Computer Aided Simulation and Process Design of a Hydrogenation Plant Using Aspen HYSYS 2006

By

Mohammad Hossein Ordouei

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2009

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

ABSTRACT

Nowadays, computers are extensively used in engineering modeling and simulation fields in many different ways, one of which is in chemical engineering. Simulation and modeling of a chemical process plant and the sizing of the equipment with the assistance of computers, is of special interests to process engineers and investors. This is due to the ability of high speed computers, which make millions of mathematical calculations in less than a second associated with the new powerful software that make the engineering calculations more reliable and precise by making very fast iterations in thermodynamics, heat and mass transfer calculations. This combination of new technological hardware and developed software enables process engineers to deal with simulation, design, optimization, control, analysis etc. of complex plants, e.g. refinery and petrochemical plants, reliably and satisfactorily.

The main chemical process simulators used for static and dynamic simulations are ASPEN PLUS, ASPEN HYSYS, PRO II, and CHEMCAD. The basic design concepts of all simulators are the same and one can fairly use all simulators if one is expert in any of them.

Hydrogenation process is an example of the complex plants, to which a special attention is made by process designers and manufacturers. This process is used for upgrading of hydrocarbon feeds containing sulfur, nitrogen and/or other unsaturated hydrocarbon compounds. In oil and gas refineries, the product of steam cracking cuts, which is valuable, may be contaminated by these unwanted components and thus there is a need to remove those pollutants in downstream of the process. Hydrogenation is also used to increase the octane number of gasoline and gas oil.

Sulfur, nitrogen and oxygen compounds and other unsaturated hydrocarbons are undesired components causing environmental issues, production of by-products, poisoning the catalysts and corrosion of the equipment. The unsaturated C=C double bonds in dioleffinic and alkenyl aromatics compounds, on the other hand, cause unwanted polymerization reactions due to having the functionality equal to or greater than 2.

Hydrogenation process of the undesired components will remove those impurities and/or increase the octane number of aforementioned hydrocarbons. This process is sometimes referred to as "hydrotreating"; however, "upgrader" is a general word and is, of course, of more interest.

In this thesis, a hydrogenation process plant was designed on the basis of the chemistry of hydrocarbons, hydrogenation reaction mechanism, detailed study of thermodynamics and kinetics and then a steady-state simulation and design of the process is carried out by ASPEN HYSYS 2006 followed by design evaluation and some modifications and conclusions.

Hydrogenation reaction has a complicated mechanism. It has been subjected to hot and controversial debates over decades. Many kinetic data are available, which contradict one another. Among them, some of the experimental researches utilize good assumptions in order to simplify the mechanism so that a "Kinetic Reaction" modeling can be employed. This thesis takes the benefit of such research works and applies some conditions to approve the validity of those assumptions. Meanwhile, some other papers from reputed companies such as IFP are used in order to make sure that the present simulation and design is a practical one and applicable in real world.

On the basis of this detailed study of reaction modeling and kinetic data, a hydrogenation plant was designed to produce and purify over 98 million kilograms of different products; e.g. Benzene, Toluene, Iso-octane etc. with fairly high purity.

Acknowledgements

The author wishes to acknowledge and thank his supervisors, Dr. Ali Elkamel and Dr. Mazda Biglari, for their guidance and support throughout the thesis.

The author also wishes to thank the readers of my thesis, Dr. Leonardo Simon and Dr. Luis Ricardez for their valuable advice on this research.

And finally, thanks to my loving mother, my family and friends for their inspiration and encouragement during the working on my thesis.

Dedication

I would like to dedicate the present work to my parents and my sisters, who have been supporting me in all steps of my life.

Table of Contents

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

1.1 The advantages of computer simulators

Many of the industrial chemical processes have to be simulated, analyzed and designed by computer since it is almost impossible to solve a plenty of equations by hand. Therefore, steps to solve them are taken using complex algorithms. The available simulators, which are directly used by process engineers, are mainly spreadsheets, mathematical packages and process simulators in static and dynamic modes.

Spreadsheets have a wide variety of applications in process feasibility. The costs of the equipment, raw materials, final products and utilities are used to estimate the capital, total investments and turn over by spreadsheets and the results can be printed and/or depicted.

Mathematical package such as POLYMATH enables to do fast calculations for linear algebra, linear and non-linear systems analysis, ordinary differential equations (ODE) with appreciable accuracies. MATLAB has similar capabilities in addition to Partial differential equations (PDE) and optimization.

1.2 Process simulators

Process simulators such as ASPEN PLUS, ASPEN HYSYS, PRO II, and CHEMCAD provide the following advantages for chemical engineers:

1. Physical properties information,

2. Chemical properties information,

3. Thermodynamic properties information,

4. Process equipment models,

5. Material and energy balance,

6. Creating Process Flow Diagram (PFD),

7. Equipment sizing,

8. Capital and revolving investment.

ASPEN HYSYS along with other process simulators facilitate the design, sizing, simulation and optimization of a chemical and/or a refinery plant and the required equipment. ASPEN HYSYS and ASPEN PLUS are extensively used in the industries since they help chemical engineers in two major fields: **Design** and **Operation**.

A. **Design:** A chemical process plant is usually composed of several process units such as distillation columns, decanters, heat exchangers, filters, reactors, compressors and pumps. These equipments are used for performing "chemical reactions", creating "temperature and pressure" gradient, "mixing" of streams, or "phases separation" into its components.

In the design phase, a simulator is very useful in the following areas:

1. Comparison among different options in a process (flow sheet selection).

2. Material and energy balance.

3. Design and sizing the process equipment.

4. Evaluation of the process in different operational conditions.

5. Design a Process Flow Diagram (PFD).

6. Optimization.

B. **Operation:** It is not easy to make changes in an operating plant without taking the risks of emergency shut-down in case of sudden changes in feed, temperature, pressure etc., which may lead to lose the quantity and quality of the products and even worse, to put in danger the worker's safety.

A production engineer can get help in the following areas from a simulator in order to prevent from those risks and to keep the plant and operation on the safe side:

1. Prediction of the change effects.

2. Evaluation of the modifications on a process.

3. Estimation of the productivity and efficiency of process equipment and/or the process as a whole.

4. Training of the production operators and/or engineers with dynamic simulators.

These simulators; e.g. ASPEN PLUS, ASPEN HYSYS, PRO II, CHEMCAD etc. are being widely used in chemical, petrochemical, oil and gas industries, pulp and paper, mining, pharmaceutical, biotechnology and power plants.

Using thermodynamic data, the real operational conditions of a plant and equipment can be simulated. This will enable a chemical engineer to analyze potential problems and optimize the design and operational conditions before performing any changes in parameters.

As it is clear from the above mentioned capabilities, the simulators prevent undesirable events. To gain this goal, a design engineer or a production engineer must have a good level of understanding about many physical laws as well as chemical engineering concepts. For instance, the selection of the equipments totally depends on the physical properties of components; e.g. for a substantial difference in volatility the gas-liquid separation method is used, while for a small difference in volatility an extraction unit may be suitable.

APPENDIX C shows simulation, modeling and optimization of a distillation tower for the separation of a hydrocarbon mixture.

1.3 Hydrocarbons characteristics

The main source of hydrocarbons, which are used in industrial scale, is crude oil. In addition to hydrocarbon, sulfur, nitrogen as well as oxygen compounds and a slight amount of organo-metallic impurities are also found in crude oil. Hydrocarbons mainly contain carbon in the range from C_1 to C_{50} plus hydrogen atoms. These hydrocarbons are classified into three major groups[1]:

a. "Paraffinic Hydrocarbons" or "Alkanes" containing C-H or C-C saturated bonds. They are categorized into normal paraffins and iso-paraffins and have the general formula of $C_n H_{2n+2}$.

b. "Naphtenic Hydrocarbons" or "Cycloparaffins" containing saturated and ring-typed hydrocarbons containing saturated C-C bonds. They have the general formula of $C_n H_{2n}$.

c. "Aromatic Hydrocarbons", which are unsaturated but stable compounds and have the structure like benzene (C_6H_6). They have the general formula of $C_n H_n$.

It important to keep in mind that the unsaturated hydrocarbons such as olefins (containing C=C double bond), diolefins (containing C=C-C=C two double bonds) etc. are not found in crude oil; however, they may be produced in the course of the refining of crude oil.

Each group and even each single member of group has the individual characteristics and applications in oil and gas industries and human life. Thus, significant attempts have been made over the decades in order to perform satisfactorily separations of crude oil into its main or group components. The refineries were established and modified to fulfill these tasks. Separation methods are developed to achieve high purity of products. In addition, by means of reactors and catalysts, low price or undesired feed components may be converted into the valuable and separable products.

Even though we are not directly concerned with refinery's operations in this context, whenever we use the word refinery, it means any of the following categories:

- Regular refineries, in which fuels are made such as LPG, gasoline, kerosene, gas oil, heavy (fuel) oil etc.

- Lubricant manufacturers, in which lubricants, paraffin and asphalts are produced in addition to fuels.

- Petrochemicals, in which the raw materials of petrochemicals such as ethylene, propylene, butylenes, butadiene, and aromatics are produced in addition to fuels.

In a sense, they are sometimes referred to as downstream operations; however, oil well, oil sand and drilling are known as upstream operations.

Refinery operations can be classified in three major categories[1]:

1. Cracking including "Thermal" and "Catalytic" treatments, each of which With Hydrogen and Catalytic Treatment W/O Hydrogen. Each of which is divided into subdivisions.

2. Synthesis including "Thermal" and "Catalytic" operations.

3. Chemical Treatment, which is divided into four subdivisions.

Detailed information about these operations is provided in Table 1.1. Among many operations listed in this table, hydrogenation is of special interest for this work. Hydrogenation operation was first developed in refineries due to dramatic increase of the demands to the light products of refineries and consequently raising the price of such products. Meanwhile the decrease of the demands to heavy products such as heavy fuel oils caused a significant development in technology especially in hydrogenation catalysts and reactor design.

Table 1.1 Classification of refineries processes. Adapted from Ref. 1.

Category	Classification	Name	Process	Operating Conditions T/0C	Operating Conditions P/atm	Feeds	Products
Cracking	Thermal	Cracking of Pure Hydrocarbons (HC)	Heat and steam	800	1~2	Light Hydrocarbons (HC)	Oleffins and H2
		Steam Cracking	Heat and steam	750	2	Gasoline	Light Oleffins
		Thermal Reforming	Heat	515-550	25~50	Heavy Gasoline	Gas-Gasoline Reformate
		Thermal Cracking	Heat	370-510	20~30	Gas oil or Residues	Gas ... Fuels
		Visbreaking	Heat	460	10~20	Residues and Vacuum Residue	Gas ... Fuels and Fuel Oil
		Coking	Heat	480-520	20~35	Vacuum Residue	Gas ... Fuels and Coke
	Catalytic without Hydrogen	Houdry Catalytic Cracking	Catalyst Silicon Alumin	425-460	1~4	Gas Oil	Gas-Gasoline-Gasoil
		Thermofor Catalytic Cracking	Catalyst Silicon Alumin (Natural or Synthetic)	460-510	1~1.5	Gas Oil	Gas-Gasoline-Gasoil
		Fluid Catalytic Cracking	Catalyst Silicon Alumin (Synthetic)	400-480	1~2	Gas Oil	Gas-Gasoline-Gasoil
		Dehydrogenation	Catalyst Cr and Al Oxides	500-600	1	Butanes	Butene and Butadiene
		Isomerization	AlCl3 or Pt on Silicon-Alumin base			C4 and Light Gasoline	Light Gasoline with High Octane
	Catalytic with Hydrogen	Catalytic Reforming	Pt on Alumin or Silicon-Alumin Base	480-520	20~50	Heavy Gasoline	Reformate Gasoline and Aromatics
		Hydrocracking	Pt or Pd on Zeolyte Base	325-510 370-425	10~30 20~35	Heavy Gas Oils	Gas ... Fuels-Gasoline
		Hydrotreating	Cobalt Oxide-Molybdenum	370-410 320-400	25~45 40~65	Gasolines Lubrication Oils	Gasoline-Intermediate Distillates-Oils and Fuels
Synthesis	Thermal	Thermal Alkylation	Heat	480-540	200	C2 (Double Bond) or iC4+C3 (Double Bond)	Neohexane
		Thermal Polymerization	Heat	480-550	100	Thermal Cracking Gas	Polymer Gasoline
	Catalytic	Alkylation	HF H2SO4	20-50 0-10	8~10 1	Light Oleffins and Isoparaffins	Alkylite Gasoline
		Polymerization	H3PO4	150-230	20~40	Thermal Cracking Gas	Polymer Gasoline
		Hydrogenation	Nickel Catalyst	160-200	2~5	Iso-Octene	Iso-Octane
Chemical Treatment	Chemical Treatment	Girbotol Process	Di-Ethanol Amine			Natural Gas	Treated Gas
		Caustic Washing	Caustic			LPG and Light Gasoline	Treated Gas and Light Gasoline
		Sweetening	1) PbO2Na2 and Sulfur 2) CuCl2 3) NaOCl			Gasoline-Kerosene	Sweetened Gasoline and Kerosene
		Sulfuric Acid Treatment	H2SO4			Gasoline-Kerosene-Lubricating Oils	treated feed

Hydrotreating plant, which widely applies the hydrogenation process, is performed in different steps of refineries. Figure 1.1 shows a block diagram of a typical upgrader[2].

Hydrogenation feed is usually Naphta, gasoline and middle distillates. However, any other hydrocarbon mixtures with the same criteria and properties as in aforementioned feeds can be subjected to hydrogenation.
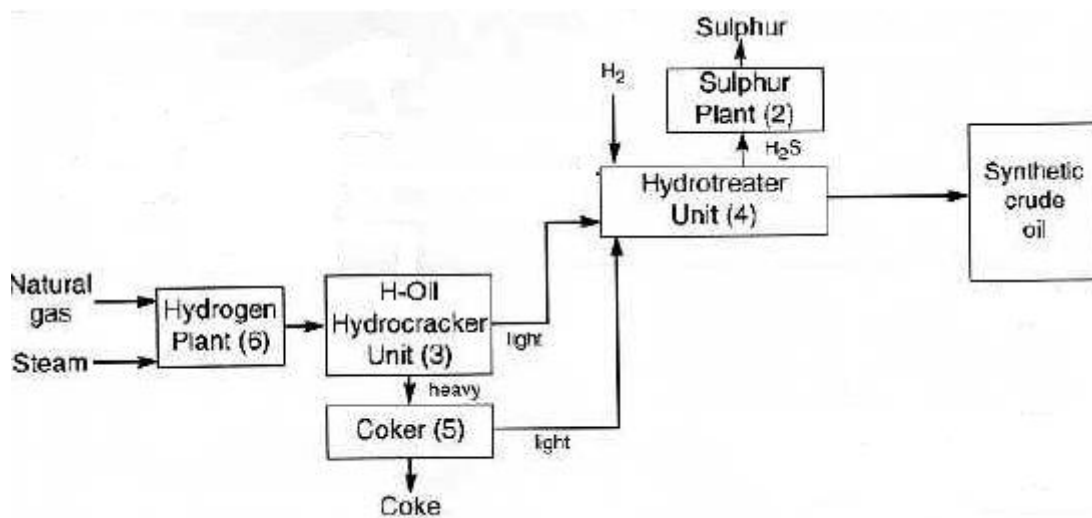
Figure 1.1 Simplified flow chart of an "upgrader unit". Adopted from Ref. 2.

1.4 The objectives of hydrogenation reactions in industries

As it was mentioned earlier, sulfur and nitrogen are already present in crude oil while unsaturated components are produced in the refineries. They cause the following problems for environment and equipment:

- Environmental pollution.

- Corrosion of equipment.

- Poisoning of the catalysts in downstream plants.

- Instability in the process.

In addition, C=C double bonds in oleffinic and dioleffinic compounds are highly active to produce gum by polymerization. That means fuels, and in particular gasoline, containing high

6

contents of unsaturated hydrocarbons has low stability with respect to temperature and therefore storage.

Apparently, each of them causes serious impact on both environment and plant operation and in turn on the company's economy. Therefore, it is crucial to build up a hydrogenation facility to overcome these problems not only in refinery plants but also in every plant, which handles hydrocarbons or solutions containing such hydrocarbons.

On the basis of the above mentioned problems, the following lists the objectives of hydrogenation operation:

1) To eliminate sulfur, nitrogen and other unsaturated hydrocarbons,

2) To decrease the above mentioned components to a standard level,

3) To hydrogenate Iso-octene into Iso-octane,

4) To stabilize the hydrocarbon mixtures by saturation of olefinic and diolefinic compounds,

5) And also when it comes to gasoline feed, the objective is to increase the octane number.

That is why this operation is sometimes referred to as "Hydrotreating".

1.5 Hydrogenation Process
Due to the above mentioned reasons, hydrogenation process has to be done in any hydrocarbon mixtures containing olefins and dioleffins and specially sulfur, nitrogen and oxygen contamination if the mixtures are to be sent to catalytic reforming process. Moreover, the end-users may need "high octane motor fuel" or "clean aromatics source" for aromatics plants, which may use "naphta" as feed.

Frank and Stadelhofer[3] have provided Table 1.2, which shows the octane number of important hydrocarbons.

Table 1.2 Octane numbers of hydrocarbons. Adapted from Ref. 3.

Hydrocarbon	Octane No.	Hydrocarbon	Octane No.
Paraffins:		**Aromatics:**	
Iso-butane	122	Benzene	99
n-Pentane	62	Toluene	124
Iso-pentane	99	o-Xylene	120
		m-Xylene	145
2,2,4-Trimethylpentane (Iso-octane)	100	p-Xylene	146
		Ethylbenzene	124
		1,2,4-Trimethylbenzene	
			171
Naphthenes:		**Olefins:**	
Methylcyclopentane	107	1-Pentene	91
Cyclopentane	91	1-Octene	29
Cyclohexane	110	Trans-3-Octene	73
1,1,3-Trimethylcyclo-hexane		4-Methyl-1-pentene	96
	85		

In our case, basically two main reactions are involved in hydrotreating operations:

1. Hydrorefining: Hydrorefining reactions contain "desulfurization", "denitrogenation" etc. Table 1.3 presents the results of desulfurization on the various feed and final product properties[4].

2. Hydrogenation: Hydrogenation is involved in saturation of oleffinic and dioleffinic compounds in the feed as mentioned before.

Table 1.3 Products from Hydrodesulfurization of Feeds with Different Sulfur Levels. Adapted from Ref. 4.

Process	VGO[*]	VRDS[**]	VGO + VRDS	RDS[***]
Feed sulfur, wt%	**2.3**	**4.1**	**2.9**	**2.9**
Product sulfur, wt%	**0.1**	**1.28**	**0.5**	**0.5**
Product yields C_1-C_4, wt%	**0.59**	**0.56**	**0.58**	**0.58**
H_2S, NH_3, wt%	2.44	3.00	2.55	2.55
C_5^+, wt%	97.51	97.34	97.46	97.67
C_5^+, LV%	100.6	102.0	101.0	101.5

*   Vacuum gas oil hydrotrater

**   Vacuum residuum hydrotreater

***   Atmospheric residuum desulfurization hydrotreating

1.6 Designing levels and modeling steps

Before defining the scope of this thesis, which is briefly mentioned in the preface, it would be informative to know about the design levels and modeling steps.

A. The designing of a process usually takes place in three steps[5]:

1. Preliminary: At this level, cost estimation will be carried out very quickly. It mainly contains an approximation with up to 50% inaccuracy and is useful for a first idea of feasibility study.

2. Detailed estimate design: After getting a reasonable result of cost estimation, the next step would be a more accurate and detailed method in order for decision makers to go for that process or to give it up. This step does not include the equipment sizing.

3. Final process design: At this level, the process is feasible and the designer has a good idea of the process, raw materials, products, capacities etc. However, the products of this step will not be sufficient to start the construction activities.

The products of this level will include equipment sizing and specifications as well as process flow diagram (PFD). It is used for more specific purposes such as process and instrument diagrams (P&ID) followed by preparation of equipment drawings, structural steel drawing, electrical and instrument hook-ups, safety equipment design etc.

However, we must remember that without PFD, it is impossible to make P&ID's and the aforementioned succeeding activities. PFD provides designers with a plenty of information including the main equipment and stream lines, flow rates, temperature, pressure, the compositions of each streams, and lots more. In this sense this thesis covers the design levels up to PFD preparation.

B. The modeling of a process usually takes place in the following steps:

1. To understand the physical system, which is to be modeled; e.g. steady state modeling or dynamic one.

2. To develop a mathematical model using conversation principle, equilibrium states, correlation etc.

3. To solve the mathematical model with the standard procedures.

4. To interpret the step 3 called simulation; i.e. solving the mathematical model, to physical system.

5. To use the approved model for future predictions, design, and operation etc.

HYSYS like other simulators; e.g. Aspen Plus, PRO II, CHEMCAD, will use typical steps of modeling together with its comprehensive library to model and simulate a process and equipment design, sizing, optimization and so on at different levels.

1.7 The levels of process simulation

Like the different level of design (sec. 3.1, part A), which can be made either manually or by simulators there are different levels of simulations by simulators, as follows, depending on the complexity of the task:

1. Process modeling and design.

2. Energy recovery for the designed process.

3. Material balance.

4. Material and energy balance.

5. Process Flow Diagram (PFD) preparation.

6. Process equipment sizing.

7. Sensitivity, optimization and case-study.

8. Technical and economical feasibility study.

The more the complexity of a simulation increases, the more mathematical equations are to be solved. As such, the more variables are to be found and the more complex algorithm of problem solving is to be developed. The good news is that even though the physical and thermodynamic properties of each process are quite different from the other, the process equipment and related equations are all the same. Therefore, a model for a special process can be developed and saved as a template in the simulator's library; however, it is possible to make and use new models in addition to the templates. In this way, combining the existing templates and creating new models it is possible to make simulated diagram and process flow diagram (PFD).

On the PFD page, each unit operations; i.e. individual equipment, uses the related equations and solvers; e.g. Newton-Rafson, based on the given data by user/designer.

1.8 The objective of the thesis

The main objective of this thesis is to turn some research papers including experimental kinetic data from a lab scale and theory to fundamentals to build up a fairly large plant on the basis of

lectures, simulation software and personal engineering practices and judgment. In this respect, the following is the list of the objectives of the present thesis:

1. As in the design basis, a feed stream containing unsaturated and saturated hydrocarbons conditions and compositions was used as mentioned in Table 3.1 and 3.2.

2. Detailed literature review in order to determine the thermodynamic and kinetic data to model hydrogenation reaction(s).

3. Steady-State Design of an upgrader plant in such a way that could be modified for using in hydrogenation of iso-octene to iso-octane, increasing the octane no. of a pyrolysis gasoline, separation of aromatics to further use in Aromatics plants and/or for hydrocarbon waste treatment. This upgrader will have the following sections:

   - Designing an integrated process which contains hydrogenation of unsaturated hydrocarbons.

   - Modeling and simulation of the further unit operations after the reactions; i.e. cooling and phase separation section.

   - Modeling and simulation of purification operations for the separation of final products including pumps, heat exchangers and storage tanks.

4. Design basis:

   Annual capacity between 98,000,000-100,000,000 kilograms per year (KGPY) consisting of:

   - Benzene: About   48,400,000   KGPY
   - Mixed aromatics   About   38,000,000   KGPY

     (Ethyl-benzene, Toluene)

   - Light Hydrocarbons (C_5^-)   About   3,100,000   KGPY

   - Iso-octane Rich HCs   About   9,100,000   KGPY

5. The modeling and simulation of process equipment including reactor, distillation column, phase separator, stabilizer, air cooler, shell and tube heat exchanger etc.

6. Sizing of tubular reactors.

7. Material balance.

8. Energy balance.

9. PFD design by HYSYS.

10. Preparation of the material and energy balance table as well as the compositions, pressure and the temperature of each stream lines.

11. Technical evaluation of the process followed by performing modifications on this basis.

12. Providing a general process description for the hydrogenation plant.

1.9 Applications of the thesis
The hydrogenation plant has a wide variety of industrial applications:

1. Elimination of sulfur according to Equations (2.1) to (2.4).

2. Elimination of nitrogen as in Equations of (2.5) to (2.6).

3. Hydrogenation of iso-octene to iso-octane in order to add into gasoline and to increase the octane no.

4. Hydrogenation of pyrolysis gasoline in order to increase the octane no. of gasoline. In this regard, the composition is a slightly different from our plant feed.

5. Hydrogenation of unsaturated hydrocarbons in order to be fed into the aromatics plant. Pyrolysis gasoline can also be used for this purpose.

6. Recovery of the solvent; i.e. toluene, benzene, thinner etc. In this case, the feed is usually free from unsaturated hydrocarbons, and even if contains, it wouldn't make serious problem when the content is low. In case of thinner feed would contain alcohols and ketones; e.g. IPA, Acetone etc.

Note 1: The changing of the stream feed influences the equipment sizing and process in terms of operability, performance and feasibility. However, the equipment arrangement might remain unchanged.

Note 2: For hydrotreatment; i.e. hydrodesulforization and hydro denitrification etc., the operation requires a high temperature.

Note 3: For applications such as solvent recovery, there is no need to design a reactor and to simulate the reaction. Therefore, the modeling and simulation would be easier than the present case.

1.10 Organization of this work

In this research work an introduction is provided in chapter 1 including process simulator and its advantages, hydrogenation reaction, how to model such reaction and related plant by process simulator, design basis and the objective of the thesis. In chapter 2, a literature review is made. A more detailed study is provided in APPENDIX B. chapter 3 contains the modeling and simulation of the hydrogenation plant is made to achieve the design basis. In chapter 4, some modifications are made in "Reaction" section, Cooling and Separation" section and in "Purification" section in order to improve the plant capacity and the purity of products. Chapter 5 offers a "General Process Description" for the designed plant. Finally, chapter 6 contains "Conclusions" of what have been done in this work.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemistry of hydrocarbons

A. Carbon:

Carbon is a tetravalent atom and can be configured in a molecule in many different ways. Therefore, there is a vast diversity of carbon compounds. One of the unique characteristics of carbon atom is its ability to link to other atoms, e.g. carbon, hydrogen, oxygen etc., through single, double and triple bonds each of which give the resulted molecule specific properties. Here are some examples:

- Carbon-Carbon (or Carbon-Hydrogen) single bond:

CH_4, C_2H_6 etc., with SP^3 hybrid configuration.

- Carbon-Carbon (or Carbon-Oxygen) double bond:

C_2H_4, HCHO etc., with SP^2 hybrid configuration.
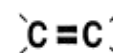
- Carbon-Carbon (or Carbon-Nitrogen) triple bond:

C_2H_2, NaCN etc., with SP hybrid configuration.

- One of the most important configurations of carbon atoms in hydrocarbons is Carbon-Carbon conjugated single and double bonds. These are known as ring type triene or aromatic rings:

C_6H_6, C_7H_8 etc., with SP^2 hybrid configuration.
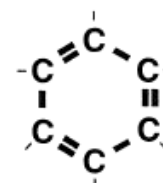
- Hydrogen atom forms merely a single bond with other atoms, and in our study with carbon atom to produce hydrocarbon. H -

Hydrocarbons are also divided into saturated and unsaturated hydrocarbons, each of which is divided into sub-divisions as following:

1. Saturated hydrocarbons:

   a) Normal Paraffins, containing a straight chain like:

   b) Iso-paraffins, containing branch(es) chain like:

   c) Naphtenes, containing saturated ring type carbon atoms like: or

2. Unsaturated hydrocarbons:

   a) Olefinic hydrocarbons, containing a Carbon-Carbon double bond like:

      i) Normal olefins like:

      ii) Iso-olefins like:
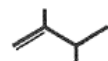
      iii) Cyclo-olefins like:

   b) Diolefinic hydrocarbons, containing two Carbon-Carbon double bonds like:

      i) Normal diolefins like:

      ii) Iso-diolefins like:
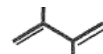
      iii) Cyclodiolefins like:

B. Sulfur:

Sulfur is a bivalent atom, capable to link to other atoms such as hydrogen, alkyl group or even in a ring type molecule:

- Hydrogen Sulfide: H_2S

- Mercaptides, containing a –SH group linked to an alkyl group: R-SH. For instance: Methyl Mercaptan CH_3-SH.

- Sulfides, in which one sulfur atom is located in between two alkyl groups; R-S-R'.

- Disulfides, in which two sulfur atoms are located in between two alkyl groups; R-S-S-R'.

- Polysulfides, in which several sulfur atoms are located in between two alkyl groups; R-S-S-…-S-R'.

- Thiocyclic compounds, containing a sulfur atom in a ring. They exist both in upstream and downstream products. Two major compounds are shown below:

  a. C_2H_4S, called Thiophene:
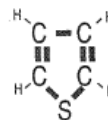
  b. C_8H_6S, called Benzothiophene:
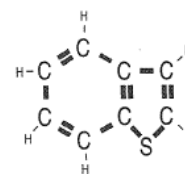
Unless mercaptides, the other sulfur compounds are not corrosive and less odorous. Mercaptides are acidic and therefore, corrosive and due to higher volatility are very odorous. They are injected in very small amounts in natural gas, which is to be used in houses and factories. Therefore, in case of any leakages the user takes a quick action.

C. Nitrogen:

Nitrogen compounds and reactions can be found in chemical reactions as shown in equations (2.5) and (2.6).

2.2 Reactions, kinetics and thermodynamics of hydrogenation

The following typical hydrogenation reactions will take place in the presence of H_2 at sufficient temperature and partial pressure[4]:

A. **Desulfurization:** Sulfur compounds in petroleum, are usually in the following forms and will be reduced to H_2S in the course of hydrotreating (hydrodesulfurization) process:

$$R\text{-}SH + H_2 \rightarrow RH + H_2S \tag{2.1}$$

$$R\text{-}S\text{-}R + 2H_2 \rightarrow 2RH + H_2S \tag{2.2}$$

$$RS\text{-}SR + 3H_2 \rightarrow 2RH + 2H_2S \tag{2.3}$$

 $+ \; 4\,H_2 \longrightarrow CH_3(CH_2)_2CH_3 + H_2S$ (2.4)
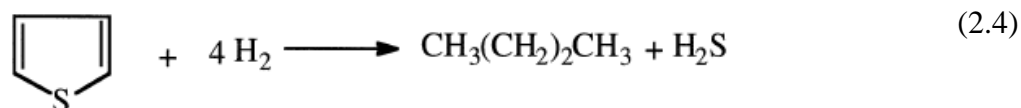
B. Denitrification: Nitrogen compounds in petroleum, are usually in the following forms and will be reduced to NH_3 in the course of hydrotreating (hydrodenitrogenation) process:

$$+ 4 H_2 \longrightarrow C_4H_{10} + NH_3 \qquad (2.5)$$

$$+ 3 H_2 \longrightarrow C_2H_5 \text{ (benzene ring)} + NH_3 \qquad (2.6)$$
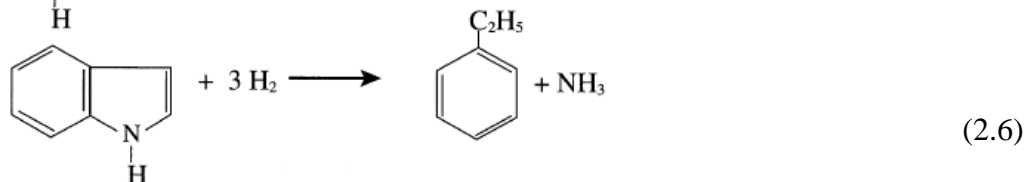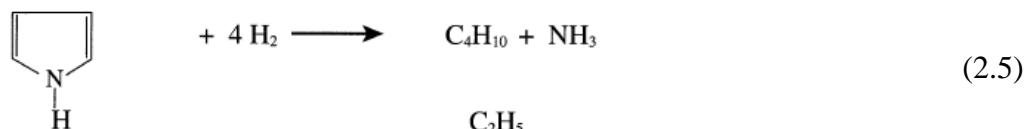
C. Hydrogenation of olefinic, diolefinic and alkenyl aromatics compounds: As mentioned above, these compounds are not originally present in crude oil but they are made in the course of separation and purification of separation processes in the refineries. The typical hydrogenation reactions are the following:

Oleffinic Compounds:
$$C_n H_{2n} + H_2 \rightarrow C_n H_{2n+2} \qquad (2.7)$$

Dioleffinic Compounds:
$$C_n H_{2n-2} + 2H_2 \rightarrow C_n H_{2n+2} \qquad (2.8)$$

Alkenyl Aromatics Compounds:
$$C_n H_n + H_2 \rightarrow C_n H_{n+2} \qquad (2.9)$$

The last two unsaturated compounds; i.e. chemical equations (2.8) and (2.9), are extremely unstable and subjected to polymerization in the presence of oxygen and at high temperature. Any monomers containing divinyl group or with functionality greater than 2, may cause branching or interconnection of a copolymer to produce large molecular weights under certain conditions similar to gel formation. In other words, gel or gum formation is carried out by polyfunction monomers[6]. Gums are very harmful for gasoline end users.

Hydrogenation reaction is an equilibrium reaction. The equilibrium is influenced by temperature and/or pressure.

Equilibrium composition is basically determined by thermodynamics at an infinite time. However, at a finite time the final composition of the reaction is calculated by kinetics. As it will

be discussed later, almost all of the reactions in industries take place at a limited time. In addition, even in the case of dealing with fast equilibrium reactions, we can shift the equilibrium to the desired direction according to the Le Chatelier's principle (see 2.3). Therefore, **almost in all of the industrial reactions, kinetics is predominant.**

According to Arrhenius equation, reaction (or in a sense, the conversion) rate is increased by increasing the temperature. For instance, in case of 1st order reaction, the reaction rate constant is generally increased by the temperature rise, which in turn influences the reaction (or conversion) rate:

$$k = A \exp (-E/RT) \tag{2.10}$$

$$-r_A = k\,C_A \tag{2.11}$$

where k is the rate constant, A is a pre-exponential term, R is the gas constant, T is temperature, r_A is rate of consumption of A, and C is the concentration of reactant A.

Hydrogenation is an exothermic reaction upon which the number of moles of products is less than that of reactants. As shown below, the production of aniline and cyclohexane from nitrobenzene and benzene, respectively, are good examples for this reaction[7]:

$$\tag{2.12}$$

$$\tag{2.13}$$
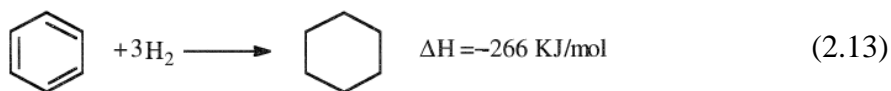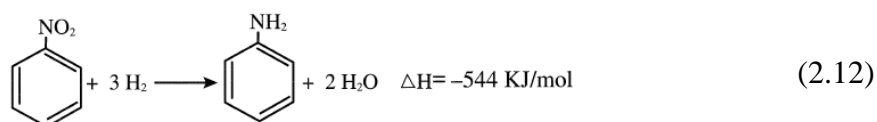
This is the fact that the decrease of the total number of moles in hydrogenation reaction causes a decrease in reaction volume. Frank and Stadelhofer[8] compared the hydrogenation of cyclohexene, 1, 3-cyclohexadiene, and benzene including their resonance energy (See Figure 2.1). They also concluded that this process is exothermic and resonance energy of benzene with its hypothetical 1, 3, 5-cyclohexatriene makes it more stable. Generally speaking, it can also be

concluded that species with two C=C double bonds, i. e. diolefins, are more unstable than those with mono C=C double bonds; i.e. olefins.
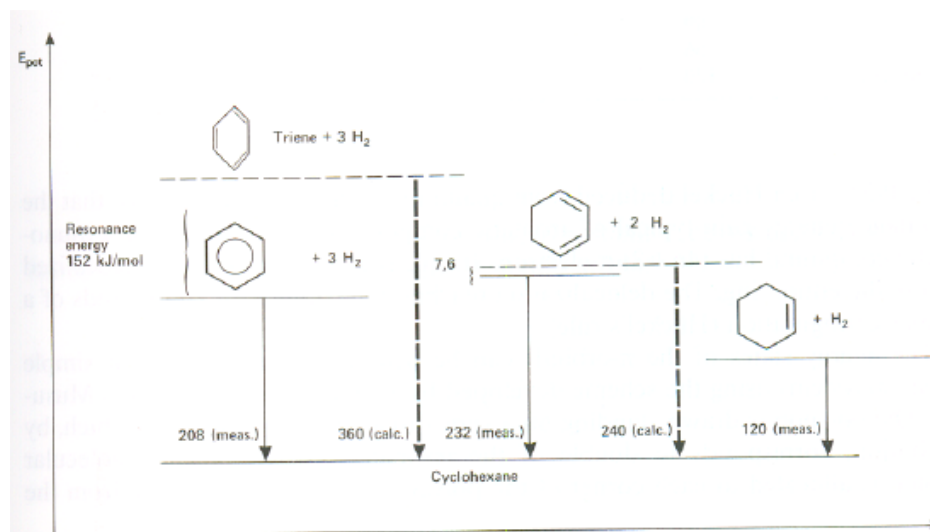
Figure 2.1 Energy diagram for the hydrogenation of benzene. Copied from Ref. 8.

On the other hand, the conversion rate of hydrogenation is affected by the hydrogen pressure and purity. Abraham and Chapman[7] performed a number of experiments to determine the effects of purity and inlet pressure of hydrogen on hydrogenation reaction of benzene to produce cyclohexane. As shown in Figure 2.2 the H_2 purity raises from 75 vol% to 100 vol% (pure hydrogen), the benzene content in the final product decreases, which means higher conversion since benzene is more consumed in the reaction. This is also the case for H_2/benzene ratio. For instance, at 100 vol% hydrogen, higher conversion (less content of benzene in final product) is achieved in 550 psig rather than 450 psig.

2.3 The Le Chatelier's principle

Recalling from general chemistry, the following expresses the Le Chatelier's principle:

"In an equilibrium reaction, the conversion rate increases when operating conditions are modified in a manner contrary to the natural trends of the reaction".
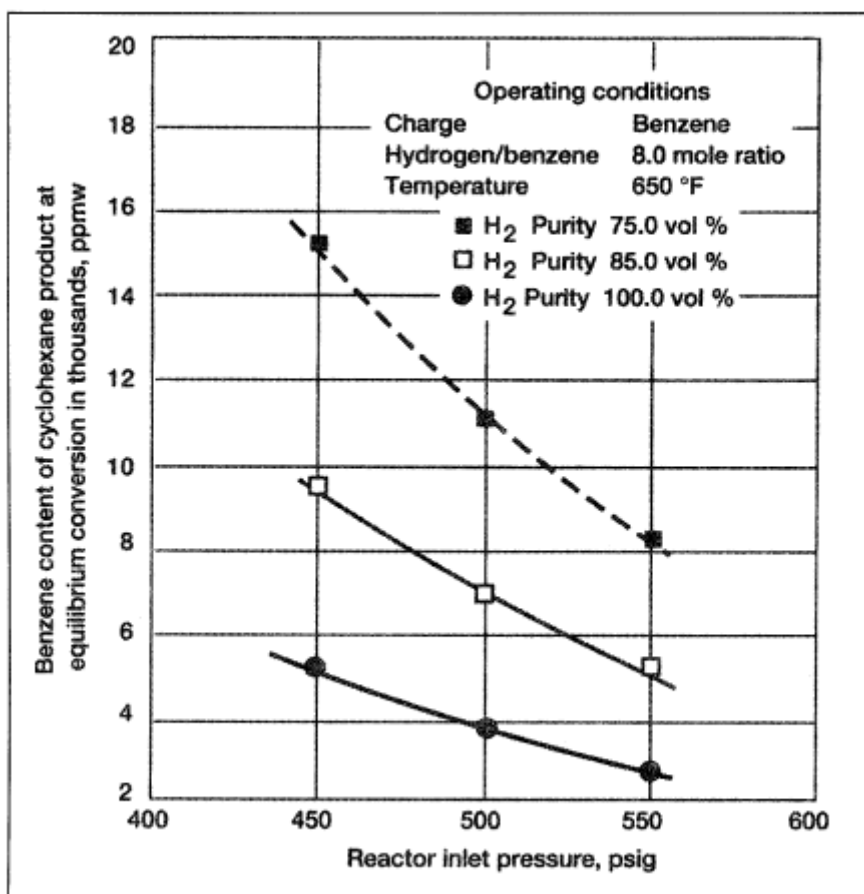
Figure 2.2 Effect of hydrogen purity and pressure on benzene hydrogenation to produce cyclohexane. Copied from Ref. 7.

