# REFINERY OPERATIONS

# PLANNING

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**05/08/2009**

**Executive Summary**

This report summarizes the use of a linear programming model used to optimize refinery crude oil purchasing while meeting a specific uncertain demand. The model was optimized by maximizing the gross refinery margin (GRM). The model includes catalytic reforming units, naphtha pre-treating units, a kerosene treating unit, a hydrodesulfurization unit, and an isomerization unit.

This base of the model is an LP model which was developed to model the Bangchak Refinery. The model incorporates uncertainty into the demand of refinery products and the purchase price of six available types of crude oil (Oman, Tapis, Labuan, Seria Light, Phet, and Murban).

The LP model is made even better by accounting for refinery utility cost, hydrogen production, and refinery fuel gas production. These inclusions allow the model to reflect the cost of operating at certain conditions. The model also gives a more accurate representation of the GRM function since the cost of utilities has been taken into account.

When compared with commonly-used industrial software, the LP model in GAMS is able to test a variety of operating variables to find a gross refinery margin value near the global optimum. Industrial software operates on a successive linear programming principle, which depends on the starting point of the solver. This can lead to industrial software finding only a local optimum.

Compared to the model without utilities, the LP utility model gives a larger gross refinery margin. While the model takes utility cost into account, it is still able to optimize the use of each unit in the refinery, increasing the total throughput for each time period evaluated.

Using the basic linear Bangchak Refinery model in GAMS, it was shown that the results of a successive linear programming (SLP) method depend on the starting point selected. Different initial conditions resulted in different stream output values.

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**Introduction**

A refinery is composed of many different unit processes and unit operations that are used to separate crude oil into products of value. In recent times, energy prices have fluctuated. Therefore, refineries are looking for ways to increase profits and margins and at the same time meet the demanding market. Changing market demands make refinery planning very difficult to handle. Therefore, refinery planning is needed to achieve profits. The selection of crudes to purchase is very important, since different crudes yield a different palate of optimum products. Examples of crudes are Labuan, Oman, Tapis, Seria Light, Phet, and Murban. The quality of crude to purchase and how much a refinery wants to produce are also important for refinery planning. The aim of this project is to focus on production in refining. This will be achieved by analyzing how each of the units operates and modeling using GAMS.

Refinery planning is an important part of refinery operations and is used in order to achieve maximum profit and satisfy market demands. With growing demand for petroleum products, increasing crude oil costs, and new environmental emissions limits, production planning has become the key to maintaining refinery margins. However, crude oil contains different hydrocarbons and other impurities, which makes modeling reactions difficult. Therefore, modeling methods such as the deterministic model have been developed to aid in refinery planning. The deterministic model was developed by Pinto and Moro and it models the units from crude oil distillation to blending (Aleskandrov). Existing Linear Programming methods consider each unit as a black box and do not consider the operating conditions of each unit in the refinery. However, our proposed model: global optimization discrete, takes into account the operating conditions of each unit, and how these change the specific products. In addition, utilities are accounted for in this model, making it a more accurate representation of the refinery processes and gross refinery margin calculation.

The Bangchak refinery, which can be seen in Figure 1, was developed by Pongsakdi et al (Pongsakdi). This is the refinery that will be used for the project. It has eight units: two distilling, two naphtha pretreating, isomerization, catalytic reforming, kerosene treating, and hydrodesulfurization. However, for this project, only the isomerization, catalytic reforming, and

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hydrotreater will be modeled. The objective is to maximize the gross refinery margin, which is the revenue minus the materials cost, operating cost and add utility cost of fuel gas consumed by heaters, and power to the whole refinery model.
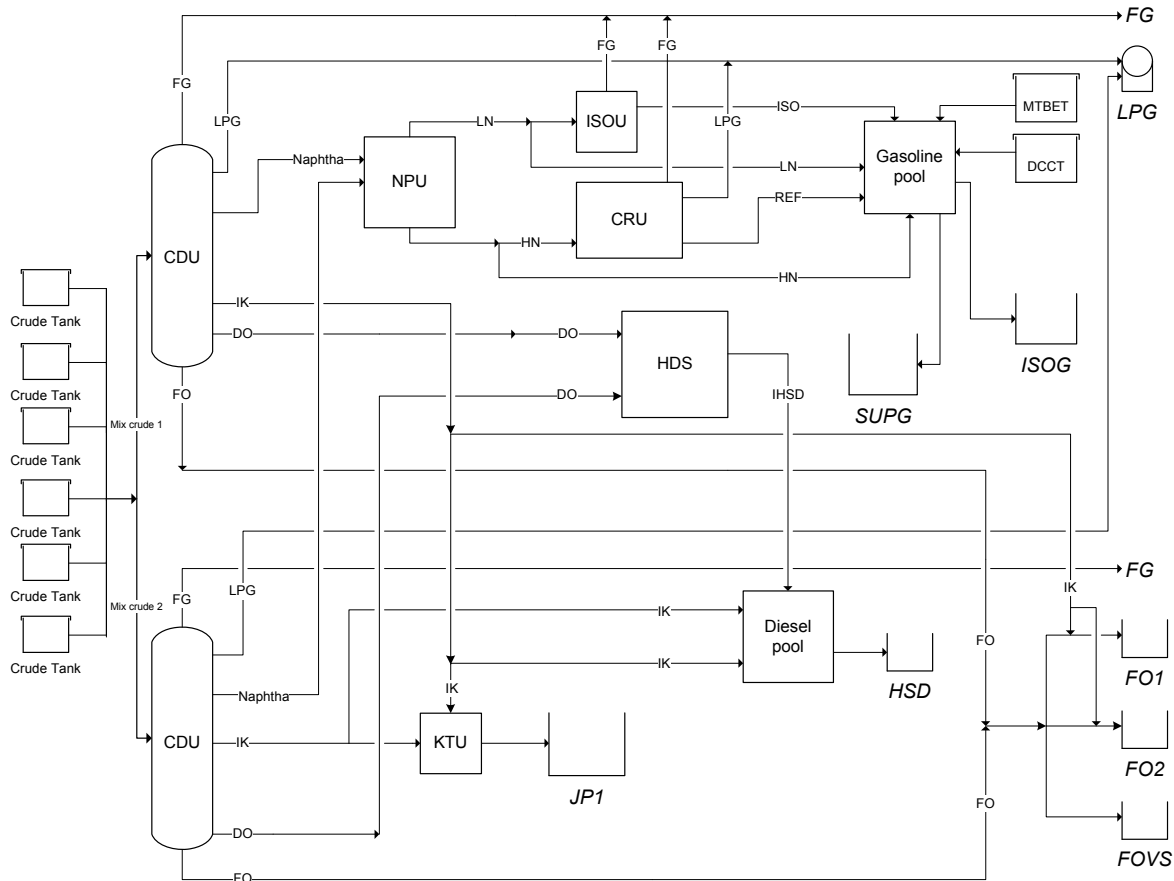


