

REFINERY OPERATIONS PLANNING

Advanced Chemical Engineering Design

Dr. Miguel J. Bagajewicz

University of Oklahoma

May 3, 2007

Andy Hill, Sarah Kuper, Sarah Shobe

EXECUTIVE SUMMARY

This report is a refinery planning model to optimize crude purchasing and unit operations to meet an uncertain demand over a three month timespan while maximizing profit. The model involves seven typical refinery processes and a blending section. Each unit has been modeled off of existing correlations and kinetic data. An optimization model (run using GAMS/CPLEX) was used to best determine purchasing requirements and operating conditions.

Six crudes were available for purchase: Oman (OM), Tapis (TP), Labuan (LB), Seria Light (SLEB), Phet (PHET), and Murban (MB). The product prices for each of the crudes is \$27.40, \$30.14, \$30.14, \$30.14, \$25.08, and \$28.19 per barrel, respectively. Two additives are also available, MBET and DCC, and are purchased for \$44.13 and \$35.01 per barrel, respectively. Product demands and prices vary over the three month timespan.

An existing LP model was used as the groundwork for this project. The existing model treated all units using input/output relationships in order to keep the model linear. This is an effective method to model crude processing, but compromises any unit operations decision making.

Modeling unit operations is highly nonlinear. Nonlinear unit models were added to the LP model unsuccessfully. The refinery model was not able to handle the nonlinearities in multiple units. To linearize the model, all unit operations variables were discretized. This converted the existing LP model to a MIP model. Now, all nonlinear equations can be evaluated as parameters and not as variables. Additional work to make the refinery model more user friendly was done by running all unit models in separate programs and producing tables, which are then called by the refinery model. This addition was also projected to reduce the run time of the program.

Inconsistencies concerning mass balances for each of the units were allowed due to their minimal effect. The units can become more balanced by simply adding additional flow rate scenarios for each unit. A balance must exist in the amount of scenarios because additions require a longer run time by the program, which currently requires around two hours to determine the optimal solution.

The results comparing a LP model without unit operations and a MIP program with unit operations shows that modeling unit operations drastically increases the gross refinery margin, which is the objective function. The profit margin for the LP model was approximately \$16.5 billion, while the margin the unit operations model was nearly \$34 billion – over twice as large. The recommendations changed significantly for the crude purchasing decisions. Specifying unit conditions (mimicking a LP model) places additional constraints on the optimal solution. This project shows that the addition of unit operations to pre-existing LP models will make the process more profitable and more accurate.

Table of Contents

Introduction	4
Refinery Planning	6
Planning	6
Existing LP Models.....	7
Unit Operations	8
Hydrotreating	8
Introduction and Background	8
Purpose of Model	9
Model Development.....	10
Catalytic Reforming.....	11
Introduction and Background	11
Purpose of Model	12
Model Development.....	13
Reaction Stoichiometry ¹⁸	13
Reaction Rates ¹⁸	14
Heat Balances ¹⁸	15
Isomerization.....	16
Introduction and Background	16
Reaction Chemistry.....	18
Catalysts	19
Purpose of Model	20
n-Butane Model	22
n-Pentane Model'	23
n-Hexane Model.....	24
Isomerization Model Results	26
Blending Model	28
Octane Number	29
Vapor Pressure	29
Liquid Viscosity.....	30
Pour Point.....	32
Diesel Index and Cetane Index	33
Sulfur Content.....	34
Decision Making	34
Unit Operations Decision Making	34
Refinery Modeling	36
Modeling.....	36
Unit Models	40
Fuel Balance / Hydrogen Balance.....	41
Results and Conclusions	42
Future Work	44

INTRODUCTION

A refinery is used to convert crude oil (a less valuable product) into more valuable products, such as motor gasoline, jet fuel, and fuel oil. A refinery consists of thirty or more processes, so a change in one process will inevitably affect all processes downstream. Due to the complex nature of the reactions and separations that take place in each process, modeling them can be difficult. Various methods are in place to estimate product yields of each unit, such as previous operational data, experimentation, correlations, and kinetic modeling. Among these methods, kinetic modeling typically yields the most accurate results, but requires information regarding the complex reactions taking place within the units. Because crude oil contains thousands of hydrocarbon compounds and other impurities, modeling reactions at the molecular level can be extremely difficult. However, in order to efficiently operate a refinery, modeling and planning are essential to the infrastructure of a refinery.

Effective refinery planning plays an essential part in achieving maximum profits and meeting market demands. Due to the current soaring energy prices, refineries are seeking ways to increase profits and margins. Refinery planning is a very complex problem with numerous inputs and outputs. Constantly changing market demands complicate refinery planning. The selection of which crudes to purchase is of primary importance, since different crudes yield a different palate of optimum products. Due to the complex nature of refinery planning, a model is necessary to aid in the planning process.

A comprehensive refinery planning model has been developed for the Bangchak refinery in Thailand. The model was developed by Pongsakdi *et al.*¹ The Bangchak refinery, which can be seen in Figure 1, has six purchased crudes, two purchased intermediates, and eight products. The purchased crudes and intermediates can be seen in Table 1 and the products in Table 2. The refinery has eight units: two distilling, two naphtha pretreating, isomerization, catalytic reforming, kerosene treating, and hydrodesulfurization. The objective function is set to maximize the gross refinery margin, which is the revenue minus the materials cost, operating cost, and a discount factor for unsupplied contract amounts.

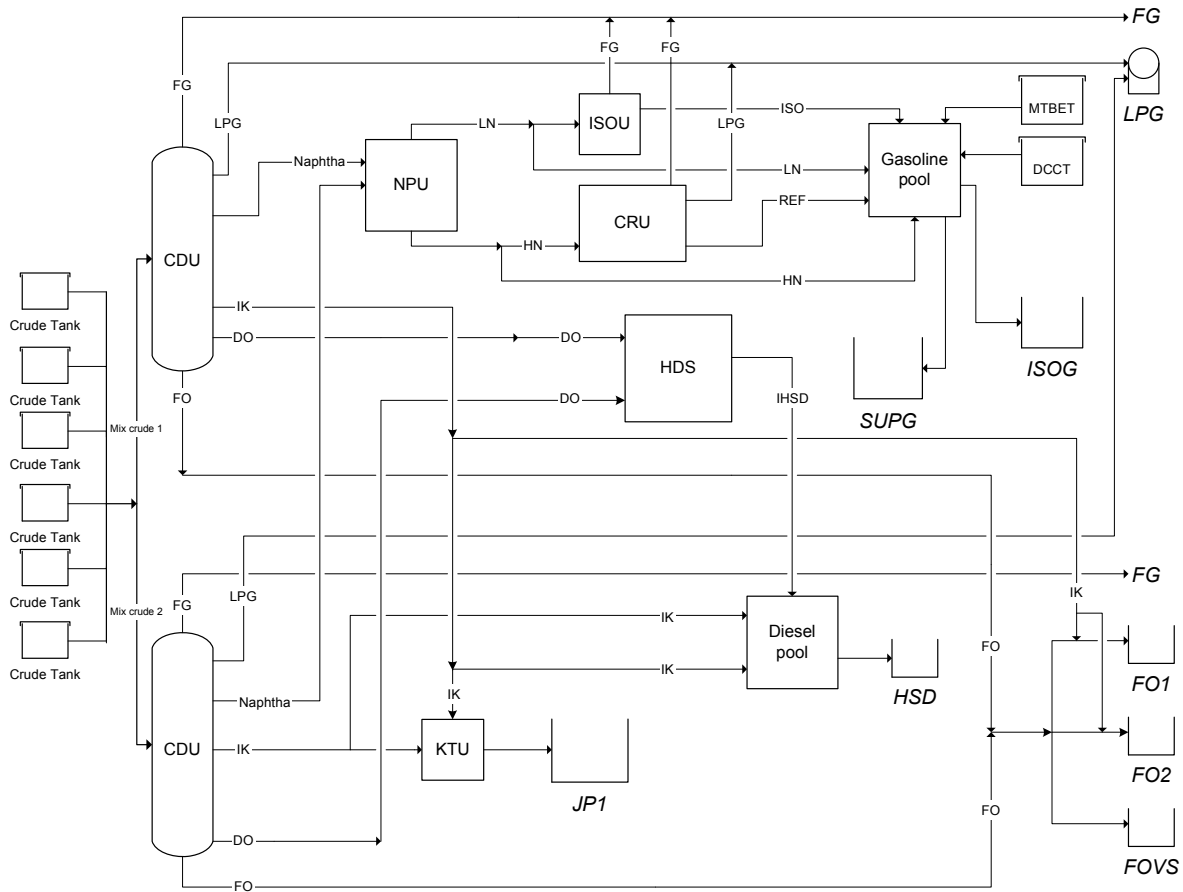


Figure 1: Bangchak Refinery²

Bangchak Crudes	
OM	Oman
TP	Tapis
LB	Labuan
SLEB	Seria Light
PHET	Phet
MB	Murban
Bangchak Intermediates	
MTBE	Methyl Tertiary Butyl Ether
DCC	Dicyclohexylcarbodiimide

Table 1: Purchased Crudes and Intermediates

LPG
SUPG
ISOG
JP-1
HSD
FO #1
FO #2
FOVS

Table 2: Bangchak Products

The model evaluates risk management for uncertain prices and demands. It is a two-stage stochastic model (a technique described in Appendix A) with the first stage variable being purchased crudes and intermediates. The comprehensive model evaluates all of the units by simple linear relationships. Each unit is modeled using correlated data or theoretical equations so that for any given feed the products of the unit can be estimated. The intermediate streams within the refinery are characterized by specific properties which are important for the prediction of products for the unit that they, in turn, feed. The aim of this project was to investigate each individual unit within a refinery, create a computer model of each unit, and integrate these models into an existing comprehensive refinery model that could be used to maximize profit for given product demands and prices. This is different than existing LP models currently in use at many refineries.

Existing LP models consider each unit as a black box and do not take into account how the operating conditions of each unit affect the product of the unit and the overall refinery. The proposed model takes into account the operating conditions of each unit, and how these change the specific refinery products, making it a more accurate representation of the refinery processes.

REFINERY PLANNING

PLANNING

Refineries have a planning department which exists to optimize the revenue of the refinery. Two of the areas where planning decisions are made include crude purchasing and crude processing³.

Recommendations for crude purchasing involve the specific amounts and types of crudes and additives the refinery needs to purchase. For example, the Bangchak refinery (case study) has the choice to purchase up to six different crude types and two additives. The choices of crude types depend on its characteristics. During the summer, light crudes will be in higher demand due to low demands for fuel oils and higher demands for gasoline. In the winter, fuel oils are in higher demand, so the cheaper heavy weight crudes will be purchased in a larger quantity. In general, the heavier the crude, the cheaper the price because heavier crude types require more work to extract useful products.

Recommendations for crude processing are very much tied into the recommendations for crude purchasing. If heavier crudes are purchased, then the daily flow rates to the units such as isomerization, reforming, and gasoline blending will decrease. Unit operations often put limitations on the crude processing decisions beyond the unit capacity constraints. Turnarounds and plant failures cause planning to constrain the flow rates to different units.

