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Advanced Process Analysis for Source Reduction in the Sulfuric Acid Petroleum Refining Alkylation Process

Final Technical Report

by

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ABSTRACT

Advanced Process Analysis System was successfully applied to the 15,000 BPD alkylation plant at the Motiva Enterprises Refinery in Convent, Louisiana. Using the flowsheeting, on-line optimization, pinch analysis and pollution assessment capabilities of the Advanced Process Analysis System an average increase in the profit of 127% can be achieved. Energy savings attained through reduced steam usage in the distillation columns total an average of 9.4×10^9 BTU/yr. A maximum reduction of 8.7% (67×10^9 BTU/yr) in heating and 6.0% (106×10^9 BTU/yr) in cooling requirements is shown to be obtainable through pinch analysis. Also one of the main sources of the pollution from the alkylation process, sulfuric acid consumption, can be reduced by 2.2 %.

Besides economic savings and waste reductions for the alkylation process, which is one of the most important refinery processes for producing conventional gasoline, the capabilities of an integrated system to facilitate the modeling and optimization of the process has been demonstrated. Application to other processes could generate comparable benefits.

The alkylation plant model had 1,579 equality constraints for material and energy balances, rate equations and equilibrium relations. There were 50 inequality constraints mainly accounting for the thermodynamic feasibility of the system. The equality and inequality constraints described 76 process units and 110 streams in the plant. Verification that the simulation described the performance of the plant was shown using data validation with 125 plant measurements from the distributed control system. There were 1,509 unmeasured variables and 64 parameters in the model.

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CHAPTER 1

INTRODUCTION

This report documents the results of applying the Advanced Process Analysis System for energy conservation and pollution reduction in a commercial, sulfuric acid catalyzed, alkylation plant at the Motiva Enterprises Refinery in Convent, Louisiana. The Advanced Process Analysis System was developed for use by process and plant engineers to perform comprehensive evaluations of projects in depth significantly beyond their current capabilities. The strategy has the advanced process analysis methodology identify sources of excess energy use and of pollutant generation. This program has built on results from research on source reduction through technology modification in reactions and separations, energy conservation (pinch analysis) and on-line optimization (process control) by Professors Hopper and Yaws at Lamar and Professor Pike at Louisiana State University. The System uses the Lamar chemical reactor analysis program, the LSU on-line optimization and pinch analysis programs, and the EPA pollution index methodology. Visual Basic was used to integrate the programs and develop an interactive Windows interface where information is shared through the Access database. This chapter gives an overview of Advanced Process Analysis System and an introduction to the alkylation process. These are described in greater detail subsequent chapters.

1.1 Overview of the Advanced Process Analysis System

The advanced process analysis methodology identifies sources of excess energy use and of pollutant generation was based on the framework shown in Figure 1.1. The main components of this system are flowsheet simulation, on-line optimization, reactor analysis, pinch analysis, and pollution assessment. The flowsheet simulation program is used

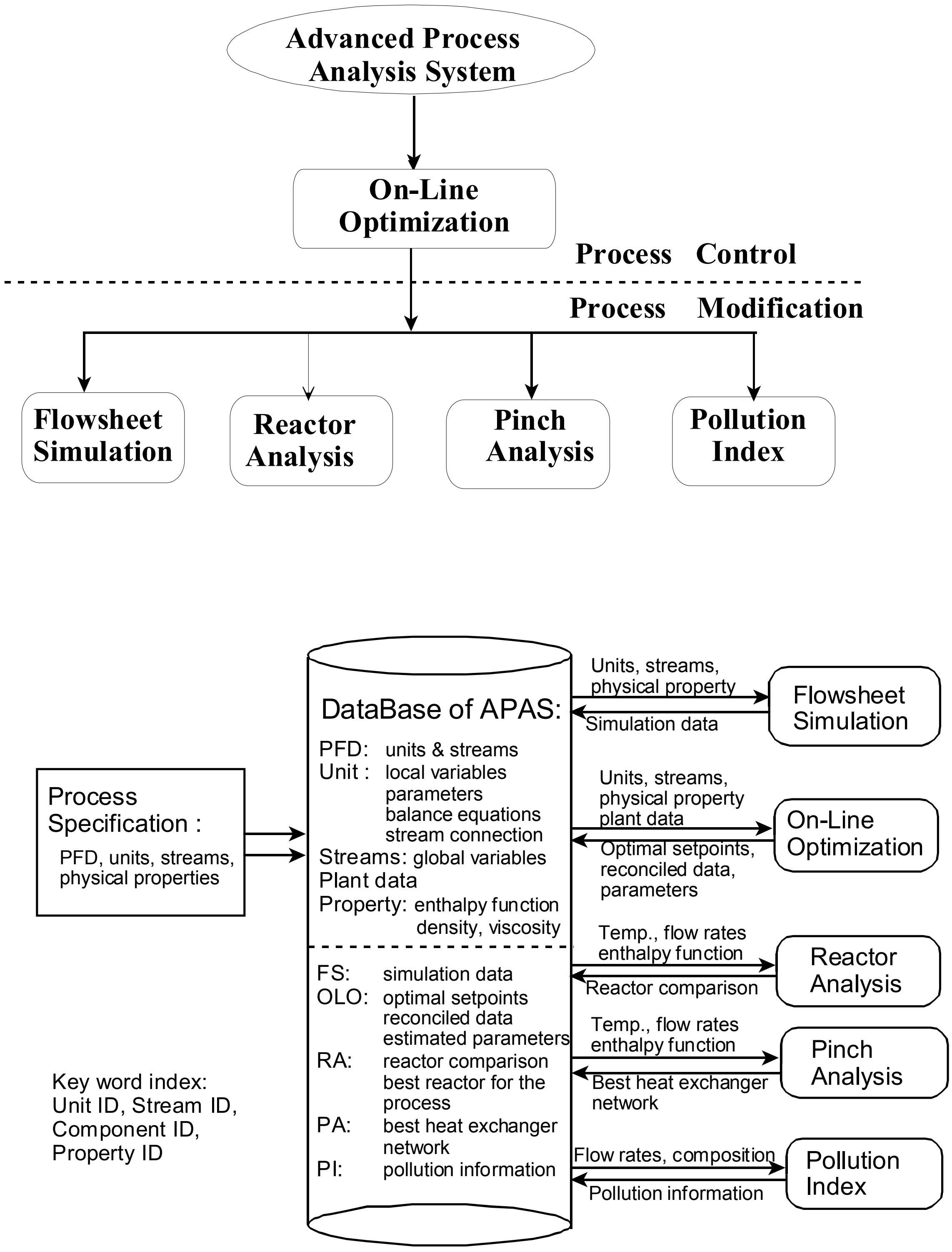


Figure 1.1: Framework of Advanced Process Analysis System

for process material and energy balances. Online optimization gives an accurate description of the chemical or refinery process being evaluated. This process simulation is used for offline studies using reactor analysis, pinch analysis and pollution assessment, to achieve process improvements that reduce pollution and energy consumption.

The Advanced Process Analysis System has been applied to two contact processes at the IMC Agrico Company's agricultural chemical complex. The results of the application of the System showed a potential annual increase in profit of 3% (or $350,000) and a 10% reduction in sulfur dioxide emissions over current operating conditions using the on-line optimization component of the System. The chemical reactor analysis component showed that the reactor conversion could be increased by 19% and that the reactor volume decreased by 87% by using a reactor pressure of 10.3 atm rather than the current 1.3 atm. The pinch analysis component showed that the minimum amount of cooling water was being used, and the heat exchanger network could be reconfigured to reduce the number of heat exchangers being used and reduce the total heat exchanger area by 25%. The pollution assessment component of the System identified the sulfur furnace and converters as the parts of the process to be modified to minimize emissions. Details of these results were given in the thesis of Kedar Telang, 1998.

1.2 Flowsheet Simulation

The flowsheet simulation, Flowsim, is used to develop the process model, and it has a graphical user interface with interactive capabilities. Process units are represented as rectangular shapes whereas the process streams are represented as lines with arrows between these units. Each process unit and stream included in the flowsheet must have a name and a description. Process information is divided into the following six categories: equality constraints, inequality constraints, unmeasured variables, measured variables, parameters and constants. All of this process information is entered with the help of the interactive, user-customized graphic screens of Flowsim, and the information is stored in an Access database for use by the other programs.

The information in the first five categories is further classified by associating it with either a unit or a stream in the flowsheet. For example, for a unit that is a heat exchanger, the relevant information includes the mass balance and heat transfer equations, limitations on the flowrates and temperatures if any, the heat transfer coefficient parameter and all the intermediate variables defined for that exchanger.

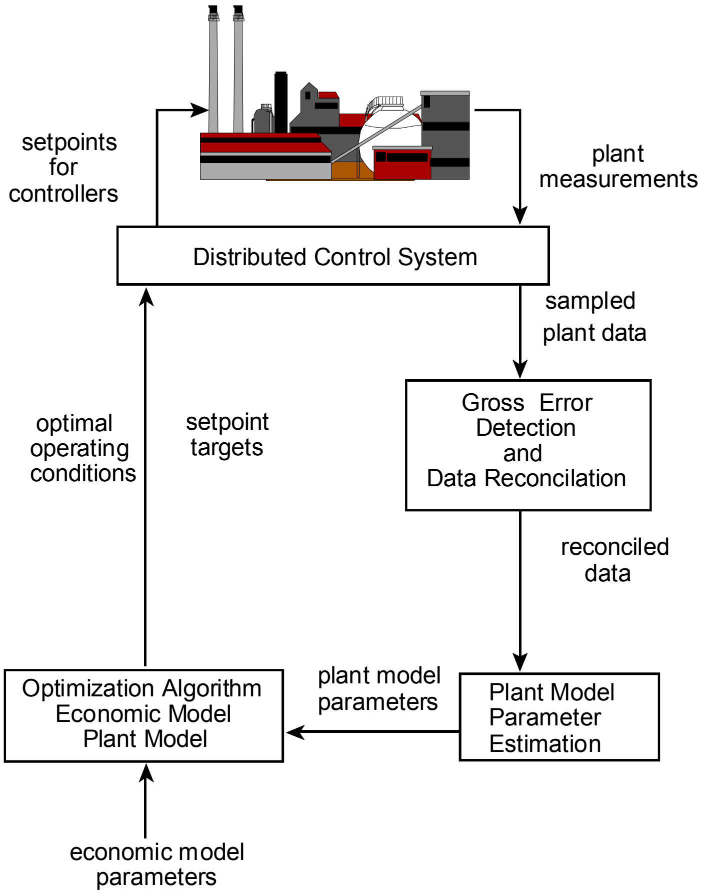
For a stream, the information includes its temperature, pressure, total flowrate, molar flowrates of individual components etc. Also, information not linked to any one unit or stream is called the 'Global Data'. For example, the overall daily profit of the process is a global unmeasured variable.

The formulation of process model for the alkylation process is described in detail in the users' manual in Appendix J. The on-line optimization program uses the process model as constraint equations to maintain the process operating at optimal set points in the distributed control system

1.3 On-line Optimization

Online optimization is the use of an automated system which adjusts the operation of a plant based on product scheduling and production control to maximize profit and minimize emissions by providing setpoints to the distributed control system. This is illustrated in Figure 1.2. Plant data is sampled from the distributed control system, and gross errors are removed from it. Then, the data is reconciled to be consistent with the material and energy balances of the process. An economic model is used to compute the profit for the plant and the plant model is used to determine the operating conditions, e.g. temperatures, pressures, flowrates of the various streams. These are variables in the material and energy balance of the plant model. The plant and economic model are together used with an optimization algorithm to determine the best operating conditions (e.g. temperatures, pressures etc.) which maximizes the profit. These optimal operating conditions are then sent to the distributed control system to provide setpoints for the controllers.

Figure 1.2: Simplified Structure of Online Optimization



1.4 Chemical Reactor Analysis

The Chemical Reactor Analysis program is a comprehensive, interactive computer simulation for three-phase catalytic gas-liquid reactors and their subsets, and an outline is shown in Figure 1.3. The program has been developed by Professor Hopper and his research group at Lamar University (Saleh et al., 1995). It has a wide range of applications such as oxidation, hydrogenation, hydrodesulfurization, hydrocracking and Fischer-Tropsch synthesis. This program interactively guides the engineer to select the best reactor design for the reacting system based on the characteristics of ten different types of industrial catalytic gas-liquid reactors which includes catalyst particle diameter and loading, diffusivities, flow regimes, gas-liquid and liquid-solid mass transfer rates, gas and liquid dispersions, heat transfer, holdup among others. The program solves the conservation equations and has checks for the validity of the design, e.g., not allowing a complete catalyst-wetting factor if the liquid flowrate is not sufficient. A more detailed description is in the user's manual.