**Figure 1: Model Basis:  Bangchak Refinery, Thailand** (Bagajewicz)

## Refinery Planning

Production planning is a routine business process where purchases are commonly made on biweekly or monthly basis.  The delivery of procured crude takes time, yet those who purchase crude do not want to commit to buying specific products too far in advance for fear of changing market demand.  Also, purchase price plays a role in the acquisition of crude.  This is

coordinated between the crude oil acquisition, product sales, and refinery operations departments. The refinery operations department determines the operating rates for the various refinery units, and determine for example, if any of the process units are scheduled for planned outage during a period. The sales department estimates sales for each product in a given period of time and helps to forecast the demand for specific distillation cuts that will be required to meet those demands. Finally the refinery planner will determine the crude oils that are scheduled for delivery during a specified period.

Purchasing of crude oil depends on available crudes and the predicted demand that the refinery is supposed to meet. The predicted demand can change based on product pricing, the economy, or even the weather. For example, if a hurricane causes damage to several refineries in the gulf coast, other refineries might be able to purchase crude from these refineries at a discount.

## Available Models

Linear Programming (LP) provides a way of finding an optimal solution to a set of linear equations by minimizing or maximizing a particular variable. These equations represent the technology and economics of complex systems an oil refinery. Typical models contain between 1000 and 5000 equations. These equations are used to describe the process yields, utility requirements, and blending operations. Since most of these equations represent highly nonlinear processes, they must be made linear using careful assumptions and accurate linear equations. The most commonly used LP programs include RPMS (by Honeywell Hi-Spec Solutions), PIMS (by Aspentech), and GRMPTS (by Haverly) (Bagajewicz). These models require the input of specific process variables to create accurate equations and process values that are used in refinery modeling.

## Linear Modeling

Historically, models that have been used in refineries have been linear. The models have followed a black box approach, where the outputs were related to inputs through basic linear functions. The internal complexities of units are ignored, and models are based on simple assumptions. Outputs are often modeled as functions of input flow rate multiplied by a yield factor. These approximations simplify reaction kinetics from partial differential equations and sets of non-linear equations down to simple linear relationships. For instance, in the hypothetical reactor in Figure 2 below, the flow rate of product $F_2$ would be related to the reactor feed by a simple function such as:

$$F_2 = \alpha_{2,1} * F_1$$ Eq. 1

Where $\alpha_{2,1}$ is a conversion factor. This allows the model to operate using simple, linear equations. What this type of model gains in simplicity, it loses in accuracy. Reactors often contain hundreds of different hydrocarbons undergoing many reactions at a wide range of temperatures and pressures. A simplified conversion factor cannot accurately account for multiple components undergoing multiple reactions for all conditions.
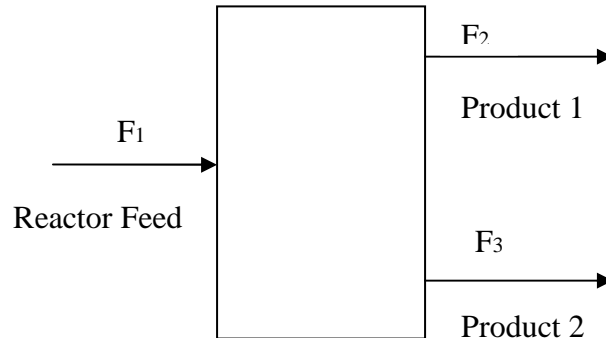


**Figure 2: Hypothetical reactor with 2 products and 1 feed stream.**

Using programs such as AspenTech's PIMS to obtain similar purchasing forecasts requires that the user have access to many specific operating parameters of the units being modeled. In GAMS, utility functions are modeled as linear functions of throughput. Rather than using simple generated numbers of utility usage per unit flow, heat balance equations were used. These equations were solved using the specific unit properties and flow values. This reduces the

accuracy of the utility equations for a specific process, but allows them to be easily adapted to fit a dynamic refinery model. The ranges of the operating variables used in this model are guided by petroleum refining literature.

The modeling method used for the Linear Models in GAMS is to create a table of values which contain some information about the way a function output is related to multiple function inputs, instead of a conversion factor alpha. This can be done by creating a multi-dimensional table that allows multiple variables to be altered for a calculation to create an output that is valid over a range of multiple variables. This table is then read by the model and the appropriate value is selected and used in the model. This allows more complex (often non-linear) equations to be used in a linear model.

## Linearity vs. Non-linearity

Historically, models that have been used in refineries have been linear. The models have followed the black box theory where only the inputs and outputs were accounted for. The black box theory uses average operating conditions to calculate output data. This project however, is aimed at modeling the units by allowing nonlinearities, and therefore, making the overall model accurate. Equations 15 and 16 are examples of the kerosene pretreating unit—showing the degree of nonlinearity.

$$F_{ar} = \alpha_1 F_{total} \qquad\qquad \text{Eq.2}$$

$$F_{ar} = fo + W * LHSV * \frac{\left(\dfrac{1000*P}{R*T}\right)}{F_{total}} * \left(\dfrac{1000*P}{R*T}\right) * \left(\dfrac{885000}{F_{total}}\right) \qquad\qquad \text{Eq. 3}$$

Where $F_{ar}$ is the flowrate of aromatics, $\alpha_1$ is alpha, $F_{total}$ is the total flowrate, $f_o$ is the initial flowrate, W is the weight of the catalyst, LHSV is liquid hourly space velocity, P is pressure, R is the gas constant and T is temperature.

Modeling the units is done out by breaking down the units into the products as a function of temperature, flowrate and pressure. This is the most accurate method of approach to modeling

unit operations because of its completeness. Utilizing multiple nonlinear unit models makes it impossible to find the global optimum.

The solution to nonlinearities is to linearize. This is done by discretizing the variables of the units. Discretizing the variables achieves linearity since it is variables existing in nonlinearities that create the problems. The discretization of the variables changes equation 17 into the following form:

$$X = f(T,F,P)$$
<div align="right">Eq.4</div>

$$X = \sum Z(T,F,P) * f(T,F,P)$$
<div align="right">Eq.5</div>

Where Z (a,b,c) is a binary variable that is used to choose the operation conditions. This reduces all variables present to zero, and therefore the model is run as a mixed integer program.

