

OPTIMIZATION OF A COMMERCIAL HYDRO-ISOMERIZATION PROCESS

by

Ülfet Ece Küçük

B.S., Chemical Engineering, Istanbul University, 2013

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Chemical Engineering

Boğaziçi University

2015

OPTIMIZATION OF A COMMERCIAL HYDRO-ISOMERIZATION PROCESS

APPROVED BY:

Assoc. Prof. Ahmet Kerim Avcı

(Thesis Supervisor)

Assoc. Prof. Burak Alakent

(Thesis Co-Supervisor)

Assoc. Prof. Hasan Bedir

Assoc. Prof. Abdullah Kerem Uğuz

Prof. Ahmet Erhan Aksoylu

DATE OF APPROVAL:

ACKNOWLEDGEMENTS

Firstly, I would like to thank and express my gratitude to my supervisor Assoc. Prof. Ahmet Kerim Avcı and Assoc. Prof. Burak Alakent for their support, inspiration, patience, guidance and precious comments throughout my thesis. I would like to thank them for giving me the chance to study with them.

My sincere gratitude is due to my thesis committee members, Prof. Ahmet Erhan Aksoylu, Assoc. Prof. Abdullah Kerem Uğuz, and Assoc. Prof. Hasan Bedir who dedicated their valuable time to read and comment on my thesis.

In addition to that, I would like to R&D department of Tüpraş for enabling the attendance to this valuable project and providing the comfortable conditions during the project.

I would like to thank specially my team mates Fırat Uzman and Işıl Kabacaoğlu for their effort, aid, technical and moral support in this project. Without them, lack of motivation and help would demotivating for me.

Very special thanks to my family, for supporting, loving and believing me in every situation. Without their support, I could not do even half of what I've done in my entire life.

I want to also thank to my dear friend Ezgi Mamus especially for being there whenever I need. She proved there is no need to be in the same major to understand the process, developments and nuisance.

I also want to thank my mates Hilal Fidan Acar, Sadık Ödemiş, Fatih Demir, Emre Can Bilir, and Selin Gündür for their support, interest, help and friendship. They showed me it's possible being in a friendly environment even you are at work. Their fellowships have been my biggest motivation and source of energy during the project.

ABSTRACT

OPTIMIZATION OF A COMMERCIAL HYDRO-ISOMERIZATION PROCESS

Isomerization process is one of the most commonly used processes in the petroleum refinery. Product of isomerization unit is “isomerate” that has a great importance for gasoline pool, since its research octane number (RON) is easy to be adjusted and it obeys the legislations about sulfur and benzene content of the gasoline pool. UOP PenexTM process is mostly used application for isomerization. PenexTM is created for the catalytic isomerization of low octane light straight run (LSR) naphtha to obtain high octane and branched isomers. Benzene reduction reactions also occur in the unit, product can be obtained with high octane number and low benzene content. In this thesis, the PenexTM unit at Tüpraş İzmir Refinery are operated at steady state, and optimized for given conditions. Optimization of the process is performed in HYSYS Optimizer Tool. Decision variables are determined after applying degree of freedom analysis to whole flow-sheet and constraints are determined by taking into account of top product rate and quality. Optimization is carried out in mixed mode, which is combination of both SQP and BOX methods, with nine decision variables and two constraints. Objective function of the process is chosen as maximum isomerate barrels production (maximum liquid yield). During the current study, catalyst of the PenexTM unit has been changed and difference between previous and current situation is investigated. The results show that, current state of the unit with changing 0.5-5 °C range of temperature for all unit elements, changing 180 m³/d of deisohexanizer column recycle rate and changing 35 ton/h of stabilizer overhead vapor rate gives optimized process with 85.5 RON and 4673 isomerate barrel value, for first condition. With the change of trickle bed catalyst, value of change in deisohexanizer recycle rate decreases 100 m³/d and change in stabilizer overhead vapor rate decreases 15 ton/h. Change in temperatures range remains constant for second condition. Also, in second condition, 87 RON and 5232 isomerate barrel value is obtained for optimized process.

ÖZET

TİCARİ BİR HİDRO-İZOMERİZASYON SÜRECİNİN OPTİMİZASYONU

İzomerizasyon prosesleri, petrol rafinerilerinde en sık kullanılan proseslerden biridir. İzomerizasyon ünitesinin ürünü olan izomerat, oktan sayısı kolaylıkla ayarlanabildiği ve benzin içeriğindeki benzen ve sülfür kısıtlamalarına uyduğu için önemlidir. UOP Penex™ prosesi, izomerizasyon için en çok tercih edilen uygulamadır. Penex™ düşük oktanlı hafif naftanın katalitik izomerizasyonu, yüksek oktanlı ve dallanmış izomerler elde etmek için üretilmiştir. Proseste aynı zamanda benzen azaltma reaksiyonları da olduğundan, ürün yüksek oktanlı ve düşük benzen içerikli olarak elde edilir. Bu tez kapsamında, Tüpraş İzmir Rafinerisinde bulunan kararlı halde ve belirlenen koşullarda çalışan Penex™ ünitesinin optimizasyonu yapılmıştır. Optimizasyon için HYSYS Optimizer yazılımı kullanılmıştır. Karar değişkenleri serbest değişkenlerin analizi yapılarak, kısıtlar alınmak istenilen ürünün özelliklerine dayanarak belirlenmiştir. Optimizasyon, SQP ve BOX yöntemlerinin birleşimi olan karışık modda, dokuz tane karar değişkeni ve iki tane kısıt ile yapılmıştır. Amaç fonksiyonu maksimum izomer varil miktarı olarak belirlenmiştir. Optimizasyon yapılırken ünitenin katalizörü değiştiğinden, öncesi ve sonrası olmak üzere iki farklı optimizasyon yapılmıştır. Sonuçlar, ünitenin tüm elemanlarının sıcaklığının 0.5-5 °C aralığında, ve deizohexanizer kolonu geri besleme hızının 180 m³/d ve stabilizer tepe buharı miktarının 35 ton/h değerlerinde, birinci durum için optimum koşula 85.5 oktan numarası ve 4673 izomerat varil miktarıyla ulaşılabileceğini göstermiştir. Katalizör değişimiyle, deizohexanizer geri besleme hızının değişimi 100 m³/d'ye, stabilizer tepe buhar miktarının değişimi 15 ton/h'ye düşmüştür. Ünite elemanlarının sıcaklık değişimleri ikinci durum için aynı kalmıştır. İkinci durumun optimize edilmiş hali için elde edilen oktan numarası 87, izomerat varil miktarı 5232'dir.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	iii
ABSTRACT.....	iv
ÖZET	v
LIST OF FIGURES	xii
LIST OF TABLES.....	xv
LIST OF ACRONYMS/ABBREVIATIONS	xvi
1. INTRODUCTION.....	1
2. LITERATURE SURVEY	4
2.1. Isomerization for Octane Upgrading	4
2.2. Simulation of Isomerization Reactors.....	8
2.2.1. The Black Box Model	9
2.2.2. Modified Black Box Reactor.....	10
2.2.3. Empirical Predictive Reactor.....	10
2.2.4. Free Energy Minimization Reactor (Gibbs).....	10
2.2.5. Equilibrium Reactor	10
2.2.6. Stoichiometric Conversion Reactor	11
2.3. Optimization	12
2.3.1. Optimization Methods.....	14
2.3.1.1. Response Surface Methodology (RSM).....	14
2.3.1.2. Heuristic Methods	14
2.3.1.3. Line Search.....	16
2.3.1.4. Golden Section Search	16
2.4. Isomerization Processes in Petroleum Refinery	18

2.5. Dehydro-isomerization	20
2.6. Linear Programming	21
3. MATHEMATICAL TECHNIQUES	24
3.1. Linear Programming	24
3.1.1. Geometry of Linear Programs	24
3.1.2. Standard Form for Linear Programs	26
3.1.3. Pivoting	26
3.1.4. Simplex Algorithm	26
3.1.5. The Column (Recipe/Activity) Approach	28
3.1.6. The Row (Material Balance) Approach	29
3.1.6.1. Define the decision variables	29
3.1.6.2. Define item set	29
3.1.6.3. Set up constraints and the objective function	29
3.2. Linear Programming Software	29
3.3. Process Simulation	30
3.3.1. General Properties of Process Simulators	30
3.3.1.1. Data processing	31
3.3.1.2. Engineering models	31
3.3.1.3. Numerical analysis	31
3.3.2. Advantages of Simulation	32
3.3.3. Disadvantages of Simulation	32
3.3.4. The Basic Steps of a Simulation Study	32
3.3.4.1. Problem Definition	33
3.3.4.2. Project Planning	33
3.3.4.3. System Definition	33
3.3.4.4. Model Formulation	33

3.3.4.5. Input Data Collection & Analysis	33
3.3.4.6. Model Translation	33
3.3.4.7. Validate the Model	33
3.3.4.8. Experimentation & Analysis	33
3.3.4.9. Documentation & Implementation	33
3.3.5. Steady State Simulation Programs	34
3.3.5.1. Pure Component Data Library	34
3.3.5.2. Non-Library Components	34
3.3.6. Unit Operation Calculations	34
3.3.6.1. Type of Problem	35
3.3.6.2. Availability of Resources	35
3.3.6.3. Costs	35
3.3.6.4. Availability of Data	36
3.4. Simulation Optimization	37
3.5. Penex TM Unit	38
3.5.1. Function of the Unit	39
3.5.2. Feed Characteristics	42
3.5.2.1. Hydrotreated Light Naphtha	42
3.5.3. Products Specifications	42
3.5.3.1. Isomerase	42
3.5.4. Thermodynamics of Isomerization Reactions	44
3.5.5. Process Principles	44
3.5.6. Reaction Mechanisms	46
3.5.6.1. Dual-Function Hydro-Isomerization Catalyst	46
3.5.6.2. Naphtene Ring Opening	47
3.5.6.3. Naphtene Isomerization	48

3.5.6.4. Benzene Saturation.....	48
3.5.6.5. Hydrocracking.....	48
3.5.7. Acidizing	49
3.5.8. Chloride (Catalyst) Promoter	49
3.5.9. Process Contaminants	50
3.5.9.1. Contaminants.....	50
3.5.9.2. Undesirable Hydrocarbons	50
3.5.10. Isomerization Reactors	50
3.5.11. Process Variables of The Reactor Section	51
3.5.11.1. Reactor Temperature.....	52
3.5.11.2. Liquid Hourly Space Velocity	56
3.5.11.3. Hydrogen To Hydrocarbon Mol Ratio.....	56
3.5.11.4. Pressure	56
3.5.12. Reactions.....	57
3.5.13. Stabilizer	59
3.5.14. Net Gas Scrubber	59
3.5.15. Caustic Scrubbing.....	60
3.5.16. Deisohexanizer Column (DIH): Theory of Fractionation.....	61
3.5.17. DIH Column	63
3.5.18. DIH Properties	64
3.5.18.1. Objective	64
3.5.18.2. Overhead Temperature and Reflux Liquid Control.....	64
3.5.18.3. Side Draw Flow and Column Bottom Level Control	64
3.5.18.4. Reboiler Heat Input Control	64
3.5.19. Process Variables of DIH	65
3.5.19.1. Feed Composition	65

3.5.19.2. Pressure	65
3.5.19.3. Inlet Temperature.....	66
3.5.19.4. Reflux Feed Ratio	66
3.5.19.5. Reboiler Heat Input.....	66
3.5.19.6. Side Draw Rate	67
3.5.19.7. Side Draw Tray Temperature	67
3.6. Process Optimization	67
3.6.1.HYSYS.....	67
3.6.2.Optimization in HYSYS.....	68
3.6.3.Original Optimizer	73
3.6.4.Box Method.....	75
3.6.4.1. Procedure for Minimization Optimization	75
3.6.5.SQP Method	76
3.6.6.Mixed Method	76
3.6.7.Degree of Freedom Analysis.....	77
3.6.8.Degree of Freedom Analysis for Multi-System Processes.....	78
3.7. Case Study	79
3.7.1.Objective Function	80
3.7.2.Decision Variables	81
4. RESULTS AND DISCUSSION	82
4.1. Optimization Results.....	82
4.1.1.Sensitivity Analyses For Isomerization Reactors.....	84
4.1.2.Sensitivity Analyses For Stabilizer	88
4.1.3.Sensitivity Analyses For DIH	91
4.2. Parameter Estimation.....	95
5. CONCLUSIONS AND RECOMMENDATIONS	98

5.1. Conclusions.....	98
5.2. Recommendations.....	99
6. REFERENCES	100

LIST OF FIGURES

Figure 2.1. Outcome Octane Number Comparison for Different Process Types.	7
Figure 2.2. RON and Performance of the Processes with % C ₆ Component in Feed.	7
Figure 2.3. Golden Section Method Explanation.	16
Figure 2.4. In case of $f(a_1) < f(b_1)$, x represents the extremum.	17
Figure 3.1. Geometry of Linear Programming.	25
Figure 3.2. Decision Algorithm of Steady-State Simulation.	37
Figure 3.3. Simplified Flowsheet of the Penex TM Unit with Light Naphtha Feed.	40
Figure 3.4. nC ₆ and nC ₅ Isomerization Reactions.	45
Figure 3.5. 2MP and 3MP Isomerization Reactions.	46
Figure 3.6. Dual-Function Catalyst Mechanism.	47
Figure 3.7. Isoparaffin Formation by Hydrogenation.	47
Figure 3.8. Naphtene Isomerization.	48
Figure 3.9. Hydrocracking Reaction.	49
Figure 3.10. 22DMB Curve.	54
Figure 3.11. Equilibrium Curves.	55
Figure 3.12. Octane Numbers of Components.	55
Figure 3.13. Caustic Scrubbing Operation.	60

Figure 3.14. Distillation Column.	62
Figure 3.15. Optimizer Spreadsheet.	69
Figure 3.16. Variables Tab in HYSYS Optimizer.	70
Figure 3.17. Monitor Tab of HYSYS Optimizer.	72
Figure 3.18. Type of Optimizer Selection.	73
Figure 3.19. Constraints and Objective Function Value Tab.	74
Figure 4.1. RON Changes in Lead Reactor for First Condition.	85
Figure 4.2. RON Changes in Lead Reactor for Second Condition.	86
Figure 4.3. RON Changes in Lag Reactor for First Condition.	87
Figure 4.4. RON Changes in Lag Reactor for Second Condition.	87
Figure 4.5. RVP Changes in Stabilizer for First Condition.	88
Figure 4.6. RVP Changes in Stabilizer for Second Condition.	89
Figure 4.7. RVP Changes with Stabilizer Reflux Feed Ratio for First Condition.	90
Figure 4.8. RVP Changes with Stabilizer Reflux Feed Ratio for Second Condition.	90
Figure 4.9. 22DMB Changes with DIH Recycle Rate for First Condition.	91
Figure 4.10. 22DMB Changes with DIH Recycle Rate for Second Condition.	92
Figure 4.11. 2MP Changes with DIH Recycle Rate for First Condition.	92
Figure 4.12. 2MP Changes with DIH Recycle Rate for Second Condition.	93

Figure 4.13. 22DMB Changes with DIH Reflux Feed Ratio for First Condition. 94

Figure 4.14. 22DMB Changes with DIH Reflux Feed Ratio for Second Condition. 94

LIST OF TABLES

Table 2.1. General Process Simulators.	12
Table 2.2. Number of Comparisons.	22
Table 3.1. Feed Characteristic of Naphtha.	42
Table 3.2. Isomerase Specifications.	43
Table 3.3. Results of Case Studies.	43
Table 3.4. Naphtha Fractionation.	54
Table 3.5. Isomerization Reactions.	57
Table 3.6. Ring Opening and Hydrogenation of Benzene.	57
Table 3.7. Hydrocracking Reactions.	58
Table 3.8. Label of Degree of Freedom Analysis.	78
Table 3.9. Control Parameters and Decision Variables.	79
Table 3.10. Decision Variables and Ranges.	81
Table 4.1. Optimization Results for the First Condition.	82
Table 4.2. Optimization Results for the Second Condition.	83
Table 4.3. First Condition Parameter Estimation Results.	95
Table 4.3. Second Condition Parameter Estimation Results.	96

LIST OF ACRONYMS/ABBREVIATIONS

22DMB	2,2 Dimethylbutane
23DMB	2,3 Dimethylbutane
2MP	2 Methylpentane
3MP	3 Methylpentane
AHP	Analytic Hierarchy Process
AIDES	Adaptive Initial Design Synthesizer
BASIC	Beginners' All-purpose Symbolic Instruction Code
BZN	Benzen
C ₁	Methane
C ₂	Ethane
C ₂ Cl ₄	Perchloroethylene
C ₃	Propane
C ₄ , nC ₄	Butane
C ₅ , nC ₅	Pentane
C ₆ , nC ₆	Hexane
C ₇ , nC ₇	Heptane
CH	Cyclohexane
CHEMCAD	Chemical Computer Aided Design
Cl	Chloride
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CP	Cyclopentane
DIH	Deisohexanizer
DIP	Deisopentanizer
EM	Eigenvalue Method
EOS	Equation of State
Fe ₂ O ₃	Iron Oxide
FeCl ₃	Iron Chloride

FORTTRAN	Formula Translation
FTS	Fischer Tropsch Synthesis
H ₂ /HC	Hydrogen Hydrocarbon ratio
H ₂ O	Water
H ₂ S	Hydrogen Sulfide
HCl	Hydrochloric Acid
HSL	Harwell Subroutine Library
HYSYS	Hyprotech Systems
iC ₄	Isobutane
iC ₅	Isopentane
LHS	Left Hand Side
LHSV	Liquid Hourly Space Velocity
LP	Linear Programming
LSR	Light Straight Run
LV	Liquid Velocity
MCP	Methylcyclopentane
MINLP	Mixed Integer Linear Programming
MON	Motor Octane Number
MOO	Multi Objective Optimization
MTBE	Methyl Tertiary Butyl Ether
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NIST	National Institute of Standards and Technology Database
PFD	Process Flow Diagram
PIN	Paraffin Isomerization number
PIP	Process Invention Procedure
PROSIM	Production and Operations Simulator
PROSYN	Process Synthesizer
Pt	Platinum
R&D	Research and Development
RHS	Right Hand Side

RON	Research Octane Number
RSM	Response Surface Methodology
RVP	Reid Vapor Pressure
SRK	Soave-Redlich-Kwong
TIP	Total Isomerization Process
UOP	Universal Oil Products
USA	United States of America
ZSM-5	Zeolite Socony Mobil-5

1. INTRODUCTION

In comparison between past and present, there is a discernible difference at petroleum refinery processes. Continuously increasing concerns about the Earth's environment and health issues have set path to a number of new legal regulations, which substantially involve clean fuel processing. Accordingly, environmental problems became more significant in refinery design and operation since the last two decades in USA. One of the outcomes of the environmental regulations is the termination of the use of lead as an agent for improving the octane number in gasoline fuel. The poisonous features of lead caused its termination for commercial use. The lead termination in gasoline together with reductions in sulfur, aromatics and olefins content can have a serious effect not only on the octane number but also on the total amount of gasoline produced at the end of the process. In addition, aromatics and vapor pressure limitations that result in reduced use of C₄ and reformate, respectively, manipulation of toxic benzene content problem in the gasoline pool became important [1]. Therefore, engineers have to find techniques to manage the octane number reduction in the gasoline pool.

The investigations have shown that increasing the percentage of branched alkanes can improve the octane number in gasoline without disturbing the economic and environmental constraints. In a manner, the isomerization of light alkanes can be a suitable process to yield gasoline compliance with environmental regulations. It is reported that light naphtha hydro-isomerization is a process that is able to meet the requirements in octane number improvement as described above [2].

Hydro-isomerization involves the transformation (i.e. isomerization) of linear alkanes to branched ones. The branched alkanes are able to provide high-octane levels and yields when they are compared with linear alkanes. In hydro-isomerization process, the feed is not naphtha, since it cannot provide the desired levels of research octane number (RON). The feed is more likely a "light" naphtha which is also an alkane that contains mostly C₄-C₆ hydrocarbons.

The products of hydro-isomerization reaction are methyl cyclopentane (MCP), 2,3 dimethylbutane (23DMB) and 3 methylpentane (3MP). Octane numbers of MCP and 23DMB are high, however 3MP has a low octane number. So the amount of 3MP in the gasoline pool must be eliminated or kept in trace number by adjusting the reaction temperature. Since hydro-isomerization process is exothermic, reaction temperature is critical for the process.

Apart from the need for linear to branched alkane isomerization, the amount of benzene in the gasoline pool needs to be minimized because of its known highly carcinogenic properties. Reduction of benzene content from distilled petroleum streams has become one of the most challenging issues in the last years. Simultaneous isomerization and benzene reduction can be achieved in the commercial UOP PenexTM Unit (process). The PenexTM process accomplishes the isomerization of normal alkanes under conditions of relatively low temperature, near-equilibrium reactor conversions and high efficiency.

Isomerase, the product of isomerization unit, is a high octane number gasoline blending component characterized by low aromatic and sulfur content which also satisfies both economic and ecological demands. Quality of the isomerase is affected by a number of parameters such as feed composition, process parameters and process engineer attention to daily operation due to lack of controllers. During the optimization, reactor inlet temperatures, stabilizer inlet temperature, overhead vapor pressure, reflux feed ratio, deisohexanizer column inlet temperature, recycle rate, reflux feed ratio and value of MP's in top product are manipulated to maximize the octane barrel of the product and maximize the RON of product. This combination maximizes the desired component product ratio, the so-called iso-ratio.

In this project, optimization of the unit is carried out by the Aspen HYSYS program tools. Steady-state operations of the PenexTM unit, stabilizer column and the distillation column (DIH) will be optimized. This approach brings a new perspective into optimization of isomerization unit by maximizing octane number and producing maximum isomerase barrels (maximum liquid yield).

In optimization of the process, reactor inlet temperatures, stabilizer inlet temperature, overhead vapor pressure, reflux feed ratio, deisohexanizer column inlet temperature, recycle rate, reflux feed ratio and value of MP's in top product are the decision variables due to operation conditions. The primary purpose is reaching the intended RON, according to this plan, setting RON around 86-87 range and total isomerate Reid Vapor Pressure should be less than 13 psi, are chosen to be process constraints. With these constraints, mass flow rate of isomerate x isomerate octane number is decided to be the objective function. Objective function value equals maximum isomerate barrels.

The detailed literature survey about isomerization, linear programming, optimization are given in Chapter 2. In Chapter 3, process description, process variables and simulation environment of the unit are explained.

Optimization method and other details about optimization, results of optimization, sensitivity analyses for units and parameter estimation with discussions of outcomes are given in Chapter 4.

2. LITERATURE SURVEY

2.1. Isomerization for Octane Upgrading

Isomerization process, which can be applied to any isomerizable organic compound, is performed in hydrogen atmosphere, hence it can be named as hydro-isomerization process. In prior processes that are applied with this aim, undesired decomposition and hydrocracking are eliminated by low temperature and catalyst agents.

Isomerization of light paraffins comprises the straight light naphtha chain isomers to branched isomers which have higher octane number than straight ones. Isomerization is also exploited to increase anti-knock quality, which is a measure of the gasoline quality in time of initialization of engine, of light paraffins [3].

Bloch *et al.* proposed an invention for this drawback. The invention was adding sulfur and a halogen compound to the process. This addition compensated the acid-acting support effect of the catalyst [4].

In 1979, Holcombe offered a basic process for octane upgrading, Total Isomerization Process (TIP). TIP has a feed stream derived from refinery operations and consist of isomeric forms of saturated hydrocarbons which have five and six carbon atoms [5]. End of the isomerization, the stream contains n-pentane, isopentane and n-hexane which have high octane numbers and dimethylbutanes. But since methylpentanes having low octane numbers, are needed to be drawn from mixture and recycle back to isomerization reactors.

A second Holcombe patent, is about a normal paraffin isomerization separation process. A molecular sieve is engaged to feed drum to separate normal paraffins from feed that is comprising both normal and branched paraffins. Only normal paraffins are adsorbed and fed to the isomerization reactor after void space purging of the molecular sieve adsorbent [6].

Evans *et al.* discussed a process about different isomerization unit feed that contains C_6 or C_{6+} normal paraffins with mono-methyl-branched paraffins and normal paraffins [7]. A separation zone downstream has a sieve with pore size that differs between $4.5 \times 4.5 \text{ \AA}$ and $5.5 \times 5.5 \text{ \AA}$. This sieve allows the adsorption of mono methyl branched paraffins and normal paraffins while allowing the dimethyl paraffins to pass through the sieve and be the product. The drawback of this method is that it is limited with C_6 or greater carbon atoms. Since normal olefins and all the mono branched olefins are adsorbed and recycled to the isomerization zone, with the feed that consists of pentanes, this process would conclude with recycling of high octane isopentane and this would be a deviation from the aim of having high octane product blend. In 1989, Evans made an enhancement on separation technique in this process and used a sieve, which has a smaller pore size than or equal to $4.5 \times 4.5 \text{ \AA}$ to adsorb normal paraffins, while allowing mono methyl branched paraffins and dibranched paraffins to pass through the sieve. But still, this enhancement did not work with the feed comprising pentane like compounds.

In recent years, there is an increasing need for high octane number gasoline without sulfur, aromatics, and olefin contents with an appropriate Reid Vapor Pressure (RVP) regulations. Reid Vapor Pressure is a measurement of the volatility of gasoline. Vapor pressure is important for automotive gasoline since it influences starting, warming up and tendency to vapor lock with high temperatures in engines. If liquid fuel evaporates and becomes gas while it is still in fuel delivery system, this change causes vapor lock. Vapor lock interrupts fuel pump operation, causes loss of feed pressure to the fuel injection system. This is why, RVP has to be under control. In winter conditions, high level vaporization is demanded to start the engine and this can be provided with high RVP. But in summer, lower level of vaporization is desired since gasoline can evaporate easily and evaporation can cause vapor lock. To avoid these, RVP should be regulated seasonally for engine reliability. Due to a rapidly developed and polluted environment, governments strictly regulate gasoline production. These regulations direct producers to find much cost effective and profitable production solutions. Koncsag *et al.* [8], Anderson *et al.* [9], and Chekantsev [10] proposed the isomerization of light straight run gasoline for development of traditional techniques.

Unfortunately, there is only moderate increment in branched paraffins with a single run. To increase the octane number much more, molecules with higher octane number are isolated from the product stream, molecules with lower octane number are recycled to the isomerization zone. Rice proposed a development technique to increase efficiency of the process with a single run. The technique contains an improvement in heat integration to stabilizer with the aim of regaining a recycle stream and a product stream from fractional distillation [11].

Another invention for the high octane number product is experienced with a feed that consist of pentane and hexane. Process has usual steps for isomerization like contacting with the catalyst, fractionation of iC_5 as overhead product and bottom stream with nC_5 , nC_6 , mono branched C_6 and dibranched C_6 . In this invention, instead of having a plain recycle stream, bottom stream penetrates through an adsorption zone with a molecular sieve which absorbs dibranched C_5 in the mixture, desorb nC_5 , nC_6 and monobranched C_6 from mixture, and recycles back to the isomerization reactor [12]. The developed technology in PenexTM and TIP technologies helps to decrease cost, saves energy and money. Hydrogen-once-through design in PenexTM has concluded in savings up to 20%.

PenexTM uses the I-8 catalyst, which provides the highest catalytic isomerization activity. The PenexTM process is also advantageous in technique way, since PenexTM can process once through operation, fractionation or recycle the side stream. Comparison between different isomerization processes can be seen from Figure 2.1.

The TIP process becomes distinct from PenexTM with catalyst selection. In TIP, generally zeolitic catalyst, which demands high operating temperatures in the reactor, has been used. High operating temperatures leads the process with low conversion with I-8 catalyst.

Hydrogen once through process has economical advantage due to elimination of some PenexTM unit sections, such as recycle compressor, product separator and associated heat exchanger. Comparison between processes according to C_6 feed component is given in Figure 2.2.

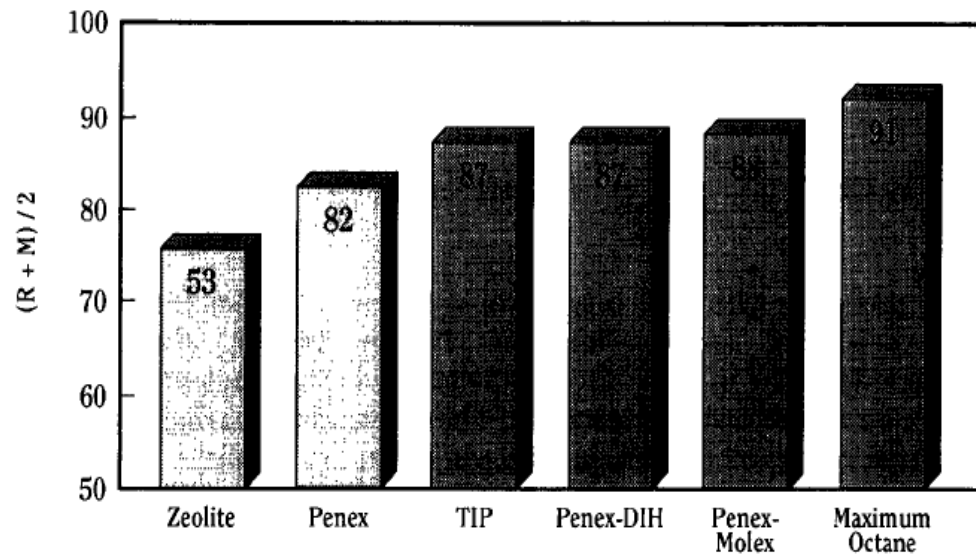


Figure 2.1. Outcome Octane Number Comparison for Different Process Types [13].