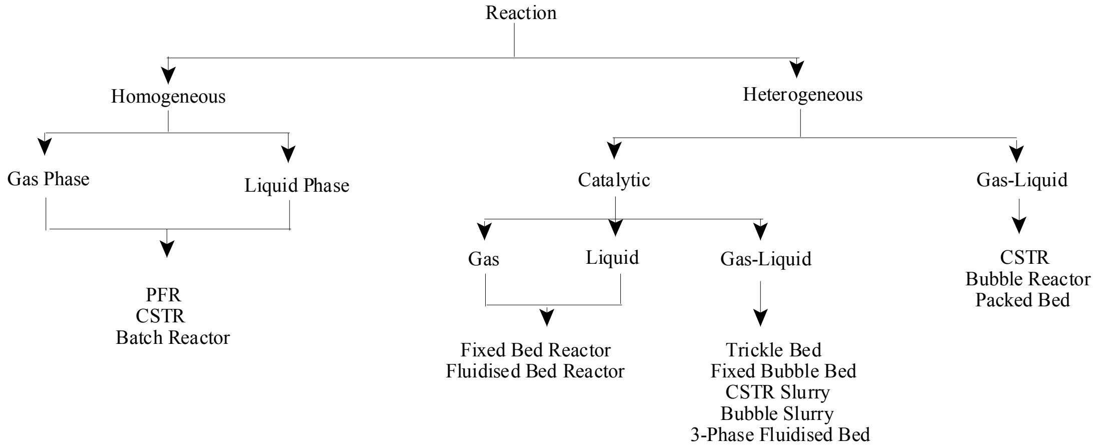


Figure 1.3: The Reactor Design Program Outline

1.5 Pinch Analysis

Pinch technology was developed in the late 1970's as a method for the design of heat exchanger networks, and it has since been extended to site energy integration including distillation and utility systems, mass exchangers, and a number of other applications (Linnhoff, 1993; Gupta and Manousiouthakis, 1993). Pinch analysis determines the best design for separations, recycle and heat exchanger networks. It employs three concepts: the composite curves, the grid diagram of process streams and the pinch point; and these are applied to minimize energy use in the process. Illustrations of composite curves and the grid diagram are shown in Figure 1.4 and Figure 1.5 respectively. The composite curves are plots of temperature as a function of enthalpy from the material and energy balances for the streams that need to be heated, called cold streams, and those that need to be cooled, called hot streams. From the composite curves of the hot and cold streams, the potential for energy exchange between the hot and cold streams can be determined, as well as the process requirements for external heating and cooling from utilities such as steam and cooling water. At one or more points the curves for the hot and cold streams may come very close, the process pinch; and this means there is no surplus heat for use at lower temperatures. The grid diagram has vertical lines to represent the hot and cold streams with lengths corresponding to the temperature range with the hot streams going from top left and the cold streams from bottom right. With this arrangement the heat recovery network for the process design can be determined. A grand composite, temperature-enthalpy curve can be assembled from the composite curves and the grid diagram to help select utilities and appropriately place boilers, turbines, distillation columns, evaporators and furnaces. Also, the heat transfer surface area can be determined with the corresponding capital cost for both energy and cost minimization. This methodology is incorporated in computer program THEN which is incorporated in the Advanced Process Analysis System.

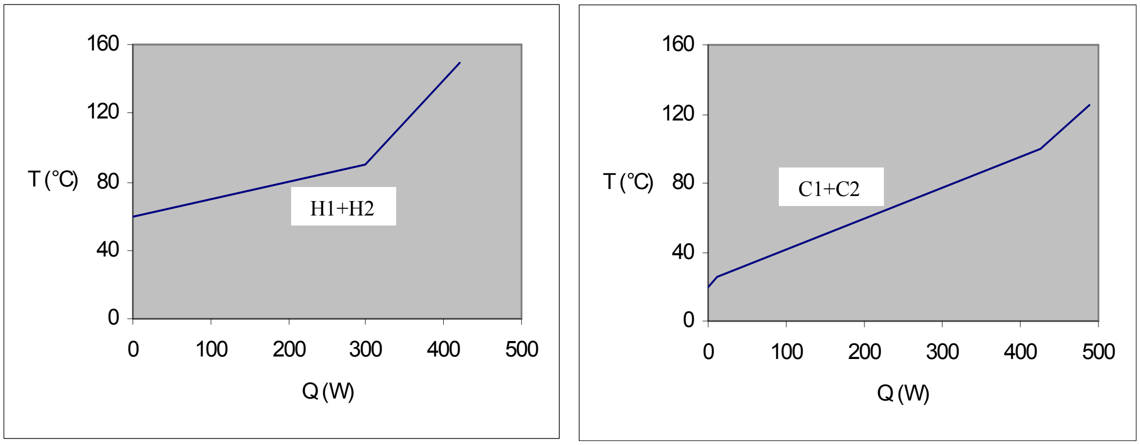


Figure 1.4: Composite Curves for Hot Streams (on the left side) and Cold Streams (on the right side) for the Simple Process

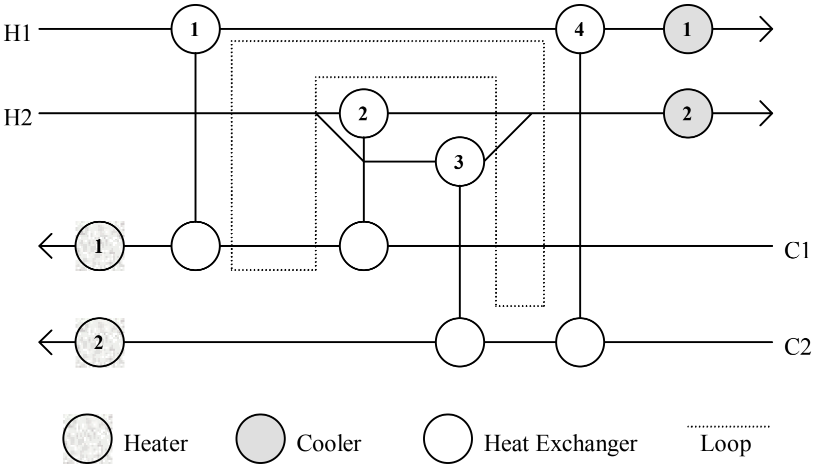


Figure 1.5: Grid Diagram

in selecting utilities and appropriate placement of boilers, turbines, distillation columns, evaporators and furnaces.

1.6 Pollution Assessment

The pollution assessment module of the Advanced Process Analysis System is called ‘The Pollution Index Program’. It is based on the Waste Reduction Algorithm (WAR) (Hilaly, 1994) and the Environmental Impact Theory (Cabezas et. al., 1997). The WAR algorithm is based on the generic pollution balance of a process flow diagram.

Pollution Accumulation = Pollution Inputs +

Pollution Generation -Pollution Output (1)

It defines a quantity called as the 'Pollution Index' to measure the waste generation in the process. This pollution index is defined as:

$$I = \text{wastes/products} = -(\Gamma\text{Out} + \Gamma\text{Fugitive}) / \Gamma P_n \quad (2)$$

This index is used to identify streams and parts of processes to be modified. Also, it allows comparison of pollution production of different processes. The WAR algorithm can be used to minimize waste in the design of new processes as well as modification of existing processes.

The Environmental Impact Theory (Cabezas et. al., 1997) is a generalization of the WAR algorithm. It describes the methodology for evaluating potential environmental impacts, and it can be used in the design and modification of chemical processes. The environmental impacts of a chemical process are generally caused by the energy and material that the process takes from and emits to the environment. The potential environmental impact is a conceptual quantity that can not be measured. But it can be calculated from related measurable quantities.

1.7 Alkylation

Alkylation is an important petroleum refining process that is used to convert light isoparaffins and light olefins into high octane number isoparaffins. Isoparaffins containing a tertiary carbon atom undergo catalytic alkylation with C_3-C_5 olefins to produce highly branched paraffins in the C_7-C_9 range. This involves a composite of consecutive and simultaneous reactions including polymerization, disproportionation, cracking and self-alkylation reactions (Corma and Martinez, 1993). Commercially, isobutane is used for the process because isopentane and higher isoparaffins have octane numbers that are quite desirable.

Catalytic alkylation occurs in the presence of sulfuric (H_2SO_4) or hydrofluoric acid (HF) catalysts, at mild temperatures and at sufficient pressure to maintain the hydrocarbons in the liquid state. With sulfuric acid it is necessary to carry out the reactions at 10 to 20°C (50 to 70°F) or lower, to minimize oxidation-reduction reactions, which result in formation of tars and production of sulfur dioxide. When hydrofluoric acid is the catalyst, reaction temperature is usually limited to 35°C (100°F) or lower. The catalyst exists as a separate phase, and the reactants and products must be transferred to and from the catalyst (Gruse and Stevens 1960, Rosenwald 1978).

Commercial alkylation plants use either sulfuric acid (H_2SO_4) or hydrofluoric acid (HF) as catalysts. About 20 years ago almost three times as much alkylate was produced using H_2SO_4 as the catalyst as compared to processes using HF. Since then the relative importance of processes using HF has increased substantially and currently these processes produce in the U.S. about 47% of the alkylate. However, in the last five years, more H_2SO_4 than HF type units have been built due to environmental and safety concerns. Recent information clarifying the dangers of HF is causing refineries that use

HF to reconsider the catalyst, or improve the safety of equipment and procedures (Albright 1990a, Cupit et al. 1961).

1.8 Summary

An overview of the Advanced Process Analysis System was given and successful applications to other processes were described briefly. Also, the current status of commercial alkylation processes was given.

In the next chapter a literature survey is given on current status of the techniques incorporated in the Advanced Process Analysis System and alkylation process chemistry and operations. The third chapter of this report describes the application of the Advanced Process Analysis System to the alkylation process. The fourth chapter gives the description of the development of the process model of the alkylation process using Advanced Process Analysis System. The fifth chapter presents the results of the analysis for the process.

CHAPTER 2

LITERATURE REVIEW

In this chapter the current status of the methodology and literature is reviewed for the methods used in the Advanced Process Analysis System. Also the current understanding of the alkylation process and its technology is given.

2.1 Advanced Process Analysis System

Advanced Process Analysis System, based on the framework given in Figure 1.1, includes chemical reactor analysis, process flowsheeting, pinch analysis and on-line optimization. All of these programs use the same information of chemical processes (material and energy balances, rate equations and equilibrium relations). Consequently, an advanced and integrated approach for process analysis is available now.

The need of an integrated approach to process analysis has been given by Van Reeuwijk et al. (1993) who proposed having a team of computer aided process engineering expert and a process engineer with technology knowledge to develop energy efficient chemical processes. A process engineer software environment is described by Ballinger et al. (1994) called '*epee'* whose goal is have to a user interface to create and manipulate objects such as processes, streams and components with sharing of data among process engineering applications in an open distributed environment. The Clean Process Advisory System (CPAS) has been described by Baker et al.(1995) as a computer based pollution prevention process and product design system that contains ten PC software tools being developed by an industry-government-university team. This includes technology selection and sizing, potential and designs, physical property data, materials locators and regulatory guidance information. An article by Shaney (1995) describes the various modeling software and databases available for process analysis and design. A review of computer aided process engineering by Winter (1992) predicts linking various applications will result in better quality of process design, better plant operations and increased productivity. It also describes the PRODABAS concept, which focuses on capturing information from multiple sources into a common multi-user framework for analysis, process definition and process engineering documentation rather than the original concept of a common user interface and datastore linked with a range of applications computing tools.

2.1.1 Industrial Applications of On-Line Optimization

Boston, et al., (1993) gave a wide review of computer simulation and optimization as well as advanced control in chemical process industries. He described the new computing power for process optimization and control that leads to higher product qualities and better processes, which are cleaner, safer, more efficient, and less costly.

Lauks, et al., (1992) reviewed the industrial applications of on-line optimization reported in the literature from 1983 to 1991 and cited nine applications – five ethylene plants, a refinery, a gas plant, a crude unit and a power station. The results showed a profitability increase of 3% or $4M/year. Also, intangible profits from a better understanding of plant behavior were significant.

Zhang (1993) conducted a study of on-line optimization for Monsanto- designed sulfuric acid plant of IMC Agrico at Convent, Louisiana. Economic optimization can achieve a 17% increase in plant profit and 25% reduction in sulfur dioxide emission. The plant was studied by Chen (1998), in developing the optimal way to conduct on-line optimization. Also, Chen (1998) reported a number of other successful applications of on-line optimization in improving chemical processes.

2.1.2 Key Elements of On-Line Optimization

The objective of on-line optimization is to determine optimal process setpoints based on plant's current operating and economic conditions. As shown in Figure 1.2, the key elements of on-line optimizations are (Chen, 1998):

- Gross Error Detection
- Data Reconciliation
- Parameter Estimation
- Economic Model (Profit Function)
- Plant Model (Process Simulation)
- Optimization Algorithm

The procedure for implementing on-line optimization involves steady-state detection, data validation, parameter estimation, and economic optimization.