A multi dimensional table was created X(a,b,c). This table was then uploaded into the model and equation 5 changed to equation 6 below.

$$X = \sum Z(T,F,P) * X(T,F,P)$$
<div align="right">Eq.6</div>

Galiasso determined that there were reaction orders for the removal of nitrogen, and aromatics. Below are the ordinary differential equations that show the rate of removal of the components based on their concentrations.

$$r_N = \frac{dC_N}{dW} = k_N C_N^{1.4} C_{H_2}^{0.6}$$
<div align="right">Eq.7</div>

$$r_{BN} = \frac{dC_{BN}}{dW} = k_{BN} C_{BN}^{1.2} C_{H_2}^{0.5}$$
<div align="right">Eq. 8</div>

$$r_{Ar} = \frac{dC_{Ar}}{dW} = k_{Ar} C_{Ar} C_{H_2}$$
<div align="right">Eq. 9</div>

## Utility Modeling

The existing LP refinery model did not take into account the effect of utility demand on gross refinery margin (GRM).  The utility cost amounts to a significant percentage of the total operating cost for a refinery.  Including the cost of utilities in the model provides more accurate results, even if the resulting GRM is less than that for the model without utilities.  The inclusion of utility cost into the purchasing model should also affect the amount of each type of crude purchased.

The amount of each utility required for a unit is calculated based on specific operating conditions of temperature, pressure, and flow rate through each unit.  This method is more accurate than modeling the demand equations as linear functions of a single variable (such as flow rate) through each unit.    For example, when modeling a heat exchanger, basic equations for heat transfer are used.

For a fluid that does not undergo a phase change,

$$Q = \dot{m} C_p \Delta T \qquad \text{Eq. 10}$$

where $\dot{m}$ is the mass flow rate and $C_p$ is the specific heat of the fluid.  For a fluid that undergoes an isothermal phase change,

$$Q = \dot{m} \lambda \qquad \text{Eq. 11}$$

where $\dot{m}$ is the mass flow rate and $\lambda$ is the latent heat of vaporization/condensation.  For this model, heat exchangers are assumed to be adiabatic with their surroundings, and the heat transfer to the material of the heat exchanger itself is assumed to be negligible.  This allows us to say that the heat lost by the process stream is equal to the heat gained by the utility stream or vice versa.  Then, for steam-fed heat exchangers, we can say that:

$$steam \ use = \sum \frac{\dot{m}_p * Cp_p * \Delta T}{\lambda_{steam}} \qquad \text{Eq. 12}$$

In this model, it is assumed that when possible, utility requirements are met using

facilities located within the refinery. This includes a boiler system used to produce refinery steam. In this boiler system refinery fuel gas, fuel oils, and excess hydrogen are used as fuel in fired heaters used to create 900 pound steam.

The 900 pound steam can be fed through a turbine system to create the electricity necessary to operate refinery pumps and compressors. The steam used in this application provides 150 pound steam for use in low-pressure steam applications. Turbines were assumed to operate at 80 percent efficiency to recover the energy released when transforming steam at 900 psia to 150 psia.

Once electricity requirements in the refinery are known, the amount of steam that is needed to generate the required electricity can be found. Once the total of steam directly used in processes or as a heating medium in a heat exchanger is determined, the amount of steam necessary to supply the plant with electricity can be added to obtain the total amount of steam that must be produced in refinery boilers. Once the amount of water used as cooling water in process coolers and condensers is determined, this can be added to the water required to meet the refinery's steam requirements, and the total amount of water required by the refinery can be determined. The utility cost can then be calculated using values obtained from <u>Petroleum Refining</u> (Gary, 25).

| Utility Cost | |
|---|---|
| Cooling Water | $0.05/1000 gal |
| | Source : Petroleum Refining by Gary et al |

**Figure 3: Utility Unit Cost**

Compressor and pump work was calculated using Pro-II software. The amount of required work was divided by the flow rate of the stream to obtain the unit work required for the specific stream composition. The Bernoulli equation is used to calculate the required pressure differential between the discharge and suction sections of the compressor. Using this work,

power can be calculated as a function of flow rate:

$$power\ use = \sum \frac{F_T * W_{F_T}}{\eta}$$ 

Eq. 13

In fuel gas calculations, the heat taken from burning fuel gas is modeled as a flow rate times a $\Delta H_{combustion}$ per unit amount of fuel gas. This value is calculated by modeling the combustion in a Gibbs Reactor using a vapor stream with equal $H_2$ and $C_1$-$C_5$ mass fractions. Fuel gas usage can then be related to refinery throughput by:

$$fuel\ gas\ usage = \sum \frac{\dot{m}_p * Cp_p * \Delta T}{\Delta H_{fg}}$$ 

Eq. 14

According to the <u>Refining Process Handbook</u>, about 10% of the refined crude ends up being used as refinery fuel gas. This provides the refinery with a large energy source to burn for use in fired heaters and steam boilers.

The maximum hot return temperature for cooling water is assumed to be 182°F, selected so the cooling water is not too near its boiling temperature. The minimum temperature for provided cooling water is assumed to be 80°F. The specific heat of water was assumed to be independent of temperature. The values were taken from property tables in Perry's Chemical Engineers' Handbook.

For cooling water processes involving condensation, the process stream was modeled in Pro-II as being cooled by an adiabatic, utility-driven heat exchanger. The operating specification was that the process stream liquid fraction be equal to 1 at the outlet. The total usage of refinery cooling water in heat exchangers results from the combination of all cooling and condensation processes as:

$$water\ cost = \sum_{coolers} \frac{\left(\frac{\$}{lb}\right) * \dot{m}_p * Cp_p * \Delta T_p}{\Delta T_w * Cp_w} + \sum_{condensers} \frac{\left(\frac{\$}{lb}\right) * \dot{m}_p * \lambda_{vap}}{\Delta T_w * Cp_w}$$ 

Eq. 15

Combining this usage with the water required to produce process steam as well as to produce

electricity gives the total water consumption of the refinery.