EXISTING LP MODELS

Presently, most refineries use linear programming (LP) techniques for their planning. LP programs utilize an objective function, typically maximizing the refinery profit. The objective function is tied to several recommendations based on linear relationships. Constraints are placed on several variables, such as all unit capacities and the amount of crude available for purchase. A few of the big LP models in industry today include RPMS (by Honeywell Hi-Spec Solutions), PIMS (by Aspentech), and GRMPTS (by Haverly). These models require a large amount of data collection by the refinery, which is used to create the linear relationships for each unit.

One of the major concerns of the LP programs in place today is the blending process. Blending in gasoline and diesel oil pools actually blends non-linearly and LP models use a linearization technique. This technique uses blending indices which can then be added to the LP program which keep it linear.

UNIT OPERATIONS

Within a refinery there are many units operating simultaneously to produce valuable products. Each unit has a specific purpose and affects the overall operation of the refinery. The specific units modeled for the refinery are as follows: Hydrotreater, Catalytic Reformer, Isomerization, and Blending units.

HYDROTREATING

Introduction and Background

Sulfur content in gasoline and diesel are now seeing new regulations for lower content set by the Environmental Protection Agency. In particular, refineries are currently expected to produce diesel with 60 ppm sulfur or less as of June of 2006.¹⁰ The processes that refineries utilize to remove sulfur is called hydrotreating. Not only does hydrotreating remove sulfur from hydrocarbons, but it also removes nitrogen from hydrocarbons and decreases the aromatic content from the given feed. The reactions for sulfur and nitrogen removal are carried out in a similar fashion. For the removal of aromatics, hydrogen is added to the aromatic ring to increase the saturation of the molecule, which eliminates the double bonds to produce naphthenes. An example of sulfur removal can be seen below in Figure 2.

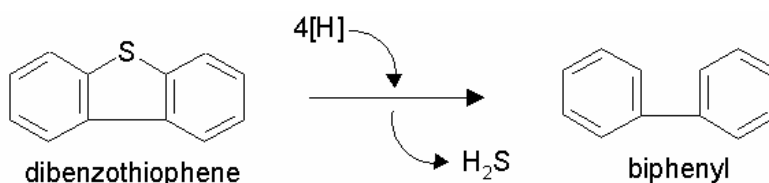


Figure 2: Sulfur Removal¹¹

Hydrotreating takes place in a packed bed reactor. The feed stream from the distillation column is mixed with a hydrogen stream and heated prior to entering the reactor. This vapor mixture then flows through the reactor where the sulfur compounds, nitrogen compounds, and hydrogen molecules adsorb onto the surface of the catalyst and react with one another. Leaving the reactor is the treated product along with byproducts of the reaction such as H₂S and NH₃. These byproducts are partially removed by the condensation of the exiting stream. They are completely

removed after distilling at the end of the hydrotreating process. The process flow diagram for this process can be seen below in Figure 3.

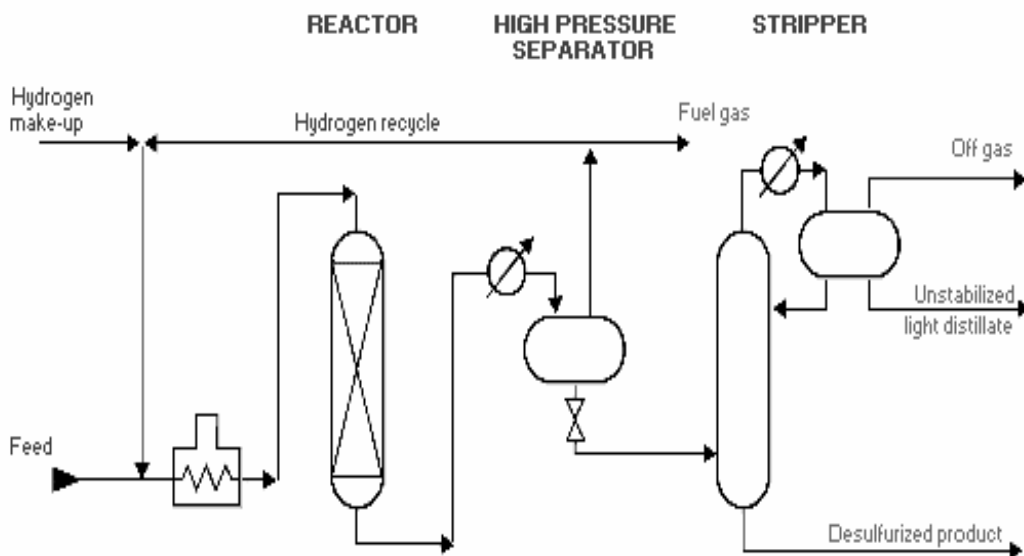


Figure 3: Hydrotreating Unit PFD¹²

There are four hydrotreater units in the Bangchak refinery: two naphtha pretreating (NPU2 and NPU3), kerosene treating (KTU), and hydrodesulfurization (HDS). For each of these units, a capacity (catalyst weight) must be determined in order to model them. Since direct contact with the Bangchak refinery is unavailable, the catalyst weight will be projected for each unit based on the inlet flow rate.

Purpose of Model

The purpose of all hydrotreater models is to integrate the cost of the operating conditions into the objective function. All variables for the unit will have an affect on the GRM. These variables can be seen in Table 3. The hydrotreating models are expected to show the highest dependence on the operating temperatures and pressures.

Operating Variables	Input Variables
Temperature	Flow Rate
Pressure	Sulfur wt%
Space Velocity	SG (Oil)
H ₂ /HC ratio*	MW (Oil)*

*currently set as a constant

Table 3: HDS variables

Model Development

In work performed by Galiasso¹³ there were reaction orders for the removal of sulfur and nitrogen containing compounds as well as aromatics. The reaction orders that they determined for a molybdenum cobalt (MoCo) catalyst are shown in the Table 4. Nitrogen removal is not determined by the model since nitrogen data is not given for the set of crudes in the original comprehensive model and is not provided in the published assays found for the crude types.¹⁴

Reaction	Hydrocarbon Order	Hydrogen Order
Sulfur	1	0.45
Aromatics	1	1

Table 4: Reaction Orders

Activation energies determined for the each of the reactions as shown in Table 5.

	Activation Energy
Reaction	(J/mol)
Sulfur	132000
Armoatic	150000

Table 5: Activation Energies

The rate law used is the Langmuir-Hinshelwood rate law¹⁵. It is dependant on the concentrations of the sulfur impurity, hydrogen, product gas, and an adsorption equilibrium term:

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

and the rate constant is determined by:

$$k = A_s \cdot e^{-\frac{E}{R \cdot T}} \quad \text{Eq. 2}$$

The Arrhenius constant is now the only unknown in the equations. A preliminary value was developed from a set of operating conditions and sulfur contents entering and exiting the hydrotreater, which can be seen in Table 6. The determined value for hydrotreating is 6×10^6 . Future work should be done to confirm this value.

Feed Properties:	
Sulfur In (ppm)	500
Sulfur Out (ppm)	20
Temperature (F)	800
Pressure (psi)	950
Catalyst Weight (lb)	500000
Density	0.89
Molecular Weight	200

Table 6: Experimental Feed Conditions to Determine Arrhenius Constant¹⁶

CATALYTIC REFORMING

Introduction and Background

Catalytic reforming is a process that is used to increase the octane number of naphtha distillation cuts by converting naphthenes and paraffins into aromatics, light end hydrocarbons ($C_1 - C_5$), and hydrogen. In the model, the feed for the catalytic reforming unit (CRU) comes from the naphtha pre-treating unit. The feed is heavy naphtha, which includes hexanes and heavier hydrocarbons that come from the atmospheric crude tower's distillation cut. The reactions take place in a series of packed bed reactors at high temperatures (900 °F – 950 °F) and lower pressures (30 atm – 40 atm) while flowing over a platinum bi-function catalyst on an alumina support. Reactions are further facilitated by large hydrogen partial pressures through a recycle stream.

A typical catalytic reforming unit consists of multiple reactors to increase the conversion to aromatics. Multiple intermediate heaters are also needed due to the reactions being highly

endothermic. A flash drum is usually included to remove the hydrogen before fractionation so that the hydrogen can be recycled and join the feed before being preheated. Following the flash drum, there is a stripping column which removes any light ends created through the reaction process. These light ends exit through the top of the column to the fuel gas system, and the reformat product exits at the bottom. A typical refinery reformer set-up is shown in Figure 4.

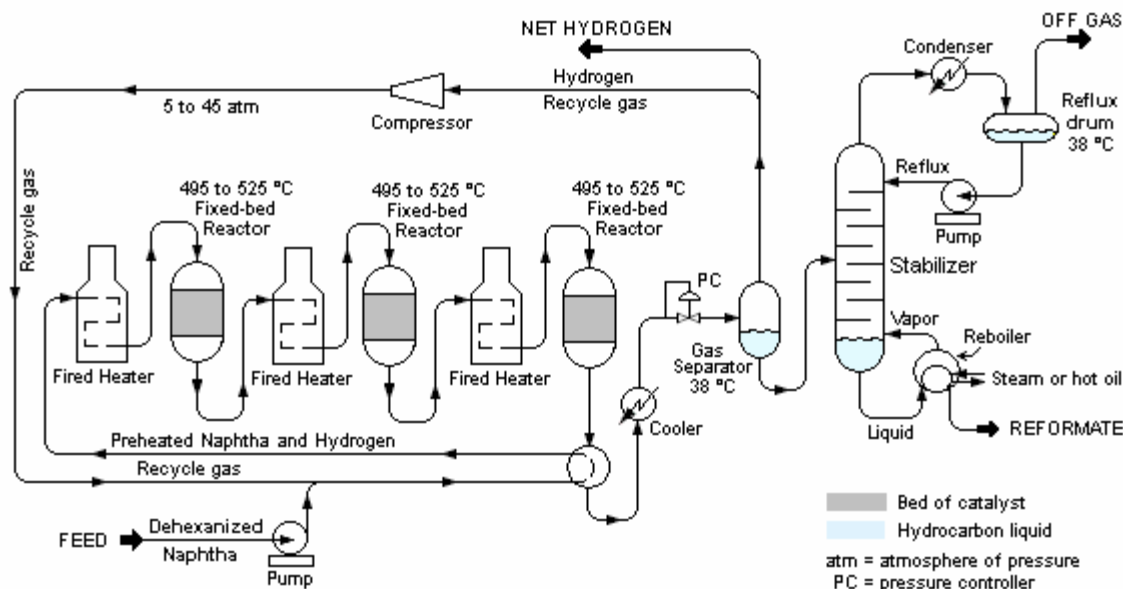


Figure 4: Typical Reformer Process¹⁷

Purpose of Model

The purpose of this model is to predict the output of the reactor system through simplified inputs. While more than a hundred individual species enter the system, the model will take into account two types of compounds to simplify the reaction stoichiometry and kinetic parameters. The two types are naphthenes and aromatics. Naphthenes are typically cyclic hydrocarbons, such as cyclohexane or methylcyclopentane, with slightly lower hydrogen to carbon ratio than paraffins. Aromatics are cyclic hydrocarbons, such as benzene or para-xylene, with the lowest hydrogen to carbon ratio of the three groups.