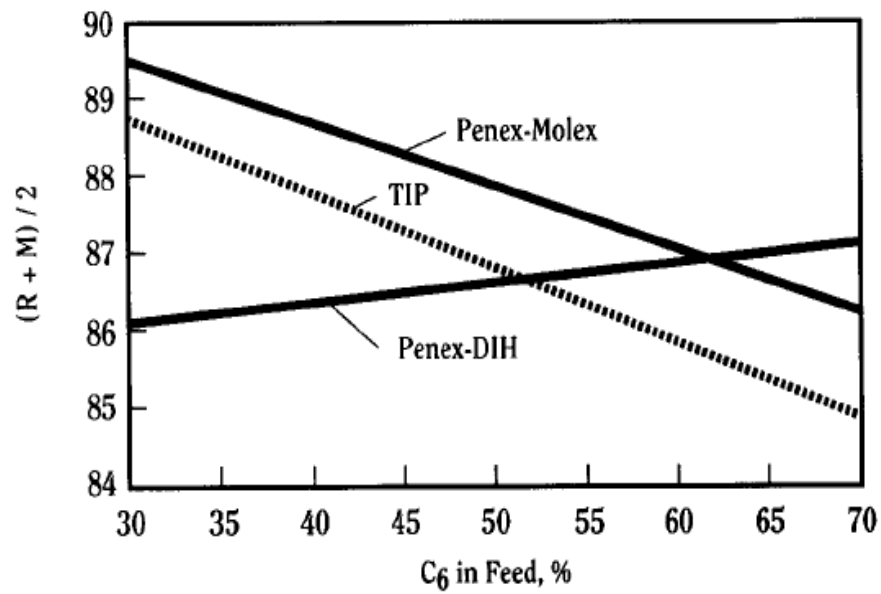


Figure 2.2. RON and Performance of the Processes with % C₆ Component in Feed.

Li *et al.*, suggested synthesis of isoparaffin rich hydrocarbons with end product of Fischer–Tropsch synthesis (FTS) over Co/SiO₂ catalyst [14]. In this study, primary product of FTS is used to get isomerized secondarily and attain isoparaffin rich hydrocarbons. Fischer–Tropsch synthesis (FTS) is the process of producing hydrocarbons, which has high paraffinic and low sulfur content, from carbonmonoxide and hydrogen gas. Fraenkel *et al.*, and Nijs *et al.* have carried out a process to obtain isoparaffins over acidic zeolites with FTS [15]. Nevertheless, zeolites were not a durable and solid choice of catalyst, conversion, activity and selectivity affected negatively the yield [14-15].

According to Li, the direct production of isoparaffins from syngas may be achieved with FTS, continuous hydrocracking and hydro-isomerization of the products, either in one or two stages [16].

2.2. Simulation of Isomerization Reactors

In petroleum refinery, process simulator is beneficial in every way. A simulation that gives updated information about the process, operating conditions and status of the catalyst, ensures maximum efficiency. This kind of simulator provides abundant information to control the process. Sughrue *et al.* suggested a simulation for pentane isomerization, that contains a reaction mechanism for producing isopentane [17]. In simulation, there were information about initial input data including feed compositions of the process, rate behaviors, process conditions, reactor size and description of concentration and temperature profiles. With these information, simulation evaluated the physical properties, heat capacities, heats of formation, equilibrium constants of equilibrium, rate constants of isomerization reaction, cracking rate constants and reaction rate. Afterwards, simulation proceeded to solve differential equations for concentrations and temperature that change along the length of the reactor, since material balances used the equations to calculate new situation of the simulation. Lastly, simulation sent the results as outputs and product yields to monitor.

There are design purpose programs in industry, especially process synthesis programs are developed to correspond this demand. Process synthesis creates a flow sheet

and this flow sheet involves specific information about units and the process conditions of the process, products or raw materials.

The process flow sheet describes the process flow, duties of the chemical reactors in the flow and sequential unit operations and material and energy streams in the process. Process synthesis software, has arisen in the late 1980s. “Flow-sheeting,” basically means simulate the attitude of the process to see, if it is profitable. It also performs the essential calculations to design the equipment and to determine values for operating conditions. Also, mass and energy balances, process equipment parameters, cost estimation for the equipment and economical analysis of the process are evaluated in flow-sheeting.

Spreadsheet softwares have broadly used around the world due to its availability for non-commercial and commercial users. They have user friendly interface and it can be applied to many processes. Coding a program, such as FORTRAN and BASIC, for solution of the process can be compelling task beside spreadsheeting.

In spreadsheeting, there are rows and columns in organizational form for entering input and obtaining output. It has a wide-range usage area comprising mathematical functions, user definable functions, formula and data replication, iteration, statistical, financial, matrix operations etc. functions and graphical output. However, spreadsheeting is not applicable for detailed and complex algorithms, since transferring all data of the process may be difficult [18]. There are different type of reactor processes. These can be defined as following:

2.2.1. The Black Box Model

The black box model compels basically the mass balance between feed and products of the reactor. There is no intervention to concentration of products while introducing them to the simulator. Also, reactor outlet temperature and reactor pressure are defined for the reactor effluent.

2.2.2. Modified Black Box Reactor

The modified black box reactor is similar to the black box reactor. It has a different property from the black box model and that is, net product of the reactor is evaluated by the reactor itself, it is not adjusted.

2.2.3. Empirical Predictive Reactor

This reactor is used to predict the amount of product that can be produced with significant feed. For real-time control, estimated composition for the product must be updated, since composition changes during the operation continuously.

2.2.4. Free Energy Minimization Reactor (Gibbs)

This reactor type establishes the distribution of products for a reaction system that is at thermodynamic equilibrium, according to user defined species. The distribution that provides minimum free energy is the output of this reactor type.

Method does not take into account the reaction rate. Advantage of this method is, supplying stoichiometric equations is not necessary for calculation and the equilibrium constants are found from the free energy data.

2.2.5. Equilibrium Reactor

Same as Gibbs reactor, equilibrium reactor also tries to reach thermodynamic equilibrium. More than one reaction can be handled in the reactor at the same time. To use the reactor, specific stoichiometric reactions must be defined and the corresponding equilibrium constants must be supplied as functions of the reaction temperature.

2.2.6. Stoichiometric Conversion Reactor

Stoichiometric equation and a starting reacting component must be written for each reaction in the solution procedure for this type of reactor. There are options for model builder, for depletion of a reacting component. These options can be listed as executing the reaction or providing the depleted component until all the reaction is completed [19].

Inverno *et al.*, proposed a steady state simulation of a plant that is located in GALPenergia Sines Refinery [20]. The model was simulated in HYSYS to analyze all the settings and calibrations for the process and confirm the results of the model for real time operations. Peng-Robinson equation of state is chosen and characterization of feed composition are determined to identify the thermodynamic properties of simulation. Using distillation curves, the bulk properties and the light end analysis are attained and a back blending procedure is operated. Consequently, simulation software can be used by eliminating debottlenecking. Settings of the real plant column has accommodated using HYSYS simulation. The demonstrated results are attained in steady state version of the software, but all the simulations that are done in steady state may be expanded to dynamic simulation or to a real time optimization system. With these arrangements, process can be controlled in advanced.

The steady state simulations are commonly used in design, analysis and the optimization fields. They also give information about process flow-sheets regarding material and energy balances. Steady state models use the equilibrium equations that provide the relationships between the system and the state. Steady state also means that all these equations used in the model are independent from time variable. With a little amount of information, simulation can run. Modern simulators permits the user express the nature of the problem easily rather than creating distress to write an appropriate energy and mass balance equations. In addition to that simulations provide state-of-the-art features like rigorous column calculations, sizing and rating of heat exchangers and separators, with allowance of addition to flow-sheet for a wide variety of processing applications. Other than these facilities, pure component library, thermodynamic methods, creation of non-

library components, physical properties, unit operation calculations and input and output interface can be found from inside of the simulation.

Steady state simulations are the base simulations for dynamic simulations that evaluates the transient behavior of the system. Hence, steady state simulation is mainly operated for optimization of the process and computing the plant performance [21]. Below listed programs are general process simulators with petroleum pseudo-component capabilities:

Table 2.1. General Process Simulators.

Program Name	Program Vendor	Vendor Location
Aspen Plus	Aspen Technology	Cambridge. MA, USA
CHEMCAD IV	Chemstations, Inc.	Houston, TX, USA
DESIGN II	Windows Simulation Company	Houston, TX, USA
Aspen HYSYS	ASPEN Technology	Cambridge. MA, USA
PD-PLUS	Deerhaven Technical Software	Burlington, MA, USA
PROVISION	Simulation Sciences, Inc.	Brea, CA, USA
PROSIM	Bryan Research & Engineering	Bryan, TX, USA

HYSYS and PROSIM simulation programs are both capable of steady state and dynamic simulations.

2.3. Optimization

Petroleum refinery applications come into prominence and as a result, refining becomes a competitive business. Legislations about the gasoline ingredients such as benzene and sulfur content with environmental regulations compel the refiners to become more successful to survive financially [22].

Optimization has a considerable benefit in finance. With aid of degrees of freedom analysis, it can be known whether optimization can be applied or not. Inputs of the process determine the number of the degrees of freedom and they can be adjusted to optimize an output. In typical optimization, the controlled inputs of the related process are manipulated to attain the best optimization result. Solving an optimization problem with global optimum is difficult task. To solve an optimization problem, three things are essential: a mathematical model that contains all process variables which can be adjusted and controlled, an economic model that provides profit, and the last one is the critical one, finding optimal profit that supports economic model and constraints [23].

Classification in optimization can be listed according to type of search space, continuous or discrete, type of objective function, convex or differentiable, and type of constraints, equal- inequal or linear-nonlinear [24].

All the types of optimization problem can be implemented to different areas such as modeling, synthesis, design, operation and control of chemical processes, with a usage of broad range of numerical methods to compute them [25-26].

Solution of optimization problems may have multiple optima, but finding global optimum or the best solution for the process is the aim. According to problem convergence, presented solution may be local or global optimum. Generally, in optimization, global solution is wanted.

Many optimization problems have only one objective function to satisfy. However in chemical engineering, optimization problems include more than one objective function which may cause conflicts during the optimization. Examples of these conflicting objectives are capital investment versus operating cost, cost versus safety, quality versus recovery/cost and environmental impact versus profitability. This kind of optimization is called multi objective optimization (MOO), also known as multi criteria optimization and it is essential to find the optimal solution(s) in the existence of tradeoffs between two or more conflicting objectives [27].

Simulation optimization is an arising field that merges optimization approach into simulation analysis. However, due to complexity of the simulation, determination and computation of the objective function may be costly. Additionally, sometimes finding an objective function that covers the process every possible profitable way makes calculations complicated. Reviews about simulation optimization method are quite abundant [28-30].

Common subject of these papers is optimization add-ons for discrete event simulation software that is developing fast nowadays. Andradóttir also discussed how stochastic approximation methods may be used for the evaluation of continuous simulation optimization problems [31].

2.3.1. Optimization Methods

2.3.1.1. Response Surface Methodology (RSM). The idea of Response Surface Methodology is, building a mathematical model that is called surrogate model, to explore the fundamental function, for each response variables. Mathematical model of RSM is chosen generally linear or quadratic. Polynomial models are formed easily but they are inadequate for complex models. RSM is used to solve the simulation model as a black box and it examines only the input/output of the simulation model, but it does not serve for internal variables and specific functions. RSM performs a sequence of local experiments to find the optimum input combinations, so it can be defined as a sequential heuristic. More specifically, RSM carries out a sequence of local approximations that are first-order polynomials in the inputs; once the optimum seems close, RSM amplifies the latest first-order polynomial to a second-order polynomial [32].

2.3.1.2. Heuristic Methods. Heuristic methods are in a close relationship with real world applications. Two well known techniques of that are tabu search and simulated annealing. Tabu search is a local search method which makes iterations to find a reasonable solution and then use this solution in current iteration to find global solution. Search permits to find worst objective function value to eliminate it while preventing the previous solution from infinite loop. To achieve this aim, a list of tabu or forbidden moves are kept in short time

memory and updated at each iteration. Tabu tenure is a short term memory tabu list and the most used type of tabu search.

Simulated annealing tries to find local moves from a list of candidate neighbor point. If a superior candidate for neighbor point is discovered, it replaces the current iterate with the one which has probability value that equals one, or if a worse point is found, it replaces the iterate with a probability value strictly less than one. For convergence, the probability of moving towards a worse point should mitigate along the iterations. These two algorithms are contemplated as global optimization methods, since they can continue the iterations out of regions where locally optimal solutions reside [33].

In consideration with all optimization models, Linear Programming (LP) models are the easiest to build and analyze. The simplex method that are used for solving LPs is an enhanced form of classical Gauss-Jordan method. Simple to understand, study and it helps to comprehend the algorithms. Since LP has numerous applications in wide variety of areas, using LP in suitable models for a decision problem, and the interpretations of the outputs of a model. A process can be modeled using LP if the decision variables are continuous variables with reasonable lower and upper bounds, and there must be only one linear objective function to be optimized in the problem with linear constraints. Linearity is affirmed in words with two assumptions. First assumption is the additivity or separability assumption, that is defined as the objective function is the sum of the n different functions but each function consists of only one of the decision variables that are all in same unit. Second one is the proportionality assumption that is summed as every decision variable is a proportion of the objective function with a constant value multiplication [34].

Floquet *et al.* examined the different optimization methods in process synthesis with three different approaches, discrete, continuous and large scale approaches. In the paper, first the process is constructed as a mixed-integer programming problem. With discrete approach, design variables of unit operations are fixed and heuristic and algorithmic approaches were successful to proceed in solution in spite of the fact that optimal solution is not guaranteed with heuristic approach. For continuous approach, the process is built as nonlinear programming problem. Design, which contains operating conditions and

input/output streams of each unit operations and structural variables are both optimized simultaneously. As a result, merging these both approaches with application of efficient large scale nonlinear programming is the best solution for the process [32].

2.3.1.3. Line Search. In optimization, while minimizing or maximizing the objective function, $f : \mathbb{R} \rightarrow \mathbb{R}$ over a closed interval $[a_0, b_0]$, line search method can be used. This method searches the region iteratively to find feasible optimum point. Line search method may be applied effectively to multivariable problems. Golden section method and Fibonacci method are the most popular and trustworthy methods that are used in line search. Also, in line search, objective function is assumed as unimodal that means f has only one local extremum.

2.3.1.4. Golden Section Search. Golden section search is established calculation of the objective function over $[a_0, b_0]$ interval at different points. These interval points are determined to reach the extremum with least evaluation as possible. The aim is to abate the internal until the optimizer is “ambushed” with enough certainty. As an example, evaluating a unimodal function within specific range at only one side of range is not logical, with this strategy, narrowing down the range is nearly impossible and time consuming. Choosing two points to narrow down as shown in Figure 2.3 would be more efficient and accurate.

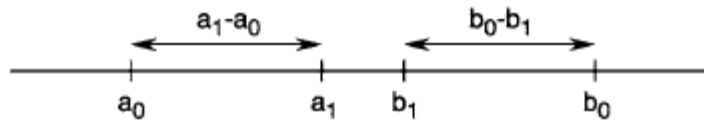


Figure 2.3. Golden Section Method Explanation.

Reducing the range with symmetry is the easiest to search method. This procedure is carried out like:

$$a_1 - a_0 = b_0 - b_1 = \rho(b_0 - a_0) \quad (2.1)$$

where

$$\rho < \frac{1}{2} \quad (2.2)$$

If $f(a_1) < f(b_1)$, then the extremum is found between $[a_0, b_1]$, as can be seen from Figure 2.4. If $f(a_1) \geq f(b_1)$, then the extremum is located in the range of $[a_1, b_0]$.

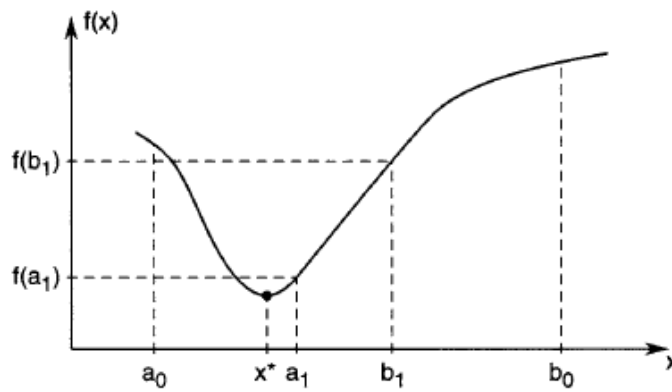


Figure 2.4. In case of $f(a_1) < f(b_1)$, x represents the extremum [35].

Powell claimed that variable metric methods are designated to minimize the chosen objective function subject to equality and in equality constraints. For unconstrained case, evaluation of variables is obtained with quadratic approximation. For optimum value, line search or trust region method can be used since problem does not converge due to selection of unsuitable starting point, in this way problem can be compelled to be converged [36].

With constraints, an algorithm is presented to attain variable metric method with second derivative of previous iterations.

In line search method, an initial estimate x^1 is needed and the k th iteration of the procedure is determined as following: after deciding search direction S^k , to minimize the objective function $f(x^k + \alpha^k S^k)$ respect to α , an α^k value is found and then equalized next iteration to, $x^{k+1} = x^k + \alpha^k S^k$. In fact, line search should be terminated when an approximate extremum along the line is found. However, it is hard to found extremum with

high certainty when next iteration point and previous one is far away from each other. For a situation like this, line search method is called “approximate or inexact line search”.

Zhang *et al.* [37], Ahookhosh *et al.* [38], Grippo *et al.* [39] examine the nonmonotone line search technique for unconstrained optimization. Previous works demonstrate that monotone line search (i.e. $f(x_{k+1}) \leq f(x_k)$) technique could be the reason of non-convergence, since the iteration is limited with a narrow area.

The nonmonotone line search technique does not use narrow area condition, with this change, the disadvantage can be eliminated. Firstly this method was proposed by Grippo *et al.*, for Newton’s method. Other proposed works are generally based on Grippo *et al.*’s work. Leong *et al.*, also examined the stability of the method beside convergence [39].

2.4. Isomerization Processes in Petroleum Refinery

Isomerization process is essential in the production of oil and gasoline. Obtaining maximum yield in octane number, gasoline amount and other desired qualifications is the purpose of every process cycle.

Lukec *et al.*, proposed an advancement in optimal processing area in refinery with using model predictive control by applying optimal control to real time operation at Rijeka Refinery. While optimizing the deisopentanizer (DIP) and deisohexanizer (DIH) columns, minimum energy consumption per unit feed, maximum overhead isopentane attainment and minimum effect of disturbance were the benchmarks of the optimization. He also offered the optimization application all over the entire process with criteria of maximum octane number, maximum usage of the capacity, expanded catalyst life and stability of the process [40].

Vahedi developed an optimization model for gasoline processing area of the refinery. Model consisted of the estimation of product qualities from reforming and examine the gasoline blending over multiple periods.

Objective of this model was minimizing the cost of operation with strict quality and quantity constraints. A linear relationship between in the qualities of final product and the blended component streams is postulated for optimization model. The objective function included cost of gasoline production operation plus inventory cost. The optimum solution should increase the yield of blended component streams in quality and quantity. As a result, a feasible local optimum is attained from a case study application that proved specifications and demands, constraints, were in agreement [41].

Modelling and optimization can be performed in same program according to the program features. These features comes with a wide variety of easiness beside its cons. Commonly used approaches for flow-sheet simulation and optimization problems are the modular (also known as black-box) and the equation-oriented approaches.

Modular (closed form) approach is the most recently used simulation method in industry. In this approach, equations are gathered in modules and these modules are used to solve the problem sequentially, in the appropriate alignment. Optimization problem can be solved after process convergence at steady state. Then, objective function and the constraints are determined. Modular approach is generally locally robust and it can be basically initialized at the beginning of the process. Nonetheless, the flow-sheet that contains black box modules, has a drawback for simulation model. Model of black box modules usually convert slowly. Furthermore, calculation of derivatives causes disturbance and recalculation of the entire flow-sheet with respect to the decision variables in optimization. With this procedure, reaching convergence and finding optimum solution is hard and time consuming.

The modular approach is also used for offline design and analysis in the industry. Aspen Plus, PRO II, and Aspen HYSYS are the general process simulators that evaluate optimization problem by firstly calculating the model, secondly defining the constraints and objective function. There is two different loop cycle in the programs, one of them is outer loop that solves the optimization problem and inner loop that solves model equations and helps the model to converge.

Equation-oriented (open form) approach is the other common approach in modelling and optimization program. In this approach, model is assumed as a block of equations that would be evaluated with a large scale nonlinear algorithm. For process optimization, Murtagh *et al.* suggested inserting model equations to solution procedure from a different point of view. Open form approach contains simultaneous linearization of all of the equations and iteration on all of the variables, with processing the Newton-Raphson method or some variation. In this kind of situation, with very large system of sparse linear equations can be evaluated adequately. Deficiency of this approach is, in working with multiple models, individual model structure may not be achieved by equation-oriented approach, solution can not be found properly. Initialization of approach could be difficult, but dividing the set into small algebraic equations can be useful. For a large system, objective function and constraint derivatives can be obtained in analytical form that prevents the model from multiple levels of iteration. This means model must not be converged before optimization, all process is handled simultaneously. Alkaya *et al.* proposed a general plan for coupling and optimizing multiple models multiplier free, reduced Hessian successive quadratic programming to avoid disadvantages of modular and equation-oriented approaches. Proposed approach facilitates the usage of current process simulators and the optimizer simultaneously with a best optimum solution [42]. Addition to that, simultaneous-modular approach is consolidation of sequential-modular and equation-oriented as the name refers.

2.5. Dehydro-isomerization

Dehydro-isomerization is a way of producing aromatic hydrocarbons from naphthenes. Carter *et al.* proposed a process that effects dehydro-isomerization rate of five membered naphthene ring hydrocarbons to aromatics [43].

Also Pirngruber *et al.* suggested to investigate the effect of the metal loading and acid site concentration on dehydro-isomerization of butene. As a result of this investigation, butenes over the acid sites are found the main route of by product formation, during dehydro-isomerization. As metal to acid sites ratio increased, for example with 0.5% wt. Pt-ZSM5 highest yield of isobutene is attained, yield of dehydrogenated products

are increased. Catalysts with a high Brønsted acid site concentration reached the equilibrium in dehydro-isomerization fast [44].

Another work on dehydro-isomerization is conducted by López *et al.*, with the aim of disclosure the catalytic potential of 0.5% wt. Pt/SAPO-11 catalyst and set up the best operating conditions for n-pentane dehydro-isomerization. Hence the best operating condition of n-pentane on catalyst is found to be at 500 °C with maximum selectivity for pentene formation. Addition to that, below 500 °C, especially between 350 °C and 400 °C range, total n-pentane conversion is varied between 8 and 18%, it is oriented as same as isopentane, this simply means changing process temperature leads selective isomerization of n-pentane to isopentane and dehydro-isomerization, in thermodynamic equilibrium [45].

2.6. Linear Programming

Moghaddam *et al.* proposed a linear programming technique to find an approach to compute CO₂ emission cooperated with the marginal production of gasoline and diesel oil. The simulation is created through the duality in LP. It combines the complete interdependency and economic effects that come with any marginal variation in the refinery. Then, the proposed methodology is applied to a typical French refinery model in order to estimate the refinery CO₂ contribution of diesel oil and gasoline. Result of this study shows, marginal production of diesel causes more CO₂ emission. According to the new European standard requirements, since diesel is more efficient in energy supplying, the gap between marginal CO₂ coefficients of gasoline and diesel oil would be enlarged [46].

According to Karwan *et al.*, linear programming is not practical. He justified, since assumptions must be made before modelling, details of the system can be overlooked. With assumptions, sometimes model contradicts the real world systems. Addition to that, in formulation of large systems, modelers add implicit preferences to add more constraints to find the solution of the model [47]. If gasoline blending production is assumed as a batch process, also the quality and volume of the products are set by refinery schedule, linear programming approach can be applied to the process successfully [48].

Chandran *et al.*, proposed an approach based on linear programming (LP) that estimates the weights for a pairwise comparison matrix generated suitable with the analytic hierarchy process [49]. Saaty developed the analytic hierarchy process (AHP) for multi criteria decision making [50]. This method is used to derive ratio scales from paired comparisons. Ratio scales are acquired from principal eigenvectors, the consistency index is derived from the principal eigenvalue. Pairwise comparison means choosing among two or more entities in pairs, to find which one is favored [51]. Number of things is the key element of the number of comparisons. Number of the comparisons may be formulated as shown (Table 2.2) below:

Table 2.2. Number of Comparisons [52].

Number of things	1	2	3	4	5	6	7	n
Number of comparisons	0	1	3	6	10	15	21	$\frac{n * (n + 1)}{2}$

In the AHP, problem is modeled as a hierarchy of criteria, subcriteria and alternatives. After the hierarchy is constructed, pairwise comparison matrix is constituted by comparison each of the matrix element. With this procedure, importance of every element is identified. Eigenvector method is used to form a priority vector which helps to find relative weights of the elements due to the hierarchy level. The AHP technique involves four-step procedure.

- Organize a decision hierarchy with reasonable part of the decision problem and hierarchy of interrelated elements.
- Create input data of pairwise comparison matrix with decision elements.
- By using eigenvalue method (EM) evaluate the relative weights of the decision elements to form a priority vector.
- Combine the relative weights of the decision elements to arrive at a set of ratings for the decision alternatives [53-55].

Process flow-sheeting with simulations was firstly introduced by Siirola *et al.*, Siirola and Rudd and Powers [56-58]. In these investigations, being a guideline is contemplated, validity of the proposed method was not depended on the type of the design problem and sophistication of the techniques. AIDES (Adaptive Initial Design Synthesizer) was developed and improved to create the model and solve more complex processes counting on the heuristic methods and linear programming. They were coordinated through a means-ends-analysis search.

BALTAZAR, was another process synthesizer [59]. It was operated just like AIDES, relying on heuristic methods and linear programming, and used a tree search to prove the theorem. Nowadays, flow-sheet synthesis is generally performed with two different approaches: one of them is hierarchical decomposition which helps to solve the process step by step with logical design decisions. For example, for a continuous process, first step is to construct input-output structures of the flow-sheet by asking some questions to create heuristics of the process. After this step, necessity of the recycle is questioned for heuristic interpretation. Third and fourth steps consists of separation, with vapor recovery and liquid separation, and heat exchanger network construction [60].

Computer version of hierarchical decomposition is PIP (Process Invention Procedure). It combines the qualitative knowledge and process organization appropriately in hierarchical structure. It tries to find a suitable flow-sheet to see why none of the alternatives are cost-effective. In case of unprofitable process, PIP searches the other alternatives which can be profitable. In this perspective, flow-sheet can be designed in PIP and evaluation of optimum conditions can be obtained quickly [61].

The second approach is mathematical programming and computer version of mathematical programming is PROSYN (PROcess SYNthesizer). It is developed by Kocis and Grossmann for modelling and decomposition strategy and MINLP optimization of process flow-sheets [62-63].

3. MATHEMATICAL TECHNIQUES

3.1. Linear Programming

The development of linear programming is announced in the most important scientific advances of the mid-20th century. Linear programming works with a mathematical model to determine the objective problem. Linear programming is named after linear objective and constraint functions [64-65]. It is not only used for programming, but also for planning of the endeavor of the process to attain best optimal results.

In mathematical view, every process contains many variables, many equations, many equalities and many inequalities to cope with. And also, the solution must please all the constraints and it must be global optimum solution for the problem.

With an assistance of a process model software, linear programming can be formulated and solved with thousand of variables and constraints. LP uses the simplex method for the optimum solution of the process even if it is enormous [66].

3.1.1. Geometry of Linear Programs

A maximization problem can be formulated as;

$$\text{Maximize: } f = x_1 + 3x_2 \quad (3.1)$$

$$\text{Subject to: } -x_1 + x_2 \leq 1 \quad (3.2)$$

$$x_1 + x_2 \leq 2 \quad (3.3)$$

$$x_1 \geq 0, x_2 \geq 0 \quad (3.4)$$

Graph of feasible region can be shown with unshaded area of the Figure 3.1. This area contains the linear inequalities. Numbers that are labeled on the graph represents the extreme points or vertices of this equations. If constraints are linear, there are only finite number of vertices.

Objective function is assumed as it is equal to a constant. When this constant value changes, shown contour goes parallel upward or downward according to change sign. Maximum value of the objective function is obtained when the contour line coincides with the constraint function at least one point.

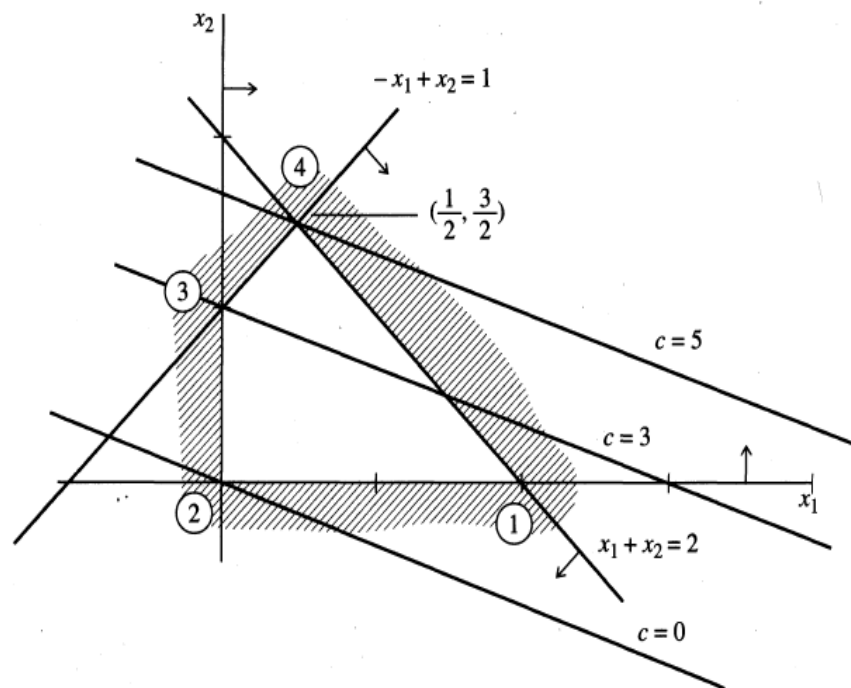


Figure 3.1. Geometry of Linear Programming.