## Catalytic Reforming

Catalytic reforming processes produce a product called reformate.   The reformate is used as an additive in blending to create high octane gasoline.   The reactors operate at high temperatures (900 to 950°F) and pressures of 30 to 40 atm.
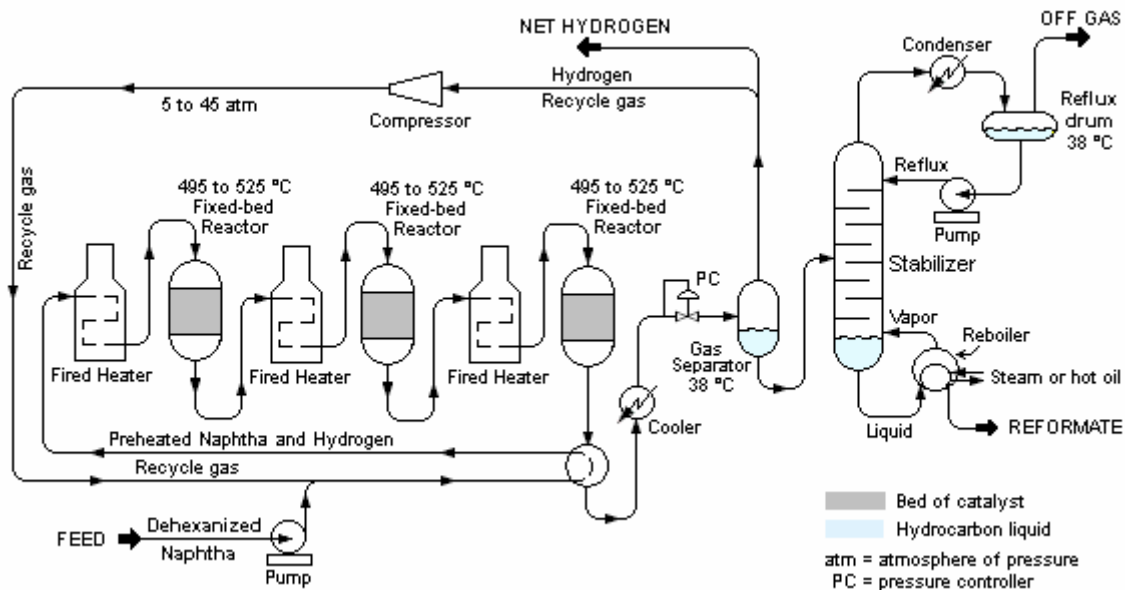


**Figure 4: Typical Reformer Process** [Leprince]

## Kinetic Modeling

The kinetic relationships that were used by Bagajewicz et al.  to model the catalytic reforming units in a mixed-integer program (Bagajewicz) are in very non-linear forms and make the current GAMS model a mixed-integer programming (MIP) model.  These equations need to be linearized and included in the LP model.

## Utility Model Development

A utility model was developed which calculates steam usage, electricity usage, and water usage as functions of temperature, pressure, initial stream composition, and flow rate. These utility demands and costs were calculated using Microsoft Excel and were inserted into the GAMS simulation in the form of tables. In this model, the utilities are supplied from within the refinery. The demand of fuel for the steam boilers is first provided by the excess hydrogen, refinery fuel gas, and fuel oils created by the refinery, and then is supplemented as needed by purchasing additional fuel gas from outside the refinery.

An average utility model was created for comparison with the more accurate model. In this model, rather than being modeled as functions of temperature, pressure, flow rate, and initial compositions, the values of temperature, pressure, and initial composition were fixed and the utility cost for the refinery was calculated as a function of only flow rate. In this model, the utilities were all assumed to be purchased from outside the refinery. In this model, temperatures, pressures, and concentrations were selected as the median value included in modeling scenarios. These values were verified by researching typical ranges for these variables in similar equipment across the petroleum refining industry. The catalytic reforming unit reactor temperatures are around 495°F to 525°F (Gary and Handwerk). Suggested temperatures of the reflux drum and gas separator are given to be about 100°F. Using these temperatures and calculated process stream properties, the cost for steam is found by:

$$scost = \frac{\left(\frac{\$2.50}{1000\ lb}\right)*2.5*(F_T)*0.429\left(\frac{BTU}{lb\cdot °F}\right)*(381-356)F*18.01\left(\frac{lb_W}{mol}\right)*1055\left(\frac{J}{BTU}\right)*1712\left(\frac{lb_p}{m^3}\right)}{4.4733*10^7\left(\frac{J}{mol}\right)}$$ 

Eq. 16

The cost of power required in the unit is given by:

$$pcost = (\$0.04/kWh)*(F_T)*0.0029\left(\frac{HP}{\frac{lbmol}{hr}}\right)*.0027\left(\frac{HP}{\frac{lbmol}{hr}}\right)*.7545\left(\frac{kW}{HP}\right)*1712\left(\frac{lb_p}{m^3}\right)$$ 

Eq. 17

The cost of cooling water used in the reformer unit's cooler and condenser are calculated as:

$$wcost = \frac{\left(\frac{\$0.05}{1000\ gal}\right)*(F_T)*16\left(\frac{BTU}{lb*°F}\right)*(920-100)°F*1712\left(\frac{lb}{m^3}\right)*1055.06\left(\frac{J}{BTU}\right)*2.16\left(\frac{gal}{mol}\right)}{(182-60)°F*8.277*10^4\left(\frac{J}{mol*K}\right)} +$$

$$\frac{\left(\frac{\$0.05}{1000\ gal}\right)*2.5*\frac{(F_T)}{2}*0.0139\left(\frac{MMBTU}{hr}\right)*2.16\left(\frac{gal}{mol}\right)*1.06*10^9\ (J/MMBTU)}{(182-60)°F*8.277*10^4\left(\frac{J}{mol*K}\right)}$$

Eq. 18

Using $C_p$ values calculated by Bagajewicz, Hill, et al in 2007 and using some Pro-II simulated process stream properties; fuel gas consumption of the three fired heaters is calculated using:

$$fguse = \frac{(F_T)*\left[18.08\left(\frac{BTU}{lb*°F}\right)*(1402-1359)K+16.93\left(\frac{BTU}{lb}°F\right)*(1402-1287)K+16.28\left(\frac{BTU}{lb*°F}\right)*(1402-1331)K\right]*1712\left(\frac{lb_p}{m^3}\right)}{\frac{0.00106MMBTU}{hr*(lbmol\ of\ FG)}*10^6\left(\frac{BTU}{MMBTU}\right)}$$

Eq. 19

Comparing the average utility model with the more accurate utility model, average monthly utility cost in the refinery was within 5 percent for the models.