Predicting the change in reactants to products allows one to predict the different amounts of gasolines, ISOG and SUPG, the refinery can produce for sale. Aromatics have relatively large research and motor octane numbers (RON & MON) and are typically blended with other components in premium gasoline (SUPG), fractionated and sold as solvents, or isomerized and sold as chemical feed stocks. In our model, the reformat will be blended to create a premium gasoline. There is not a large demand for napthene products currently, and it is desired to convert them into more valuable products.

Model Development

The model utilizes a kinetic rate law for the conversion of napthenes to aromatics to produce a higher value product that can be blended in the gasoline pool to create the premium gasoline. The following sets of equations were taken from Smith in 1959.

Reaction Stoichiometry¹⁸

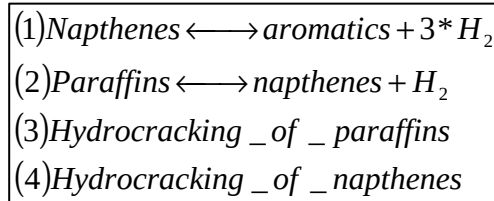
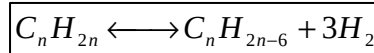


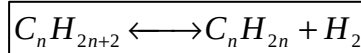
Figure 5: Lumped Reaction Stoichiometry¹⁹

Reaction (1) – Conversion of napthenes to aromatics



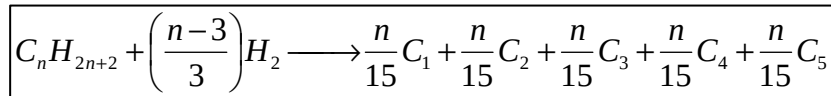
Eq. 3

Reaction (2) – Conversion of paraffins to napthenes



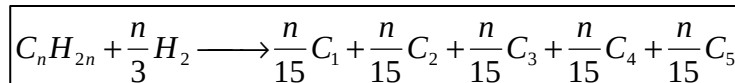
Eq. 4

Reaction (3) – Hydrocracking of parffins



Eq. 5

Reaction (4) – Hydrocracking of napthenes



Eq.6

Reaction Rates¹⁸

Reaction (1) – Conversion of naphthenes to aromatics

Equilibrium for Reaction (1)

$$K_{P1} = \frac{P_A * P_H^3}{P_N} = \exp\left(46.15 - \frac{46045}{T}\right), [=] atm^3 \quad \text{Eq. 7}$$

Kinetic constant for Reaction (1)

$$\hat{k}_{P1} = \exp\left(23.21 - \frac{34750}{T}\right), [=] \frac{\text{moles}}{(hr)(lb_cat.)(atm)} \quad \text{Eq. 8}$$

Reaction rate for Reaction (1)

$$-\hat{r}_1 = \hat{k}_{P1} \left(P_N - \frac{P_A * P_H^3}{K_{P1}} \right) [=] \frac{\text{moles_naphthene_converted_to_aromatics}}{(hr)(lb_cat.)} \quad \text{Eq. 9}$$

$$\left(-\hat{r}_1 \right) \left(\frac{\Delta W}{F_T} \right) = \Delta X_1 \quad \text{Eq. 10}$$

Reaction (2) – Conversion of naphthenes to paraffins

Equilibrium for Reaction (2)

$$K_{P2} = \frac{P_P}{P_N * P_H} = \exp\left(\frac{8000}{T} - 7.12\right), [=] atm^{-1} \quad \text{Eq. 11}$$

Kinetic constant for Reaction (2)

$$\hat{k}_{P2} = \exp\left(35.98 - \frac{59600}{T}\right), [=] \frac{\text{moles}}{(hr)(lb_cat.)(atm)^2} \quad \text{Eq. 12}$$

Reaction rate for Reaction (2)

$$-\hat{r}_2 = \hat{k}_{P2} \left(P_N * P_H - \frac{P_P}{K_{P2}} \right) [=] \frac{\text{moles_naphthene_converted_to_paraffins}}{(hr)(lb_cat.)} \quad \text{Eq. 13}$$

$$\left(-\hat{r}_2 \right) \left(\frac{\Delta W}{F_T} \right) = \Delta X_2 \quad \text{Eq. 14}$$

Reaction (3) – Hydrocracking of paraffins

Kinetic constant for Reaction (3)

$$\hat{k}_{p3} = \exp\left(42.97 - \frac{62300}{T}\right), [=] \frac{\text{moles}}{(\text{hr})(\text{lb}_{\text{cat.}})} \quad \text{Eq. 15}$$

Reaction rate for Reaction (3)

$$-\hat{r}_3 = \hat{k}_{p3} \left(\frac{P_p}{P}\right) [=] \frac{\text{moles}_{\text{paraffins converted by hydrocracking}}}{(\text{hr})(\text{lb}_{\text{cat.}})} \quad \text{Eq. 16}$$

$$\left(-\hat{r}_3\right) \left(\frac{\Delta W}{F_T}\right) = \Delta X_3 \quad \text{Eq. 17}$$

Reaction (4) Hydrocracking of naphthenes

Kinetic constant for Reaction (4)

$$\hat{k}_{p4} = \exp\left(42.97 - \frac{62300}{T}\right), [=] \frac{\text{moles}}{(\text{hr})(\text{lb}_{\text{cat.}})} \quad \text{Eq. 18}$$

Reaction rate for Reaction (4)

$$-\hat{r}_4 = \hat{k}_{p4} \left(\frac{P_N}{P}\right) [=] \frac{\text{moles}_{\text{naphthenes converted by hydrocracking}}}{(\text{hr})(\text{lb}_{\text{cat.}})} \quad \text{Eq. 19}$$

$$\left(-\hat{r}_4\right) \left(\frac{\Delta W}{F_T}\right) = \Delta X_4 \quad \text{Eq. 20}$$

Heat Balances¹⁸

$$\Delta W \left[\left(-\hat{r}_1\right)(-\Delta H_1)(3) + \left(-\hat{r}_2\right)(-\Delta H_2) + \left(-\hat{r}_3\right)(-\Delta H_3) \left(\frac{n-3}{3}\right) + \left(-\hat{r}_4\right)(-\Delta H_4) \left(\frac{n}{3}\right) \right] = \sum_j C_{pj} \Delta T \quad \text{Eq. 21}$$

$$Q = \dot{n} * C_{p, \text{Molar}} * \Delta T \quad \text{Eq. 22}$$

The equations were entered into an optimization model aimed at maximizing the conversion of naphthenes to aromatics for the catalytic reforming unit. The main parameters that are manipulated are the temperature and pressure in the given operating ranges to maximize the conversion to aromatics. The optimization of this unit will change once it is incorporated in the overall refinery model. Typical operating ranges for a catalytic reformer unit can be seen in Table 7.

Temperature	925-975 F
Pressure	50-350 psig
H ₂ /Feed Ratio (mol)	3-8
LHSV	1-3 hr ⁻¹

Table 7: Typical Operating Ranges for CRU²⁰

ISOMERIZATION

Introduction and Background

Isomerization converts linear alkanes, such as butane, pentane, and hexane, to their branched isomers in a fixed bed reactor. When isomerization occurs, the configuration of the molecule changes, but the number of atoms (chemical formula) of the molecule is unchanged. It is typically a gas-phased catalyzed reaction for the conversion of butane to iso-butane. Whereas the conversion of pentanes and hexanes to their respective branched isomers can occur in both the gas phase and liquid phase. Pentane is converted into isopentane, while hexane can be converted into 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethyl butane. The isomerization of the straight-chained alkanes results in an increase in octane number of the product stream of the isomerization unit. Equilibrium of isomerization reactions are favored by lower temperatures. As the temperature of the unit increases the equilibrium shifts towards the straight chain molecules.

Feed for the isomerization comes from the naphtha pre-treating unit. It usually contains roughly 50wt% pentanes and 50wt% hexanes. The butane fraction will range from 0 to approximately four weight percent.³⁰ Typical isomerization processes include a fixed catalyst bed reactor with separation and recycle equipment. The overall process varies according to the catalyst used. All processes require the input of hydrogen to support the reaction mechanism. The hydrogen to hydrocarbon ratio is a process variable. Hydrogen is not consumed in any significant amounts, but it is consumed to convert benzene to cyclohexane through hydrogenation. Any hydrogen that is not converted to other products is recycled. If chlorinated platinum on alumina catalyst is used, driers and scrubbers for HCl removal are necessary process steps. However, with the platinum on zeolite catalysts these steps can be omitted.³¹

Typically pentane and hexane are isomerized in one unit and butane in a separate unit. This is not always the case. It depends on the purpose of the unit as well as the amount to be processed. The isomerization model supposes that the feed to the unit contains butane through hexane.³²

As seen in Figure 6, the process feed is passed through the reactor, and the product is sent directly to a separator. The hydrogen is separated from the product stream and recycled. The remaining alkanes are sent to an adsorption column, where the lighter alkanes are sent to the fuel gas system. The heavier alkanes are sent to a distillation column where the remaining straight chained pentanes and hexanes are recycled back to the front of the unit, mixed with the feed stream, and fed back through the reactors. The remaining product is fed upstream as the isomerate. A simplified block diagram can be seen in Figure 7 for the isomerization unit.

