 (MIP)

- Did not attempt to use
  - Overall model would theoretically work
  - Model would become extremely long
  - Would require more memory and resources
  - Less user friendly than option #3
Option #3 (MIP Brute Force)

- Take Excel model
- Model MIP in GAMS
- Have MIP write to an overall table
- Utilize binary variables in overall model to select variables based on the table and constraints
\[ X = \sum_{(T, C_{A0}, C_{B0})} Z(T, C_{A0}, C_{B0}) \cdot X(T, C_{A0}, C_{B0}) \]

<table>
<thead>
<tr>
<th>T</th>
<th>C_{A0} =</th>
<th>0.50 mol/L</th>
<th>0.55 mol/L</th>
<th>0.60 mol/L</th>
<th>0.65 mol/L</th>
<th>0.70 mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 F</td>
<td>0.92 mol/L</td>
<td>0.74</td>
<td>0.22</td>
<td>0.75</td>
<td>0.54</td>
<td>0.93</td>
</tr>
<tr>
<td>500 F</td>
<td>0.94 mol/L</td>
<td>0.10</td>
<td>0.39</td>
<td>0.79</td>
<td>0.32</td>
<td>0.38</td>
</tr>
<tr>
<td>500 F</td>
<td>0.96 mol/L</td>
<td>0.72</td>
<td>0.70</td>
<td>0.06</td>
<td>0.28</td>
<td>0.22</td>
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<tr>
<td>500 F</td>
<td>0.98 mol/L</td>
<td>0.54</td>
<td>0.57</td>
<td>0.53</td>
<td>0.24</td>
<td>0.22</td>
</tr>
<tr>
<td>500 F</td>
<td>1.00 mol/L</td>
<td>0.91</td>
<td>0.41</td>
<td>0.80</td>
<td>0.66</td>
<td>0.97</td>
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<tr>
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<td>0.70</td>
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<td>0.79</td>
<td>0.58</td>
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<tr>
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<td>0.86</td>
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<td>600 F</td>
<td>1.00 mol/L</td>
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<td>0.00</td>
<td>0.62</td>
<td>0.69</td>
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<td>0.85</td>
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<tr>
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<tr>
<td>700 F</td>
<td>0.96 mol/L</td>
<td>0.83</td>
<td>0.45</td>
<td>0.46</td>
<td>0.54</td>
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</tr>
<tr>
<td>700 F</td>
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<td>0.94</td>
<td>0.43</td>
<td>0.69</td>
<td>0.25</td>
<td>0.88</td>
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<tr>
<td>700 F</td>
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<td>0.01</td>
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<td>0.26</td>
<td>0.07</td>
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<tr>
<td>800 F</td>
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<td>0.25</td>
<td>0.64</td>
<td>0.55</td>
<td>0.40</td>
<td>0.68</td>
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<tr>
<td>800 F</td>
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<td>0.87</td>
<td>0.14</td>
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<td>0.96</td>
</tr>
<tr>
<td>800 F</td>
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<td>0.58</td>
<td>0.37</td>
<td>0.61</td>
<td>0.71</td>
</tr>
<tr>
<td>800 F</td>
<td>0.98 mol/L</td>
<td>0.46</td>
<td>0.20</td>
<td>0.17</td>
<td>0.99</td>
<td>0.37</td>
</tr>
<tr>
<td>800 F</td>
<td>1.00 mol/L</td>
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<td>0.82</td>
<td>0.81</td>
<td>0.81</td>
<td>0.86</td>
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<tr>
<td>900 F</td>
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<td>0.39</td>
<td>0.50</td>
<td>0.57</td>
<td>0.10</td>
</tr>
<tr>
<td>900 F</td>
<td>0.94 mol/L</td>
<td>0.27</td>
<td>0.52</td>
<td>0.35</td>
<td>0.81</td>
<td>0.96</td>
</tr>
<tr>
<td>900 F</td>
<td>0.96 mol/L</td>
<td>0.71</td>
<td>0.09</td>
<td>0.63</td>
<td>0.45</td>
<td>0.03</td>
</tr>
<tr>
<td>900 F</td>
<td>0.98 mol/L</td>
<td>0.61</td>
<td>0.47</td>
<td>0.30</td>
<td>0.29</td>
<td>0.09</td>
</tr>
<tr>
<td>900 F</td>
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<td>0.35</td>
<td>0.52</td>
<td>0.84</td>
<td>0.02</td>
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</tbody>
</table>
Option #3 (MIP Brute Force)