For the existing MIP model developed by Bagajewicz et al in 2007, reformer reactor temperatures are modeled as being isothermal. Based on Langmuir-Hinshelwood kinetics, each reactor experiences a temperature drop. The reactors contain different weights of catalyst, which affects reaction kinetics. Also, each reactor should have a different feed temperature. The reactor beds are connected in series, so the reactors should see vastly different feed compositions and should therefore experience varying reaction rates when compared against one another. Using the calculations set forth by Bagajewicz et al, the temperature drop through each reactor bed was related to the flow sent into the unit. This allows the temperature used in the model to be averaged over the bed, providing a more accurate value for the simulation.

Reactor Temperature Profile (CRU2, CRU3)

$$T_{R1} = T_{in1} + 460 + \left[\frac{.0008*(F_T)-136.68}{2}\right] [=] °R$$

Eq. 20

$$T_{R2} = T_{in2} + 460 + \left[\frac{.0014*(F_T)-107.82}{2}\right] [=] \,^\circ R \qquad \text{Eq. 21}$$

$$T_{R3} = T_{in3} + 460 + \left[\frac{.0018*(F_T)-70.34}{2}\right] [=] \,^\text{c}R \qquad \text{Eq. 22}$$

## Hydrotreating

Hydrotreating is the process of removing sulfur, nitrogen and aromatic content of feed from process streams. These impurities can poison catalysts, foul heat transfer surfaces, and create EPA CFR40 emissions violations if they remain in the process streams that are sent to downstream units. The process stabilizes petroleum products by converting olefins to paraffin's in the presence of a catalyst and reacting them with hydrogen. Hydrotreating for sulfur is called hydrodesulfurization (Leprince).

The main hydrotreating reaction is desulfurization. Some of the desulfurization reactions can be seen below.

Desulfurization (Gary and Handwerk)

a. Mercaptans : RSH+ $H_2 \rightarrow$ RH +$H_2$S
b. Sulfides : $R_2$S +$2H_2 \rightarrow$ 2RH + $H_2$S
c. Disulfides : $(RS)_2$ + $3H_2 \rightarrow$ 2RH + $2H_2$S
d. Thiophenes : $H_4$S + $4H_2 \rightarrow C_4H_{10}$ + $H_2$S

Hydrotreating takes place on a packed bed reactor. The feed steam from the distillation column is de-aerated, mixed with hydrogen, preheated, and charged under pressure prior to entering the reactor. In the reactor, the sulfur and nitrogen compounds are converted into $H_2$S and $NH_3$. The hydrogen-rich gas from the high-pressure separation is recycled to combine with the feed stream, and the low-pressure gas stream rich in $H_2$S is sent to a gas treating stripper where $H_2$S is removed. The process flow diagram for this process can be seen below in Figure 4.
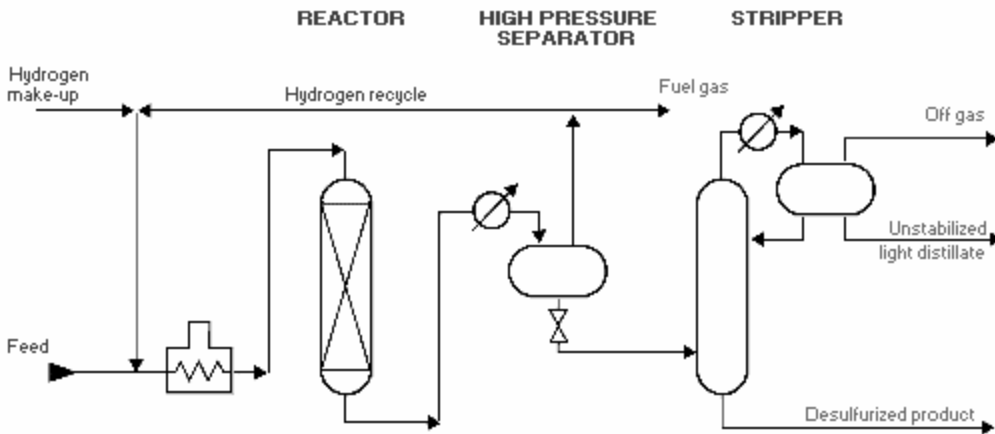
**Figure 5: Hydrotreating Unit PFD** [(Leprince)]

Bangchak refinery has four hydrotreater units:  hydrodesulfurization (HDS), a kerosene treating unit, (KTU) and two naphtha pretreating units (NPU2 and NPU3).

**Utility Model Development**

An average utility model was created for comparison in the hydrotreating units as well. The hydrotreating units are modeled using similar operating parameters due to the fact from 625°F to 698°F for the hydrodesulfurization unit, as given by Parkash (p. 32).  Using these values and simulated property values and work requirements, the cost for power can be calculated by:

$$pcost = (\$0.04/kWh) * (F_T) * .0027\left(\frac{HP}{\frac{lbmol}{hr}}\right) * .7545\left(\frac{kW}{HP}\right) * 1522.85\left(\frac{lb_F}{m^3}\right) \qquad \text{Eq. 23}$$

For the two utility-driven heat exchangers, cooling water cost is calculated by:

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$$wcost =$$

$$\frac{\left(\frac{\$0.05}{1000\ gal}\right)*(F_T)*0.477\left(\frac{BTU}{lb\cdot°F}\right)*(662-140)°F*1522.85\left(\frac{lb_p}{m^3}\right)*1055\left(\frac{J}{BTU}\right)*2.16\left(\frac{gal_W}{mol}\right)}{(182-60)°F*8.277*10^4\left(\frac{J}{mol\cdot K}\right)} +$$

$$\frac{\left(\frac{\$0.05}{1000\ gal}\right)*(F_T)*0.477\left(\frac{BTU}{lb\cdot°F}\right)*(662-140)°F*152\ 2.85\left(\frac{lb_p}{m^3}\right)*1055\left(\frac{J}{BTU}\right)*2.16\left(\frac{gal_W}{mol}\right)}{(182-60)°F*8.277*10^4\left(\frac{J}{mol\cdot K}\right)}$$

Eq. 24

In the hydrodesulfurization unit's fired heat exchanger, refinery fuel gas consumption is calculated as:

$$fguse = \frac{(F_T)*0.477\left(\frac{BTU}{lb\cdot°F}\right)*(662-200)°F*1522.85\left(\frac{lb_p}{m^3}\right)}{\frac{0.00106\ MMBTU}{hr*(lbmol\ of\ FG)}*10^6\left(\frac{BTU}{MMBTU}\right)}$$

Eq. 25

## Isomerization

The isomerization unit creates a product largely consisting of a single isomer called isomerate. Blending this isomerate into end use gasoline products increases the octane number of the gasoline products. The reaction is an equilibrium reaction where undesired products are recycled back to the reactors to help the equilibrium reaction to produce more of the desired product. The reaction is a gas-phase, catalyzed reaction that converts butane to iso-butane. Figure 5 shows the composition of the feed to the isomerization unit. This composition was determined by Bagajewicz et al. and was used for property estimation during utility model development for the LP Utility model.