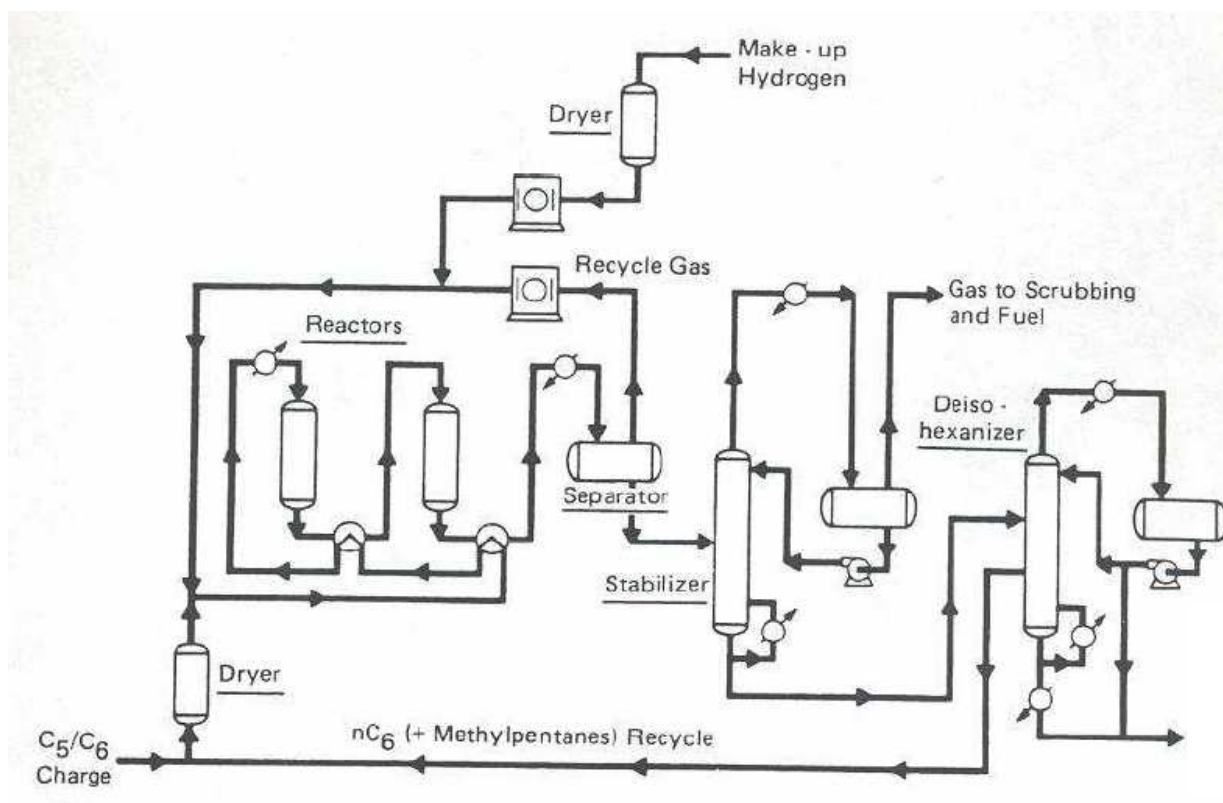


Figure 6: Typical Isomerization Unit³³

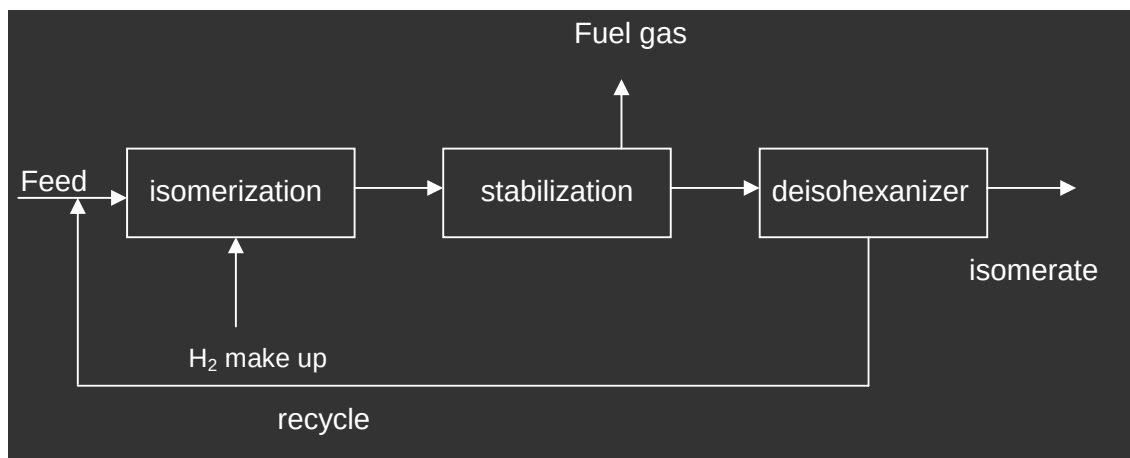


Figure 7: Isomerization Unit Block Diagram

Reaction Chemistry

Isomerization of n-alkanes is an equilibrium limited reaction. The equilibrium favors the isoparaffins at low temperatures; this being especially true for butane and pentane. However, this trend does not hold for all the isomers of hexane (Figure 8). Isomer 2,2-dimethylbutane (2,2-DMB) is the most stable and prevalent isomer of hexane at room temperature. Its presence

decreases rapidly with increasing temperature. The other isomers of hexane, including n-hexane, all increase in mole percent as the temperature increases. The most prevalent at high temperatures, 250°C, is 2-methylpentane (2-MP). The double branched carbon chains have the highest octane rating and are therefore the most desired. They are, however, due to the equilibrium described, typically not as stable at the operating conditions of most industrial processes. Also, due to the conditions of most industrial operations and the catalysts that are used, only one, 2-methylbutane, of the two pentane isomers forms, because of this, 2,2-dimethylpropane is not considered in the reaction process.³⁴

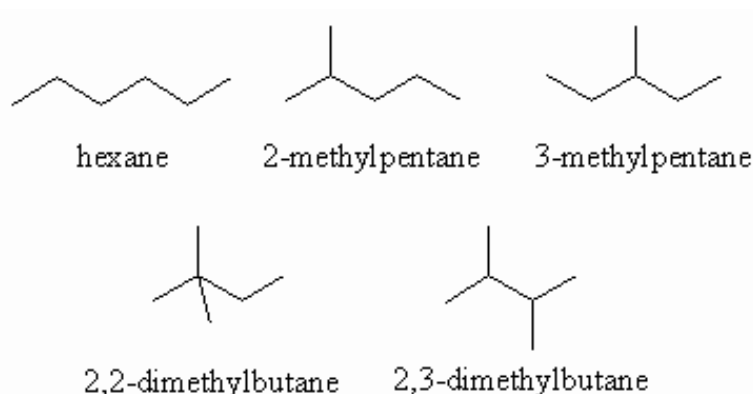


Figure 8: Isomers of Hexane³⁵

The side reactions that accompany the isomerization process include cracking and coking. The amount of these reactions is typically dependent on the functionality of the catalyst used. However, if the hydrogenating function of the catalyst is greater than 15% of the acidic function, then these side reactions are minimal.³⁶ In the proposed model, all side reactions are neglected.

Catalysts

Two types of catalysts, platinum/chlorinated alumina and platinum/zeolite, have become the most prevalent in industry. Both catalysts are bifunctional, with acidic and metallic sites, reacting by either a mono-functional or bi-functional mechanism. The operating conditions for a standard isomerization unit are given in Table 8. The platinum/alumina catalyst operates at significantly lower temperatures. However, it requires that the feed is pretreated, particularly for water, and chlorine, usually in the form of carbon tetrachloride, must be continuously injected into the process stream. The injection of chlorine keeps the acidity of the catalyst at a maximum. One advantage of the platinum/zeolite catalyst is that it does not require that the feed be pretreated.

However, the unit must operate at higher temperatures, which reduces the amount of isomerate achievable with a single run.³⁷

As stated earlier, the side reactions for this unit can be minimized through the catalyst choice. If the catalyst hydrogenating function to acid function ratio is above 0.15, then the catalyst activity, stability, and selectivity are maximized and the side reactions are minimized.³⁸

Typical Operating Ranges		
Reactor Temperature	200-400	F
Pressure	250-500	psig
Hydrogen/Hydrocarbon Ratio	0.1-4	
Single Pass LHSV	1-2	hr ⁻¹

Table 8: Typical Operating Ranges for an Isomerization Unit

Purpose of Model

Microsoft Excel and GAMS were used to create a model to predict the output weight percents of the isomerate stream of the isomerization unit. This model required the inputs, hydrogen to hydrocarbon ratio, mass flow rate (g/s), weight percent of the feed stream components, and temperature. Typical feed compositions for an isomerization unit are shown in Table 9 and were used as the input weight percent concentrations of the feed stream to the isomerization unit. Utilizing these inputs, the model is able to calculate the necessary variables to optimize the isomerization unit product and octane number. It does this by using kinetic rate laws that model the reactions occurring inside the reactor.

Feed Components	wt% ^[1]
i-C4	0
C4	0.4
Isopentane	19.6
n-pentane	28.5
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

Table 9: Isomerization Feed Compositions ²⁹

Using the input weight percents of the feed stream, Antoine's equation determines the vapor pressures of each of the components at the unit temperature. Antoine's equation is shown in Equation 23.

$$\log_{10} P^o = A - \frac{B}{T + C} \quad \text{Eq. 23}$$

Constants for Antoine's equation are shown in Table 10. The components partial pressure can be found from using the inlet mole fractions.⁴¹ The sum of the individual partial pressures gives the total pressure of the unit. The desired hydrogen to hydrocarbon ratio of 0.1 to 4 gives the pressure of hydrogen supplied to the reaction. An approximation of the process stream volume and the concentration of hydrogen can then be found with the ideal gas law. These calculations give the feed in all the forms needed for the rate law calculations.

Feed Components	A	B	C	Temp Range (°C)
i-C4	6.91048	946.35	246.68	-87 to 7
C4	6.80896	935.86	238.73	-77-19
Isopentane	6.83315	1040.73	235.45	-57 to 49
n-pentane	6.85296	1064.84	233.01	-50 to 58
cyclopentane	6.88676	1124.162	231.36	-40-72
dimethyl-2,2-butane	6.75483	1081.176	229.34	-42-73
2,3-dimethylbutane	6.80983	1127.187	228.9	-35-81
2-methyl pentane	6.8391	1135.41	226.57	-32 to 83
3-methyl pentane	6.84887	1152.368	227.13	-30 to 87
n-c6	6.87601	1171.17	224.41	-25-92
methylcyclopentane	6.86283	1186.059	226.04	-24 to 96
cyclohexane	6.8413	1201.53	222.65	20-81
benzene	6.90565	1211.033	220.79	8-103
hydrogen	5.81464	66.7945	275.65	----

Table 10: Antoine Equation Constants⁴²

Constants and data were required for the model. These included Arrhenius equation constants, molecular weights, gas constants, and the Antoine equation constants given in Table 10.

Arrhenius equation constants are given in Tables 11, 12, 14, and 15 for the respective models.