The relationship between these key elements is outlined in Figure 2.1. Both plant model and optimization algorithms are required in the three steps of on-line optimization – data validation, parameter estimation, and economic optimization. Plant model serves as constraint equations in the three nonlinear optimization problems, which are solved by the optimization algorithm. For data validation, errors in plant measurements are rectified by optimizing a likelihood function subject to plant model, and a test statistic is used to detect gross errors in the measurements. For parameter estimation, parameters in plant model are estimated by optimizing an objective function, such as minimizing the sum of squares of measurement errors, subject to constraints in the plant model. For economic optimization, the plant model is used with economic model to maximize plant profit and provide optimal setpoints for the distributed control system to operate.

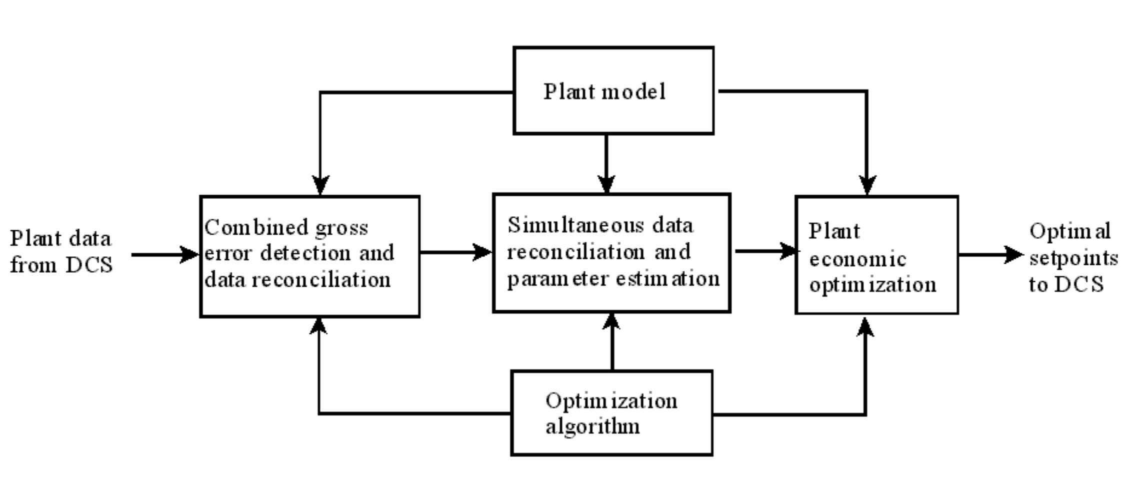


Figure 2.1 Relationship between key elements of on-line optimization

2.1.3 Energy Conservation

Heat Exchanger Network Synthesis (HENS) for maximum heat recovery is the key to energy conservation in a chemical plant. The problem of design and optimization of heat exchanger networks has received considerable attention over the last two decades (Ahmad et al., 1990, Duran et al., 1986, Linhoff et al. 1978, 1979, 1982).

The problem of HENS can be defined as the determination of a cost-effective network to exchange heat among a set of process streams where any heating and cooling that is not satisfied by exchange among these streams must be provided by external utilities (Shenoy, 1995). Attempts at solving this problem have been based on the following approaches.

Heuristic Approaches: The HENS problem was first formulated by Masso and Rudd (1969). At that time, the design methods were generally based on heuristic approaches. One of the commonly used rules was to match the hottest stream with the coldest stream. Several other methods were based on tree search techniques (Lee et al., 1970). This generally led to feasible but non-optimal solutions.

Pinch Analysis: Hohmann (1971) made significant contributions to the development of the thermodynamic approach. In the late 1970s, Linnhoff and Hindmarsh (Linnhoff et al., 1979) first introduced Pinch Analysis; a method based on thermodynamic principles. They also introduced a number of important concepts, which formed the basis for further research. These concepts were reviewed by Gundersen et al. (1987), and summarized by Telang (1998).

Mathematical Programming: Developments in computer hardware and software enabled the development of methods based on mathematical programming. Paoulias and Grossman (1983) formulated Maximum Energy Recovery (MER) problem as a linear programming (LP) model based on the transshipment model, which is widely used in operations research. This model was expanded to make restricted hot and cold stream matches by using mixed integer linear programming (MILP) formulation.

HEXTRAN, SUPERTARGET and ASPEN PINCH are some of the commonly used commercial heat exchanger design programs.

2.1.4 Pollution Prevention

Cost minimization has traditionally been the objective of chemical process design. However, growing environmental awareness now demands process technologies that minimize or prevent production of wastes. The most important issue in development of such technologies is a method to provide a quantitative measure of waste production in a process.

Waste Reduction Algorithm: Many different approaches (Telang, 1998) have been suggested to deal with this problem. One of these is the Waste Reduction Algorithm (WAR) (Hilaly, 1994). The WAR algorithm is based on the generic pollution balance of a process flow diagram.

$$\text{Pollution Accumulation} = \text{Pollution Inputs} + \text{Pollution Generation} - \text{Pollution Output} \qquad (2.1)$$

It defines a quantity called as the 'Pollution Index' to measure the waste generation in the process. This pollution index is defined as:

$$I = \text{wastes/products} = -(\Gamma\text{Out} + \Gamma\text{Fugitive}) / \Gamma P_n \qquad (2.2)$$

This index is used to identify streams and parts of processes to be modified. Also, it allows comparison of pollution production of different processes. The WAR algorithm can be used to minimize waste in the design of new processes as well as modification of existing processes.

Environmental Impact Theory: This theory (Cabezas et. al., 1997) is a generalization of the WAR algorithm. It describes the methodology for evaluating potential environmental impacts, and it can be used in the design and modification of chemical processes. The environmental impacts of a chemical process are generally caused by the energy and material that the process takes from and emits to the environment. The potential environmental impact is a conceptual quantity that can not be measured. But it can be calculated from related measurable quantities.

The generic pollution balance equation of the WAR algorithm is now applied to the conservation of the Potential Environmental Impact in a process. The flow of impact $\dot{I}$, in and out of the process is related to mass and energy flows but is not equivalent to them. The conservation equation can be written as

$$\frac{dI_{sys}}{dt} = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \tag{2.3}$$

where I_{sys} is the potential environmental impact content inside the process, $\dot{I}_{in}$ is the input rate of impact, $\dot{I}_{out}$ is the output rate of impact and $\dot{I}_{gen}$ is the rate of impact generation inside the process by chemical reactions or other means. At steady state, equation 2.3 reduces to:

$$0 = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \tag{2.4}$$

Application of this equation to chemical processes requires an expression that relates the conceptual impact quantity $\dot{I}$ to measurable quantities. The input rate of impact can be written as

$$\dot{I}_{in} = \sum_{j} \dot{I}_{j} = \sum_{j} \dot{M}_{j}^{in} \sum_{k} x_{kj} \Psi_{k} \tag{2.5}$$

where the subscript 'in' stands for input streams. The sum over j is taken over all the input streams. For each input stream j, a sum is taken over all the chemical species present in that stream. M_j is the mass flow rate of the stream j and the x_{kj} is the mass fraction of chemical k in that stream. Ψ_k is the characteristic potential impact of chemical k.

The output streams are further divided into two different types: Product and Non-product. All non-product streams are considered as pollutants with positive potential impact and all product streams are considered to have zero potential impact.

The output rate of impact can be written as:

$$\dot{I}_{out} = \sum_j \dot{I}_j = \sum_j \dot{M}_j^{out} \sum_k x_{kj} \Psi_k \tag{2.6}$$

where the subscript 'out' stands for non-product streams. The sum over j is taken over all the non-product streams. For each stream j, a sum is taken over all the chemical species.

Knowing the input and output rate of impact from the equations 2.5 and 2.6, the generation rate can be calculated using equation 2.4. Equations 2.5 and 2.6 need values of potential environmental impacts of chemical species. The potential environmental impact of a chemical species (Ψ_k) is calculated using the following expression

$$\Psi_k = \sum_l \alpha_l \Psi_{k,l}^s \tag{2.7}$$

where, the sum is taken over the categories of environmental impact. α_l is the relative weighting factor for impact of type l independent of chemical k. $\Psi^s_{k,l}$ l (units of Potential Environmental Impact/mass of chemical k) is the potential environmental impact of chemical k for impact of type l. Values of $\Psi^s_{k,l}$ for a number of chemical species can be obtained from the report on environmental life cycle assessment of products (Heijungs, 1992). Some non-zero values of $\Psi^s_{k,l}$ for the components used in the modeling of the alkylation process are given in Table 2.1.

There are nine different categories of impact. These can be subdivided into four physical potential impacts (acidification, greenhouse enhancement, ozone depletion and photochemical oxidant formation), three human toxicity effects (air, water and soil) and two ecotoxicity effects (aquatic and terrestrial). The relative weighting factor α_l allows the above expression for the impact to be customized to specific or local conditions. The suggested procedure is to initially set values of all relative weighting factors α_l to one, and then allow the user to vary them according to local needs. More information on impact types and choice of weighting factors can be obtained from the report on environmental life cycle assessment of products (Heijungs, 1992).

Table 2.1. $\Psi^{s}_{k,l}$ Values used in Alkylation Process Model

Component	Ecotoxicity (aquatic)	Ecotoxicity (terrestrial)	Human Toxicity (air)	Human Toxicity (water)	Human Toxicity (soil)	Photochemical Oxidant Formation
C_3-	0.0305	0	9.06E-7	0	0	1.1764
C_4=	0.0412	0.3012	0	0.3012	0.3012	1.6460
iC_4	0.1566	0.2908	8.58E-7	0.2908	0.2908	0.6473
nC_4	0.1890	0.2908	8.58E-7	0.2908	0.2908	0.8425
iC_5	0.0649	0.2342	0	0.2342	0.2342	0.6082
nC_5	0.3422	0.2342	5.53E-7	0.2342	0.2342	0.8384
iC_6	0.2827	0.1611	0	0.1611	0.1611	1.022
H_2SO_4	0.0170	0.1640	0.2950	0.1640	0.1640	0

To quantitatively describe the pollution impact of a process, the conservation equation is used to define two categories of Impact Indexes. The first category is based on generation of potential impact within the process. These are useful in addressing the questions related to the internal environmental efficiency of the process plant, i.e., the ability of the process to produce desired products while creating a minimum of environmental impact. The second category measures the emission of potential impact by the process. This is a measure of the external environmental efficiency of the process i.e. the ability to produce the desired products while inflicting on the environment a minimum of impact.

Within each of these categories, three types of indexes are defined which can be used for comparison of different processes. In the first category (generation), the three indexes are as follows.

1) $\dot{I}^{NP}_{gen}$ This measures the the total rate at which the process generates potential environmental impact due to nonproducts. This can be calculated by subtracting the input rate of impact ($\dot{I}_{in}$) from the output rate of impact ($\dot{I}_{out}$), i.e. $\dot{I}^{NP}_{gen} = \dot{I}_{out} - \dot{I}_{in}$.

2) $\hat{I}^{NP}_{gen}$ This measures the potential impact created by all nonproducts in manufacturing a unit mass of all the products. This can be obtained from dividing $\dot{I}^{NP}_{gen}$ by the rate at which the process outputs products, i.e.

$$\hat{I}^{NP}_{gen} = \frac{\bar{I}^{NP}_{gen}}{\sum_p \bar{P}_p}.$$

3) $\hat{M}^{NP}_{gen}$ This is a measure of the mass efficiency of the process, i.e., the ratio of mass converted to an undesirable form to mass converted to a desirable form. This can be calculated from $\hat{I}^{NP}_{gen}$ by assigning a value of 1 to the potential impacts of all non-products, i.e.

$$\hat{M}^{NP}_{gen} = \frac{\sum_j \bar{M}_j^{(out)} \sum_k x_{kj}^{NP} - \sum_j \bar{M}_j^{(in)} \sum_k x_{kj}^{NP}}{\sum_p \bar{P}_p}.$$

The indexes in the second category (emission) are as follows.

4) $\dot{I}^{NP}_{out}$ This measures the the total rate at which the process outputs potential environmental impact due to nonproducts. This is calculated using equation 2.6, i.e. $\dot{I}^{NP}_{out} = \sum_j \bar{M}_j^{(out)} \sum_k x_{kj}^{NP} \Psi_k$.

5) $\hat{I}^{NP}_{out}$ This measures the potential impact emitted in manufacturing a unit mass of all the products. This is obtained from dividing $\dot{I}^{NP}_{out}$ by the rate at which the process outputs products, i.e. $\hat{I}^{NP}_{out} = \frac{\bar{I}^{NP}_{out}}{\sum_p \bar{P}_p}$.

6) $\hat{M}^{NP}_{out}$ This is the amount of pollutant mass emitted in manufacturing a unit mass of product. This can be calculated from $\hat{I}^{NP}_{out}$ by assigning a value of 1 to the potential impacts of all non-products, i.e.

$$\hat{M}^{NP}_{out} = \frac{\sum_j \bar{M}_j^{(out)} \sum_k x_{kj}^{NP}}{\sum_p \bar{P}_p}.$$

Indices 1 and 4 can be used for comparison of different designs on an absolute basis whereas indices 2, 3, 5 and 6 can be used to compare them independent of the plant size. Higher values of indices mean higher pollution impact and suggest that the plant design is inefficient from environmental safety point of view. Negative values mean that the input streams are actually more harmful to the environment than the non-products if they are not processed.