For this figure maximum objective function value is attained at 5, with $x_1 = 0.5$, $x_2 = 1.5$

3.1.2. Standard Form for Linear Programs

An LP problem can be written in the following form:

Choose $x = (x_1, x_2, \dots, x_n)$ to minimize

$$f = \sum_{j=1}^n c_j x_j \quad (3.5)$$

$$\text{Subject to: } \sum_{j=1}^n a_{ij} x_j = b_j, i=1,2, \dots, m \quad (3.6)$$

$$l_j \leq x_j \leq u_j, j=1,2, \dots, n \quad (3.7)$$

where c_j are the n objective function coefficients, a_i and b_i are parameters in the m linear equality constraints, and l_j and u_j are lower and upper bounds, respectively.

3.1.3. Pivoting

Pivot operation contains a specific sequence of elementary row operations in linear programming. A pivot operation contains m elementary operations which take the place of in a linear system that has a specified variable and has a coefficient of unity and zero in one equation, somewhere in it. Steps can be explained broadly:

- Select a term $a_{rs}x_s$ in equation r , variable s , with $a_{rs} \neq 0$ called pivot term.
- Replace the r th equation E_r by the r^{th} equation multiplied by $1/a_{rs}$.
- For each $i = 1, 2, \dots, m$ except $i=r$, replace the i th equation E_i by $E_i - a_{is}/E_r a_{rs}$, that is, by the sum of E_i and the replaced r th equation multiplied by $-a_{is}$.

3.1.4. Simplex Algorithm

The simplex method, which consists of two-phase procedure, is utilized in search of optimal solution to an LP problem.

In simplex method, Phase 1 is formed of procuring an initial basic feasible solution and it is not easy to find, even it may not exist since constraints may be inconsistent.

Phase 2 uses the solution found in the Phase 1, as a starting point and it can find the minimum value for a minimization problem or it decides the problem is unbounded.

Phase 1 starts with an initial starting point A and an initial basic (possibly infeasible) solution (x_B, x_N) satisfying

$$Bx_B + Nx_N = b \quad (3.8)$$

In the previous expression, all components of x_N that represent bounds and N is the corresponding matrix of coefficients for x_N . Since B is nonsingular

$$B^{-1}(b - Nx_N) = x_B \quad (3.9)$$

If x_B is between the bounds, the solution will be feasible and it can be used in Phase 2 which optimizes the true objective. Otherwise, some components of x_B violate their bounds.

At the beginning of the simplex method, objective function is assumed just like it is another equation in the problem,

$$f = c_1x_1 + c_2x_2 + \cdots + c_nx_n \quad (3.10)$$

That can be shown as,

$$-f + c_1x_1 + c_2x_2 + \cdots + c_nx_n = 0 \quad (3.11)$$

In this way, objective function can be included in the set to form an augmented system of equations. The simplex algorithm is always initiated with this augmented system in canonical form.

Finding a good initial basis is the crucial part of linear programming. If there are doable sets of parameter values, after the first set is solved, the optimal basis is stored in the program and used as the initial basis for the LP problem. Choosing a good starting point mitigates computation time observably when compared with a cold start, where no good start point is known.

There are two general ways that linear program can be constructed: the column (recipe/activity) approach and the row (material balance) approach. Since both approach gives same final result, choice depends on organizing the data for the problem.

3.1.5. The Column (Recipe/Activity) Approach

In column approach, a system is considered as dividable into a number of elementary functions and the activities. An activity is the thought of a “black box” and it can be filled with tangible inputs. The various kind of inputs are called items. The quantity of each activity is called activity level. To change the activity level, it is necessary to change the quantity of each kind of inputs, in and out of the activity. In linear programming, the activity levels are not given but are the decision variables are required to cover certain specified requirements. Steps for formulating the column approach,

- Define the activity set
- Define the item set
- Define the input and output coefficients
- Specify the outside items of the “box”
- Set up the material balances equations

This approach requires nonnegative activities and material balances should be introduced as constraints. Because of this necessity, validation of the model cannot be checked easily.

3.1.6. The Row (Material Balance) Approach

The row approach is generally easier and natural way to construct linear programming. In this approach, constraints are defined in terms of decision variables. Steps for row approach are explained below:

3.1.6.1. Define the decision variables. This step resembles the step in the activity approach. Introducing process decision variables is the target of the step.

3.1.6.2. Define item set. This part generally covers choosing a unit for measuring the quantity of variables. i is general nomenclature for referring to a type of item.

3.1.6.3. Set up constraints and the objective function. After defining the items, if there is any restrictions in the process, they must be defined to the program as constraints.

3.2. Linear Programming Software

Linear programming software involve two kind of merged but in some way different kind of programs. One of the solver software adopts the data that comes from linear programming or mixed integer linear programming input, process to resolve the input and send output as a result. Software uses generally one of two algorithms: simplex or interior point method for linear programming solvers and branch and bound methods for mixed integer linear programming [67].

Other type of solver is the spreadsheet solver. In this kind, there are columns to introduce the decision variables, constraints and the objective function of the modeled simulation. After plugged in, linear programming or mixed integer linear programming solver is enforced.

3.3. Process Simulation

Process simulation performs notable role in deciding how to operate the plant efficiently at the very beginning of the construction, starting from feasibility studies through detailed engineering design, personnel training and plant operation. Simulation studies are used for coherent choice of operation and acquisition in manufacturing, economy and return on investment.

Flow diagrams of unit operations are used to simulate the purpose and assignment of each unit in the plant. Software solves the mass and energy balance of the whole plant with the real data that are used to reach steady state conditions for the process. Generally, process simulations are employed to provide optimum conditions.

Process simulators can be particularly beneficial in determining the catalyst replacement cycle with estimation of the catalyst impact. With this estimation fresh, regenerated or completely different kind of catalyst should be loaded to the reactor would be released.

Model find the solutions through approximations and assumptions, with a broad range of variables such as temperature and pressure. It also uses interpolation and extrapolation to facilitate the hypothetical conditions for the process and questions for the best results [68].

3.3.1. General Properties of Process Simulators

Process simulators is not only used for the design but also it can be used in the simulation, performance and rating mode. Simulation mode is more balanced numerically between over all the modes, but generally design problems are taken seriously than simulation problems. By using iterations in the simulation, valid results may be obtained.

Process simulation programs that can carry out optimization, equipment sizing and economic evaluation, conduction between all these is generally feeble. Also for

introducing input to simulator, there is common rule for all the simulators. If simulator demands less information about simulation, it prevents the user from trouble. In designing a process simulator program, there is few crucial steps:

3.3.1.1. Data processing. Data processing contains reasonable input data and best testing methods for the simulator.

3.3.1.2. Engineering models. Thermodynamic and physical properties, chemical process units and logical correlations demand intimate knowledge about modelling of the chemical processes.

3.3.1.3. Numerical analysis. For iterative solution of complicated unit modules calculations, numerical analysis must be applied [69].

In this modern age of powerful computers, making calculations by hand is waste of time. With right simulation software for the process, all the chemical engineering calculations can be operated in little time even it has iterations. Setting a simulation with real data of a plant is always easier than computing all the necessary calculations. Construction of the simulation compensates the loss of energy with its speed and accurateness [70].

Using simulation is convenient, if there is a complex system that is in a relationship with an internal interaction of subsystem. A lot of changes and effects of these changes can be simulated such as informational, organizational and environmental. Through the instrumentality of simulation model, it is possible to establish ability to understand process conditions, consequences of the development and enhancement of the system. Simulation of a model with distinct capabilities is also a tool for regulating the requirements of the process. Up until this point, solving the process by hand is only time consuming. Nevertheless, the process conditions can change due to some regulations. If the problem can be solved analytically, or carried out with direct experiments, it is not logical to simulate a model. Because for obvious and clear case that can be solved easily, simulation

can become cost consumer and exclusive to return into profitability. Also for some cases, simulation can be tough, due to convoluted system behavior.

3.3.2. Advantages of Simulation

In simulation, newly introduced parameters can be analyzed without disturbing ongoing operation of the process. Also, time variable can be controlled due to speed requirements of the process, it can be compressed or expanded. With simulation, it is effortless to see the relationship between variables and the effects of them on the other variables to examine the simulation result and impact of change. Every possible situation for the model can be analyzed. In addition, simulations, especially agent-based ones, support malleable techniques for finding solutions to a wide range of research questions [71].

3.3.3. Disadvantages of Simulation

Besides advantages of simulations, there are some drawbacks in simulation. Model building can be tough, expensive and time consuming. Even though waste of time can be mitigated with aid of introducing simple assumptions to simulation, output can create burden to decipher for some cases. Furthermore, for some simulators, results can not be analyzed immediately after the simulation has started. This is an important drawback, since in real case, an event that may occur instantaneously and it takes hours to adapt the new information to the simulation. Although simulation can be carried out in a variety of contexts, templates contain a formalized set of rules and best practices are not readily accessible. For this reason, simulation modeling requires training. Since simulation needs creativity and patience, beginners find it appalling [72].

3.3.4. The Basic Steps of a Simulation Study

A simulation needs an algorithm order which associates specific steps to obtain the desired results. Independent from the type of problem and the objective of the study, the algorithm is nearly same for every process. Basic steps of the simulation process are:

3.3.4.1. Problem Definition. In this step, deciding the goals and objective of the study is handled.

3.3.4.2. Project Planning. With project planning, project is divided into parts to use time and budget properly and efficiently.

3.3.4.3. System Definition. Identifying the components of the system, the analyzation of the performance and selecting the bounds of the system are handled in this step.

3.3.4.4. Model Formulation. System flowchart can be created in this step. It may be useful to understand the interaction between variables, system behavior, and basic requirements of the model.

3.3.4.5. Input Data Collection & Analysis. New data from the real world application or existing data is gathered to create an input for the formulated model.

3.3.4.6. Model Translation. Given data to simulation is interpreted into programming language.

3.3.4.7. Validate the Model. Comparison of model and the real system behavior and performance under process conditions is crucial for the simulation.

3.3.4.8. Experimentation & Analysis. In experiment part, multiple runs for the simulation and comparison with alternative system that, are developed simultaneously when the runs have been continued, are made.

3.3.4.9. Documentation & Implementation. The best alternative system is chosen to implement through documentation that contains written report and presentations.

3.3.5. Steady State Simulation Programs

Commercial simulation programs contribute some features that help users to construct a model. These can be listed as: a pure component data library, estimation procedures for non-library components, thermodynamic methods, physical and transport properties, simulated laboratory tests, unit operation modules for calculations, special flow sheet building modules and a user interface for program input and output. All of these features may be used in the modelling, comparison of the models and laboratory calculations. In addition to that, every monetary simulation program has an interface, that inputs of process are entered and restored along a process flow diagram (PFD). Streams of the process are primary members of the flow sheet construction, since product stream of one unit operation is the feed of another unit operation.

3.3.5.1. Pure Component Data Library. All commercial simulators have broad numbers of pure component libraries that contain chemical compound data for plants. For example, HYSYS uses generally NIST, FACTV and APV libraries.

3.3.5.2. Non-Library Components. In refining process, unfortunately there is no possibility that blend contains only pure components. For pseudo components in the mixture, there are non-library components. From literature, simulator calculates the thermophysical properties with estimation of normal boiling point, specific gravity and molecular weight of non-library components.

3.3.6. Unit Operation Calculations

In chemical engineering, splitting flow sheets into parts is appropriate, since this procedure makes simulation evaluation straightforward. This is unit operations. Methods and scientific principles, which are used in computing the unit operations, are identical. Every separate unit operation constructed as building blocks that may be connected via the process streams to form the process flowsheet.

To understand, if simulation is the correct approach to solving a particular problem, four items should be evaluated before deciding to conduct the study:

- Type of Problem
- Availability of Resources
- Costs
- Availability of Data

3.3.6.1. Type of Problem. If a problem can be solved by common sense or analytically, the use of simulation is unnecessary. Additionally, using algorithms and mathematical equations may be faster and less expensive than simulating. Also, if the problem can be solved by performing direct experiments on the system, then conducting direct experiments may be more desirable than simulating. However, degree of disturbance of the real system needs to be considered, when performing experiments on the simulation. If a high degree of disruption to the real system occurs, then another approach may be necessary. Also, the real system itself plays another role in deciding for simulation. If the system is too complex, cannot be defined or not understandable then simulation do not give meaningful results. This situation often occurs when operator behavior is involved.

3.3.6.2. Availability of Resources. People and time are the determining resources for conducting a simulation study. An experienced analyst is the most important resource since such a person has the ability and experience to determine both the model's appropriate level of detail and how to verify and validate the model. Without a trained simulator, the wrong model may be developed that gives unreliable results. Additionally, the allocation of time should not be limited, since this may force the simulator to take shortcuts in designing the model. Also, the schedule should allow enough time for the implementation of any necessary changes with performing verification and validation of the results whether they are meaningful.

3.3.6.3. Costs. Cost considerations should be thought at each step in the simulation process. Such as purchasing simulation software and computer resources, if it's not already

available. Obviously, if these costs exceed the potential savings in altering the current system, then simulation should not be pursued.

3.3.6.4. Availability of Data. The necessary data should be identified and located, and if the data does not exist, at least it should be collectible. If the data does not exist and cannot be collected, then continuing the simulation study eventually yield unreliable and useless results, since the simulation output cannot be compared to the real system's performance. Comparison is vital for verifying and validating the simulation model.

The basic steps and decisions for a simulation study are incorporated into a flowchart as shown in Figure 3.2.

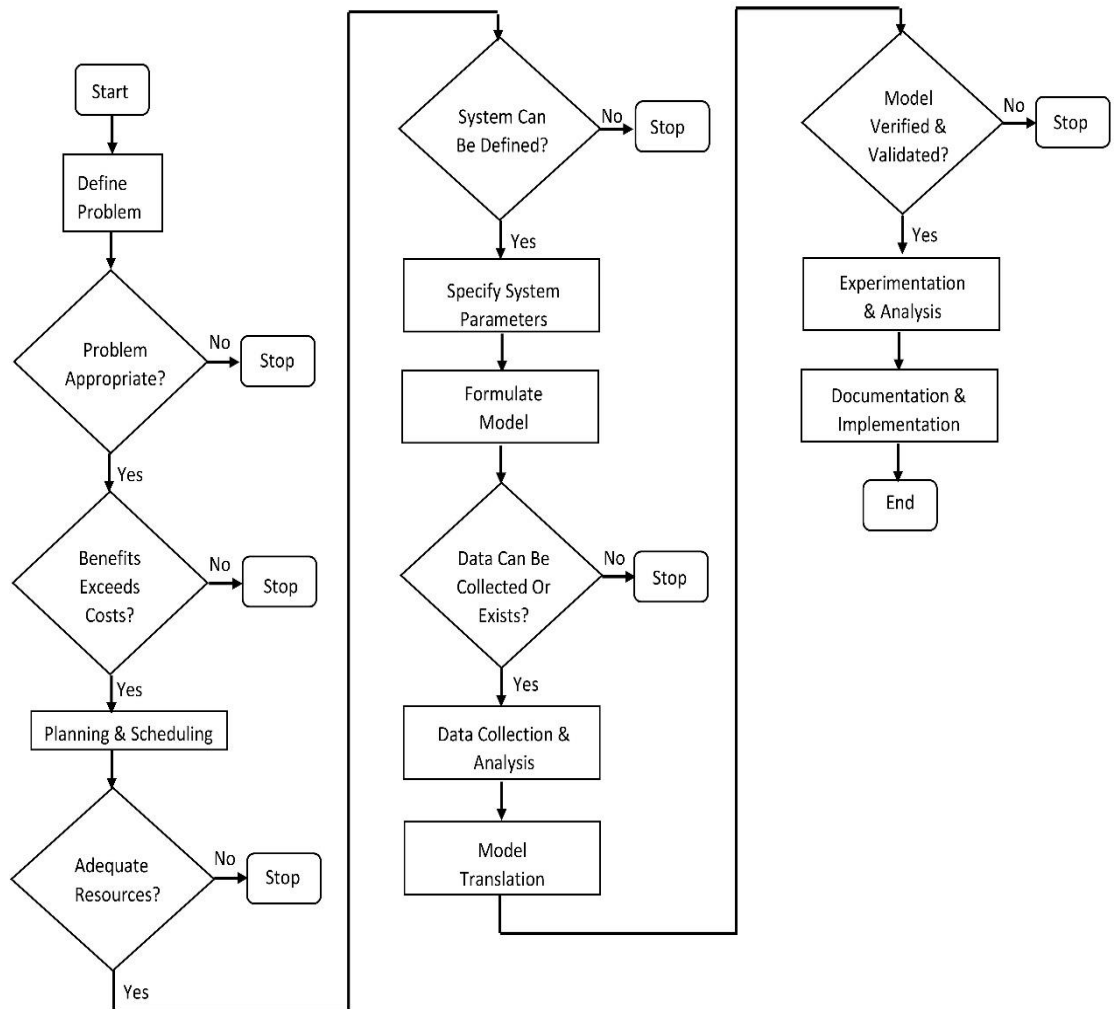


Figure 3.2. Decision Algorithm of Steady-State Simulation.

There are two types of simulation states that are established on the behavior of the model with respect to time. Steady state and dynamic state.

3.4. Simulation Optimization

This kind of optimization study can be explained as seeking the best input variables. Objective of this work is to minimize the resources that used while the maximizing the outputs of simulation.

One of popular optimization of simulation method is finite difference method, in linear programming. The method consists of approximation of the differential operator by replacing the derivatives in the equation, using differential quotients. The domain is partitioned in space and time, approximations of the solution are computed in the space or time points. The error between the numerical solution and the exact solution is called the discretization error or truncation error. The term truncation error reflects the fact that, a finite part of a Taylor series is used in the approximation. Partial derivatives of the output variable $f(x)$ are estimated by the following:

$$\frac{\partial f}{\partial x_i} = \frac{f(x_1, \dots, x_i + \Delta i, \dots, x_n) - f(x_1, \dots, x_i, \dots, x_n)}{\Delta i} \quad (3.12)$$

Estimation of gradient at significant value of x can be executed by $n+1$ configurations of the simulation. To increase the accuracy, multiple observations for each partial derivatives must be evaluated.

The other one is Nelder And Mead's Simplex Search named after John Nelder and Roger Mead. The procedure begins with simplex points that contains $p+1$ vertices, which are not all of them in the same plane and feasible region. It is carried out with elimination of the worst point in the simplex and adding a new reasonable point that is considered as a reflection of eliminated worst point through the centroid of the remaining vertices. Disadvantages of this method include the assumption of convex feasible region and handling of feasibility constraints of implementation problems.

3.5. Penex™ Unit

Optimization case study is handled for Penex™ unit and in the following, there are operational information for the unit. Detailed explanation is given in process order.

3.5.1. Function of the Unit

The function of the PenexTM unit is processing straight run light naphtha from the overhead of the naphtha splitter column to produce a high octane isomerate naphtha product. The light straight run naphtha is derived from either 100% Bach Ho Crude or Mixed Crude (85% Bach Ho / 15% Arabian Light).

The UOP PenexTM Process flow scheme affects capital expenditure in a good way by wiping out product separation and compression.

The process is a catalytic isomerization of pentanes, hexanes and blends of them, also it continues uninterruptedly. In PenexTM unit, reactions, which occurs in hydrogen atmosphere and over a trickle bed catalyst, are limited by equilibrium. Process operating conditions supports isomerization reactions, while diminishing hydrocracking reactions. Product of this process is blend of isoparaffins with a high octane number.

The process allows minimum staffing and supervision. If normal hydrotreating is not taken into account, the PenexTM process does not demand special feed pretreatment or intense prefractionation to eliminate C₆ cyclics or C₇₊. This characteristic of PenexTM unit gives refiner flexible feedstock selection.

The main elements of the PenexTM unit are the liquid feed driers, make-up gas driers, the feed surge drum, the reactors, heat exchangers, product stabilizer, net gas scrubber and deisohexanizer (Figure 3.3).

The PenexTM system has normally two reactors in series with equal amount of catalyst loaded. Two reactors is not necessary for the achievement of the operation, but in catalyst regeneration time for lead reactor, it goes offline for reloading. PenexTM catalyst is so susceptible and it is deactivated by water easily. Water deactivation progresses quickly, goes down the bed in a piston-like fashion, downstream of the catalyst bed stays unaltered.

In catalyst regeneration time of lead reactor, lag reactor is qualified to keep operation going at design throughput and yield. After regeneration, reactors may be returned into the first position. The design of two reactors permits 100% unit flow efficiency, decreases catalyst usage costs by chance of practical part of catalyst replacement. With this characteristic, catalyst capital expenditure demand can be reduced by designing the unit for a smaller catalyst inventory which also provides higher space velocity.

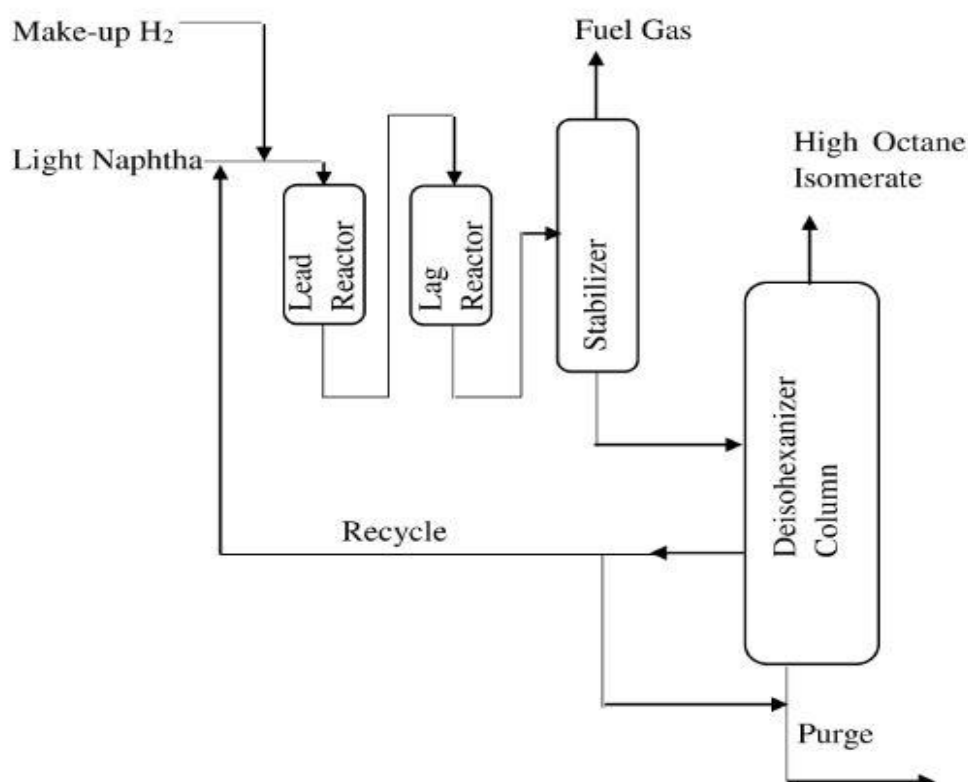


Figure 3.3. Simplified Flowsheet of the PenexTM Unit with Light Naphtha Feed.

Both isomerization and benzene hydrogenation reactions are exothermic, temperature-riser reactions in the reactor. The outlet temperature has to be as low as the catalyst allows, since equilibrium reaction demands low temperature. Using a single reactor, low inlet temperature leads low isomerization rate in the catalyst bed. With two reactors in the unit, the imposition of an inverse temperature gradient can be accomplished between reactors through exchange between warm feed and cold feed. With this

imposition, the lead reactor can be operated at higher temperature and attains a higher reaction rate. To take the benefit of more favorable equilibrium, most part of isomerization reactions takes place in lead reactor at high rate and subsequently lag reactor is carried out at lower temperature. Since some of catalysts tend to coke or sludge, all type of catalysts cannot handle the inverse temperature gradient principle. PenexTM catalyst is chosen to handle the inverse temperature gradient.

PenexTM catalyst continuously requires chloride promoter (perchloroethylene) to be activated, which is transformed into hydrogen chloride in the reactor. After it is used, it leaves the unit inside the stabilizer gas.

At the beginning of the process, liquid feed is sent to feed dryers and feed surge drum as a purpose of preserving the catalyst. Hydrogen make-up gas dryers are used to blend, the combined feed from the feed surge drum with hydrogen make-up gas.

The effluent from the lag reactor is loaded to the stabilizer to eliminate the residual hydrogen, light gases (C₁ through C₄) are formed as a result of cracking, from isomerate. The stabilizer gas is sent to the caustic scrubber to get rid of the hydrogen chloride before entering the refinery fuel gas system.

Stabilizer bottom stream is the feed of deisohexanizer (DIH) column. DIH is used for splitting C₅, 2,2-dimethylbutane (22DMB) and 2,3-dimethylbutane (23DMB) from the other C₆ isomers, heavier components in isomerate and increasing the octane number of product to 88-90 RON. With hydrocarbon once-through operation, acquired maximum research octane number is roughly 84 RON, so addition of DIH gives significant increase.

The DIH overhead product contains mostly C₅ and dimethylbutanes which are gasoline mixture components. Bottom product of DIH is also generally sent to storage to blend with DIH overhead product. Nevertheless, the bottoms might be thought as reformer feedstock. The DIH side draw, which contains mostly methylpentanes (MP), trace amount of dimethylbutanes (DMB) and nC₆, is recycled back to the isomerization unit to blend with fresh feed to compose combined feed.

3.5.2. Feed Characteristics

3.5.2.1. Hydrotreated Light Naphtha.

The feed definition for the PenexTM unit has given in Table 3.1.

Table 3.1. Feed Characteristic of Naphtha.

Feed Composition wt %			
Feed	Naphtha Splitter Overhead with low C ₆ in the feed	Naphtha Splitter Overhead with low C ₇ in the feed	Hydrocracker
Isobutane	-	-	0.1
n-butane	-	-	0.3
Isopentane	1.22	1.3	16.97
n-pentane	23.95	25.37	15.81
CP	2.47	2.61	1.7
22DMB	0.45	0.48	0.38
23DMB	2.7	2.86	3.03
2MP	12.79	13.55	19.88
3MP	9.54	10.1	12.06
n-hexane	25.15	26.57	6.64
MCP	10.31	10.5	16.02
Dimethylpentane	2.96	1.57	-
Benzene	2.71	2.78	2.18
Cyclohexane	4.73	1.88	3.76
Dimethylcyclopentane	0.58	0.24	-
2-methylhexane	0.27	0.11	-
3-ethylpentane	0.14	0.06	-
n-heptane	0.01	0.01	-
Methylcyclohexane	0.02	0.01	-
Toluen	-	-	1.04
Olefin	-	-	0.09
Total	100	100	100
Sulfur. wt.ppm	800	800	10
Nitrogen. wt.ppm	1	1	1

3.5.3. Products Specifications

3.5.3.1. Isomerate. In refinery, two different isomerate types are stated: one of them contains high benzene contaminant with cut points C₅ – 82 °C and the other one contains low benzene with cut points C₅ – 70 °C. Operating case selection affects the isomerate properties (Table 3.2). Hereafter are given the composition of the isomerate obtained for

each case at start of run (SOR) (fresh catalyst) and end of run (EOR) (spent catalyst) (Table 3.3).

Table 3.2. Isomerase Specifications.

Property	Value
C ₅ + Product Yield at Start of Run(wt. % Fresh Feed, minimum)	95.2
C ₅ + RON	87
C ₅ + MON	85
RVP, kg/cm ²	0.82
Benzene, vol.-%	0
Aromatics, vol.-%	0
Olefins, vol.-%	0
Sulfur, wt-ppm	1 max.
Nitrogen, wt-ppm	1 max.
Oxygenates, wt-ppm	1 max.

Table 3.3. Results of Case Studies.

	SOR	EOR	SOR	EOR
Density at 15°C	0.656	0.656	0.647	0.648
Composition, kmol/h				
Propane	Trace	Trace	Trace	Trace
Isobutane	0.79	0.58	0.2	0.14
n-Butane	1.67	1.35	0.73	0.61
Isopentane	108.87	104.52	99.34	95.85
n-Pentane	33.69	38.76	28.49	32.65
Cyclopentane	0.33	0.35	0.33	0.35
22DMB	104.08	79.78	110	95.94
23DMB	18.83	22.92	10.9	14.19
2MP	31.44	46.7	16.26	24.65
3MP	5.18	9.13	2.63	4.56
n-Hexane	0.45	0.77	0.3	0.47
MCP	0.44	0.84	0.13	0.23
CH	3.28	3	1.36	1.27
Benzene	Trace	Trace	Trace	Trace
2-Methylhexane	0.2	0.26	Trace	Trace
n-Heptane	0.16	0.26	Trace	Trace
Methylcyclohexane	25.39	22.24	8.21	7.74

3.5.4. Thermodynamics of Isomerization Reactions

The isomerization reaction is limited by equilibrium and naturally exothermic with heat of reaction in the range of -4 to -20 kJ/mol, so normal paraffins cannot be converted into isoparaffins completely. Reactor temperature is the key element for maximum possible conversion. Using thermodynamics, n-paraffin isomerization can be carried out at low temperatures to reach equilibrium.

Isomerization reactions are comparatively slow and residence time distribution is wide for efficient conversions. In isomerization reactor blend consists of multibranched paraffins, that are more inclined to cracking, and monobranched paraffins are also inclined to isomerization and hydrocracking. The products of consecutive isomerization and hydrocracking reactions include monobranched isomers, dibranched isomers and cracked light products. Only traces of tribranched isomers are usually observed in the products, since they are cracked rapidly. According to isomerization and hydrocracking reaction rates, product distribution is regulated. It is important to optimize operating conditions to prevent hydrocracking and olefin formation.

3.5.5. Process Principles

The PenexTM process reaction is carried out on a trickle bed catalyst, that is coated with a noble metal material and an acidic component to activate the catalyst. In hydrogen atmosphere, with injection of perchloroethylene as a catalyst promoter, reaction is performed.

The catalyst is easy to be poisoned, so it needs a dry, low sulfur feedstock that helps to less hydrocracking. The C₅/C₆ paraffin isomerization reactions, are shown in Figure 3.4, 2MP and 3MP isomerization reactions are also shown in Figure 3.5. The octane numbers presented in this section are for pure components.