The Arrhenius equation is described in Equation 2. The ideal gas constant (0.0820575 atm*L/(mol*K)) was used in the ideal gas law to describe the volume of the reactor. By utilizing the constants, equations, and kinetic relationships, a model was produced in Excel and GAMS to describe the isomerization process and its product characteristics, such as weight percent of product stream components and octane number.

n-Butane Model⁴³

Inputs of the isomerization unit model include feed stream composition, feed stream flow rate, temperature, and hydrogen to hydrocarbon ratio. The isomerization of n-butane can be modeled based on the partial pressure of n-butane and hydrogen according to the rate law:

$$r_{n-C4} = -K_1 \cdot \frac{P_{n-C4}}{P_{H_2}} + K_2 \cdot \frac{P_{iso-C4}}{P_{H_2}} \quad \text{Eq. 24}$$

where K_1 and K_2 (atm/s) are the rate constants for the forward and reverse reactions respectively. This rate law was determined using NIP-66 catalyst. This catalyst contains 0.6% Pt and 6-10% Cl on n-Al₂O₃.⁴⁴

	E, J/mole	A
K_1	58,615	3,953,058
K_2	66,989	25,140,735

Table 11: Activation Energy and Frequency Factor for n-Butane Isomerization

n-Pentane Model^{45,46}

Due to the selectivity of the catalysts used in industry one of the isomers of the n-pentane, 2,2-dimethylpropane, does not form in an appreciable amount and thus can be disregarded when considering the isomerization reaction.⁴⁷ The reaction of n-pentane to isopentane or 2-methylbutane can be based on a general first order rate law. Based on molar concentration, a rate law can be developed that takes into account the effective rate of reaction accounting for the actual rates variation with both hydrogen and hydrocarbon content. The equation

$$R \ln K_{eq} = \frac{1861}{T} - 1.299 \quad \text{Eq. 25}$$

allows calculation of the equilibrium constant for variations in temperature. Using the equilibrium constant, a rate (Equation 25) based on the molar concentration of n-pentane, isopentane, and hydrogen can be used to predict the product of the isomerization reaction. This rate is also determined on the NIP-66 catalyst.

$$r_{n-C5} = - \left[K_2 \cdot \left(\frac{C_{n-C5}}{[H_2]} \right)^{0.125} - 0.0000197 \cdot t \right] \left[K_{eq} \cdot C_{n-C5} - (K_{eq} + 1) \cdot C_{i-C5} \right] \quad \text{Eq. 26}$$

	E, J/mole	A
K₁	42,287	4,024
K₂	50,032	7,332

Table 12: Activation Energy and Frequency Factor for n-Pentane Isomerization

n-Hexane Model⁴⁸

N-Hexane has four different isomers that it can form as shown in Figure 8. All of these reactions must be taken into account in the model. For a constant pressure, all of these reactions can be modeled by a first order rate law. Thus, the general rate (Equation 27) can be used to predict the products of the n-hexane isomerization reaction. Equation 27 uses molar concentrations of the components. The rate was developed using a Pt-H-for mordenite (Pt/HM) catalyst.

$$\frac{dC_i}{dt} = -\left(\sum_{j=1}^5 K_{j,i}\right) \cdot C_i + \sum_{j=1}^5 K_{i,j} C_j \quad \text{Eq. 27}$$

n-Hexane	1
3-MP	2
2-MP	3
2,3-DMB	4
2,2-DMB	5

Table 13: Nomenclature used in the reaction rate equation for n-Hexane

The rates of each of the reactions are dependent on the equilibrium constant that can be found by rearranging the Arrhenius equation to the form of

$$\ln(K) = \ln(A) - \left(\frac{E}{R}\right)\left(\frac{1}{T}\right) \quad \text{Eq. 28}$$

The activation energies and the pre-exponential factors for these reactions are listed in Table 14 and Table 15. With these values and Equation 28, the products of the isomerization reaction of n-hexane can be predicted.

	n-C6		3MP		2MP	
	-E/R	A	-E/R	A	-E/R	A
n-C6	0	0	-19406	1.25E+16	-19666	2.57E+16
3MP	-23035	1.12E+19	0	0	-15184	4.7E+13
2MP	-20758	7.68E+16	-16076	1.68E+14	0	0
23DMB	-23784	1.97E+18	-21259	2.66E+17	-19478	5.56E+16
22DMB	-14552	7.10E+09	-27669	4.48E+21	-9480	1.97E+06

Table 14: Activation Energy and Frequency Factor for n-Hexane Isomerization

	23DMB		22DMB	
	-E/R	A	-E/R	A
n-C6	-29556	1.2E+24	-25756	9.3E+19
3MP	-15982	1.61E+13	-26796	3.53E+21
2MP	-16134	2.8E+13	-25562	3.02E+20
23DMB	0	0	-16446	2.00E+13
22DMB	-18192	2.98E+14	0	0

Table 15: Activation Energy and Frequency Factor for n-Hexane Isomerization

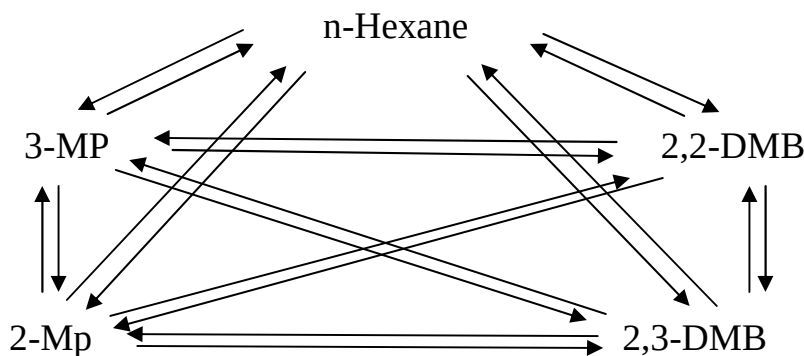


Figure 9: Reaction Pathways for n-Hexane and its isomers⁴⁹

By using the kinetic models for the reactions occurring in the isomerization unit, Excel and GAMS can be used to determine the outlet concentration of the isomerate stream. The octane number of this stream can be found as well, which is necessary for the blending model to predict the octane number of product streams of the refinery.

Isomerization Model Results

From the reaction equilibrium, the unit is expected to obtain a greater conversion of straight-chained alkanes to isomers at lower temperatures. This occurs in the model as shown in Figure 10. It can be seen that as the temperature of the isomerization unit increases, the octane rating of the product stream decreases. Despite the temperature increase, the octane number of the product stream of the isomerization unit is greater than that of the feed stream to the unit (see pink line in Figure 10). It can be seen that the model is not extremely sensitive to the change in temperature. This can be explained by the reaction conditions of the isomerization unit. The conditions of this reaction are not extreme, so sensitivity is not expected.

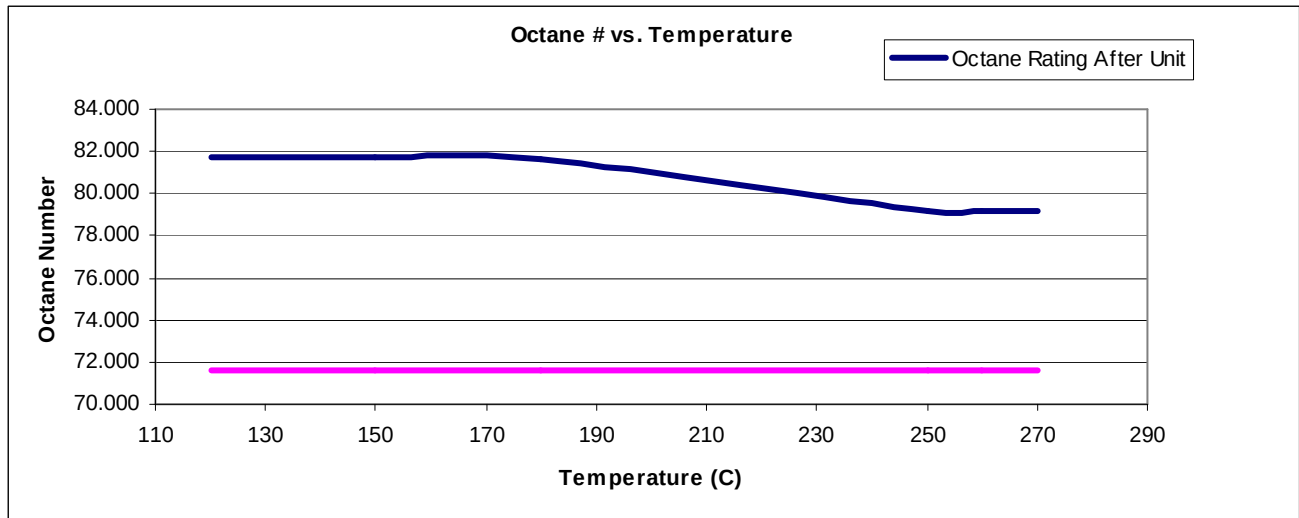


Figure 10: Octane Number vs. Temperature

The model is not sensitive to the hydrogen to hydrocarbon ratio as shown in Figure 11. As the ratio increased, there was no drastic change in the octane number of the isomerate stream. Typically, the hydrogen is used to minimize carbon deposits on the catalyst⁵⁰. Once again, the octane number of the isomerate stream is higher than that of the feed stream, showing that the isomerization unit is increasing the octane number of the feed. This is consistent with typical isomerization units, which can result in an octane number increase from 70 to 84⁵¹.

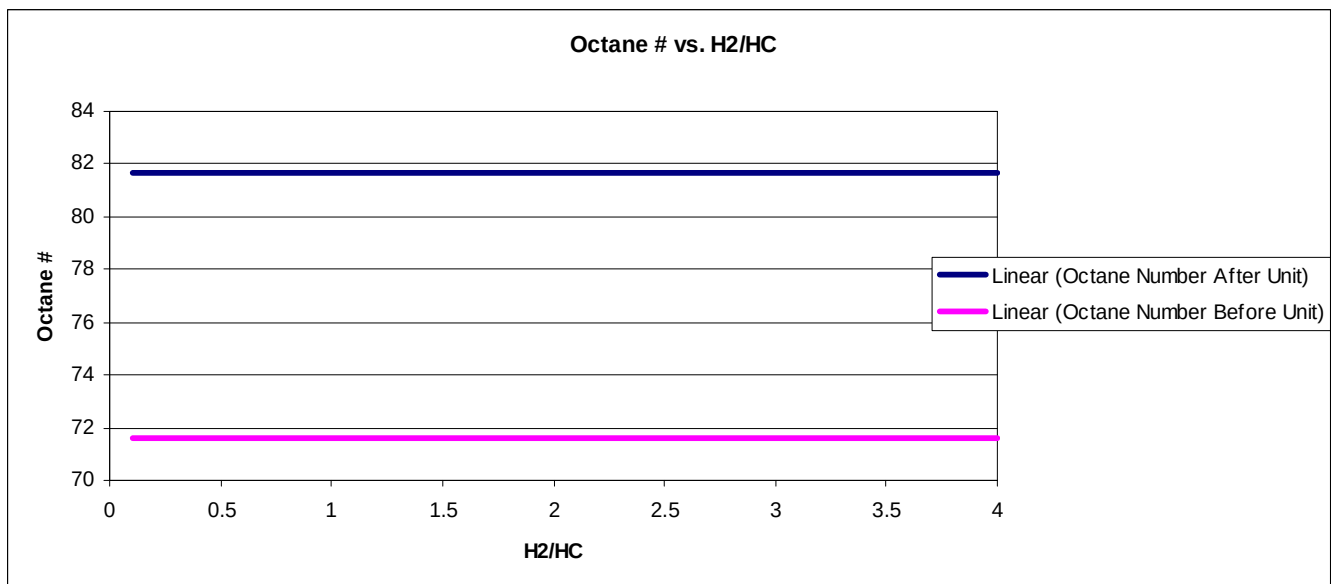


Figure 11: Octane # vs. H2/HC

BLENDING MODEL

The current refinery model has six petroleum streams coming into the blending section of the refinery from three different process units. These streams are then blended into gasoline products. There is also a diesel pool, which blends diesel from the three petroleum streams.