2.2 Sulfuric Acid Alkylation Process

Alkylation offers several key advantages to refiners, including the highest average quality of all components available to the gasoline pool, increased amounts of gasoline per volume of crude oil and high heats of combustion. Alkylates permit use of internal combustion engines with higher compression ratios and hence the potential for increased miles per gallon. Alkylates burn freely, promote long engine life, and have low levels of undesired emissions (Albright 1990a, Corma and Martinez 1993).

The catalytic alkylation of paraffins involves the addition of an isoparaffin containing tertiary hydrogen to an olefin. The process is used by the petroleum industry to prepare highly branched paraffins mainly in the C_7 to C_9 range for use as high-quality fuels for spark ignition engines. The overall process is a composite of complex reactions, and consequently rigorous control is required of operating conditions and of catalyst to assure predictable results.

2.2.1 Alkylation in the Petroleum Industry

Isoparaffin-olefin alkylation entails the manufacture of branched paraffins that distill in the gasoline range (up to ca. 200 ^{o}C). Commercial refinery plants operate with the C_3 and C_4 hydrocarbon streams; alkylation involving high molecular weight olefin or isoparaffins (over C_5) are not attractive, partly because of numerous side reactions such as hydrogen transfer (Rosenwald 1978).

Sulfuric acid concentration is maintained at about 90%. Operation below this acid concentration generally causes polymerization. Product quality is improved when temperatures are reduced to the range of 0-10 ^{o}C. Cooling requirements are obtained by flashing of unreacted isobutane. Some form of heat removal is essential because the heat of reaction is approximately 14×10^5 J/kg (600 Btu/lb.) for butenes. In order to prevent polymerization of the olefin, an excess of isobutane is charged to the reaction zone. Isobutane-to-olefin molar ratios of 6:1 to 14:1 are common. More effective suppression of side reactions is produced by the higher ratios (Vichailak 1995).

The alkylation reaction system is a two-phase system with a low solubility of isobutane in the catalyst phase. In order to ensure intimate contact of the reactant and the catalyst, efficient mixing with fine subdivision must be provided. Presence of unsaturated organic diluent in the acid catalyst favors the alkylation reaction. The organic diluent has been considered to be a source of carbonium ions that promote the alkylation reaction (Rosenwald 1978).

2.2.2 Commercial Sulfuric Acid Alkylation Process

More than 60% of the worldwide production of alkylate using a sulfuric acid catalyst is obtained from effluent refrigeration process of Stratco Inc. A typical process flow diagram is as shown in Figure 2.2.

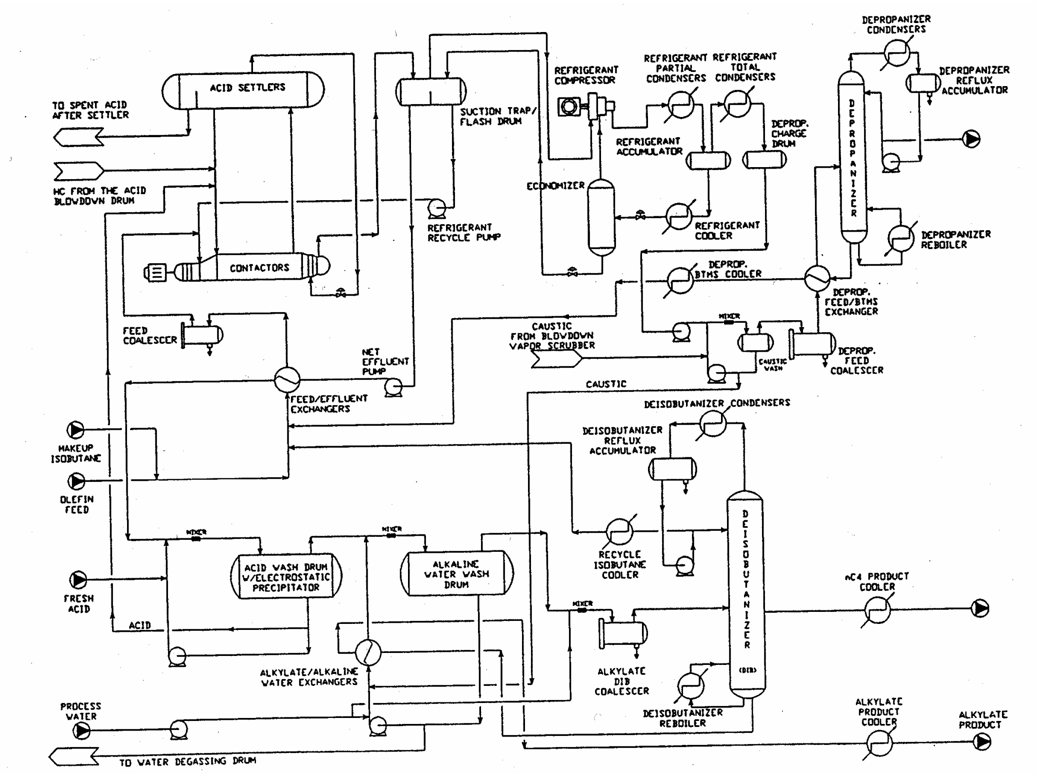


Figure 2.2. Sulfuric Acid Alkylation Process (Vichailak 1995)

The Stratco reactor or contactor, shown in Figure 2.3, is a horizontal pressure vessel containing a mixing impeller, an inner circulation tube and a tube bundle to remove the heat generated by the alkylation reaction. The hydrocarbon and acid feeds are injected into the suction side of the impeller inside the circulation tube. The impeller rapidly disperses the hydrocarbon feed with the acid catalyst to form an emulsion. The emulsion is circulated by the impeller at high rates within the contactor.

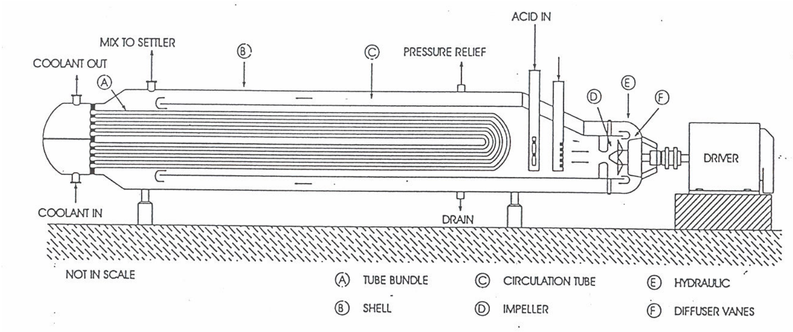


Figure 2.3. STRATCO Effluent Refrigeration Reactor (Yongkeat, 1996)

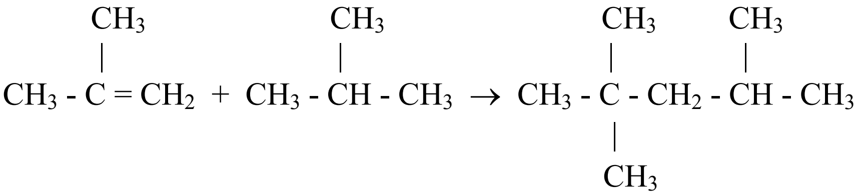
Stratco contactors are usually sized to produce 2,000 bbl/day of alkylate (Albright 1990a). Improvements introduced in recent years include: longer coils to increase the overall heat transfer coefficients; improved pump/agitator system and injection devices for introducing the hydrocarbon feed and the acid into the contactor, which in turn improves alkylate quality and lowers refrigeration costs. The pump/agitator has been positioned below the centerline in order to minimize partial settling of acid at the bottom of the contactor.

A part of the emulsion is continuously removed and sent to the acid settler or decanter, where the acid and hydrocarbon phases separate. Then in a flash drum the hydrocarbon phase is flashed to separate C_4 and lighter components from the heavier hydrocarbons. The lighter components are sent to the contactor as refrigerants and are then recycled. The heavier components are sent to the deisobutanizer column, where alkylate is separated from unreacted butane and isobutane. The C_3 content in the system is decreased by sending the lighter components through the depropanizer column. The process is described in greater detail in Chapter 4.

2.2.3 Theory of Alkylation Reactions

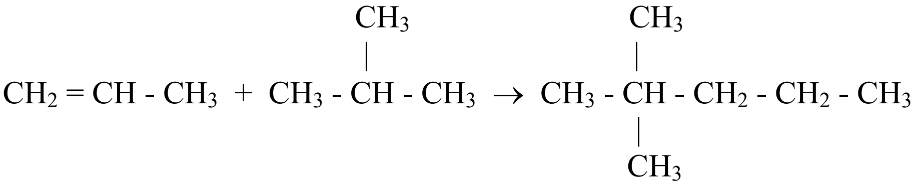
Alkylation of isobutane with C_3-C_5 olefins involves a series of consecutive and simultaneous reactions (Corma and Martinez 1993). Only isoparaffins containing a tertiary carbon atom are found to undergo catalytic alkylation with olefins. Reactions and products are readily explained by the carbonium ion mechanism.

The principal reactions that occur in alkylation are the combinations of olefins with isoparaffins as follows:



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

isobutylene isobutane 2,2,4 - trimethylpentane (isooctane)

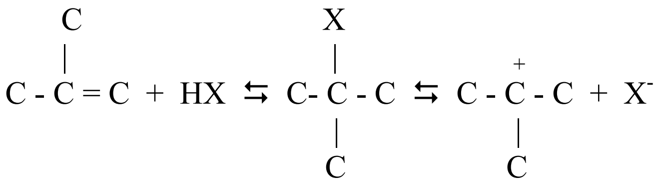


$$CH_2=CH-CH_3 + CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{CH}}}}-CH_2-CH_2-CH_3$$

propylene isobutane 2,2 - dimethylpentane (isoheptane)

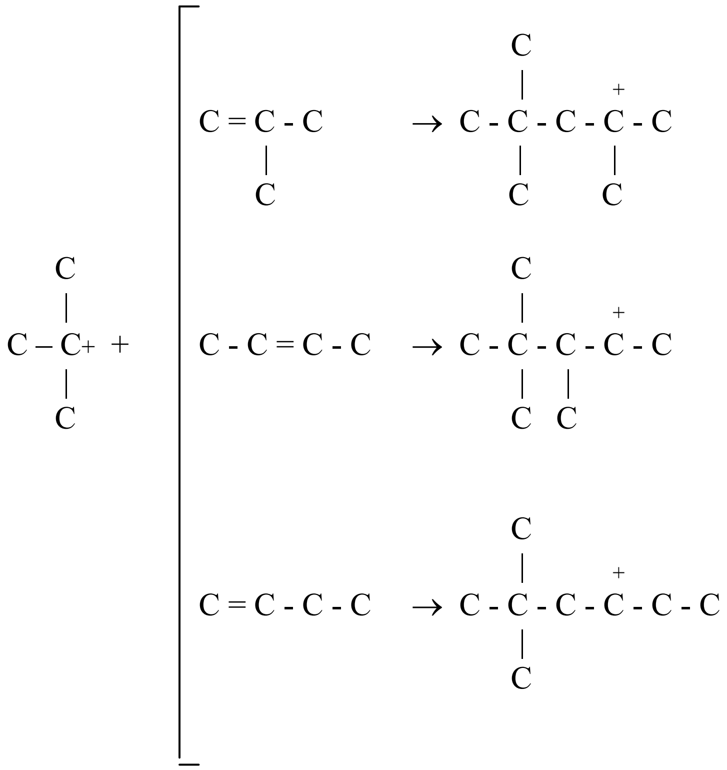
Steps in the alkylation reaction mechanism involving carbonium ions are shown below, with typical examples to illustrate each reaction step (Cupit 1961). (X is OSO_3H or F):

1. The first step is the addition of proton to olefin molecule to form a tertiary butyl cation:



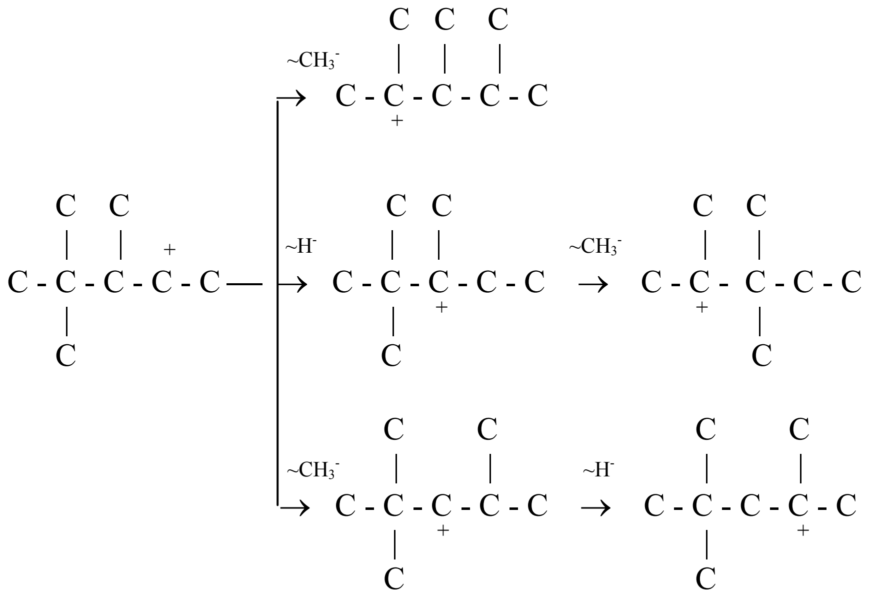
$$C-\overset{\overset{C}{|}}{C}=C + HX \leftrightarrows C-\underset{\underset{C}{|}}{\overset{\overset{X}{|}}{C}}-C \leftrightarrows C-\underset{\underset{C}{|}}{\overset{+}{C}}-C + X^{-} \qquad (2.8)$$