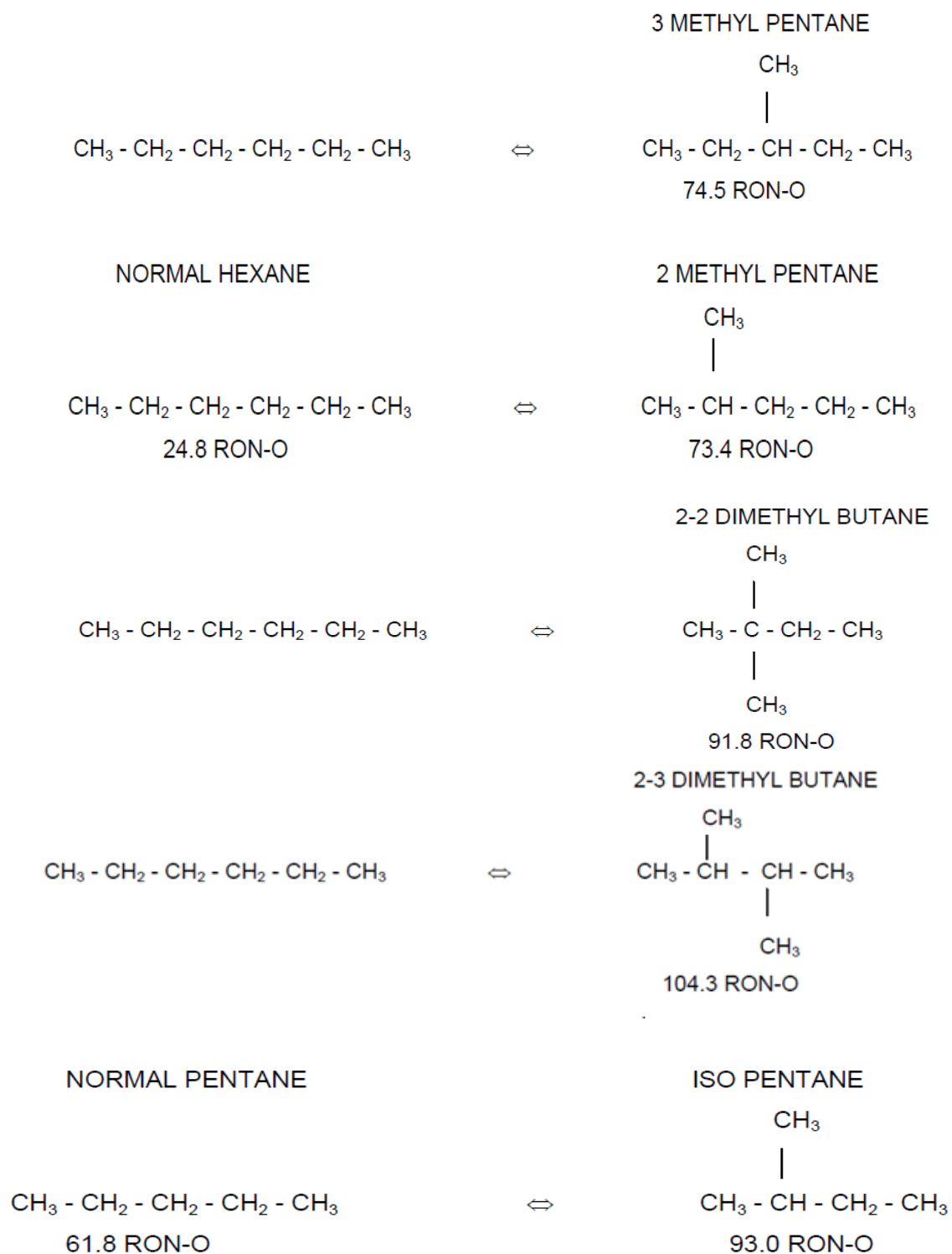


Figure 3.4. nC6 and nC5 Isomerization Reactions.

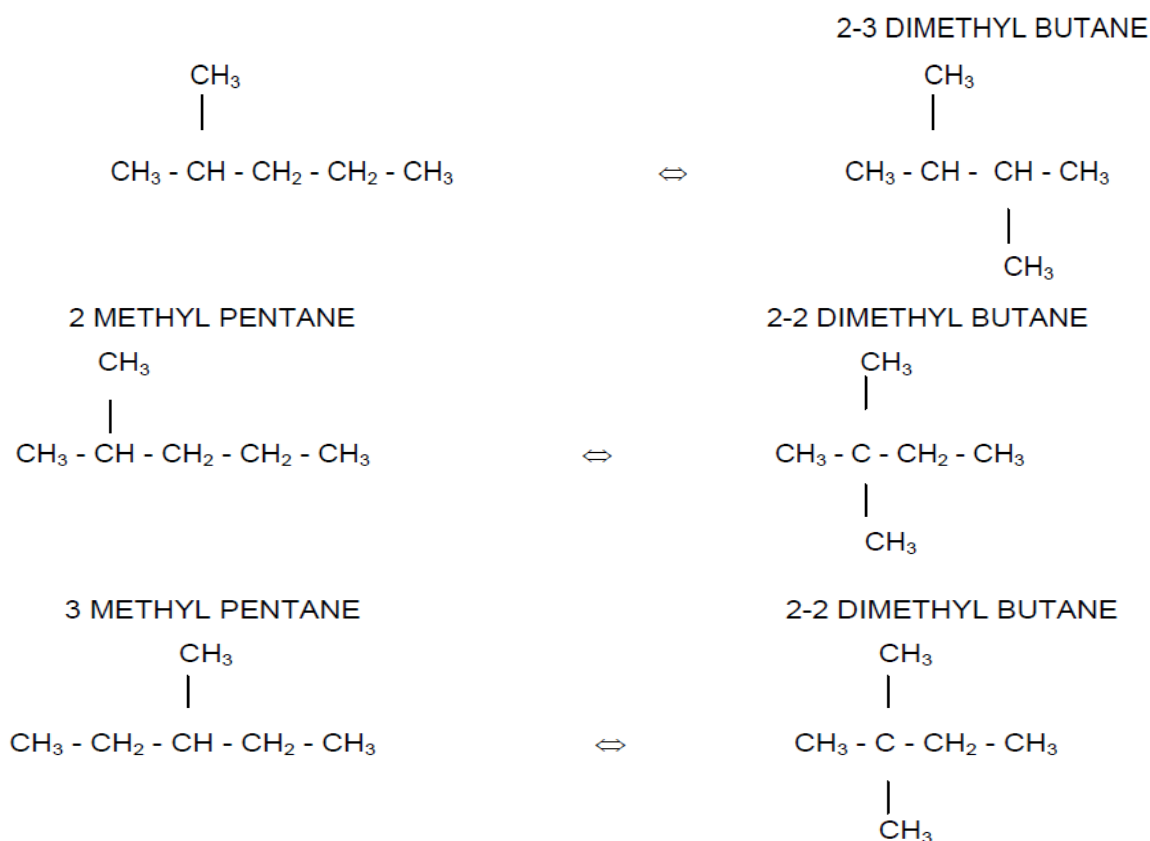


Figure 3.5. 2MP and 3MP Isomerization Reactions.

3.5.6. Reaction Mechanisms

In isomerization unit, dual-function hydro-isomerization type of catalysts are used. This catalyst is also known as "low temperature" catalyst, it can be operated under 200 °C operating temperature. General properties of catalysts are given above in the process principles part.

3.5.6.1. Dual-Function Hydro-Isomerization Catalyst. The dual-function hydro-isomerization catalysts are considered to conduct through an olefin intermediate whose structure is composed by the metallic component. This mechanism can be illustrated with platinum (Figure 3.6).

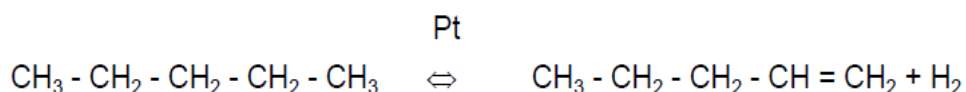


Figure 3.6. Dual-Function Catalyst Mechanism.

In this reaction, equilibrium is unfavorable for the left side, but since this is a reversible reaction, in spite of unobtainable equilibrium, the acid function of catalyst depletes olefin by formation of a carbonic ion, so it allows more olefin to form.

The isoparaffin is the final form that is created by hydrogenation:

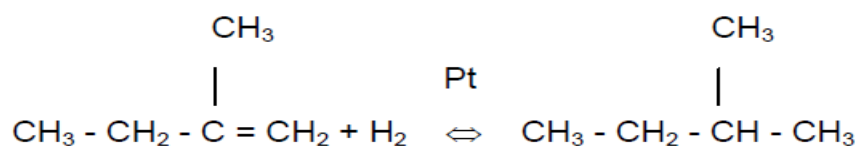


Figure 3.7. Isoparaffin Formation by Hydrogenation.

Other than the paraffin isomerization reactions, there are considerable reactions that are occurred in the reactor, including:

- Naphthene ring opening
- Naphthene isomerization
- Benzene saturation
- Hydrocracking

3.5.6.2. Naphtene Ring Opening. Cyclopentane (CP), methyl cyclopentane (MCP) and cyclohexane (CH) are found in the feed of isomerization reactor. Since the aim of the isomerization unit is attaining maximum possible high octane number paraffin amount, these naphthene rings are hydrogenated to form paraffins. The ring opening reaction is

proportional with increasing reactor temperature. At typical operating conditions for isomerization reactor, the naphthene rings are converted to paraffins about 20-40 percent.

3.5.6.3. Naphtene Isomerization. MCP production is tend to be formed from the naphthene CH with increasing temperature.

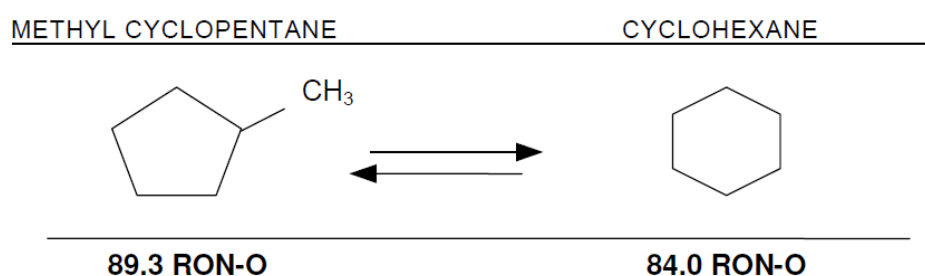


Figure 3.8. Naphtene Isomerization.

3.5.6.4. Benzene Saturation. Benzene saturation reaction is not limited by equilibrium and the conversion will be %100 at relatively low temperatures, very rapidly. Since the benzene saturation is exothermic, there will be heat release in the reactor and these discharged heat restricts the amount of benzene, which the Penex™ unit feed can abide. Benzene saturation is handled by the platinum function of the isomerization catalyst. Addition to these all information, Penex™ feed can consist of 4% benzene.

3.5.6.5. Hydrocracking. Hydrocracking takes place in the Penex™ reactors and degree of hydrocracking depends on the feed specifications, whether it contains high percent of C₇, C₇₊ or not. Because C₇ and C₇₊, are big molecules, incline to hydrocracking easily rather than smaller molecules. C₅ and C₆ paraffins also crack at certain extent. As C₅/C₆ paraffin isomerization reaches equilibrium, the extent of hydrocracking increases. And subject to this, one of purposes of DIH is decreasing the amount of C₅ in the feed with side draw. If isomerization is compelled too hard, degree of hydrocracking increases with the products of methane, ethane, propane and butane. They reduce the yield and raise the heat generation. Hydrocracking reaction can be shown as below (Figure 3.9).

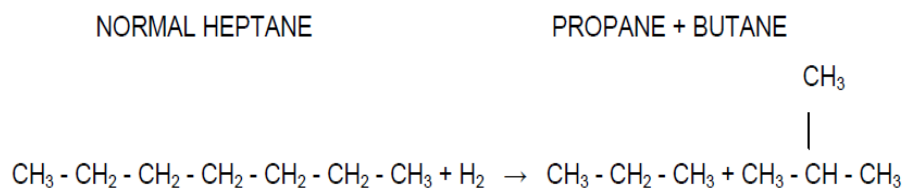
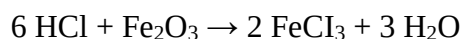


Figure 3.9. Hydrocracking Reaction.

3.5.7. Acidizing

While the initializing of the unit is continuing, hydrogen chloride (HCl) is injected into the feed stream to procure the reaction between iron oxide (Fe_2O_3) and hydrogen chloride to obtain iron chloride (FeCl_3) and water (H_2O). The aim of this application is, depleting the rust in the unit. When H_2O in the unit is run out, moisture analyzers detect this change that indicates the rust has been minimized.

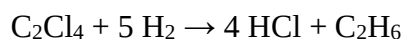
Hydrogen chloride + iron oxide $\rightarrow$ Iron chloride + water



3.5.8. Chloride (Catalyst) Promoter

Catalyst acid function is provided by the injection of the chloride promoter (perchloroethylene, C_2Cl_4) with chloride atoms (Cl). When reaction temperature reaches 105°C or higher, the organic chloride will be turned into HCl, with activation of the catalysts.

Perchloroethylene + hydrogen $\rightarrow$ Hydrogen chloride + ethane



3.5.9. Process Contaminants

The contaminants and undesirable components on the PenexTM Process have to be removed in Unifiner process.

3.5.9.1. Contaminants.

- Sulfur
- Water or other Oxygenated Compounds
- Nitrogen
- Fluoride

3.5.9.2. Undesirable Hydrocarbons.

- Olefins
- Cyclic Compounds
- C₇ Hydrocarbons
- Butane

Since feed of PenexTM unit is hydrotreated and dried, these contaminants and hydrocarbons can be found in the feed in trace amounts.

3.5.10. Isomerization Reactors

The reactors of the isomerization process are essential part of the unit. From time to time, it's possible one of the reactor is either lead or lag reactor can be used as need-based. A single reactor can carry out the whole process with a bypass operation.

Thermocouples are used to measure the isomerization catalyst bed of each reactor temperature to obtain the catalyst activity on the monitor in conjunction with product ratios. Reactors are loaded with I-8 catalyst.

After the combined feed is heated against the lag reactor exit and MP steam, flows to the lead reactor. The combined feed enters the reactor vessel top through an inlet distributor and leaves at the bottom.

Above the catalyst bed, a vapor/liquid distributor tray is inserted to provide even distribution. The bottom head of the reactor has a screen basket that allows the process stream to pass through it, but prevents any ceramic support material to migrate into the unit. The vessels are made of carbon steel. After the stream exits from the first reactor, it passes to the hot combined feed exchanger at 182-188 °C and the heat of exothermic reaction in the reactor is relatively mitigate, temperature decreases down to 112-155 °C.

There is a temperature controller at the lead reactor exit, and this temperature controller adjusts the lag reactor's inlet temperature. The relatively cooled stream is sent to the lag reactor, where the final reactions will be completed.

The hydrogen purge, is used to clear away hydrocarbons from the reactor, exists at the inlet of each reactor. Hydrogen quench line is located at the lead reactor inlet header to assist to cool the catalyst during a temperature change as well as to remove hydrocarbon. After exiting the lag reactor, the stream is then transmitted to the tube side of the cold combined feed exchanger to be cooled down to 115 °C. Then, the cold combined feed exchanger tube side effluent is sent to the stabilizer.

3.5.11. Process Variables of The Reactor Section

At the beginning of the normal operation of the isomerization unit, operating pressure, fresh feed rate and make-up hydrogen flows, are set up.

In the following, the "product isomer ratio" refers to the weight percentage ratio of isopentane to total C₅ aliphatic paraffins, or the weight percentage ratio of 2,2 and 2,3 dimethyl butane to the total C₆ aliphatic paraffins in the stabilizer bottoms stream. This is also expressed in the PIN number as is shown below.

$$PIN = \frac{iC_5}{nC_5} + \frac{22DMB}{nC_6} + \frac{23DMB}{nC_6} \quad (3.13)$$

The term "liquid feed" means C₅/C₆ charge of the liquid feed driers of the unit, "reactor charge" is the effluent from the liquid feed driers and "combined feed" refers to the reactor charge plus make-up hydrogen.

3.5.11.1. Reactor Temperature. As it is expressed above, reactor temperature is the main process control. At any given outlet temperature, a definite upper limit exists for the isoparaffins quantity in the converted product in the reactor, as shown in Figures 3.10, 3.11 and 3.12. From thermodynamics, this is an equilibrium state that can be reached only with an infinite time in infinitely large reactor. In reality, the product always consists of less amount of isoparaffins than expected (equilibrium state). If reactor temperature is raised to promote the rate of isomerization, the equilibrium composition can be achieved more closely. But as a reverse effect, at excessively high temperatures, despite the fact that the high temperature leads a higher reaction rate, the amount of isoparaffins in the product actually mitigate, since the equilibrium curves, which are provided in Figures 3.10, 3.11 and 3.12, shift downward after some temperature rise.

In equilibrium curves, process conditions is for the PenexTM reactor and composition is in mixed phase. The amount of liquid is regulated by the feed composition, reactor temperature and pressure. The equilibrium values for liquid phase operation are lower than for vapor phase operation. The actual equilibrium values for isopentane and 22DMB for the mixed phase content of the reactor lies between the liquid and vapor curves shown in Figure 3.11.

While targeting to approach to the equilibrium, using excessively higher temperatures than required, achieves nothing but increasing the degree of hydrocracking. High temperatures not only causes more hydrocracking, but also lead to an increased rate of carbon laydown on the catalyst. The catalyst of PenexTM unit has inherently low carbon forming inclination, so excessive hydrocracking would be experienced before carbon formation problems.

One of the other reason of isomerization unit has two reactors in series is independent temperature control. Any benzene in the feed is hydrogenated in the lead reactor, even if catalyst has lost its activity because of paraffin isomerization. Reactions, ring opening, cyclohexane and methylcyclopentane conversions to hexanes also occur in the lead reactor with hydrocracking of C_7 to C_3 and C_4 . These three reactions (benzene hydrogenation, naphthene ring opening to hexane, and C_7 hydrocracking) are exothermic as stated above, and they causes more temperature rise in the lead reactor than paraffin isomerization.

Generally, the temperature of lead reactor system is chosen to maximize the concentration of isopentane and 2,2 dimethyl butane (22DMB) in its effluent. The amount of active catalyst present affects the concentrations and the required outlet temperature. The temperature of lead reactor system is also determined by the amount of C_6 cyclic and C_{7+} components that are presented in the feed. Higher the temperatures is required with high concentrations of these components in the feed. By this procedure, the lag reactor temperature is reduced and it is possible to operate at equilibrium favorable conditions.

The lead reactor system temperature is normally independent from the isomer content of the final stabilizer bottoms product. To obtain optimum overall operation, it should be carried out by analyzing the quantitative relationships which is developed through operating experience on each unit and changed with catalyst age. When catalyst is fresh and the operation is at early stages, the final product will probably be made as rich in isopentane and 22DMB. Then, the lead reactor is chosen to be operated with a lower isopentane and 22DMB content, since lower lead reactor temperature means slightly less hydrocracking and slightly higher liquid yield.

Table 3.4. Naphtha Fractionation.

Component	Boiling Temperature (°C)	Relative Volatility
Isopentane	28	3.18
n-Pentane	36	2.71
22DMB	50	1.9
23DMB	58	1.59
2MP	60	1.53
3MP	63	1.42
n-Hexane	69	1.26
MCP	72	1.21
Benzene	80	1.25
CH	81	1

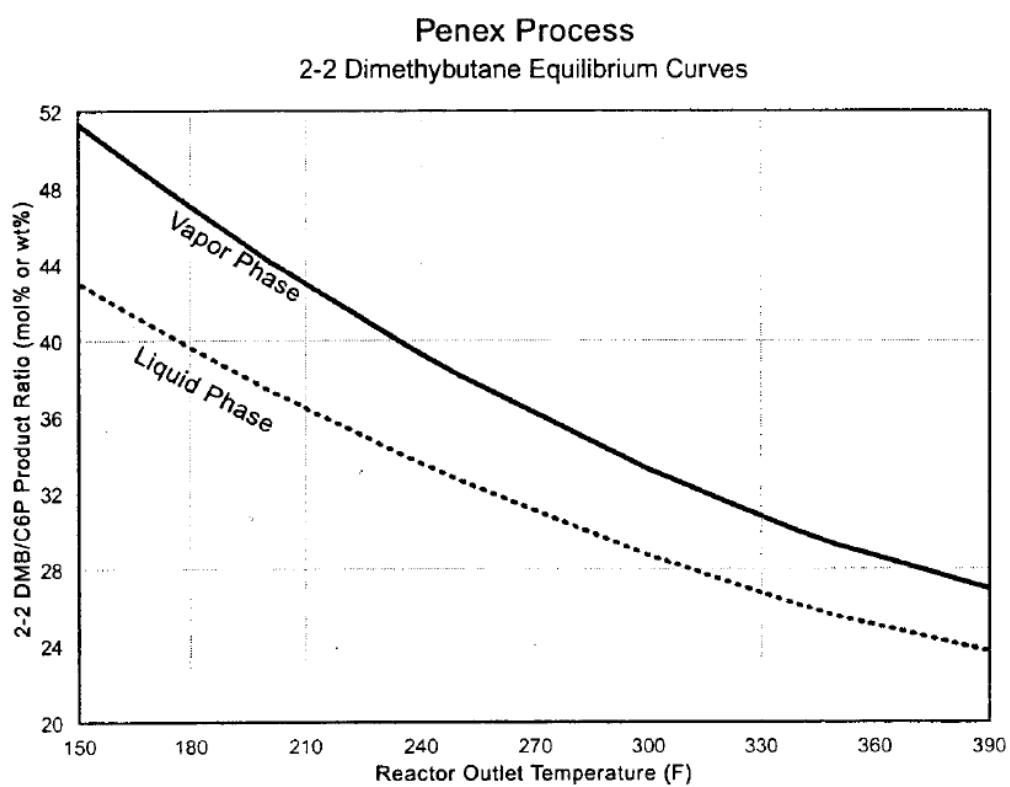


Figure 3.10. 22DMB Curve [73].

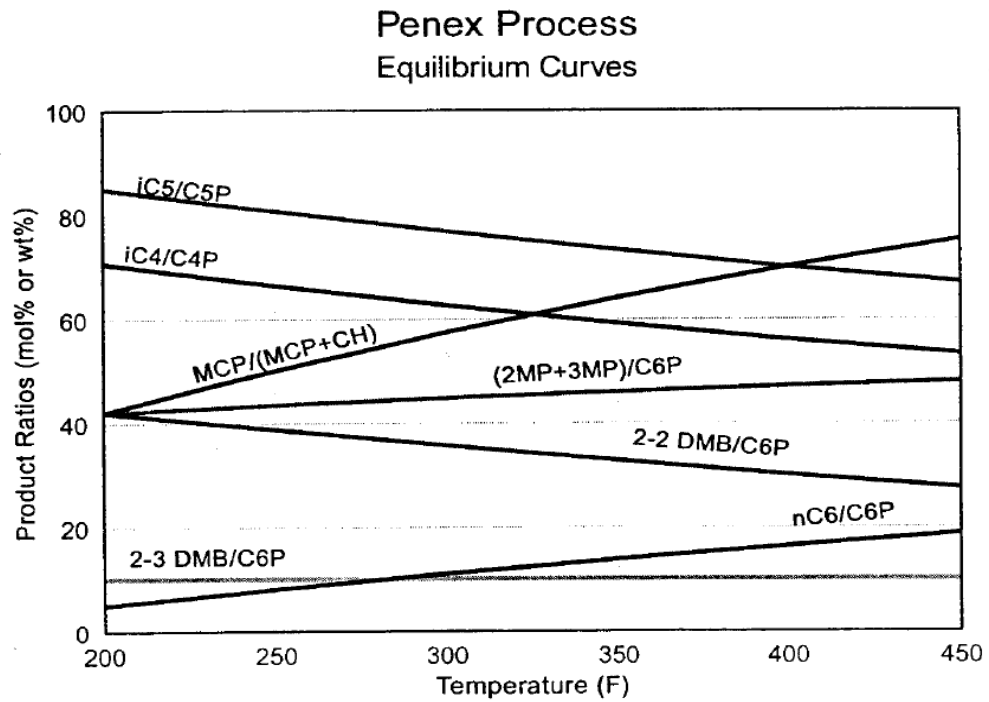


Figure 3.11. Equilibrium Curves [73].

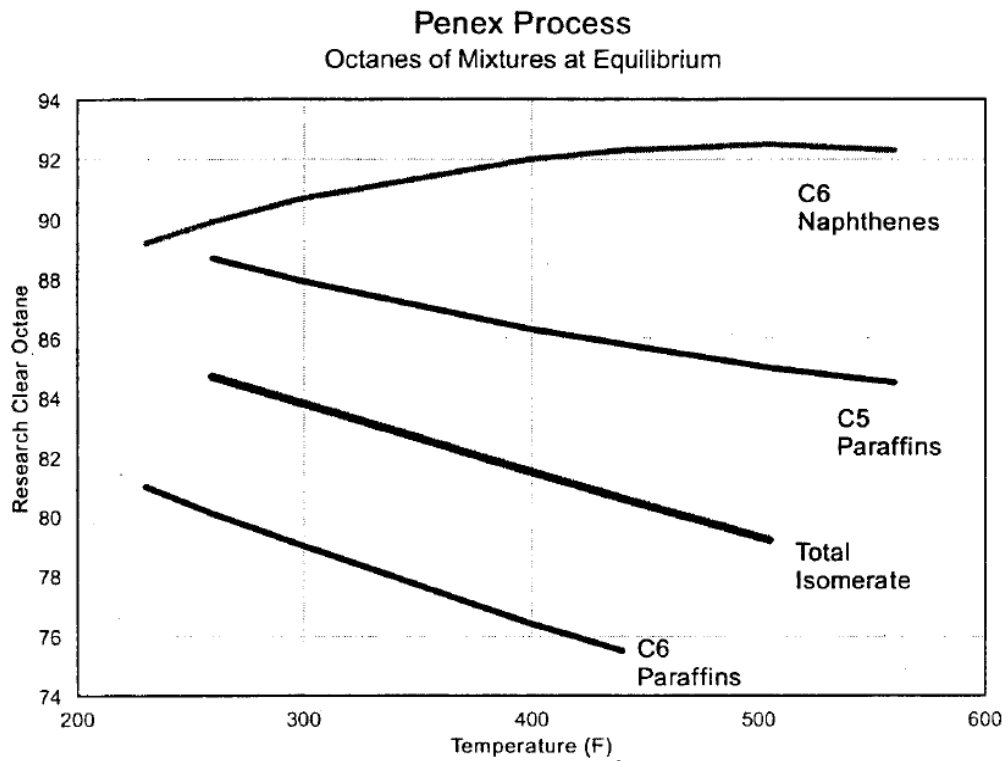


Figure 3.12. Octane Numbers of Components [73].

3.5.11.2. Liquid Hourly Space Velocity. This term is defined as, the volumetric flow of reactor charge hourly is divided by volume of catalyst in the reactors. It is generally abbreviated to LHSV. The design LHSV for C₅/C₆ PenexTM operation is normally between 1 and 2. Raising the LHSV affects negatively product isomer ratios. To abstain excessive reactor severity, PenexTM reactor should be operated above 0.5 hr⁻¹ overall or 0.1 hr⁻¹ minimum per reactor.

3.5.11.3. Hydrogen To Hydrocarbon Mol Ratio. This ratio is described as, the number of moles hydrogen at the reactor outlet per mol of reactor charge going through the catalyst. It is designated at 0.05 moles H₂/mol HC. Keeping ratio at significant range facilitates the prevention from carbon deposition on catalyst and cultivate the H₂ atmosphere. In necessary situations, to provide optimum hydrogen to hydrocarbon ratio, reactor feed rate can be decreased. The H₂/HC ratio can be found by calculating the total moles of hydrogen in the stabilizer overhead gas over the total moles of fresh feed.

3.5.11.4. Pressure. The PenexTM unit is constructed to run at 31.2 kg/cm² g at the reactor outlet. Higher pressure provide help to compensate the effect of methylcyclopentane (MCP) and cyclohexane (CH) that are absorbed on the catalyst. Also, it decrease the rate of isomerization reactions. Lowering the unit pressure or operating at a slightly lower level would not alter the catalyst life but the degree of isomerization would be affected.

3.5.12. Reactions

Table 3.5. Isomerization Reactions [74].

$nC_4 \rightarrow iC_4$	$iC_4 \rightarrow nC_4$	$nC_5 \rightarrow iC_5$	$iC_5 \rightarrow nC_5$
$nC_6 \rightarrow 2MP$	$2MP \rightarrow nC_6$	$nC_6 \rightarrow 3MP$	$3MP \rightarrow nC_6$
$23DMB \rightarrow 2MP$	$2MP \rightarrow 23DMB$	$23DMB \rightarrow 22DMB$	$22DMB \rightarrow 23DMB$
$MCP \rightarrow CH$	$CH \rightarrow MCP$	$3MP \rightarrow 2MP$	$2MP \rightarrow 3MP$

Table 3.6. Ring Opening and Hydrogenation of Benzene [74].

$CP + H_2 \rightarrow nC_5$	$CP + H_2 \rightarrow iC_5$	$CH + H_2 \rightarrow nC_6$
$MCP + H_2 \rightarrow 2MP$	$MCP + H_2 \rightarrow 3MP$	$MCP + H_2 \rightarrow 23DMB$
$MCP + H_2 \rightarrow 22DMB$	$BZN + 3H_2 \rightarrow MCP$	$BZN + 3H_2 \rightarrow CH$

Table 3.7. Hydrocracking Reactions [74].