For each of the gasoline streams, the mass flow rate, API gravity, octane numbers (MON, RON), and Reid Vapor Pressure (RVP) are known. From these values, the volumetric flow rates and vapor pressure blending index are calculated. Two grades of gasoline are produced: normal grade (87 octane) and premium grade (91 octane). Both grades have the Environmental Protection Agency mandated constraint on RVP of 8.7 psi for the summer months, and 12 psi for the winter months. Both grades also have the same constraint on total n-butane content of 8%. The other inputs into the gasoline blending model are the predicted market demands and market prices for the two grades of gasoline.

With these inputs, the blending model optimizes the amount of each of the six streams that blends to produce the two grades of gasoline. The maximized objective function is the profit, and the constraints are the component mass balances, and the gasoline specifications (octane, RVP, and maximum n-butane content). The octane requirement is calculated by using a volume percent weighted average for both the MON and RON, and averaging the resulting MON and RON. The RVP requirement is calculated by using a volume percent weighted average of the vapor pressure blending index and comparing this to the vapor pressure blending index of the required RVP. The n-butane content restriction is met by requiring the volume percent of n-butane to be less than or equal to the maximum value.

Diesel blending consists of optimizing the amount of diesel and kerosene to produce high speed diesel. For diesel, the aniline point and the API gravity are required to calculate the diesel index. For fuel oils, properties such as flash point, pour point, and cloud point are also important.

OCTANE NUMBER

Octane number is an important characteristic of fuels used in spark engines, such as gasoline. It represents the antiknock characteristic of a fuel. There are two methods used to determine the octane number of a fuel. The motor octane number (MON) of a fuel is measured under road conditions, and the research octane number (RON) is measured under city conditions. The average of the MON and RON is the posted octane number that consumers see at the gas pump and is the specification that must be met for the specific type of gasoline.

The octane number of a fuel is highly dependent on the chemical structure of the individual components in the mixture, and affected by the interaction between molecules. Due to these properties, octane numbers blend nonlinearly. Weighted averages can be used when the contribution of each component is less than approximately 15% of the total volume, without introducing a large amount of error. Many blending approaches have been developed, including a blending index for the RON given by the following analytical relation:

$$BI_{RON} = 3.205 + (0.279 * \text{EXP}(0.031 * \text{RON})) \quad \text{Eq. 29}$$

After the octane numbers have been converted to the octane blending index, they blend linearly, and the resulting research octane number is obtained by solving the equation above for RON.

VAPOR PRESSURE

The Reid Vapor Pressure (RVP) is a measure of a petroleum mixture's vapor pressure at 100°F, and is used to determine the volatility of the mixture. It differs from the mixture's true vapor pressure at temperatures other than 100°F, and may include measurement error from the equipment used. RVP is used to standardize volatility measurements. It does not blend linearly, and a blending index is used to linearize blending calculations. Vapor pressure blending index (VPBI) is determined from RVP by:

$$VPBI = (RVP)^{1.25} \quad \text{Eq. 30}^{52}$$

A theoretical model for vapor pressure blending can be determined from thermodynamics, and is feasible for the case in which the input streams from the refinery units have relatively constant compositions. The composition of the petroleum mixture would have to be known. In refineries, the composition of the purchased crude oils changes, which changes the composition of the inputs and outputs of the refinery process units, despite blending different crude oils to keep the blend entering the refinery relatively constant. This provides the blending units, on the very end of the refinery, with inputs of varying composition.

For the model to be developed, the fugacity of each component, relative to the interactions with the other components in the mixture, would be calculated. Then the overall fugacity of the system would be the sum of the fugacities of each component. Once the true vapor pressure from this method is known, the RVP of the mixture is determined by solving for the true vapor pressure at 100°F.

LIQUID VISCOSITY

Liquid viscosity can be estimated using empirical correlations. Most correlations used estimate liquid viscosity as only a function of temperature, because most applications for which viscosities are important are at low to moderate pressure. Viscosity is inversely proportional to temperature. Eyring developed the following semi-theoretical model from thermodynamics and tuned the coefficients using experimental data.

$$\mu = \frac{N_A h}{V} * \exp\left(\frac{3.8T_b}{T}\right) \quad \text{Eq. 31}^{53}$$

where:

μ is the absolute liquid viscosity in poise at temperature T;

T is the temperature in Kelvin;

T_b is the normal boiling point in Kelvin;

h is Planck's constant (6.624×10^{-27} g*cm²/s); and

N_A is Avogadro's number (6.023×10^{23} gmol⁻¹).

For petrochemicals, an empirical correlation has been developed that gives the liquid viscosity within +/-5% of the actual value. Five experimentally determined parameters (A, B, C, D, and E) are used. This data is available from the American Petroleum Institute's Technical Databank (API-TDB).⁵⁴

$$\mu = 1000 * \exp\left(A + \frac{B}{T} + C \ln T + D * T^E\right) \quad \text{Eq. 32}$$

For defined liquid mixtures, the following mixing rules are recommended in the API-TDB and Design Institute for Physical Properties (DIPPR) manuals:

$$\mu_m = \left(\sum_{i=1}^N x_i \mu_i^{1/3}\right)^3 \text{ for liquid hydrocarbons} \quad \text{Eq. 33}^{55}$$

$$\ln \mu_m = \sum_{i=1}^N x_i \ln \mu_i \text{ for liquid nonhydrocarbons} \quad \text{Eq. 34}$$

where:

μ_m is the absolute viscosity of the mixture;

μ_i is the absolute viscosity of component i, with the same units as μ_m is desired in; and

x_i is the volume fraction of component i.

For liquid petroleum fractions of unknown compositions, an experimental data point can be taken for the viscosity at 100°F, and then the following correlation can be used:

$$\log_{10}[\nu_T] = A \left(\frac{311}{T}\right)^B - 0.8696 \quad \text{Eq. 35}^{56}$$

$$A = \log_{10}(\nu_{100}) + 0.8696$$

$$B = 0.28008 * \log_{10}(\nu_{100}) + 1.8616$$

where:

T is the liquid's temperature in Kelvin;

ν_{100} is the viscosity data point taken at 100F, in cSt; and
 ν_T is the viscosity at temperature T, in cSt.

Once the viscosity is known, the viscosity-blending index can be calculated using the correlation below, which was developed by the Chevron Research Company. Once the blending index is known, the viscosity index of a mixture can be determined using the volume-weighted averages of the blending indices of the constituents.⁵⁷

$$BI_v = \frac{\log_{10} \nu}{3 + \log_{10} \nu}$$

$$BI_{v,mix} = \sum x_{vi} BI_{v,i}$$
Eq. 36

Where:

ν is the kinematic viscosity in cSt;
 $BI_{v,i}$ is the viscosity blending index of component i; and
 $x_{v,i}$ is the volume fraction of component i.

POUR POINT

“The pour point of a petroleum fraction is the lowest temperature at which the oil will pour or flow when it is cooled without stirring under standard cooling conditions. When the temperature is less than pour point of a petroleum product it cannot be stored or transferred through a pipeline.”

Pour point depressant additives are used in producing engine oils, and can achieve pour points as low as -25 to -40°C. Pour point depressants inhibit the growth of wax crystals in the oil.

The pour point of a petroleum fraction can be estimated from viscosity, average molecular weight, and specific gravity using the following empirical equation, which was developed with data from over 300 petroleum fractions⁵⁸:

$$T_p = 130.47 \left[SG^{2.970566} \right] * \left[M^{(0.61235 - 0.47357 SG)} \right] * \left[\nu_{100}^{(0.310331 - 0.32834 SG)} \right]$$
Eq. 37

Where:

T_p is the pour point in Kelvin;

M is the molecular weight; and

ν_{100} is the kinematic viscosity at 100°F

The pour point of petroleum mixtures does not blend linearly, and the pour point blending index is used to linearize the system. The pour point blending index is related to the pour point temperature by the following relation⁵⁹:

$$BI_p = T_p^{\left(\frac{1}{0.08}\right)} \quad \text{Where } T_p \text{ is the pour point in Kelvin.} \quad \text{Eq. 38}$$

$$BI_{p,mix} = \sum x_{vi} BI_{p,i} \quad \text{Eq. 39}$$

DIESEL INDEX AND CETANE INDEX

The diesel index and cetane index measure the favorability of auto-ignition in a petroleum mixture. This property is essential for diesel engines. The diesel index can be calculated from the API gravity and the aniline point using the following empirical correlation:

$$DI = \frac{(API)(1.8AP + 32)}{100} \quad \text{Eq. 40}^{60}$$

where:

AP is the aniline point in °C; and

API is the API gravity

The cetane index can then be found from the diesel index using the following empirical correlation:

$$CI = 0.72DI + 10 \quad \text{Eq. 41}^{61}$$

Once either the diesel or cetane indexes are known, a final diesel product can be blended.

SULFUR CONTENT

Sulfur is considered an impurity when blending gasolines. Sulfur is also a toxin regulated by the Environmental Protection Agency. In gasoline, the regulated sulfur content limit is 60 ppm, while the regulation for diesel fuel is 15 ppm. A sulfur balance was completed for the all streams in the refinery leading to the blending unit to ensure that all EPA regulations were met.

DECISION MAKING

Decision making in a refinery can be separated into two different categories: planning and scheduling. Planning is based on the forecasted market demands and prices. Scheduling is based on the given equipment, materials, and time⁶². Planning decisions are made months and sometimes years in advance, while scheduling decisions operate on a much shorter timetable. It is important to note that all scheduling decisions are dependent on the planning decisions made previously. Scheduling decisions can be only as good as the planning decisions made⁶³. Therefore, the decision making for planning must be based on the most accurate representation of refinery processes. Any inaccuracy has the potential to lead to poor decisions and lead to a lower profit margin.

UNIT OPERATIONS DECISION MAKING

Modeling unit operations, which is the main scope of this project, will provide recommendations based on more detailed models of each unit. In the current LP models, basic relationships between input data are used to calculate the output data. This allows for the program to remain linear. This project is aimed at expanding the unit models to allow nonlinearities, and therefore make the overall model more accurate and recommendations more economical.

Existing LP models utilize input/output relationships shown by equations 42 and 43, while the actual unit operates following nonlinear equations such as equations 44.

$$F_{ref,CRU2} = F_{i,CRU2} \cdot 0.86 \quad \text{Eq. 42}$$

$$ON_{ref,CRU2} = 99 \quad \text{Eq. 43}$$

$$r_{n-C5} = - \left[K_2 \cdot \left(\frac{C_{n-C5}}{[H_2]} \right)^{0.125} - 0.0000197 \cdot t \right] \left[K_{eq} \cdot C_{n-C5} - (K_{eq} + 1) \cdot C_{i-C5} \right] \quad \text{Eq. 44}$$

As can be seen, the degree of nonlinearity is fairly drastic, meaning that the accuracy of linear models is substituted for model simplicity.

In order to model unit operations, the unit models are broken down into the products as a function of the input variables. This is by far the most accurate approach to modeling unit operations because of its completeness. Although it provides good results, it is not feasible to add these to LP models. Utilizing multiple nonlinear unit models makes it impossible to find the global optimum. The difficulty in finding a global optimum can possibly be attributed to variables being based on compounded multiple nonlinear models. The nonlinear HDS model was added to the LP (making it a nonlinear program (NLP)) Bangchak model. This showed the exact same recommendations as the LP model, but the gross refinery margin was different due to the different associated costs. After the HDS unit was added, the NPU2 unit was added. This provided an infeasible solution for the model. After only two units were added, the program had difficulty reaching an optimum; therefore, another approach was sought out.