• Currently being used
  – Offers ease of use for the overall model
  – Drawback - more files are required to run the model
    • 26 tables utilized
Specific Modeling Issues

- “Best Choice” scenario
- Mass Balance
- Blending
- Additions
“Best Choice” Scenario

- Unit operations flow rates chosen by which scenario is nearest to the actual flow rate
- Allows for degrees of freedom in crude purchasing
“Best Choice” Scenario

\[ F_{\text{overall}} - F_{\text{unit}} \leq d \]

\[ F_{\text{unit}} - F_{\text{overall}} \leq d \]

<table>
<thead>
<tr>
<th>F =</th>
</tr>
</thead>
<tbody>
<tr>
<td>15000 m³/d</td>
</tr>
<tr>
<td>16000 m³/d</td>
</tr>
<tr>
<td>17000 m³/d</td>
</tr>
<tr>
<td>18000 m³/d</td>
</tr>
<tr>
<td>19000 m³/d</td>
</tr>
</tbody>
</table>

\[ d = \frac{F_2 - F_1}{2} \]

\[ e.g. = \frac{16000 - 15000}{2} = 500 \]

- F = flow rates
- d = difference between discretized unit flow rates
Mass Balance (CRU2, CRU3, ISOU)

- Solving the mass balance (2 options)
  - \( F_{\text{overall}} = F_{\text{out}} \)
  - Requires a non-linear equation (\( Z \cdot F_{\text{overall}} \))
  - Linearization possible, but requires massive amounts of memory (takes the program a long time to run)
Linearization of $Z^*F_{\text{overall}}$

\[
\Gamma(a,b,c) - x \cdot Z(a,b,c) \leq 0
\]
\[
\Gamma(a,b,c) \geq 0
\]
\[
(F_{\text{overall}} - \Gamma(a,b,c)) - x \cdot (1 - Z(a,b,c)) \leq 0
\]
\[
F_{\text{overall}} - \Gamma(a,b,c) \geq 0
\]

\[
x = 1 \cdot 10^{10}
\]

where \[
\sum_{(a,b,c)} \Gamma(a,b,c) = \sum_{(a,b,c)} Z(a,b,c) \cdot F_{\text{overall}}
\]
Mass Balance (CRU2, CRU3, ISOU)

• Successful solution
  – Advantage - requires far less memory
  – Disadvantage - mass is not completely balanced
  • Model not based on mass flow rates
  • Volumetric balances are inexact
  • If large amount of flow rate scenarios used, the error is minimized
    – Large amounts of scenarios does not slow down model

\[ F_{\text{reformate,out}} = F_{\text{reformate,unit}} \]
Blending Model

\[ F_a \cdot ON_a + F_b \cdot ON_b + F_c \cdot ON_c \geq F_{tot} \cdot ON_x \]

\( x = ISOG, SUPG \)

\( ON_{SUPG} = 91 \)

\( ON_{ISOG} = 95 \)

- \( ON_a \) dependant on \( Z \), therefore \( Z*F \) appears again
  - Linearization used (only 3 required this time)
Linearization of $Z^*F_{\text{overall}}$

$$
\Gamma(a,b,c) - x \cdot Z(a,b,c) \leq 0
$$

$$
\Gamma(a,b,c) \geq 0
$$

$$
(F_{\text{overall}} - \Gamma(a,b,c)) - x \cdot (1 - Z(a,b,c)) \leq 0
$$

$$
F_{\text{overall}} - \Gamma(a,b,c) \geq 0
$$

$$
x = 1 \cdot 10^{10}
$$

where

$$
\sum_{(a,b,c)} \Gamma(a,b,c) = \sum_{(a,b,c)} Z(a,b,c) \cdot F_{\text{overall}}
$$
Additions