Combining this principle with the aforementioned studies pertinent to the number of moles in the reaction, the pressure and temperature (enthalpy) of the reaction, and the nature of the equilibrium reaction, one may conclude the following:

1. In an exothermic reaction, in which the temperature increases continuously, the remedial action would be to decrease the reactor temperature.

2. When the number of the moles of reactants is less than the number of moles of products, the pressure will drop in gas phase reaction. Therefore, the pressure should be increased to gain a higher conversion.

3. In particular case; i.e. hydrogenation, the hydrogen content of the medium decreases as the hydrogen is consumed in the reaction. Thus, the hydrogen concentration (H_2 inlet pressure) should be increased.

4. In a hydrodesulfurization reaction, H_2S is produced (increasing the concentration). The proper action is therefore, to decrease the hydrogen sulfide concentration in the medium.

Consequently, the reaction rate is mainly affected by any of the following factors:

- Temperature

- Pressure

- The proportion of chemicals, i.e. the reactants and/or products.

2.4 Catalyst selection

The reaction rate also highly depends on the particular catalyst used for the reaction. Table 2.1, gives general information about the catalysts groups and functions for hydrogenation, hydrocracking reaction and so on in addition to the related examples[9].

Table 2.1 Classifications of solid catalysts. Adapted from Ref. 9.

Group	Function	Example
Metals	Hydrogenation, dehydrogenation, hydrogenolysis[*] (hydrocracking)	Fe, Ni, Pd, Pt, Ag

* Addition of hydrogen across a single bond to cause splitting into two molecules, e.g., $C_2H_6 + H_2 \rightarrow 2\ CH_4$.

Depending on the catalytic reaction type there are several reaction mechanisms, kinetics and reaction rates on the basis of existing theories. Langmuir is one of the scientists who offered invaluable theory in this regard. Table 2.2 lists some examples of Langmuir-Hinshelwood rate expression including reaction description, individual steps, reaction rates and constants[10].

For a typical catalytic hydrogenation, ethylene to ethane, see Appendix A. Also, for more details on reaction description, individual steps, reaction rates and constants, see Table 2.2 in previous page, which lists some examples of Langmuir-Hinshelwood rate expression.

For a detailed study of catalyst effects, catalyst selection and related kinetic data refer to Appendix B. The kinetic data resulted from the discussion will be applied to the reaction modeling and reactor design.

2.5 Typical hydrogenation plant

Figure 2.3 shows a schematic process flow diagram of a hydrotreating plant of Exxon Mobil Company[4], in which hydrogenation reaction is carried out in order to remove or decrease sulfur content to an acceptable standard level; i.e. hydrodesulfurization.
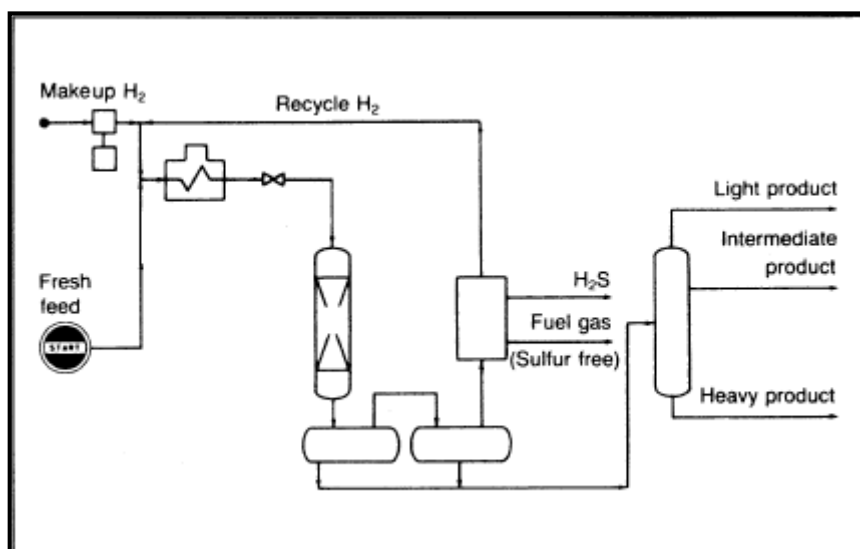
Figure 2.3 Flow diagram of an Exxon hydrotreating unit. Adapted from Ref. 4.

Table 2.2 Examples of Langmuir-Hinshelwood Rate Expression. Copied from Ref. 10.

Reaction Description	Individual Steps	Equation $(-r_A)$	Constants
(1) Isomerization: $A \rightleftharpoons B$	$A + S \rightleftharpoons A \cdot S$ $A \cdot S \rightleftharpoons B \cdot S$ $B \cdot S \rightleftharpoons B + S$	$-r_A = k_{s1}C_{AS} - k_{s2}C_{BS}$ $= \dfrac{k'_{s1}K_A C_A - k'_{s2}K_B C_B}{1 + K_A C_A + K_B C_B}$	$k'_{s1} = k_{s1}C_t$ $k'_{s2} = k_{s2}C_t$
(2) Decomposition: $A \rightleftharpoons B + C$	$A + S \rightleftharpoons A \cdot S$ $A \cdot S + S \rightleftharpoons B \cdot S + C \cdot S$ $B \cdot S \rightleftharpoons B + S$ $C \cdot S \rightleftharpoons C + S$	$-r_A = k_{s1}C_{AS}C_t - k_{s2}C_{BS}C_{CS}$ $= \dfrac{k'_{s1}K_A C_A - k'_{s2}K_B K_C C_B C_C}{(1 + K_A C_A + K_B C_B + K_C C_C)^2}$	$k'_{s1} = k_{s1}C_t$ $k'_{s2} = k_{s2}C_t$ $C_c = \dfrac{C_t}{(1 + K_A C_A + K_B C_B + K_C C_C)}$
(3) Bimolecular: $A + B \rightleftharpoons C + D$	$A + S \rightleftharpoons A \cdot S$ $B + S \rightleftharpoons B \cdot S$ $A \cdot S + B \cdot S \rightleftharpoons C \cdot S + D \cdot S$ $C \cdot S \rightleftharpoons C + S$ $D \cdot S \rightleftharpoons D + S$	$-r_A = k_{s1}C_{AS}C_{BS} - k_{s2}C_{CS}C_{DS}$ $= \dfrac{k_{s1}K_A K_B C_A C_B - k_{s2}K_C K_D C_C C_D}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2}$	$k'_{s1} = k_{s1}C_t$ $k'_{s2} = k_{s2}C_t$
(4) Bimolecular, different sites: $A + B \rightleftharpoons C + D$	$A + S_1 \rightleftharpoons A \cdot S_1$ $B + S_2 \rightleftharpoons B \cdot S_2$ $A \cdot S_1 + B \cdot S_2 \rightleftharpoons C \cdot S_1 + D \cdot S_2$ $C \cdot S_1 \rightleftharpoons C + S_1$ $D \cdot S_2 \rightleftharpoons D + S_2$	$-r_A = k_{s1}(C_{AS})_1(C_{BS})_2 - k_{s2}(C_{CS})_1(C_{DS})_2$ $= \dfrac{k'_{s1}(K_A)_1(K_B)_2 C_A C_B - k'_{s2}(K_C)_1(K_D)_2 C_C C_D}{[1 + (K_A)_1 C_A + (K_C)_1 C_C][1 + (K_B)_2 C_B + (K_D)_2 C_D]}$	$k'_{s1} = k_{s1}C_{t1}C_{t2}$ $k'_{s2} = k_{s2}C_{t1}C_{t2}$
(5) Bimolecular with dissociation of one reactant; $\frac{1}{2}A_2 + B \rightleftharpoons C + D$	$A_2 + 2S \rightleftharpoons 2A \cdot S$ $B + S \rightleftharpoons B \cdot S$ $A \cdot S + B \cdot S \rightleftharpoons C \cdot S + D \cdot S$ $C \cdot S \rightleftharpoons C + S$ $D \cdot S \rightleftharpoons D + S$	$-r_A = k_{s1}C_{AS}C_{BS} - k_{s2}C_{CS}C_{DS}$ $= \dfrac{k'_{s1}(K_A C_A)^{1/2}K_B C_B - k'_{s2}K_C C_C C_D}{[1 + (K_A C_A)^{1/2} + K_B C_B + K_C C_C + K_D C_D]^2}$	$k'_{s1} = k_{s1}C_t$ $k'_{s2} = k_{s2}C_t$
(6) Bimolecular with one reactant not adsorbed; $A(g) + B \rightleftharpoons C$	$B + S \rightleftharpoons B \cdot S$ $A(g) + B \cdot S \rightleftharpoons C \cdot S$ $C \cdot S \rightleftharpoons C + S$	$-r_A = k_{s1}C_{BS}C_A - k_{s2}C_{CS}$ $= \dfrac{k'_{s1}K_B C_B(C_A) - k'_{s2}K_C C_C}{1 + K_B C_B + K_C C_C}$	$k'_{s1} = k_{s1}C_t$

An "Upgrader Gas Oil Hydrotreater" plant, which is part of Oilfield Technical Society's website[11,] is shown in Figure 2.4. The related links can also be found on the website.
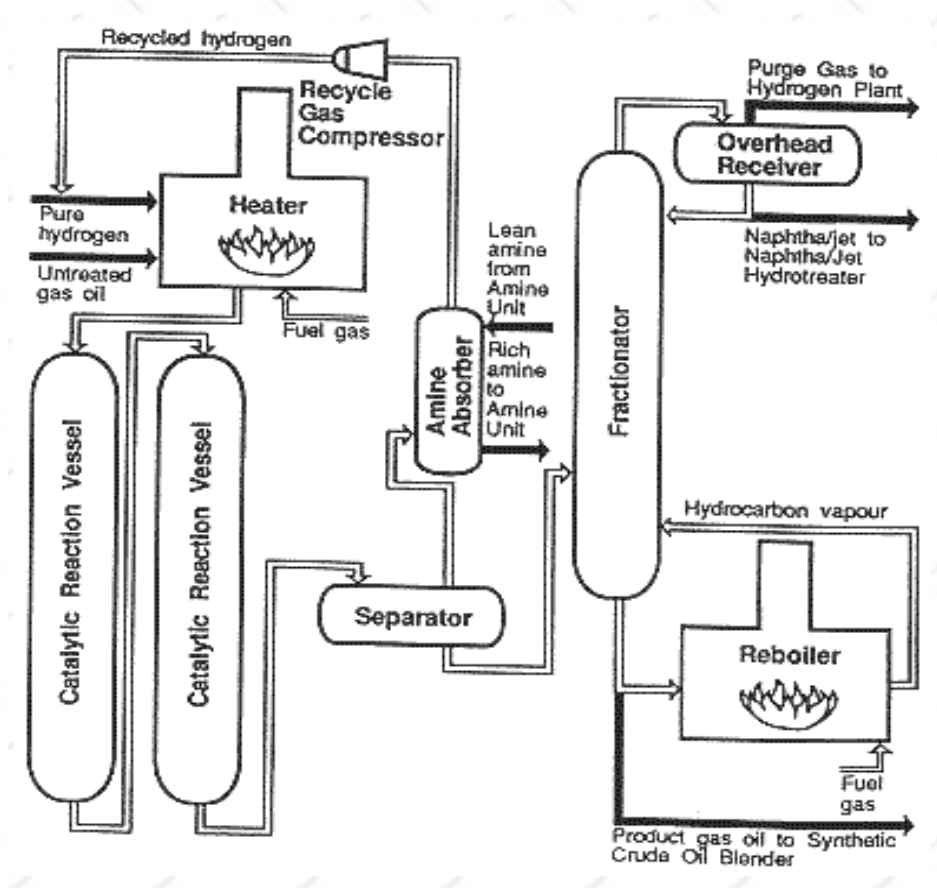
Figure 2.4 The block flow diagram of an upgrader gas hydrotreater. Adapted from Ref 11.

Another block flow diagram[12] can be found in Figure 2.5. The feed of this plant is pyrolysis gasoline. It contains a reactor and distillation columns.
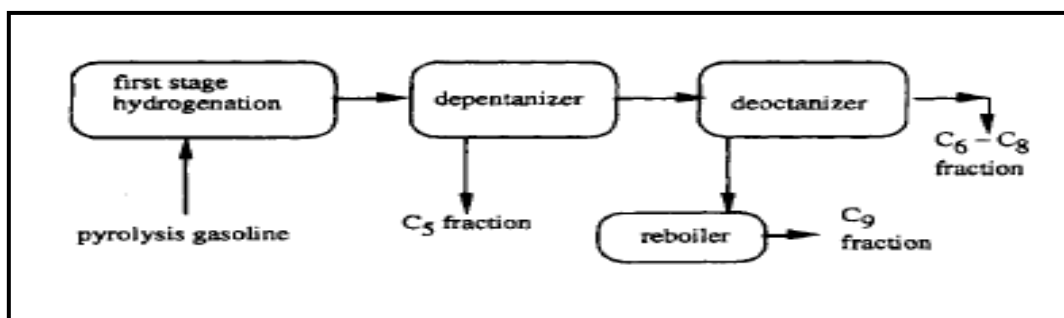
Figure 2.5 Block flow diagram of the selective hydrogenation of pyrolysis gasoline stabilization process. Adapted from Ref. 12.

2.6 Review on simulation on hydrogenation plants

Many researchers have issued papers with respect to computer aided simulation for designing a hydrogenation and hydrotreating as a part of an upgrader plant. There are similarities and differences between this thesis and their works as mentioned below.

A. Similarities:

1. Using the similar (but not exactly the same) mathematical equations for their modeling.

2. Using almost the same software applications for the modeling; e.g. MATLAB, Polymath, Aspen Plus, Aspen HYSYS, PRO II etc.

3. Using the similar process flow chart; but not the same, of course, for starting the modeling.

B. Differences:

1. Having different objectives of a simulation; e.g. only a reaction, or a sole reactor, or a complete plant etc.

2. Using different feedstock in terms of compositions.

3. Using different physical properties for the feedstock.

4. Using different thermodynamic property.

5. Using different operational conditions; e.g. temperature and pressure.

6. Using different catalysis.

7. Using different unit operations or different type of equipment; e.g. PBR reactor not CSTR or vertical phase separator not horizontal.

8. Producing different products depending on the process conditions and catalysis used.

9. Different states of simulation; e.g. steady-state simulation or dynamic.

C. Examples:

Below are some examples of the previous jobs of computer-aided simulation of hydrogenation reaction that are different from this thesis:

1. **Dynamic Modeling:** A mathematical and computational dynamic modeling is developed for the catalytic hydrogenation of pyrolysis gasoline in a trickle-bed reactor is performed by A. Arpornwichanop et al.[13]

2. **Dynamic Modeling:** Santana et al.[14] have studied a hybrid mathematical modeling for a three-phase hydrogenation reactor.

3. **Chiral Catalyst Effect:** Noyori et al.[15] have studied the effect of a chiral molecular catalyst as the most powerful way to produce enantio-enriched compounds. This phenomenon takes place in asymmetric hydrogenation reactions.

4. **Dynamic Modeling:** A simulation analysis of the impact of phase change on three-phase slurry reactor is dynamically performed by Mariano et al.[16,17]. A non-isothermal heterogeneous reactor containing Ni/SiO_2 catalysts was used for this dynamic modeling. They used HYSYS software and Fortran 90.

5. **Dynamic Simulation of Complex Chemical Processes:** A framework for dynamic simulation is performed for complex chemical processes by Oh and Moon from South Korean LG Engineering Co.[18].

6. **Upgrading a Petroleum Naphtha Fraction:** Butchanan et al.[19] have patented a naphtha upgrading process in a petroleum factory. They improved the conversion of hydrocarbons under severe conditions; i.e. at above 50 psig and 427 ^{o}C.

There are few companies that have license for their processes, which are not available in the open literatures.

7. **Modeling reactive Distillation:** A review study of combined reactor and distillation column is performed by Taylor and Krishna[20]. They have developed models that are used for design of such combined reactive distillation.

CHAPTER 3

MODELING OF A HYDROGENATION PLANT

3.1 Starting the modeling

This hydrogenation model contains 3 major steps: Hydrogenation Reaction, Phase Separation, and Purification. This is just a nomenclature and in reality as can be seen later some unit operations such as coolers are used in more than one step. Figure 3.1 shows the Block Flow Diagram (BFD) of the current design of hydrogenation upgrader process. There are 3 outlet streams from deiso-octanizers: overhead, side cut and bottom streams containing benzene, iso-octane rich solvent and mixed aromatics, respectively.
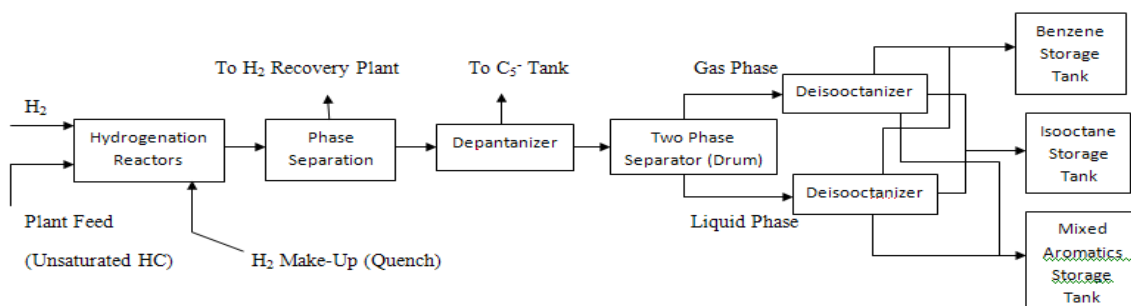
Figure 3.1 The Block flow diagram (BDF) of the present hydrogenation process.

3.2 Feed streams

There are two feed streamlines, which are received at plant battery limit (B.L.) at certain conditions and flow rates and introduced to the reactor after being mixed in a static mixer. The name, compositions and the status of each stream lines are in Table 3.1 and 3.2.

Table 3.1 The conditions of the feed stream lines at Battery Limit.

No.	Parameter	Plant Feed	H_2 Feed	H_2 Make-Up
1	Pressure (bar)	29	29	27
2	Temperature (^oC)	100	100	25
3	Mass Flow Rate (Kg/hr)	12,500	500	100

Table 3.2 The compositions of the feed streams at Battery Limit in wt%.

No.	Components	Hydrocarbon Feed Stream (wt %)	H$_2$ Feed Stream (wt %)	H$_2$ Make-Up Stream (wt %)
1	Iso-Butane	1.02	0	0
2	n-Butane	0.79	0	0
3	Iso-Pentane	0.96	0	0
4	n-Pentane	0.17	0	0
5	Iso-Butene	0.91	0	0
6	Iso-octene	10.92	0	0
7	Iso-octane	0	0	0
8	1-Butene	0.54	0	0
9	Styrene	15.53	0	0
10	Ethyl-Benzene	2.31	0	0
11	Benzene	48.01	0	0
12	Toluene	18.84	0	0
13	Hydrogen	0	100	100

As shown in Table 3.2, there are some unsaturated components containing C=C double bonds that are harmful for the hydrocarbon stream; e.g. in terms of storage due to capability of gum formation, the lack of octane no. etc.

Therefore, the unsaturated hydrocarbons are not desirable and have to be converted into saturated hydrocarbons by hydrogenation reaction to make high value products. This product will be subjected to stabilization in order to remove light hydrocarbons to produce more valuable products.

3.3 Reaction modeling by HYSYS

For the modeling of reactions, we need to define the reactions for the simulator first and then provide the thermodynamic and kinetic data according to the available and trustworthy information. A detailed survey has been made in open literature to find that information. More information is provided in APPENDIX B for this part of the present research. Table 3.3 shows five types of reactions that can be modeled in HYSYS.

Table 3.3 Five types of reactions that HYSYS can model. Adapted from Ref. 21.

Reaction Type	Requirements
Conversion	Requires the stoichiometry of all the reactions and the conversion of a base component in the reaction.
Equilibrium	Requires the stoichiometry of all the reactions. The term Ln (K) may be calculated using one of several different methods, as explained later. The reaction order for each component is determined from the stoichiometry coefficients.
Kinetics	Requires the stoichiometry of all the reactions as well as the Activation Energy and Frequency Factor in the Arrhenius equation for forward and reverse (optional) reactions. The forward and reverse orders of reaction for each component can be specified.
Heterogeneous Catalytic	Requires the kinetics terms of the Kinetics reaction as well as the Activation Energy, Frequency Factor and Component Exponent terms of the Adsorption kinetics.
Simple Rate	Requires the stoichiometry of all the reactions, as well as the Activation Energy and Frequency Factor in the Arrhenius equation for the forward reaction. The Equilibrium Expression constants are required for the reverse reaction.

The hydrogenation reaction kinetics follows Langmuir-Hinshelwood rate expression (APPENDIX A) and the reaction mechanism is dissociative type. Consider the following general reaction and compare it with hydrogenation reactions B-13 to B-16 in APPENDIX B.

$$aA + bB \rightarrow cP \tag{3-1}$$

where a, b and c are equal to 1 in this thesis.

"Heterogeneous Catalytic" reactions can be modeled by HYSYS[21] in accordance with Langmuir-Hinshelwood rate expression as mentioned in Table 2.2.

Due to the difficulty of determination of parameters of Langmuir-Hinshelwood and other rate expressions, many studies have been made by researchers on the hydrogenation reaction kinetics and therefore, some assumptions have been made to model the reaction as a kinetics reaction rather than equilibrium one and then proved the validity of the assumtions[22]. The following section is considered for modeling the reactions in HYSYS Simulation Basis Manager (SBM) based on the aforementioned equations.

3.4 Reaction section of hydrogenation plant

A. The reaction rate model:

As it is shown in APPENDIX B, equation (B-10) represents a "Kinetic" reaction rate model that fits to hydrogenation reactions of our unsaturated hydrocarbons and can be introduced to HYSYS. Therefore, we deal with the simplified 1st order reaction with respect to unsaturated reactants.

The equation (B-10) will be then modified as follows:

$$-r_A = k\, C_A\, (C_{H2})^{1/2}; \qquad where\ k = k\,(T)\ and \qquad\qquad (3-2)$$

$$k\,(T) = A\, T^{\beta} exp\,\{-E/RT\}; \qquad where\ 0 \leq \beta \leq 1 \qquad\qquad (3-3)$$

where r_A is the rate of consumption of species A, k is the rate constant, C_A is the concentration of the unsaturated species A and C_{H2} is the concentration of hydrogen gas.

When $\beta = 0$, we are dealing with Arrhenius equation, otherwise with collision theory ($\beta = 0.5$) and transition-state theory ($\beta = 1$).

Collision theory assumes that collision has low energy to precede the reaction and therefore, it is the limiting step. Whereas transition-state theory assumes that the collision energy is high

enough for reaction but the conversion of transition complex to the final product takes place very slow and therefore, it is the limiting step.

On the basis of the data provided in Table 3.4, the kinetics follows the Arrhenius's equation as mentioned in equation (B-17).

B. Chemical reactions in PFR:

The reactions of the equations (B-13) to (B-16) take place in our tubular reactor. Other data such as the frequency factors and activation energies of the above reactions can be found in Table 3.4.

Table 3.4 The kinetics data of hydrogenation reactions (1) to (4). Adapted from Refs. B.19, B.20, And B.27.

Reaction	**Reactant**	**k** [mol/(s)(kg cat)] $\times$ (m^3/mol)$^{3/2}$	**K** [mol/(h)(m^3)] $\times$ (m^3/mol)$^{3/2}$	**E** J / mol	**Reference No.**
(B-13)	1-Butene	1.482×10^{-5}	32.93	34,900	B-19
(B-14)	Iso-butene	2.0958×10^{-6}	4.66	39,100	B-19
(B-15)	Iso-octene	1.23×10^{-4}	273.68	10,506	B-20
(B-16)	Styrene	0.0415	9.23×10^4	26,030	B-27

C. Catalyst specifications

Hydrogenation catalyst was chosen so that it has to be selective, durable and produces the highest conversion. Fortunately, this catalyst for our purpose is commercially available. Palladium among other catalysts such as Co-Mo, NiO/MoO_3 and NiO/WO_3 has a good reputation for our reactions in industrial scales on the basis of the experimental investigations that are studied in APPENDIX B.

The selected catalyst has the following specifications[23]:

- Porosity = 0.5,

- Particle diameter = 4 mm,

- Tortuosity = 4,

- Bulk density = 618 Kg/m^3 (and therefore, solid density = 1236 Kg/m^3).

These data is slightly different from the typical values reported by Fogler[24]; i.e. 0.4 and 3 for porosity and tortuosity, respectively.

D. Reaction parameters

The operation conditions are determined by many references. Following is an example[4]:

- Temperature range from 260 ^{o}C to 425 ^{o}C.

- Total pressure from 100 psi to 3000 psi.

However, different and more practical reactor temperatures are also reported[12] as the following:

- Reactor SOR (Start of Reaction) inlet and outlet Temperature in ^{o}C: 60 and 140, respectively.

- Reactor EOR (End of Reaction) inlet and outlet Temperature: 120 and 180 ^{o}C, respectively.

- Reactor pressure in Kg/cm^2: 30.

The temperatures from 260 ^{o}C to 425 ^{o}C are considered to be severe conditions, which is suitable for tough compounds such as sulfur and nitrogen removal; e.g. reaction equations (2.1) to (2.6). Thus, the inlet feeds to the B.L. has a fairly mild conditions for our reactions as mentioned in Table 3.1.

$$R\text{-}SH + H_2 \rightarrow RH + H_2S \tag{2.1}$$

$$R\text{-}S\text{-}R + 2H_2 \rightarrow 2RH + H_2S \tag{2.2}$$

$$RS\text{-}SR + 3H_2 \rightarrow 2RH + 2H_2S \tag{2.3}$$

 $+ \ 4\,H_2 \longrightarrow CH_3(CH_2)_2CH_3 + H_2S$ (2.4)

$$\text{(pyrrole)} + 4\,H_2 \longrightarrow C_4H_{10} + NH_3 \qquad (2.5)$$

$$\text{(indole)} + 3\,H_2 \longrightarrow \text{(ethylbenzene, } C_2H_5) + NH_3 \qquad (2.6)$$
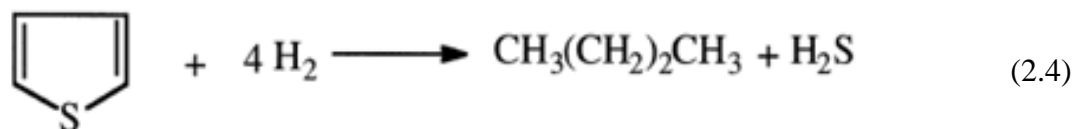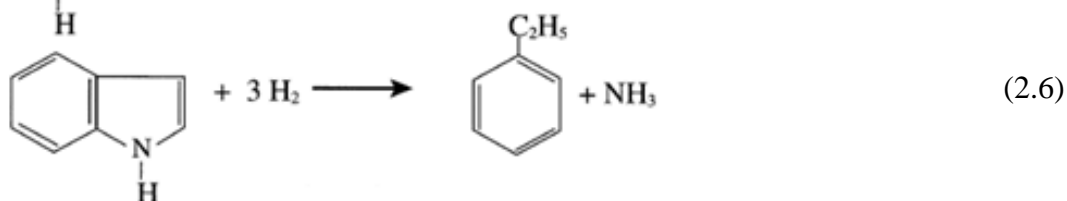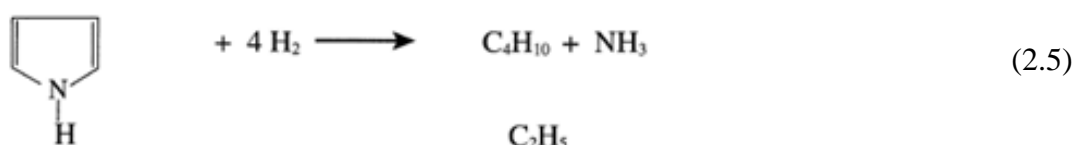
According to APPENDIX B, the hydrogenation of olefins and even diolefins takes place in mild conditions with fairly high conversion of unsaturated hydrocarbons.

However, some other conditions might also be wise to take into account. For instance, from the studies that led to Figure 2.2, the following results can be obtained:

- The more pure H_2 inlet gas is used, the higher conversion is achieved (less benzene in final product)

- The higher pressure at reactor inlet, the higher conversion will be achieved.

- The above mentioned results are achievable when H_2/Benzene ratio is equal to 8.0 for benzene hydrogenation.

Consequently, the higher hydrogen partial pressure and also the higher molar ratio of H_2/HC (here benzene) are, the higher conversion in the course of hydrogenation reaction will take place.

Moreover, the higher hydrogen partial pressure, the less coke deposits and similarly the less polymerization in the reactor. Therefore, in our modeling, the above mentioned factors are carefully followed with the exception that the H_2 to unsaturated ratio is about 7.3 since the reactants are unsaturated olefins, which need not to severe conditions as in desulfurization and in hydrogenation of aromatic rings.

E. Reactor modeling

For our kinetic reaction model, which is in fact a simplified catalytic equilibrium reaction, a plug reactor filled with palladium catalysis is modeled in this thesis.

Two types of plug flow reactors are currently used in industries: "Isothermal" and "Adiabatic".

In an "isothermal reactor", catalysis is filled inside the reactor and a cooling/heating fluid is flowing in the tubes of outer side of the reactor just like a shell and tube heat exchanger, while in an "adiabatic reactor", catalysis is filled as packing inside the reactor in one or more beds. In case of multi-bed reactor, cooling/heating operation is performed in between each bed.

In order to achieve a maximum mixedness of feed streams a mixer is used prior to the plug flow reactor. Since it is not possible to enter a material stream into the middle of the plug flow reactor in HYSYS, two reactors are designed in this research in order to introduce make-up hydrogen, which also acts as a quenching medium. Figures 3.2a, b and c show the conditions and compositions of the First Hydrogenation Reactor inlet stream.

Stream Name	Hydrogenation Rea	Vapour Phase	Liquid Phase
Vapour / Phase Fraction	0.6605	0.6605	0.3395
Temperature [C]	88.21	88.21	88.21
Pressure [kPa]	2901	2901	2901
Molar Flow [kgmole/h]	393.0	259.6	133.4
Mass Flow [kg/h]	1.300e+004	1520	1.148e+004
Std Ideal Liq Vol Flow [m3/h]	21.95	8.431	13.51
Molar Enthalpy [kJ/kgmole]	1.424e+004	2802	3.649e+004
Molar Entropy [kJ/kgmole-C]	74.31	99.79	24.73
Heat Flow [kJ/h]	5.596e+006	7.274e+005	4.869e+006
Liq Vol Flow @Std Cond [m3/h]	<empty>	<empty>	13.41
Fluid Package	Basis-1		

(a)

	Molar Flows
i-Butane	2.1883
n-Butane	1.6922
i-Pentane	1.6630
n-Pentane	0.29176
i-Butene	2.0277
224-Mpentane	0.00000
244M2pentene	12.167
1-Butene	1.2108
Styrene	18.644
E-Benzene	2.7134
Benzene	76.837
Toluene	25.559
Hydrogen	248.02
Total	393.00888 kgmole/h

	Mole Fractions
i-Butane	0.005568
n-Butane	0.004306
i-Pentane	0.004232
n-Pentane	0.000742
i-Butene	0.005159
224-Mpentane	0.000000
244M2pentene	0.030958
1-Butene	0.003081
Styrene	0.047439
E-Benzene	0.006904
Benzene	0.195508
Toluene	0.065033
Hydrogen	0.631069

(b)   (c)

Figure 3.2 The mixed stream resulted from HC and H_2 feed streams (Table 3.2). (a) Conditions, (b) Compositions in molar flow, (c) Compositions in mole fractions.

F. Tubular reactor (PFR) sizing

Having had the compositions, conditions and the properties of feed stream and the outlet temperature and pressure, in addition to the design equation of PFR etc. we sized the Plug Flow Reactor manually and by using POLYMATH software. Other applications such as MATLAB will also be useful.

The maximum volume is found to be for the hydrogenation of Iso-Butene, i.e. 3.19 m^3. But this is the volume of the catalyst whose porosity and bulk density are 0.5 and 618 Kg/m^3, respectively. Therefore, the volume of the reactor would be around 6.38 m^3. For a detailed analysis refer to APPENDIX D.

A quick and also appropriate way to size the reactor is using the best space velocity for the hydrogenation reactor.

Generally, the space velocity is the reciprocal of the space time (τ), which in turn is equal to:

$$\tau = V/v_0 \tag{3-4}$$

where V is the volume of the reactor and v_0 is the volumetric feed flow rate to the reactor by definition[25]. Similarly, the space velocity is defined as the volumetric flow rate of reactant streams at the reference conditions:

$$SV = 1 / \tau \tag{3-5}$$

Space time and the volumetric flow rate are measured at the entrance conditions, whereas the space velocity (SV) is measured, as stated in reference conditions.

There are two types of space velocity, which are commonly used in industries: LHSV and GHSV:

LHSV or liquid-hourly space velocity is the liquid volumetric feed rate (v_0) measured at 60 ^{o}F or 70 ^{o}F, although the feed stream may be a vapor at a higher temperature. But in GHSV the v_0 is measured at standard temperature and pressure (STP)[26].

Lin and Chou[12] reported the best LHSV for the hydrogenation of pyrolysis gasoline to be 3.5 h^{-1}. In this regard, the standard volumetric liquid flow rate of the feed stream to the reactor is equal to 21.95 m^3/h. Combining the equations (3-4) and (3-5) gives:

$$SV = v_0 / V \qquad \qquad (3\text{-}6)$$

Or

$$V = v_0 / SV \qquad \qquad (3\text{-}7)$$

Thus,

$$V = 21.95 / 3.5 = 6.27 \text{ m}^3.$$

It is close enough to 6.38 m^3 that is found from POLYMATH for the hydrogenation of Iso-Butene. Moreover, it looks to be more practical. So, we consider it as our PFR volume. For a detailed study, please refer to APPENDIX D

However, in order to control the temperature without using a cooling system, i.e. heat exchanger, we consider two reactors with 3.5 m^3 of volume each and then insert the make-up hydrogen at ambient temperature to the second reactor in order for the reaction to yield higher saturated hydrocarbons and to quench the products of the first reactor at the entrance of the second hydrogenation reactor. Figure 3.3 shows the arrangement of the streams and the PFR reactors.

It is important to keep in mind that the "rate of reaction" and the "residence time" or "space velocity" are established in laboratory and in pilot plant, respectively[27].
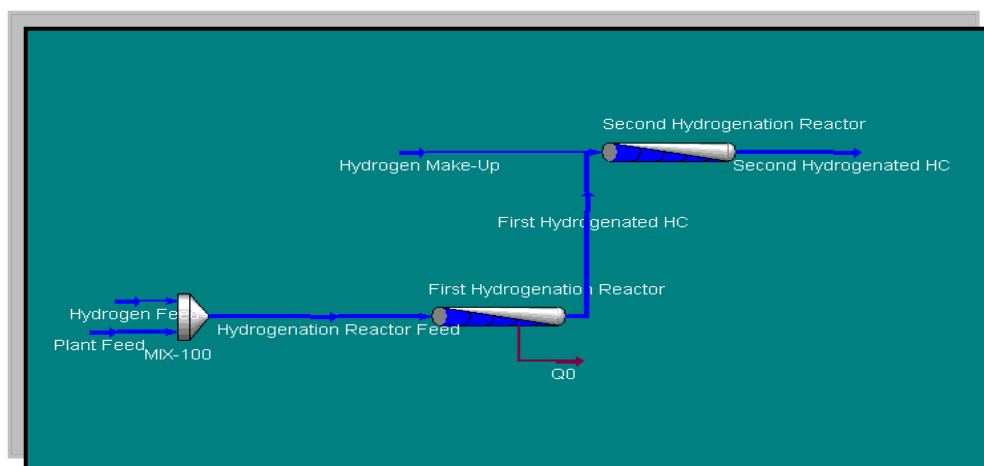
Figure 3.3 The feed streams and PFR arrangement for the Hydrogenation plant.

This arrangement is a typical way to show graphically a multi-bed tubular reactor by HYSYS. This arrangement is not necessarily applicable in industries; instead there are different arrangements for multi-bed reactors depending on the reaction type, heat produced or consumed and other factors. Figure 3.4 show these arrangements[28].

In the system like Figure 3.4e the cooling is carried out by an external heat exchanger (cooler). Our tubular reactor is very close to the one shown in Figure 3.4b. Its difference with Figure 3.4e system is that the cooling in our system takes place by direct injection of Hydrogen Make-Up stream line, which is called quenching operation.
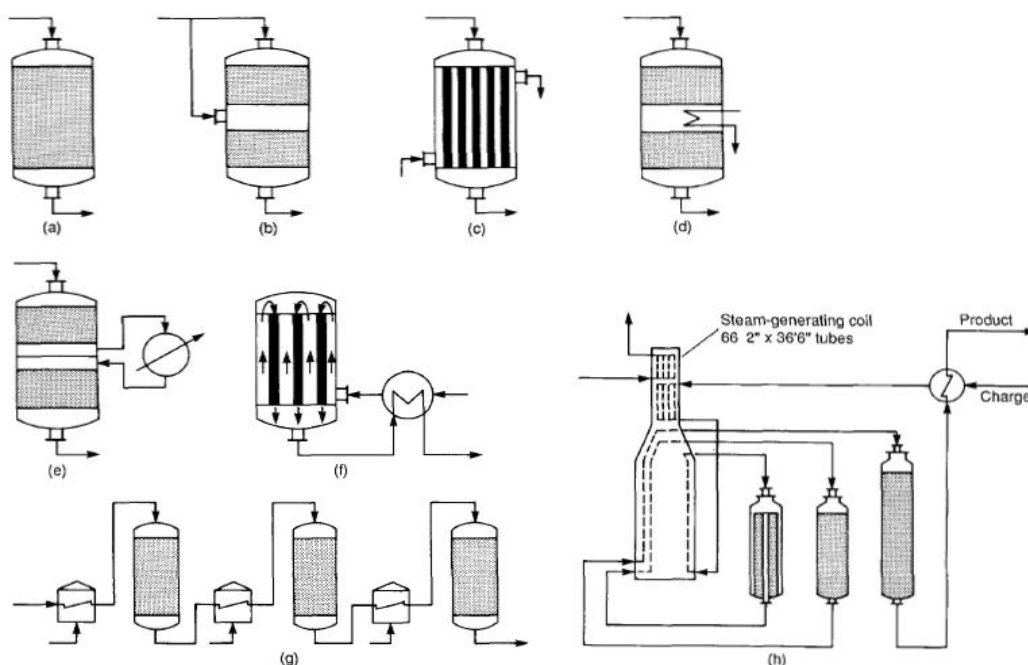
Figure 3.4 Multibed catalytic reactors: (a) adiabatic; (b) interbed coldshot injection; (c) shell and tube; (d) built-in interbed heat exchanger; (e) external interbed exchanger; (f) autothermal shell, outside influent-effluent heat exchanger; (g) multishell adiabatic reactor with interstage fired heaters; (h) platinum-catalyst, fixed bed reformer for 5000 bpsd charge rate; reactors 1 and 2 are 5.5 ft dia by 9.5 ft high and reactor 3 is 6.5 × 12.0 ft.   Copied from Ref. 28

G. PFR modeling results and analyses

Figures 3.5a and b show the conditions and compositions of the First Hydrogenation Reactor outlet stream, respectively, which is called First Hydrogenated HC (Hydrocarbons). This product line is a two-phase flow stream and introduced to the Second Hydrogenated HC in order to get higher conversions of unsaturated hydrocarbons.

Figures 3.6a and 3.6b also show the conditions and compositions of the Second Hydrogenation Reactor outlet stream, which is called Second Hydrogenated HC (Hydrocarbons).

In this step, it would be a good idea to calculate the conversion factor after the Second Hydrogenation Reactor with comparison to the First Hydrogenation Reactor Feed. The total remaining number of moles of reactant is calculated by equation (3-8):

$$N = N_o - N_o x = N_o (1-x) \tag{3-8}$$

Or

$$x = 1 - N / N_o \tag{3-9}$$

(a)

(b)

Figure 3.5 The 1st Hydrogenation Reactor outlet stream. (a) Conditions, (b) Compositions.

(a)

(b)

Figure 3.6 The two-phase outlet stream from the 2nd Hydrogenation Reactor. (a) Conditions, (b) Compositions.