2. Then, the tertiary butyl cation is added to the olefin :



$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{+} + \left[\begin{array}{lll} C=\underset{\underset{C}{|}}{C}-C & \rightarrow & C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\underset{\underset{C}{|}}{\overset{+}{C}}-C \qquad (2.9) \\ C-C=C-C & \rightarrow & C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{C}{|}}{C}-\overset{+}{C}-C \qquad (2.10) \\ C=C-C-C & \rightarrow & C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C-\overset{+}{C}-C-C \qquad (2.11) \end{array}\right.$$

3. Carbonium ions may isomerize via hydride and methyl shifts to form more stable carbonium ions:

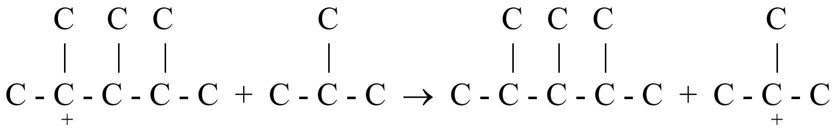


$$C-\underset{C}{\overset{C}{C}}-\overset{C}{C}-\overset{+}{C}-C \xrightarrow{\sim CH_3^-} C-\underset{+}{\overset{C}{C}}-\overset{C}{C}-\overset{C}{C}-C \quad (2.12)$$

$$\xrightarrow{\sim H^-} C-\underset{C}{\overset{C}{C}}-\underset{+}{\overset{C}{C}}-C-C \xrightarrow{\sim CH_3^-} C-\underset{+}{\overset{C}{C}}-\underset{C}{\overset{C}{C}}-C-C \quad (2.13)$$

$$\xrightarrow{\sim CH_3^-} C-\underset{C}{\overset{C}{C}}-\underset{+}{C}-\overset{C}{C}-C \xrightarrow{\sim H^-} C-\underset{C}{\overset{C}{C}}-C-\underset{+}{\overset{C}{C}}-C \quad (2.14)$$

4. These carbonium ions suffer rapid hydride transfer from isobutane, leading to the different paraffin isomers and generating tertiary butyl cation:



$$C-\underset{+}{\overset{C}{C}}-\overset{C}{C}-\overset{C}{C}-C + C-\overset{C}{C}-C \rightarrow C-\overset{C}{C}-\overset{C}{C}-\overset{C}{C}-C + C-\underset{+}{\overset{C}{C}}-C \quad (2.15)$$

Unfortunately, these are not the only reactions occurring during alkylation. There are a number of secondary reactions that in general reduce the quality of the alkylate. These reactions include polymerization, disproportionation, cracking and self-alkylation reactions (Corma and Martinez 1993).

5. Polymerization results from the addition of a second olefin to the carbonium ion formed in the primary reaction, as was seen in step 2 of the above mechanism:

$$iC_8H_{17}^+ + C_4H_8 \rightarrow iC_{12}H_{25}^+ + C_4H_{10} \rightarrow iC_{12}H_{26} + iC_4H_9^+ \quad (2.16)$$

The $iC_{12}H_{25}^+$ can continue to react with an olefin to form a larger isoalkyl cation:

$$iC_{12}H_{25}^+ + C_4H_8 \rightarrow iC_{16}H_{33} + iC_4H_{10} \rightarrow iC_{16}H_{34} + iC_4H_9^+ \qquad (2.17)$$

6. Disproportionation causes the disappearance of two molecules of alkylate to give a lower and a higher molecular weight isoparaffin than the initial one:

$$2iC_8H_{18} \rightarrow iC_7H_{16} + C_9H_{20} \qquad (2.18)$$

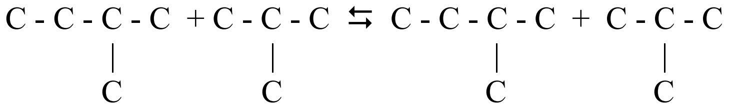
7. Larger isoalkyl cations can crack, leading to smaller isoalkyl cations and olefins:

$$iC_{12}H_{25}^+ \rightarrow iC_5H_{11}^+ + iC_7H_{14} \qquad (2.19)$$

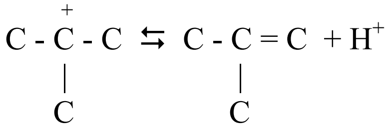
$$iC_{12}H_{25}^+ \rightarrow iC_6H_{13}^+ + iC_6H_{12} \qquad (2.20)$$

$$iC_6H_{13}^+ \rightarrow iC_5H_{11}^+ + iC_5H_{10} + iC_6H_{12} \qquad (2.21)$$

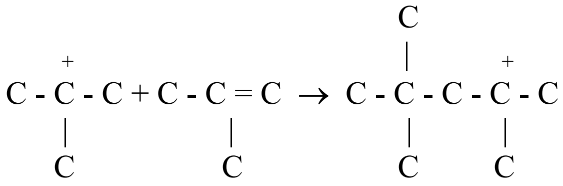
8. Self-alkylation accounts for the formation of trimethyl-pentanes when isobutane is alkylated with olefins other than butanes. At the same time, saturated paraffin of the same carbon number as the olefin is obtained. The reaction scheme for pentene, for example is :



$$C-C-\underset{\substack{|\\ C}}{\overset{+}{C}}-C + C-\underset{\substack{|\\ C}}{C}-C \leftrightarrows C-C-\underset{\substack{|\\ C}}{C}-C + C-\underset{\substack{|\\ C}}{\overset{+}{C}}-C \qquad (2.22)$$



$$C-\underset{\substack{|\\ C}}{\overset{+}{C}}-C \leftrightarrows C-\underset{\substack{|\\ C}}{C}=C + H^+ \qquad (2.23)$$



$$C - \underset{\substack{|\\ C}}{\overset{+}{C}} - C + C - \underset{\substack{|\\ C}}{C} = C \rightarrow C - \underset{\substack{|\\ C}}{\overset{\substack{C\\ |}}{C}} - C - \underset{\substack{|\\ C}}{\overset{+}{C}} - C \qquad (2.24)$$

The above reactions are believed to be fundamental to the alkylation process and are used to explain the formation of both primary and secondary products. Although isobutane and butenes were used as examples, these reactions also applied to other isoparaffins and olefins.

2.2.4 Reaction Mechanism for Alkylation of Isobutane with Propylene

Langley and Pike (1972) studied the sulfuric acid alkylation of isobutane with propylene and proposed seventeen-reaction mechanism model (Table 2.2) based on Schmering carbonium ion mechanism with modification introduced to account for iC_9 and iC_{10} formation. Experimental measurements were made in an ideally mixed, continuous flow stirred tank reactor at the temperature range 18-57 ^{o}C. The model was found to be valid in the range of 27-57 ^{o}C using 95% sulfuric acid catalyst. Lower concentration of sulfuric acid (around 90%) resulted in increased rates of formation of iC_9 and iC_{10} and decreased rates of alkylate formation.

2.2.5 Reaction Mechanism for Alkylation of Isobutane with Butylene and Pentylene

Vichailak (1995) extended the mechanism given by Langley and Pike (1972) to a nineteen-reaction mechanism model for isobutane with butylene alkylation and twenty one-reaction mechanism model for isobutane with pentylene alkylation. The reaction mechanism model for alkylation of isobutane with butylene is shown in Table 2.3. The reaction rate constants (frequency factor and activation energy) for each reaction of these mechanisms that were taken to be identical to the reactions in the propylene mechanism. A list of these rate constants, k values, are given in Appendix C.8. The results from this reaction model showed a fair agreement (90%) with the published data (Albright, 1992, Srichanachaikul, 1996). The reaction mechanism and rate constants shown in Table 2.3 to describe the alkylation reaction were used for the STRATCO reactors in the Motiva plant model.

Table 2.2. Reaction Mechanism and Material Balances for Sulfuric Acid Alkylation of Isobutane with Propylene (Langley, 1969)

Initiation reactions

$$C_3^{=} + HX \xrightarrow{k_1} C_3^{+} X^-$$

$$C_3^{+} X^- + iC_4 \xrightarrow{k_2} C_3 + iC_4^{+} X^-$$

Primary reactions

$$iC_4^{+} X^- + C_3^{=} \xrightarrow{k_{11}} iC_7^{+} X^-$$

$$iC_7^{+} X^- + iC_4 \xrightarrow{k_5} iC_7 + iC_4^{+} X^-$$

$$iC_4^{+} X^- \xrightarrow{k_9} iC_4^{=} + HX$$

$$iC_4^{+} X^- + iC_4^{=} \xrightarrow{k_{10}} iC_8^{+} X^-$$

$$iC_8^{+} X^- + iC_4 \xrightarrow{k_6} iC_8 + iC_4^{+} X^-$$

Destructive alkylation reactions

$$iC_7^{+} X^- \xrightarrow{k_{12}} iC_7^{=} + HX$$

$$iC_7^{=} + iC_4^{+} X^- \xrightarrow{k_{13}} iC_5^{=} + iC_6^{+} X^-$$

$$iC_5^{=} + HX \xrightarrow{k_{14}} iC_5^{+} X^-$$

$$iC_5 + X^- + iC_4 \xrightarrow{k_3} iC_5 + iC_4^{+} X^-$$

$$iC_6^{+} X^- + iC_4 \xrightarrow{k_4} iC_6 + iC_4^{+} X^-$$

$$iC_7^{+} X^- + C_3^{=} \xrightarrow{k_{15}} iC_{10}^{+} X^-$$

$$iC_{10}^{+} X^- + iC_4 \xrightarrow{k_8} iC_{10} + iC_4^{+} X^-$$

$$iC_5^{=} + iC_4^{+} X^- \xrightarrow{k_{16}} iC_9^{+} X^-$$

$$iC_9^{+} X^- + iC_4 \xrightarrow{k_7} iC_9 + iC_4^{+} X^-$$

$$iC_{10}^{+} X^- \xrightarrow{k_{17}} iC_5^{=} + iC_5^{+} X^-$$

(a) Material balance on reactants and
Associated consumption rates.

$$-r_{iC4} = k_2[C_3^{+} X^-][iC_4] + k_3[iC_5^{+} X^-][iC_4] + k_4[iC_6^{+} X^-][iC_4] + k_5[iC_7^{+} X^-][iC_4] + k_6[iC_8^{+} X^-][iC_4] + k_7[iC_9^{+} X^-][iC_4] + k_8[iC_{10}^{+} X^-][iC_4]$$

$$-r_{C3=} = k_1[C_3^{=}][HX] + k_{11}[iC_4^{+} X^-][C_3^{=}] + k_{15}[iC_7^{+} X^-][C_3^{=}]$$

Self-alkylation reactions

(b) Product formation equations.

$$r_{C3} = k_2[C_3^{+} X^-][iC_4]$$

$$r_{iC5} = k_3[iC_5^{+} X^-][iC_4$$

$$r_{iC6} = k_4[iC_6^{+} X^-][iC_4]$$

$$r_{iC7} = k_5[iC_7^{+} X^-][iC_4]$$

$$r_{iC8} = k_6[iC_8^{+} X^-][iC_4]$$

$$r_{iC9} = k_7[iC_9^{+} X^-][iC_4]$$

$$r_{iC10} = k_8[iC_{10}^{+} X^-][iC_4]$$

(c) Olefinic intermediate rate equations.

$$r_{iC4=} = 0 = k_9[iC_4^{+} X^-] - k_{10}[iC_4^{=}][iC_4^{+} X^-]$$

$$r_{iC5=} = 0 = k_{13}[iC_7^{=}][iC_4^{+} X^-] + k_{17}[iC_{10}^{+} X^-] - k_{14}[iC_5^{=}][HX] - k_{16}[iC_5^{=}][iC_4^{+} X^-]$$

$$r_{iC7=} = 0 = k_{12}[iC_7^{+} X^-] - k_{13}[iC_7^{=}][iC_4^{+} X^-]$$

(d) Carbonium ion rate equations.