• Revised Fuel Balance
  – Fuel Gas and Fuel Oil burned
• Added Operating Costs associated with compression
• Added Hydrogen Balance
Results

• Executed using CPLEX
  – Approximately 50 minutes to reach integer solution
  – Approximately 2 hours to reach optimal solution
It Works!
Over $1 \times 10^{16}$ combinations of operating conditions
Planning

• Currently planning is optimized and then unit operations are optimized

• Planning is highly dependent on unit operations
  – e.g. turnarounds, unit capacities
Results

• GRM has increased
  – Optimizing unit operations is more efficient

<table>
<thead>
<tr>
<th></th>
<th>GRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model without Unit Operations</td>
<td>$16,492,336.72</td>
</tr>
<tr>
<td>Model with Unit Operations</td>
<td>$34,130,901.06</td>
</tr>
</tbody>
</table>
## Results

- Purchased crudes and intermediates

### Model without Unit Operations

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oman (OM):</td>
<td>167734.3</td>
<td>167339.3</td>
<td>165082.6</td>
</tr>
<tr>
<td>Tapis (TP):</td>
<td>13427.7</td>
<td>14317</td>
<td>19397.5</td>
</tr>
<tr>
<td>Labuan (LB):</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Seria Light (SLEB):</td>
<td>95392.2</td>
<td>95392.2</td>
<td>95392.2</td>
</tr>
<tr>
<td>Phet (PHET):</td>
<td>57235.3</td>
<td>57235.3</td>
<td>57235.3</td>
</tr>
<tr>
<td>Murban (MB):</td>
<td>95392.2</td>
<td>95392.2</td>
<td>95392.2</td>
</tr>
<tr>
<td>MTBE:</td>
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<td>13700.7</td>
<td>13921.7</td>
</tr>
<tr>
<td>DCC:</td>
<td>68088</td>
<td>68301.8</td>
<td>69523.2</td>
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### Model with Unit Operations

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oman (OM):</td>
<td>244486.2</td>
<td>262303.1</td>
<td>267899.8</td>
</tr>
<tr>
<td>Tapis (TP):</td>
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<td>41126.2</td>
<td>47392.2</td>
</tr>
<tr>
<td>Labuan (LB):</td>
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<td>0</td>
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<tr>
<td>Seria Light (SLEB):</td>
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<td>95392.2</td>
<td>95392.2</td>
</tr>
<tr>
<td>Phet (PHET):</td>
<td>57235.3</td>
<td>57235.3</td>
<td>57235.3</td>
</tr>
<tr>
<td>Murban (MB):</td>
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<td>95392.2</td>
<td>95392.2</td>
</tr>
<tr>
<td>MTBE:</td>
<td>18266</td>
<td>19392.8</td>
<td>20404.2</td>
</tr>
<tr>
<td>DCC:</td>
<td>87059.5</td>
<td>91153.7</td>
<td>93941.2</td>
</tr>
</tbody>
</table>
Results
Discussion

Reformer Sensitivity

- Varying Flow (15-25 Mm3/day)
- Varying Pressure (400-800 psi)
- Varying Temperature (800-980 °F)

Octane Number

- Linear (Varying Flow (15-25 Mm3/day))
- Poly. (Varying Pressure (400-800 psi))
- Poly. (Varying Temperature (800-980 °F))
Discussion

• Optimizing unit operations adds another dimension to optimize refinery processing

• Can provide more thorough insight for decision making
Acknowledgments

- Dr. Miguel Bagajewicz
- DuyQuang Nguyen
- Mike Mills

- Sunoco Refinery (Tulsa, OK)
  - John Paris
Please, No Questions!

....Just Kidding