The reactants are 1-Butene, Iso-Butene, Iso-octane and Styrene. The total conversion of each reactant is given in following list.

Table 3.5 Total conversion of unsaturated HC's after Second Hydrogenation Reactor.

Reactant	1-Butene	Iso-Butene	Iso-octene	Styrene
Total Conversion, x	0.108	6.95×10^{-3}	1.00	1.00

The reactions overall information including "Integration Information" and "Catalyst Data" in the both tubular reactors can be found from Figures 3.7 and 3.8.

The Reaction Set is defined for HYSYS in SBM window, "Reaction" tab according to reactions (B-13) through (B-16) and in this page all we need to do is to click on the drop down list and select "Global Rxn Set". The other data is gathered from the research papers that have been mentioned earlier in this chapter; e.g. particle size, bulk density, porosity etc.

In the Number of Segment box, the reactor is divided into the given number by user, here 30 segments, to make the integration calculations in 30 steps by software. This number gives a fairly accurate result for a 3.5 m^3 volume PFR without doing lots of calculations.
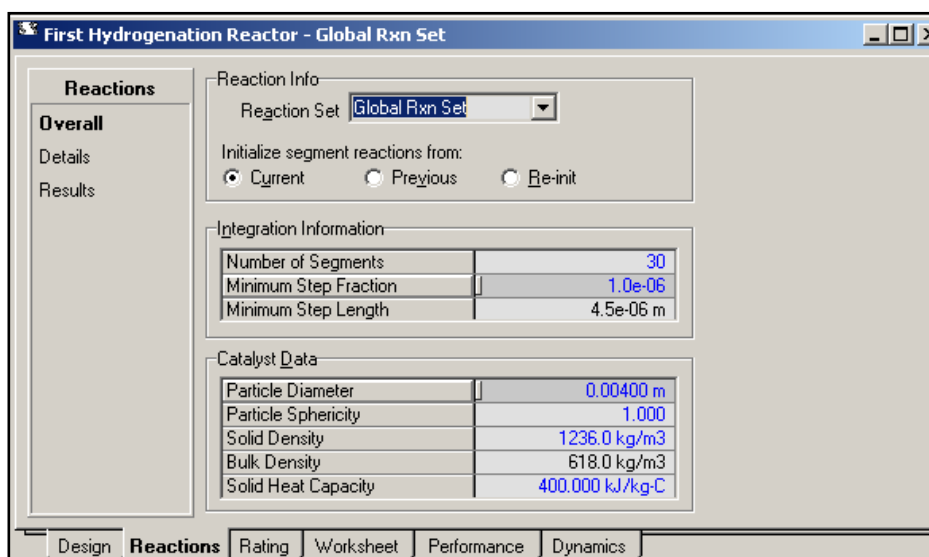
Figure 3.7 Reaction Overall Information page of the 1st Hydrogenation Reactor.

In the Number of Segment box, the reactor is divided into the given number by user, here 30 segments, to make the integration calculations in 30 steps by software. This number gives a fairly accurate result for a 3.5 m^3 volume PFR without doing lots of calculations. Minimum Step Fraction is a default value made by HYSYS and we let it be and Minimum Step Length will be calculated by software on the basis of the given data in Integration Information part by user. As such, the default value of "Solid Heat Capacity" is left as it is.

Sizing the reactor is carried out in Rating tab of the reactor property page and by clicking on the Sizing option. Reactor diameter is considered to be 82 cm (about 32 in.) because firstly, the L/D

ratio for such volume is about 8, which is good enough to fill and discharge the catalyst inside the reactor conveniently. And secondly, the reactor would be less expensive with higher safety factor due to using a seamless pipe for manufacturing it. The void fraction is also obtained from the papers. The length of the reactor is calculated by HYSYS. Wall thickness is left as in default form. Figure 3.8 shows the input data for sizing the tubular reactor.
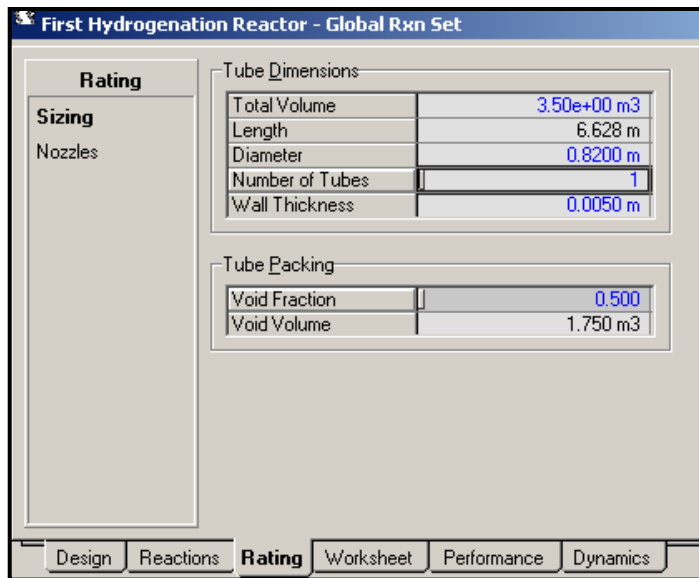
Figure 3.8 The input data for Sizing the 1st and the 2nd Hydrogenation Reactors.

Figures 3.9a and b show the molar flow rate changes of Iso-octane and Styrene along the reactor length, respectively.
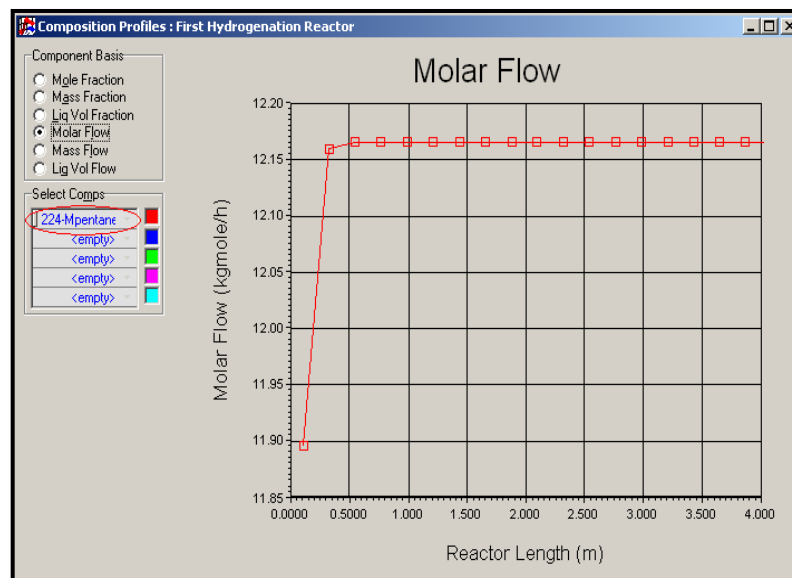
(a)
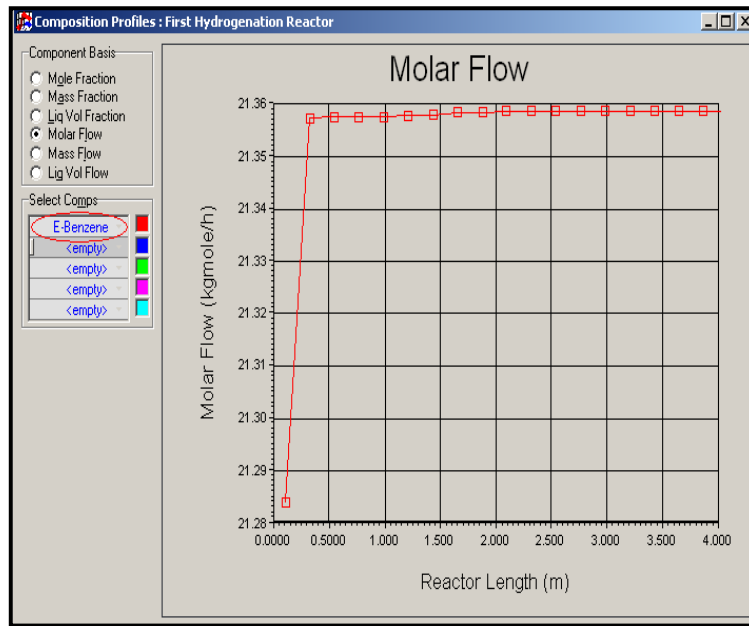
(b)

Figure 3.9 Changes in the Molar Flow rate of (a) Iso-octane (244-Methyl Pentane) and (b) Ethyl Benzene in First Hydrogenation Reactor.

Figures 3.10a and b show the molar flow rate changes of n-Butane and Iso-Butane along the reactor length, respectively.
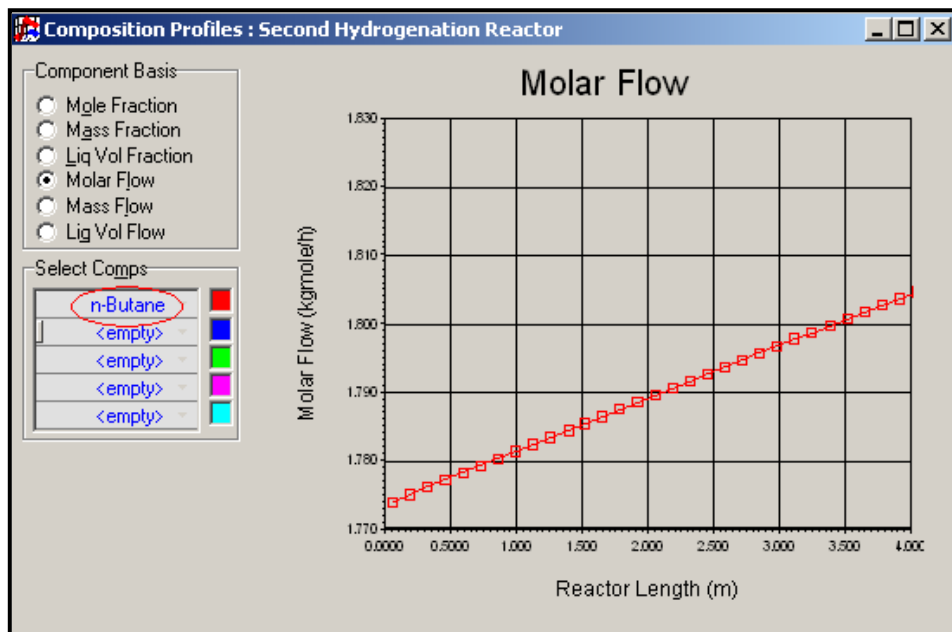
(a)
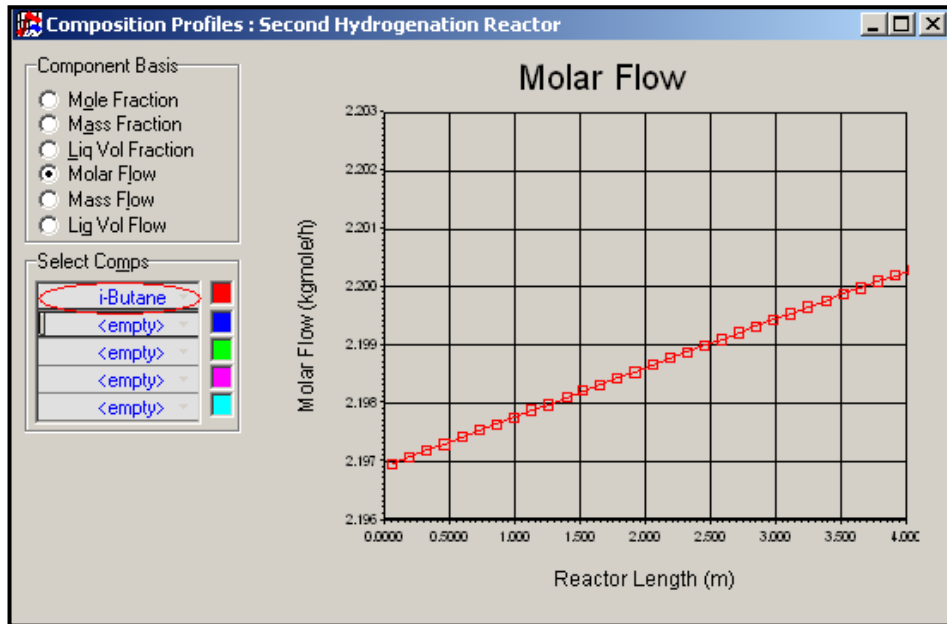
(b)

Figure 3.10 Changes in the Molar Flow rate of (a) n-Butane and (b) Iso-Butane in Second Hydrogenation Reactor.

3.5 Cooling and separation section of hydrogenation plant
A. The modeling of cooling heat exchangers

From the 1st and the 2nd Hydrogenated HC's conditions (Figs. 3.5a and 3.6a), it can be seen that the majority of the streams contain vapor phase (0.8114), which is to be separated by gas-liquid (phase) separator. However, it is wise to cool down the 2nd Hydrogenated HC stream to get higher liquid prior to send it to drum separator in order to isolate HC from hydrogen.

In this regard, three cooling steps including an air cooler are considered:

1. First Step Pre-Cooler: It is a shell and tube heat exchanger, drops the temperature by almost 20 ^{o}C from 150.4 ^{o}C to 130.5 ^{o}C resulting in dropping the vapor fraction from 0.8114 down to 0.7527 consuming 1.232×10^6 Btu/h. See Figures 3.11a and b.

    Pressure drop about 50 kPa, for a high vapor fraction stream, seems to be true on the basis of literatures. For instance, for liquid service, ΔP= 5-10 psi is a minimum requirement[27, 29].
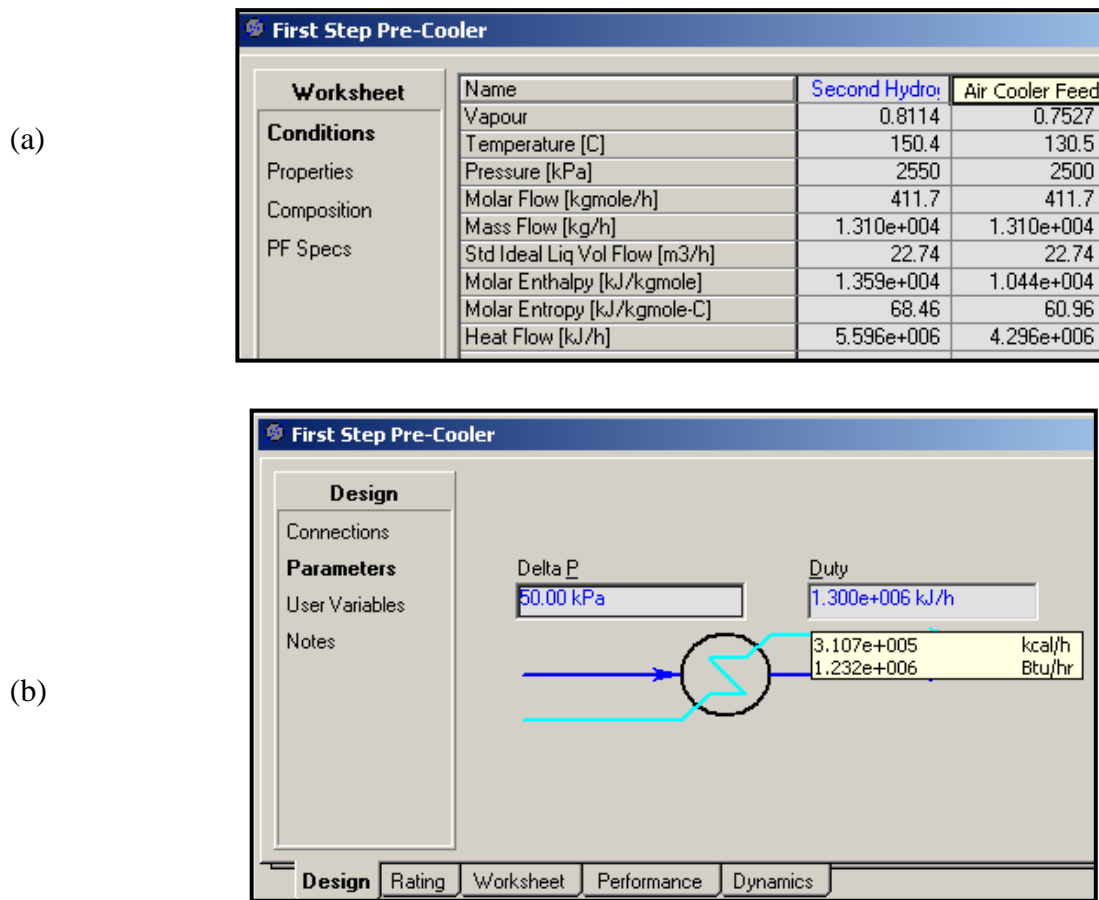
Figure 3.11 (a) Conditions of inlet stream to and outlet stream from First Step Pre-Cooler. (b) Duty of the First Step Pre-Cooler.

2. Air cooler: This type of cooler uses air at ambient temperature as coolant to remove the heat from the fluid passing through the tubes inside the cooler. The air flow then, passes perpendicular to the finned tubes, which improves heat transfer by increasing the substantial heat transfer surfaces.

All costs including capital, operating and maintenance costs plus required spaces are very important to be questioned and investigated in advance to selection of an air cooler. The list on next page fairly answers to these questions depending on the location and facilities of a plant; e.g. climatic condition, water resources etc. This table enumerates the advantages and disadvantages of such system[30].

Table 3.6 Advantages and disadvantages of air-cooler heat exchangers. Adapted from Ref. 30.

Advantages
Since the water is not used as cooling medium, the disadvantages of using water are eliminated.
Eliminates high cost of water including expenses of treating water.
Thermal or chemical pollution of water resources is avoided.
Installation is simplified due to elimination of coolant water piping.
Location of the air-cooled heat exchangers is independent of water supply location.
Maintenance may be reduced due to elimination of water fouling characteristics which could require frequent cleaning of water cooled heat exchangers.
Air-cooled heat exchangers will continue to operate (but at reduced capacity) due to radiation and natural convection air circulation should a power failure occur.
Temperature control of the process fluid may be accomplished easily through the use of shutters, variable pitch fan blades, variable speed drives, or, in multiple fan installations, by shutting off fans as required.
Disadvantages
Since air has relatively poor thermal transport properties when compared to water, the air-cooled heat exchanger could have considerably more heat transfer surface area. A large space requirement may result.
Approach temperature differences between the outlet process fluid temperature and the ambient air temperature are greatly in the range of 10 ^{o}K to 15 ^{o}K. Normally, water cooled heat exchangers can be designed for closer approaches of 5 ^{o}K. Of course, closer approaches for air-cooled heat exchangers can be designed, but generally these are not justified on an economic basis.
Outdoor operation in cold winter environments may require special consideration to prevent freezing of the tube side fluid or formation of ice on the outside surface.
The movement of large volumes air is accomplished by the rotation of large diameter fan blades rotating at high speeds. As a result, noise due to air turbulence and high fan tip speed is generated.

Technical data for air-cooler tube size, fans, power consumptions etc. can be found in reference 29.

The result of our modeling of air cooler is found in Figures 3.12a and b.

(a)

(b)

(c)

Figure 3.12 (a) The conditions of the fluids before and after the air-cooler. (b) Design parameters of the air-cooler including the pressure drop HC and overall UA. (c) The performance results for designing the air-cooler.

3. After Cooler: It is a shell and tube heat exchanger similar to First Step Pre-Cooler. Therefore, the same discussion as for the air cooler is applicable here. Figures 3.13a and b show the result of modeling of this cooler.

(a)

Name	Second Cooler	To FirstSep
Vapour	0.6754	0.6586
Temperature [C]	78.34	48.48
Pressure [kPa]	2475	2455
Molar Flow [kgmole/h]	411.7	411.7
Mass Flow [kg/h]	1.310e+004	1.310e+004
Std Ideal Liq Vol Flow [m3/h]	22.74	22.74
Molar Enthalpy [kJ/kgmole]	4230	1558
Molar Entropy [kJ/kgmole-C]	44.64	36.75
Heat Flow [kJ/h]	1.741e+006	6.415e+005

Worksheet — Conditions, Properties, Composition, PF Specs

(b)

After Cooler — Design

Connections, Parameters, User Variables, Notes

Delta P: 20.00 kPa
Duty: 1.100e+006 kJ/h
2.629e+005 kcal/h
1.043e+006 Btu/hr

Design | Rating | Worksheet | Performance | Dynamics
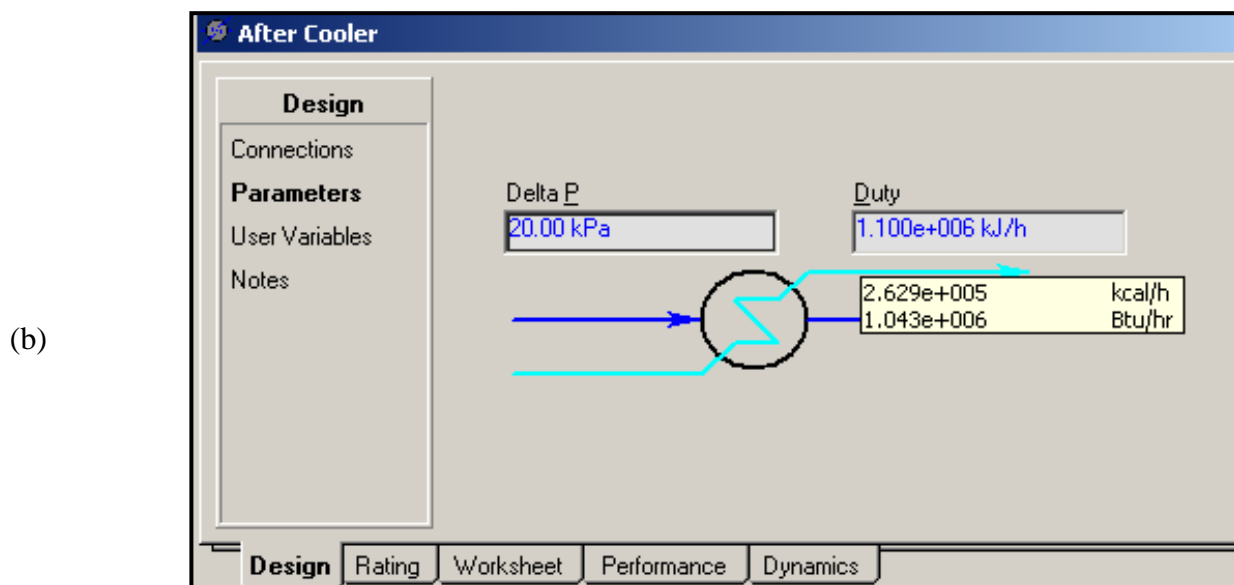
Figure 3.13 (a) Conditions of inlet stream to and outlet stream from After Cooler. (b) Duty of the After Cooler.

If we reconsider the cooling operation now, comparing the Second Hydrogenated HC stream and the outlet stream from After Cooler called To FirstSep stream, we will see that the liquid flow rate is increased significantly. In the former stream the mass flow rate of gas and liquid portions are 6245 Kg/h and 6855 Kg/h, respectively, while in the latter stream the mass flow rate of gas and liquid portions are 958.6 Kg/h and 12,140 Kg/h, respectively, which is acceptable.

B. Two-phase separator modeling

We are concerned with a two-phase flow and need to do a phase separation. The vital conditions under which fluid phases tend to be separated are "difference in phase densities" and "phase immiscibility"[31].

We will use "separator" equipment or more common used words, Gas-Liquid Separator, in this step of process design. In this equipment, liquid droplets are influenced by two different forces in two different directions: Drag force caused by gas upward movement and the gravity force caused by gravitational acceleration. Figure 3.14 illustrates both types of forces.
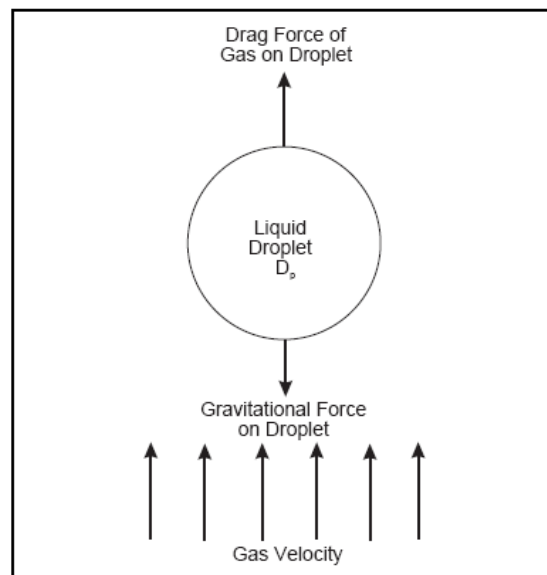
Figure 3.14 Forces on liquid in gas stream. Adapted from Ref. 31.

In this type of phase separator, the maximum gas velocity is important to be calculated first. The standard equation with the relevant graph is given below[32] to find the value of constant K:

$$U_{\text{Vapor max}} = K \left[(\rho_L - \rho_V) / \rho_V \right]^{0.5} \tag{3-10}$$

Where U = Velocity (ft/sec), ρ = Density of gas or liquid (lbs/ft^3), K = System constant, K_H and K_V are considered for the vertical and horizontal separator, respectively. Figure 3.15 and following descriptions explain how to design the gas velocity factor at 85% of flooding, which is a typical value. Other curves with different flooding values are also available.
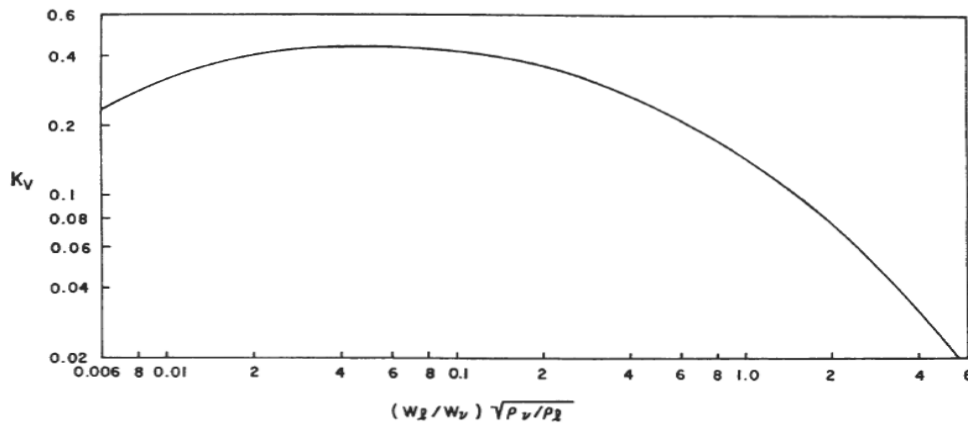
Figure 3.15 Designing the gas velocity factor for vertical gas-liquid drum. Adopted from Ref. 32.

where W_l and W_v are the mass flow rates of liquid and vapor in lb/sec, respectively.

This factor is applicable for vertical separator drums; however, the following equation relates K_H and K_V:

$$K_H = 1.25 \, K_V \tag{3-11}$$

$$W_L / W_V \, (\rho_V / \rho_L)^{0.5} \tag{3-12}$$

A separator drum, which usually handles a large quantity of liquid and/or receives a mixture of hydrocarbons containing water or functions as a surge drum, is usually horizontal. On the other hand, when the gas to liquid ratio is high or the gas volume is low or the drum functions as a compressor knock-out drum, a vertical drum is advisable.

C. Sizing of vertical drum separator and analyses

A two-phase flow enters into the drum and is separated into gas or vapor and liquid flows. Figures 3.17a and b also show typical vertical and horizontal drums, respectively[33].

(a)   (b)
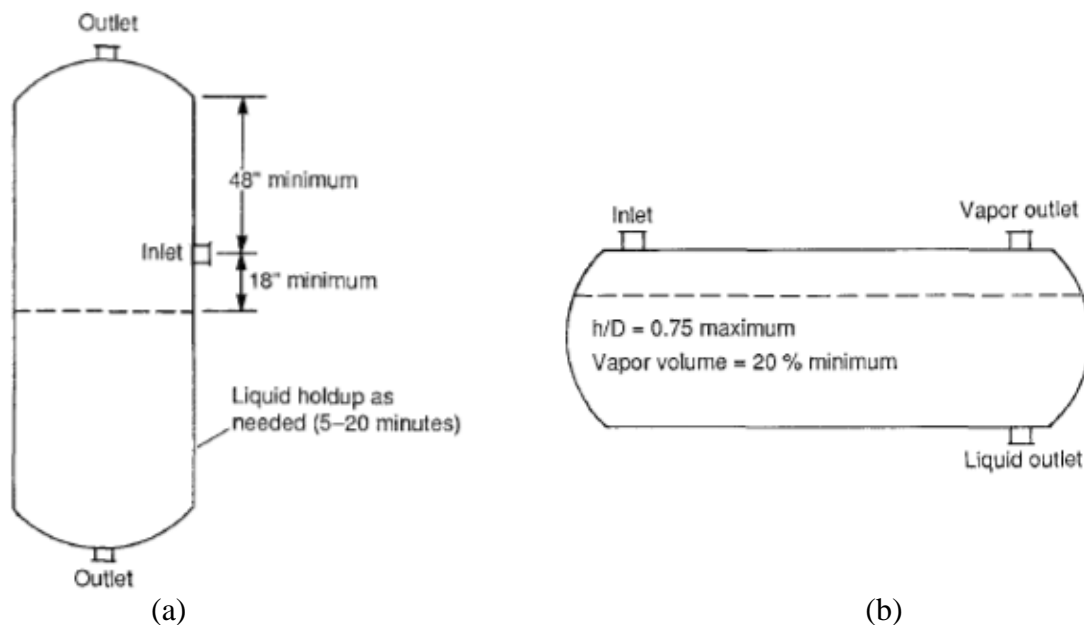
Figure 3.16 Key dimensions for a **(a)** Vertical knock-out drum (Liquid holdup between 5-20 minutes). **(b)** Horizontal knock-out drum. Adapted from Ref. 33.

Referring to equation (3-10) and Figure 3.16, we need to know the properties of the "To FirstSep" stream in order to make calculations for sizing the drum. Fortunately, HYSYS has provided the flow properties as it can be seen in Figure 3.17.

Stream Name	To FirstSep	Vapour Phase	Liquid Phase
Molecular Weight	31.82	3.535	86.40
Molar Density [kgmole/m3]	1.317	0.9108	9.425
Mass Density [kg/m3]	41.91	3.220	814.3
Act. Volume Flow [m3/h]	312.6	297.7	14.91
Mass Enthalpy [kJ/kg]	48.97	85.06	46.12
Mass Entropy [kJ/kg-C]	1.155	27.84	-0.9519
Heat Capacity [kJ/kgmole-C]	71.17	30.33	150.0
Mass Heat Capacity [kJ/kg-C]	2.236	8.578	1.736
Lower Heating Value [kJ/kgmole]	1.422e+006	3.037e+005	3.579e+006
Mass Lower Heating Value [kJ/kg]	4.468e+004	8.591e+004	4.143e+004
Phase Fraction [Vol. Basis]	0.3625	0.3625	0.6375
Phase Fraction [Mass Basis]	7.317e-002	7.317e-002	0.9268

Figure 3.17 The properties of the stream "To FirstSep" provided by HYSYS simulator.

Another way, which is more practical and general and therefore more applicable, is to calculate the liquid hold-up time in the vessel (drum) and then relate the calculated volume to the drum height and diameter having L/D ratio and liquid volumetric flow rate, then to size the liquid section of the drum. The similar calculations should be done for vapor phase and finally to add up both liquid and vapor volumes and heights to size a two-phase separator drum.

Liquid hold-up (residence) time for half full drum varies from 5-20 minutes as shown in Figure 3.16a[33], 5-10 minutes is also reported[26]. Thus, we opt 10 minutes as the residence time of the liquid for half full drum based on the company experience. We use also Figure 3.16 for other data such as Q_L.

$$V_L = Q_L \times t \tag{3-13}$$

$$V_L = 526.54 \text{ ft}^3/ \text{h} \times 1 \text{ h} / 60 \text{ mins} \times 10 \text{ mins} = 87.757 \text{ ft}^3 = 2.485 \text{ m}^3$$

$$V_L = A_L \times L_L \rightarrow V_L = (\pi \times D^2_L) \times L_L / 4 \tag{3-14}$$

But the L/D ratio is reported[32] to be equal to 4 for the pressure range from 251-500 psig per following table.

Table 3.7 Rough estimations for dependency of height to diameter ratio in a drum to inlet pressure. Adopted from Ref. 32.

P (psig)	0-250	251-500	501$^+$
L/D	3	4	5

Therefore, for our inlet pressure 2455 kPa (356.1 psia):

$$L_L / D_L = 4 \rightarrow L_L = 4 \times D_L \tag{3-15}$$

Combining equations (3-14) and (3-15) and rearrangement for D_L gives:

$$D_L = [(4 \times V_L) / (4 \times \pi)]^{1/3} = (V_L / \pi)^{1/3} \tag{3-16}$$

Thus; $D_L = (2.485 / \pi)^{1/3} = 0.925$ m

$L_L = 4 \times D_L$ ➔ $L_L = 3.699$ m

From Figure 3.16a the height of gas is the sum of the liquid level in the drum up to the inlet line flange plus the inlet line flange up to the top end seam. Thus:

$$L_V = 18" + 48" = 66" = 1.676 \text{ m} \tag{3-17}$$

Since the drum is a uniform cylinder type vessel, $D_L = D_V = 0.925$ m

$V_V = (\pi \times D_V^2) \times L_V / 4 = \pi \times (0.925)^2 \times 1.676 / 4 = 1.126 \text{ m}^3$

$V_t = V_L + V_V = 2.485 + 1.126 = 3.611 \text{ m}^3$

$L_t = L_V + L_L = 1.676 + 3.699 = 5.375$ m

$L_L / L_t \times 100 = 68.8\%$ or almost 70%, which is acceptable.

The arrangement of a vertical drum separator in HYSYS is shown in Figure 3.18.
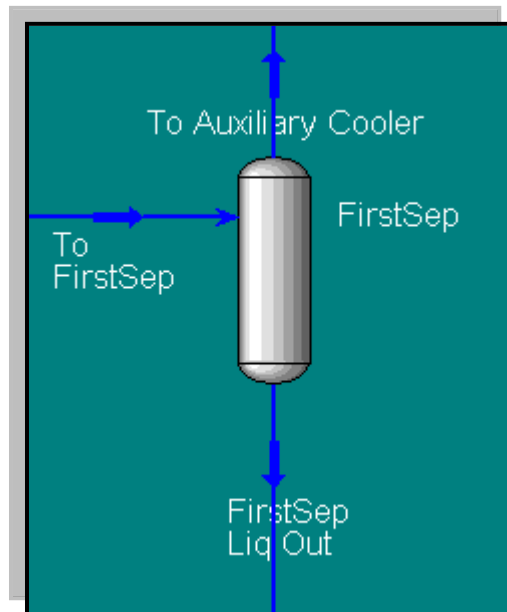
Figure 3.18 Modeling and the arrangement of a vertical drum separator in HYSYS.

The upward outlet flow from the drum, which is in gas phase, has the following compositions and mass flow rates as in Figure 3.19.

Figure 3.19 The compositions and flow rates of the gas outlet from the FirstSep drum.

Obviously, there are some heavy components, which have slightly high mass flow rate and therefore, it is better to cool it down in order to remove part of those heavy components and that is why it is called "To Auxiliary Cooler" stream.

After passing through the Auxiliary Cooler, the stream is conducted to a second drum and from where the outlet gas steam is then sent to the Hydrogen Recovery Plant in order to separate HC's from H_2. The composition of "To H_2 Recovery Plant" stream is shown in Figure 3.20. The heavy HC's are fairly decreased comparing with "To Auxiliary Cooler" stream (Figure 3.19).

Figure 3.20 The compositions and flow rates of the gas outlet from the SecondSep drum.

Similar calculations for FirstSep can be made here for the SecondSep for sizing the drum. The inlet flow to the SecondSep has the properties shown in Figure 3.21.

Figure 3.21 The properties of the stream "To SecondSep" provided by HYSYS simulator.

Considering the liquid hold-up time to be equal to 20 minutes and L/D ratio to be equal to 4 (the inlet pressure is equal to 348.8 psia); from equation (3-13) we will calculate the liquid volume:

$$V_L = Q_L \times t \tag{3-13}$$

$V_L = 0.1889 \text{ m}^3/\text{h} \times (1\text{h} / 60 \text{ mins}) \times 20 \text{ mins} = 0.063 \text{ m}^3$

From Equation (3-17):

$D_L = (V_L / \pi)^{1/3} = (0.063 / \pi)^{1/3} = 0.27 \text{ m}$ ➔

$L_L = 4 \times D_L = 1.087 \text{ m}$

From equation (3-18):

$L_V = 18" + 48" = 66" = 1.676 \text{ m}$

Since the drum is a uniform cylinder type vessel, $D_L = D_V = 0.27 \text{ m}$

$V_V = (\pi \times D^2_V) \times L_V / 4 = \pi \times (0.27)^2 \times 1.676 / 4 = 0.095 \text{ m}^3$

$V_t = V_L + V_V = 0.063 + 0.095 = 0.158 \text{ m}^3$

$L_t = L_V + L_L = 1.676 + 1.087 = 2.763 \text{ m}$

$L_L / L_t \times 100 = 39.3$ % or almost 40%.

The accumulated liquid from the bottom parts of FirstSep and SecondSep are sent to stabilizer. Figure 3.22 shows the second part of the plant; i.e. cooling and phase separation.
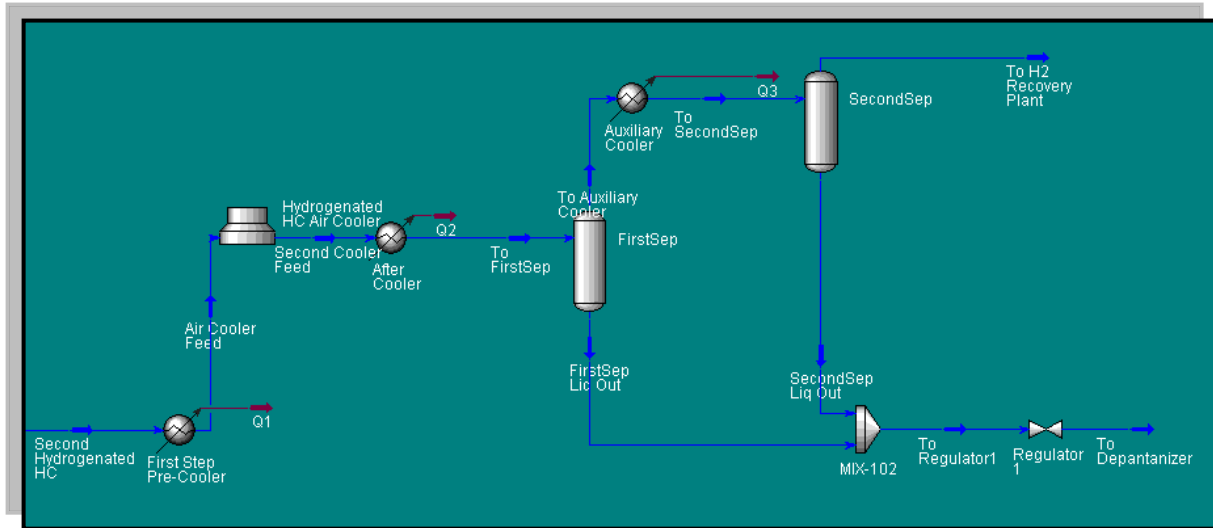
Figure 3.22 The arrangement of the Cooling and Separation Section of Hydrogenation Plant.

The liquid phase from the bottom outlet streams of FirstSep and SecondSep drums are sent to a mixer to make a uniform fluid prior to sending it to stabilizer. Figure 3.23a and b show the conditions and compositions (in mole fraction) of the aforementioned streams before and after mixing.