The solution to the nonlinear problems is to simply linearize it. In order to linearize a unit model, the variables are discretized. Discretizing the variables achieves linearity since it is variables existing in nonlinearities that creates the problems. The discretization of the variables changes equation 45 into the following form:

$$X = f(T, C_{A0}, C_{B0}) \quad \text{Eq. 45}$$

$$X = \sum_{(T, C_{A0}, C_{B0})} Z(T, C_{A0}, C_{B0}) \cdot f(T, C_{A0}, C_{B0}) \quad \text{Eq. 46}$$

where $Z(a,b,c)$ is a binary variable that is used to choose the operating conditions. This reduces all variables present to zero, and therefore the model can be ran as a mixed integer program (MIP) and not an NLP.

This option was altered slightly before it was added to the problem. Instead of adding the binary variable times the function, a multi-dimensional table was created $X(a,b,c)$. This table was then uploaded into the model, and the equation became:

$$X = \sum_{(T, C_{A0}, C_{B0})} Z(T, C_{A0}, C_{B0}) \cdot X(T, C_{A0}, C_{B0}) \quad \text{Eq. 47}$$

This method should produce identical results to equation 47 because the variables are discretized the same way and should provide identical outputs. This method was chosen in order to keep the overall model much simpler. Not only will model run statistics (rows and columns) be decreased, but it would reduce the lines of code by approximately three or four times. Reducing the length of the program will allow the overall model to be much easier to work with. The downside is that the unit models are separate. This means the models must be ran separate, and the results are added to a table that is then called from the overall model. It should be noted that the unit models output their results in a very simple way that they may be cut-and-pasted into the desired location.

REFINERY MODELING

Each unit is modeled individually and then put into a comprehensive refinery model. The purpose of this model is to predict optimum outputs for each unit as well as the entire refinery, and to optimize gross refinery margin (GRM).

MODELING

All of the units were modeled following these steps:

1. Model in Microsoft Excel

This step is done in order to ensure that all input constants and variables are known. It is also used to compare to the GAMS model (following step) to make sure that the final GAMS model

is accurate. Modeling in Excel first allows the user to be able to see immediate results after changes of inputs or equations instead of having to run a program and extrapolate results.

2. Model in GAMS

The type of model built in GAMS depended on the timetable of the project. Near the beginning, a nonlinear model was built immediately after the Excel model. Once the nonlinear models were ruled out of the final design of the project, linear models were built in GAMS. These unit models were run using the CPLEX solver. The models were built with all variables and constants entered as parameters and scalars. The variables and equations that were used to initiate the program are listed below:

```
Variable a,b;  
a.lo = 0;  
a.up = 0;  
Equation aa;  
aa.. a = b;  
solve (model) using lp maximizing b
```

The LP unit models call the discretized unit variables from an excel file and utilize a put function to calculate the desired outputs for all possible combinations. The desired outputs are put into separate output Excel files. For example, the catalytic reforming units output the amount of reformate, LPG, fuel gas, and hydrogen produced, as well as the octane number of the reformate. Each of these is organized into a separate file ready to copy and paste for the overall model to use.

As discussed before, the variables in the overall model are chosen from a discretized list. In order to do this, the binary variable (Z) is utilized. To ensure that only one option is chosen the sum of all Z variables is set to equal 1 as seen in equation 48. Constraints placed on outputs of

$$\sum_{(a,b,c)} Z(a,b,c) = 1 \quad \text{Eq. 48}$$

several units, along with operating costs, determine the optimum operating conditions. The constraints that are placed on different units can be seen in table 15. The outlet sulfur contents are

	Outlet Sulfur (ppm)	SUPG (ON)	ISOG (ON)
NPU2	60	NA	NA
NPU3	60	NA	NA
CRU2	NA	91	95
CRU3	NA	91	95
ISOU	NA	91	95
KTU	5	NA	NA
DGO-HDS	15	NA	NA

Table 15: Unit Constraints

used based on current EPA regulations except for the KTU constraint⁶⁴. The purpose of the KTU is to reduce the content of the mercaptan sulfur. Since no mercaptan sulfur content data is available for the crude types, the sulfur content and constraint are made up. Since this project is a proof of concept project, as long as the data and constraint is reasonable, it will not affect the accuracy of the program. The octane number constraints are not directly applied to the unit output. The octane number of each of the gasoline products is calculated by the following equation 49:

$$ON_{gas} = \frac{\sum_{i=LNT,HNT,REF,ISOM,DCC,MTBE} (F_i \cdot ON_i)}{F_{gas}} \quad \text{Eq. 49}$$

Therefore, the output octane number of reformat or isomerase had no actual requirement, just as long as the gasoline meets requirements. Since the outlet octane of the units is dependent on the flow rate, the model must optimize the correct combination of flow and octane number.

One problem with running the overall model became how to determine the flow rate for each of the unit models. The first attempt was to simply set the flow rate from the overall model equal to the unit model flow rate. This became a problem because now flow rates for the units in the

$$F_{overall} - F_{unit} \leq \frac{d}{2} \quad \text{Eq. 50}$$

$$F_{overall} - F_{unit} \leq \frac{d}{2}$$

$$d = \text{difference between discretized flow rates}$$

overall model are now discretized, and the degrees of freedom are decreased. The model began having disastrous problems with resource limits when the fourth unit was added to the model. When degrees of freedom were given back to the model by implementing equations 50 and 51, the model was not constrained by resource limits and solved in less than two seconds. Using these equations, as stated before, offers the advantage of an increased amount of degrees of freedom, but the major disadvantage is that the unit model is not as accurate. One solution to increasing accuracy is to increase the amount of discretized flow rates; therefore making the difference between each flow less.

Another problem that stemmed from adding equations 50 and 51 is that the mass balance out of the unit is not completely balanced. Each scenario ran using the unit models is completely balanced, but when the flow rate of the overall model does not match the flow rate from the unit model, the overall model had an unbalanced mass balance for that unit. This, of course, is a big problem, but seeing that there is another inconsistency in the mass balance and a way to minimize it makes it a reasonable problem. The inconsistency is that the model utilizes volumetric flow rates (at standard conditions); therefore, it is currently operating under a volumetric flow balance and not a mass balance. The problem with this is that if streams have a different molecular weight, then the volumetric flow balance does not correspond to a mass balance. Just off the distillation units, all streams have different molecular weights. The residue and diesel oil cuts are going to have a much higher molecular weight than the fuel gas, LPG, and naphtha cuts. Also, as already discussed, if the amount of discretized flow rates is increased, then the difference is decreased, and the unit will become more balanced.

There was an attempt to keep the mass balance balanced by multiplying an average product flow rate times the inlet flow as shown in equation 52. The problem is that this is a nonlinear equation because two variables are multiplied by each other (remember that the

$$F_{product} = F_{avg, product} \cdot F_{overall} \quad \text{Eq. 52}$$

average product flow rate is a variable because it is dependent on the binary variable Z). The process to linearize it is expressed in equations 53 through 56. It introduces a gamma function that

$$\Gamma(a, b, c) - x \cdot Z(a, b, c) \leq 0 \quad \text{Eq. 53}$$

$$\Gamma(a, b, c) \geq 0 \quad \text{Eq. 54}$$

$$(F_{overall} - \Gamma(a, b, c)) - x \cdot (1 - Z(a, b, c)) \leq 0 \quad \text{Eq. 55}$$

$$F_{overall} - \Gamma(a, b, c) \geq 0 \quad \text{Eq. 56}$$

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

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

exists as a linearized product of the binary variable Z and the variable flow rate. The gamma function is used along with a couple of tables (overall flow rate to unit and product flow rates out of unit) to determine the balanced product flow rates. This method was used in the model and produced results that showed it was exceeding the resource limit. This resource limitation was produced with only three of the six required linearizations of a binary variable and variable flow rate (three linearizations for the mass balance of ISOU, CRU2, and CRU3 and the other three for the octane blending of the isomerate and reformat streams). Since there are no ways around the octane blending linearization equations, it was necessary to remove the three mass balance linearizations in order to allow the program not to bump into resource limitations.

UNIT MODELS

All of the unit models are solved using ordinary differential equations (ODE). The ordinary differential equations are modeled in Excel and GAMS using Euler steps. All units were modeled with 20 steps. This number was chosen because a limit had to be set on the number of steps based on the work required to add each step to the GAMS model and based on the accuracy of the model using that many steps. The work required on each model was limited since the

$$F_{n,S} = F_{n-1,S} - r_{n-1} \cdot \Delta W \quad \text{Eq. 57}$$

$$F_{n,H_2} = F_{n-1,H_2} - r_{n-1} \cdot \Delta W \quad \text{Eq. 58}$$

$$C_{n,S} = \frac{C_{tot} \cdot F_{n,S}}{F_{tot}} \quad \text{Eq. 59}$$

$$C_{n,H_2} = \frac{C_{tot} \cdot F_{n,H_2}}{F_{tot}} \quad \text{Eq. 60}$$

project had to keep moving forward. The accuracy of each unit model would effectively be increased if more steps were added, but any steps added past twenty was only a minimal addition in terms of accuracy. Equations 57 through 60 show an example of Euler's steps used in the hydrotreater models.

As ordinary differential equations, each of the units operates based on an independent variable. The independent variable for the hydrotreaters is catalyst weight. The reforming and isomerization models use volume. The values that the independent variables are evaluated between are shown in table 16.

Unit	Independent Variable	Evaluated to:
NPU2	W (g)	1.00E+08
NPU3	W (g)	3.90E+07
Reformer Reactor 1	W (lb)	1.40E+03
Reformer Reactor 2	W (lb)	1.40E+03
Reformer Reactor 3	W (lb)	2.30E+03
ISOU	V (L)	5.60E+03
KTU	W (g)	1.10E+08
DGO-HDS	W (g)	1.80E+08

Table 16: ODE Independent Variables

FUEL BALANCE / HYDROGEN BALANCE

The existing LP model included a fuel balance, the used fuel gas, and one of the fuel oil products (FOVS) to heat the refinery. This was altered so that the amount of fuel gas and fuel oil burnt

$$Q = \dot{m} \cdot c_p \cdot \Delta T \quad \text{Eq. 61}$$

$$Q = \sum_{i=FG,FOVS} H_{vap,i} \cdot \dot{m} \quad \text{Eq. 62}$$

was based on the inlet temperature and flow rate. Equations 61 and 62 show the energy balance between energy required and amount of fuel burnt. The heat of combustion used for the fuel gas is 15.6 MMBtu/m³ and for the fuel oil is 37.5 MMBtu/m³. The model will choose to burn the fuel gas first since there is no selling price for it and thus is more profitable to conserve as much of the fuel oil as possible.