**Figure 6: Isomerization Feed Compositions** [Bagajewicz]

| Feed Components | Weight % |
|---|---|
| i-C4 | 2 |
| C4 | 1.4 |
| Isopentane | 19.6 |
| n-pentane | 28.6 |

| | |
|---|---|
| cyclopentane | 1.4 |
| dimethyl-2,2-butane | 0.9 |
| 2,3-dimethylbutane | 2.2 |
| 2-methyl pentane | 13.1 |
| 3-methyl pentane | 10.2 |
| n-c6 | 18.6 |
| methylcyclopentane | 2.8 |
| cyclohexane | 0.4 |
| benzene | 1.9 |
| Sum | 100 |

There are two distinct processes of isomerization: butane isomerization and pentane/hexane isomerization ($C_5/C_6$). Butane isomerization is a structural process where the carbon arrangement of the molecule is rearranged with no change in the molecular formula (Leprince). This is an equilibrium reaction where the composition is a function of temperature. On the other hand, $C_5/C_6$ isomerization is used to increase the octane numbers of the products.

**Figure 7: Typical operating condition for Isomerization**

| Operating Ranges | |
|---|---|
| Variable | Range |
| Reactor Temperature | 250 - 550°F |
| Pressure | 250 - 400 psig |
| Hydrogen/Hydrocarbon Ratio | 2:1 |
| Single pass LHSV | 1.5 – 2.5 v/hr/v |
| Liquid product yield | > 98 wt % |

**Figure 8:  Isomerization Unit with Deisohexanizer Recycle** [Bagajewicz]

## Utility Model Development

The Isomerization unit used for this model is an Isomerization with deisohexanizer recycle.  The unit is assumed to operate with a reactor temperature ranging from 250°F to 550°F, as described by McKetta.  Using stream property data, we find that the cost of power required for the Isomerization unit can be calculated as:

$$pcost = 2*(\$0.04/kWh)*(F_T)*.00273\left(\frac{HP}{\frac{lbmol}{hr}}\right)*.7457\left(\frac{kW}{HP}\right)*1440.6(\frac{lb_g}{m^3})\quad\text{Eq. 26}$$

The unit contains four coolers that use utility cooling water.  After finding stream property values and estimating temperatures of some internal streams, the cost of the cooling

water can be calculated using:

$wcost$

$$
\begin{aligned}
=\ & \frac{\left(\frac{\$0.05}{1000\,gal}\right)*(F_T)*.515\left(\frac{BTU}{lb*\degree F}\right)*(575-140)\degree F*2.16\left(\frac{gal_w}{mol}\right)*1055\left(\frac{J}{BTU}\right)*1440.6(\frac{lb_g}{m^3})}{(182-60)\degree F*8.277*10^4(\frac{J}{mol*K})} \\[6pt]
& +\frac{\left(\frac{\$0.05}{1000\,gal}\right)*(F_T)*.515(\frac{BTU}{lb*\degree F})*(140-60)\degree F*2.16\left(\frac{gal_w}{mol}\right)*1055\left(\frac{J}{BTU}\right)*1440.6(\frac{lb_g}{m^3})}{(182-60)\degree F*8.277*10^4(\frac{J}{mol*K})} \\[6pt]
& +\frac{\left(\frac{\$0.05}{1000\,gal}\right)*(F_T)*.515\left(\frac{BTU}{lb*\degree F}\right)*(100-60)\degree F*2.16\left(\frac{gal_w}{mol}\right)*1055\left(\frac{J}{BTU}\right)*1440.6(\frac{lb_g}{m^3})}{(182-60)\degree F*8.277*10^4(\frac{J}{mol*K})} \\[6pt]
& +\frac{\left(\frac{\$0.05}{1000\,gal}\right)*(F_T)*.515(\frac{BTU}{lb*\degree F})*(100-60)\degree F*2.16\left(\frac{gal_w}{mol}\right)*1055\left(\frac{J}{BTU}\right)*1440.6(\frac{lb_g}{m^3})}{(182-60)\degree F*8.277*10^4(\frac{J}{mol*K})}
\end{aligned}
$$

Eq. 27

The Isomerization unit contains three fired heaters which use refinery fuel gas. The use of fuel gas can be calculated by:

$$
\begin{aligned}
fguse =\ & \frac{(F_T)*.515(\frac{BTU}{lb*\degree F})*(575-460)\degree F*1440.6(\frac{lb_g}{m^3})}{\frac{0.00106\,MMBTU}{hr*(lbmol\ of\ FG)}*10^6(\frac{BTU}{MMBTU})} \\[6pt]
& +\frac{(F_T)*.515(\frac{BTU}{lb*\degree F})*(475-140)\degree F*1440.6(\frac{lb_g}{m^3})}{\frac{0.00106\,MMBTU}{hr*(lbmol\ of\ FG)}*10^6(\frac{BTU}{MMBTU})} \\[6pt]
& +\frac{(F_T)*.515(\frac{BTU}{lb*\degree F})*(160-100)\degree F*1440.6(\frac{lb_g}{m^3})}{\frac{0.00106\,MMBTU}{hr*(lbmol\ of\ FG)}*10^6(\frac{BTU}{MMBTU})}
\end{aligned}
$$

Eq. 28

**Successive Linear Programming**

Refinery operations involve many variables for optimization. Therefore, optimization has a critical influence towards refinery profitability. Maximum optimization is carried out using Successive linear programming (SLP). SLP solves non linear optimization problems using a sequence of linear programs. In SLP, a starting point is selected and the nonlinear model and constrains are linearized about the starting point. The point from where the linear program solution can be used as a new point to linearization the non linear problem. This is continued till a stopping criterion is met. It is necessary to bind the steps taken in the iterations to insure that the model improves and the values of the independent variable are specified. Below is the general form of equation used.

$$
\begin{aligned}
&\text{Optimize:} && y(x) \\
&\text{Subject to:} && fj(x) \leq bi && \text{for } i=1,2,\ldots,m \\
& && uj \geq xj \geq 1j && \text{for } j=1,2,\ldots,n
\end{aligned}
$$