(a)

MIX-102			
Worksheet	Name	FirstSep Liq Ou	SecondSep Liu	To Regulator 1
Conditions	Vapour	0.0000	0.0000	0.0000
Properties	Temperature [C]	130.5	25.77	104.2
	Pressure [kPa]	2500	2475	2475
Composition	Molar Flow [kgmole/h]	101.8	40.57	142.4
PF Specs	Mass Flow [kg/h]	8922	3348	1.227e+004
	Std Ideal Liq Vol Flow [m3/h]	10.59	4.061	14.65
	Molar Enthalpy [kJ/kgmole]	1.861e+004	13.44	1.331e+004
	Molar Entropy [kJ/kgmole-C]	-45.10	-91.51	-56.73
	Heat Flow [kJ/h]	1.894e+006	545.3	1.895e+006

Design | Rating | **Worksheet** | Dynamics

Delete | OK | ☐ Ignored

(b)

Figure 3.23 Liquid outlet streams from FirstSep and SecondSep drums (a) The conditions and (b) The compositions.

3.6 Purification section

In a purification process, the objective is to separate the components in order to make valuable products from a less valuable mixture.

A. Mass transfer operation

Mass transfer is carried out by driving forces such as concentration gradient, electrical potential gradient, chemical potential gradient, temperature gradient and pressure gradient. In most separation processes, two phases come into contact and then mass transfer takes place. This contact can be "Direct Contact of two Immiscible Phases" or "Indirect Contact of two Immiscible Phases" categories. The majority of the separation processes falls into "Direct Contact of two Immiscible Phases"[34]. Depending on the phases concerned; i.e. liquid, solid or gas, new separation methods are defined.

The most important method of the "Direct Contact of two Immiscible Phases" category is gas-liquid separation, which is divided into the following operations:

1. Absorption: In this operation, gas comes into contact with liquid and one or more components in gas phase diffuse into liquid, so the mass transfer takes place from gas into liquid.

2. Stripping (or gas desorption): Mass transfer takes place from liquid into gas phase. Usually, this operation is applied to recover the less amount of a desired component in a less valuable fluid; e.g. a hydrocarbon in process water.

3. Evaporation: When the temperature difference is high enough to separate two immiscible components and the more volatile component can be found in gas phase, this operation becomes important.

4. Distillation: In this operation the gas and liquid phases are made by operation staffs. The separation is accomplished on the basis of the temperature difference and/or the partial pressure difference of the components.

When it comes to purification of hydrocarbons, distillation column is the first equipment that comes into mind. Distillation column is the most applicable and economic purification equipment for oil and gas and petrochemical industries. In this work, we use distillation columns for purification of hydrogenated hydrocarbons as well as light hydrocarbons.

B. Modeling of distillation columns

A detailed procedure for modeling, simulation and optimization of a distillation column including a practical example of a mixture of hydrocarbons is provided in APPENDIX C. Therefore, we skip such modeling here and refer the readers to APPENDIX C for detailed information.

The general arrangement of the purification section of our hydrogenation plant is shown in Figure 3.24. The major reason for selecting distillation column in purification section is the relative volatility; i.e. partial pressure differences. The main advantages of the tray columns compared with packed ones are:

1. The heating up of liquid inside the column much easier and therefore, more economical.

2. The installation of side cut in order to withdraw the pure products is possible.

3. Low maintenance cost.

4. Higher resistivity against thermal shocks.

The outlet liquid streams from separating drums have different conditions and compositions, and therefore are mixed in MIX-102 (Figure 3.23) to make a uniform conditions and compositions of flow advance to being sent to Depantanizer.

Depantanizer is a distillation column and its function is to stabilize the hydrogenated HC's as the outlet stream from the hydrogenation reactors by eliminating the light HC's, which are dissolved in liquid phase in both drums under high pressure operation (about 25 bar) prior to further purifications. Thus, the stream is introduced to a regulating valve in order to release part of light HC's and also to economize the distillation column by lowering the design pressure. The regulator 1 is designed for this purpose to decrease the pressure by 17 bars.
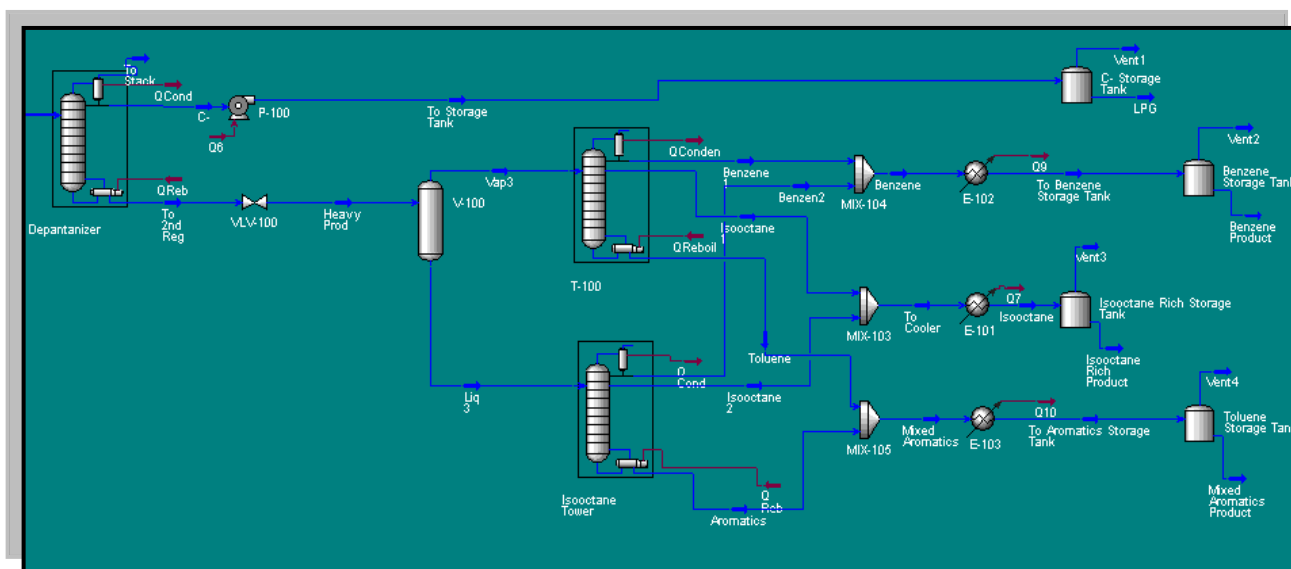
Figure 3.24 The arrangement of Purification Section of Hydrogenation Plant.

The Depantanizer column is sometimes referred to as "Stabilizer" and as mentioned above its function is to remove C_5^- components from the stream. The stream to Depantanizer is a two phase flow with a dominant liquid phase (liquid fraction, 0.986) and has the compositions and conditions in accordance with Figure 3.25a and b.

(a)

(b)

Figure 3.25 The inlet stream to Depantanizer (a) Conditions, (b) Compositions.

The inlet stream is therefore separated into 3 streams under heat treatment provided by re-boiler, which is located on the bottom of Depantanizer. The re-boiler is usually a shell and tube type heat exchanger and steam is injected to the tube side whereas the HC's are circulated in shell side via thermosiphon circulation. The inlet stream to the Depantanizer enters the column at 104.5 ^{o}C and 7.8 bar and on the tray #7. The gas/liquid contact takes place on each tray and therefore the vapor phase moves upward while the liquid phase overflows from the tray weirs to down comer. The vapor is then cooled down in a condenser and the majority of the condensed fluid is returned to the top of the column as a reflux. The reflux ratio here is equal to 5. The rest of vapor phase has a mass flow rate about 11 Kg/h mostly contained H_2 (> 93%) and therefore, is sent to stack. The remaining part of condensed fluid contains C^-_5 and therefore, is sent to the

C⁻$_5$ Storage Tank. The bottom product contains heavy HC's containing Iso-octane, Benzene, Styrene and Ethyl-Benzene etc. Thus, a further separation is required. But prior to applying another distillation separation, we first decrease the pressure of the Heavy HC's stream in order to apply an atmospheric distillation; otherwise the costs of distillation column and energy consumptions would be high. In this regard, another regulating valve is installed before the next distillation column. The compositions of the inlet and the outlet streams to Depantanizer are shown in Figure 3.26.

Column: Depantanizer / COL1 Fluid Pkg: Basis-1 / Peng-Robinson				
	To Depantanizer	To Stack	C-	To 2nd Reg
i-Butane	0.0084	0.0197	0.1779	0.0000
n-Butane	0.0083	0.0121	0.1778	0.0000
i-Pentane	0.0097	0.0045	0.2102	0.0000
n-Pentane	0.0018	0.0006	0.0383	0.0000
i-Butene	0.0085	0.0164	0.1818	0.0000
224-Mpentane	0.0846	0.0000	0.0026	0.0898
244M2pentene	0.0000	0.0000	0.0000	0.0000
1-Butene	0.0046	0.0086	0.0987	0.0000
Styrene	0.0000	0.0000	0.0000	0.0000
E-Benzene	0.1500	0.0000	0.0000	0.1595
Benzene	0.5318	0.0003	0.1090	0.5603
Toluene	0.1790	0.0000	0.0002	0.1904
Hydrogen	0.0133	0.9379	0.0035	0.0000

Figure 3.26 The compositions of the inlet and the outlet streams to Depantanizer.

The conditions and the compositions of the bottom stream from Depantanizer (named "To 2ⁿᵈ Reg") are shown in Figures 3.27a and b. The stream is free from light HC's and only contains Iso-octane, Benzene, Ethyl-Benzene and Toluene.

Stream Name	To 2nd Reg
Vapour / Phase Fraction	0.0000
Temperature [C]	175.4
Pressure [kPa]	720.0
Molar Flow [kgmole/h]	133.9
Mass Flow [kg/h]	1.185e+004
Std Ideal Liq Vol Flow [m3/h]	13.92
Molar Enthalpy [kJ/kgmole]	3.198e+004
Molar Entropy [kJ/kgmole-C]	-34.84
Heat Flow [kJ/h]	4.282e+006
Liq Vol Flow @Std Cond [m3/h]	13.77
Fluid Package	Basis-1

	Mass Fractions
i-Butane	0.000000
n-Butane	0.000000
i-Pentane	0.000000
n-Pentane	0.000000
i-Butene	0.000000
224-Mpentane	0.115967
244M2pentene	0.000000
1-Butene	0.000000
Styrene	0.000001
E-Benzene	0.191325
Benzene	0.494501
Toluene	0.198205
Hydrogen	0.000000

Figure 3.27 The outlet bottom stream from Depantanizer. (a) Conditions. (b) Compositions.

After passing through the regulating valve (VLV-100) the stream (called Heavy Prod) will change to a two-phase flow stream and have the conditions and compositions shown in Figures 3.28a and b.

(a)

Stream Name		Heavy Prod	Vapour Phase	Liquid Phase
Vapour / Phase Fraction		0.4673	0.4673	0.5327
Temperature [C]		100.3	100.3	100.3
Pressure [kPa]		120.0	120.0	120.0
Molar Flow [kgmole/h]		133.9	62.57	71.31
Mass Flow [kg/h]		1.185e+004	5365	6483
Std Ideal Liq Vol Flow [m3/h]		13.92	6.316	7.607
Molar Enthalpy [kJ/kgmole]		3.198e+004	5.236e+004	1.411e+004
Molar Entropy [kJ/kgmole-C]		-30.93	5.009	-62.47
Heat Flow [kJ/h]		4.282e+006	3.276e+006	1.006e+006
Liq Vol Flow @Std Cond [m3/h]		13.77	6.249	7.528
Fluid Package		Basis-1		

(b)

	Mass Fractions	Vapour Phase	Liquid Phase
i-Butane	0.000000	0.000000	0.000000
n-Butane	0.000000	0.000000	0.000000
i-Pentane	0.000000	0.000000	0.000000
n-Pentane	0.000000	0.000000	0.000000
i-Butene	0.000000	0.000000	0.000000
224-Mpentane	0.115967	0.130370	0.104048
244M2pentene	0.000000	0.000000	0.000000
1-Butene	0.000000	0.000000	0.000000
Styrene	0.000001	0.000000	0.000002
E-Benzene	0.191325	0.089994	0.275182
Benzene	0.494501	0.621299	0.389571
Toluene	0.198205	0.158337	0.231198
Hydrogen	0.000000	0.000000	0.000000

Figure 3.28 The two-phase stream "Heavy Prod" (a) Conditions, (b) Compositions.

C. Comparison with other possible arrangement

Figure 3.29 shows another proposed arrangement, which differs from that in Figure 3.24. The reason is that, lacking of regulating valve and drum separator and utilizing one distillation column has less efficiency comparing to the arrangement in Figure 3.24.

The resulted compositions of outlet streams from system in Figure 3.29; i.e. "Iso-octane" and "Aromatics", can be found in Figures 3.30a and b.
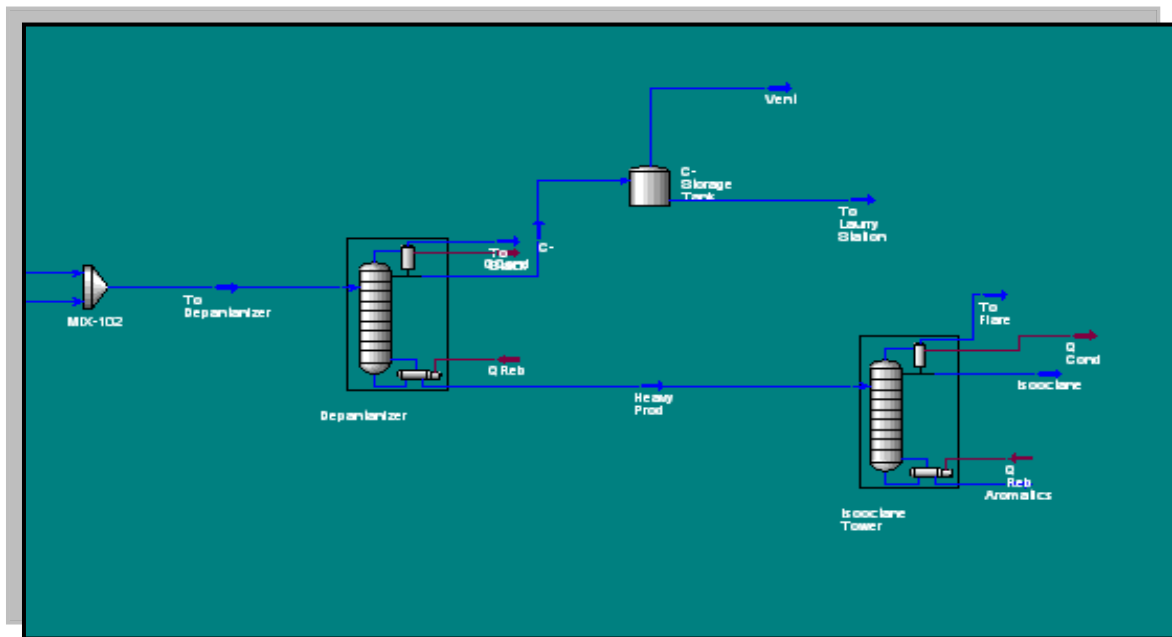
Figure 3.29 Purification arrangement without regulating valve and drum separator.

Figure 3.30 Mass flow rate of the compositions of (a) "Aromatics" and (b) "Iso-octane" streams.

The flow rate of Benzene, which has the highest wt% in Iso-octane stream, is not so attractive comparing that in Aromatics stream as to follow this arrangement. Therefore, we discard this design for now and will keep our arrangement in Figure 3.24. According to this arrangement, the mass flow rates and the compositions of liquid and vapor phases are close, however, it is preferred to use two different distillation column for each individual streams.

The liquid outlet from drum separator is sent to a tower called "Aromatics Column" in order to isolate Aromatics containing Toluene and Ethyl-Benzene from Iso-octane and Benzene.

The vapor outlet from drum separator is sent to a tower called "Benzene Column" in order to isolate Benzene from Toluene and Ethyl-Benzene and Iso-octane.

Despite of trying to isolate each component from the others, they are not absolutely pure and contain slight percentage of other components. For instance, Iso-octane is not pure at all; however, the stream can be called "Iso-octane Rich Stream".

Similar streams; i.e. Toluene, Benzene etc, are sent to dedicated mixers before cooling them down and then are sent to the relevant "Storage Tanks".

3.7 Annual capacity

It would be a good practice to evaluate how much production capacity would have this plant in a fiscal year.

In such a plant, total working hour would be calculated as following for 365 days, 24 hours per annum:

Total Working Hour = 365 Day / Year × 24 Hours / Day = 8,760 Hours / Year

However, to be realistic there will be a need for plant annual overhaul to perform maintenance works for instance, catalyst change in reactors. Annual overhaul, usually takes a month each year. Therefore, the total plant annual working hour will be round down to 8,000 hours;

Total Working Hour = 8,000 Hours / Year.

This is the design basis. Figure 3.31a to d show the mass flow rates of LPG, Benzene, Iso-octane Rich HC and Mixed Aromatics, respectively. Here, the word LPG is borrowed to represent the Light Products. In fact, LPG is commonly used for a mixture of propanes, butanes, butenes etc.

(a)   (b)

(c)   (d)

Figure 3.31 Conditions of (a) LPG. (b) Benzene. (c) Iso-octane. (d) Aromatics.

Table 3.8 shows the mass flow rate, purity and annual production of each component the based on data provided in Figures 3.31a, b, c and d.

Table 3.8 Annual capacity including individual mass flow rates and yearly production rates for each component.

Components	LPG	Benzene	Iso-octane Rich	Mixed Aromatics
Kg / h	410.7	6,068	1,163	4,618
Purity, wt%	A mixture of butanes, propanes and butenes	93.6	51.7	Ethyl-Benzene: 47.3 Toluene: 44.3
Kg / Year	3,285,600	48,544,000	9,304,000	36,944,000
Total	**98,077,600 KGPY**			

Figures 4.32a to c show the compositions in wt% of Benzene, Iso-octane Rich, and Mixed Aromatics streams, respectively.

(a)

(b)

Figure 3.32 The compositions of:

(a) Benzene,

(b) Iso-octane,

(c) Mixed Aromatics.

(c)
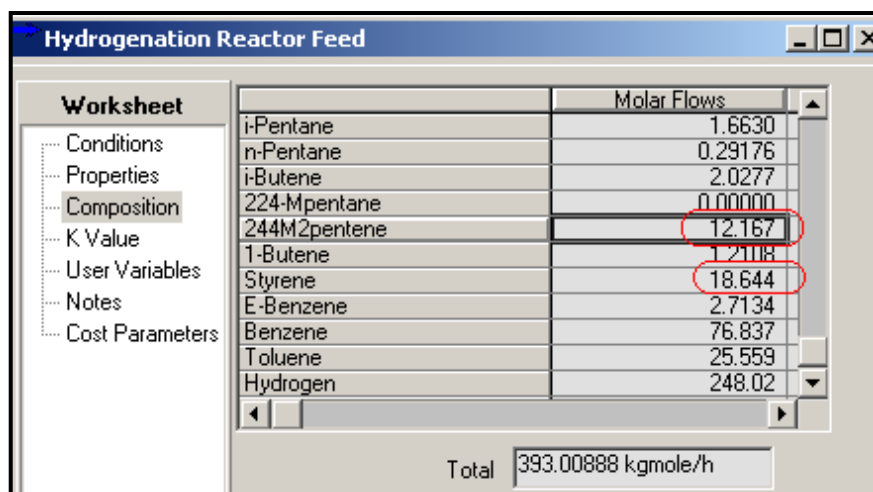
CHAPTER 4

MODIFICATIONS

The process design shown in chapter 4 is not the final design. Therefore, some modifications should be done on the design, if possible. Fortunately, there are some important items to be considered in order to modify the process design in all three sections.

4.1 Reaction section

Iso-octane is produced from Iso-octene, so is Ethyl-Benzene from Styrene. The initial molar flow rates of Iso-octene and Styrene to the First Hydrogenation Reactor are 12.167 and 18.644 Kgmole / h, respectively. See Figure 4.1.

Figure 4.1 The initial molar flow rates of all components into the First Hydrogenation Reactor, including Iso-octene (224M2pentene) and Styrene.

Taking a closer look to Figures 4.2 and 4.3, we can see that the maximum conversion can be achieved in the first 0.5 m of the reactor length for both components.

Note that the initial molar flow rate of Ethyl-Benzene is 2.7134 Kgmole / h and its final molar flow rate is 21.361 Kgmole / h. However, the total molar flow rate at about 0.35 m length of the reactor will be 21.357 Kgmole / h.
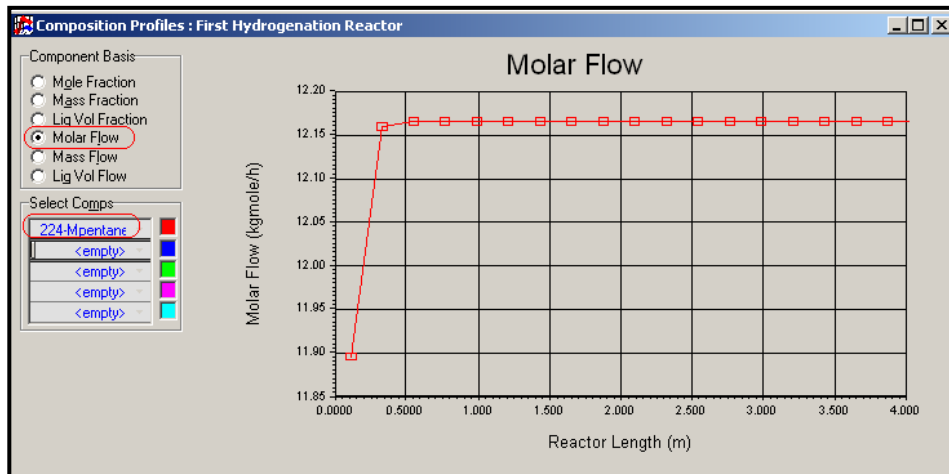
Figure 4.2 The maximum conversion (12.167 Kgmole / h) of Iso-octane from the same molar flow rate of Iso-octene is achieved at about 0.35 m of the reactor length.
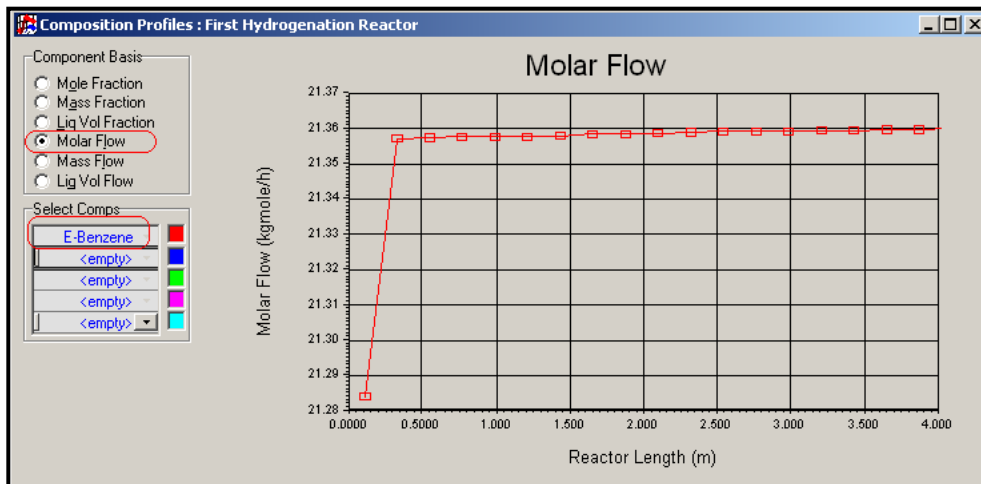
Figure 4.3 The maximum conversion (18.644 Kgmole / h) of Ethyl-Benzene from the same molar flow rate of Styrene is achieved at about 0.35 m of the reactor length.

A. Re-sizing the tubular reactors

Therefore, the reactor can be re-sized for a better and economical design. There are a couple of reasons for decreasing the reactor size:

1. The maximum conversion of Iso-Butene and n-Butene at the full length of the first reactor is not appreciable; neither is in the second one. See Figure 4.4.

2. Iso-Butene and n-Butene do make the products unstable due to the high volatility comparing with that of heavy HC's and as it is shown in Purification Section; they are removed from

the products by Stabilizer Column as LPG. LPG is usually used as fuel for combustion in boilers in large scale industries and/or if there is an Olefin Plant near our plant, LPG can be sent for thermal cracking in order to make C=C double bonds from alkanes.
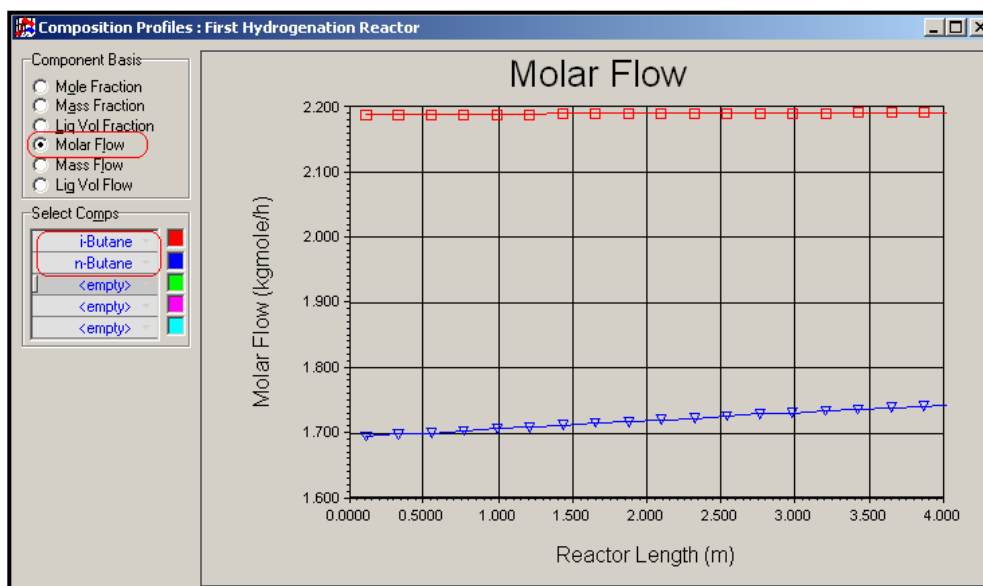
Figure 4.4 The conversion of Iso-Butene and n-Butene along the reactor length are not considerable.

The calculation made by POLYMATH, which is shown in Table D.3 is also good evidence that proves that 7 m^3 for both reactors is too large while the conversion of both Iso-Butene and n-Butene are very low. The calculated catalyst volume is about 0.04 m^3 and due to the porosity of catalyst equal to 0.5 the reactor volume would be about 1.0 m^3; more precisely:

$V_{PFR} = 0.0407 / 0.5 = 0.081$ m^3

However, the engineering practice shows that 1.0 m^3 is not practical but to keep a total volume of 3.5 m^3 for both reactors. This is because of needing to free space for mixing of "Hydrogen Feed" and "Plant Feed" streams as well as mixing of the product of the first catalyst bed in the reactor and "Make-Up Hydrogen" stream. Not to mention, needing to some spaces for other accessories such as catalyst holders, rings and ring supports etc. therefore, we keep the volume of both reactors totally 3.5 m^3.

Again, there would not be necessarily two tubular reactors and can be one combined PFR with one inlet line for Hydrogen Make-Up Stream right from the middle of the reactor length. Figure 3.4b shows a typical tubular reactor, which is very similar to our design.

Figure 4.5 shows sizing data for First Hydrogenation Reactor, which is similar for both reactors. Diameter 0.82 m is sufficient for this volume in order to keep plug flow inside the reactor while it is large enough for further maintenance and catalyst filling/discharging. The total length of 6.28 m for reactors is practical for operation, control instruments and maintenance.
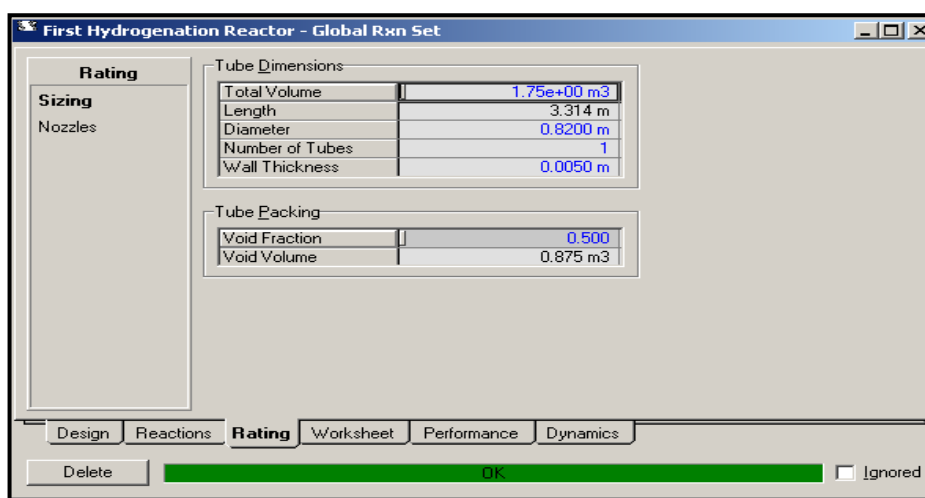
Figure 4.5 The sizing data for "1st Hydrogenation Reactor".

B. Comparison the new design with old design

The result of such change in reactor volumes can be found by comparison of Figures 4.6a and b (the conditions of Second Hydrogenated HC's before and after volume change) as well as Figures 4.7a and b (the compositions of Second Hydrogenated HC's before and after volume change). From the aforementioned figures, we can see that the condition of the stream remains almost unchanged while the fixed capital expenses will be dramatically dropped in this section due to decreasing the reactor volume by half.

(a)   (b)

Figure 4.6 The conditions of the "2nd Hydrogenated HC from the 2nd Hydrogenation Reactor (a) at total $V_{PFR} = 7$ m^3. (b) at total $V_{PFR} = 3.5$ m^3. There is no significant change.

(a)   (b)

Figure 4.7 The compositions of the "2nd Hydrogenated HC from the 2nd Hydrogenation Reactor (a) at total $V_{PFR} = 7$ m^3. (b) at total $V_{PFR} = 3.5$ m^3.

Therefore, we keep the new sizing of the reactors by 3.5 m^3 the total volume of plug flow reactor. In this case, we keep the conditions and compositions of product stream as it was when $V_{PFR} = 7$ m^3 while decreasing the total costs of the reactor.

4.2 Cooling and phase separation section

In this section, we may perform some modifications in order to improve and/or decrease the energy consumption and also vessel size, which is led to a decrease in capital and revolving investment as well as declining the operating and maintenance expenses.

71

A. New arrangement

Therefore, a new arrangement is considered in this section as shown in Figure 4.8. Compare it with Figure 3.22.

In this new arrangement, the "2nd Hydrogenated HC" is cooled in a shell and tube cooler heat exchanger similar to the old arrangement. The temperature will drop by almost 20 ^{o}C. But in the new process design (Figure 4.8) instead of further cooling the stream, it is sent to a drum separator since the vapor phase is above 0.75.

This new arrangement not only keeps the conditions and the compositions of the outlet streams from this section almost the same (see Figures 4.9a & b and 4.10a & b for the conditions of the streams "To H$_2$ Recovery Plant" and "To Regulator 1" respectively and also Figures 4.11a & b and 4.12a & b for the compositions of the streams "To H$_2$ Recovery Plant" and "To Regulator 1" respectively) but it also reduces the duties of Air cooler and After Cooler comparing with the old arrangement while the duties of Pre-Coolers remain the same.
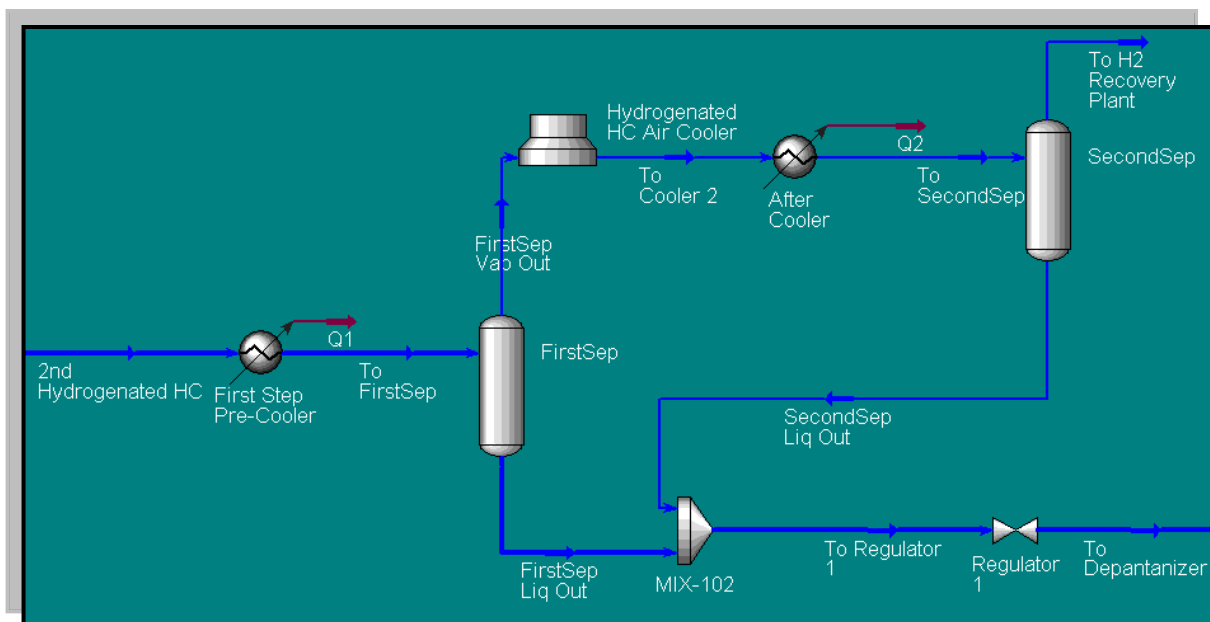
Figure 4.8 The new arrangement of Cooling and Phase Separation Section.

(a)   (b)

Figure 4.9 The conditions of the streams "To H$_2$ Recovery Plant" in (a) Old Arrangement as in Figure 3.22. (b) New Arrangement as in Figure 4.8.

(a)   (b)

Figure 4.10 The compositions of the streams "To H$_2$ Recovery Plant" in (a) Old Arrangement as in Figure 3.22. (b) New Arrangement as in Figure 4.8.

(a)   (b)

Figure 4.11 The conditions of the streams "To Regulator 1" in (a) Old Arrangement as in Figure 3.22. (b) New Arrangement as in Figure 4.8.

	Mass Flows
i-Butane	78.487
n-Butane	74.387
i-Pentane	101.64
n-Pentane	18.373
i-Butene	75.213
224-Mpentane	1375.6
244M2pentene	0.00000
1-Butene	40.662
Styrene	0.00000
E-Benzene	2266.7
Benzene	5914.5
Toluene	2349.4
Hydrogen	2.9383

(a)

	Mass Flows
i-Butane	69.665
n-Butane	66.447
i-Pentane	99.497
n-Pentane	18.074
i-Butene	68.622
224-Mpentane	1376.3
244M2pentene	0.00000
1-Butene	39.301
Styrene	0.00000
E-Benzene	2266.2
Benzene	5916.3
Toluene	2348.7
Hydrogen	3.8253

(b)
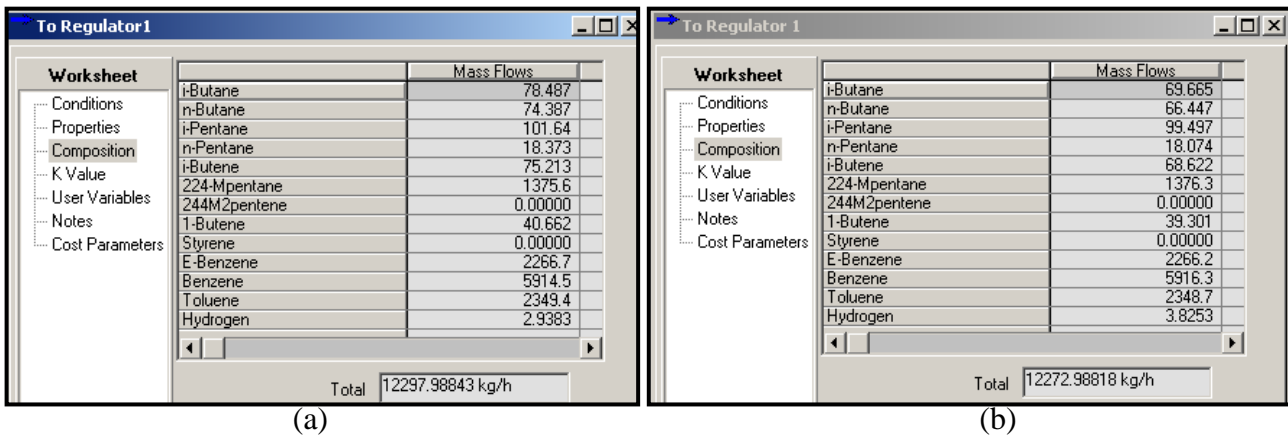
Figure 4.12 The compositions of the streams "To Regulator 1" in (a) Old Arrangement as in Figure 3.22. (b) New Arrangement as in Figure 4.8.

B. Comparison the new arrangement with the old one

Table 4.1 shows the comparison among the duties of heat exchangers in both old and new arrangements.

Table 4.1 Comparison of the duties of heat exchangers in Cooling and Phase Separation Section.

Item	First Step Pre-Cooler	Hydrog. HC's Air Cooler (Absolute Value of Working Fluid Duty)	After Cooler	Auxiliary Cooler
Duty 1[*]	1.3×10^6 kJ / h	2.554×10^6 kJ / h	1.1×10^6 kJ / h	2.6×10^5 kJ/h
Duty 2[**]	1.3×10^6 kJ / h	1.709×10^6 kJ / h	9×10^5 kJ / h	N/A
Difference	0	8.45×10^5 kJ / h	2×10^5 kJ / h	2.6×10^5 kJ/h
Total Energy Saving		1.035×106 kJ / h		

*   Duty 1 refers to the arrangement in Figure 3.22.

**   Duty 2 refers to the arrangement in Figure 4.8.

As shown in Table 4.1 except for the First Step Pre-Cooler, which is absolutely the same for both arrangement due to receiving the same stream with the same conditions and compositions, the duties have considerably changed for "Hydrogenated HC's Air Cooler", "After Cooler" and "Auxiliary Cooler". These modifications save energy up to 1035 MJ / h, which has influence on

the size and the fixed and revolving investments of the equipment. Therefore, we keep the new arrangement.

4.3 Purification section

Table 3.8 shows the plant capacity including the purity of streams based on the arrangement depicted in Figure 3.24. This arrangement fulfils the design basis mentioned in section 1.8.

However, we could achieve higher capacity, purity and one more product as we splitted the stream "Mixed Aromatics" into its components by new design and equipments arrangement.

A. New arrangement

Although the plant capacity is close to the design basis, the purity of each product might be questionable. Fortunately, by using almost the same equipment higher purity products may be achieved. Applying some modifications will result in a better arrangement to gain more product purity. Appendix B shows a detailed procedure including case study of modeling and optimization of a distillation column. The number of trays and the operating pressures and other parameters of distillation columns are available in many reference books for an initial and practical estimations[35, 36, 37].

Figure 4.13 shows the arrangement of the Purification Section. The major difference between this arrangement and the old one is:

1) the elimination of the drum separator.

2) the columns are used in series not in parallel, and

3) taking more product streams and therefore, needing to another storage tank.