$$r_{C3+X-} = 0 = k_1[C_3^{=}][HX] - k_2[C_3^{+} X^-][iC_4]$$

$$r_{iC4+X-} = 0 = r_{iC4} - k_9[iC_4^{+} X^-] - k_{10}[iC_4^{=}][iC_4^{+} X^-] - k_{11}[iC_4^{+} X^-][C_3^{=}] - k_{13}[iC_7^{=}][iC_4^{+} X^-] - k_{16}[iC_5^{=}][iC_4^{+} X^-]$$

$$r_{iC5+X-} = 0 = k_{14}[iC_5^{=}][HX] + k_{17}[iC_{10}^{+} X^-] - k_3[iC_5^{+} X^-][iC_4]$$

$$r_{iC6+X-} = 0 = k_{13}[iC_7^{=}][iC^{+} X^-] - k_4[iC_6^{+} X^-][iC_4]$$

$$r_{iC7+X-} = 0 = k_{11}[iC_4^{+} X^-][C_3^{=}] - k_5[iC_7^{+} X^-][iC_4] - k_{15}[iC_7^{+} X^-][C_3^{=}] - k_{12}[iC_7^{+} X^-]$$

$$r_{iC8+X-} = 0 = k_{10}[iC_4^{=}][iC_4^{+} X^-] - k_6[iC_8^{+} X^-][iC_4]$$

$$r_{iC9+X-} = 0 = k_{16}[iC_5^{=}][iC_4^{+} X^-] - k_7[iC_9^{+} X^-[iC_4]$$

$$r_{iC10+X-} = 0 = k_{15}[iC_7^{+} X^-][C_3^{=}] - k_{17}[iC_{10}^{+} X^-] - k_8[iC_{10}^{+} X^-][iC_4]$$

Table 2.3. Reaction Mechanism and Material Balances for Sulfuric Acid Alkylation of Isobutane with Butylene (Vichailak, 1995)

Initiation reactions

$$C_4^{=} + HX \xrightarrow{k_1} C_4^{+}X^{-}$$

$$C_4^{+}X^{-} + iC_4 \xrightarrow{k_2} C_4 + iC_4^{+}X^{-}$$

Primary reactions

$$iC_4^{+}X^{-} + C_4^{=} \xrightarrow{k_{11}} iC_8^{+}X^{-}$$

$$iC_8^{+}X^{-} + iC_4 \xrightarrow{k_6} iC_8 + iC_4^{+}X^{-}$$

Self-alkylation reactions

$$iC_4^{+}X^{-} \xrightarrow{k_9} iC_4^{=} + HX$$

$$iC_4^{+}X^{-} + iC_4^{=} \xrightarrow{k_{10}} iC_8^{+}X^{-}$$

$$iC_8^{+}X^{-} + iC_4 \xrightarrow{k_6} iC_8 + iC_4^{+}X^{-}$$

Destructive alkylation reactions

$$iC_8^{+}X^{-} \xrightarrow{k_{12}} iC_8^{=} + HX$$

$$iC_8^{=} + iC_4^{+}X^{-} \xrightarrow{k_{13}} iC_5^{=} + iC_7^{+}X^{-}$$

$$iC_5^{=} + HX \xrightarrow{k_{14}} iC_5^{+}X^{-}$$

$$iC_5^{+}X^{-} + iC_4 \xrightarrow{k_3} iC_5 + iC_4^{+}X^{-}$$

$$iC_7^{+}X^{-} + iC_4 \xrightarrow{k_5} iC_7 + iC_4^{+}X^{-}$$

$$iC_7^{+}X^{-} + C_4^{=} \xrightarrow{k_{15}} iC_{11}^{+}X^{-}$$

$$iC_{11}^{+}X^{-} + iC_4 \xrightarrow{k_{18}} iC_{11} + iC_4^{+}X^{-}$$

$$iC_5^{=} + iC_4^{+}X^{-} \xrightarrow{k_{16}} iC_9^{+}X^{-}$$

$$iC_9^{+}X^{-} + iC_4 \xrightarrow{k_7} iC_9 + iC_4^{+}X^{-}$$

$$iC_{11}^{+}X^{-} \xrightarrow{k_{17}} iC_5^{=} + iC_6^{+}X^{-}$$

$$iC_6^{+}X^{-} + iC_4 \xrightarrow{k_4} iC_6 + iC_4^{+}X^{-}$$

$$iC_6^{+}X^{-} + C_4^{=} \xrightarrow{k_{19}} iC_{10}^{+}X^{-}$$

$$iC_{10}^{+}X^{-} + iC_4 \xrightarrow{k_8} iC_{10} + iC_4^{+}X^{-}$$

(a) Material balance on reactants and
Associated consumption rates.

$$\begin{aligned}-r_{iC4} = {} & k_2[C_4^{+}X^{-}][iC_4] + k_3[iC_5^{+}X^{-}][iC_4] + \\ & k_4[iC_6^{+}X^{-}][iC_4] + k_5[iC_7^{+}X^{-}][iC_4] + \\ & k_6[iC_8^{+}X^{-}][iC_4] + k_7[iC_9^{+}X^{-}][iC_4] + \\ & k_8[iC_{10}^{+}X^{-}][iC_4] + k_{18}[iC_{11}^{+}X^{-}][iC_4]\end{aligned}$$

$$\begin{aligned}-r_{C4=} = {} & k_1[C_4^{=}][HX] + k_{11}[iC_4^{+}X^{-}][C_4^{=}] + \\ & k_{15}[iC_7^{+}X^{-}][C_4^{=}] + k_{19}[iC_6^{+}X^{-}][C_4^{=}]\end{aligned}$$

(b) Product formation equations.

$$r_{C4} = k_2[C_4^{+}X^{-}][iC_4]$$

$$r_{iC5} = k_3[iC_5^{+}X^{-}][iC_4]$$

$$r_{iC6} = k_4[iC_6^{+}X^{-}][iC_4]$$

$$r_{iC7} = k_5[iC_7^{+}X^{-}][iC_4]$$

$$r_{iC8} = k_6[iC_8^{+}X^{-}][iC_4]$$

$$r_{iC9} = k_7[iC_9^{+}X^{-}][iC_4]$$

$$r_{iC10} = k_8[iC_{10}^{+}X^{-}][iC_4]$$

$$r_{iC11} = k_{18}[iC_{11}^{+}X^{-}][iC_4]$$

(c) Olefinic intermediate rate equations

$$r_{iC4=} = 0 = k_9[iC_4^{+}X^{-}] - k_{10}[iC_4^{=}][iC_4^{+}X^{-}]$$

$$\begin{aligned}r_{iC5=} = 0 = {} & k_{13}[iC_8^{=}][iC_4^{+}X^{-}] + k_{17}[iC_{11}^{+}X^{-}] - \\ & k_{14}[iC_5^{=}][HX] - k_{16}[iC_5^{=}][iC_4^{+}X^{-}]\end{aligned}$$

$$r_{iC8=} = 0 = k_{12}[iC_8^{+}X^{-}] - k_{13}[iC_8^{=}][iC_4^{+}X^{-}]$$

(d) Carbonium ion rate equations.

$$r_{C4+X-} = 0 = k_1[C_4^{=}][HX] - k_2[C_4^{+}X^{-}][iC_4]$$

$$\begin{aligned}r_{iC4+X-} = 0 = {} & -r_{iC4} - k_9[iC_4^{+}X^{-}] - k_{10}[iC_4^{=}][iC_4^{+}X^{-}] - \\ & k_{11}[iC_4^{+}X^{-}][C_4^{=}] - k_{13}[iC_8^{=}][iC_4^{+}X^{-}] - k_{16}[iC_5^{=}][iC_4^{+}X^{-}]\end{aligned}$$

$$r_{iC5+X-} = 0 = k_{14}[iC_5^{=}][HX] - k_3[iC_5^{+}X^{-}][iC_4]$$

$$r_{iC6+X-} = 0 = k_{17}[iC_{11}^{+}X^{-}] - k_4[iC_6^{+}X^{-}][iC_4] - k_{19}[iC_6^{+}X^{-}][C_4^{=}]$$

$$r_{iC7+X-} = 0 = k_{13}[iC_4^{+}X^{-}][iC_8^{=}] - k_5[iC_7^{+}X^{-}][iC_4] - k_{15}[iC_7^{+}X^{-}][C_4^{=}]$$

$$\begin{aligned}r_{iC8+X-} = 0 = {} & k_{11}[C_4^{=}][iC_4^{+}X^{-}] + k_{10}[iC_4^{+}X^{-}][iC_4^{=}] - \\ & k_6[iC_8^{+}X^{-}][iC_4] - k_{12}[iC_8^{+}X^{-}]\end{aligned}$$

$$r_{iC9+X-} = 0 = k_{16}[iC_5^{=}][iC_4^{+}X^{-}] - k_7[iC_9^{+}X^{-}[iC_4]$$

$$r_{iC10+X-} = 0 = k_{19}[iC_6^{+}X^{-}][C_4^{=}] - k_8[iC_{10}^{+}X^{-}][iC_4]$$

$$r_{iC11+X-} = 0 = k_{15}[iC_7^{+}X^{-}][C_4^{=}] - k_{18}[iC_{11}^{+}X^{-}][iC_4] - k_{17}[iC_{11}^{+}X^{-}]$$

2.2.6 Influence of Process Variables

The most important process variables are reaction temperature, acid strength, isobutane concentration, and olefin space velocity. Changes in these variables affect both product quality and yield (Gary and Handwerk, 1984).

Reaction Temperature

The reaction temperature in sulfuric acid alkylation is usually in the range of 32-50 ^oF. At higher temperatures, oxidation reactions become important and acid consumption increases (Corma and Martinez, 1993). At temperatures above 65 ^oF, polymerization of the olefins becomes significant and yields are decreased. If the operation takes place at lower temperatures, the effectiveness decreases due to the increase in the acid viscosity and the decreased solubility of hydrocarbons in the acid phase (Gary and Handwerk, 1984).

Acid Strength

Acid strength has varying effects on alkylate quality, depending on the effectiveness of the reactor mixing and the water content of the acid. In sulfuric acid alkylation, the best quality and highest yields are obtained with acid strengths of 93-95% by weight of acid, 1-2% of water and the remainder hydrocarbon diluents. The water content in the acid lowers its catalytic activity by about 3-5 times as much as hydrocarbon diluents, thus, an 88% acid containing 5% water is much less effective catalyst than the same strength acid containing 2% water. At concentrations higher than 99%, isobutane reacts with SO_3, and below 85-88% concentration, the catalyst becomes a polymerization rather than an alkylation catalyst. Poor mixing in a reactor requires higher acid strength necessary to keep acid dilution down. Increasing the acid strength from 89% to 93% increases the alkylate quality by 1-2 octane numbers (Cupit et.al., 1962).

Isobutane Concentration

Isobutane concentration in the feed to the reactor is generally expressed in terms of isobutane/olefin ratio. This is one of the most important process variables that controls acid consumption, yield and quality of the alkylate. When the isobutane/olefin ratio in the feed is high (15:1), the olefin is more likely to react with an isobutane molecule to form the desired product than to undergo butene-butene polymerization. Thus undesired reactions are minimized. If this ratio is kept low (<5:1), production of heavy polymers increases due to polymerization reactions, and the acid consumption increases (Corma and Martinez, 1993). An increase in this ratio produces a decrease in acid consumption while increasing both the yield and the quality of the alkylate. The external isobutane to olefin ratio in sulfuric acid plants are usually in the range of 5:1 to 15:1 (Gary and Handwerk, 1984).

Olefin Space Velocity

Olefin space velocity is defined as the volume of olefin charged per hour divided by the volume of acid in the reactor.

$$Olefin\ space\ velocity = \frac{Volumetric\ \ Flow\ Rate\ of\ \ Olefin}{Vol.\ Fraction\ of\ \ acid\ in\ reactor * Volume\ of\ \ reactor}$$

Lowering the olefin space velocity reduces the amount of high boiling hydrocarbons produced, increase the product octane and lowers acid consumption (Gary and Handwerk, 1984). Olefins space velocity is one way of expressing space-time, another is by using contact time.

2.2.7 Feedstock

Olefins and isobutane are used as alkylation feedstocks. The chief sources of olefins are catalytic cracking and coking operations. Butenes and propenes are the most common olefins used but ethylene and pentenes are included in some cases. Olefins can be produced by dehydrogenation of paraffins and isobutane is cracked commercially to provide alkylation unit feed.

Hydrocrackers and catalytic crackers produce a majority of the isobutane used in alkylation, moreover it is obtained from catalytic reformers, crude distillation, and natural gas processing. In some cases, normal butane is isomerized to produce additional isobutane for alkylation unit feed.

2.2.8 Products

In addition to the alkylate stream, the products leaving the alkylation unit include the propanes and normal butane that enter with the saturated and unsaturated feed streams as well as a small quantity of tar produced by polymerization reactions.