A hydrogen balance was added to model. All hydrogen is being produced by the catalytic reforming units and is consumed by the hydrotreating units. The model did not sell the hydrogen, but simply reported the amount of the product.

RESULTS AND CONCLUSIONS

The final model of the Bangchak refinery was solved using the CPLEX solver in GAMS. This was ran on a 2.8 GHz Pentium 4 processor. The program requires about 50 minutes to reach an integer solution and 2 hours to solve for the optimum solution. The solution requires over 300,000 iterations to determine the optimal solution. The iteration limit and time limit are set well above the required amounts to solve.

The model showed the exact results as hypothesized. Adding unit operations to a LP model significantly affects the recommendations and refinery margin. Two different programs were run to compare the addition of unit operations. First, the model with all unit operations decisions set as constants, and the second with all unit operations decisions as variables. Setting unit operations decisions as constants is an accurate representation of LP models since the desired outputs are only based on the inlet flow rate. It actually does not even completely reflect LP models because most models show that output data does not form a linear relationship with the inlet flow rate. Therefore, the model representing current LP models actually should be more accurate than the LP model, but will still prove the hypothesized concept.

The two models showed drastic differences in gross refinery margin and recommendations. The gross refinery margin of the model using unit operations was over twice the profit as the model

without unit operations. This data can be seen in Table 17. The recommendations also changed a great deal. These changes can be seen in Tables 18 and 19, and are highlighted in yellow below.

	GRM
Model without Unit Operations	\$16,492,336.72
Model with Unit Operations	\$34,130,901.06

Table 17: Gross Refinery Margin

Model without Unit Operations				Model with Unit Operations			
	1	2	3		1	2	3
Oman (OM):	167734.3	167339.3	165082.6	Oman (OM):	244486.2	262303.1	267899.8
Tapis (TP):	13427.7	14317	19397.5	Tapis (TP):	32853.3	41126.2	47392.2
Labuan (LB):	0	0	0	Labuan (LB):	0	0	9041.4
Seria Light (SLEB):	95392.2	95392.2	95392.2	Seria Light (SLEB):	95392.2	95392.2	95392.2
Phet (PHET):	57235.3	57235.3	57235.3	Phet (PHET):	57235.3	57235.3	57235.3
Murban (MB):	95392.2	95392.2	95392.2	Murban (MB):	95392.2	95392.2	95392.2
MTBE:	13662	13700.7	13921.7	MTBE:	18266	19392.8	20404.2
DCC:	68088	68301.8	69523.2	DCC:	87059.5	91153.7	93941.2

Table 18: Model Without Unit Operations

Table 19: Model With Unit Operations

This change was anticipated because optimization of a refinery exists on a multi-dimensional field. Both crude processing decisions along with unit operations decisions are important to the optimization. Restricting the unit operations adds additional constraints on the optimization (e.g. the octane number of reformate is considered to be constantly 99 in the LP model while depending on operating conditions, the octane number can be as high as 101). These additional constraints reduce the thoroughness and accuracy of the model and will result in a distorted view of the global optimum.

As discussed before, refineries typically make planning decisions months in advance and scheduling decisions are made only days or possibly a week in advance. Tying these decisions together would effectively enhance the productivity and profit of the refinery. Upper-management in refineries do not show much interest in the difference in operating conditions from day-to-day; they are simply concerned with whether the unit is running or not.

FUTURE WORK

Additional work to further this project can be done to increase the number of scenarios used in this model. Currently over 1×10^{17} scenarios are being evaluated, but that is not enough to effectively implement in any refinery. Refinery processing will require a great deal more scenarios to be evaluated. Even for a small refinery such as Bangchak, many more less significant variables are present including some possibly between units. In order to commercially develop this project, more work needs to be done in order to be as accurate and effective as possible.

Also, additional work could create a more accurate operating cost equation associated with each of the units. Currently, only basic equations utilizing the fuel balance and compressor work are used to associate the cost with each unit.

Another project that could possibly be connected to this one in the future would be to model the uncertainty associated with crude processing units. This project would utilize a unit model (or the overall model) and use the percent uncertainty in measurement readings to make recommendations based on the degree of risk the company is willing to give.

References

Note: In-text numbers correspond to the footnotes found at the end of this section.

1. Aleksandrov, A.S. et al. Kinetics of low-temperature n-pentane isomerization over NIP-66 catalyst. *Khimiya i Teckhnologiya Topliv i Masel*. No. 10, pp. 5-8, October, 1976.
2. Burisan, N.R., N.K. Volnukhina, A.A. Polyakov, and I.S. Fuks. Kinetic relationships in the low-temperature isomerization of n-butane. *Khimiya i Teckhnologiya Topliv i Masel*. No. 10, pp. 6-8, October, 1972.
3. Cheng-Lie Li, Zhe-Lin Zhu. Network of n-Hexane isomerization over Pt/Al₂O₃ and Pd/HM catalysts. *Fuel Science and Technology Int’L*. v. 9 n. 9. Jan. 01 1991 pg 1103-1122.
4. Conversion Process. Petroleum Refining. Ed. Pierre Leprince. Institut Français du Petrole Publications. 1998 Editions Technip, France.
5. Encyclopedia of Chemical Processing and Design. 62 Vent Collection System, Design and Safety to Viscosity-Gravity Constant, Estimation. Ed. John McKetta. 1998 Marcel Dekker, Inc. New York, NY.
6. Galiasso et al., Hydrotreat of Light Cracked Gas Oil, Heinz Heinemann, copyrighted 1984, pg 145-153
7. Gary, J.H. and G.E. Handwerk. Petroleum Refining: Technology and Economics. Marcel Dekker Inc: New York, 2001, 121-141. and A.V. Mrstik, K.A. Smith, and R.D. Pinkerton, *Advan. Chem. Ser.* 5 , 97. 1951.
8. Liang. Et. Al. A Study on Naphtha Catalytic Reforming Reaction Simulation and Analysis. *Journal of Zhejiang University Science*. 2005 6B(6): 590-596.
9. Meyers, Robert A. Handbook of Petroleum Refining Processes. 3rd edition. McGraw-Hill: NewYork, 2004, 14.35.
10. Pongsakdi, Arkadej, et. al. Financial Risk Management in the Planning of Refinery Operations. *International Journal of Production Economics*. Accepted for publication, 20 April 2005.

11. Riazi, M.R. Characterization and Properties of Petroleum Fractions. West Conshohocken, PA: ASTM International, 2005., p. 335
12. Rodriguez, M.A. and Ancheyta, J. *Modeling of Hydrodesulfurization, Hydrodenitrogenation, and the Hydrogenation of Aromatics in Vacuum Gas Oil Hydrotreaters*. Energy and Fuels. 2004, 18, 789-794.
13. Speight, James G. Lange's Handbook of Chemistry (15th Edition). McGraw-Hill., Table 5.9.
14. Sulfur Removal, <http://library.wur.nl/wda/abstracts/ab3328.html>

¹ Pongsakdi, *et al.*

² Pongsakdi, *et al.*

³ http://www.cheresources.com/refinery_planning_optimization.shtml

¹⁰ NPRA "Diesel Sulfur" www.npradc.org/issues/fuels/diesel_sulfur.cfm

¹¹ Sulfur Removal, <http://library.wur.nl/wda/abstracts/ab3328.html>

¹² Gary and Handwerk

¹³ Galiasso et al., *Hydrotreat of Light Cracked Gas Oil*, Heinz Heinemann, copyrighted 1984, pg 145-153

¹⁴ Oil and Gas Journal (Aaland and Rhodes)

¹⁵ Rodriguez and Ancheyta

¹⁶ <http://www.eia.doe.gov/oiaf/servicerpt/ulsd/chapter3>.

¹⁷ Gary and Handwerk

¹⁹ Liang, Et. Al. A Study on Naphtha Catalytic Reforming Reaction Simulation and Analysis. Journal of Zhejiang University Science. 2005 6B(6): 590-596.

²⁰ Gary and Handwerk

³⁰ *Conversion Process*.

³¹ *Conversion Process*.

³² *Encyclopedia of Chemical Processing and Design*. 27

³³ Gary and Handwerk, 4th edition

³⁴ *Conversion Process*.

³⁵ *Conversion Process*.

³⁶ *Conversion Process*.

³⁷ *Conversion Process*.

³⁸ *Conversion Process*.

⁴¹ *Properties of gases and liquids, the*. Reid, Robert C.

⁴² *Conversion Process*

-
- ⁴³ Burisan, N.R., N.K. Volnukhina, A.A. Polyakov, and I.S. Fuks. *Kinetic relationships in the low-temperature isomerization of n-butane*. Khimiya i Teckhnologiya Topliv i Masel. No. 10, pp. 6-8, October, 1972.
- ⁴⁴ Aleksandrov, A.S. et al. *Kinetics of low-temperature n-pentane isomerization over NIP-66 catalyst*. Khimiya i Teckhnologiya Topliv i Masel. No. 10, pp. 5-8, October, 1976.
- ⁴⁵ Aleksandrov, A.S. et al. *Kinetics of low-temperature n-pentane isomerization over NIP-66 catalyst*. Khimiya i Teckhnologiya Topliv i Masel. No. 10, pp. 5-8, October, 1976.
- ⁴⁶ Aleksandrov, A.S. et al. *Kinetics of low-temperature n-pentane isomerization over NIP-66 catalyst*. Khimiya i Teckhnologiya Topliv i Masel. No. 10, pp. 5-8, October, 1976.
- ⁴⁷ *Encyclopedia of Chemical Processing and Design*. 27
- ⁴⁸ Cheng-Lie Li, Zhe-Lin Zhu. *Network of n-Hexane isomerization over Pt/Al₂O₃ and Pd/HM catalysts*. Fuel Science and Technology Int’L. v. 9 n. 9. Jan. 01 1991 pg 1103-1122.
- ⁴⁹ Cheng-Lie Li, *Network*
- ⁵⁰ Catalytic Reforming and Isomerization
- ⁵¹ Catalytic Reforming and Isomerization
- ⁵² Gary and Handwerk, 166
- ⁵³ Riazi, M.R. *Characterization and Properties of Petroleum Fractions*. West Conshohocken, PA: ASTM International, 2005., p. 335
- ⁵⁴ Riazi, p. 335
- ⁵⁵ Riazi, p. 335
- ⁵⁶ Riazi, p. 335
- ⁵⁷ Riazi, p. 335
- ⁵⁸ Riazi, p. 135
- ⁵⁹ Riazi, p. 135
- ⁶⁰ Riazi, p. 138
- ⁶¹ Riazi, p. 138
- ⁶² Kelly and Mann
- ⁶³ Kelly and Mann
- ⁶⁴ EPA paper
- ⁶⁴ http://www.cheresources.com/refinery_planning_optimization.shtml
- ⁶⁴ http://www.conocophillips.com/NR/rdonlyres/199287F3-9CDC-4C6C-8D61-EE1591281F5D/0/FB_entire.pdf
- ⁶⁴ Kelly and Mann
- ⁶⁴ Kelly and Mann
- ⁶⁴ EPA paper