Heat exchangers are designed in this section only for the bottom outlet lines as well as the side cut of distillation columns. There is no need to them in overhead from columns since they are already considered by HYSYS as a part of column package similar to re-boilers. Therefore, for the overhead lines coming from condensers, we do not design further cooler since the capacity of storage tanks are high enough to provide a complete heat transfer in the tanks over the time.
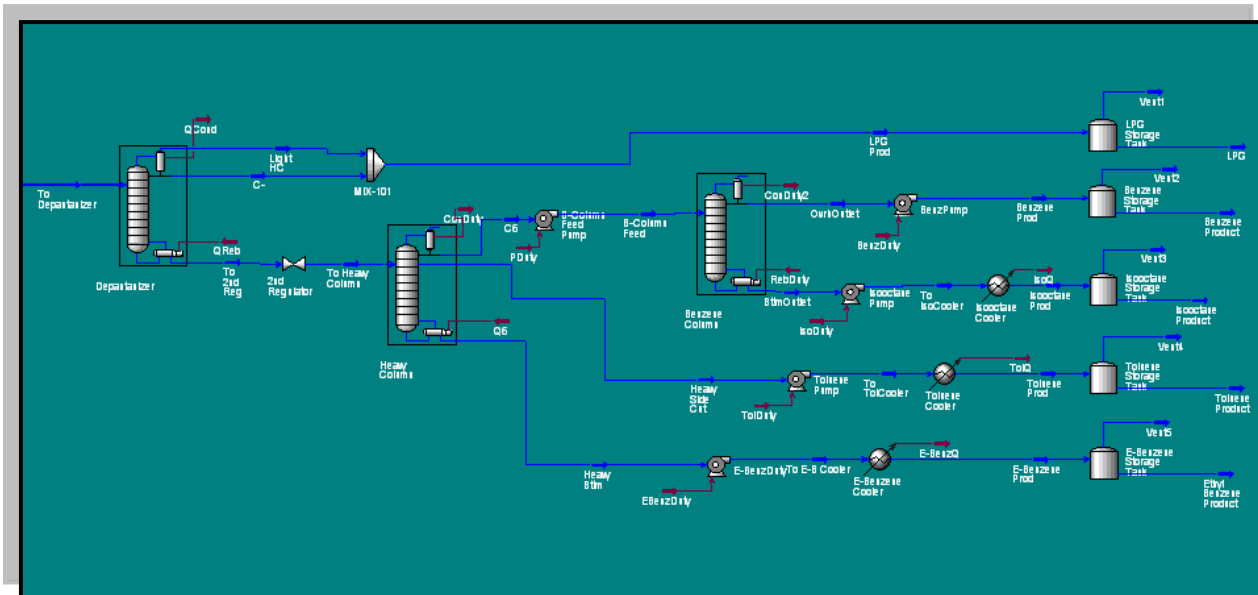
Figure 4.13 The new arrangement of Purification Section of Hydrogenation Plant.

Usually, a 30 day production capacity is considered for the design of a storage tank[27]; for instance, for LPG product the volume flow rate is 29.58 m^3 / h (Figure 4.14).

Figure 4.14 Volumetric flow rate of LPG product is equal to 29.58 m^3 / h

Therefore, for a 30 day production capacity of LPG, we will need a storage tank with 20,000 m^3 minimum volume. Due to the existing of the risk of breathing losses, tank may be equipped with the floating or expansion roofs for conservation.

Figures 4.15a and b to Figures 4.19a and b, show the conditions and the compositions of the final products.

	LPG Prod
Stream Name	LPG Prod
Vapour / Phase Fraction	0.9937
Temperature [C]	65.90
Pressure [kPa]	690.0
Molar Flow [kgmole/h]	7.970
Mass Flow [kg/h]	379.4
Std Ideal Liq Vol Flow [m3/h]	0.6785
Molar Enthalpy [kJ/kgmole]	-6.743e+004
Molar Entropy [kJ/kgmole-C]	143.0
Heat Flow [kJ/h]	-5.374e+005
Liq Vol Flow @Std Cond [m3/h]	0.7641
Fluid Package	Basis-1

	Mass Fractions
i-Butane	0.183603
n-Butane	0.175120
i-Pentane	0.260569
n-Pentane	0.046985
i-Butene	0.180855
224-Mpentane	0.000554
244M2pentene	0.000000
1-Butene	0.103579
Styrene	0.000000
E-Benzene	0.000000
Benzene	0.038634
Toluene	0.000021
Hydrogen	0.010081

(a)   (b)

Figure 4.15 The LPG Product stream to storage tank: (a) conditions and (b) compositions.

	Benzene Prod
Stream Name	Benzene Prod
Vapour / Phase Fraction	0.0000
Temperature [C]	79.02
Pressure [kPa]	100.9
Molar Flow [kgmole/h]	78.88
Mass Flow [kg/h]	6283
Std Ideal Liq Vol Flow [m3/h]	7.240
Molar Enthalpy [kJ/kgmole]	4.430e+004
Molar Entropy [kJ/kgmole-C]	-115.3
Heat Flow [kJ/h]	3.494e+006
Liq Vol Flow @Std Cond [m3/h]	7.205
Fluid Package	Basis-1

	Mass Fractions
i-Butane	0.000000
n-Butane	0.000000
i-Pentane	0.000100
n-Pentane	0.000039
i-Butene	0.000000
224-Mpentane	0.061186
244M2pentene	0.000000
1-Butene	0.000000
Styrene	0.000000
E-Benzene	0.000000
Benzene	0.938675
Toluene	0.000000
Hydrogen	0.000000

(a)   (b)

Figure 4.16a and b The Benzene Product stream to storage tank: (a) Conditions and (b) Compositions.

	Isooctane Prod
Stream Name	Isooctane Prod
Vapour / Phase Fraction	0.0000
Temperature [C]	99.29
Pressure [kPa]	103.0
Molar Flow [kgmole/h]	7.671
Mass Flow [kg/h]	872.4
Std Ideal Liq Vol Flow [m3/h]	1.251
Molar Enthalpy [kJ/kgmole]	-2.344e+005
Molar Entropy [kJ/kgmole-C]	58.79
Heat Flow [kJ/h]	-1.798e+006
Liq Vol Flow @Std Cond [m3/h]	1.247
Fluid Package	Basis-1

	Mass Fractions
i-Butane	0.000000
n-Butane	0.000000
i-Pentane	0.000000
n-Pentane	0.000000
i-Butene	0.000000
224-Mpentane	0.983664
244M2pentene	0.000000
1-Butene	0.000000
Styrene	0.000000
E-Benzene	0.000000
Benzene	0.002711
Toluene	0.013625
Hydrogen	0.000000

(a)   (b)

Figure 4.17a and b The Iso-octane Product stream to storage tank: (a) Conditions and (b) Compositions.

Toluene Prod

Worksheet	Stream Name	Toluene Prod
Conditions	Vapour / Phase Fraction	0.0000
Properties	Temperature [C]	107.9
Composition	Pressure [kPa]	97.41
K Value	Molar Flow [kgmole/h]	23.80
User Variables	Mass Flow [kg/h]	2248
Notes	Std Ideal Liq Vol Flow [m3/h]	2.622
Cost Parameters	Molar Enthalpy [kJ/kgmole]	1.159e+004
	Molar Entropy [kJ/kgmole-C]	-54.51
	Heat Flow [kJ/h]	2.758e+005
	Liq Vol Flow @Std Cond [m3/h]	2.608
	Fluid Package	Basis-1

(a)

	Mass Fractions
i-Butane	0.000000
n-Butane	0.000000
i-Pentane	0.000000
n-Pentane	0.000000
i-Butene	0.000000
224-Mpentane	0.059370
244M2pentene	0.000000
1-Butene	0.000000
Styrene	0.000000
E-Benzene	0.099428
Benzene	0.000793
Toluene	0.840409
Hydrogen	0.000000

(b)

Figure 4.18a and b The Toluene Product stream to storage tank: (a) Conditions and (b) Compositions.

E-Benzene Prod

Worksheet	Stream Name	E-Benzene Prod
Conditions	Vapour / Phase Fraction	0.0000
Properties	Temperature [C]	128.8
Composition	Pressure [kPa]	103.0
K Value	Molar Flow [kgmole/h]	24.10
User Variables	Mass Flow [kg/h]	2491
Notes	Std Ideal Liq Vol Flow [m3/h]	2.863
Cost Parameters	Molar Enthalpy [kJ/kgmole]	1.338e+004
	Molar Entropy [kJ/kgmole-C]	-26.72
	Heat Flow [kJ/h]	3.226e+005
	Liq Vol Flow @Std Cond [m3/h]	2.854
	Fluid Package	Basis-1

(a)

	Mass Fractions
i-Butane	0.000000
n-Butane	0.000000
i-Pentane	0.000000
n-Pentane	0.000000
i-Butene	0.000000
224-Mpentane	0.000035
244M2pentene	0.000000
1-Butene	0.000000
Styrene	0.000000
E-Benzene	0.820197
Benzene	0.000000
Toluene	0.179768
Hydrogen	0.000000

(b)

Figure 4.19a and b The Ethyl Benzene Product stream to storage tank: (a) Conditions and (b) Compositions.

B. Column design properties

Figures 4.20 to 4.22 show the design properties page of distillation columns used in this thesis; i.e. "Depantanizer", "Heavy Column" and "Benzene Column", respectively. The information of each page contains "Inlet Stream", "Outlet Streams" including side cut, "Number of Trays", "Inlet Stage", "The Pressure of Column Condenser and Re-boiler", "Pressure Difference" inside condenser and re-boiler etc.
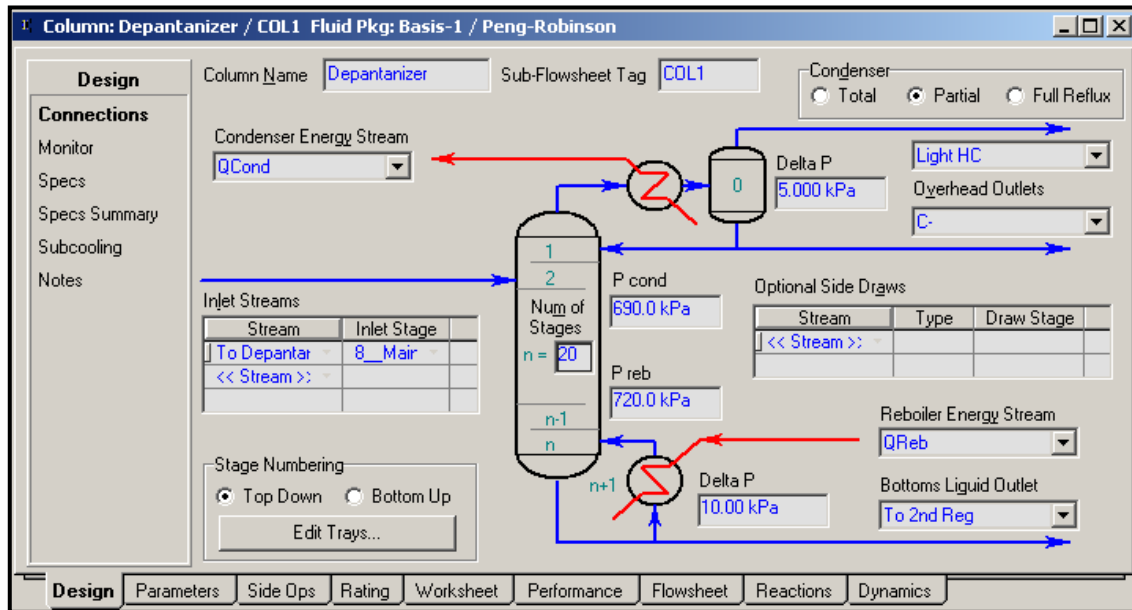
Figure 4.20 The design properties page of "Depantanizer" column.
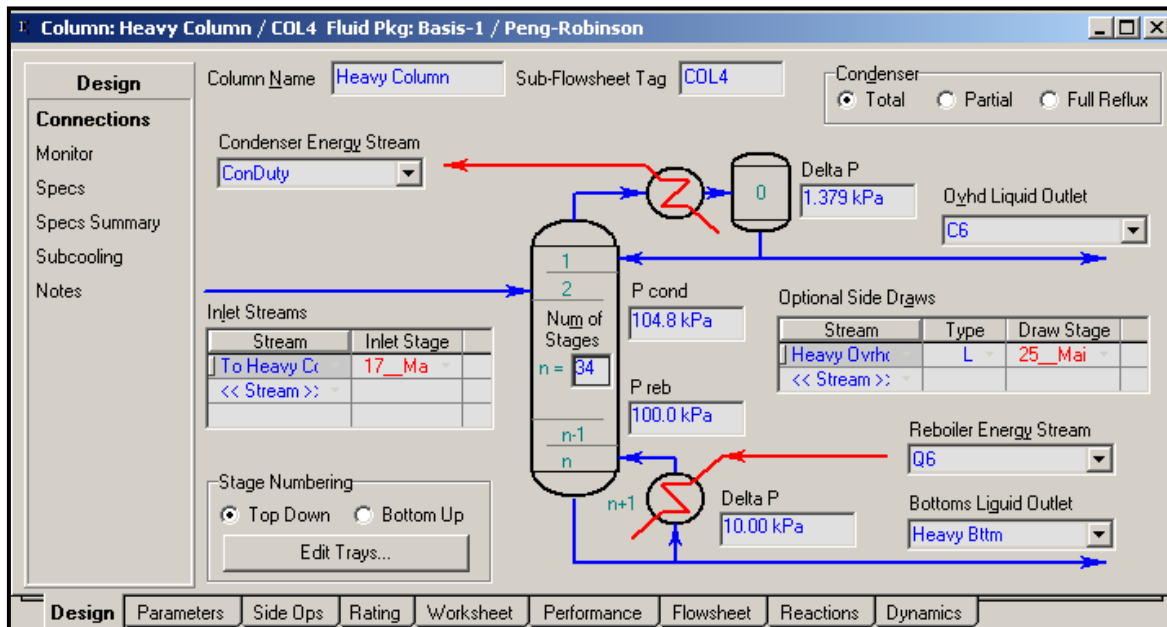
Figure 4.21 The design properties page of "Heavy Column".
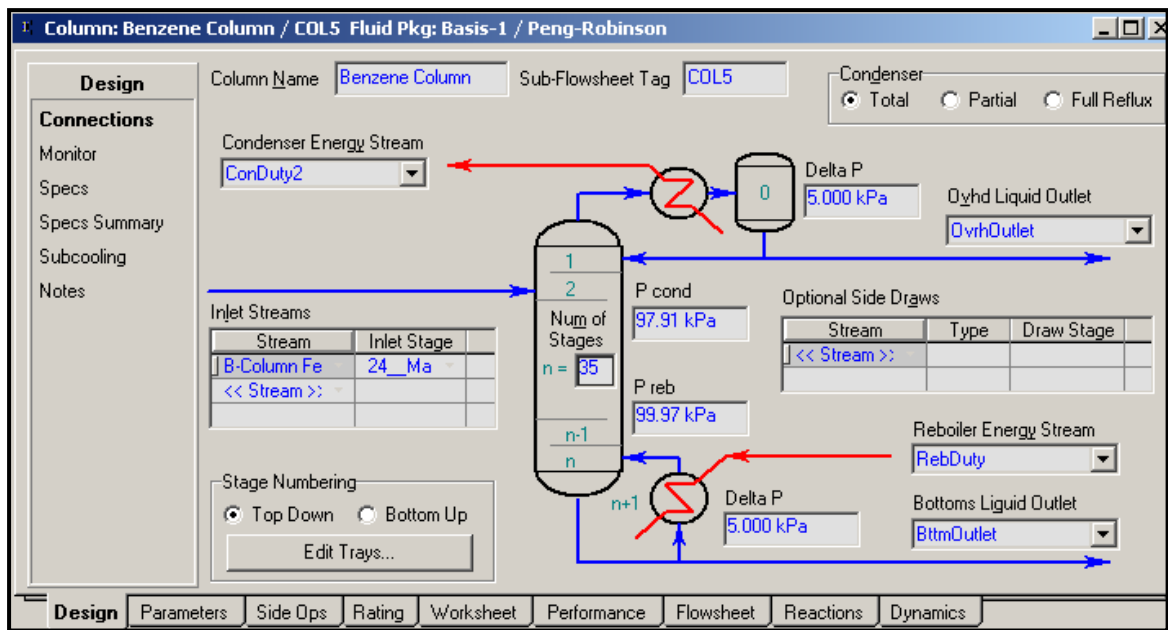
Figure 4.22 The design properties page of "Benzene Column".

C. The result of new arrangements

Table 4.2 show the outcome based on the new design in Figures 4.16a and b to 4.20a and b, comparing with Table 3.8. A good comparison is performed thereafter between the two arrangements.

Table 4.2 Annual capacity including individual mass flow rates and yearly production rates for each component in new (second) arrangement.

Components	LPG	Benzene	Iso-octane	Toluene	Ethyl Benzene
Kg / h	379.4	6,283	872.4	2,248	2,491
Purity, wt%	A mixture of butanes, propanes and butenes.	93.9	98.4	84.0	82.0
Kg / Year	3,035,200	50,264,000	6,979,200	17,984,000	19,928,000
Total	**98,190,400 KGPY**				

Even though detailed cost estimation is out of the scope of the present work, a rough estimation was made to decide if the new design was attractive. The following equation[38] is used for cost estimation:

$$C_e = a + b\ S^n \qquad\qquad (4\text{-}1)$$

Where C_e is the cost of the equipment in \$US, S is the size of equipment in terms of units; e.g. shell mass in kg for pressure vessels, heat transfer area in m^2 for heat exchangers etc. a, b and n are parameters which can be found from the relevant tables in reference books[38].

Table 4.3 shows the cost estimation (in \$US) of two arrangements. As shown in this table, the new (second) arrangement is more economical in terms of capital cost and provides higher plant capacity and purity. The difference is not big (< \$US 40,000) while the performance of the new arrangement is better as discussed before.

Table 4.3 Cost estimations and comparisons between two arrangements

No.	Equipments	First Arrangement, Refer to Table 3.8	Second Arrangement, Refer to Table 4.2
1	Reactors and Drum Separators	75,553	43,554
2	Air Cooler and Heat Exchangers	78,343	65,344
3	Distillation Columns including Trays, Reboilers and Condensers	283,586	273,450
4	Storage Tanks and Pumps	690,789	708,786
	TOTAL COST	**\$US 1,128,271**	**\$US 1,091,133**

D. Comparison of two arrangements

1. Although a drop appears in new arrangement for LPG, it accounts for lack of Benzene in LPG stream. This means higher recovery for Benzene, which means a better design.

2. The purity of Benzene stream has not increased significantly; however, an increase in the mass flow rate by more than 200 Kg / h results in an annual increase of almost 1,700,000 Kg of fairly pure Benzene.

3. Iso-octane has about 52 wt% for the capacity of about 9.3 million Kg/Year in old arrangement. In new arrangement, the annual capacity drops down to about 7 million Kg/ Year. However, the purity has significantly increased by more than 98 wt%.

4. Mixed Aromatics stream in old arrangement also has 47.3 wt% and 44.3 wt% for Ethyl Benzene and Toluene, respectively. Whereas in new arrangement, it is separated into two different streams by the same number of distillation tower to achieve almost 18 million Kg/Year of 84 wt% and almost 19.9 million Kg/Year of 82 wt% for Toluene and Ethyl-Benzene, respectively (totally, 37,912,000 Kg / Year). On the other word, we gain two different streams with a good degree of purity of each components and an increase of total capacity by 1,000,000 Kg / Year.

The above mentioned facts and figures are attractive enough to convince the designer to go for the new arrangement.

CHAPTER 5

PROCESS DESCRIPTION

5.1 General process descriptions

The catalyst used in the experiments[22, 23] is Palladium. The commercial form of industrial scale Palladium catalyst is palladium oxide[39] on γ-alumina as base metal. Therefore, it is crucial to pay attention to this matter that in initial start-up the catalyst should undergo the reduction reaction by the injection of hydrogen rich gas into the reactor bed in order for the oxygen atoms of the palladium oxide to react with catalyst. Otherwise, the catalyst would be inactive and any free oxygen would be harmful in terms of reactor safety and reaction by-product.

The Plant Feed stream enters the plant battery limit and goes directly to the tubular reactor with the flow rate of 12,500 Kg/hr, at 29 barg and 100 ^{o}C. The H_2 Feed stream with the flow rate of 500 Kg/hr, at 29 barg and 100 ^{o}C is mixed with the Plant Feed stream in the mixer MIX-100. From where, the mixture is sent to the First Hydrogenation Reactor. The Plant Feed has unsaturated hydrocarbons (HC's); i.e. 1-Butene, Iso-Butene, Iso-octene and Styrene, and therefore, the hydrogenation reaction takes place on the palladium catalyst bed inside the PFR reactor. The outlet of the First Hydrogenation Reactor is then sent to the Second Hydrogenation Reactor after mixing up with H_2 Make-Up Stream, which has a flow rate of 100 Kg/h, at 25 ^{o}C and 27 barg and functions as a make-up hydrogen in order to compensate the hydrogen gas pressure and concentration drops and as a dilution medium in order to prevent the outlet flow from the reactor from thickening. And finally and more importantly, it quenches the outlet flow in order to control the reaction temperature.

The outlet temperature and pressure of the First Hydrogenation Reactor and the Second Hydrogenation Reactor are shown in Table 5.1. The two phase flow products of hydrogenation reactions are then sent to the FirstSep Pre-Cooler, which drops the temperature by 20 ^{o}C and increases the liquid phase fraction by almost 24% (from 0.189 to 0.248).

The cooled products are flashed in the FirstSep in order to separate liquid phase from gas phase in the "To FirstSep" stream. The vapor phase is then sent to the secondary and ternary cooling systems to cool the fluid down to about 25 ^{o}C just before flashing it in SecondSep. The vapor phase from SecondSep, is rich in hydrogen gas and cannot be condensed anymore. Therefore, it is sent to hydrogen recovery plant via the stream "To H_2 Recovery Plant". The purity of the

hydrogen gas in this stream is more than 98 Mol%, and therefore, it can be used in this plant as a pure hydrogen (see Figure 2.2).

Table 5.1 The conditions of the outlet streams from the 1st and the 2nd Hydrogenation Reactors.

Conditions	1st Hydrogenated HC Stream	2nd Hydrogenated HC Stream
Flow Rate, Kg/h	13,000	13,100
Temperature, ^{o}C	158.8	150.3
Pressure, barg	27.26	25.50

The liquid phases from both separators bottom outlets; i.e. FirstSep and SecondSep, are then mixed in the mixer MIX-102, followed by depressurizing the combined streams in order to send it to Depantanizer. The "Regulator1" is utilized in order to depressurize the stream by 17 bars.

Depantanizer is in fact, a stabilizer having 20 trays in total, in which the light HC's that cause instability in the system due to their volatility are eliminated in the column. The inlet stream to the "To Depantanizer" will enter to the 8th tray of Depantanizer and undergo the heat treatment in the distillation column and the light HC's will be then sent to LPG Storage Tank.

The bottom outlet from Depantanizer contains heavy hydrocarbons, therefore, it is sent to "Heavy Column" (a 34 tray distillation column). But we do not need to use a pressurized tower, since the equipment, operation and maintenance will become so expensive, while atmospheric distillation operation suffices for a good purification. Thus, the "2nd Regulator" is designed to provide a $\Delta P = 6$ bars in order for the stream "To Heavy Column" to enter to the 17th tray of Heavy Column at 1.1 bar and 97.5 ^{o}C.

The bottom product of Heavy Column contains Ethyl Benzene and therefore, it is sent to the Ethyl Benzene Storage Tank via E-Benzene pump and after cooling the stream in E-Benzene Cooler, which drops the temperature from 128.8 ^{o}C to 43.3 ^{o}C.

The Heavy Column is equipped with a side-cut at 25th tray in order to withdraw Toluene product and pump it via Toluene Pump to Toluene Cooler, which drops the temperature from 107.9 ^{o}C to 45.87 ^{o}C and from where to Toluene Storage Tank.

The overhead of this column, which is cooled down to 81.8 ^{o}C in condenser, contains Benzene and Iso-octane. Therefore, it is sent to Benzene Column for further purification via B-Column Feed Pump. The column has 35 trays and the feed enters to 24th tray and separated into Benzene from overhead and Iso-octane from the bottom outlet.

Benzene, which is condensed in the overhead condenser, goes to Benzene Storage Tank at 79 ^{o}C via Benzene Pump, while Iso-octane is sent to Iso-octane Cooler via Iso-octane Pump. The Iso-octane stream is first cooled down from 99.3 ^{o}C to 43.7 ^{o}C and then delivered to Iso-octane Storage Tank.

5.2 Energy streams

The following table shows the quantity of energy, applied to or removed from equipment such as condensers, re-boilers, coolers etc.

Table 5.2 The energy consumptions or removal from the heat exchangers.

Energy Streams									
		Q2	QCond	QReb	Q6	Q1	ConDuty	ConDuty2	RebDuty
Heat Flow	kJ/h	9.000e+005	1.024e+006	2.905e+006	1.373e+007	1.300e+006	1.573e+007	1.449e+007	1.449e+007
		PDuty	BenzDuty	IsoDuty	TolDuty	EBenzDuty	IsoQ	TolQ	E-BenzQ
Heat Flow	kJ/h	3668	31.33	5.615	11.63	13.00	1.120e+005	2.542e+005	3.986e+005

Also material balance and heat balance of each material stream can be generated by HYSYS. Table 5.3 provides the following information of each stream:

- Vapor Fraction

- Temperature in (^{o}C) and Pressure in (kPa)

- Molar Flow (in kgmol/h) and Mass Flow (in kg/h)

- Liquid Volume Flow (in m^3/h)

- Heat Flow (in kJ/h)

Table 5.3 The table of heat and energy balances of "Material Stream".

		Plant Feed	Hydrogen Feed	First Hydrogenated HC	Hydrogenation Reactor Feed	Hydrogen Make-Up	2nd Hydrogenated HC	FirstSep Vap Out
Vapour Fraction		0.0000	1.0000	0.7761	0.6605	1.0000	0.8110	1.0000
Temperature	C	100.0	100.0	158.8	88.21	25.00	150.3	130.3
Pressure	kPa	2901	2901	2726	2901	2700	2550	2500
Molar Flow	kgmole/h	145.0	248.0	362.2	393.0	49.60	411.7	309.8
Mass Flow	kg/h	1.250e+004	500.0	1.300e+004	1.300e+004	100.0	1.310e+004	4167
Liquid Volume Flow	m3/h	14.79	7.157	21.31	21.95	1.431	22.74	12.14
Heat Flow	kJ/h	5.063e+006	5.329e+005	5.596e+006	5.596e+006	-74.23	5.596e+006	2.399e+006

		SecondSep Liq Out	To Regulator 1	C-	Light HC	Vent1	LPG	To Depentanizer
Vapour Fraction		0.0000	0.0000	0.0000	1.0000	1.0000	0.0000	0.0140
Temperature	C	25.26	104.0	104.0	65.90	65.90	65.90	104.3
Pressure	kPa	2475	2475	2475	690.0	690.0	690.0	774.5
Molar Flow	kgmole/h	40.47	142.4	142.4	7.920	7.920	5.000e-002	142.4
Mass Flow	kg/h	3340	1.227e+004	1.227e+004	376.1	376.1	3.325	1.227e+004
Liquid Volume Flow	m3/h	4.051	14.65	14.65	0.6733	0.6733	5.197e-003	14.65
Heat Flow	kJ/h	-1318	1.895e+006	1.895e+006	-5.323e+005	-5.323e+005	-5125	1.895e+006

		Isooctane Product	Vent4	Toluene Product	To FirstSep	C6	Heavy Side Cut	Heavy Bttm
Vapour Fraction		0.0000	1.0000	0.0000	0.7524	0.0000	0.0000	0.0000
Temperature	C	43.65	43.65	45.87	130.3	46.87	107.9	128.8
Pressure	kPa	92.97	47.41	47.41	2500	47.41	94.41	100.0
Molar Flow	kgmole/h	7.694	0.0000	23.80	411.7	23.80	23.80	24.10
Mass Flow	kg/h	875.1	0.0000	2247	1.310e+004	2247	2247	2491
Liquid Volume Flow	m3/h	1.255	0.0000	2.622	22.74	2.622	2.622	2.863
Heat Flow	kJ/h	-1.916e+006	0.0000	2.273e+004	4.296e+006	2.273e+004	2.769e+005	3.225e+005

		LPG Prod	Benzene Prod	Isooctane Prod	Toluene Prod	E-Benzene Prod	Vent5	Ethyl Benzene Product
Vapour Fraction		0.9937	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
Temperature	C	65.90	79.02	43.65	45.87	81.62	43.33	43.33
Pressure	kPa	690.0	100.9	92.97	47.41	104.8	53.00	53.00
Molar Flow	kgmole/h	7.970	78.86	7.694	23.80	86.55	24.10	24.10
Mass Flow	kg/h	379.4	6281	875.1	2247	7156	2491	2491
Liquid Volume Flow	m3/h	0.6785	7.236	1.255	2.622	8.491	2.863	2.863
Heat Flow	kJ/h	-5.374e+005	3.499e+006	-1.916e+006	2.273e+004	1.710e+006	-7.605e+004	-7.605e+004

Table 5.3 The table of heat and energy balances of "Material Stream" (Cont'd).

		FirstSep Liq Out	To SecondSep	To Cooler2	To H2 Recovery Plant
Vapour Fraction		0.0000	0.8693	0.8978	1.0000
Temperature	C	130.3	25.26	72.36	25.26
Pressure	kPa	2500	2475	2475	2475
Molar Flow	kgmole/h	101.9	309.8	309.8	269.3
Mass Flow	kg/h	8933	4167	4167	827.2
Liquid Volume Flow	m3/h	10.60	12.14	12.14	8.087
Heat Flow	kJ/h	1.896e+006	-2.091e+005	6.909e+005	-2.078e+005

		To 2nd Reg	Vent2	Benzene Product	Vent3
Vapour Fraction		0.0000	1.0000	0.0000	1.0000
Temperature	C	175.3	79.02	79.02	43.65
Pressure	kPa	720.0	100.9	100.9	92.97
Molar Flow	kgmole/h	134.5	0.0000	78.86	0.0000
Mass Flow	kg/h	1.189e+004	0.0000	6281	0.0000
Liquid Volume Flow	m3/h	13.98	0.0000	7.236	0.0000
Heat Flow	kJ/h	4.313e+006	0.0000	3.499e+006	0.0000

		To Heavy Column	OvrhOutlet	BttmOutlet	B-Column Feed
Vapour Fraction		0.4804	0.0000	0.0000	0.0000
Temperature	C	97.50	79.02	99.29	81.79
Pressure	kPa	110.5	97.91	99.97	404.8
Molar Flow	kgmole/h	134.5	78.86	7.694	86.55
Mass Flow	kg/h	1.189e+004	6281	875.1	7156
Liquid Volume Flow	m3/h	13.98	7.236	1.255	8.491
Heat Flow	kJ/h	4.313e+006	3.499e+006	-1.804e+006	1.713e+006

		To IsoCooler	To TolCooler	To E-B Cooler	
Vapour Fraction		0.0000	0.0000	0.0000	
Temperature	C	99.29	107.9	128.8	
Pressure	kPa	103.0	97.41	103.0	
Molar Flow	kgmole/h	7.694	23.80	24.10	
Mass Flow	kg/h	875.1	2247	2491	
Liquid Volume Flow	m3/h	1.255	2.622	2.863	
Heat Flow	kJ/h	-1.804e+006	2.769e+005	3.226e+005	

CHAPTER 6

CONCLUSIONS AND OTHER APPROACH

6.1 Conclusions

Followings are the conclusions drawn from this research work:

1. Computer assisted modeling and simulation has increasingly become popular in all fields of engineering and in particular in chemical engineering, oil & gas and petrochemical industries. Nowadays, a number of simulators are developed and/or updated in order for engineers to make fast and precise calculations. Among all of the simulators, chemical engineering simulators assist a chemical engineer to simulate design and operation of a chemical equipment and plant, which saves a lot of time and money.

   They also enable chemical engineers to design large plants by using defined thermodynamic or other equations of state, kinetic data, practical and mathematical models and equations, and other user input data. Without simulators modeling and design of such large plants would be expensive and time consuming.

2. In this thesis, a hydrogenation plant was designed by using one of the chemical engineering simulators, called ASPEN HYSYS 2006. The art of the thesis was to turn the hydrogenation reaction experiments in lab scale to a large scale hydrogenation plant.

3. The feed, which enters to the plant battery limit, is a mixture of hydrocarbons including unsaturated ones; i.e. 1-Butene, Iso-Butene, Iso-octene, and Styrene, plus saturated HC's containing Benzene, Light HC's, and Toluene etc. The conditions and compositions of the feed are known.

4. The objective of this thesis was to model and simulate the reaction, reactors, coolers, heaters, separation and purification equipment. For this purpose, ASPEN HYSYS 2006 was used and other information and data was collected from the literatures and papers. Having had the above mentioned objective and other necessary data in addition to the extensive skills of using the simulator and personal experience and judgment, a hydrogenation plant including purification process was modeled and designed to achieve over 98,000,000 kilograms per annum of different products from the initial components.

5. A literature survey was carried out to obtain the rate of reaction and other kinetic data from the literatures and papers. Despite of what scientists found over decades about the simplicity

of the catalytic hydrogenation mechanism, the hydrogenation catalytic reaction is absolutely complicated and follows "Langmuir-Hinshelwood Rate Expression". For that, the catalytic reaction has to be modeled as an "**Equilibrium**" reaction and therefore, many experiments have to be done in order to find the adsorption rate to catalyst, desorption rate from the catalyst, forward and backward reaction rates plus other necessary information to provide for the simulator.

6. However, many oriented experiments have been done followed by assumptions to simplify the hydrogenation catalytic reaction so that it can be modeled as a "**Kinetic**" reaction. Besides, the selection of catalyst type is crucial to gain a good result for our reaction. Palladium was found to be the best catalyst for our purpose due to its selectivity, higher conversion factor and durability. A literature survey was made in APPENDIX B.

7. The hydrogenation plant was designed in three sections: Reaction, Cooling and Phase Separation, And Purification.

8. The capacity was 98,077,600 Kgs per year with the wt% purity of 93.6 and 51.7 for Benzene and Iso-octane, respectively. Further modifications improved our plant capacity up to 98,190,400 kg per year and product purity as the following (See Table 4.2).

9. Further separation of aromatics from non-aromatics; e.g. Toluene from Iso-octane Prod stream, Iso-octane from Benzene Prod and Toluene Prod streams, are carried out by extractive distillation. Many companies have license for this operation due to using commercial solvents for this purpose, which will be then regenerated and returned to the process.

Krupp Udeh is one of those companies. This German company employs Morphylane process for this separation. The solvent used for this separation is N-formylmorpholyne (NFM). In the presence of NFM, vapor pressure of non-aromatic hydrocarbons will change resulting in changing in their boiling points. In other words, aromatics have originally lower boiling point or almost the same BP as of non-aromatics become less volatile and higher BP and can be dissolved in NFM and withdrawn from the extractive distillation column and separated from non-aromatics HC's. NFM will remove from aromatics compounds by further heat treatment.

10. As stated before, hydrogenation reaction can be applied for removing sulfur compounds from hydrocarbons, which is called hydrodesulfurization. The process is almost the same as our process except the reaction tale place in severe conditions; e.g. high temperature about 350 °C or more. This might mean that the catalyst or catalyst support might change. There are references for hydrodesulfurization reaction[40,41,42,43].

6.2 Other approaches:

The current design needs additional cooperation with other design engineers. This thesis is in fact, a conceptual design as a part of basic design. More engineering works should be done in future in order to provide a detailed design prior to procurement and construction works to establish such a large scale hydrogenation plant. The main tasks include:

1. There is an opportunity to decrease the energy consumption in the plant; e.g. using the hot medium for heating the cold medium and vice versa. This can be done on heat exchangers.

2. Develop a controllability analysis on this plant.

3. Develop a detailed sizing of equipment.

4. Study the dynamic behavior of this plant.

REFERENCES

1. Abolhamd G., "Petroleum Refining Bases", 3rd Edition, Tehran University Press 2296, 2002 (Farsi).

2. OTS Heavy Oil Science Centre Website (dated Jan. 2009):

   http://www.lloydminsterheavyoil.com/petrochem01.htm

3. Frank H. G., Stadelhofer J. W., "Industrial Aromatics Chemistry; Raw Materials, Processes, Products", 1st Edition, Chapter 3, Springer-Verlag, 1988.

4. Matar M., "Chemistry of Petrochemical Processes", Chapter 3, 2nd Edition, Gulf Publishing Company, 2000.

5. Anderson W.A., "Process Equipment Sizing", Chapter 1, P. 20, University of Waterloo, 2003.

6. Rudin, A., "The Elements of Polymer Science and Engineering", 2nd Edition, Chapter 7, Academic Press, 1999.

7. Abraham, O. C. and Chapman, G. L., *Hydrocarbon Processing*, Vol. 70, No. 10, 1991, pp. 95–97.

8. Frank H. G., Stadelhofer J. W., "Industrial Aromatics Chemistry Raw Materials, Processes, Products", Chapter 2, Springer-Verlag, 1988.

9. Lee, H. H., "Heterogeneous Reactor Design", Chapter 1, Butterworth Publishers, 1985.

10. Lee, H. H., "Heterogeneous Reactor Design", Chapter 2, Butterworth Publishers, 1985.

11. http://www.lloydminsterheavyoil.com/upgradgasoilhy.htm   (dated Jan. 2009).

12. Lin T.B. and Chou T. C., *Industrial and Engineering Chemistry Research*, Vol. 34, No. 1, P. 128-134 (1995).

13. Arpornwichanop A., Kittisupakorn P., and Mujtaba I.M., European Symposium on Computer Aided Process Engineering-12, Elsevier Science B.V, P. 421-426 (2002).

14. Santana P.I., Vasco de Toledo E.C., Meleiro L.A.C., Scheffer R., Freitas Jr., Maciel M.R.W., and Maciel Filho R., *European Symposium on Computer Aided Process Engineering-11*, Elsevier Science B.V, P. 279-284 (2001).

15. Noyori R., Kitamura M., and Ohkuma T., *Proc. Natl. Acad. Sci. USA*, April 13, 101 (15): 5356-5362 (2004).

16. Mariano A.P., Vasco de Toledo E.C., Francisco da Silva J.M., Maciel M.R.W., and Maciel Filho R., 2nd Mercosur Congress on Chemical Engineering, 4th Mersocur Congress on Process System Engineering, ENPROMER Co. Click on the following link (dated Jan. 2009):

http://www.enpromer2005.eq.ufrj.br/nukleo/pdfs/0509_mariano_et_al_509.pdf

17. Mariano A.P., Vasco de Toledo E.C., Francisco da Silva J.M., Maciel M.R.W., and Maciel Filho R., 2nd Mercosur Congress on Chemical Engineering, 4th Mersocur Congress on Process System Engineering, ENPROMER Co. Click on the following link (dated Jan. 2009): http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6TFT-4G002JF-1&_user=1067412&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000051246&_version=1&_urlVersion=0&_userid=1067412&md5=02ddb3daa5aed9f07bd4ee16a7c2a4a6

18. Oh M. and Moon I., *Korean J. Chem. Eng.*, 15(3), 231-242 (1998).

19. Buchanan et al., Hydrocarbon Conversion, United States Patent No. 5, 865, 986, Date of Patent Feb. 02, 1999.

20. Taylor R. and Krishna R., *Chemical Engineering Science*, 55, 5183-5229 (2000).

21. SimBasis, HYSYS Training Document, Chapter 4, P. 4-11 (2001).

22. Sarkar A., Seth D., Ng Flora T. T. and Rempel G. L., *American Institute of Chemical Engineering Journal* (2006) Vol. 52, No. 3, 1142-1156.

23. Seth D., Sarkar A., Ng Flora T.T. and Rempel G. L., *Chemical Engineering Science*, (2007) Vol. 62, 4544 – 4557.

24. Fogler H. S., "Elements of Chemical Reaction Engineering", 4th Edition, Chapter 12, Pearson Prentice Hall, 2007.

25. Hill Charles G., "An Introduction to Chemical Engineering Kinetics and Reactor Design", Chapter 8, John Wiley and Sons, 1977.

26. Fogler H. S., "Elements of Chemical Reaction Engineering", 4th Edition, Chapter 2, Pearson Prentice Hall, 2007.

27. Walas Stanley M., "Chemical Process Equipment-Selection and Design", Rules of Thumb Reactors, Butterworth-Heinemann, 1990.

28. Walas Stanley M., "Chemical Process Equipment-Selection and Design", Chapter 17, Butterworth-Heinemann, 1990.

29. Walas Stanley M., "Chemical Process Equipment-Selection and Design", Chapter 8, Butterworth-Heinemann, 1990.

30. Cheremisinoff Nicholas P., "Handbook of Chemical Processing Equipment", Chapter 1, Butterworth Heinemann, 2000.

31. Engineering Data Book, SI Version, "Gas Processing Suppliers Association", Chapter 7, 1998.

32. Branan Carl, "Rules of Thumb for Chemical Engineers", 3rd Edition, Chapter 8, Gulf Professional Publishing, 2002.

33. Walas Stanley M., "Chemical Process Equipment-Selection and Design", Chapter 18, Butterworth-Heinemann, 1990.

34. Treybal Robert E., "Mass-Transfer Operation", Chapter 6, McGraw-Hill Book Company, 1980.

35. Seader J.D., Henley Ernest J., "Separation Process Principles", Chapter 7, John Wiley & Sons Inc., 1998.

36. Ludwig Ernest E., "Applied Process Design For Chemical and Petrochemical Plants", Vol.2, 3rd Edition, Chapter 8, Gulf Professional Publishing, 1997.