The product streams leaving an alkylation unit are:

1. LPG grade propane liquid
2. Normal butane liquid
3. C_5^+ Alkylate
4. Spent Acid (with tar)

Only about 0.1 % by volume of olefin feed is converted into tar. This is not truly a tar but a thick dark brown oil containing complex mixtures of conjugated cyclopentadienes with side chains (Thomas, 1970).

2.2.9 Catalysts

Concentrated sulfuric and hydroflouric acids are the only catalysts used commercially today for the production of high octane alkylate gasoline but other catalysts are used to produce ethylbenzene, cumene and long chain (C_{12} to C_{16}) alkylated benzenes (Thomas, 1970).

The desirable reactions are the formation of C_8 carbonium ions and the subsequent formation of alkylates. The main undesirable reaction is polymerization of olefins. Only strong acids can catalyze the alkylation reaction but weaker acids can cause polymerization to take place. Therefore the acid strengths must be kept above 88 % by weight H_2SO_4 or HF in order to prevent excessive polymerization. Sulfuric acid containing free SO_3 also causes undesired side reactions and concentrations greater than 99.3 % H_2SO_4 are not generally used (Thomas, 1970).

Isobutane is soluble in the acid phase only to the extent of about 0.1 % by weight in sulfuric acid and about 3 % in hydroflouric acid. Olefins are more soluble in the acid phase and a slight amount of polymerization of the olefins is desirable as the polymerization products dissolve in the acid and increase the solubility of isobutane in the acid phase.

If the concentration of the acid becomes less than 88 %, some of the acid must be removed and replaced with stronger acid. In hydroflouric acid units, the acid removed is redistilled and the polymerization products removed as thick dark oil. The concentrated HF is recycled in the unit and the net consumption is about 0.3 lb per barrel of alkylate produced (Templeton and King, 1956).

The sulfuric acid removed must be regenerated in a sulfuric acid plant which is generally not part of the alkylation unit, and the acid consumption ranges from 18 to 30 lb per barrel of alkylate produced. Makeup acid is usually 99.3 % by weight H_2SO_4.

2.3 Summary

This chapter reviewed the literature for chemical process analysis and for the current understanding of alkylation process. The next chapter describes the methodology of Advanced Process Analysis System. Subsequent chapters describe Motiva's Alkylation process and the results of applying the system to this process.

CHAPTER 3

METHODOLOGY

In this chapter a detailed description is given for the methodology used in the Advanced Process Analysis System. The framework for the Advanced Process Analysis System was shown in Figure 1.1. The main components of this system are a flowsheeting program for process material and energy balances, an on-line optimization program, a chemical reactor analysis program, a heat exchanger network design program and a pollution assessment module. An overview of each of these programs was given in Chapter 1.

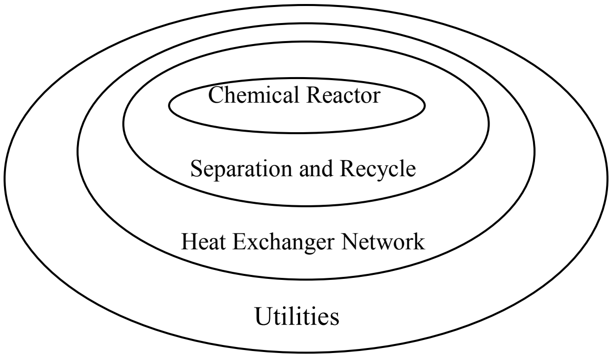


Figure 3.1: 'Onion Skin' Diagram for Organization of a Chemical Process and Hierarchy of Analysis.

The Advanced Process Analysis System methodology to identify and eliminate the causes of energy inefficiency and pollutant generation is based on the onion skin diagram shown in Figure 3.1. Having an accurate description of the process from online optimization, an evaluation of the best types of chemical reactors is done first to modify and improve the process. Then the separation units are evaluated. This is followed by the pinch analysis to determine the best configuration for the heat exchanger network and determine the utilities needed for the process. Not shown in the diagram is the pollution index evaluation, which is used to identify and minimize emissions. The following gives a detailed description of the components of the Advanced Process Analysis System and how they are used together to control and modify the process to maximize profit and minimize wastes and emissions.

3.1 Flowsheeting Program

The first step towards implementing the Advanced Process Analysis System is the development of the process model, which is also known as flowsheeting. The process model is a set of constraint equations, which represent a mathematical model of material and energy balances, rate equations and equilibrium relation for the process. Formulation of the process model can be divided into two important steps.

Formulation of Constraints for Process Units: A process model can be formulated either empirically or mechanistically. A mechanistic model makes use of constraint equations depicting conservation laws (mass and energy balances), equilibrium relations and empirical formulas. Advanced Process Analysis System uses mechanistic models for analysis.

Mathematically, constraints fall into two types: equality constraints and inequality constraints. Equality constraints are material and energy balances or any other exact relationship in a process. Inequality constraints include demand for product, availability of raw materials and capacities of process units.

Classification of Variables and Determination of Parameters: After the constraints are formulated, the variables in the process are divided into two groups: measured and unmeasured variables. Measured variables are the variables which are directly measured from the distributed control systems (DCS) and the plant control laboratory. The remaining variables are the unmeasured variables. For redundancy, there must be more measured variables than the degree of freedom of the equality constraints.

Parameters in the model can also be divided into two types: constant and time varying parameters. Constant parameters do not change with time and include reaction activation energy, heat exchanger areas. Time-varying parameters include fouling factors in heat exchangers and catalyst deactivation parameters. They change slowly with time and are related to the degradation of performance of equipment.

Flowsim: The program used for flowsheeting in the Advanced Process Analysis System is called 'Flowsim'. Flowsim provides a graphical user interface with interactive capabilities. An example of this interface is shown in Figure 3.2 for a simple refinery, and the comparable diagram for the alkylation process is given in the next chapter, Figure 4.5. Process units are represented as rectangular shapes whereas the process streams are represented as lines with arrows between these units. Process units and streams can be drawn by clicking the corresponding icons on the Flowsim window. Each process unit and stream in the flowsheet must have a name and a description. Process information is divided into the following six categories; equality constraints, inequality constraints, unmeasured variables, measured variables, parameters and constants.

The information in the first five categories is further classified by associating it with either a unit or a stream in the flowsheet. For example, for a unit that is a heat exchanger, the relevant information includes the mass balance and heat transfer equations, limitations on the flowrates and temperatures if any, the heat transfer coefficient parameter and all the intermediate variables defined for that exchanger.

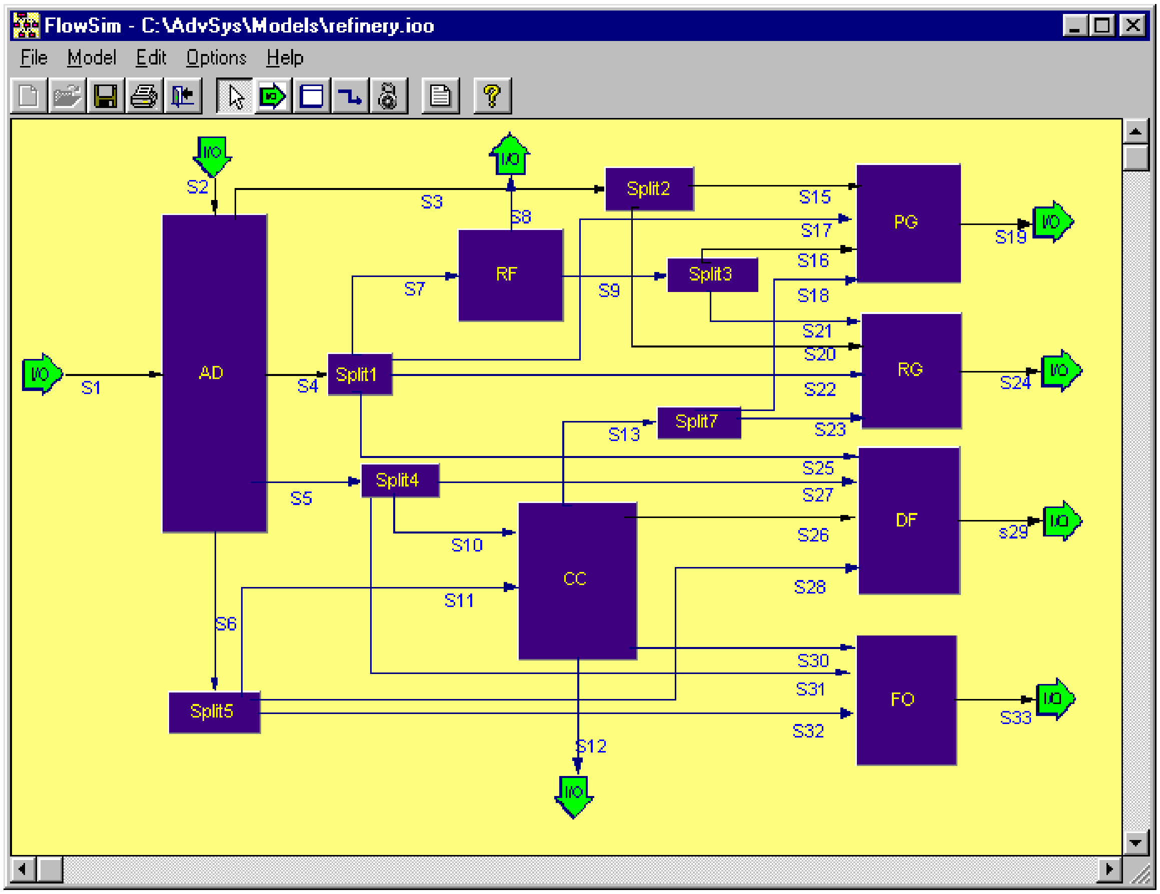


Figure 3.2 Example of Flowsim Screen for a Simple Refinery

For a stream, the information includes its temperature, pressure, total flowrate, molar flowrates of individual components etc. Information not linked to any one unit or stream is called the ‘Global Data’. For example, the overall daily profit of the process is a global unmeasured variable because it is not related to any particular process unit or stream.

The sixth category of constants can be grouped into different sets based on their physical significance. For example, constants related to heat exchangers can be placed in one group and those related to reactors into another group.

Flowsim also has a seventh category of information called as the ‘enthalpy coefficients’. This stores the list of all the chemical components in the process and their enthalpy coefficients for multiple temperature ranges. All of this process information is entered with the help of the interactive, user-customized graphic screens of Flowsim. This concludes the description of the flowsheeting part of the Advanced Process Analysis System. Appendix J is the user’s manual, which gives a step-by-step description of creating process models.

3.2 Online Optimization Program

Once the process model has been developed using Flowsim, the next step is to conduct on-line optimization. On-line optimization is the use of an automated system which adjusts the operation of a plant based on product scheduling and production control to maximize profit and minimize emissions by providing setpoints to the distributed control system. As shown in Figure 1.5, it includes three important steps: combined gross error detection and data reconciliation, simultaneous data reconciliation and parameter estimation and plant economic optimization. In combined gross error detection and data reconciliation, a set of accurate plant measurements is generated from data extracted from the plant’s Distributed Control System (DCS). This set of data is used for estimating the parameters in plant models. Parameter estimation is necessary to have the plant model match the current performance of the plant. Then economic optimization is conducted to optimize the economic model using this current plant model as constraints. This generates set points for the distributed control system to move the plant to optimal operating conditions.

Each of the above three-optimization problems in on-line optimization has a similar mathematical statement as following:

Optimize: *Objective function*
Subject to: *Constraints from plant model.*

where the objective function is a joint distribution function for data reconciliation, least squares for parameter estimation and a profit function (economic model) for plant economic optimization. The constraint equations describe the relationship among variables and parameters in the process, and they are material and energy balances, chemical reaction rates, thermodynamic equilibrium relations, and others.

To perform data reconciliation, there has to be redundancy in the measurements, i.e. there should be more measurements than the degrees of freedom in the process model. For redundancy, the number of measurements to determine the minimum number of measured variables is given by the degree of freedom, which is calculated using the following equation (Felder and Rousseau, 1986).

Degree of freedom = Total number of variables – Total number of equality constraints + Number of independent chemical reactions.

Also, the unmeasured variables have to be determined by the measured variables, called observability. If an unmeasured variable can not be determined by a measured variable, it is unobservable. This is called the 'observability and redundancy criterion', which needs to be satisfied (Chen, 1998).

Combined Gross Error Detection and Data Reconciliation: Process data from distributed control system is subject to two types of errors, random errors and gross errors. Gross errors must be detected and rectified before the data is used to estimate plant parameters. Combined gross error detection and data reconciliation algorithms can be used to detect and rectify gross errors in measurements for on-line optimization. These algorithms are: measurement test method using normal distribution, Tjoa-Biegler's method using contaminated Gaussian distribution, and robust statistical method using robust functions. The theoretical performance of these algorithms has been evaluated by Chen, 1998.

Based on Chen's study, Tjao-Biegler's method or robust method is used to perform combined gross error detection and data reconciliation. It detects and rectifies gross errors in plant data sampled from distributed control system. This step generates a set of measurements containing only random errors for parameter estimation. Then, this set of measurements is used for simultaneous parameter estimation and data reconciliation using the least-squares method.