$nC_4 + H_2 \rightarrow C_1 + C_3$	$nC_4 + H_2 \rightarrow 2C_2$	$iC_4 + H_2 \rightarrow C_1 + C_3$
$nC_5 + H_2 \rightarrow C_1 + nC_4$	$nC_5 + H_2 \rightarrow C_2 + C_3$	$iC_5 + H_2 \rightarrow C_1 + nC_4$
$iC_5 + H_2 \rightarrow C_1 + iC_4$	$iC_5 + H_2 \rightarrow C_2 + C_3$	$nC_6 + H_2 \rightarrow C_1 + nC_5$
$nC_6 + H_2 \rightarrow C_2 + nC_4$	$nC_6 + H_2 \rightarrow 2C_3$	$2MP + H_2 \rightarrow C_1 + nC_5$
$2MP + H_2 \rightarrow C_1 + iC_5$	$2MP + H_2 \rightarrow C_2 + iC_4$	$2MP + H_2 \rightarrow 2C_3$
$3MP + H_2 \rightarrow C_1 + nC_5$	$3MP + H_2 \rightarrow C_1 + i - C_5$	$3MP + H_2 \rightarrow C_2 + nC_4$
$23DMB + H_2 \rightarrow C_1 + iC_5$	$23DMB + H_2 \rightarrow 2C_3$	$23DMB + H_2 \rightarrow C_1 + iC_5$
$22DMB + H_2 \rightarrow C_2 + iC_4$	$nC_7 + H_2 \rightarrow C_1 + nC_6$	

3.5.13. Stabilizer

Lag reactor bottom is the feed of stabilizer and it enters at pressure of 15.9 kgf/cm² and temperature of 113 °C.

Duty of stabilizer is, separating any dissolved hydrogen, HCl and cracked gases (C₁, C₂ and C₃'s) from the isomerase. These gases are formed during reactions in isomerization unit.

The stabilizer column overhead vapor contains the light hydrocarbon components of the feed of column. It is directed to the air cooled stabilizer condenser for condensation and cooled to 50°C. Via stabilizer trim condenser, it is sent to the stabilizer receiver. All liquid from the stabilizer overhead receiver is refluxed to the stabilizer column on first tray.

The column is reboiled by MP steam in stabilizer reboiler. The amount of heat input is adapted to supply enough reflux rate, to strip the HCl and light ends from the stabilizer bottoms effluent. The typical design external reflux to feed ratio is approximately 0.5 on a volume basis.

3.5.14. Net Gas Scrubber

Net gas scrubber neutralizes the hydrogen chloride in the stabilizer off gas. The HCl is formed in the reactor section and then vented off through the stabilizer overhead receiver. In scrubber, the off gas from the stabilizer receiver goes through a liquid. With a counter current flow system, it meets caustic solution (10 wt % NaOH) which reacts with HCl to form sodium chloride and water.

The incoming gas is contacted with the caustic, in bottom portion of the scrubber. In this section, most of HCl is evacuated as possible, before it reaches the top portion or the scrubbing section of the column.

The scrubbed gas leaves the top of the column and it is directed as net gas to the refinery fuel gas unit on pressure controller. The hydrogen purity of the net gas is monitored in order to regulate the hydrogen to hydrocarbon ratio.

3.5.15. Caustic Scrubbing

In the net gas scrubber, with the of acid base neutralization, hydrogen chloride (HCl) is neutralized with sodium hydroxide (NaOH). After neutralization, sodium chloride (NaCl) and water are formed in the stream. A diagram of the caustic scrubbing operation is shown in Figure 3.13.

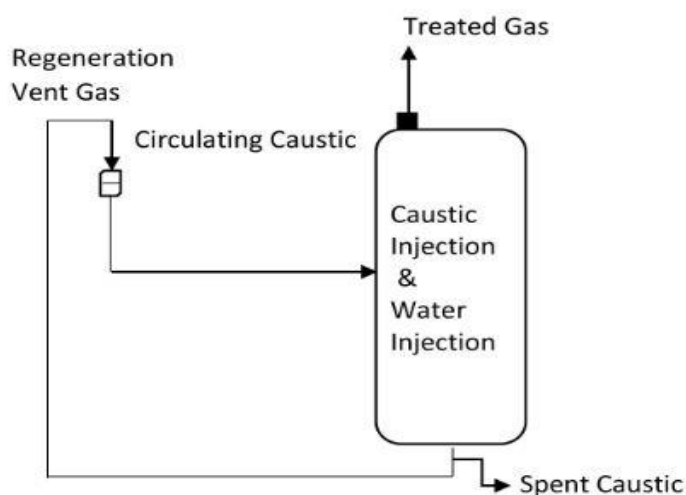
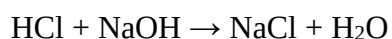


Figure 3.13. Caustic Scrubbing Operation.

Hydrogen Chloride+ Sodium Hydroxide → Sodium Chloride + Water



3.5.16. Deisohexanizer Column (DIH): Theory of Fractionation

If boiling points of two components with comparably close boiling points are heated, obtained vapor above the liquid consist of both components. For example, the simple distillation of a mixture of 50:50 A and B, with a postulation of A has a lower boiling point than B. When boiling occurs, in the vapor phase, A will have higher ratio, presence of B is negligible, supposing that the ratio between is 66:33 A:B. To make this vapor richer in A, vapor is cooled in the condenser and collected into the receiving flask. At the end of the simple distillation, to get purer A, another simple distillation has to been set up. To get pure A, series of vaporization/condensation cycles are required, which cause more capital and utility cost.

Fractional distillation is a series of simple distillations, but it takes place in a single distillation column, instead of having many condensers and receivers. Distillation columns are tubes with high surface area and permit favorable multiple vaporization/condensation cycles to happen at once.

In fractional distillation, vapor moves up through column and condenses on a "fractionating tray". Then it continues to evaporate, rises further up the column and condenses again on another fractionating tray. Fractionating trays are constructed to gather some amount of boiling liquid on the tray while vapors from the tray below are bubbled through the liquid. One type of fractionating tray used widely in the past is commonly called "bubble cap". The component with lower boiling point in the mixture, becomes more and more pure by courtesy of evaporation/condensation cycle.

For improved separation, mixture should go into more evaporation/condensation cycles. Bigger surface area in the column, affects the separation quality in a good way. But, it causes slower distillation process, furthermore, there is part of liquid that always stays on the column walls and cannot be distilled. The liquid, condensed on the surfaces in the column and cannot be distilled, is known as hold-up.

During fractional distillation, temperature gradient is seen through the length of the column. The mixture boiling point depends on the mixture composition, if mixture contains more low boiling component, mixture boils at lower temperature. Each component has different vapor pressure, that is a indicator of the tendency of a molecule of the component. The total vapor pressure of a mixture is the sum of all the partial pressures of each component in the mixture. The vapor pressure of this mixture is in the range of the vapor pressures of the components, just like boiling points.

If thermometer on the column head shows the temperature of lower boiling compound, that means the distilled liquid is pure. If the thermometer shows above the boiling point of the low boiling compound, it indicates that distilled liquid contains high boiling component apart from low boiling component. To guarantee a temperature gradient over the column, reflux can be used. Reflux can be explained as, the most of vapor in the boiling still pot should be condensed and dripped back into still pot by heating the still pot slowly. Some of the trays have been omitted to simplify the sketch Figure 3.14.

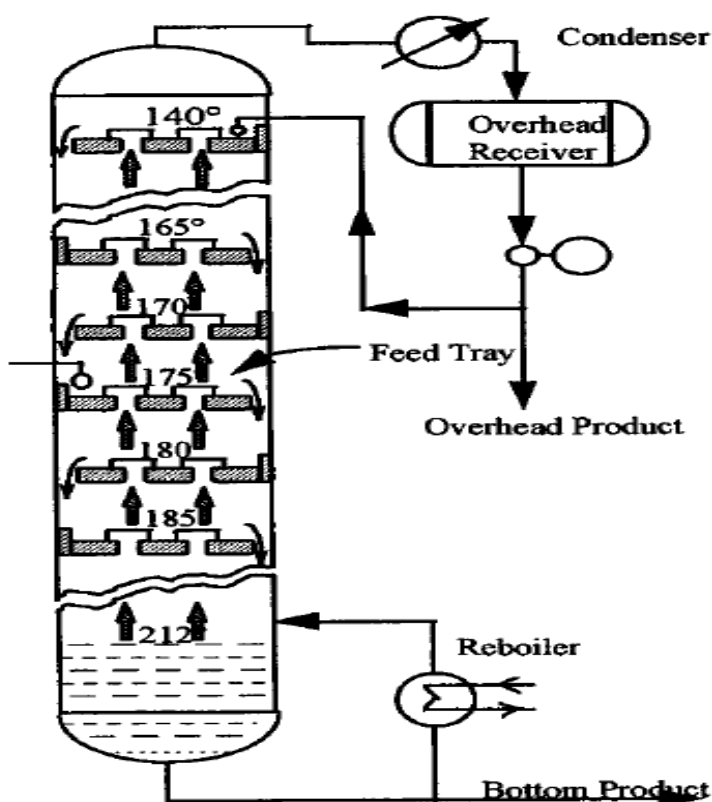


Figure 3.14. Distillation Column.

Top reflux is explained above. There is also internal reflux. The surplus liquid, that goes down from one tray to another is internal reflux. If some of surplus liquid is wanted to be removed, heat of reboiler can be increased. Less internal reflux and same amount of heated vapors are the source of the tray temperature increment. This increment affects the equilibrium state of the reaction.

As can be seen, top reflux is more important than the internal reflux. Top reflux regulate the state of fractionation. Also, if there is too much top reflux, there will be too much internal reflux.

The contact between the rising vapors and the liquid on each tray should be calculated for the optimum results and efficiency. If the vapors do not have enough time to establish an equilibrium with the liquid, less vapors condenses.

Top reflux amount of a fractionating tower can be determined by quantity of the overhead vapors and given heat. To have better fractionation, top reflux may be increased. This alteration usually increases the given heat quantity.

3.5.17. DIH Column

The DIH column in the isomerization unit, fractionates the C_5/C_6 naphtha mixture. The DIH overhead contains C_5 's and dimethyl butanes, the DIH side draw is generally composed of methylpentane which decreases the total research octane number (RON) of the mixture that is sent to gasoline blending. Operation in the DIH column continues with blending the bottom stream of DIH and DIH overhead. DIH bottom stream has low flow rate and it consists of heavier boiling components, like cyclohexane and C_{7+} .

Desired products isopentane and its isomer, neopentane, boil at the lowest temperatures in the DIH column effluent. Since isohexane boils between the range of nC_5 and nC_6 boiled, isohexane generally left in the recycle and sent again into combined feed. To avoid this, more than one DIH column with high reflux ratio is required.

3.5.18. DIH Properties

3.5.18.1. Objective. The objective of deisohexanizer column is, attaining the isohexane and pentanes from the stabilizer bottom products. A side draw is used to recycle relatively low octane number products, methylpentanes, and nC_6 . They are recycled back to isomerization unit for further enhancing.

3.5.18.2. Overhead Temperature and Reflux Liquid Control. Tray temperature is controlled by sending the overhead product to storage for temperature measurement and flow controller resets the tray temperature according to this information. In the case of reported temperature is above set point, temperature controller diminishes flow controller set point. In the new situation, opening value of flow controller will be at lower temperature. Sum of product and reflux gives the value of flow controller, thus if the overhead product flow mitigates, flow controller measures decreased flow temperature. To remove flow loss effect, flow controller output increases, then more reflux is sent to the column. Compositional control (chromatograph) is used to take the desired amount of net overhead product. If the composition sensor is not satisfied, the overhead product is refluxed back to the column. This assures the feed will be separated well, then sent to composition sensor again to check whether it is at its desired value or not.

3.5.18.3. Side Draw Flow and Column Bottom Level Control. Compositional control also operates with the heavies on the side draw. They should be decreased to attain best performance from the isomerization reactor. Flow controller, which is cascaded the column bottom level control, measures the side cut that is recycled back to isomerization unit.

3.5.18.4. Reboiler Heat Input Control. Desuperheated MP steam gives the heat via a thermosyphon reboiler to DIH column. Reflux feed ratio are arranged with the help of adjustment of the reboiler heat input.

3.5.19. Process Variables of DIH

The purpose of this section is examining the effects of these variables consequences and conferring the principal process variables on DIH performance. The process variables are:

- Feed Composition
- Pressure
- Inlet Temperature
- Reflux/Feed Ratio
- Reboiler Heat Input
- Side Draw Recycle Rate
- Side Draw Tray Temperature

3.5.19.1. Feed Composition. Type of feed that is charged to the column affects the DIH performance. If the feed components differ from design specifications, DIH cannot be able to make separation efficiently. Feed composition cannot be handled easily with a basic change in the column environment, so DIH feed properties should be checked daily basis. If feed contains more heavies or light ends from design specifications, this condition upsets the DIH operation and products that are generated in that condition are off-spec. Operation with lighter feed demands lower top tray temperature to regulate the same recovery percentage of pentanes and 22DMB compounds in DIH overhead. Heavier feed tends to demand the opposite conditions. DIH sensitivity range for feed composition fluctuation also depends on how the column design agrees with the specified unit construction. With a reboiler, column can be adjusted to get more duty or column with extra trays may be used in the operation. These modifications help the operation to continue. Normally 10-20% change in composition does not affect performance significantly.

3.5.19.2. Pressure. The DIH pressure is typically set by design specifications and does not change. DIH columns are designed to operate in a very limited pressure range between 0.3-1.0 bar. Big changes in the column pressure causes flood and affects the separation efficiency. Lower operating pressures are used to rise the component relative volatility

which increases the efficiency of the separation. This application also decreases the reflux requirement or required tray numbers because of decrement in the reboiler duty. Regardless, good column operation requires fixed pressure and continuous changes upset the column and have negative effect on column operation.

3.5.19.3. Inlet Temperature. The DIH feed temperature is merged with DIH side draw stream behavior. Inlet feed temperature is selected to be identical with side draw tray temperature due to column design. An abrupt change to a colder feed will act as reflux and push the reboiler harder to heat the liquid to its bubble point. This change upsets the DIH heat balance and the bottom net stream, thus more light ends is sent to bottom net stream, until reboiler heat input is raised and the balance is set up again. Colder feed also mitigates the column efficiency. Comparatively, too high inlet temperature causes more heavy material to migrate into the overhead product, it has similar effect with having high reboiler duty. Compositional temperature control tries to diminish the effect by reducing product draw and increasing reflux to attain desired temperature and composition profiles.

3.5.19.4. Reflux Feed Ratio. This variable is dependent both on reboiler heat duty and top temperature control. Separation efficiency raises with reflux to feed ratio until the tower begins to flood. It can be used as ratio controller. Also, liquid reflux balances the top column temperature by heat extraction. When reflux rate increases, top of the column temperature is cooled down. Tower pressure and feed composition have effects on obtaining the desired overhead product composition. As already explained above, if the DIH pressure goes down, the temperature controller steps in to regulate temperature, to come up to same overhead feed composition.

3.5.19.5. Reboiler Heat Input. DIH reboiler and side draw reboiler are heat provider to the column. There is no direct control on the side draw reboiler heat input. The column reboiler flow rate is independent variable and maintains the heat input of DIH. The reboiler heat input manages the reflux feed ratio in the column, for a significant feed rate and tower top temperature. High reflux rate enhances the separation until the tower begins to flood. In case of higher reflux, operation for attaining higher efficiency causes additional cost as a

form of higher utilities consumption. In general, reboiler heat input is adjusted to operate at the minimum reflux to provide the demanded separation for DIH feed.

3.5.19.6. Side Draw Rate. The DIH recycle side draw is recycled back to the isomerization unit upstream. Flow controller on the side draw is cascaded from the column bottoms level controller.

3.5.19.7. Side Draw Tray Temperature. The side draw temperature is generally adjusted by taking the base of the side draw recycle composition. The heavies on the side draw should be at lowest concentration, as possible to attain the best performance from the isomerization reactor section. The side draw tray temperature should also be maintained to draw the maximum methylpentanes to the side draw, while maximizing 23DMB in the overhead product. Side draw reboiler heat input is directly responsible from side draw tray temperature. If side draw reboiler heat input is too high, side draw tray temperature raises and causes more heavy compounds in the overhead product. On the contrary, if side draw reboiler heat input is too low, side draw tray temperature decreases and light compounds are drawn into side draw effluent. In this case, compositional controller shows off spec and it causes net overhead product flow rate to be raised. As a result, reflux flow rate decreases to acquire the required temperature and composition profiles [73].

3.6. Process Optimization

PenexTM unit optimization was carried out in HYSYS optimizer. In the following, there are information about general optimization procedure and optimization study.

3.6.1. HYSYS

Aspen HYSYS Refining is leaned on flowsheet facility of HYSYS. Existing HYSYS simulation cases can be leveraged in Aspen HYSYS Refining by adding petroleum assays information and specific refinery unit operations.

A petroleum assay takes information about physical properties with a significant component list. In simulation environment, if each stream has a different physical properties, all of them have its own petroleum assay. This kind of structure permits the simulation of refinery wide flowsheets using one single component list, this characteristic provides optimal performance on speed and calculations.

With “degrees of freedom” approach, which increases the flexibility with obtained solutions, estimations in Aspen HYSYS Refining are carried out easily. When enough information is supplied to Aspen HYSYS Refining, the results come out immediately. This characteristic gives the users better understanding about effect of each process variable.

Calculations are made accurately by using integrated steady state and dynamic modelling features of HYSYS. It is an effective tool for steady state process modeling with courtesy of various components. Aspen HYSYS Refining can be integrated to third party design options and custom built unit operations.

The multi flowsheet architecture of HYSYS is essential to overall modeling approach. For huge processes, flowsheets can be prepared for smaller components in the processes and refinery operations can be divided into controllable and efficient pieces. Each of these sub-processes is part of the overall simulation, and they are calculated as main process. This feature makes possible detailed analysis for each part of process [75].

Aspen HYSYS supplies the certainty, speed and veracity for the process calculations [76]. Also, with featured services, HYSYS has the facility for simultaneous translation of the commands immediately, when they are given to simulation [77].

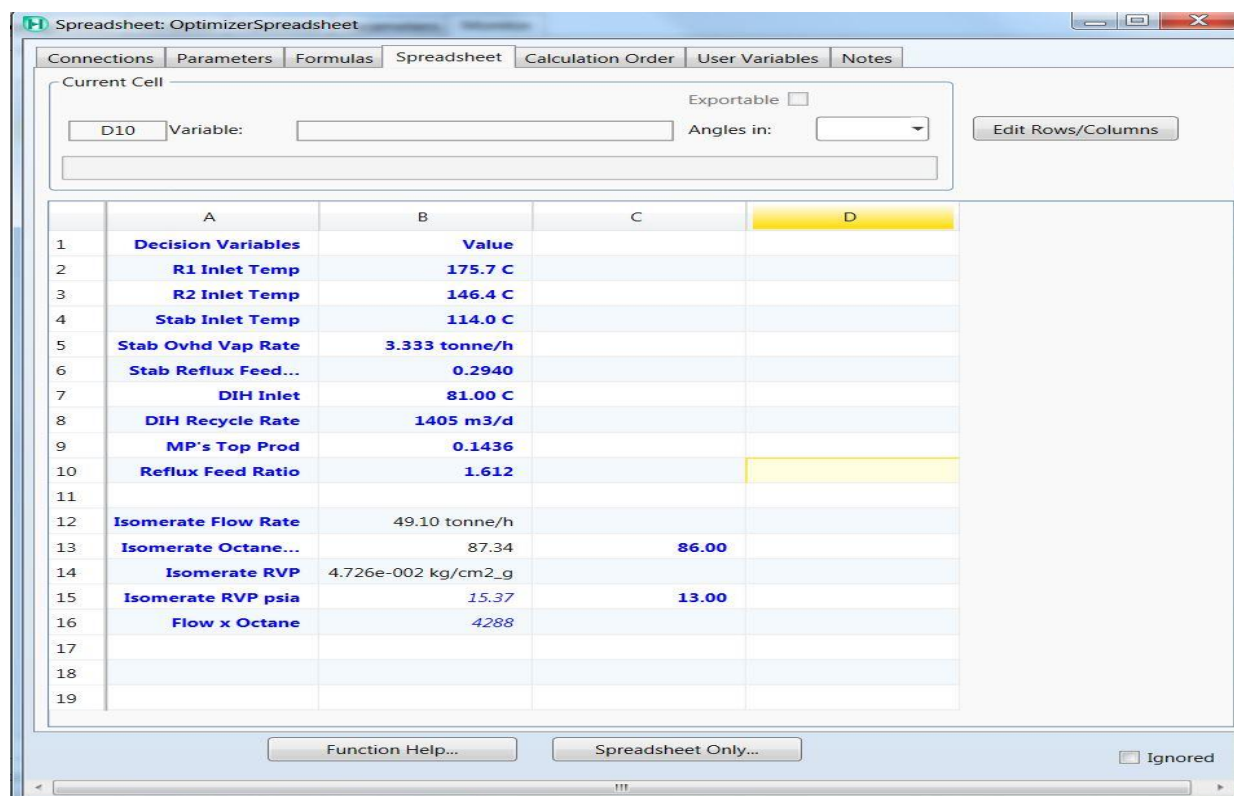
3.6.2. Optimization in HYSYS

The process optimization is an important quantitative tool, in industrial decision making. Generally the objective functions in the optimization are minimizing cost, maximizing yields of desired products while minimizing side products, and decreasing the time for maintenance.

HYSYS consists of a multi variable steady state optimizer. After flowsheet of process is built and converged, the optimizer can be used to provide the maximum or minimum value of objective function. Only drawback of the optimizer is, that can only be used in steady state mode, not in dynamic mode.

The optimizer spreadsheet (Figure 3.15) is used for characterization and calculation of objective function, with unlimited constraints and variables. The flexibility of optimizer permits the construction of any type of objective function.

In optimizer, primary variables are decision variables, that are manipulated to attain best value of objective function, can be imported from the flowsheet of the simulation. Constraint function part comprises both inequality and equality constraint functions. Methods of the Box, Mixed and Sequential Quadratic Programming (SQP) can handle the problems with inequality constraints. The Fletcher-Reeves and Quasi-Newton methods are available for unconstrained optimization problems. These methods are identified in modes section of HYSYS.



	A	B	C	D
1	Decision Variables	Value		
2	R1 Inlet Temp	175.7 C		
3	R2 Inlet Temp	146.4 C		
4	Stab Inlet Temp	114.0 C		
5	Stab Ovhd Vap Rate	3.333 tonne/h		
6	Stab Reflux Feed...	0.2940		
7	DIH Inlet	81.00 C		
8	DIH Recycle Rate	1405 m3/d		
9	MP's Top Prod	0.1436		
10	Reflux Feed Ratio	1.612		
11				
12	Isomerate Flow Rate	49.10 tonne/h		
13	Isomerate Octane...	87.34	86.00	
14	Isomerate RVP	4.726e-002 kg/cm2_g		
15	Isomerate RVP psia	15.37	13.00	
16	Flow x Octane	4288		
17				
18				
19				

Figure 3.15. Optimizer Spreadsheet.

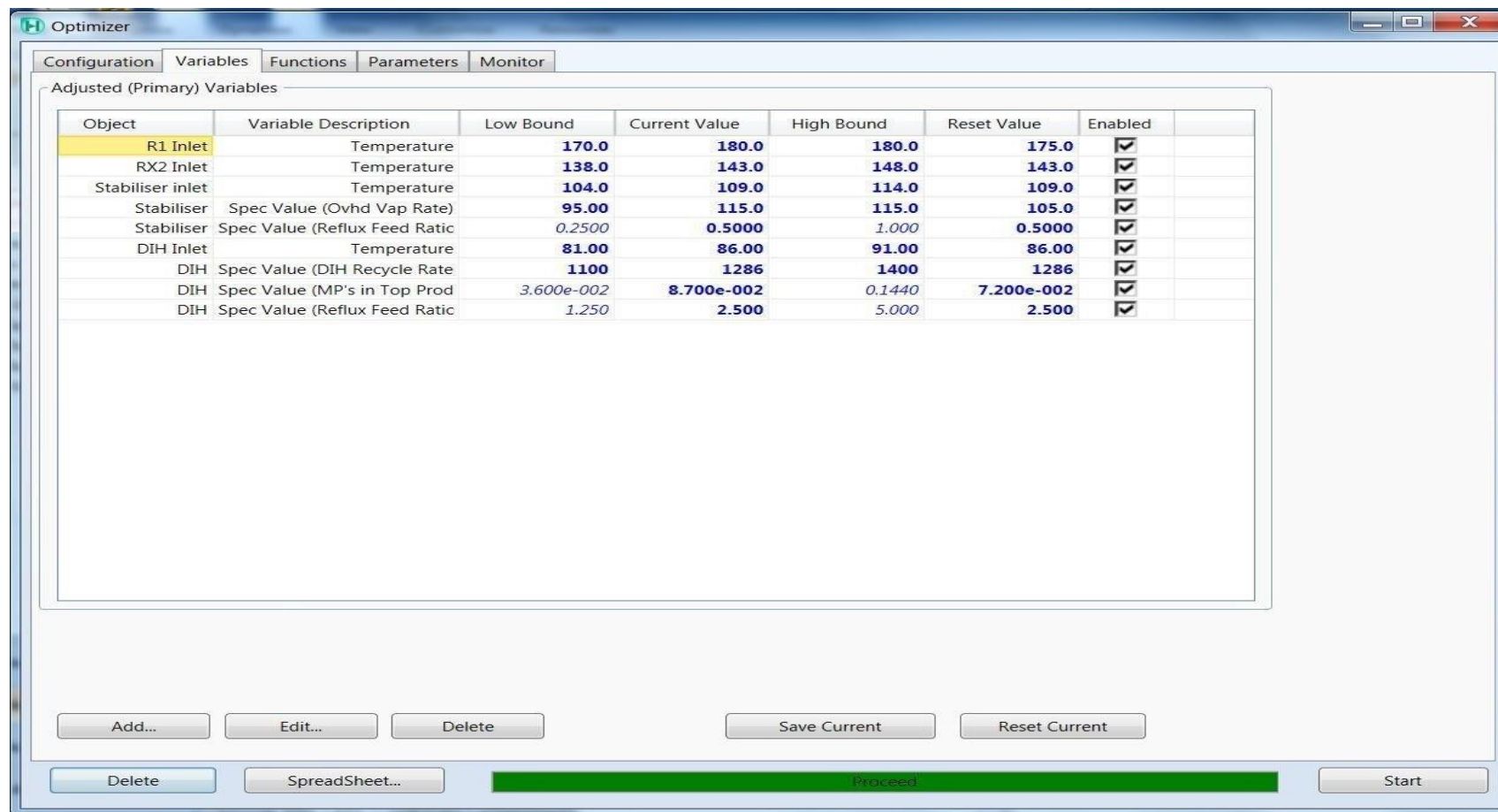


Figure 3.16. Variables Tab in HYSYS Optimizer.

Variables tab of HYSYS is shown in Figure 3.16. All independent variables are assigned for the overall process. To have reasonable results, independent results have to be between logical upper and lower bounds. Bounds are used to normalize the decision variables values. Normalization can be formulated as:

$$x_{norm} = \frac{x - x_{low}}{x_{high} - x_{low}} \quad (3.14)$$

The constraint functions tab are used for designate the left and right sides of the constraint function (in the LHS cell and RHS cell columns). In original optimizer section relationships between left and right hand sides can be greater, smaller or equal (LHS > RHS, LHS < RHS, LHS = RHS). Penalty value on the screen represents the importance of the constraint. Greater penalty value gives the constraint more weight and optimizer tries to be met the given constraint value. The Penalty Value is equal to 1 by default.

Optimizer gives the opportunity of changing the maximum function evaluation and maximum iteration number of the function. That means operation on the optimizer can be modified as desired to reach global optimum, which defines only exact solution of the function. Error of the solution can be characterized with tolerance value change. In the monitor tab (Figure 3.17), all evaluations, objective function value, primary variables, constraint functions and error values on the constraint functions, that are made by the optimizer can be examined. Positivity and negativity of constraints are the results of whether the constraint function is rewarded or not.

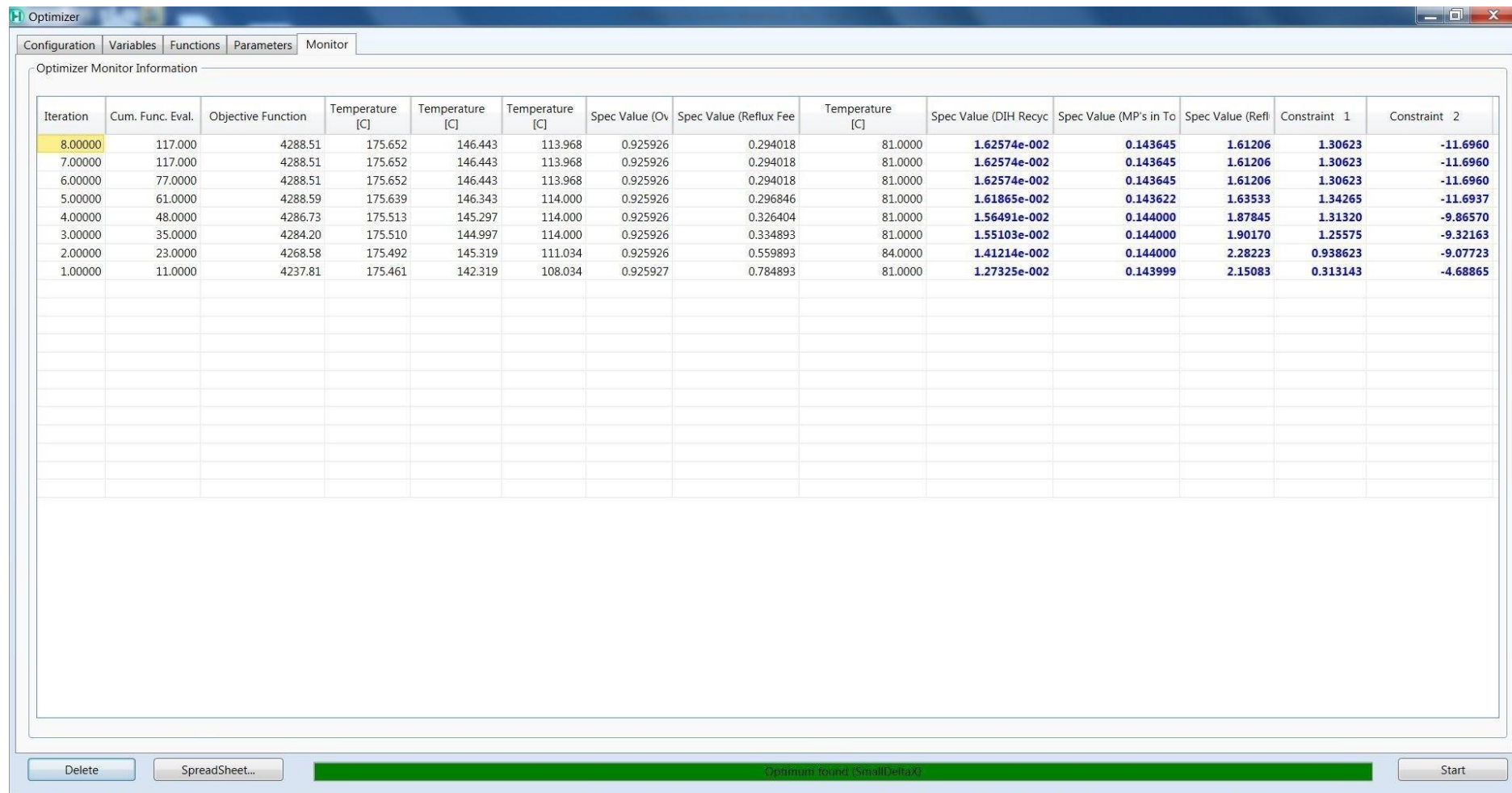


Figure 3.17. Monitor Tab of HYSYS Optimizer.