In this case, the non-linear variables would be variables involving α. These variables include temperatures, flow rate, concentration and pressure. Using Taylor series expansion, the linear model written with α can be solved. SLP algorithms with proper LP (α) should give solutions more accurate and precise than GRM obtained from LP model. This implies that implementing a SLP model would depend on the number of non-linear variables present in the refinery. For example, Equation 29 shows the flow rate of paraffin from the catalytic reforming unit and its non-linear variables.

$$
F_{par,1} = F_0 C_{0,par} - W_{cat} * \left[ \begin{array}{l} \left[ \exp\left(35.98 - \dfrac{59600}{T}\right) \right] * \left( C_{0,nap} * C_{0,hyd} * P^2 - \dfrac{C_{0,par} P}{\exp\left[\dfrac{8000}{T} - 7.12\right]} \right) \\[3em] -C_{0,par} \exp\left[ 42.97 - \dfrac{62300}{T} \right] \end{array} \right] \qquad \text{Eq. 29}
$$

$$F_{par,1,i+1} = F_{par,1,i} + \left[\frac{\partial F_{par,1}}{\partial P}\right]_i (P - P_i) + \left[\frac{\partial F_{par,1}}{\partial T}\right]_i (T - T_i) + \left[\frac{\partial F_{par,1}}{\partial C_{0,par}}\right]_i (C_{0,par} - C_{0,par,i}) + \left[\frac{\partial F_{par,1}}{\partial F_0}\right]_i (F_0 - F_{0,i})$$

$$+ \left[\frac{\partial F_{par,1}}{\partial C_{0,hyd}}\right]_i (C_{0,hyd} - C_{0,hyd,i}) + \left[\frac{\partial F_{par,1}}{\partial C_{0,nap}}\right]_i (C_{0,nap} - C_{0,nap,i})$$

Eq. 30

Where
    O = inlet conditions
    i= numbers calculated using the output from GAMS

Equation 30 shows the linearized equation that is put into the GAMS program to optimize the gross refinery margin. The initial condition value ($F_{par,Ji}$) is calculated by the reforming unit supertables and called A. Partial derivatives with respect to initial concentrations, temperature, pressure, and flow rate were taken for each product stream exiting the reactor. The partial derivative terms were calculated by supertables and are called $B_i$. These allow us to write the equation into the linear model in a linear form, like that shown in Equation 30.

A Successive Linear Programming (SLP) method was used to analyze the basic Linear programming Bangchak Refinery model in GAMS. This method was used as a comparison between SLP and LP modeling. For the basic LP model, temperature, concentration, and pressure are not process variables that are accounted for in the program. This leads to using a first-order Taylor-series expansion for the linear representation of functions similar to Equation 30, which only contains a correction term for initial flow rate, $F_0$. The equations are included in the model, and then the model gave results for the outlet flow rate. All A and $B_i$ variables were re-calculated, and then re-entered into a new equation in the GAMS model. This process was repeated until all $B_i$ values were sufficiently close to zero.

Initially, the partial derivatives (when calculated from the starting point results in supertables) were of the order of magnitude between $10^{-3}$ and $10^{-6}$. These numbers are very near to zero. A condition for $B_i$ values to be sufficiently close to zero was that the $B_i$ value dropped below $1*10^{-4}$. This is would represent approximately a $10^{-7}$ percentage (0.0000001) of the flow rate being calculated. That is on the order of one one-hundred-thousandth of one percent of the flow rate.

To create a new, completely SLP model, there would have to be a new Linear Model modification for each starting point to be tested. This means tailoring a model to very specific conditions of flow. For illustrative purposes, this has been done for the reforming units of the basic linear Bangchak Refinery Model, but to make the complete SLP model worth the time investment, much more refinery-specific data would need to be known to make the model more accurate so that a good starting point could be carefully selected. This is why commercially available packages require so much refinery-specific input about ranges of process variables, size of unit components, and detailed configuration of refining units. For comparison, the basic linear Bangchak Refinery model was analyzed using SLP techniques. The model was tested using two different initial starting points. As the models were re-run, it was clear that the values for reactor products converged toward different numbers. This is a clear indicator that successive linear programming is only as good as its initial guess, since the initial guesses dictate which maximum the program will find in the GRM objective function.

**Sulfur**

Sulfur content is one of the important properties of crude oil. It is an undesirable impurity that brings about corrosion and pollution concerns. Sulfur content is expressed as a percentage of sulfur by weight and varies from less than 0.1 % to greater than 5% (Gary and Handwerk). Environmental Protection Agency (EPA) specifications for sulfur content of gasoline is < 30 wppm (weight parts per million) (Gary and Handwerk). A sulfur balance was completed for each of the units and the overall model refinery.

Sulfur may be present in crude oil as hydrogen sulfide ($H_2S$), as compounds (e.g. mercaptans, sulfides, disulfides, thiophenes, etc.) or as elemental sulfur. Each crude oil has different amounts and types of sulfur compounds, but as a rule the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions. Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptans.

In US refineries, the largest source of sulfur oxide emissions is caused by the burning of high sulfur fuels, including sour refinery gases, residue oil, heavy refinery oils, and petroleum coke (Myers). The combustion of petroleum products containing sulfur compounds produces undesirables such as sulfuric acid and sulfur dioxide. Catalytic Hydrotreating processes such as hydrodesulfurization remove sulfur compounds from refinery product streams. Sweetening processes either remove the sulfur compounds or convert them to odorless disulfides, as in the case of mercaptans.

Sulfur content regulations have been set by the Environmental Protection Agency, EPA, in gasoline. Refineries are now expected to produce diesel with 60 ppm sulfur as of June of 2006 (Parkash).

## Hydrogen Balance

A hydrogen balance was added to the model to determine whether the refinery produces excess hydrogen or has to purchase hydrogen to meet unit demands. If the plant requires more hydrogen than it produces, then those costs should be added to the model as a utility cost. The use of these equations requires that the model be solved as a mixed integer model. The mixed integer model allows values for a continuous function to be selected based on other process variables like flow rate, temperature, and pressure. The net amount of hydrogen produced in the refinery is equal to the amount of hydrogen created by the reforming units less the amount used in the hydrotreating units. Assuming that the refinery has the capacity to pipe the excess hydrogen throughout the refinery to provide make-up hydrogen, an excess of hydrogen produced can be used to supplement hydrogen need in reforming units and as fuel in refinery steam boilers.