37. Engineering Data Book, SI Version, "Gas Processing Suppliers Association", Chapter 19, 1998.

38. Towler G., Sinnott R., "Chemical Engineering Design; Principles, Practice and Economics of Plant and Process Design", Chapter 6, Elsevier Inc., 2008.

39. Nishimura S., "Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis", Chapter 1, A Wiley-Interscience Publication, 2001.

40. Ali, M, Al-Malki, A, El-Ali, B, Martinie, G, & Siddiqui, M (2006). Deep desulphurization of gasoline and diesel fuels. Elsevier, from (dated Mar. 2009):

http://www.sciencedirect.com

41. Leitao, Anabela, and Rodrigues Alfredo, "Studies on the Merox process: Kinetics of n-Butyl Mercaptan oxidation", Chemical Engineering Science, 44 (1989): 1245-1253.

42. Leitao, Anabela, and Rodrigues Alfredo, "Fixed-bed Reactor for gasoline sweetening: Kinetics of Mercaptan oxidation and simulation of the Merox reactor unit", Chemical Engineering Science, 45(1990): 679-685.

43. Ito, Eri, and Rob van Veen. J.A.. "On novel processes for removing sulphur from refinery streams." Catalysis Today 116(2006): 446-460.

APPENDICES

APPENDIX A: The mechanism of ethylene hydrogenation[1]

Consider the following saturation reaction for ethelyne, which takes place by hydrogenation reaction:

$$C_2H_4 \rightleftharpoons C_2H_6$$
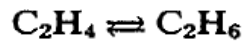
 Turkevich et al. proposed the mechanism of ethelyne hydrogenation based on H-D exchange between C_2H_4 and D_2 molecules as follows:

$$H_2 + 2S \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} 2H \cdot S$$

$$H_2C = CH_2 + 2S \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} \underset{\underset{S}{\cdot} \; \underset{S}{\cdot}}{H_2C - CH_2}$$

$$H \cdot S + \underset{\underset{S}{\cdot} \; \underset{S}{\cdot}}{H_2C - CH_2} \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} \underset{\underset{S}{\cdot}}{H_2C - CH_3} + 2S$$

$$\underset{\underset{S}{\cdot}}{H} + \underset{\underset{S}{\cdot}}{H_2C - CH_3} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} C_2H_6 + 2S$$
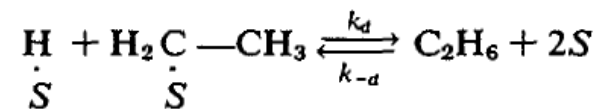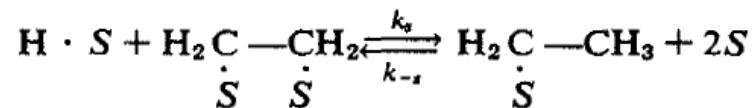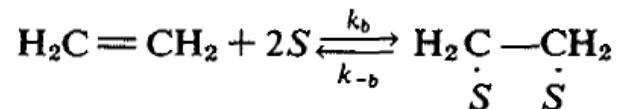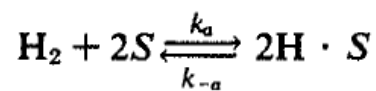
They reported that found out that hydrogen olefin are adsorbed by catalyst on two different sites and two different steps. Then, make an adsorbed intermediate. The mechanism is, in fact, a dissociative reaction. They used infrared spectra for their studies.

1. Lee, H. H., "Heterogeneous Reactor Design", Chapter 2, Butterworth Publishers, 1985.

APPENDIX B: Catalyst Effect, Catalyst Selection and Related Kinetic Data

A general definition of a catalyst is that:

"*A catalyst is a substance that affects the rate or the direction of a chemical reaction, but is not appreciably consumed in the process*"[1]

Catalysts are divided into two major categories:

- Homogeneous, which deals with only one phase reactions.

- Heterogeneous, which deals with more than one phase reactions.

A heterogeneous catalyst usually has a supporting metal, which is sometimes referred to as "porous solid" and contains the oxide of earth metals such as magnesium, aluminum, silicon etc. On the porous solid other metal(s) atoms are deposited. This dispersed metal provides "active sites", which is fundamentally responsible for the catalytic reaction. These kinds of catalysts are called supported catalysts. The porosity of heterogeneous catalyst provides a high surface area to achieve a reasonable reaction rate.

An active site on a metal surface is a point on which a strong chemically bonded atoms or molecules can be formed.

Turnover number gives the activity of the site and is defined as the number of molecules reacting per active site per second and would be very high.

Seven steps are to be done in order for a catalytic reaction to take place[2]:

1. Diffusion of the reactants to the external surface of the catalyst.

2. Diffusion of the reactants to the catalyst pores from the external surface.

3. Adsorption of the reactants onto the catalyst.

4. Reaction on the surface of the catalyst.

5. Desorption of products from the surface after reacting on the catalyst surface.

6. Diffusion of the products from the internal surface of catalyst into the pores.

7. Diffusion of the products from the exterior surface of the catalyst to the bulk fluid.

As it can be seen, there are four steps, which contain mass transfer (transport phenomenon); i.e. steps 1, 2, 6, and 7. Also the remaining steps contain kinetics phenomenon (heterogeneous chemical kinetics); i.e. steps 3, 4, and 5.

These two phenomena compete in a catalytic reaction. In order for the kinetics to prevail the transport (diffusion) phenomenon, the reactants and products should easily access to/and move

out from the active site of the catalyst surface. To do so, special attention should be paid to the following parameters while a catalyst is being selected:

"Special Surface Area" of the supporting metal, "Dispersion Rate of the Active Agents" on the supporting metal, and finally, "Pore Distribution" of the support.

For the hydrogenation of hydrocarbon, the supporting metal may be alumina or silica with the formula of Al_2O_3 and SiO_2, respectively. The availability of the surface area for making the catalyst-reactants contact is up to hundreds of square meters per gram catalyst, in practice. Consider a pellet; i.e. a simple cylindrical catalyst model, the total surface area (S in m^2) per unit volume (V in m^3) symbolized by a_c can be calculated for different radius of r:

$$S = 2 \pi r L \tag{B-1}$$

$$V = \pi r^2 L \tag{B-2}$$

$$a_c = (2 \pi r L)/(\pi r^2 L) = 2/r \tag{B-3}$$

For instance, for r equal to 1 mm, 1 µm and 1 nm, the a_c will be equal to 2×10^3, 2×10^6, 2×10^9 m^2/m^3, respectively. Therefore, for a pellet catalyst with a density of 1800 Kg/m^3 or 1.8×10^6 g/m^3 and a radius of 1 nm, the surface area per g catalyst would be 1.11×10^3 m^2/g.

Many companies in chemical and petroleum fields, specially the licensing companies produce and offer their own catalysts for their designed reactors. One can find an endless list of the catalyst providers from all around the world just by checking the Internet and companies' websites. One of the providers is AXENS IFP Group Technologies, who provide their clients and other customers with their list of products including adsorbents, guard beds, grading materials and so on, which can be found from the company's website[3]. Table B.1a and B.1b show the list of catalysts used for hydrogenation and other industrial chemical reactions, respectively.

It goes without saying that before putting any order for purchasing a catalyst, it is crucial to consult the providers to get and check the necessary kinetic and properties data for different catalysts. This is true because each company has its own trading numbers for different products, which have different characteristic and therefore different applications. Thus, purchasing a product without taking company's advice could be a big mistake.

Usually, the metallic catalysts are used for hydrogenation reactions of hydrocarbons such as Platinum, Rhodium, and Palladium etc. Each catalyst has its own conversion effects depending on the shape, porosity and other characteristics.

Table B. 2 shows the different types of catalysts, which are used in industrial reactors for different types of chemical reactions[4].

Studies show that palladium is on the top rank of hydrogenation catalysts for industrial applications due to significant conversion factor and high selectivity effect, meaning that using

palladium catalyst consumes not only the reactants in vast portions in the course of reaction but it also produces desired products.

Mitsui and Kasahara[5] have compared the selectivity of different catalysts for the hydrogenation of butene and found out that **Pd has the highest selectivity** among Ru, Rh, Os, Ir and Pt.

Nishimura[6] offered an order of hydrogenation selectivity over a number of unsupported catalysts for 1-octene at 25 ^{o}C and P_{H2} = 1 atm used isopropyl alcohol as solution. **Pd is the highest selective catalyst** as it can be seen below:

$$Pd\ (2.05) \gg Rh\ (0.125) \geq Ru\ (0.12) \gg Pt\ (0.025) \cong Ir\ (0.025) > Os\ (0.009) \qquad \text{(B-4)}$$

This reference book also studies a number of catalysts for hydrogenation reactions of alkenes and other hydrocarbons; e.g. alkynes, and organic substances. Up to this point we got a fair understanding about catalyst and its effect on the rate of reaction. Also, it is now clear that Palladium catalyst is the best option for the selective hydrogenation reactions, on the basis of the available references.

The next step would be to look for the necessary kinetic data for our modeling. Therefore, there is still a highly demand to search for other references and text books as well as research works containing the required kinetic data. Unfortunately, the old references and source of information provided no exact kinetics data and there are so hot controversies among the new research papers that make it difficult to choose one of which among the others. References B.7 to B.9 are typical examples of the old sources, which are not reliable for our upgrader.

Denisov[7] has proposed the following formula to find the frequency (or pre-exponential) factor in Arrhenius equation; i.e. $k = z_0 \exp(-E/RT)$: $\qquad$ (B-5)

$$z_0 = 3\,\pi\,\eta\,\sigma\,/\,2\,m \qquad \text{(B-6)}$$

where η is viscosity, σ is diameter, and m is the molecular weight.

He also provided tables 43 and 44 of the reference no. 7, which contains k factors in terms of log k for the hydrogenation of a number of alkenes; however, they are associated with radical addition of hydrogenation reactions. Therefore, they cannot be applied to our simulation. Moreover, we need both frequency factor and activation energy to enter in HYSYS software. Although equation (B-6) is a good estimation for frequency factor, we are still going out of activation energy data.

Kerr and Parsonage[8] have also provided the tables of thermodynamics and kinetics data. However, there is no complete information in some cases such as the activation energy of the hydrogenation of 1-Butene.

Tables B.1. The lists of catalysis. Downloaded from Ref. B. 3.

HYDROTREATING

	Applications	Material	Size (mm)	Shape	Form
Distillates					
HR 406	Mid-activity HDS for naphtha and pygas	CoMo	1.2 and 1.6	TL	1, 2, 3
HR 426	High-activity HDS for diesel and VGO	CoMo	1.2 and 1.6	TL	1, 2
HR 448	High-activity HDS and HDN for diesel and VGO	NiMo	1.2, 1.6 and 2.5	TL	1, 2
HR 506	Mid-activity HDS for naphtha	CoMo	1.2 and 1.6	TL	1, 2
HR 526	Very high-activity HDS for ULSD and VGO	CoMo	1.2 and 1.6	TL	1, 2
HR 538	High-activity HDS and HDN for diesel and VGO	NiMo	1.2, 1.6 and 2.5	TL	1, 2
HR 548	Very high-activity HDS and HDN for diesel and VGO	NiMo	1.2 and 1.6	TL	1, 2
HR 626	Very high-activity HDS for ULSD	CoMo	1.6	TL	1, 2
HR 945	Hydrogenation of olefins and diolefins for Delta P management	NiMo special alumina	2–4	S	1, 2, 3
Hydrocracking					
HRK 558	Hydrocracking pretreat	NiMo	1.2 and 1.6	TL	1, 2
HDK 776	HDC for mid distillates and lube oils	NiW amorphous Si/alumina	1.6	TL	1, 2
HYC 642	HDC for mid distillates and lube oils	NiMo zeolites	1.6	E	1, 2
HYC 652	HDC for mid distillates and lube oils	NiMo zeolites	1.6	E	1, 2
HYK 742	HDC for mid distillates and lube oils	NiMo zeolites	1.6	TL	1, 2
HTS 358	HDS and HDN of VGO in ebullated bed (H-Oil DC)	Proprietary	0.9	E	1, 2
HTS 458	HDS and HDN of VGO in ebullated bed (H-Oil DC)	Proprietary	1.2	E	1, 2
Residue					
HMC 841	HDM of atmospheric and vacuum residues	NiMo special alumina	1.5–3	S	1, 2
HMC 845	HDM of atmospheric and vacuum residues	NiMo special alumina	1.5–3	S	1, 2
HMC 868	HDM and asphaltene conversion of atmospheric and vacuum residues	NiCoMo	1.5–3 and 4–6.3	S	1, 2
HMC 945	HDM of atmospheric and vacuum residues	NiMo special alumina	4–6.3	S	1, 2
HT 428	HDS and HDN of demetallized residues	NiMo	1.2 and 1.6	TL	1, 2
HT 438	HDS and HDN of demetallized residues	NiCoMo	1.2 and 1.6	TL	1, 2

a) The list of AXENS IFP Technologies' catalysis used in hydrotreating processes.

HYDROGENATION

	Applications	Material	Size (mm)	Shape	Form
Hydrogenation					
AX 744	Aromatics hydrogenation	Ni	1.2	TL	7
AX 745	Aromatics hydrogenation	Ni	1.2	TL	7
AX 746	Olefins and aromatics hydrogenation	Ni	1.3	TL	7
LD 402	Aromatics hydrogenation	Pt, promoter	1.2	E	1
LD 412R	Olefins and aromatics hydrogenation	Pt	1.2	E	4
LD 746	Aromatics hydrogenation	Ni	1.6	TL	7
Prime-G+™					
HR 806	Prime-G+ HDS (selective HDS of cracked naphtha)	Proprietary	2–4	S	1, 3
HR 841	Prime-G+ HDS (selective HDS of cracked naphtha)	Proprietary	1.4–2.8	S	1, 3
HR 845	Prime-G+ SHU (diolefins and light sulfur removal)	Proprietary	2–4	S	1, 3
Selective Hydrogenation					
LD 143	Benzene hydrogenation	Ni	2–4	S	1
LD 145	Cracked gasoline hydrogenation	NiMo, special alumina	2–4	S	1, 2, 3
LD 241	Pyrolysis gasoline selective hydrogenation	Ni	2–4	S	1, 5
LD 265	Diolefins selective hydrogenation and Olefins hydrogenation	Pd	2–4	S	1,4
LD 267R	Selective hydroisomerization and Arofining	Pd	2	S	6
LD 269	Diolefins selective hydrogenation and olefins hydrogenation	Pd	2	S	1, 4
LD 271	Butadiene hydrogenation with maximum 1-butene yield	Pd plus promoter	2	S	1, 4
LD 273	MAPD hydrogenation with maximum propylene yield	Pd plus promoter	2	S	1, 4
LD 277	Acetylenes selective hydrogenation	Pd plus promoter	2	S	1, 4
LD 2773	Sulfur-rich C$_4$ cut selective hydrogenation or phenylacetylene selective hydrogenation	Pd plus promoter	2	S	1, 4
LD 341	Pyrolysis gasoline selective hydrogenation	Ni	2–4	S	5
LD 365	Pyrolysis gasoline selective hydrogenation	Pd	2–4	S	1, 4
LD 441	Pyrolysis gasoline selective hydrogenation	Ni	2–4	S	1
LD 465	Pyrolysis gasoline selective hydrogenation	Pd	2–4	S	1, 4
LD 485	Pyrolysis gasoline selective hydrogenation	Pd	2–4	S	1, 4
LT 279	C$_2$ and C$_3$ cut selective hydrogenation	Pd	3	S	1

b) The list of AXENS IFP Technologies' catalysis used in hydrogenation processes.

Key; **Shape**: S (Sphere), E (Cylindrical extrudate), TL (Trilobal extrudate)

Form: 1 (Oxide), 2 (Presulfided), 3 (Fully sulfided), 4 (Reduced), 5 (Resucat™), 6 (Activated), 7 (Reduced and stabilized)

Table B.2. Catalysts for Different Types of Reactions. Adapted from Ref. B.4.

Reactors	Reaction	Catalyst	Temperature	Pressure
Hydrogenation (Chemicals)	Reduction	Nickel Platinum Palladium Copper Cobalt Silver	Low to medium	High

There is a suggestion that in case of lack of data for frequency factor and activation energy for a gas-phase 1st order reaction, the values 10^{13} S[-1] and 200 KJ/mol for z_0 and E, respectively, would be a good guess[9].

Although the aforementioned information is a good point to start a modeling and simulation by process engineering software, we need more precise experimental data for the current thesis. Therefore, we need some more experimental data, which are close to our hydrogenation reactions. Searching for such a data, the some of the previous results were approved again such as using palladium catalyst in industrial reactors for selective hydrogenation reactions.

Boitiaux et al.[10] have studied the selectivity ranking of Pt, Pd and Rhodium catalysts in hydrogenation of 1-Butene, 1,3-Butadiene and 1-Butyne quantitatively in a single reaction scheme and concluded that unlike palladium, platinum and rhodium produce plenty of butane. Also the trans to cis ratio of 2-butene production from butadiene in hydrogenation reaction is much higher in case of palladium (12) than in platinum and rhodium (3.5). They have also found out that there is a relationship between trans to cis ratio and the initial butane production. The less the trans to cis ratio is, the more initial butane is produced. Table B.3 is adapted from their paper, which compares the selectivity and the trans to cis ratios of different catalysts at different temperatures.

The similar study was carried out by Goetz et al.[11] on butadiene at atmospheric pressure and the temperature range from 0-20 °C over the wide range of conversion. They found out that **palladium catalysts are the best option for the selective hydrogenation reaction of butadiene**. However, there is a limitation in conversion factor, i.e. 85-90% of the total conversion and from that point the selectivity will decrease.

Table B.3: The selectivity and trans/cis ratio for 1, 3-butadiene hydrogenation. Adapted from Ref. B. 10.

Catalyst	Temperature, ^{o}C	Trans/cis	S
Pd-Al$_2$O$_3$	0	13.8	1.000
	21	13.2	1.000
	43	9.7	1.000

Silvestre-Albero et al.[12], have studied the same reaction (hydrogenation of butadiene) on nano sized palladium catalysts and found that the activity and the selectivity of catalysts; e.g. Pd/Al$_2$O$_3$ and Pd/SiO$_2$, will drop with decreasing the particle size. They also reported a reaction rate of zero-order with respect to butadiene. The former results were also reported by Boitiaux et al.[13] and Tardy et al.[14]
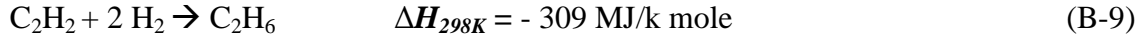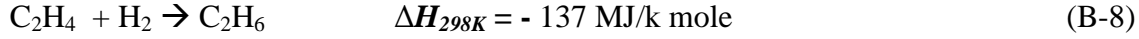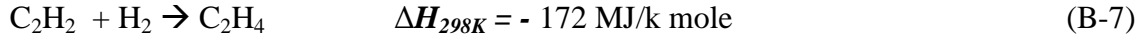
A detailed and attractive study of selective and competitive hydrogenation of C$_5$ diolefins; i.e. 1, 3-cyclopentadiene, isoprene, 1, 4-pentadiene, cis-1, 3-pentadiene, trans-1, 3-pentadiene, over a heterogeneous palladium catalyst, was made by Krupka et al.[15]

Germain[16] has concluded from the hydrogenation reactions of unsaturated and aromatics hydrocarbons that **the hydrogenation reactions at temperatures < 100 ^{o}C are irreversible and highly exothermic**, however, it is also possible the hydrogenation reactions of such compounds at high pressure and temperature; e.g. 500 ^{o}C.

The hydrogenation of ethylene at low temperatures is 1st and zero order for hydrogen and ethylene, respectively. However, **the reaction order for ethylene goes up to 1st order at higher temperatures.**

Bos and Westerterp[17], have reviewed the kinetics and mechanism of ethyne and ethylene selective hydrogenation using palladium catalysts (Pd/Al$_2$O$_3$), while there is high concentration of ethyne and concluded that the classical theory; i.e. thermodynamic factors, cannot explain the kinetics due to the complexity of the reactions. Therefore, it is assumed that two or more different active sites of catalysts are involved in selective hydrogenation as Langmuir-Hinshelwood mechanism provides a good explanation for this type of reactions. For a detailed mechanism refer to APPENDIX A.

Palladium catalysts can diminish the ethyne concentrations down to < 5 ppm while keeping ethylene almost unreacted. The following reactions including direct hydrogenation of ethyne to ethane as well as oligomerisation, which produces C$_4^+$ mixture will take place:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \qquad \Delta H_{298K} = -172 \text{ MJ/k mole} \qquad \text{(B-7)}$$
$$C_2H_4 + H_2 \rightarrow C_2H_6 \qquad \Delta H_{298K} = -137 \text{ MJ/k mole} \qquad \text{(B-8)}$$
$$C_2H_2 + 2 H_2 \rightarrow C_2H_6 \qquad \Delta H_{298K} = -309 \text{ MJ/k mole} \qquad \text{(B-9)}$$

The adiabatic packed bed reactors in addition to egg shell type catalysts (preventing mass transfer resistance) are used for those reactions in industries.

The fact is that the hydrogenation reaction is very complex, that is why just a few practical kinetic rate expressions are available.

The similar reaction over Pd catalyst was studied by Borodzinski A. and Bond G.C.[18] in order to investigate the effect of changes to catalyst in the course of reaction.

Seth et al.[19], have performed an investigation on the kinetic of Pd/α-Al$_2$O$_3$ catalytic reaction of selective hydrogenation of 1,3-butadiene in the liquid-phase at reference temperature 50 $^{\circ}$C and pressure ranging from 1205 kPa to 2170 kPa in the presence of iso-butene and resulted that Pd/α-Al$_2$O$_3$ was highly selective with no significant deactivation. The same investigations were performed on iso-octane by the same team[20] and the similar results were reported. They used a simplified Langmuir-Hinshelwood mechanism to develop a kinetic model, which precisely explains the experimental data even though many parameters could not be determined accurately and therefore dropped off from the final rate expression. They also have reported that an external fixed bed reactor would have the best performance (rather than a combined distillation).

On the basis of Langmuir–Hinshelwood mechanism, the rate of a single reaction in presence of other components is related to the square-root of the hydrogen concentration, which is assumed to adsorb dissociative.

"The reaction rate is therefore expressed as:

$$-r_A = k \, C_A \, (C_{H2})^{1/2} \, \theta_S^2 \qquad \text{(B-10)}$$

where, r_A is the rate of consumption of species A, k is the rate constant for the hydrogenation, C_A is the concentration of the unsaturated species and C_{H2} is the hydrogen concentration in the solution, and θ_s is the fraction of vacant sites on the catalyst surface."

θ_s is a complex term in our case and is equal to:

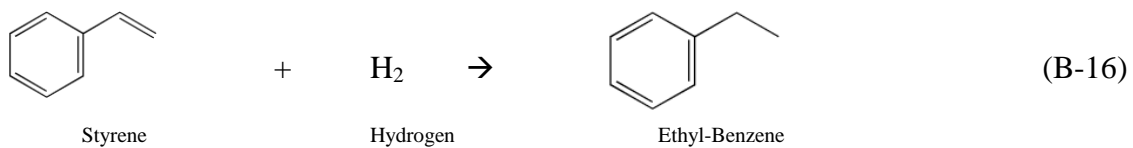$$1/(1 + \sqrt{K_{H_2}C_{H_2}} + K_A C_A + K_B C_B + K_C C_C + K_D C_D + K_E C_E), \qquad \text{(B-11)}$$

where, A, B, C, D and E are the four isomers of butene and butadiene. As mentioned earlier parameters such as equilibrium constants cannot be found reliably from literature and therefore, dropped off from the rate expression assuming that $\theta_S = 1$. We also keep this procedure in our simulation. k is calculated from the following equation:

$$k = k_{\text{ref}} \exp\left[-\frac{E_{\text{app}}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \qquad \text{(B-12)}$$

where T_{ref} is equal to 50 $^{\circ}$C for 1-butene[19], iso-butene and styrene and is equal to 110 $^{\circ}$C for iso-octane[20].

Other studies on hydrogenation reactions contains C_5 alkenes[21] and 1,3-pentadiene[22] on Pd/alumina catalyst, kinetics of liquid-phase hydrogenation reaction of iso-octene[23] over Pd/alumina catalyst, mechanism of hydrocarbon conversion reactions on heterogeneous catalysts[24], the hydrogenation of alkadienes[25], the selective hydrogenation of unsaturated hydrocarbons[26].

The following reactions take place in our upgrader system in the reactor:

$$CH_3CH_2CH=CH_2 \quad + \quad H_2 \quad \rightarrow CH_3CH_2CH_2CH_3 \tag{B-13}$$

1-Butene   Hydrogen   n-Butane

$$CH_3C(CH_3)=CH_2 \quad + \quad H_2 \quad \rightarrow CH_3CH(CH)_3CH_3 \tag{B-14}$$

Iso-Butene   Hydrogen   Iso-Butane

$$CH_3C(CH_3)_2CH=CHCH_3 + \quad H_2 \quad \rightarrow CH_3C(CH_3)_2CH_2CH_2CH_3 \tag{B-15}$$

Iso-octene   Hydrogen   Iso-octane
(2, 4, 4-trimethyl-2-pentene (2-TMP))

Styrene   + H_2 →   Ethyl-Benzene   (B-16)

Hydrogen
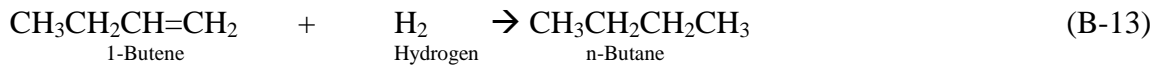
The general reaction rate, which is applicable to main reactants, here olefins, is as following:

$$-r_A = k\ C_A\ (C_{H2})^{1/2} = k_{ref}\ exp\ [-E/R\ (1/T - 1/T_{ref})]\ C_A\ (C_{H2})^{1/2} \tag{B-17}$$

As an overall result of our investigation, the parameters are so selected as to be close to an upgrader plant.

The frequency factors and activation energies of the reactions B.13 to B.16 can be found in Table 3.5[19,20,27].

Reference B:

1. Hill C. G., "An Introduction to Chemical Engineering Kinetics & Reactor Design", Chapter 6, JOHN WILEY & SONS, 1977.

2. Hagen J., "Industrial Catalysis A Practical Approach", 2nd Edition, Chapter 5, WILEY-VCH Verlag GmbH & CO., 2006.

3. The website of AXENS IFP Technologies. The list of products including catalysts (Jan. 2009):

   http://www.axens.net/pdf/products/PCA_brochure_2007.pdf?file=pdf%2Fproducts%2FPCA_brochure_2007.pdf

4. Igbinoghene D. C., "Chemical Process Calculations Manual", Chapter 17, McGraw-Hill, 2004.

5. Mitsui S. and Kasahara A.Zabicky J., "The Chemistry of Alkenes" (Edited by Zabicky J.), Vol. 2, Chapter 4, Intersciance Publishers, 1970.

6. Nishimura S., "Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis", Chapter 3, A Wiley-Interscience Publication, 2001.

7. Denisov E.T., "Liquid-Phase Reaction Rate Constants", Chapter 6, IFI/Plenum, Translated from Russian by Johnston, R.K., 1974.

8. Kerr J.A. and Parsonage M.J., "Evaluated Kinetics Data on Gas Phase Addition Reactions Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds", Chapter 2, Butterworth, 1972.

9. Fogler H. S., "Elements of Chemical Reaction Engineering", 4th Edition, Chapter 3, Pearson Prentice Hall, 2007.

10. Boitiaux J.P., Cosyns J. and Robert E., *Applied Catalysis,* 35 (1987) 193-209.

11. Goetz J., Murzin D. Yu., Ulischenko M. and Touroude R., *Chemical Engineering Science,* Vol. 5 I, No. 1 I (1996) 2879-2884.

12. Silvestre-Albero J., Rupprechter G., and Freund H. J., *Journal of Catalysis*, 240 (2006) 58–65.

13. Boitiaux J.P., Cosyns J. and Vasudevan S., *Applied Catalyst*, 6 (1983) 41.

14. Tardy B., Noupa C., Leclercq C., Bertolini J.C., Hoareau A., Treilleux M., Faure J.P. and Nihoul G., *Journal of Catalyst*, 129 (1991) 1.

15. Krupka J., Severa Z. and Pasek J., *React. Kinet. Catal. Lett.*, Vol. 89, No. 2, (2006) 359-368.

16. Germain J.E., "Catalytic Conversion of Hydrocarbons", Chapter 3, Academic Press, 1969.

17. Bos A. N. R., Westerterp K. R., *Chemical Engineering and Processing,* 32 (1993) l-7.

18. Borodzinski A. and Bond G.C., *Catalysis Reviews-Science and Engineering*, 48(2), 2006, 91-144.

19. Seth D., Sarkar A., Ng Flora T.T. and Rempel G. L., *Chemical Engineering Science,* 62 (2007) 4544 – 4557.

20. Sarkar A., Seth D., Ng Flora T. T. and Rempel G. L., *American Institute of Chemical Engineering Journal*, March, 2006, Vol. 52, No. 3, p. 1142-1156.

21. Canning A.S., Jackson S.D., Monaghan A. and Wright T., *Catalysis Today*, 116(1), 2006, 22-29.

22. Jackson S.D., Monaghan A., *Catalysis Today*, 128(1-2), 2007, 47-51.

23. Sarkar A., Seth D., Ng Flora T.T. and Rempel G. L., *American Institute of Chemical Engineering Journal,* 52(3), 2006, 1142 –1156.

24. Zaera F., *Topics in Catalysis*, 34(1-4), 2005, 129-141.

25. Bond G.C., Webb G., Wells P.B. and Winterbottom J.M., j. Chem. Society (1965), (May), 3218-3227.

26. Bond G.C., Newham J. and Wells P.B., *Actes International Congress Catalyse*, 2e, Paris 1960 (1961), 1, 1177-1188, discussion 1189.

27. Zhiming Zhou, Zhenmin Cheng, Yining Cao, Jinchi Zhang, Dong Yang, Weikang Yuan, *Chemical Engineering Technology,* 2007, 30, No. 1, 105–111.

APPENDIX C: Simulation and Optimization by ASPEN HYSYS 2006

In this appendix, the project of a new distillation column is modeled using ASPEN HYSYS 2006 process simulator software followed by the optimization of molar flow rate of the desired components in outlet streams, which are Normal Pentane (n-C5) in distillate from condenser, Normal Hexane (n-C6) in side stream 1, Normal Heptane (n-C7) and Normal Octane (n-C8) in side steam 2 and finally, Normal Nonane (n-C9) in bottom stream from re-boiler. In this investigation, SQP method of line search for optimization of our objective function is utilized, the size of equipment before and after the optimization remains unchanged and no economy considerations have been taken into account. As a result, the objective function increased by 8.85% while increasing the duties of condenser and re-boiler.

Distillation column equipment

Distillation column is one of the most important separation equipment in Chemical and Refinery Plants, in which we intentionally make both gas and liquid phases.

It is a method of separation of a solution which depends upon the distribution of the substances between a gas and a liquid phase, applied to cases where all components present in both phases. Instead of introducing a new substance into the mixture in order to provide the second phase, as it is done in gas adsorption or desorption, the new phase is created from the original solution by vaporization or condensation[1].

In this technique, a feed stream is introduced ideally at its saturated liquid phase and near its boiling point to the column tray at the similar temperature, direct contact and therefore mass transfer is then made between two phases. Separation takes place here on the basis of the difference between the boiling points or the partial pressures (relative volatilities) of the components. For this reason, the technique is one of the most energy consuming.

The successful application of distillation methods depends greatly upon an understanding of equilibria existing between the vapour and liquid phases of the mixtures encountered. A brief review of these is therefore essential. The emphasis here will be on binary mixtures[1].

A number of useful on-line sources about thermodynamic models for simulation purposes with HYSYS are listed in reference list. For more information please refer to item nos. 2 to 5 of reference list.

Optimization methods for a distillation tower

The optimization of a distillation tower is mostly made in 3 different ways:

1. The minimum required trays at a constant reflux flow

2. The optimization of an economic design for a new distillation tower

3. Minimizing the reflux flow by determination of the best inlet feed tray

However, there are also some other ways for this purpose such as:

4. Optimizing the costs of the tower, condenser or re-boiler, including utility consumption considering constant reflux flow

5. Determination of the minimum theoretical trays assuming that the purity of the products and the inlet feed tray will not change.

Note: The current research is made for optimization purpose only and utilizes the second method, in which a new distillation column is first simulated (designed), and then the optimization is performed on its products, i.e. outlet streams.

Optimization by process simulators

Optimization by process software simulators has been developed extensively as numerical methods; high speed computers and relevant software are developed to make quick and precise calculations. Process simulators such as ASPEN Plus, ASPEN HYSYS, PRO II, ChemCad etc. provide facilities for chemical engineers such as material and energy balances for a flow diagram and also data bank including:

B. Physical properties information,

C. Chemical properties information,

D. Thermodynamic properties information,

E. Transportation properties information,

F. Sizing and calculations for equipment,

G. Capital and revolving investment,

H. Physical properties models,

I. Process equipment models,

J. Determination of equipment costs etc.

For finding the details in Property Methods and Calculations please refer to the on-line sources mentioned in item nos. 5 and 6 of reference list.

ASPEN HYSYS along with other process simulators facilitate the design, sizing, simulation and optimization of a chemical or a refinery equipment and plant. ASPEN HYSYS (from now on, we call it HYSYS) and ASPEN Plus are extensively used in many plants and are one of the most important qualifications that many big companies consider for their new candidates they wish to hire.

For finding a good reference for HYSYS training see item no. 7 of reference list.

Optimization project by ASPEN HYSYS 2006

In a distillation column, a stream containing of Normal Pentane (n-C_5), Normal Hexane (n-C_6), Normal Heptane (n-C_7), Normal Octane (n-C_8) and Normal Nonane (n-C_9) is to be separated. The products leave the column through four outlet different streams, i.e. distillate from condenser mainly containing n-C_5, column bottom from re-boiler mainly containing n-C_9, side stream 1 (S1) from tray no. 6 mainly containing n-C_6, and side stream 2 (S2) from tray no. 16 mainly containing n-C_7 and n-C_8.

The condition and compositions of the feed stream as well as the following data are known:

Feed rate, feed temperature and feed pressure; 9.479 lbmole/hr, 120 ^{o}F and 25 Psia, respectively.

Molar Flow in lbmole/hr; n-C_5 = 3.0492, n-C_6 = 1.2764, n-C_7 = 1.5967, n-C_8 = 0.4377 and n-C_9= 3.1187.

   5 <= Reflux Ratio <=10

   0.1<= Distillation/Feed <= 0.7

   0.1<= S1/Feed <=0.7

   0.1<= S2/Feed <= 0.7

   0.05 <= Bottom/Feed

The objective is to maximize the desired product in the dedicated streams by HYSYS process simulation software, i.e. n-C_5 in distillate, n-C_6 in S1, n-C_7 and n-C_8 in S2 and finally n-C_9 in bottom streams.

First we define the "Objective Function" as following:

$$F = x_{n-C5} * F_{Distillate} + x_{n-C6} * F_{S1} + x_{n-C7} * F_{S2} + x_{n-C8} * F_{S2} + x_{n-C9} * F_{Bottom}$$

   Subject to:

   5 <= Reflux Ratio <=10

   0.1<= Distillation/Feed <= 0.7

   0.1<= S1/Feed <=0.7

   0.1<= S2/Feed <= 0.7

   Bottom/Feed >= 0.05

We will now maximize F by ASPEN HYSYS 2006, using SQP (Successive Quadratic Programming) method under given inequality constraints.

Successive quadratic programming (SQP) methods solve a sequence of quadratic programming approximations to a non-linear programming problem. Quadratic programs (QP's) have a quadratic objective function and linear constraints, and there exist efficient procedures for solving them; … As in **SLP***, the linear constraints are linearizations of the actual constraints about the selected point. The objective is a quadratic approximation to the Lagrangian function, and the algorithm is simply Newton's method applied to the KTC of the problem[8].

For more information about optimization methods in HYSYS please refer to the attachment no. 1.

General notes for HYSYS users:

1. In entire space of HYSYS application, blue, red and green colours are used for "Material Streams", "Energy Streams" and "Logical Operations", respectively.

2. For the values of input and output streams, the value in blue colour are input values (by user), values in red are assumed those values made by software and can be changed and the values in black are calculated by software, which cannot be changed. (Note: only blue and red values can be changed).

3. After completion of data entry for material streams and unit operations when simulation is made, the colour of streams and operations will change.

4. For n components in a stream we need n+2 thermodynamic properties to start data entry, which are: Conditions (3 parameters: Pressure, Temperature, Molar or Mass Flow) plus compositions.

* SLP stands for Successive Linear Programming

Simulation and optimization of a newly designed distillation tower

To use HYSYS simulation software for optimization, we should either use the existing file, which is already simulated the distillation column, or build up a new simulation for the column. In our case, as we notified before, we will establish a new simulation, i.e. a new design, and then optimize the objective function. For this purpose we performed the following steps:

1. To start simulation, we click on the Start button on the Desktop and go to Program, then follow Figure C.1a. in the next step, we click on the "Page" sign (Figure C.1b):
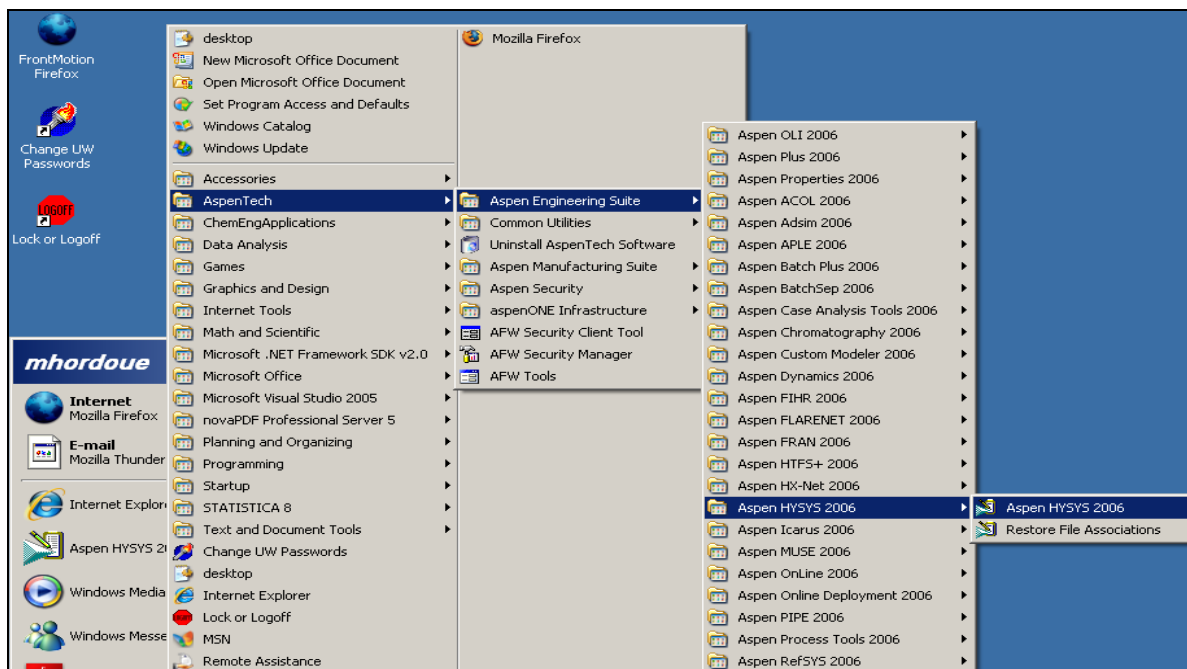
(a)

(b)
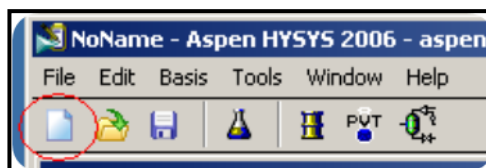
Figure C.1: (a) The path for opening HYSYS 2006 file. (b) Click on the "Page" sign to open a new case.

Note: In this project one of the computers in DWE 3521 has been used. Thus, the path on other computers in the room may be different from figure 1a.