3.6.3. Original Optimizer

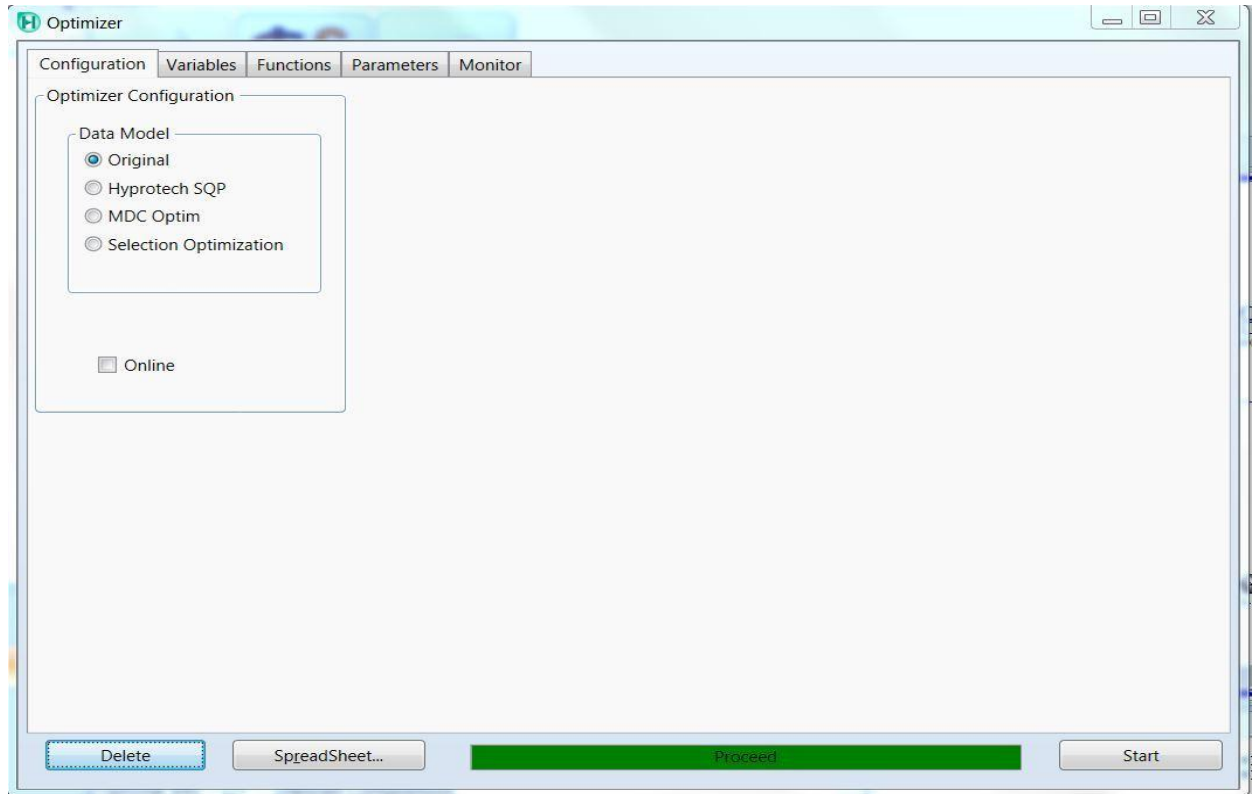


Figure 3.18. Type of Optimizer Selection.

The Optimizer maintains the values of a set of primary variables with a goal of minimization or maximization of the objective function that can be consisted of unlimited number of process variables.

$$\min f(x_1, x_2, x_3, \dots, x_n) \quad (3.15)$$

where:

$x_1, x_2, \dots, x_n$ = process variables

$$x_{i \text{ lower bound}}^0 < x_i < x_{i \text{ upper bound}}^0 \quad \text{with } i = 1, 2, 3, \dots, n \quad (3.16)$$

Every primary variable can take the every value of defined range.

x_i = a process variable used to define the objective function

x_i^0 = a primary variable which is manipulated by the optimizer

y_i = a variable used to define the constraint function

General representation of the equality and inequality constraints are:

$$c_i(y_1, y_2, y_3, \dots, y_n) = 0, i = 1, 2, 3, \dots, m_1 \quad (3.17)$$

$$c_i(y_1, y_2, y_3, \dots, y_n) = 0, i \leq 1, 2, 3, \dots, m_1 + 1, \dots, m_2 \quad (3.18)$$

$$c_i(y_1, y_2, y_3, \dots, y_n) \geq 0, i = m_2 + 1, \dots, m \quad (3.19)$$

Since lower and upper bounds are used for the calculation of normalized primary variables, feasible bounds must be selected. Exceeding high or low bounds violate the results and the reliability of the optimization. In addition all these, initial start point must be assigned carefully. Constraint functions and objective function value tab is shown at Figure 3.19.

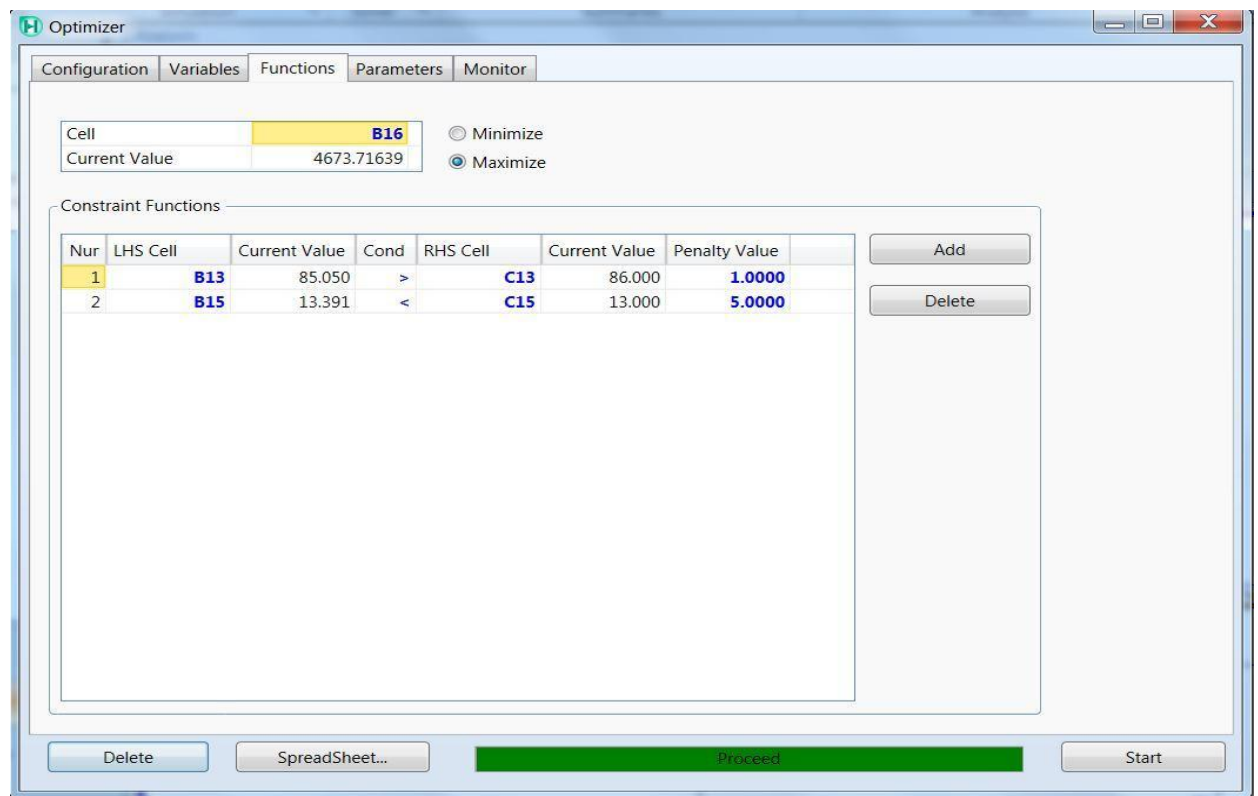


Figure 3.19. Constraints and Objective Function Value Tab.

3.6.4. Box Method

The procedure is combination of the “Complex” method of Box [78], that has been expanded from simplex method of Spendley with constraints and the Downhill Simplex algorithm that was proposed by John Nelder & Roger Mead. It can also be applied to nonlinear optimization problems in case of their derivatives are not known. Nevertheless, the Nelder–Mead technique is a heuristic search method that can converge to nonstationary points, unless any other reasonable conditions can be found by other simplex search methods on problems that can be solved by alternative methods [79] or the Box algorithm of Kuester and Mize [80]. The Box method is a sequential search technique that can be applied on nonlinear objective functions, subject to nonlinear inequality constraints. In Box method, derivatives of the functions are not necessary. Drawbacks of this method is, it can not handle the equality constraints. Besides, this method needs to evaluate large number of iterations and functions to reach the convergence.

3.6.4.1. Procedure for Minimization Optimization.

- With n variables, program creates an original “complex” of $n+1$ points around the center of the feasible region with a reasonable starting point.
- The objective function is evaluated at each point. The point having the highest function value is replaced by a point, which is obtained by extrapolating through the face of the complex across from the high point (reflection).
- If the new point is successful, in minimization of the objective function, HYSYS tries an additional extrapolation. Otherwise, if the new point is worse than the second highest point, HYSYS does a one dimensional contraction.
- If a point keeps giving high values, all points are gathered around the lowest point.
- The new point must satisfy both the variable bounds and the inequality constraints. If it violates the bounds, it is brought to the bound. If it violates the constraints, the point is moved progressively, towards the centroid of the remaining points until the constraints are satisfied.
- Steps #2 through #5 are repeated until convergence.

3.6.5. SQP Method

The Sequential Quadratic Programming (SQP) Method can handle inequality and equality constraints. In the past, many of the researchers considered SQP was the most efficient method for minimization with general linear and nonlinear constraints. Implemented procedure in HYSYS is a modification of Harwell subroutines, that is originally the Harwell Subroutine Library, embodies the collection of Fortran 77 and 95 codes by the prefix HSL, and it is the backbone of numerical analysis. It is enhanced by the Numerical Analysis Group at the Rutherford Appleton Laboratory with offering ideas of the other experts in the field. Codes are named after early versions of Fortran's limited subroutine name length, letters represents the classification of the problem they solve and the numbers to identify different codes [81].

VF13 [82] and VE17 are the names of solution codes that are used in SQP method. In these solutions, every iteration minimizes a quadratic approximation to the Lagrangian function subject to linear approximations to the constraints. At the same time, the second derivative matrix of the Lagrangian function is also calculated. A line search procedure applies the “watchdog technique” [83] that compels the convergence in algorithms for constrained optimization by relaxing the line search condition on next variable, from the initial point. The program also follows the algorithm of Powell closely [84].

3.6.6. Mixed Method

The Mixed method endeavors to combine and take advantage of the global convergence characteristics of the Box method and the capability of the SQP method. At the beginning, optimization starts with the minimization operation using Box method with a slack convergence tolerance (generally 50 times lower than the given tolerance). After convergence, the SQP method is used to find the final solution, using the given tolerance. Since handling inequality constraints is the common thread of both methods, mixed method handles only inequality constraints. Mixed method commonly demands least number of function evaluations, which means it is the most efficient method in all methods.

3.6.7. Degree of Freedom Analysis

Degree of freedom determines the state of the process with suitable independent variables. For a refinery system, degrees of freedom analysis is necessary to determine, whether process can be solved with the given information, or additional information should be defined for process. If process has a finite set of solutions, it is well defined and can be solved without supplementary information. When there is superfluous and unnecessary information about system, this system is overspecified and it can be still solvable without these excess data or impractical assumption about the system. However, the system can be underdetermined. It is occurred when there is not enough information about system to solve. This situation can be sorted out as in several ways. One of them is investigating extra data of temperatures, flow rates, reflux feed ratios of the process.

Other way may be finding supplementary equations or information about what is wanted as output from the process, such as how much conversion should be obtained in a reaction, how efficient a separation process is etc.

Degree of freedom analysis can be performed to one unit operations as follows:

- From your flowchart, determine the number of unknowns in the process.
- Subtract the number of equations can be written on the process. This can include mass balances, energy balances, equilibrium relationships, relations between concentrations, and any equations derived from extra information about the process.
- The number you are left with is the degrees of freedom of the process.
- To perform a degree of freedom analysis for a given system, it should be examined and; If N_{dof} equals zero, the problem is uniquely specified. If is N_{dof} greater than zero, the problem is underspecified. Finally, as you may have guessed, if N_{dof} is less than zero, the problem is overspecified.

$$N_{unknown} + N_{reaction} - N_{material} - N_{other} = N_{dof} \quad (3.20)$$

Table 3.8. Label of Degree of Freedom Analysis.

N_{unknown}	Find the number of unknowns in the problem
$+N_{\text{reaction}}$	Add the number of reactions in the system
$-N_{\text{material}}$	Subtract the number of independent material balances
$-N_{\text{other}}$	Subtract the number of other relationships given in the problem statement
$= N_{\text{dof}}$	

3.6.8. Degree of Freedom Analysis for Multi-System Processes

For a multiple unit operation processes, degree of freedom analysis can be made as following steps:

- Label a flowchart completely with all the relevant unknowns.
- Perform a degree of freedom analysis on each unit operation, as described above.
- Apply the degrees of freedom for each of the operations.
- Subtract the number of variables in intermediate streams, i.e. streams between two unit operations. This is because each of these was counted twice, once for the operation it leaves and once for the one it enters.

For the subject of this thesis, control parameters induce the degree of freedom. To keep in control the process, one decision variable corresponds for every control parameter. In the following, all control parameters and decision variables are shown (Table 3.9).

Table 3.9. Control Parameters and Decision Variables.

Control Parameters	Decision Variables
Reactors	Reactors
Feed Heat Treatment	Inlet Temperature
Stabilizer	Stabilizer
Feed Heat Treatment	Inlet Temperature
Condenser Heat Treatment	Overhead Vapor Rate
Reboiler Heat Treatment	Overhead Reflux Rate
DIH Column	DIH Column
Feed Heat Treatment	Inlet Temperature
Condenser Heat Treatment	RVP Value of the Isomerate
Reflux-Feed Ratio of Overhead	Reflux-Feed Ratio of Overhead
Reboiler Heat Treatment	MP values in Overhead
Side Draw Flow Rate	DIH Recycle Rate

3.7. Case Study

Research octane number is the measure of the maximum compression ratio for fuels. It indicates the self ignition of fuels, whether they are durable or not during engine initialization. If fuel has high octane number, that means it has high compression ratio, stable and protects engine against knocking. Motor octane number (MON) is another kind of octane number indicator, to determine MON, tests are applied to fuels in specific conditions that are different from RON tests conditions. Generally, stated octane number of gasoline is arithmetic average of MON and RON.

Optimization study is carried out for isomerization unit product, isomerate, which is added to commercial gasoline mixture of the refinery. Commercial gasoline must have a significant research octane number before sales. If it does not come across desired yield, methyl tertiary butyl ether (MTBE) is used as additive to reach desired octane number. Nevertheless, MTBE selling price per gallon is much higher than commercial gasoline selling price, so this procedure brings financial burden.

After some research, between other additives, which are generated in refinery, and isomerate in gasoline mixture, RON of isomerate is more controllable by the virtue of PenexTM unit operating conditions. According to this easiness, RON of isomerate number

is decided to be optimized. But after some trials, study shows maximization of RON leads decrement in liquid yield. As a result, objective function of the study is changed to maximum liquid yield x maximum isomerase octane numbers.

For this case study, data of Tüpraş İzmir refinery isomerization unit inputs and outputs are taken into consideration. Steady state optimization of the commercial Penex™ unit, that is also established the operation in Tüpraş İzmir refinery, was carried out by Aspen HYSYS program tools.

3.7.1. Objective Function

The objective of the steady state optimization of Penex™ are to produce maximum isomerase barrels. This objective is formulated as generating maximum liquid yield and high octane number product. Decreasing benzene content of total gasoline pool leads to maximum liquid yield. In that way, this is appreciable in both environment and the objective. But in that condition, having high octane number cannot be possible. If maximum liquid yield is targeted, 2MP component is drawn into the isomerase to obtain maximum liquid yield, since 2MP has high mole fraction in combined feed. But, when fraction of 2MP increases in isomerase, RON of isomerase decreases due to low RON of 2MP. Considering this trade off, objective function of study is determined as maximum isomerase barrels.

In this case study, optimization is carried out by changing values of decision variables to have both maximum octane number and liquid yields. Furthermore, optimization software provides opportunity to work with maximum octane number and liquid yield at lowest cost and highest profit within the constraints of the environmental concerns and the safety of the unit. The objective function and all constraints are linear.

$$\text{Max Isomerase Barrels}(x_1, x_2, x_3, \dots, x_9) \quad (3.21)$$

Where x_1 is lead reactor inlet temperature (°C), x_2 is lag reactor inlet temperature (°C), x_3 is stabilizer inlet temperature (°C), x_4 is stabilizer overhead vapor rate (ton/h), x_5 is

stabilizer reflux feed ratio, x_6 is DIH inlet temperature ($^{\circ}\text{C}$), x_7 is DIH recycle rate (m^3/d), x_8 is DIH reflux feed ratio, x_9 is DIH top product MP value.

3.7.2. Decision Variables

Decision variables values are imported from PenexTM unit PFD. The following decision variables are used in optimization of process: Inlet temperatures of lead and lag reactors, inlet temperature, overhead vapor pressure and reflux-feed ratio of stabilizer, inlet temperature, recycle rate, methylpentane values in top product and reflux-feed ratio of DIH column. In table 3.10 decision variables and range of values are shown.

Table 3.10. Decision Variables and Ranges.

Decision Variables	Ranges of Variables	Current Value
Lead Reactor Inlet Temperature($^{\circ}\text{C}$)	170-180	175
Lag Reactor Inlet Temperature ($^{\circ}\text{C}$)	130-150	135
Stabilizer Inlet Temperature($^{\circ}\text{C}$)	100-120	110
Stabilizer Overhead Vapor Rate (ton/h)	95-115	105
Stabilizer Reflux-Feed Ratio	0.25-1	0.5
DIH Inlet Temperature ($^{\circ}\text{C}$)	80-100	91
DIH Recycle Rate(m^3/d)	1000-1500	1200
DIH Top MP's Product Rate(ton/h)	0.1-0.25	0.15
DIH Reflux-Feed Ratio	1 – 5	2.5

The lower and upper bounds for all of the decision variables are set. Inequality constraints are determined to provide the best operating conditions and the objective of the case study. There are two constraints in steady-state optimization of PenexTM unit, both of them depend on gasoline quality. First constraint is to operate the unit at best conditions, keeping Reid vapor pressure (RVP) of isomerate at specific value. Since RVP determines the volatility of the gasoline, especially for season changes, RVP should be kept under 13 psi. Second constraint is setting research octane number (RON) around 86-87.

Constraint functions: RVP of isomerate < 13 psi

RON of isomerate > 86

4. RESULTS AND DISCUSSION

Optimization of PenexTM unit is carried out according to procedure that is explained in Section 3, at 130-160°C temperature and 33 kgf/cm² pressure with minimum 86 RON and maximum 13 psi pressure constraints. During optimization process, the catalyst is changed and optimization is executed for both conditions. In the first condition, catalyst is almost completely deactivated and operated with high temperature for satisfy the objective. Second condition is closer to PenexTM unit operating conditions. In addition, for second condition parameter estimation is performed based on Acar's investigation [84]. Optimization results for two cases and parameter estimation for second case is given in the following sections.

4.1. Optimization Results

Before catalyst change, decision variables are determined as mentioned in Section 3. Initial values represent the operating condition of PenexTM unit before optimization. Final values are the recommended values to reach maximum isomerate barrels with constraints. Optimization results before catalyst change are shown in Table 4.1.

Table 4.1. Optimization Results for the First Condition.

Decision Variables	Initial Value	Final Value	Constraint
R1 Inlet Temp (°C)	175	175.5	
R2 Inlet Temp (°C)	143	142	
Stab Inlet Temp (°C)	109	108	
Stab Overhead Vapor Rate (ton/h)	105	80	
Stab Reflux/Feed Ratio	0.5	0.8	
DIH Inlet Temp (°C)	86	81	
DIH Recycle Rate (m ³ /d)	1280	1100	
DIH MP's Top Prod	0.072	0.144	
DIH Reflux/Feed Ratio	2.5	2.2	
Optimization Values			
Isomerate Flow Rate (ton/h)	48	55	
Isomerate Octane Number	85.5	85	> 86
Isomerate RVP (psi)	13	13.4	< 13
Isomerate Flow x Octane	4102	4675	maximize

Objective of the optimization is to attain highest value of the isomerate flow x octane number with the constraints, higher octane number than 86 and lower RVP value than 13 psi. However, even though so many optimization trials with a wide range of decision variables value are performed with optimizer, since catalyst is almost completely deactivated, objective function is provided successfully but constraints are slightly violated. Although all the decision variables are important for Penex™ unit operation, value changes in DIH column have more impact on obtaining objective function, since RON of isomerate is adjusted in DIH column. According to optimization results, when DIH recycle rate decreases from 1280 to 1100 m³/d, DIH reflux feed ratio decreases from 2.5 to 2.2 and DIH overhead contains more MPs, optimum conditions are obtained. Optimum RVP value is adjusted in stabilizer column. If overhead vapor rate of stabilizer decreases from 105 to 80 and stabilizer reflux feed ratio increases from 0.5 to 0.8, RVP constraint is satisfied.

After catalyst change, even before optimization performance of the unit is increased observably. Optimization results can be seen below.

Table 4.2. Optimization Results for the Second Condition.

Decision Variable	Initial Value	Final Value	Constraint
R1 Inlet Temp (°C)	135	135.5	
R2 Inlet Temp (°C)	125	120	
Stab Overhead Vapor Rate (ton/h)	141	126	
Stab Reflux/Feed Ratio	0.575	0.5	
DIH Recycle Rate (m ³ /d)	1348	1438	
DIH Reflux/Feed Ratio	1.1	1.2	
DIH MP's Top Prod	0.18	0.2	
Optimization Values			
Isomerate Flow Rate(ton/h)	59.5	60	
Isomerate Octane Number	86.7	87	> 86
Isomerate RVP (psi)	12.3	12.8	< 13
Flow x Octane	5161.5	5232	maximize

For second optimization case, decision variables are modified according to plant controllers presence in the plant. In this way, optimization is achieved more easily.

After catalyst change, reactor operating temperatures are decreased to actual catalyst working temperature. Stabilizer overhead vapor rate is higher than first condition stabilizer overhead vapor rate. Feed with higher C_{7+} content may be the reason for this difference. Since C_7 and C_{7+} cracks into C_3 and C_4 , in second condition, stabilizer overhead vapor rate is higher than the first condition. However, stabilizer reflux feed ratio is lower and this is the evidence of splitting of the light hydrocarbons is better in second condition. In first condition, ratio is increasing during the first operating condition, when it decreases during the second operation condition. DIH recycle rate designates the recycle flow that are sent back to the reactor for better splitting. This rate is higher in second condition initial value and increases during operation. When recycle rate increases, total isomerate product is obtained in purer form. With increment of recycle rate, DIH reflux feed ratio is decreased as well, since there is no need more reflux to split more MPs in top product. With lower reflux feed ratio MP content cannot be sent back to reactor, but this effect can be neglected due to slight changes between initial and final value of MPs in second condition.

Constraints are satisfied more successfully and easily in second condition, in comparison with the first condition. Even though it has some drawbacks, second condition has better results for PenexTM unit optimization and improvement.

Exact relationships of the decision variables with stabilizer column, DIH column and reactors are found by carrying out sensitivity analyses. DIH and stabilizer related decision variables are investigated with value changes in 22DMB and 2MP, since they are dominant in determining RON of the isomerate. For reactor related decision variables, RON of the isomerate is taken into consideration itself. When sensitivity analyses are carried out for each decision variable, some of them is found more sensitive in changes. Sensitivity analyses for columns and reactors are evaluated in the following.

4.1.1. Sensitivity Analyses For Isomerization Reactors

Isomerization reactions determine the RON value of isomerate in the first place. This is why, sensitivity analyses in the reactors are carried out by taking into consideration of temperature of isomerization reactors and RON value of the isomerate. Temperature of the

reactors are different for first and second conditions due to catalyst health. In Figure 4.1 and Figure 4.2 RON changes in lead reactor for first and second condition is examined, respectively. These two figures shows in lead reactor, there is no changes in first condition. Change in second condition is negligible, since change is only 0.28, in RON value. Isomerization reactions majorly completed in lead reactor but with a single run, conversion is limited and unconverted nC_5 and nC_6 remain in the feed.

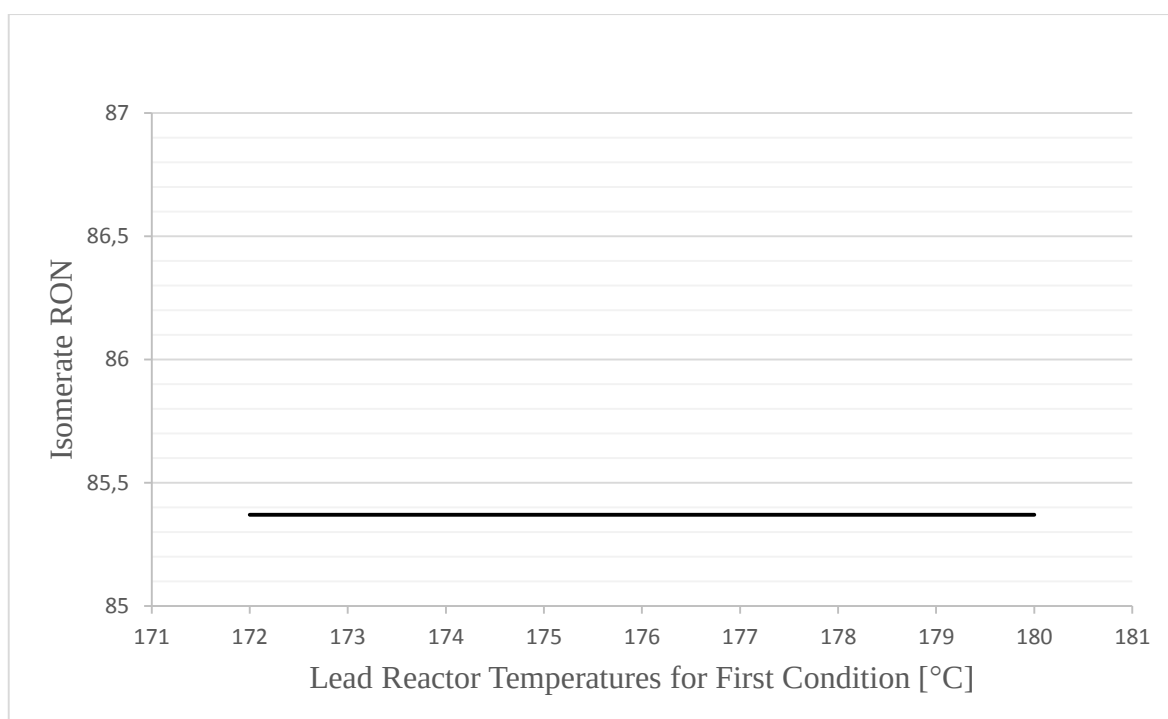


Figure 4.1. RON Changes in Lead Reactor for First Condition.

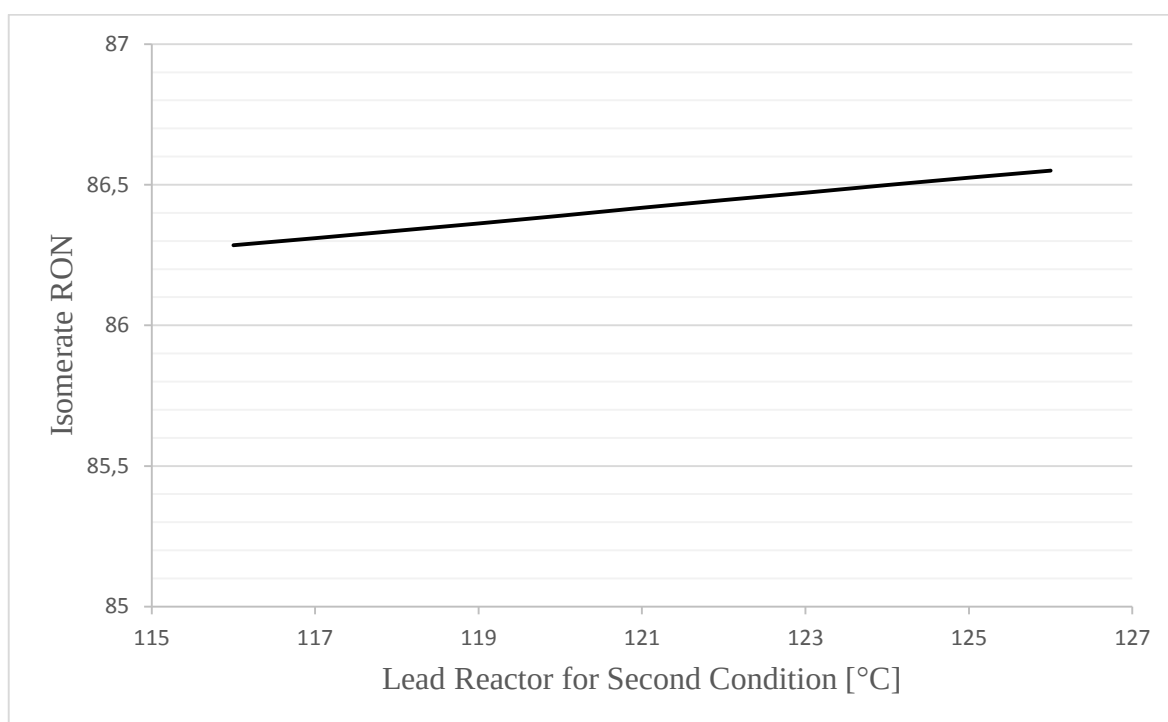


Figure 4.2. RON Changes in Lead Reactor for Second Condition.