## Results and Conclusions

The Linear Programming (LP) models are solved by maximizing gross refinery margin

(GRM) using the CPLEX solver found in GAMS software.  To maximize GRM, the solver recommends an appropriate amount of each of six types of crude oil to be purchased over three time periods based on uncertain demand.  For the Linear model with complex utilities, the GRM was $34.1 million (over a three month period).  For this model, the monthly cost for utilities was just less than $1 million per month.  The model produced enough excess hydrogen in the reforming units to supplement the demand in the hydrotreating units.  Enough refinery fuel gas is produced to provide for the demand in fired heaters and in refinery boilers to produce steam.

**Utility Models**

When compared with the linear model without utilities, and the linear model with simplified utilities, the linear model with complex utilities provided the highest GRM and had the lowest overall utility cost of the models.  Other models created for comparison were a model with no utility cost factored into the GRM equation and a model with simplified utilities.  The linear model with simplified utilities had a GRM of $31.2 million compared to the model with no utilities which produced a GRM of $34.1 million.

**Figure 9:  Gross Refinery Margin**

| Model | GRM |
|---|---|
| Complex Utilities | $34,103,151 |
| Simplified Utilities | $31,168,455 |
| No Utilities | $34,097,901 |

It was expected that the model with simplified utilities would have a lower GRM than the model without utilities due to the additional cost factored into the GRM function in the model. The surprising result was that the model with complex utilities was able to overcome this additional cost by restructuring the way the refinery was operated through the three-month model

period. This was achieved in the complex utility model because the model changed the operating conditions (pressure, temperature) in individual units to alter their products. The model also told the refinery to process more crude during the three month period. This was made possible by altering purchasing recommendations to allow the proper crudes to be refined to produce the optimal end-use products at the cheapest price possible.

In terms of crude purchasing, the linear model with complex utilities gives different purchasing recommendations for three of the six crudes over all three time periods when compared to the linear model with simplified utilities.

| | Linear Model with Simplified Utilities | | | | Linear Model with Complex Utilities | | |
|---|---|---|---|---|---|---|---|
| | Crude Purchasing Recommendations (m3/day) | | | | Crude Purchasing Recommendations (m3/day) | | |
| | | Month | | | | Month | |
| | 1 | 2 | 3 | | 1 | 2 | 3 |
| OM | 244486 | 262303 | 267899 | OM | 250361.5 | 265445 | 267700 |
| TP | 32853.3 | 41126.2 | 47392.2 | TP | 35313.8 | 42245.6 | 43073.4 |
| LB | 0 | 0 | 9041.4 | LB | 0 | 0 | 12997.8 |
| SLEB | 95392.2 | 95392.2 | 95392.2 | SLEB | 95392.2 | 95392.2 | 95392.2 |
| PHET | 57235.3 | 57235.3 | 57235.3 | PHET | 57235.3 | 57235.3 | 57235.3 |
| MB | 95392.2 | 95392.2 | 95392.2 | MB | 95392.2 | 95392.2 | 95392.2 |

**Figure 10: Crude Purchasing Recommendations of different Linear Utility Models**

Adding utility cost to the gross refinery margin calculation makes the model more realistic. Although it would seem that the gross refinery margin should decrease due to the additional cost of utilities, the model with utilities is able to produce a higher gross refinery margin than that of the model without utilities. This is possible because the model alters unit operating conditions to alter the products produced to meet demand with profitable products.

**Table 11: Output of Temperature and Pressure difference in Models**

| | No Utility Model | | | Complex Utility Model | | |
|---|---|---|---|---|---|---|
| | | | | | | |
| **Month:** | **1** | **2** | **3** | **1** | **2** | **3** |
| | NPU2 | | | NPU2 | | |
| **Temperature** | 600 | 600 | 600 | 600 | 600 | 600 |
| **Pressure** | 600 | 600 | 600 | 600 | 600 | 600 |
| | | | | | | |
| | NPU3 | | | NPU3 | | |
| **Temperature** | 700 | 700 | 700 | 700 | 700 | 700 |
| **Pressure** | 600 | 680 | 680 | 680 | 680 | 680 |
| | | | | | | |
| | ISOU | | | ISOU | | |
| **Temperature** | N/A | 275 | 275 | 275 | 275 | 275 |
| **Pressure** | N/A | 1.9 | 1.9 | 2 | 2.1 | 2.1 |
| | | | | | | |
| | CRU2 | | | CRU2 | | |
| **Temperature** | 980 | 980 | 980 | 980 | 980 | 980 |
| **Pressure** | 850 | 850 | 800 | 850 | 850 | 400 |
| | | | | | | |
| | CRU3 | | | CRU3 | | |
| **Temperature** | 980 | 980 | 980 | 980 | 980 | 980 |
| **Pressure** | 500 | 800 | 550 | 400 | 600 | 750 |

As indicated by highlighting, the linear model with complex utilities forces the model to change operating conditions in certain units in order to change the products produced in that unit. These changes allow the model to meet demand and to refine more crude in the three month time

period.

## CRU Reactor Temperature

The Non-Isothermal CRU model produces more hydrogen and almost 50 percent more reformate than the isothermal model. The Non-Isothermal model provides a more accurate depiction of the temperature inside the reactors. Temperature is critical in understanding the product output of the reformer reactors, since each reaction rate is dependent on temperature. The Isothermal CRU model operates with each of the three reactor beds having the same temperature. The model also neglects the fact that the reactors experience temperature drops from the endothermic reactions which occur inside. The Non-Isothermal CRU model takes into account the reactor temperature changes. This is done by making temperature in the reactors a function of flow rate through that reactor. This process gives three equations which alter the operating temperature of each reactor based on stream composition and flow through the reactors.

## Recommendations for Future Study

The linear refinery model developed in this study works well for a basic refinery layout of only a few refinery units. For the program to be applied to a wider range of refineries, additional units should be added to reflect the wide range of units operating at many refineries today. This would allow more complex blending processes, a higher degree of impurity removal, and would provide additional profitable products to the model.

More detailed specifications about the equipment at a particular refinery would also allow a more complete model to be created and fit to the operating conditions of an individual refinery. This would allow the software to be tested on a comparative basis now that its general methodological benefit has been shown.

If very specific refinery data were available, it might be worth creating a completely SLP model for comparison with a linear model for that refinery. This would be less of an academic exercise, since the model nor the results would translate well for any other refinery except for the one studied. This could be a good opportunity to team up with a partner in industry to try to create such a model, but its scope could be longer than what is available for a semester in class.

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