2. From the "Tools" menu we need to go to "Preferences", on "Session Preferences" page and click on "Variables" tab, and then click on "Unit". In "Available Unit Sets", we select "Field" to identify a unit set for software. See Figure C.2 below:
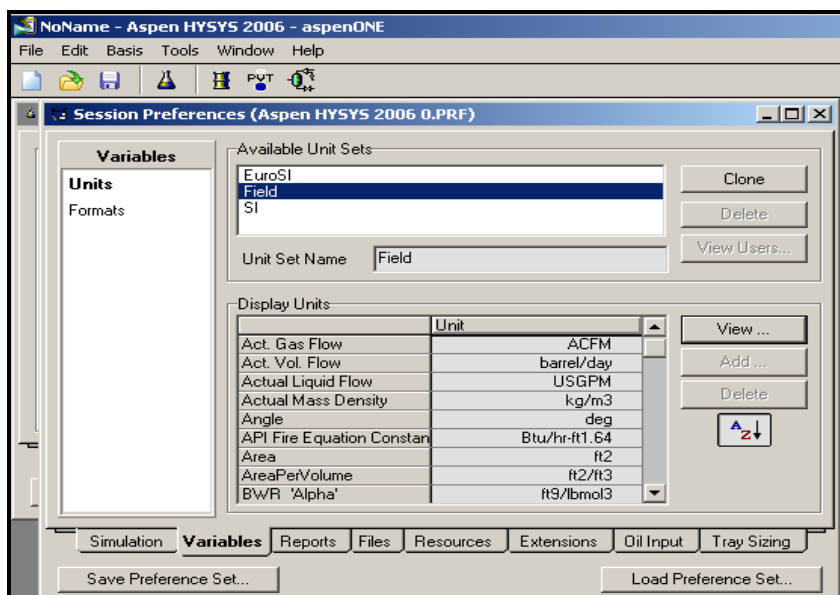

Figure C.2: Identifying a unit set for HYSYS software.

3. On SBM (Simulation Basis Manager) Window, on "Component" tab, we have to add the components, so we click on the "Add" button. See Figure C.3:
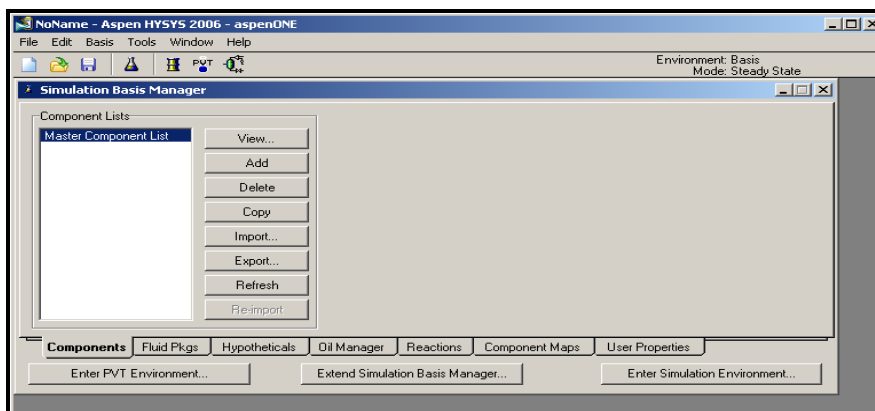

Figure C.3: Adding a Component list to SBM.

4. Now we choose the following components in "Component List" as in Figure C.4:
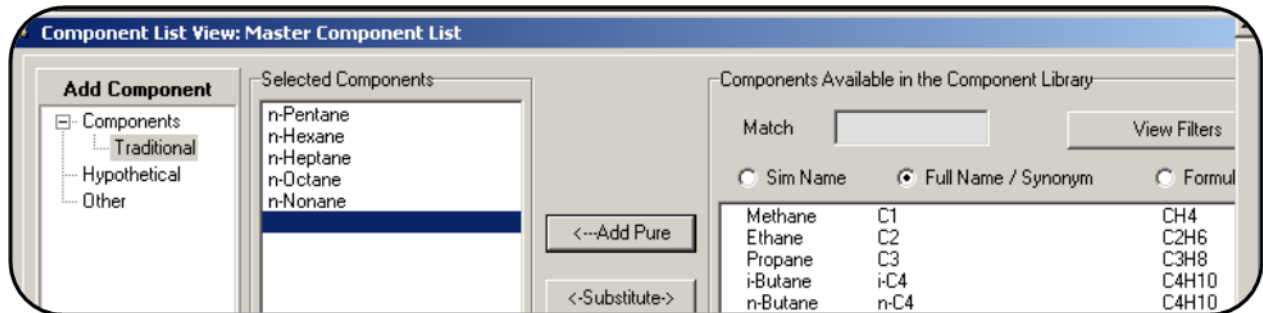
Figure C.4: Adding the list of components in the "Component List".

5. On SBM Window and on "Fluid Package" tab; we hit the "Add" button. See Figure C.5:
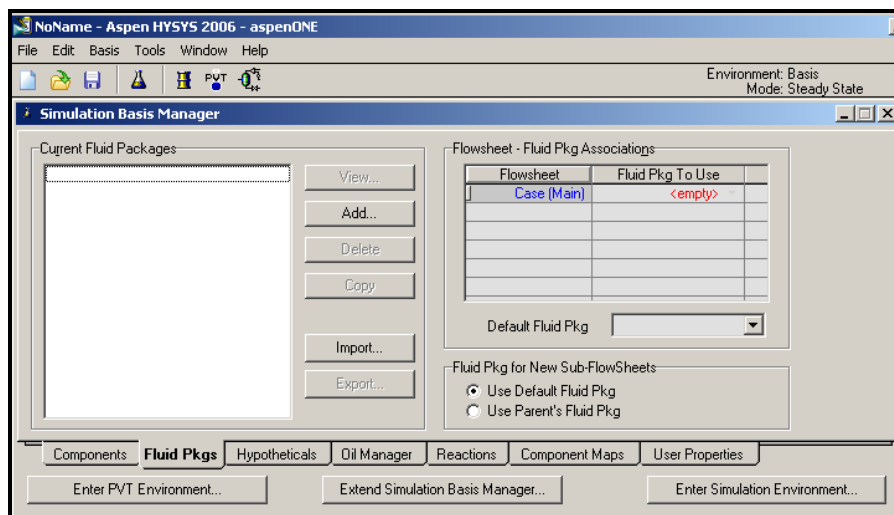

Figure C.5: Adding a Fluid Package to the SBM.

6. On the "Set Up" page of "Fluid Package" Window when "All Types" in Property Package Filter area is selected, we choose "Chao Seader Model" on the Property Package Selection area on the left. See Figure C.6:

Note: For more information on Chao Seader Models, please refer to attachment no.2 (HYSYS Help Menu)
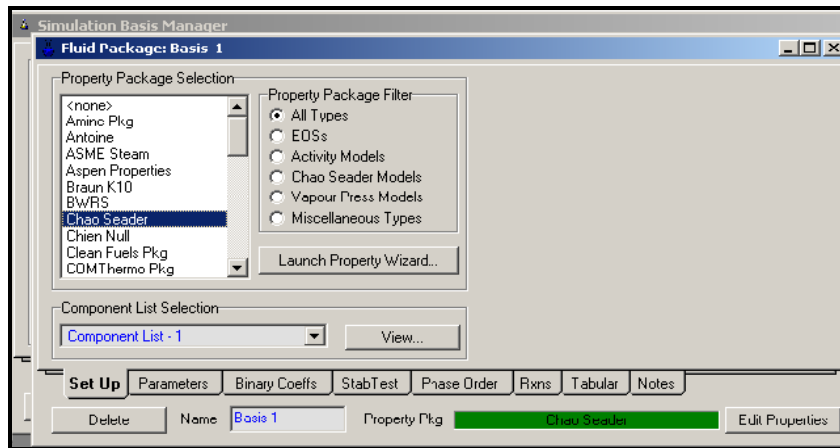
Figure C.6: Selection of a Property Package.

7. Now we want to make sure if the "User Input Expert" check box is on, so we go to SBM Window and hit the "Enter Simulation Environment" button. To see how to access "Session Preferences" Window, follow the item no. 2 above. See Figure C.7:
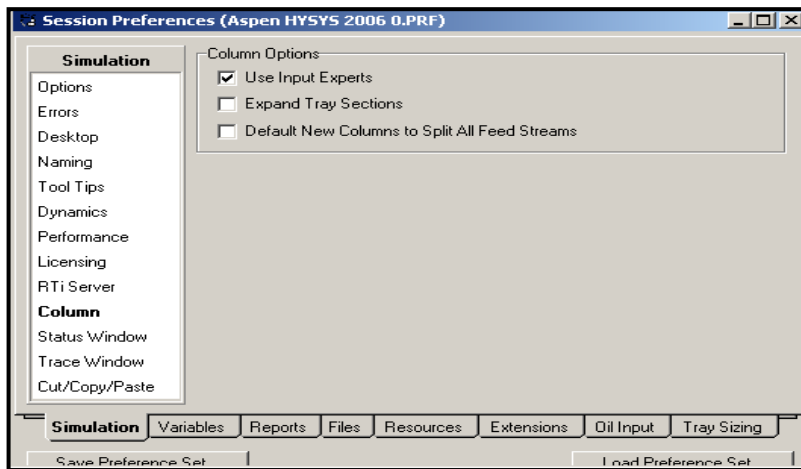

Figure C.7: Making sure that "User Input Expert" is active.

8. From the icons on the palette on PFD screen, a "Distillation Column" is to be selected and drawn to the PFD. Double clicking on the column logo, we can see "Distillation Column Input Expert" window. This window is in fact a wizard, which helps the designer to fill out the minimum data in order for HYSYS to model a distillation column. We need to follow the Figures C. 8 to C.12 and after each step click on the "Next" Button:
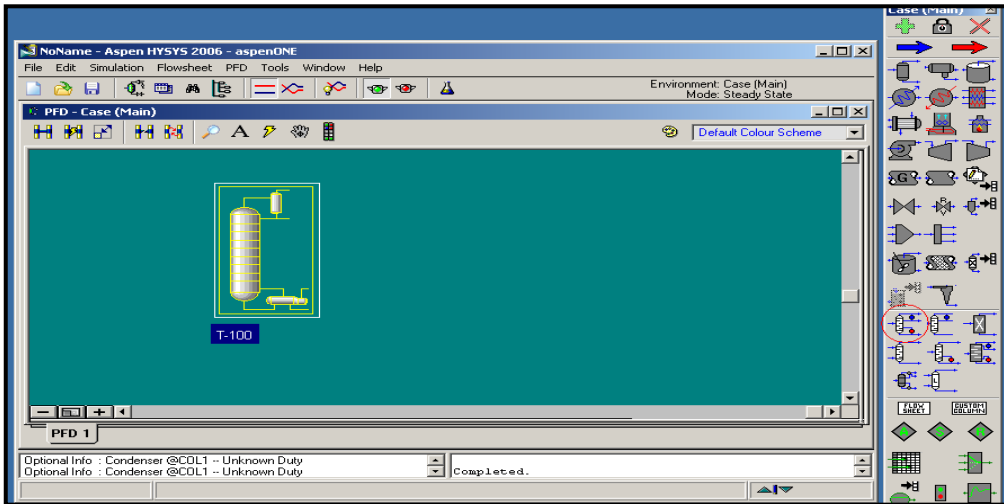
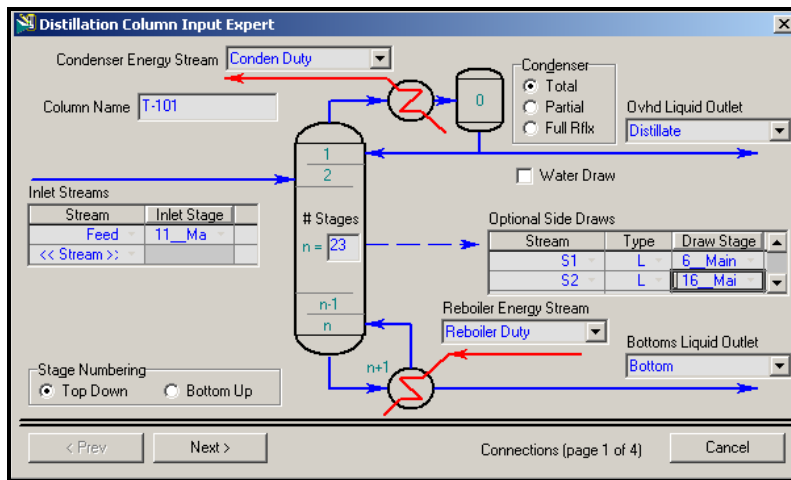**Figure C.8:** Selection of a Distillation Column form the palette on PFD screen.

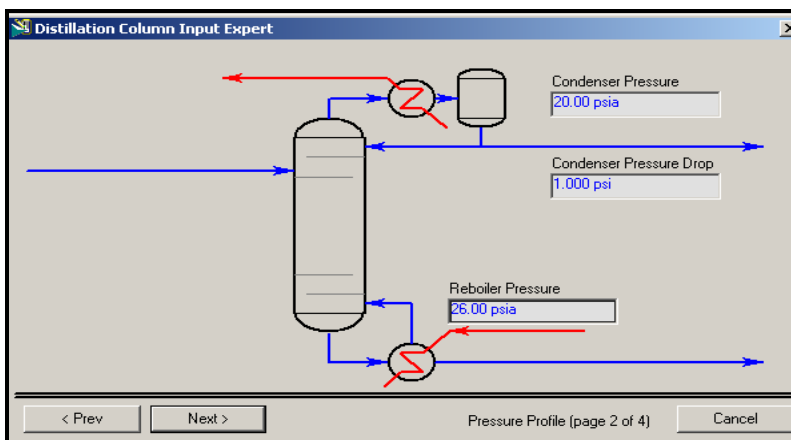**Figure C.9:** Filling out the relevant boxes as in figures 9 to 12 then clicking the "Next" button.

Figure C.10: Type 20, 1 and 26 in Pisa for Condenser Pressure, Condenser Pressure Drop and Re-boiler Pressure fields, respectively.
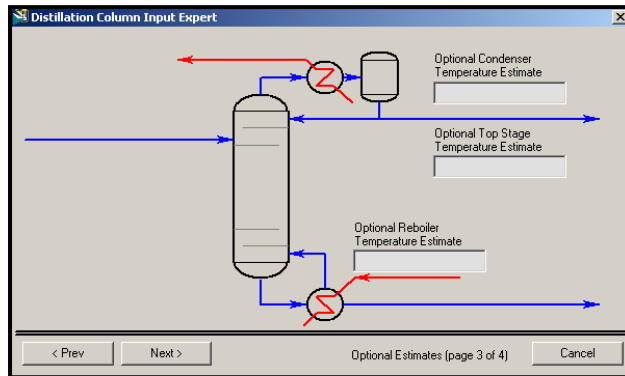
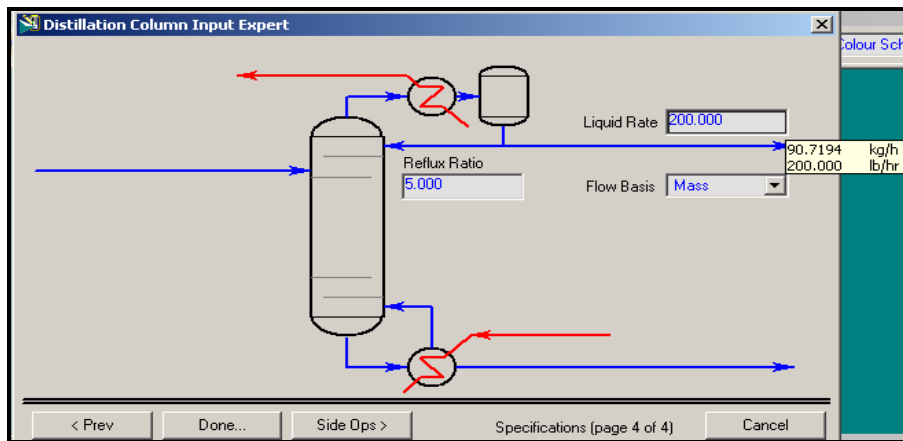**Figure C.11:** Leave this page blank and then click Next button.

Figure C.12: Type 200 lb/hr for Liquid Rate, 5 for Reflux Ratio and Mass in Flow Basis field.

9. Now the conditions of the Feed entering to the column should be given to the Feed Stream by double clicking on the Feed arrow on PFD as shown on the Table C.1:

Table C.1: Feed Stream Conditions.

Feed		
Temperature	120	F
Pressure	25	Pisa
Molar Flow	9.479	lbmole/hr
Molar Flow (n-Pentane)	3.0492	lbmole/hr
Molar Flow (n-Hexane)	1.2764	lbmole/hr
Molar Flow (n-Heptane)	1.5967	lbmole/hr
Molar Flow (n-Octane)	0.4377	lbmole/hr
Molar Flow (n-Nonane)	3.1187	lbmole/hr

10. Once HYSYS receives the above mentioned conditions, it starts calculations for other properties of the mixture. The result is shown in Figures C.13a & C.13b:
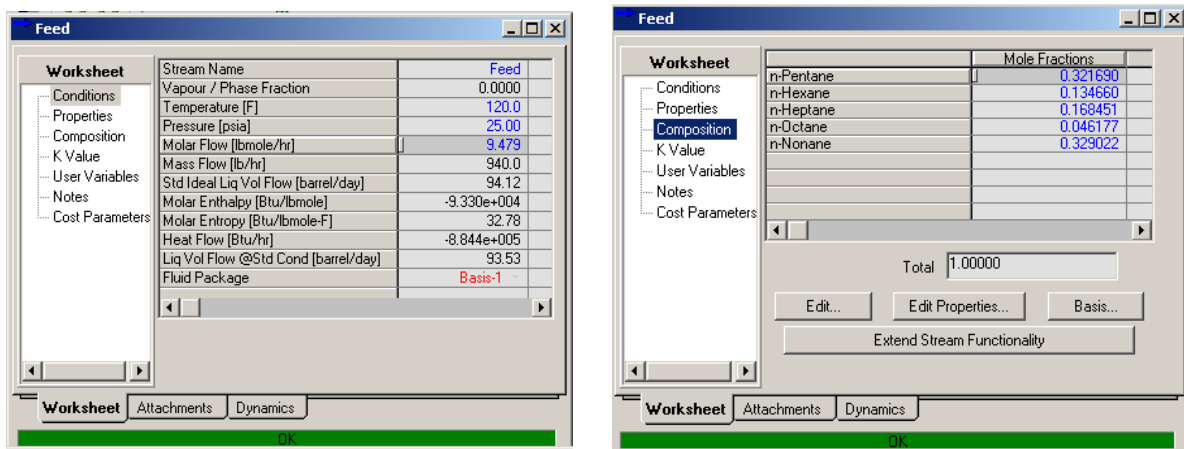

Figure C.13: (a) Feed Conditions. (b) Feed Compositions.

Note: The data in blue colour have been entered by user (designer). The data in black are the result of HYSYS simulation/calculations for the stream.

11. Now going back to the column's window, "Design" page, and selecting the "Specs Summary" we can see that HYSYS pre-assumed there would be 4 degrees of freedom, i.e. Reflux Ratio, Distillate Rate, Side Stream 1, and Side Stream 2. All of them are active check box on but two of which have no value, since we entered only Reflux Ratio and Distillate values while filling out the Column Wizard. In this step we enter 2 lbmoles/hr in the Monitor tab of Design window for each of them and click on the Run button. See Figure C.14:
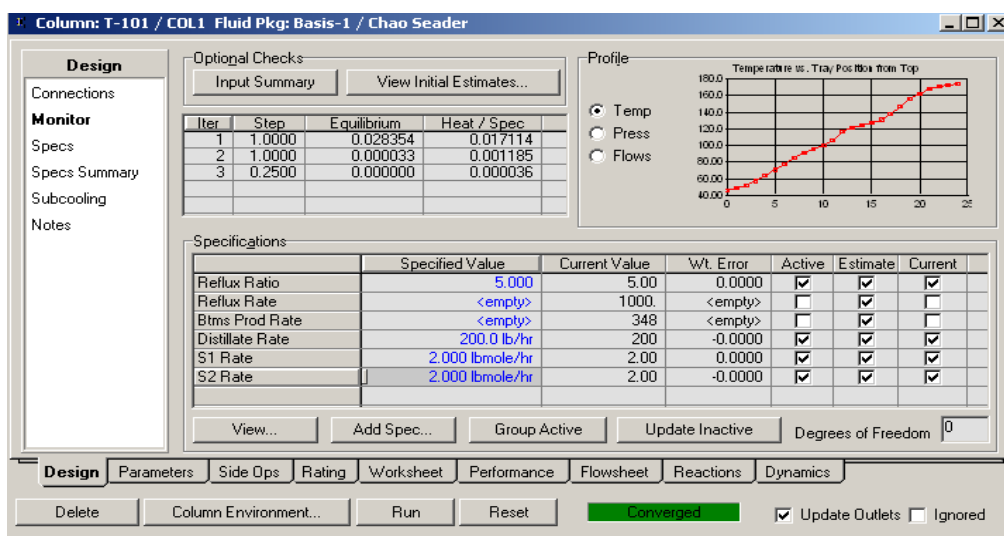

Figure C.14: Simulation of Distillation Tower by HYSYS. Note to the "Converged" message on the bottom of the column window.

117

12. At this point, we will see the graph of the mole fraction versus tray. To access the graph, "Preferences" tab on the a/m window should be selected, followed by "Plot" and then "Compositions" in "Tray by Tray Property" field and finally "By Graph". See Figure C.15:
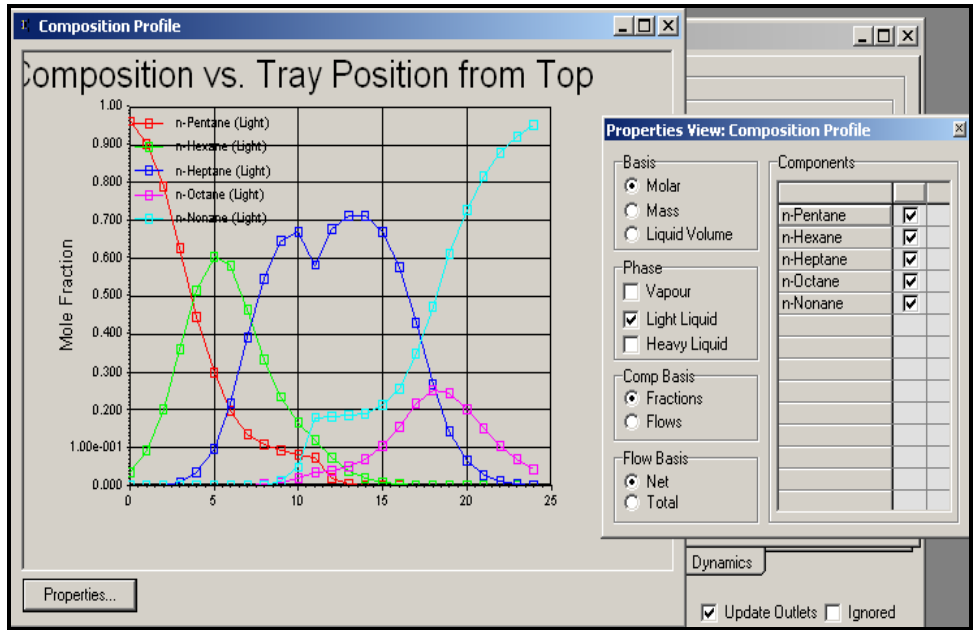

Figure C.15: The Plot of Compositions versus Tray.

13. Also see the result in Table C.2 by selecting "By Table" instead of "By Graph".

Table C.2: The Table of Composition versus Tray.

	n-Pentane [Light Liq]	n-Hexane [Light Liq]	n-Heptane [Light Liq]	n-Octane [Light Liq]	n-Nonane [Light Liq]
Condenser	0.9630	0.0369	0.0001	0.0000	0.0000
1__Main TS	0.9035	0.0960	0.0005	0.0000	0.0000
2__Main TS	0.7929	0.2046	0.0024	0.0000	0.0000
3__Main TS	0.6287	0.3609	0.0104	0.0000	0.0000
4__Main TS	0.4475	0.5168	0.0356	0.0000	0.0000
5__Main TS	0.2986	0.6034	0.0979	0.0001	0.0000
6__Main TS	0.1994	0.5825	0.2177	0.0003	0.0000
7__Main TS	0.1397	0.4666	0.3920	0.0013	0.0004
8__Main TS	0.1104	0.3361	0.5473	0.0040	0.0022
9__Main TS	0.0952	0.2353	0.6482	0.0098	0.0114
10__Main TS	0.0855	0.1684	0.6741	0.0210	0.0510
11__Main TS	0.0756	0.1206	0.5848	0.0366	0.1824
12__Main TS	0.0216	0.0745	0.6788	0.0422	0.1829
13__Main TS	0.0057	0.0415	0.7150	0.0520	0.1858
14__Main TS	0.0014	0.0219	0.7123	0.0705	0.1939
15__Main TS	0.0003	0.0109	0.6708	0.1041	0.2139
16__Main TS	0.0001	0.0049	0.5782	0.1570	0.2598
17__Main TS	0.0000	0.0019	0.4294	0.2185	0.3503
18__Main TS	0.0000	0.0006	0.2693	0.2534	0.4767
19__Main TS	0.0000	0.0002	0.1433	0.2444	0.6120
20__Main TS	0.0000	0.0000	0.0672	0.2038	0.7290
21__Main TS	0.0000	0.0000	0.0289	0.1535	0.8176
22__Main TS	0.0000	0.0000	0.0118	0.1078	0.8804
23__Main TS	0.0000	0.0000	0.0046	0.0717	0.9237
Reboiler	0.0000	0.0000	0.0017	0.0452	0.9531

Thinking about optimization

14. Up to this step we have simulated the distillation column and got the result. From now on, we will focus on the optimization (in our case maximization) of the desired flow rates of components in outlet streams from our simulated column. On the PFD we add a Spreadsheet (See attachment no. 3 for more details about HYSYS Spreadsheet) from palette, and then double click on spreadsheet icon on PFD. The variables are added to the spreadsheet by selection of "Connections" and clicking on "Import Variables" button. On the new window called "Select Import for Cell" we need to add the following variables as shown in Figure C.16:   Distillate (n-C5), S1 (n-C6), S2 (n-C7), S2 (n-C8), Bottom (n-C9).
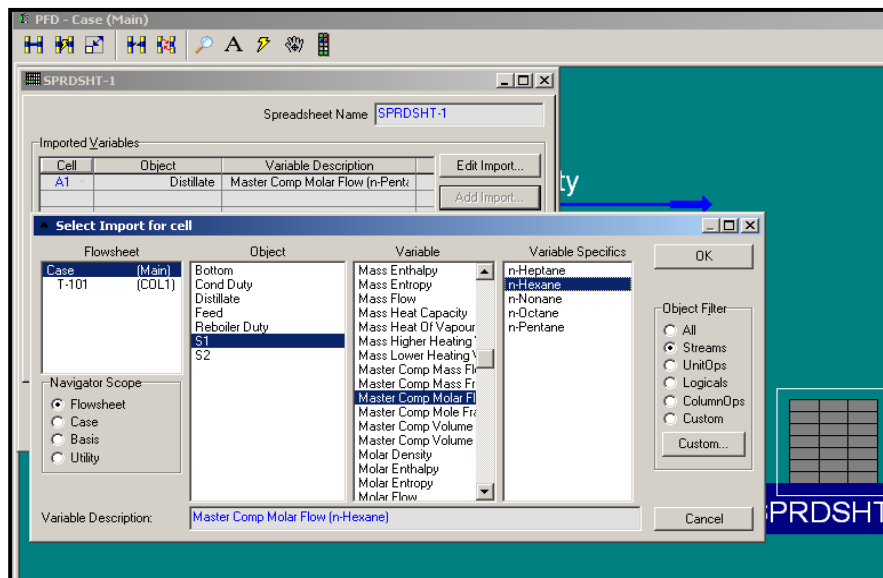

Figure C.16: Introducing the variables to cells A1 to A5 of spreadsheet.

15. After entering all of the variables, we click the "OK" button, and on the SPRDSHT-1 window, click on spreadsheet tab, select B1 cell as a summation of cells A1 to A5. See Figure C.17:
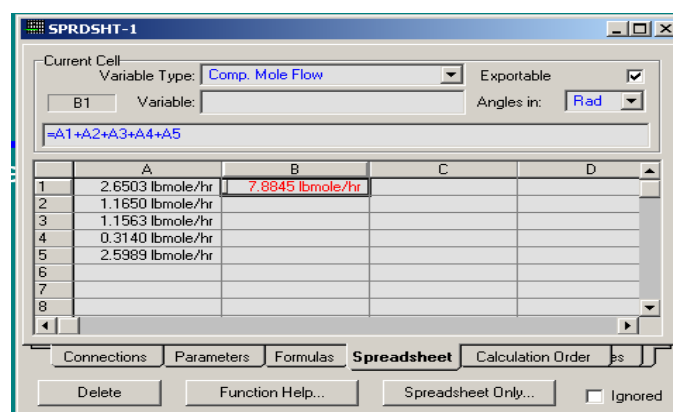

Figure C.17: The values and the sum of variables

16. We now access to "Databook" from "Tools" menu, then hit the "Insert" button to select the variables containing of 4 column specifications (see item no. 11 above) plus the bottom stream (here B1) as shown in Figure C.18.
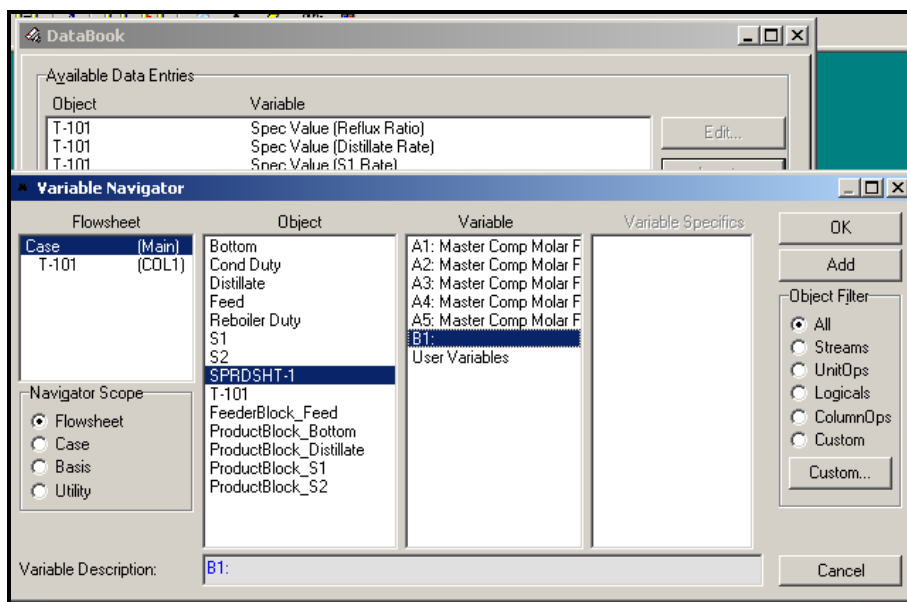

Figure C.18: Selection of variables in Databook.

17. In "Databook" window, we define the "Reflux Ratio" and "S1" as independent variables and B1 (sum of A1 to A5 in Spreadsheet-see item no. 15) as dependent variable. To do so, we selected "Case Study" page in "Databook". See Figure C.19.
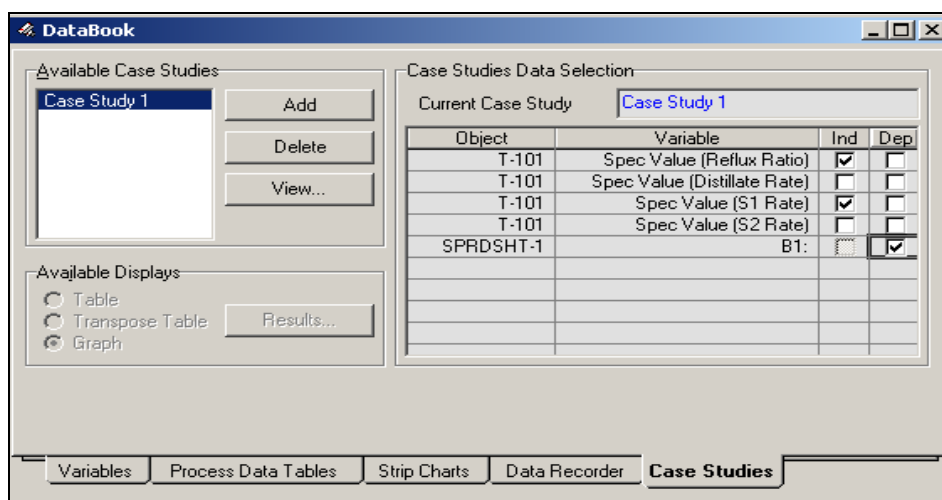

Figure C.19: Determination of dependent and independent variables in Databook.

18. Tapping on "View" button of Fig. C. 19, we can access to "Case Study Setup Main" window to determine the initial and final values including step sizes for independent variables then hit the "Start" button. See Figures C.20a and b.
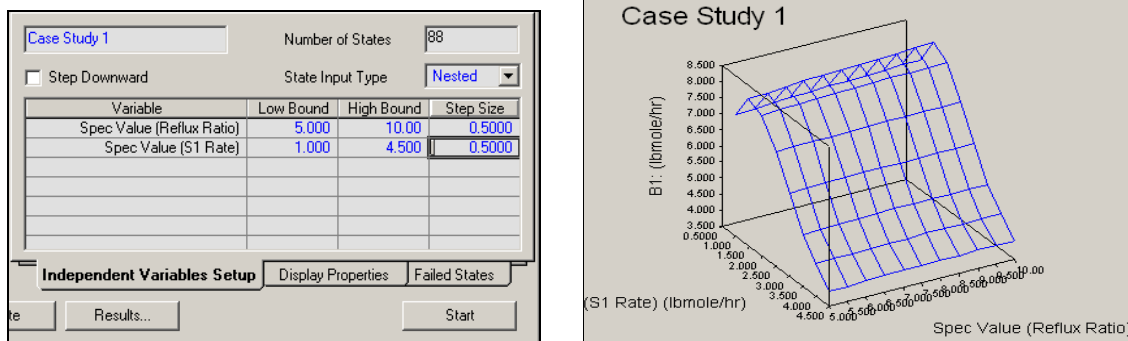

Figure C.20: (a) Case Study Setup Main Window. (b) Reflux Ratio and S1 versus B1; 3D Curve.

Optimization: For optimization purposes, all of objective functions, optimization variables and constraints must be introduced to the software.

19. The first step in optimization by HYSYS is to determine the **Optimization Variables** or Adjusted (Primary) Variables or better the **"Decision Variables"** for HYSYS. To do so, we go to "Optimizer" window from "Simulation" menu, select "Variables" page on "Optimizer" window, and then click on "Add" button to access the "Add Variable to Optimizer" window. Follow Figures C.21 to C.23:
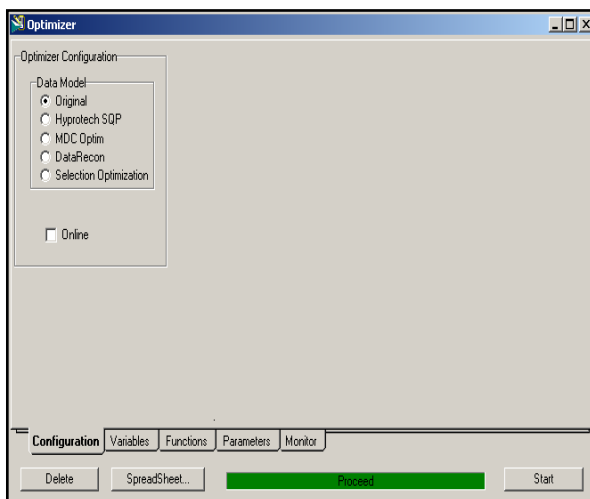

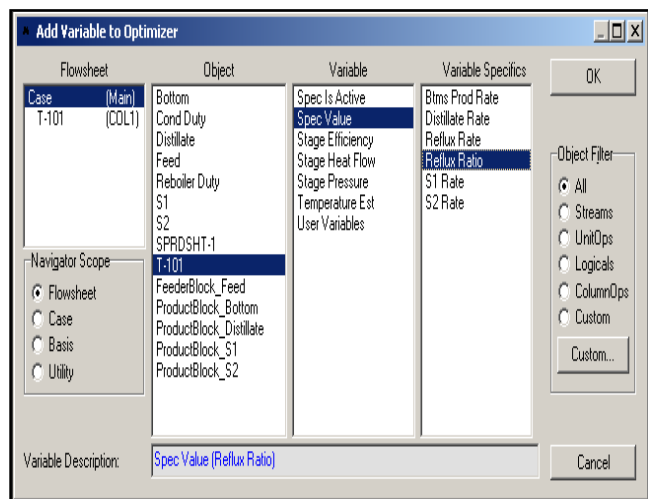
Figure C.21: "Optimizer" window.   **Figure C.22:** Adding variables to "Optimizer" window.
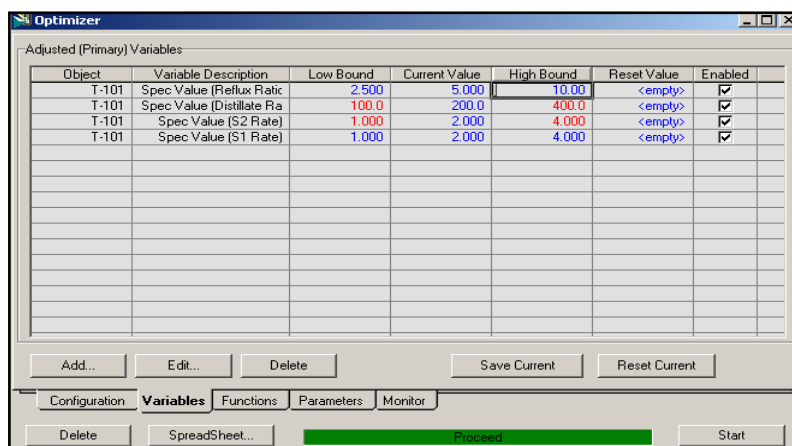
Figure C.23: Determination of Optimization Variables or Decision Variables to the "Variables" page of "Optimizer" Window.

20. The second step in optimization by HYSYS is to define all of the variables and functions, which make objective functions and constraints. On "Optimizer" window by clicking on "Spreadsheet…" button we go to "Optimizer Spreadsheet" window then click on "Add Import…" button in the new window access to the "Select Import for Cell" window. See Figures C.24 and C.25. The following variables should be added to the "Imported Variable" list on "OptimizerSpreadsheet" window:

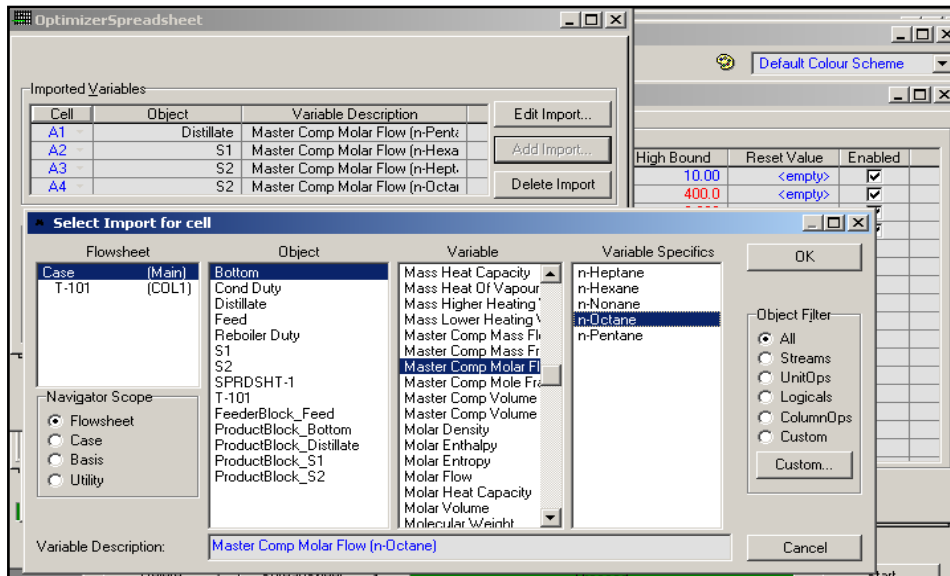|		
Distillate	Master Comp Molar Flow	n-C5,
Side Stream 1 (S1)	Master Comp Molar Flow	n-C6,
Side Stream 2 (S2)	Master Comp Molar Flow	n-C7,
Side Stream 2 (S2)	Master Comp Molar Flow	n-C8,
Bottom	Master Comp Molar Flow	n-C9.