In Figure 4.3 and 4.4 RON changes in the lag reactor, are examined respectively. Comparison with the changes in the lead reactor, lag reactor is much useful for obtaining higher RON. However, in first condition, change is less than in second condition, even lag reactor temperature is lower than first condition lag reactor temperature. This difference can be explained by catalyst change. New catalyst bed works more effectively, as expected.

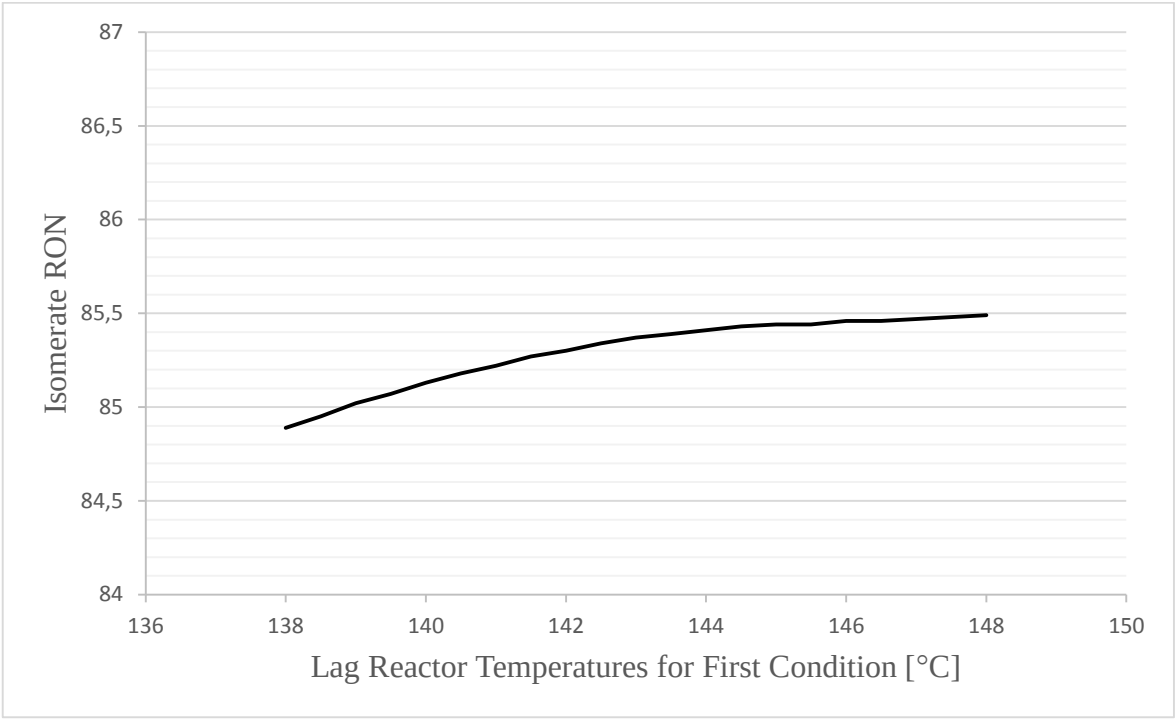


Figure 4.3. RON Changes in Lag Reactor for First Condition.

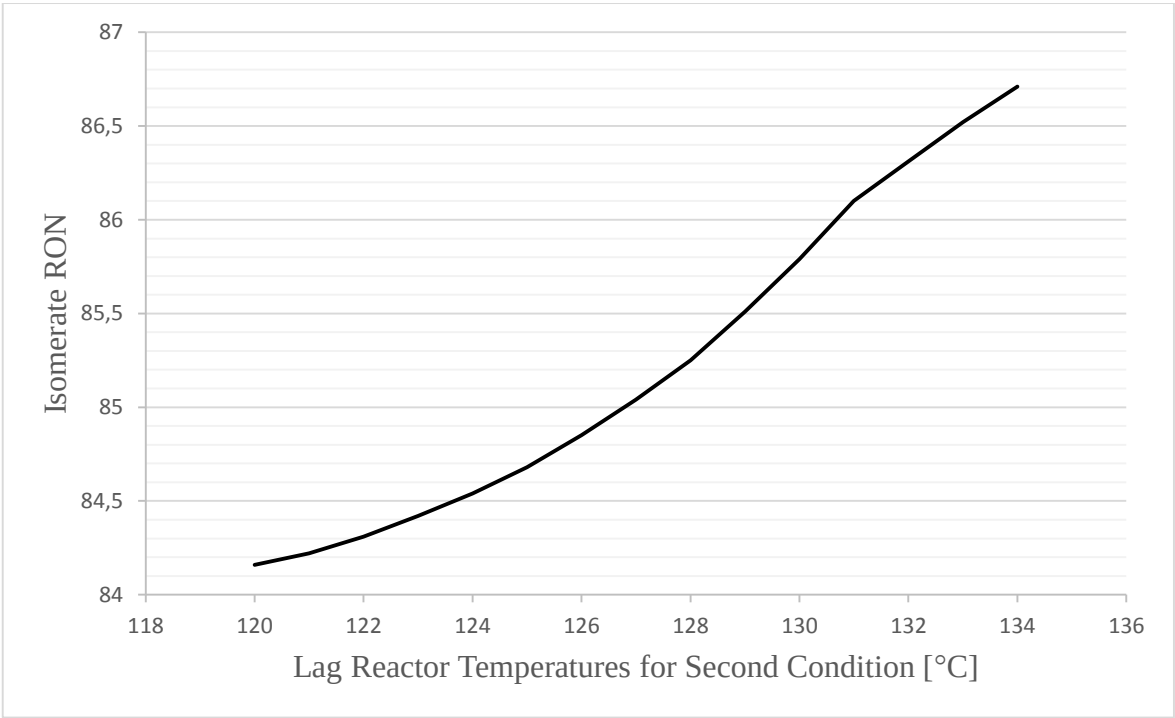


Figure 4.4. RON Changes in Lag Reactor for Second Condition.

4.1.2. Sensitivity Analyses For Stabilizer

Stabilizer sends the light compounds to stabilizer overhead, because light ends in the isomerase cause high RVP, which is restricted due to constraints. In Figure 4.5, stabilizer overhead vapor rate varies between 95 and 115 ton/h. With high overhead vapor rate, RVP value of the isomerase decreases. Figure 4.6 represents RVP change with stabilizer overhead vapor rate for second condition. In second condition, vapor rate and RVP decrement are higher, but for both condition results are expected, diversity between conditions may be explained as, feed of second condition contains more light ends.

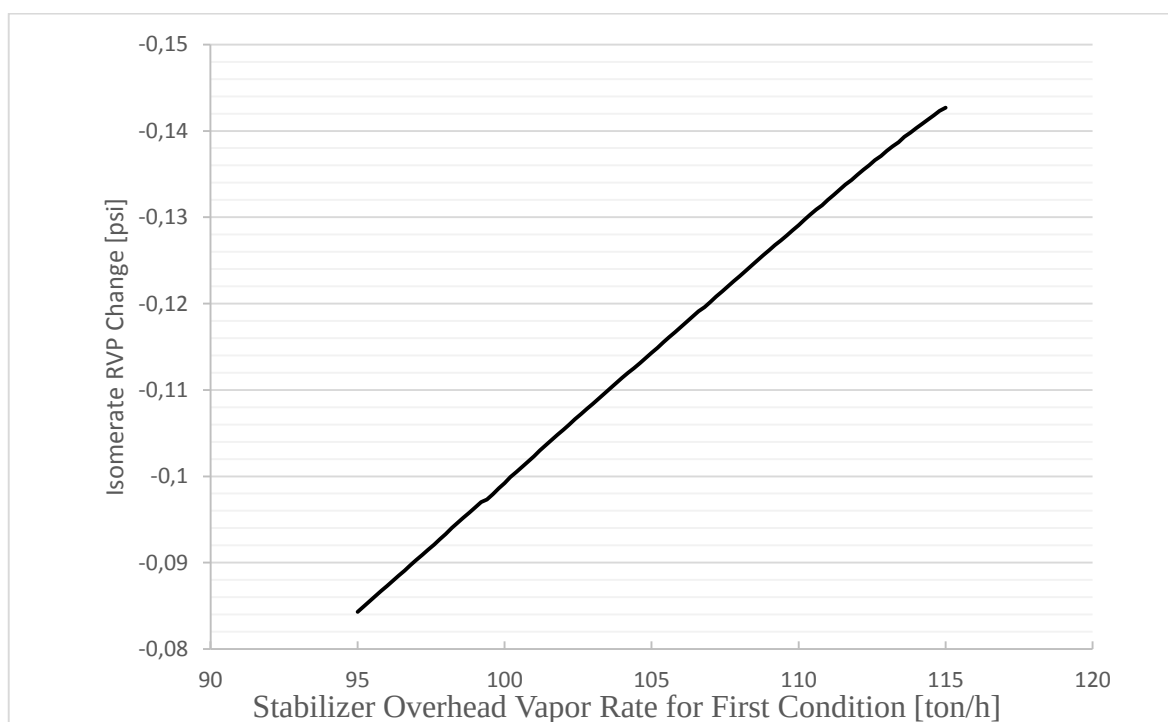


Figure 4.5. RVP Changes in Stabilizer for First Condition.

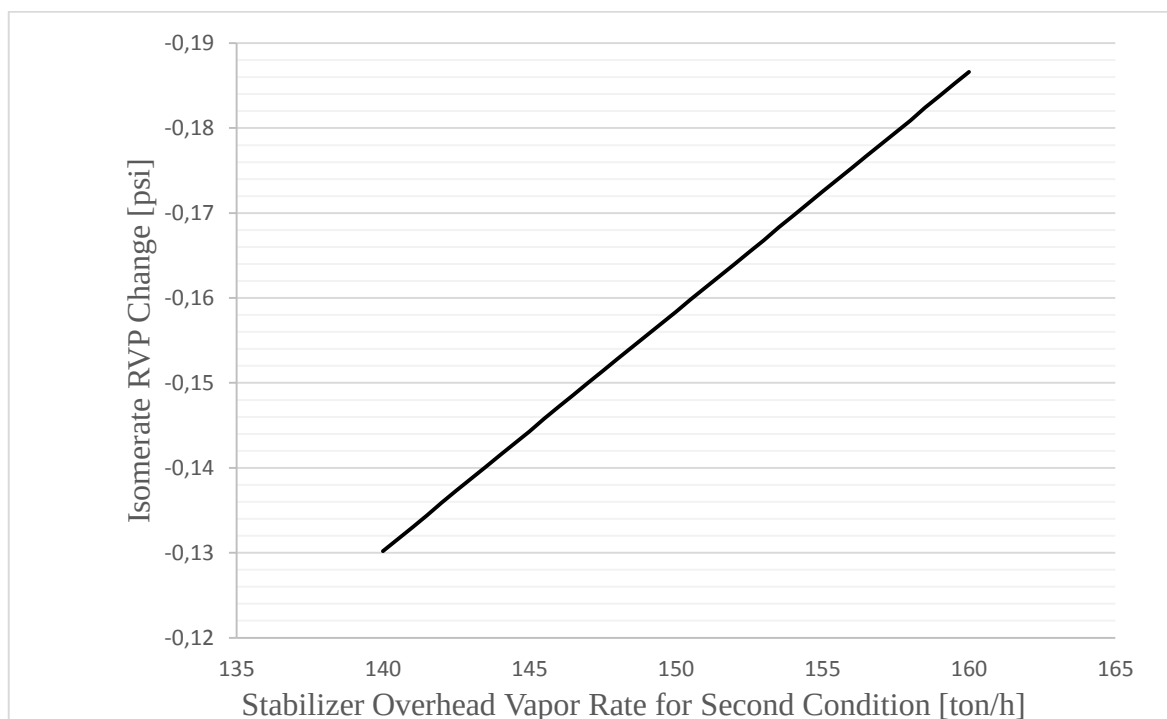


Figure 4.6. RVP Changes in Stabilizer for Second Condition.

Figure 4.7 and 4.8 represent RVP changes with stabilizer reflux feed ratio for first and second condition, respectively. Trends in figures are nearly same for same reflux feed ratio values but RVP changes are observable different. In second condition, RVP values decreases more. This indicates, there is better splitting operation in second condition. As explained above, since stabilizer overhead vapor rate is higher in second condition, results are anticipated.

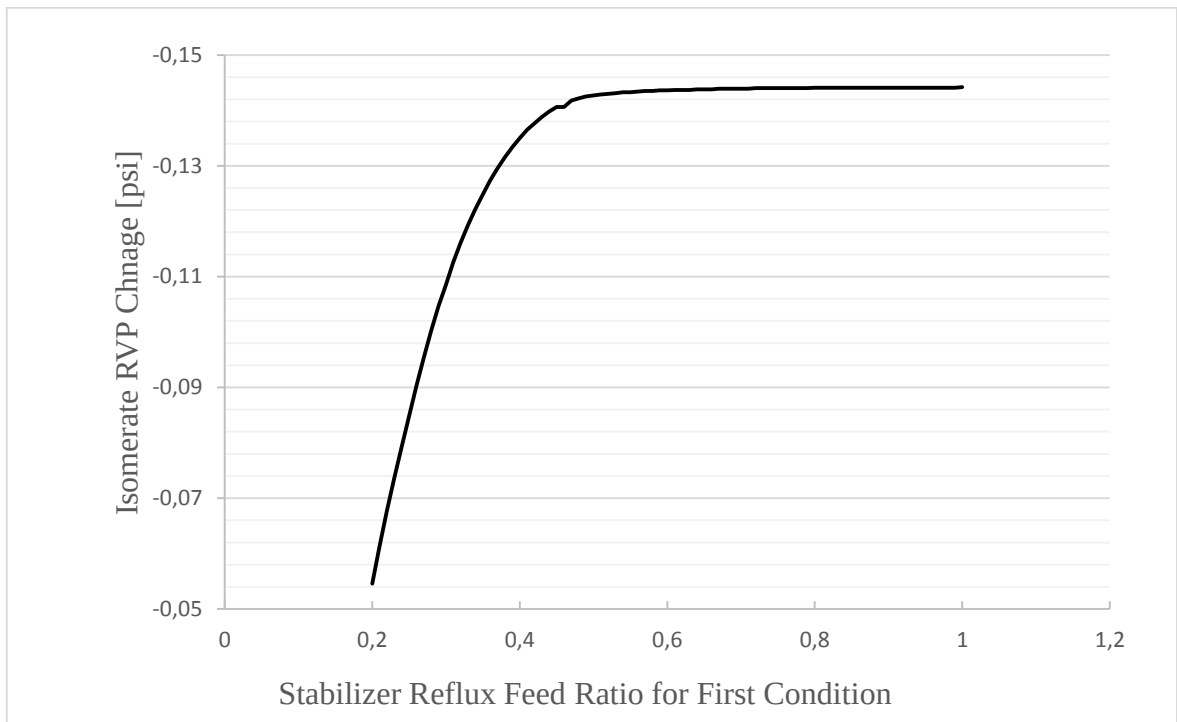


Figure 4.7. RVP Changes with Stabilizer Reflux Feed Ratio for First Condition.

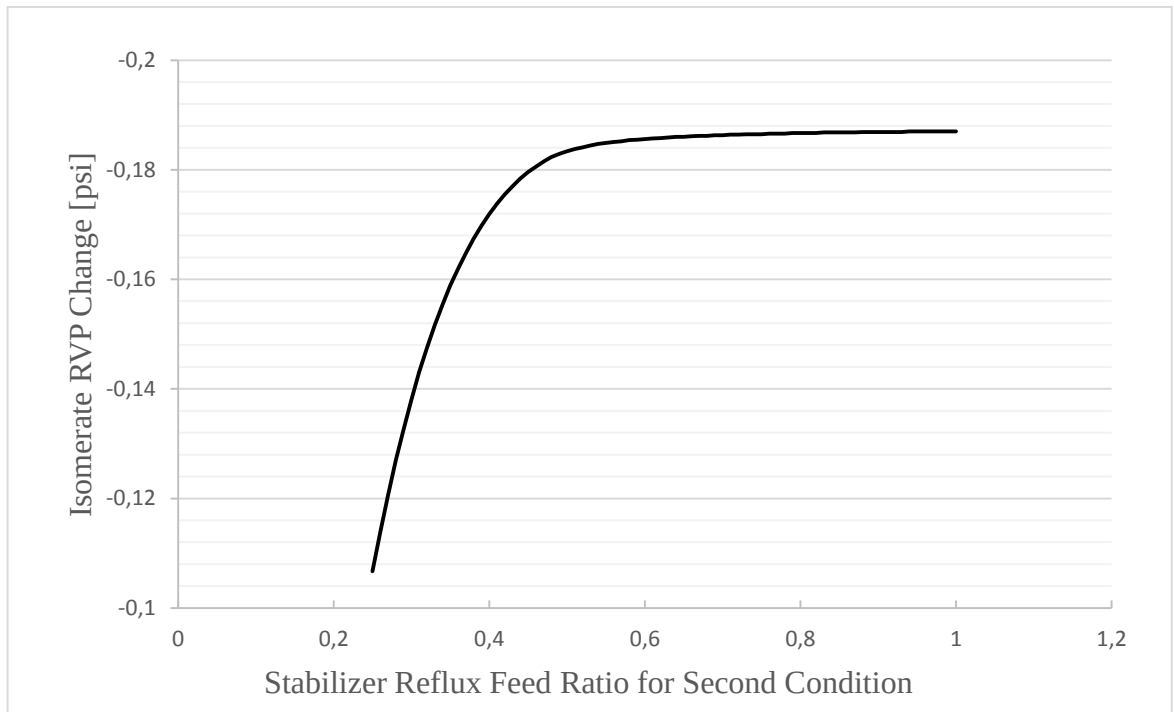


Figure 4.8. RVP Changes with Stabilizer Reflux Feed Ratio for Second Condition.

4.1.3. Sensitivity Analyses For DIH

In Figure 4.9 and 4.10, 22DMB changes in the isomerate with DIH recycle rate for first and second condition are shown. DIH recycle rate in graphs varies between 1300-1400 m³/d. As recycle rate increases, splitting is enhanced and 22DMB values increase for both condition. However, splitting in first condition is much better, since increment in recycle rate affects the 22DMB amount in isomerate. Difference in 22DMB fraction in second condition much lower for same DIH recycle rates. Figure 4.11 shows 2MP change with DIH recycle rate for first condition. When recycle rate increases, 2MP value in isomerate increases as well. For second condition, separation of 2MP is better than first condition (Figure 4.12).

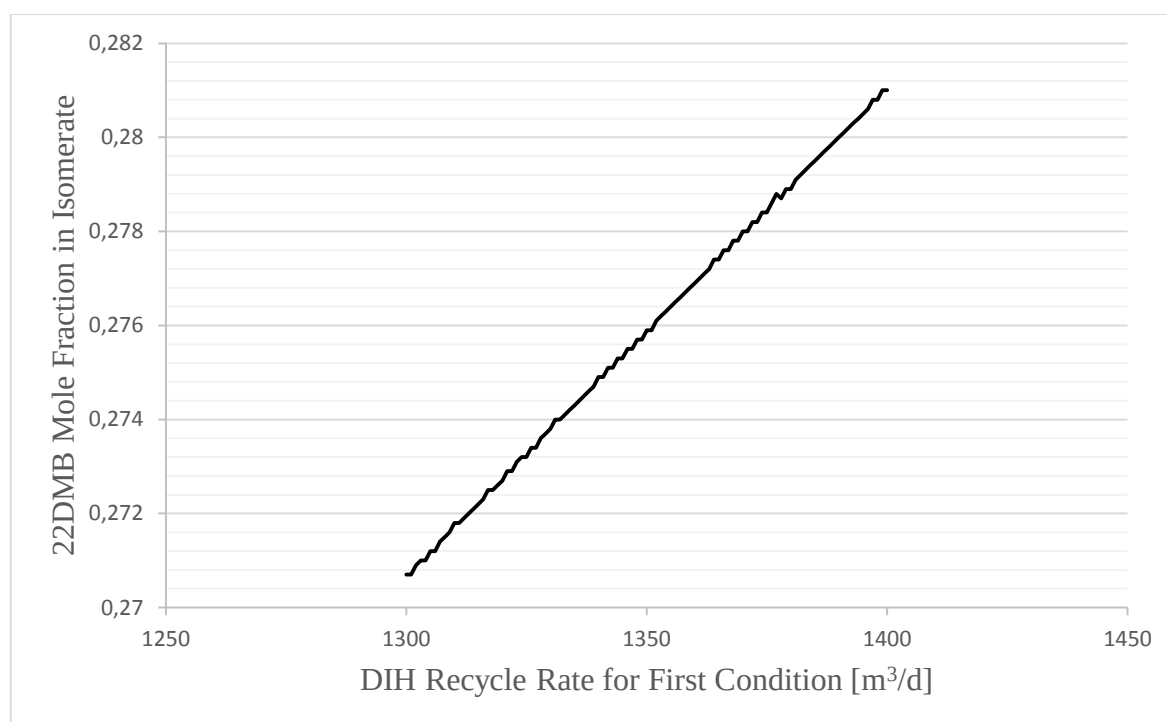


Figure 4.9. 22DMB Changes with DIH Recycle Rate for First Condition.

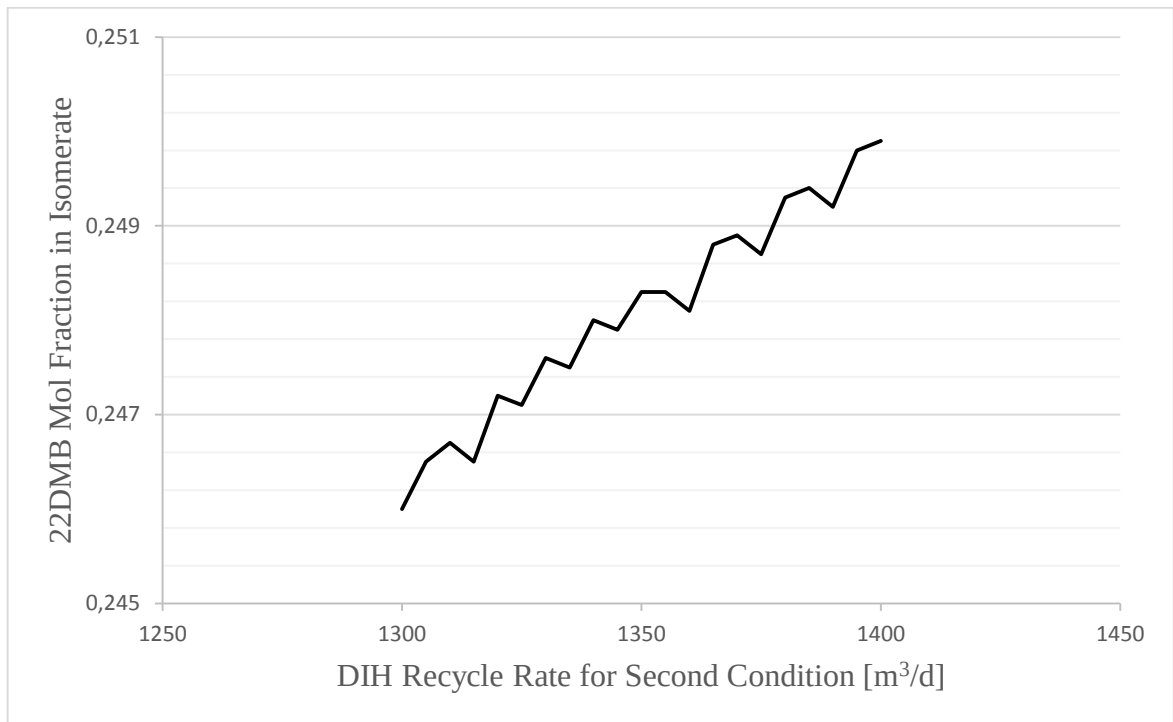


Figure 4.10. 22DMB Changes with DIH Recycle Rate for Second Condition.

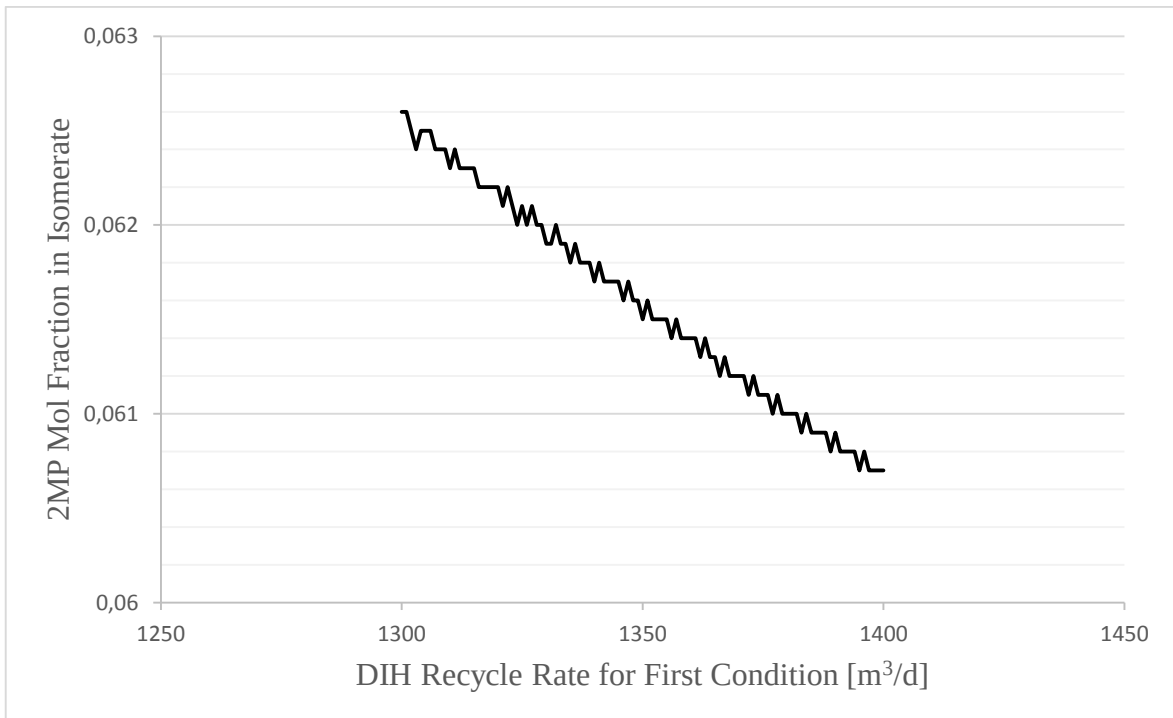


Figure 4.11. 2MP Changes with DIH Recycle Rate for First Condition.

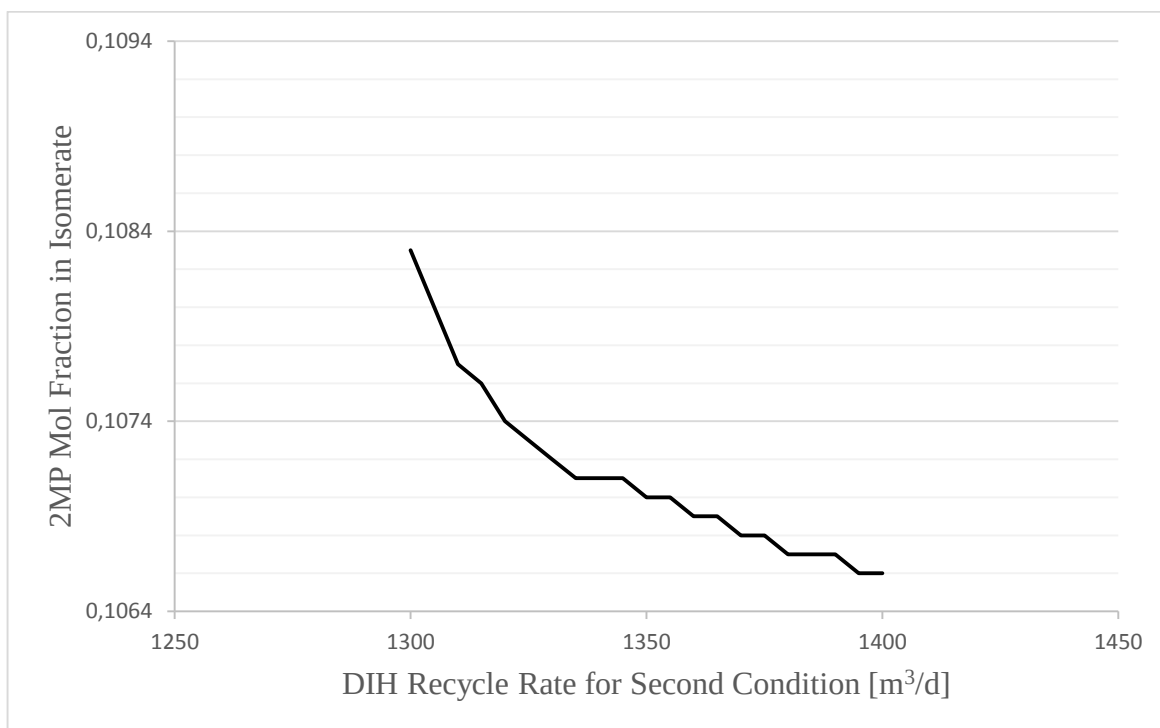


Figure 4.12. 2MP Changes with DIH Recycle Rate for Second Condition.

In Figure 4.13 and 4.14, relationship between 22DMB with DIH reflux feed ratio is examined. For second condition, 22DMB amount is slightly higher than the first condition but if reflux feed ratio is considered, second condition reaches the equilibrium at low ratios. For same 22DMB fraction, second condition has lower reflux feed ratio. Since DIH recycle rate is higher remarkably, low reflux feed ratio may be the result. Reflux is used for better splitting, with high DIH recycle rate, reflux can be decreased. Thus, changing task between DIH reflux feed ratio and recycle rate, provides the opportunity to have low condenser duty and low cost.

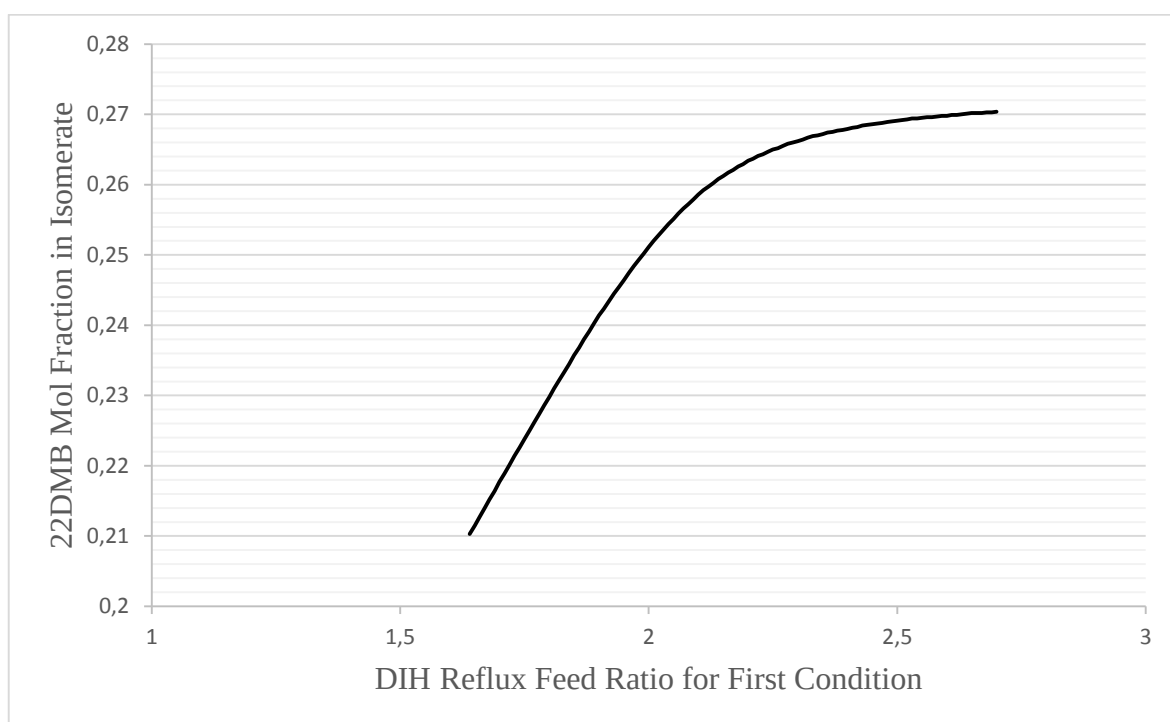


Figure 4.13. 22DMB Changes with DIH Reflux Feed Ratio for First Condition.

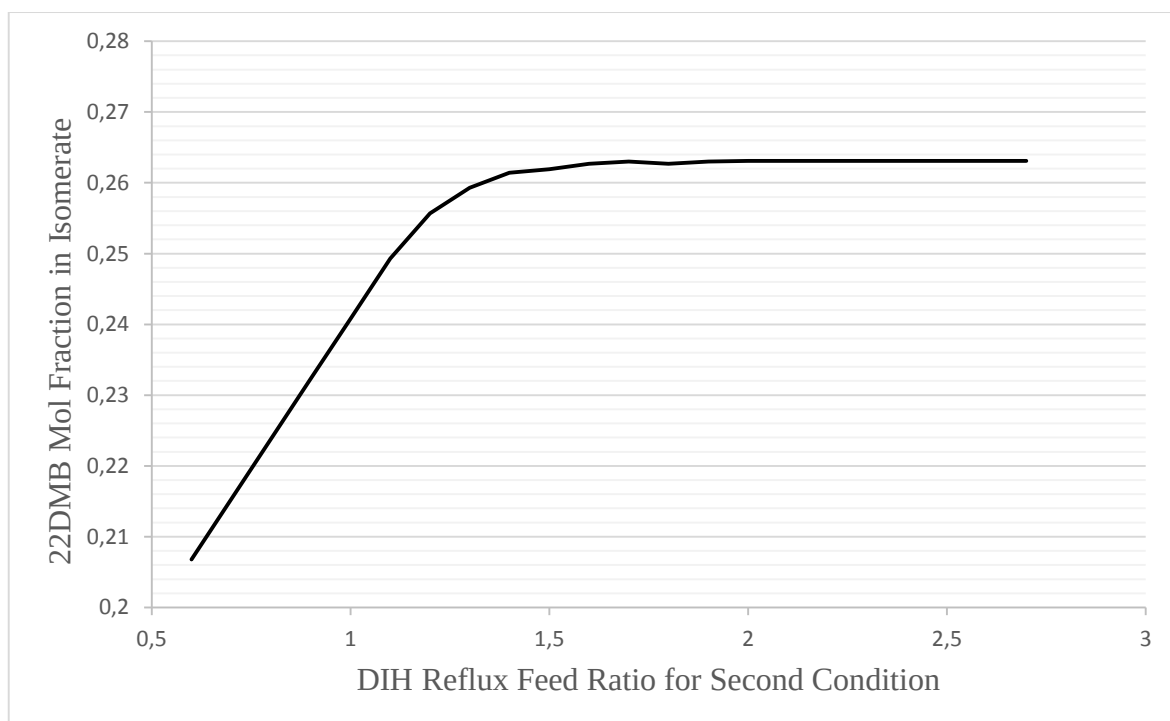


Figure 4.14. 22DMB Changes with DIH Reflux Feed Ratio for Second Condition.

4.2. Parameter Estimation

Parameter estimation is made after catalyst change for second condition with real data of the plant which does not reach steady state. Although second condition is more suitable and profitable for the process, decrement in the function of the parameter estimation is more recognizable than at the function of first condition parameter estimation. First and second condition results can be seen below for comparison (Table 4.3 and 4.4).

Table 4.3. First Condition Parameter Estimation Results.

First Condition Coefficients[74]					
	lnk ₀ [-]	E _A [kj/kmol]		lnk ₀ [-]	E _A [kj/kmol]
Rxn 1	16.1	81	Rxn 25	25.1	154.5
Rxn 2	20.5	67.7	Rxn 26	29	166.3
Rxn 3	16.3	83.5	Rxn 27	16	105.4
Rxn 4	15.9	82.1	Rxn 28	19.4	117.8
Rxn 5	13.7	78.4	Rxn 29	19.5	129.5
Rxn 6	13.6	76.7	Rxn 30	21.2	120.3
Rxn 7	13	77.5	Rxn 31	21	104.4
Rxn 8	15.9	71.5	Rxn 32	16.8	108
Rxn 9	20.2	73.3	Rxn 33	14.3	115.7
Rxn 10	19.5	77.1	Rxn 34	17.6	117
Rxn 11	15.4	72.9	Rxn 35	19.3	97.4
Rxn 12	15.4	72.5	Rxn 36	16.1	99.3
Rxn 13	18.1	64.9	Rxn 37	15.4	118.4
Rxn 14	14.5	97.8	Rxn 38	11.9	126.9
Rxn 15	21.2	62.3	Rxn 39	16.6	100.4
Rxn 16	14.2	76.4	Rxn 40	17.9	116
Rxn 17	28.2	144.4	Rxn 41	13	97
Rxn 18	30.9	182.4	Rxn 42	31.8	146.4
Rxn 19	8.1	87.2	Rxn 43	25.6	95.3
Rxn 20	9.5	87.3	Rxn 44	24.5	130.1
Rxn 21	6.9	89.2	Rxn 45	23.5	126.8
Rxn 22	24.8	172.8	Rxn 46	21.6	74.6
Rxn 23	15.1	132.5	Rxn 47	14.9	72.9
Rxn 24	22.7	191.4	Rxn 48	14.4	74.6

Table 4.3. Second Condition Parameter Estimation Results.

Second Condition Coefficients					
	$\ln k_0$ [-]	E_A [kJ/kmol]		$\ln k_0$ [-]	E_A [kJ/kmol]
Rxn 1	19.1	79.8	Rxn 25	25.7	150.3
Rxn 2	18	76.7	Rxn 26	30.8	171.2
Rxn 3	16.6	82	Rxn 27	16.9	100.5
Rxn 4	15.9	82.4	Rxn 28	20.3	125.2
Rxn 5	14.1	78.4	Rxn 29	19.6	119.1
Rxn 6	13.3	77.8	Rxn 30	21.4	112.6
Rxn 7	13.7	73	Rxn 31	22.3	101.9
Rxn 8	14.4	77.3	Rxn 32	17.4	115.6
Rxn 9	20.2	73	Rxn 33	14.4	112
Rxn 10	19.3	76.4	Rxn 34	17.2	117.1
Rxn 11	15.2	72.7	Rxn 35	19.1	102.7
Rxn 12	14.9	74.7	Rxn 36	15.9	108.1
Rxn 13	19.7	59.4	Rxn 37	15.9	115.8
Rxn 14	14.7	108.5	Rxn 38	12.2	133.1
Rxn 15	19	80.5	Rxn 39	19.1	89.1
Rxn 16	16	71.7	Rxn 40	18.8	119.1
Rxn 17	32.7	119.4	Rxn 41	13.5	98.1
Rxn 18	28.5	208.6	Rxn 42	31.2	124
Rxn 19	7.8	83.2	Rxn 43	26.2	103.5
Rxn 20	9.9	86.8	Rxn 44	24.1	125.1
Rxn 21	6.7	78.9	Rxn 45	23.6	124.9
Rxn 22	23.2	172.8	Rxn 46	20.4	82.4
Rxn 23	15.4	124	Rxn 47	14.8	75.4
Rxn 24	23.8	179	Rxn 48	15.3	73.6

For 3rd reaction, $nC_5 \rightarrow iC_5$, both $\ln k_0$ and E_a values slightly are decreased. While 4th reaction $iC_5 \rightarrow nC_5$, $\ln k_0$ and E_a values are slightly increased. This means, while converting nC_5 to iC_5 reaction becomes slower, reverse conversion becomes faster, there is much nC_5 in isomate. These result is undesired for the process, since nC_5 should be converted to high octane product.

For 9th and 10th reactions, 23DMB $\rightarrow$ 2MP and 2MP $\rightarrow$ 23DMB respectively, they become slower slightly and compensate each other.

18th reaction is CP+H₂ $\rightarrow$ iC₅, and increases with high delta. This change in the reaction covers almost all lost desirable iC₅ compound and makes second condition is favorable.

45th reaction, MCP+H₂ $\rightarrow$ 23DMB becomes slower, but 46th reaction, MCP+H₂ $\rightarrow$ 22DMB becomes faster, since 22DMB mole fraction in isomerate is appreciable and its alteration is bigger, it is an advantage for isomerization.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The aim of the study is to perform an optimization study on commercial hydro-isomerization process and to understand the relationships between decision variables and unit columns and reactors. The conclusions of the study are summarized below.

Lead reactor temperature has a role on catalyst operating temperature and handling conversion of paraffins and high octane products, since isomerization reactions are equilibrium reactions and limited by thermodynamics. Before catalyst change, optimum operating temperature is 175.5 °C, while after catalyst change, optimum operating temperature decreases to 135.5 °C to provide maximum octane number isomerate.

Lag reactor temperature is responsible for providing higher conversion and higher RON from isomerization reactions at lower temperatures, as a second run. For first condition, 142 °C is optimum temperature and for second condition, optimum temperature is found 120 °C for lag reactor. With catalyst change, unit approaches specified design conditions.

Stabilizer adjusts RVP value of the isomerate by altering its overhead vapor rate and reflux feed ratio. With 80 ton/h stabilizer overhead vapor rate and 0.8 reflux feed ratio, optimum condition is found for first condition. For second condition, overhead vapor rate is obtained as 126 ton/h and reflux feed ratio is obtained as 0.5. Also, stabilizer sensitivity analyses show that, increasing overhead vapor rate and reflux feed ratio decreases RVP of isomerate. This indicates enhancement in splitting.

Deisohexanizer column splits low octane products from isomerate to recycle them back to reactors, since in suitable conditions, these products can be converted into high octane products. For first condition, deisohexanizer column recycle rate and reflux feed ratio are found 1100 m³/d and 2.2 respectively, for optimized case. For second condition,

deisohexanizer column recycle rate is found 1438 m³/d, reflux feed ratio is found 1.2. Generally, if reflux feed ratio and recycle rate increase, splitting 2MP from isomerate is improved. However, sensitivity analyses shows, for second condition, 2MP molar fraction in isomerate is higher in comparison with first condition, although both recycle rate and reflux feed ratio are higher from their initial value.

Parameter estimation of second condition shows that, there are augmentation in $\text{CP} + \text{H}_2 \rightarrow \text{iC}_5$ and $\text{MCP} + \text{H}_2 \rightarrow \text{22DMB}$ reactions remarkably and compensate other changes in the unit.

5.2. Recommendations

The recommendations to improve the study may be summarized below.

Second condition of case study deisohexanizer column operation can be developed for better results. Since there is a different outcome from deisohexanizer column than expected, column operation would be investigated to understand whether there is a disruption.

Parameter estimation of second case may be improved after catalyst bed reaches the steady state conditions.

6. REFERENCES

1. Løften, T., *Catalytic Isomerization of Light Alkanes*, Ph.D. Thesis, Norwegian University of Science and Technology, 2004.
2. Weyda, H. and E. Kohler, "Modern Refining Concepts - an Update on Naphtha-Isomerization to Modern Gasoline Manufacture", *Catalysis Today*, Vol. 81, No. 1, pp. 51-55, 2003.
3. Kline, R. E., W. C. Starnes, and R. C. Zabor, *Hydroisomerization Process*, U.S. Patent and Trademark Office, Washington, DC., 1963.
4. Bloch, H. S., *Hydroisomerization Process*, U.S. Patent and Trademark Office, Washington, DC., 1961.
5. Holcombe, T. C., *Normal Hydrocarbon Feedstock Blended with the Zeolite Desorption Effluent*, U.S. Patent and Trademark Office, Washington, DC., 1980.
6. Holcombe, T. C., *n-Paraffin-Isoparaffin Separation Process*, U.S. Patent and Trademark Office, Washington, DC., 1979.
7. Stem, S. C. and W. E. Evans, *Total Isomerization Process with Mono-Methyl-Branched Plus Normal Paraffin Recycle Stream*, U.S. Patent and Trademark Office, Washington, DC., 1988.
8. Koncsag, C. I., I. A. Tutun, and C. Safta, "Study of C₅/C₆ Isomerization on Pt/H-Zeolite Catalyst in Industrial Conditions", *Ovidius University Annals of Chemistry*, Vol. 22, No. 2, pp. 102-106, 2011.
9. Anderson, G., R. Rosin, M. Stine, and M. Hunter, "New Solutions for Light Paraffin Isomerization", *UOP LLC*, 2004.

10. Chekantsev, N. V., M. S. Gyngazova, and E. D. Ivanchina, "Mathematical Modeling of Light Naphtha (C_5 , C_6) Isomerization Process", *Chemical Engineering Journal*, Vol. 238, No. pp. 120-128, 2014.
11. Rice, L. H., *Fractionation of Paraffin Isomerization Process Effluent*, U.S. Patent and Trademark Office, Washington, DC., 2003.
12. Foley, R. M., *C_5/C_6 Isomerization Process*, U.S. Patent and Trademark Office, Washington, DC., 1991.
13. Kuchar, P., J. Bricker, M. Reno, and R. Haizmann, "Paraffin Isomerization Innovations", *Fuel Processing Technology*, Vol. 35, No. 1, pp. 183-200, 1993.
14. Fraenkel, D. and B. C. Gates, "Shape-Selective Fischer-Tropsch Synthesis Catalyzed by Zeolite-Entrapped Cobalt Clusters", *Journal of the American Chemical Society*, Vol. 102, No. 7, pp. 2478-2480, 1980.
15. Nijs, H. H., P. A. Jacobs, and J. B. Uytterhoeven, "Chain Limitation of Fischer-Tropsch Products in Zeolites", *Journal of the Chemical Society, Chemical Communications*, Vol. 4, pp. 180-181, 1979.
16. Li, X., K. Asami, M. Luo, K. Michiki, N. Tsubaki, and K. Fujimoto, "Direct Synthesis of Middle Iso-Paraffins from Synthesis Gas", *Catalysis Today*, Vol. 84, No. 1, pp. 59-65, 2003.
17. Edward, L. S. I., R. Adarme, and F. N. Lin, *Method and Apparatus for Computer Simulation of Pentane Isomerization Reactions*, U.S. Patent and Trademark Office, Washington, DC., 1999.
18. Peters, M. S., K. D. Timmerhaus, R. E. West, K. Timmerhaus, and R. West, *Plant Design and Economics for Chemical Engineers*, Vol. 4., McGraw-Hill, New York, 1968.

19. Levenspiel O., *Chemical Reaction Engineering*, 3rd Edition, John Wiley & Sons, New York, 1999.
20. Inverno, J. E. F., E. Correiaz, and P. Jiménez-Asenjo, "Two Examples of Steady State Simulation with HYSYS at GALPenergia Sines Refinery", *European Symposium on Computer Aided Process Engineering-14: 37th European Symposium of the Working Party on Computer-Aided Process Engineering*, 2004.
21. Yela, S., *Framework for Operability Assessment of Production Facilities: An Application to a Primary Unit of a Crude Oil Refinery*, Ph.D. Thesis, Kakatiya University, 2009.
22. Kaes, G. L., *Refinery Process Modeling: A Practical Guide to Steady State Modeling of Petroleum Processes : Using Commercial Simulators*, Athens Printing Company, New York, 2000.
23. Robertson, G., *Advanced and Novel Modeling Techniques for Simulation, Optimization and Monitoring Chemical Engineering Tasks with Refinery and Petrochemical Unit Applications*, Ph.D. Thesis, Louisiana State University, 2014.
24. Biegler, L. T. and I. E. Grossmann, "Retrospective on Optimization", *Computers & Chemical Engineering*, Vol. 28, No. 8, pp. 1169-1192, 2004.
25. Grossmann, I. E. and L. T. Biegler, "Part II. Future Perspective on Optimization", *Computers & Chemical Engineering*, Vol. 28, No. 8, pp. 1193-1218, 2004.
26. Rangaiah, G. P., *Multi-Objective Optimization: Techniques and Applications in Chemical Engineering*, Vol. 2., World Scientific, Singapore, 2008.
27. Rangaiah, G. P. and A. Bonilla-Petriciolet, *Multi-Objective Optimization in Chemical Engineering: Developments and Applications*, John Wiley & Sons, New York , 2013.

28. Fu, M. C., "Optimization Via Simulation: A Review", *Annals of Operations Research*, Vol. 53, No. 1, pp. 199-247, 1994.
29. Fu, M. C., "Optimization for Simulation: Theory Vs. Practice", *Inform Journal on Computing*, Vol. 14, No. 3, pp. 192-215, 2002.
30. Andradóttir, S., *Simulation Optimization in Handbook of Simulation: Principles, Methodology, Advances, Applications, and Practice*, John Wiley & Sons, Hoboken, 1998.
31. Fu, M. C., *Handbook of Simulation Optimization*, Springer, New York, 2015.
32. Floquet, P., L. Pibouleau, and S. Domenech, "Mathematical Programming Tools for Chemical Engineering Process Design Synthesis", *Chemical Engineering and Processing: Process Intensification*, Vol. 23, No. 2, pp. 99-113, 1988.
33. Deng, G., *Simulation-Based Optimization*, Ph.D. Thesis, University of Wisconsin-Madison, 2007.
34. Murty, K. G., *Optimization for Decision Making Linear and Quadratic Models*, Springer, New York, 2010.
35. Fletcher, R., *Practical Methods of Optimization*, 2nd Edition, John Wiley & Sons, Chichester, 2000.
36. Powell, M., "Variable Metric Methods for Constrained Optimization", *Mathematical Programming the State of the Art*, pp. 288-311, 1983.
37. Zhang, H. and W. W. Hager, "A Nonmonotone Line Search Technique and Its Application to Unconstrained Optimization", *SIAM Journal on Optimization*, Vol. 14, No. 4, pp. 1043-1056, 2004.

38. Ahookhosh, M., K. Amini, and M. R. Peyghami, "A Nonmonotone Trust-Region Line Search Method for Large-Scale Unconstrained Optimization", *Applied Mathematical Modelling*, Vol. 36, No. 1, pp. 478-487, 2012.
39. Grippo, L., F. Lampariello, and S. Lucidi, "A Nonmonotone Line Search Technique for Newton's Method", *SIAM Journal on Numerical Analysis*, Vol. 23, No. 4, pp. 707-716, 1986.
40. Lukec, I., D. Lukec, K. S. Bionda, and Z. Adzamic, "The Possibilities of Advancing Isomerization Process through Continuous Optimization", *Goriva i maziva*, Vol. 46, No. 3, pp. 234-245, 2007.
41. Vahedi, V. and S. B. Jørgensen, *Data-Based Dynamic Modeling for Refinery Optimization: CAPEC*, Ph.D. Thesis, Technical University of Denmark, 2002.
42. Alkaya, D., S. Vasantharajan, and L. T. Biegler, "Generalization of a Tailored Approach for Process Optimization", *Industrial & Engineering Chemistry Research*, Vol. 39, No. 6, pp. 1731-1742, 2000.
43. Carter, N., J. Estes, and S. Kravitz, *Dehydroisomerization Process*, U.S. Patent and Trademark Office, Washington, DC., 1973.
44. Pirngruber, G., K. Seshan, and J. Lercher, "Dehydroisomerization of n-Butane over Pt-ZSM5 (I): Effect of the Metal Loading and Acid Site Concentration", *Journal of Catalysis*, Vol. 186, No. 1, pp. 188-200, 1999.
45. López, C. M., M. De Sousa, Y. Campos, L. Hernández, and L. Garcá, "Dehydroisomerization of n-Pentane on SAPO-11 Molecular Sieves Impregnated with Platinum", *Applied Catalysis A: General*, Vol. 258, No. 2, pp. 195-202, 2004.
46. Moghaddam, A. T. N. and V. Saint-Antonin, "Impact of Tightening the Sulfur Specifications on the Automotive Fuels' CO₂ Contribution: A French Refinery Case Study", *Energy Policy*, Vol. 36, No. 7, pp. 2449-2459, 2008.

47. Bialas, W. F. and M. H. Karwan, "Two-Level Linear Programming", *Management Science*, Vol. 30, No. 8, pp. 1004-1020, 1984.
48. Singh, A., J. Forbes, P. Vermeer, and S. Woo, "Model-Based Real-Time Optimization of Automotive Gasoline Blending Operations", *Journal of Process Control*, Vol. 10, No. 1, pp. 43-58, 2000.
49. Chandran, B., B. Golden, and E. Wasil, "Linear Programming Models for Estimating Weights in the Analytic Hierarchy Process", *Computers & Operations Research*, Vol. 32, No. 9, pp. 2235-2254, 2005.
50. Saaty, T. L., "How to Make a Decision: The Analytic Hierarchy Process", *European Journal of Operational Research*, Vol. 48, No. 1, pp. 9-26, 1990.
51. Brunelli, M., *Introduction to the Analytic Hierarchy Process*, Springer, New York, 2015.
52. Teknomo, K., 2006, *Analytic Hierarchy Process (AHP) Tutorial*, http://www.thecourse.us/5/library/AHP/AHP_Tutorial.pdf, [Accessed April 2015].
53. Hanratty, P. and B. Joseph, "Decision-Making in Chemical Engineering and Expert Systems: Application of the Analytic Hierarchy Process to Reactor Selection", *Computers & Chemical Engineering*, Vol. 16, No. 9, pp. 849-860, 1992.
54. Johnson, C., "Constructive Critique of a Hierarchical Prioritization Scheme Employing Paired Comparisons", *Proceedings of the International Conference of Cybernetics and Society of the IEEE*, pp. 373-378, 1980.
55. Zahedi, F., "The Analytic Hierarchy Process-a Survey of the Method and Its Applications", *Interfaces*, Vol. 16, No. 4, pp. 96-108, 1986.
56. Sirola, J., G. Powers, and D. Rudd, "Synthesis of System Designs: III. Toward a Process Concept Generator", *AIChE Journal*, Vol. 17, No. 3, pp. 677-682, 1971.

57. Siirola, J. J. and D. F. Rudd, "Computer-Aided Synthesis of Chemical Process Designs. From Reaction Path Data to the Process Task Network", *Industrial & Engineering Chemistry Fundamentals*, Vol. 10, No. 3, pp. 353-362, 1971.
58. Powers, G., "Heuristic Synthesis in Process Development", *Chemical Engineering Progress*, Vol. 68, No. 8, pp. 88, 1972.
59. Mahalec, V. and R. Motard, "Evolutionary Search for an Optimal Limiting Process Flowsheet", *Computers & Chemical Engineering*, Vol. 1, No. 2, pp. 133-147, 1977.
60. Douglas, J. M., *Conceptual Design of Chemical Processes*, McGraw-Hill, Singapore, 1988.
61. Kirkwood, R., M. H. Locke, and J. Douglas, "A Prototype Expert System for Synthesizing Chemical Process Flowsheets", *Computers & Chemical Engineering*, Vol. 12, No. 4, pp. 329-343, 1988.
62. Kravanja, Z. and I. E. Grossmann, "PROSYN—an MINLP Process Synthesizer", *Computers & Chemical Engineering*, Vol. 14, No. 12, pp. 1363-1378, 1990.
63. Grossmann, I. E., "Mixed-Integer Programming Approach for the Synthesis of Integrated Process Flowsheets", *Computers & Chemical Engineering*, Vol. 9, No. 5, pp. 463-482, 1985.
64. Dantzig, G. B., *Linear Programming and Extensions*, Princeton University Press, Princeton, 1998.
65. Vanderbei, R. J., *Linear Programming: Foundations and Extensions*, 4th Edition, Springer, New York, 2014.
66. Hillier, F. S. and G. J. Lieberman, *Introduction to Operations Research*, 9th Edition, McGraw-Hill, New York, 2010.

67. Gonzalez-Lima, M. D., A. R. Oliveira, and D. E. Oliveira, "A Robust and Efficient Proposal for Solving Linear Systems Arising in Interior-Point Methods for Linear Programming", *Computational Optimization and Applications*, Vol. 56, No. 3, pp. 573-597, 2013.
68. Schriber, T. J., "Introduction to Simulation", *Proceedings of the 9th Conference on Winter Simulation-Volume 1*, 1977.
69. Motard, R. L., M. Shacham, and E. M. Rosen, "Steady-State Chemical Process Simulation", *AIChE Journal*, Vol. 21, No. 3, pp. 417-436, 1975.
70. Kelton, W. D. and A. M. Law, *Simulation Modeling and Analysis*, 3rd Edition, McGraw-Hill, New York, 2000.
71. Banks, J., "Introduction to Simulation", *Proceedings of the 31st Conference on Winter Simulation: Simulation-A Bridge to the Future-Volume 1*, 1999.
72. Carson, Y. and A. Maria, "Simulation Optimization: Methods and Applications", *Proceedings of the 29th Conference on Winter Simulation*, 1997.
73. *UOP Training Document*, Universal Oil Products Press, 2010.
74. Acar Fidan H., *Development and Verification of Two Phase Reactor Model for Industrial Light Naphtha Isomerization Reactors*, M.S. Thesis, Boğaziçi University, 2015.
75. AspenTech, "Hysys Petroleum Refining", 2013, <http://www.aspentech.com/aspen-hysys-petroleum-refining/>, [Accessed April 2015].
76. Ejikeme-Ugwu, E., *Planning for the Integrated Refinery Subsystems*, Ph.D.Thesis, Cranfield University, 2012.

77. Banga, J. R., R. Irizarry-Rivera, and W. Seider, "Stochastic Optimization for Optimal and Model-Predictive Control", *Computers & Chemical Engineering*, Vol. 22, No. 4, pp. 603-612, 1998.
78. Box, M., "A New Method of Constrained Optimization and a Comparison with Other Methods", *The Computer Journal*, Vol. 8, No. 1, pp. 42-52, 1965.
79. Press, W., S. Teukolsky, W. Vetterling, and B. Flannery, *Numerical Recipes in C*, 2nd Edition, Cambridge University Press, Cambridge, 1992.
80. Kuester, J. L., J. H. Mize, and D. Griffin, "Optimization Techniques with Fortran", *Journal of Applied Mechanics*, Vol. 41, No. pp. 116, 1974.
81. Council, S. T. F., "The HSL Mathematical Software Library", 2015, <http://www.hsl.rl.ac.uk/>, [Accessed April 2015].
82. Council, S. T. F., "VF13", 2011, <http://www.hsl.rl.ac.uk/archive/specs/vf13.pdf>, [Accessed April 2015].
83. Chamberlain, R., M. Powell, C. Lemarechal, and H. Pedersen, "The Watchdog Technique for Forcing Convergence in Algorithms for Constrained Optimization", *Algorithms for Constrained Minimization of Smooth Nonlinear Functions*, pp. 1-17, 1982.
84. Powell, M. J., "A Fast Algorithm for Nonlinearly Constrained Optimization Calculations", *Numerical Analysis*, pp. 144-157, 1978.