Figure C.24: Selecting the variables from "Select Import for Cell" window.
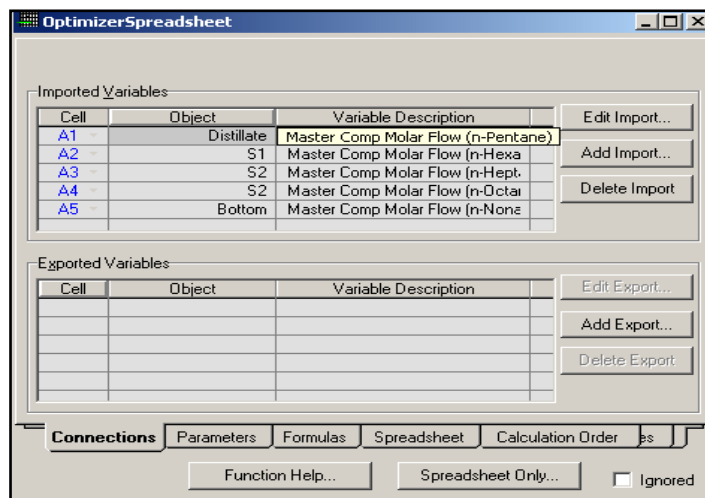
Figure C.25: Adding the variables to the "Imported Variable" list.

Then, on "Optimizer" window, clicking on the "Spreadsheet" tab, we consider A6 cell for the summation of cells A1 to A5. See Figure C.26:
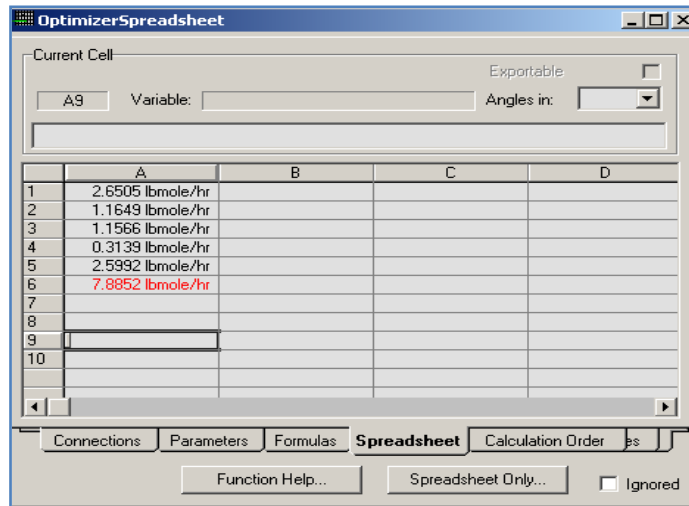
Figure C.26: Consider A6 cell for the summation of cells A1 to A5.

21. Back to the "Connections" tab on "OptimizerSpreadsheet" window, we consider the cells C1 to C5 for following variables. See Figure C.27:

Cell No.	Object Name	Type
C1	Distillation Rate Stream	Molar Flow
C2	S1 Stream	Molar Flow
C3	S2 Stream	Molar Flow
C4	Bottom Stream	Molar Flow
C5	Feed Stream	Molar Flow

Figure C.27: Input other variables in "Connections" tab of "OptimizerSpreadsheet"Window.

22. In this step, we introduce some functions of constraints in cells D2 to D5 in the "Spreadsheet" tab on "OptimizerSpreadsheet" Window as in Figure C.28:

D2 = Distillate/Feed (C1/C5)

D3 = S1/Feed (C2/C5)

D4 = S2/Feed (C3/C5)

D5 = Bottom/Feed (C4/C5)

We also consider the lower and upper limits for HYSYS, which are to be defined in cells D7 to D9:   D7 = 0.1;   D8 = 0.7;   D9 = 0.05.
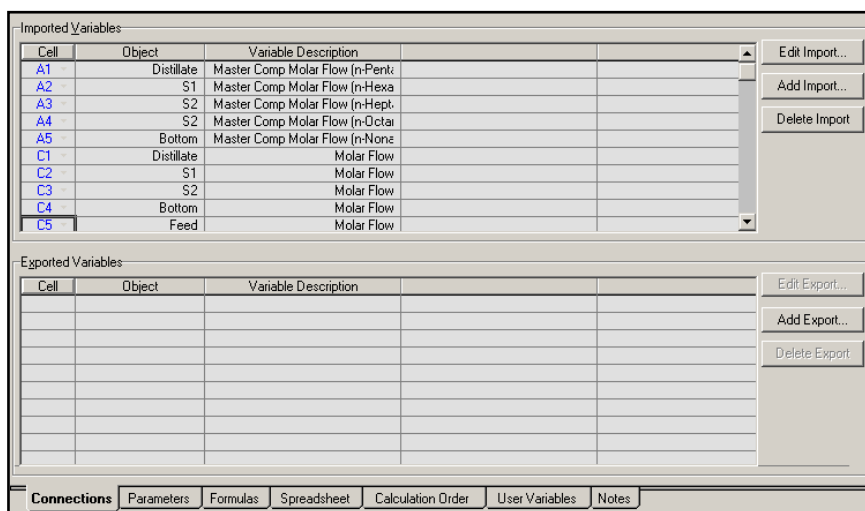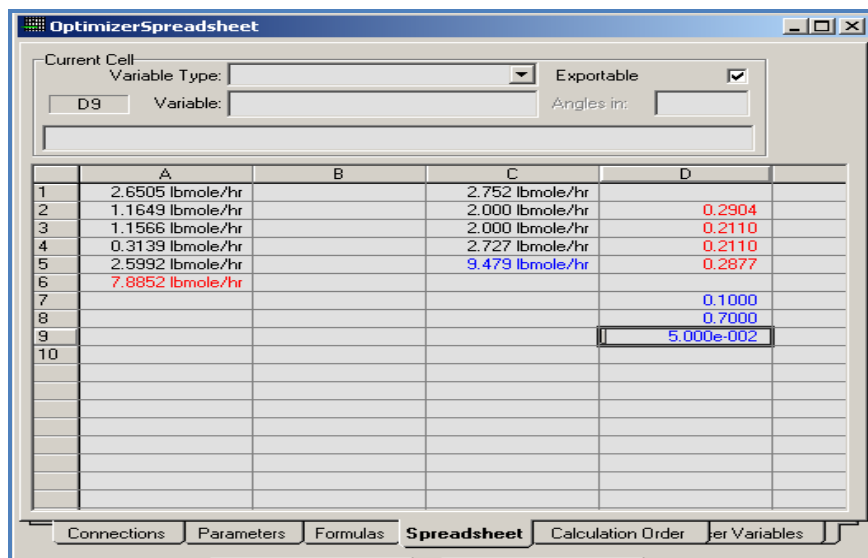

Figure C.28: Introducing functions and constraints to HYSYS.

Up to here, all variables and functions in objective function in addition to constraints are defined to HYSYS and calculated by it accordingly. The next step is to introduce these functions to Optimizer.

23. Back to Optimizer window and on "Functions" tab, A6 (the sum of A1 to A5-see item no. 20), which is of our interest for optimization as it is our **"Objective Function"** and also "Maximize" option must be selected. "LSH Cell", "Cond" and "RSH Cell" must be entered by user in "Constraint Functions" field as shown in Figure C.29.
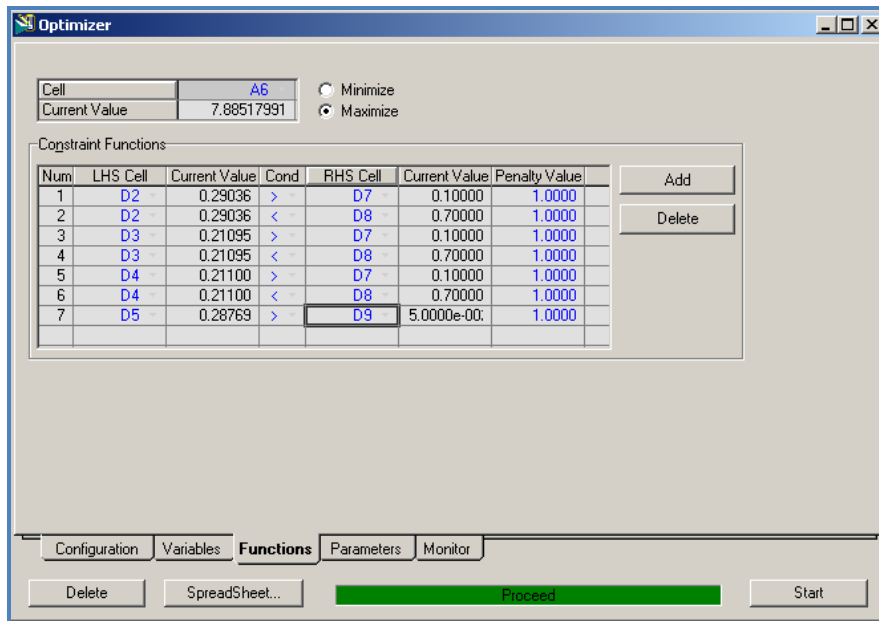
Figure C.29: Introducing the "Objective" and "Constraints" Functions to "Optimizer".

24. Now we need to introduce the first constraint to optimizer, which has not been done yet. For this reason, on the Optimizer window, we select the "Variables" tab and in "Adjusted (Primary) Variables" field, we type numbers 5 and 10 to the "Low Bound" and "High Bound" of "Reflux Ratio" (the first row of aforementioned field), respectively, recalling that Adjusted (Primary) Variables, is in fact our "Decision Variables". See Figure C.30.
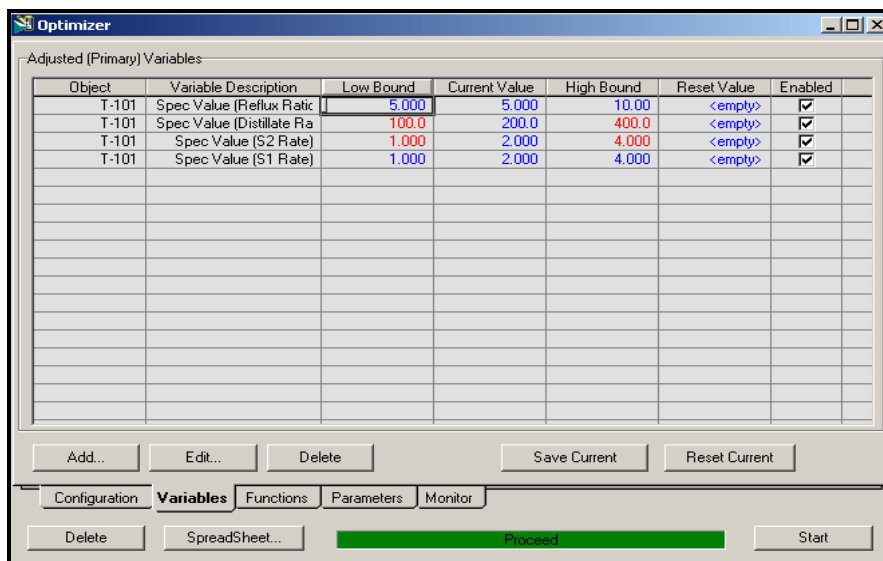
Figure C.30: Entering the Low and High Bounds of Reflux Ratio to Optimizer.

25. And now we have to clarify for HYSYS what method of optimization to choose. As mentioned in "Abstract" section at the beginning of this report, SQP is applied for the method of optimization or our case. To do so, on "Parameters" tab on the Optimizer window, the following changes should be made (see Figure C.31):

- Select "SQP" in "Scheme" field,
- Type 0.01 and 0.0 in Shift A and Shift B fields, respectively.

Note: For short descriptions about optimization methods in HYSYS please refer to attachment nos. 1. Also see the item no. 8 of the references list.
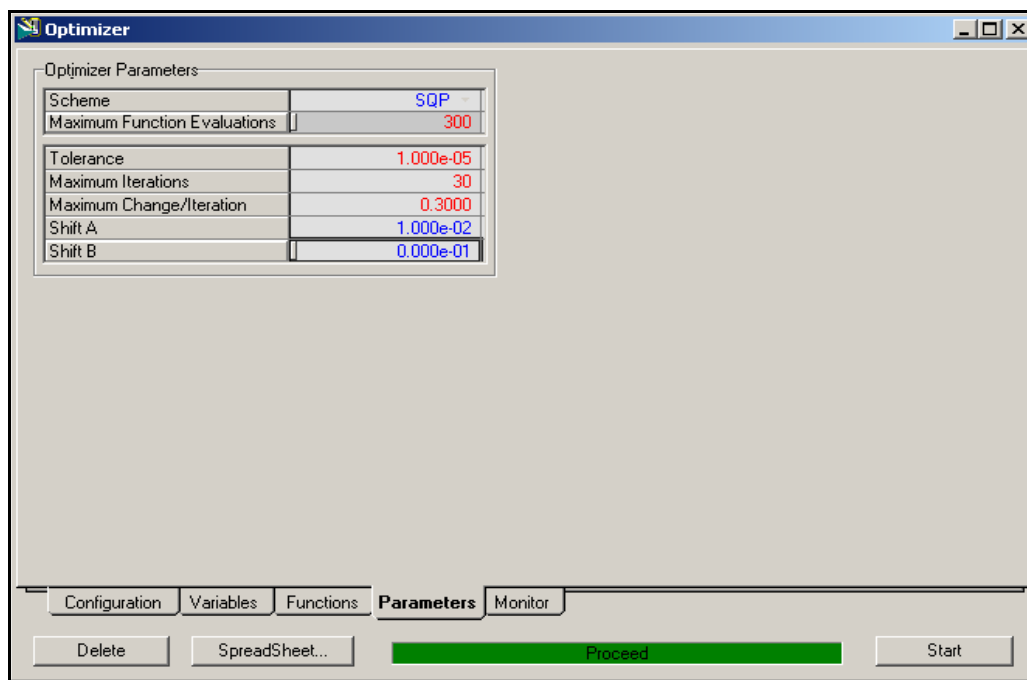
Figure C.31: Selecting the optimization method.

26. At this point, HYSYS is ready to perform calculations and graphs for optimization of our objective function. As it can be seen from Figure C.31 and other figures of Optimizer window, there is a green bar in the bottom of window with the word "Proceed" on it. All we need to do is just clicking on the "Start" button on the "Optimizer" window (See Figure C.31). After clicking on this button the word **"Proceed"** will be replaced by **"Optimum found (SmallDeltaX)"**. Please compare Figure C.32 with Figure C.31:
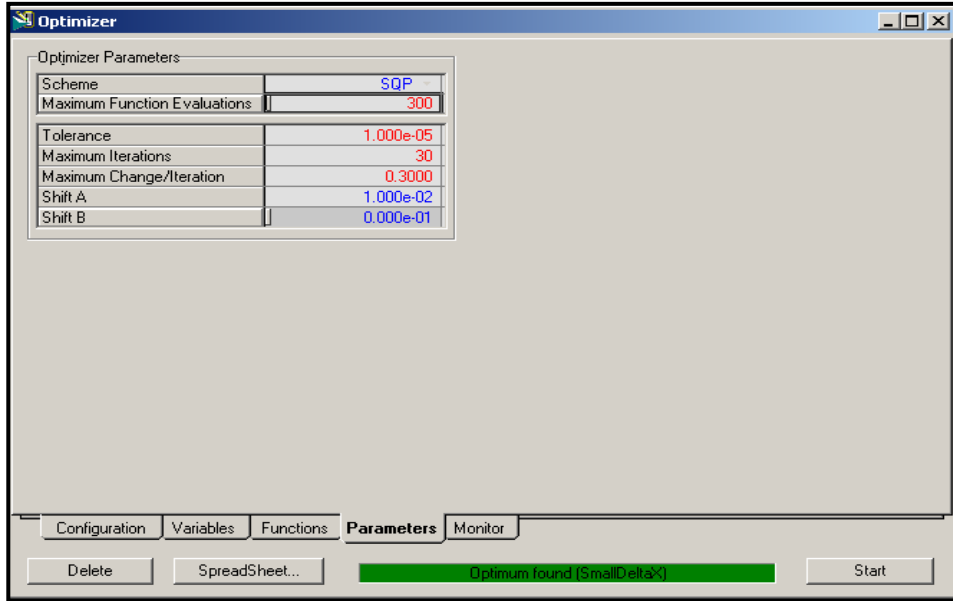
Figure C.32: HYSYS found the optimum values successfully. Compare with Fig. C.31

27. Now we see the graph of the mole fraction versus tray. To access the graph, "Preferences" tab on the a/m window should be selected, followed by "Plot" and then "Compositions" in "Tray by Tray Property" field and finally "By Graph". See Figure C.33 and compare it with Figure C.15:
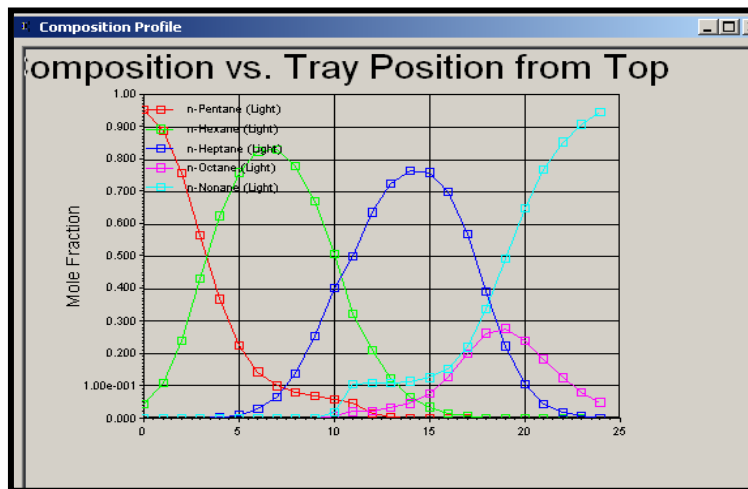
Figure C.33: The Plot of Compositions versus Tray after optimization.

Results

A. We have already introduced our objective function to HYSYS as A6 cell. Comparing the values of A6 before and after the optimization (see Figure C.34a and C.34b); we can see that A6 has increased by 8.85%.
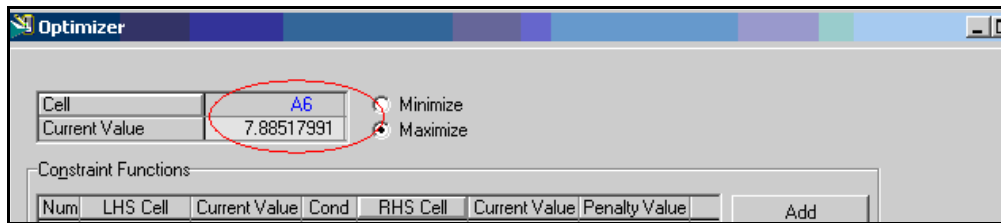
(a)
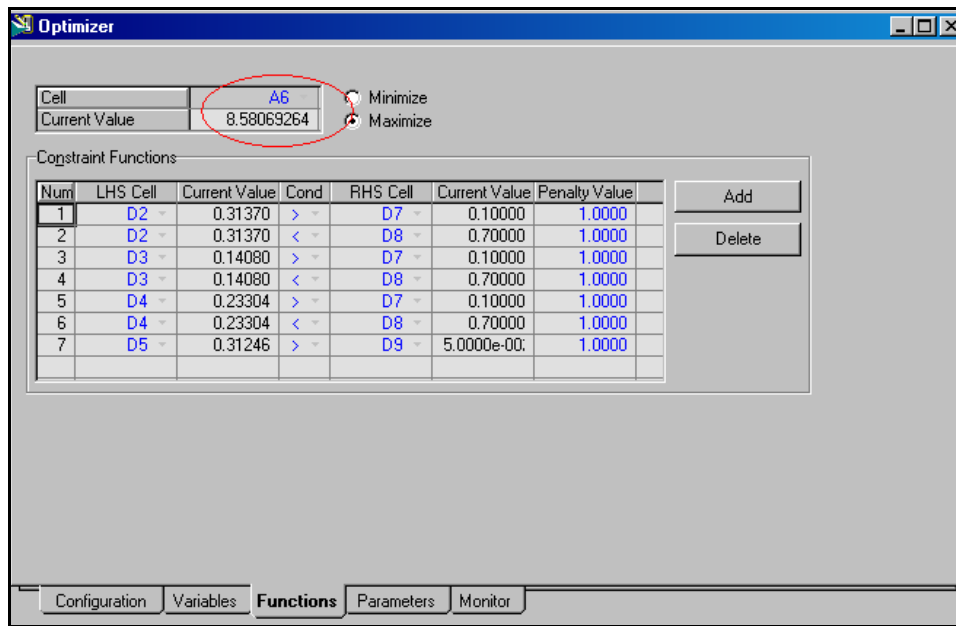
(b)

Figure C.34: (a) Optimizer Function Window before Optimization. See also Fig. C.29. (b) Optimizer Function Window after Optimization.

B. The sizes of condenser and re-boiler are the same and remained unchanged before and after optimization, as in Figure C.35:
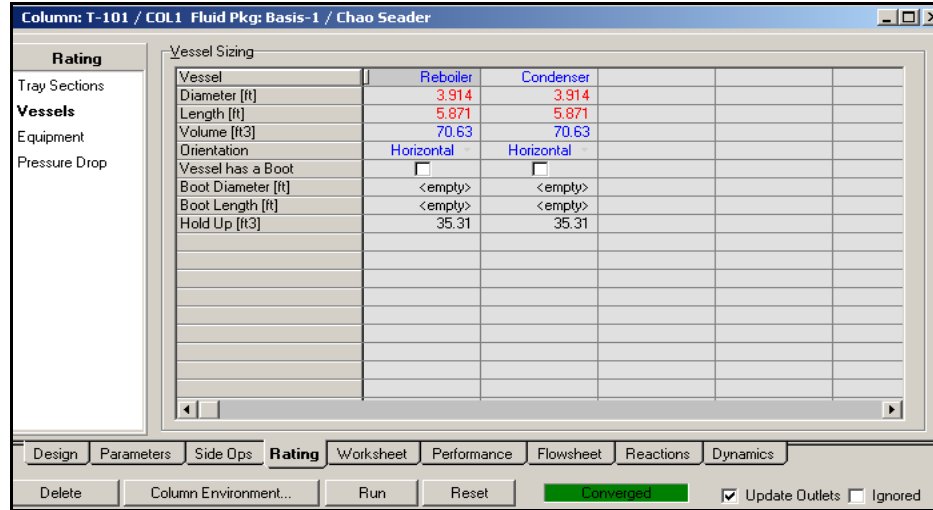
Figure C.35: On the "Rating" tab of Column sheet, check the "Vessel Sizing" field.

As mentioned before, it is not our task to optimize the energy consumptions at this point; otherwise the number of re-boilers could be discussed for instance, two instead of one.

If there would be medium pressure steam (MPS) in the plant, the replacement of low pressure steam (LPS) with MPS also could be investigated. Usually LPS is used for heating up the column re-boilers especially in small to medium scale plants.

Cooling water (CW) consumption has no significant influence on plant economy; however, it could be investigated in the last step of plant optimization.

C. For this optimization the duties of condenser and re-boiler will be increased by almost 98.34% and 70.92%, respectively. Compare Figures C.36a and C.36b:

(a)

(b)

Figure 36: (a) Duties of condenser and re-boiler before optimization. (b) Duties of condenser and re-boiler after optimization

ATTACHMENT NO. 1

Optimization methods in HYSYS[9]

HYSYS uses different methods for optimization. These methods are explained hereunder:

- **BOX method:**

a. This method uses "Sequential Search" technique for solving non-linear objective functions with non-linear constraints.

b. Gradient models are not used in this method.

c. Only inequality constraints can be used in this method of optimization. Equality constraints are not acceptable.

d. This method needs large number of iterations and generally is highly stable.

- **SQP method:**

a. It can be used for both cases; equality and inequality constraints.

b. It is a good method of optimization if there are good initial values and fewer variables.

c. This method applies "Powell" algorithm.

- **Fletcher-Reeves method:**

a. This method applies "Polak-Ribiere" algorithm, which is a modified model of "Fletcher-Reeves Conjugate Gradient" algorithm.

b. It can not be used if the optimization has constraints.

- **Quasi-Newton method:**

a. This method applies "Quasi-Newton method of Broyden-Fletcher-Goldfarb-Shanno (BFGS)" algorithm.

b. It cannot be used in case the optimization has constraints.

- **Mixed method:**

a. This method has both advantages: the stability of BOX method and the speed of SQP method.

b. This method is used only for inequality constraints.

ATTACHMENT NO. 2

Chao Seader (CS) Models for property package (adapted from HYSYS help menu)[9]

Use the Chao Seader (CS) method for heavy hydrocarbons, where the pressure is less than 10342 kPa (1500 Pisa), and temperatures range between -17.78 and 260°C (0-500°F).

The CS property package is used for the steam systems. The CS property package can also be used for three-phase flashes, but is restricted to the use of pure H_2O for the second liquid phase.

The CS method, though limited in scope, may be preferred in some instances. For example, CS is recommended for problems containing mainly liquid or vapour H_2O because the property package includes special correlations that accurately represent the steam tables.

The following tables give an approximate range of applicability for CS method and under what conditions CS is applicable.

Method	Temp (°F)	Temp (°C)	Press (Pisa)	Press (kPa)
CS	0 to 500	-18 to 260	<1,500	<10,000

Conditions of Applicability

For all hydrocarbons (except CH4): · $0.5 < Tri < 1.3$ and Prmixture < 0.8

If CH4 or H2 is present:· molal average $Tr < 0.93$ · CH4 mole fraction < 0.3·mole fraction dissolved gases < 0.2

When predicting K values for:

Paraffinic or Olefinic Mixtures · liquid phase aromatic mole fraction < 0.5

Aromatic Mixtures · liquid phase aromatic mole fraction > 0.5

Chao-Seader (CS) uses the CS-RK method for calculating VLE and the Lee Kessler method for calculating Enthalpy and Entropy.

The vapour phase fugacity coefficients are calculated with the Redlich Kwong equation of state. The pure liquid fugacity coefficients are calculated using the principle of corresponding states. Special functions are incorporated for the calculation of liquid phase fugacities for N_2,

CO2 and H2S. These functions are restricted to hydrocarbon mixtures with less than five percent of each of the above components.

As with the Vapour Pressure models, H2O is treated using a combination of the steam tables and the kerosene solubility charts from the API Data Book. This method of handling H2O is not very accurate for gas systems. Although three phase calculations are performed for all systems, it is important to note that the aqueous phase is always treated as pure H2O with these correlations.

ATTACHMENT NO. 3

HYSYS spreadsheet (adapted from HYSYS help menu)[9]:

The Spreadsheet applies the functionality of Spreadsheet programs to flowsheet modeling. With essentially complete access to all process variables, the Spreadsheet is extremely powerful and has many applications in HYSYS.

The Spreadsheet can be used to manipulate or perform custom calculations on Flowsheet variables. Because it is an operation, calculations are performed automatically; Spreadsheet cells are updated when flowsheet variables change.

Complex mathematical formulas can be created, using syntax which is similar to conventional Spreadsheets. Arithmetic, logarithmic, and trigonometric functions are examples of the mathematical functionality available in the Spreadsheet. The Spreadsheet also provides logical programming in addition to its comprehensive mathematical capabilities. Boolean logic is supported, which allows you to compare the value of two or more variables using logical operators, and then perform the appropriate action depending on that result.

Reference C:

1. Robert E. Treybal, "Mass Transfer Operations", Chapter 9, McGraw-Hill Inc. 1980, 3rd Edition.

2. Selection of a thermodynamic model in HYSYS Simulation (dated Sept. 2008): http://people.clarkson.edu/~wilcox/Design/thermodl.htm

3. Generating binary and ternary phase diagrams using HYSYS (dated Sept. 2008): http://people.clarkson.edu/~wilcox/Design/phasdiag.htm

4. Selection of Thermodynamic model, click on the following links (dated Sept. 2008):
   other methods of
   other methods with examples

5. Excellent papers for preventing the uncertainty in the physical properties, particularly phase equilibria (dated Sept. 2008):
   "Uncovering the realities of simulation," part A
   http://people.clarkson.edu/~wilcox/Design/simultr1.pdf
   and Part B:
   http://people.clarkson.edu/~wilcox/Design/simultr2.pdf

6. Other Source: For finding the details in Property Methods and Calculations please refer to the following website (dated Sept. 2008):
   http://users.rowan.edu/~hesketh/0906-316/Handouts/Pages%20from%20SimBasis%20appendix%20A%20property%20packages.pdf

7. HYSYS Training (dated Sept. 2008):

   http://support.aspentech.com/supportpublictrain/FrameTrain.asp?ProductTraining.asp?id1=2674&id2=HYSYS&id3=all&id4=2006

8. T. F. Edgar, D. M. Himmelblau and L. S. Lasdon, "Optimization of Chemical Processes", Chapter 8, 2nd Edition, McGrawHill Higher Education, 2001.

9. One of the most important references, which can be used at any time while simulating with HYSYS is the HYSYS Help menu. It provides the users with useful hints at any time. For instance, attachment nos. 1 to 3 of this report are adapted from Help menu.

APPENDIX D: Modeling and simulation of a plug flow reactor for hydrogenation reaction

A plug flow reactor or simply PFR is a tubular reactor with the following properties and assumptions[1]:

1. The conditions at any point of the PFR are time independent.

2. Constant linear velocity, temperature and composition for the reaction mixture in the reactor cross-section; i.e. no radial gradients.

3. The composition of the reacting flow varies with the distance L from the reactor inlet point.

4. No flow mixing inside the reactor.

5. Velocity profile is flat.

Figure D.1 shows a typical PFR. For the modeling of a PFR the following assumptions also should be made:

1. Steady state operation.

2. Plug flow.

3. Rate constant is constant across the reactor and independent from the reactor length.
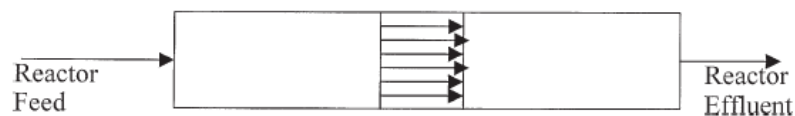
Figure D.1. A schematic tubular (plug flow) reactor. Copied from Ref. D.1

A PFR consists of one or more cylindrical pipes and is mostly used for gas phase reactions. It operates at steady state and the reactants are consumed continually as they flow down the reactor length. Concentrations and other conditions change in the axial direction but no variations in radial direction.

Design equation:

Suppose the following hydrogenation reaction takes place in a PFR:

$$aA + bH_2 \rightarrow cP \tag{D-1}$$

where A and P are unsaturated hydrocarbons and saturated ones, respectively.

For a single C=C double bond hydrogenation (saturation) reaction, $a = b = c = 1$

The following steps should be followed in order to design and size a tubular reactor[2]:

1. $dV = F_{Ao} \cdot dx / (-r_A)$ ➔ $dV / dx = F_{Ao} / (-r_A)$ $\qquad$ (D-2)

2. $C_A = C_{Ao} \cdot (1-x) / (1 + \Sigma x)$ $\qquad$ for liquid phase reaction. $\qquad$ (D-3)

   where $\Sigma = y_{Ao} \cdot \delta = (F_{Ao} / F_{To}) \cdot (c/a - b/a - 1) = (-F_{Ao} / F_{To})$ $\qquad$ (D-4)

3. $F_{Ao} = C_{Ao} \cdot v_o$ $\qquad$ (D-5)

4. $-r_A = k\, C_A\, (C_{H2})^{1/2}$ $\qquad$ (B-17)

5. $k = k_{ref} \exp [-E/R(1/T_2 - 1/T_1)]$ $\qquad$ (D-6)

Combination of the above equations and considering the available data from tables B.4 and 4.2 a, b, and c and also design criteria; e.g. reaction end temperature 158 ^oC, gives:

6. $dV/dx = (C_{Ao}v_o)/\{k_{ref} \exp[-E/R(1/T_2 - 1/T_1)]C_{Ao}[(1-x)/(1+(-F_{Ao}/F_{To})x)](C_{H2})^{1/2}\}$ (D-7)

7. $C_{H2} = C_{Ao}(\theta_{H2}+\gamma_{H2} x)/(1+\Sigma x) = C_{Ao} (\theta_{H2} + \gamma_{H2} x)/[1+(-F_{Ao}/F_{To})x]$ $\qquad$ (D-8)

where C_{Ao} is the initial concentration of unsaturated hydrocarbon and in this particular case is the initial concentration of i-Butene and

$\theta_{H2} = (F_{H2})_o / F_{Ao} = (248.02\ Kgmol/h) / (2.0277\ Kgmol/h)$ ➔ $\theta_{H2} = 122.32$

and

$\gamma_{H2} = -b/a = -1$

$F_{To} = 393.01\ Kgmol/h$

$F_{Ao}/F_{To} = (2.0277\ Kgmol/h) / (393.01\ Kgmol/h) = 0.0052\ (<< 1)$

$C_{Ao} = F_{Ao} / v_o = (2.0277\ Kgmol/h) / (285.6\ m^3/h) = 4.2\ mol/m^3$

Thus:

$C_{H2} = 4.2 \times (122.32 - x)$

$T_1 = 361.36$ K

$T_2 = 431.95$ K

$E_{i\text{-Butene}} = 39100$ J/mol

$K_{ref} = 4.66 \ [mol/(h)(m^3)] \times (m^3/mol)^{3/2}$

Note 1: k_{ref} is in $[mol/(s) \ (Kg \ Cat)] \times (m^3/mol)^{3/2}$ and therefore, in order to find the PFR volume, k_{ref} is to be multiplied by 3600 (s/h) and then by 618 $(Kg/m^3)^3$.

Results

The above data is entered into POLYMATH to find the volume of catalyst used for the hydrogenation reaction when conversion is 0.85. Table D.1 shows the result:

Table D.1. Calculations made by POLYMATH for sizing a PFR for the hydrogenation of Iso-Butene.

POLYMATH Results For Sizing the PFR for Hydrogenation of i-Butene
No Title   03-21-2009,   Rev5.1.225

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
x	0	0	0.85	0.85
V	0	0	3.1904038	3.1904038
v0	285.6	285.6	285.6	285.6
P0	29.01	29.01	29.01	29.01
P	27.26	27.26	27.26	27.26
T0	361.36	361.36	361.36	361.36
T	431.95	431.95	431.95	431.95
kref	2.096E-06	2.096E-06	2.096E-06	2.096E-06
E	3.91E+04	3.91E+04	3.91E+04	3.91E+04
R	8.314	8.314	8.314	8.314

Note 2: It should be taken into account that the calculated volume is the catalyst volume and since the porosity is 0.5^3, the result should be multiplied by 2 or divided by 0.5 to obtain the PFR volume. In our case:

$V_{PFR} = 3.19 \text{ m}^3 / 0.5 = 6.38 \text{ m}^3$

We need a more practical data to obtain more applicable sizing for our PFR. Fortunately, good evidence is available in literature by one of the well-known companies in this field, i.e. IFP technologies[4].

One of the most important parameters in designing a reactor especially a PFR is space velocity. Generally, the space velocity is the reciprocal of the space time (τ), which in turn is equal to:

$$\tau = V/v_0 \tag{D-9}$$

where V is the volume of the reactor and v_0 is the volumetric feed flow rate to the reactor by definition[5]. Similarly, the space velocity is defined as the volumetric flow rate of reactant streams at reference conditions:

$$SV = 1 / \tau \tag{D-10}$$

Space time the volumetric flow rate is measured at the entrance conditions, whereas the space velocity (SV) is measured, as stated in reference conditions.

There are two types of space velocity, which are commonly used in industries: LHSV and GHSV.

LHSV or liquid-hourly space velocity is the liquid volumetric feed rate (v_0) measured at 60 $^{\circ}$F or 70 $^{\circ}$F, although the feed stream may be a vapor at a higher temperature. But in GHSV the v_0 is measured at standard temperature and pressure (STP)[6].

Lin T.B. and Chou T.C.[4] from IFP, reported the best LHSV for the hydrogenation of pyrolysis gasoline to be 3.5 h^{-1}. In this regard, the standard volumetric liquid flow rate of the feed stream to the reactor is equal to 21.95 m^3/h. Combining the equations (3-5) and (3-6) gives:

$$SV = v_0 / V \tag{D-11}$$

Or

$$V = v_0 / SV \tag{D-12}$$

Thus,

$V = (21.95 \text{ m}^3/\text{h}) / (3.5 \text{ h}^{-1}) = 6.27 \text{ m}^3$

This is close to the volume obtained from POLYMATH for Iso-Butene as it can be seen in previous page (6.38 m3).

The same modeling for other unsaturated components; e.g. 1-Butene, Iso-octane and Styrene were done in the same way as for Iso-Butene followed by calculations made by POLYMATH. Tables D.2 to D.4 show the results.

Tables D.2 to D.4. Calculations made by POLYMATH for sizing a PFR for the hydrogenation of 1-Butene, Iso-octane and Styrene, respectively.

(D.2)

POLYMATH Results For Sizing the PFR for Hydrogenation of 1-Butene
No Title   03-21-2009,   Rev5.1.225

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
x	0	0	0.85	0.85
V	0	0	0.6688899	0.6688899
v0	285.6	285.6	285.6	285.6
P0	29.01	29.01	29.01	29.01
P	27.26	27.26	27.26	27.26
T0	361.36	361.36	361.36	361.36
T	431.95	431.95	431.95	431.95
kref	1.482E-05	1.482E-05	1.482E-05	1.482E-05
E	3.49E+04	3.49E+04	3.49E+04	3.49E+04
R	8.314	8.314	8.314	8.314

(D.3)

POLYMATH Results For Sizing the PFR for Hydrogenation of i-Octene
No Title   03-21-2009,   Rev5.1.225

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
x	0	0	0.85	0.85
V	0	0	0.0407009	0.0407009
v0	14.65	14.65	14.65	14.65
P0	29.01	29.01	29.01	29.01
P	27.26	27.26	27.26	27.26
T0	361.36	361.36	361.36	361.36
T	431.95	431.95	431.95	431.95
kref	1.23E-04	1.23E-04	1.23E-04	1.23E-04
Ca0	0.7738567	0.7738567	0.7738567	0.7738567
E	1.051E+04	1.051E+04	1.051E+04	1.051E+04
R	8.314	8.314	8.314	8.314

(D.4)

POLYMATH Results PFR for Hydrogenation of Styrene
No Title   03-21-2009,   Rev5.1.225

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
x	0	0	0.85	0.85
V	0	0	5.487E-04	5.487E-04
v0	285.6	285.6	285.6	285.6
P0	29.01	29.01	29.01	29.01
P	27.26	27.26	27.26	27.26
T0	361.36	361.36	361.36	361.36
T	431.95	431.95	431.95	431.95
kref	0.0415	0.0415	0.0415	0.0415
E	2.603E+04	2.603E+04	2.603E+04	2.603E+04
R	8.314	8.314	8.314	8.314

Figure 4.4b shows a real catalytic fixed bed plug flow reactor with a two-phase flow inlet. As it can be seen two reactors can be integrated into one with a quenching stream in the middle of the reactor and between two catalyst beds.

Reference D:

1. Coker A. Kayode, "Modeling of Chemical Kinetics and Reactor Design", Chapter 5, Gulf Professional Publishing, 2001.

2. Fogler H. S., "Elements of Chemical Reaction Engineering", 4th Edition, Chapter 2, Pearson Prentice Hall, 2007.
3. Amitava Sarkar, Deepyaman Seth, Flora T. T. Ng, and Garry L. Rempel, *AIChE Journal*, March, 2006, Vol. 52, No. 3, p. 1142-1156.
4. Lin T.B. and Chou T.C., *Ind. Eng. Chem. Res.*, Vol. 34, No. 1, P. 129, Table 2 (1995).

5. Hill Charles G., "An Introduction to Chemical Engineering Kinetics and Reactor Design", Chapter 8, John Wiley and Sons, 1977.

6. Fogler H. S., "Elements of Chemical Reaction Engineering", 4th Edition, Chapter 2, Pearson Prentice Hall, 2007.