Simultaneous Data Reconciliation and Parameter Estimation: The general methodology for this step is similar to the methodology of combined gross error detection and data reconciliation. The difference is that parameters in plant model are considered as variables along with process variables in simultaneous data reconciliation and parameter estimation rather than being constants as in data reconciliation. Both process variables and parameters are simultaneously estimated. Based on Chen's study, the least squares algorithm is used to carry out combined gross error detection and data reconciliation. The data set produced by parameter estimation is free of any gross errors, and the updated values of parameters represent the current state of the process. These parameter values are used in economic optimization.

Plant Economic Optimization: The objective of plant economic optimization is to generate a set of optimal operating setpoints for the distributed control system. This set of optimal setpoints will maximize the plant profit, satisfy the current constraints in plant model, meet the requirements for the demand of the product and availability of raw materials, and meet the restriction on pollutant emission. Optimization can be achieved by maximizing the economic model (objective function) subject to the process constraints. The objective function can be different depending on the goals of optimization. The objectives can be to maximize plant profit, minimize energy use, minimize undesired by-products, minimize waste/pollutant emission or a combination of these objectives. The result of economic optimization is a set of optimal values for all the measured and unmeasured variables in the process. These are then sent to the distributed control system (DCS) to provide setpoints for the controllers.

On-line optimization program of Advanced Process Analysis System retrieves the process model and the flowsheet diagram from Flowsim. Additional information needed to run online optimization includes plant data and standard deviation for measured variables; initial estimates, bounds and scaling factors for both measured and unmeasured variables; and economic objective function. The program then constructs three optimization problems shown in Figure 1.5 and uses GAMS (General Algebraic Modeling System) to solve them sequentially. Results of these three problems can be viewed using the graphical interface of Flowsim. This is illustrated in the user’s manual in Appendix J.

3.3 Chemical Reactor Analysis Program

Having optimized the process operating conditions for the most current state of the plant, the next step in Advanced Process Analysis System is to evaluate modifications to improve the process and reduce emission and energy consumption. First, chemical reactors in the process are examined. The reactors are the key units of chemical plants. The performance of reactors significantly affects the economic and environmental aspects of plant operation. The formulation of constraints in these types of units is very important and complicated owing to the various types of reactors and complex reaction kinetics. Unlike a heat exchanger whose constraints are similar regardless of types of equipment, there is a great variation in deriving the constraints for reactors.

The chemical reactor analysis program of Advanced Process Analysis System is a comprehensive, interactive computer simulation that can be used for modeling various types of reactors such as plug flow, CSTR and batch reactors. This is shown in Figure 1.3. Reaction phases included are homogeneous gas, homogeneous liquid, catalytic liquid, gas-liquid etc. The options for energy models include isothermal, adiabatic and non-adiabatic.

The kinetic data needed for the reactor system includes the number of reactions taking place in the reactor and the number of chemical species involved. For each reaction, stoichiometry and reaction rate expressions also need to be supplied. Physical properties for chemical species can be retrieved from Flowsim.

Feed stream for the reactor is obtained from Flowsim and its temperature, pressure and flowrate are retrieved using the results from on-line optimization. Finally, the dimensions of the reactor and heat transfer coefficients are supplied. All of this data is used to simulate reactor conditions and predict its performance. Reactant concentration, conversion, temperature and pressure are calculated as functions of reactor length or space-time. The results can be viewed in both tabular and graphical form. The user's manual in Appendix J gives a step-by-step description of the program.

As operating process conditions change, the performance of reactors can vary to a significant extent, also. The reactor design program a wide range of different types of reactors, which can be examined and compared to decide the best reactor configuration for economic benefits and waste reduction.

3.4 Heat Exchanger Network Program

The optimization of chemical reactors is followed by heat exchanger network optimization as shown in the onion skin diagram in Figure 3.1. Most chemical processes require heating and cooling of certain process streams before they enter another process unit or are released into environment. This heating or cooling requirement can be satisfied by matching these streams with one another and by supplying external source of heating or cooling. These external sources are called as utilities, and they add to the operating cost of the plant. The Heat Exchanger Network program aims at minimizing the use of these external utilities by increasing energy recovery within the process. It also synthesizes a heat exchanger network that is feasible and has a low investment cost.

There are several ways of carrying out the above optimization. Two of the most important ones are pinch analysis and mathematical programming methods. Pinch analysis is based on thermodynamic principles whereas the mathematical methods are based on mass and energy balance constraints. The Heat Exchanger Network Program (abbreviated as THEN) is based on the method of pinch analysis.

The first step in the implementation of THEN is the identification of all the process streams, which are important for energy integration. These streams usually include streams entering or leaving heat exchangers, heaters and coolers. The flowsheeting diagram of Flowsim is used in the selection of these streams.

The next step in this optimization task involves retrieval of necessary information related to these streams. Data necessary to perform heat exchanger network optimization includes temperature, flowrate, film heat transfer coefficient and enthalpy data. Enthalpy data can be in the form of constant heat capacities for streams with small temperature variations. For streams with large variations, it can be entered as temperature-dependent enthalpy coefficients. Film heat transfer coefficients are needed only to calculate the areas of heat exchangers in the new network proposed by THEN.

Temperature and flowrates of various process streams are automatically retrieved from the results of online optimization. The setpoints obtained after the plant economic optimization are used as the source data. Physical properties such as the heat capacities, enthalpy coefficients and film heat transfer coefficients are retrieved from Flowsim.

The third step in heat exchanger network optimization is the classification of streams into hot streams and cold streams. A hot stream is a stream that needs to be cooled to a lower temperature whereas a cold stream is a stream that needs to be heated to a higher temperature. Usually, streams entering a cooler or the hot side of a heat exchanger are hot streams whereas streams entering through a heater or the cold side of a heat exchanger are cold streams. The final step in this problem requires the specification of minimum approach temperature. This value is usually based on experience.

Having completed all of the above four steps, heat exchanger network optimization is now performed using THEN. Thermodynamic principles are applied to determine the minimum amount of external supply of hot and cold utilities. Grand Composite Curve is constructed for the process, which shows heat flows at various temperature levels. A new network of heat exchangers, heaters and coolers is proposed, which features the minimum amount of external utilities. This network drawn in a graphical format is called the Network Grid Diagram. An example of a network grid diagram is given in Figure 1.4. Detailed information about the network can be viewed using the interactive features of the user interface. The user's manual in Appendix J provides a step-by-step description of the program.

The amount for minimum hot and cold utilities calculated by the Heat Exchanger Network Program is compared with current amount of utilities being used in the process. If the current amounts are greater than the minimum amounts, the process has potential for reduction in operating cost. The network grid diagram synthesized by THEN can be used to construct a heat exchanger network that achieves the target of minimum utilities. Savings in operating costs are compared with cost of modification of the existing network, and a decision is made about the implementation of the solution proposed by THEN.

3.5 Pollution Assessment Program

The final step in the Advanced Process Analysis System is the determination of the emissions from the process and the location where these pollutants are generated within the process. The pollution assessment module of Advanced Process Analysis System is called 'The Pollution Index Program'. It is based on the Waste Reduction Algorithm and the Environmental Impact Theory as described in Chapter 2. It defines a quantity called as the pollution index to provide a basis for measuring the pollution generated by the process.

Environmental impact of a chemical process is caused by the streams that the process takes from and emits to the environment. Only these input and output streams are considered in performing pollution index analysis. Other streams, which are completely internal to the process, are excluded. In the Pollution Index Program, this selection of input-output streams is automatically done based on the plant information entered in Flowsim.

The next step in pollution index analysis is the classification of output streams into product and non-product streams. All streams which are either sold as product or which are used up in a subsequent process in the production facility are considered as product streams. All other output streams, which are released into the environment, are considered as non-product streams. All non-product streams are considered as pollutant streams whereas all product streams are considered to have zero environmental impact.

Pollution index of a stream is a function of its composition. The composition data for the streams is retrieved from the results of on-line optimization performed earlier. This can be either in terms of molar flowrates or fractions. Additional data needed for pollution analysis is the specific environmental impact potential values of individual chemical species present in a stream. These values for various chemical species are available in the report on environmental life cycle assessment of products.

The last piece of information required is the relative weighting factors for the process plant. According to the Waste Reduction Algorithm, environmental impact of chemical processes can be broadly classified into nine categories e.g. acidification, photochemical oxidation etc. The relative weighting factors allow the customization of the analysis to local conditions. Their values depend on the location of the plant and its surrounding conditions. For example, the weighting factor for photochemical oxidation is higher in areas which suffer from smog.

Having finished all of the above prerequisite steps, the pollution index program is now called to perform the analysis. Mass balance constraints are solved for the process streams involved, and equations of the Environmental Impact Theory are used to calculate the pollution index values. Six types of pollution indices are reported for the process. Three of these are based on internal environmental efficiency whereas the other three are based on external environmental efficiency. Higher the values of these indices, higher is the environmental impact of the process.

The pollution index program also calculates pollution indices for each of the individual process streams. These values help in identification of the streams which contribute more to the overall pollution impact of the process. Suitable process modifications can be done to reduce the pollutant content of these streams.

Every run of on-line optimization for the process can be followed by pollution index calculations. The new pollution index values are compared with the older values.

The comparison shows how the change in process conditions affects the environmental impact. Thus, the pollution index program can be used in continuous on-line monitoring of the process.

3.6 Summary

To summarize, the Flowsim program is used first to develop the process model. The On-Line Optimization program is used to control the process to maximize profit and minimize pollutants, and in doing this it has to continually update the process model to match the current state of the plant. This provides an accurate description of the process for off-line process modification analysis. The Chemical Reactor Analysis program is used to determine the best type of chemical reactors for the process and to optimize their performance. The Heat Exchanger Network Program then optimizes the heat recovery in the system and minimizes the amount of external utilities. Finally, the Pollution Index Program is called to carry out pollution analysis to measure the environmental impact of the process and to direct changes to reduce waste generation. Subsequent chapters describe applying this methodology in analyzing Motiva refinery alkylation process.

CHAPTER 4

MOTIVA ALKYLATION PROCESS

Advanced Process Analysis System was applied to a commercial alkylation process at Motiva Refinery Complex in Convent, Louisiana. This chapter describes the Motiva alkylation process and the simulation of the process developed with APAS. Also, the validation of the process simulation is given, demonstrating that the simulation predicts the performance of the plant.

4.1 Process Description

Motiva Alkylation process is a 15,000 BPD STRATCO Effluent Refrigerated Alkylation Plant. The heart of the process is the STRATCO reactor or contactor, which contacts the reactants in a high velocity propeller stream and removes heat from the exothermic reaction.

In the STRATCO Effluent Refrigerated Alkylation process, light olefins (propylene, butylenes) are reacted with isobutane in the presence of sulfuric acid catalyst to form hydrocarbon, mainly in the iC_7 to iC_8 range, called alkylate. The alkylate product is a mixture of gasoline boiling range branched hydrocarbons which is blended with the refinery gasoline pool to increase the gasoline octane.

Process flow diagrams representing Motiva alkylation process are shown in Figures 4.1, 4.2 and 4.3. These were prepared from P&ID’s of the plant. The reaction section of the process is shown in Figure 4.1. The refrigeration, depropanizer and deisobutanizer sections are shown in Figure 4.2. The saturate deisobutanizer section of the alkylation process is shown in Figure 4.3.

The process has four reactor pairs and four acid settlers as shown in Figure 4.1. In the reaction section there are three feed streams, the olefin feed (HC01), the isobutane feed (HC03) and the recycled olefin/isobutane mixture (HC32). The olefin feed contains the light olefins that are reacted with isobutane in the alkylation unit's STRATCO stirred reactors. The isobutane stream is in excess to fully react with all of the olefins being charged to the unit. The process units are described in this section.

4.1.1 STRATCO Contactor

The two feed streams (HC01 and HC03) are cooled by exchanging heat with the net Contactor effluent stream (5E-628, 5E-628, 5E-630) from the suction trap/flash drum (5C-614) as shown in Figure 4.1. The two streams are then combined and fed to the STRATCO Contactors (5C-623 to 5C-630). The recycled olefin/isobutane stream is fed to the Contactors separately (HC34, HC38, HC41, HC45).

The STRATCO Contactor, in which the alkylation reaction occurs, is a horizontal pressure vessel containing a mixing impeller, an inner circulation tube and a tube bundle to remove the heat generated by the alkylation reaction as shown in Figure 4.4. The feed is injected into the suction side of the impeller inside the circulation tube. The impeller rapidly disperses the hydrocarbon feed with acid catalyst to form an emulsion. The emulsion is circulated by the impeller at high rates within the Contactor. The sulfuric acid present within the reaction zone serves as a catalyst to the alkylation reaction. The acid absorbs a small amount of hydrocarbon from side reactions and feed contaminants which reduces the sulfuric acid concentration.

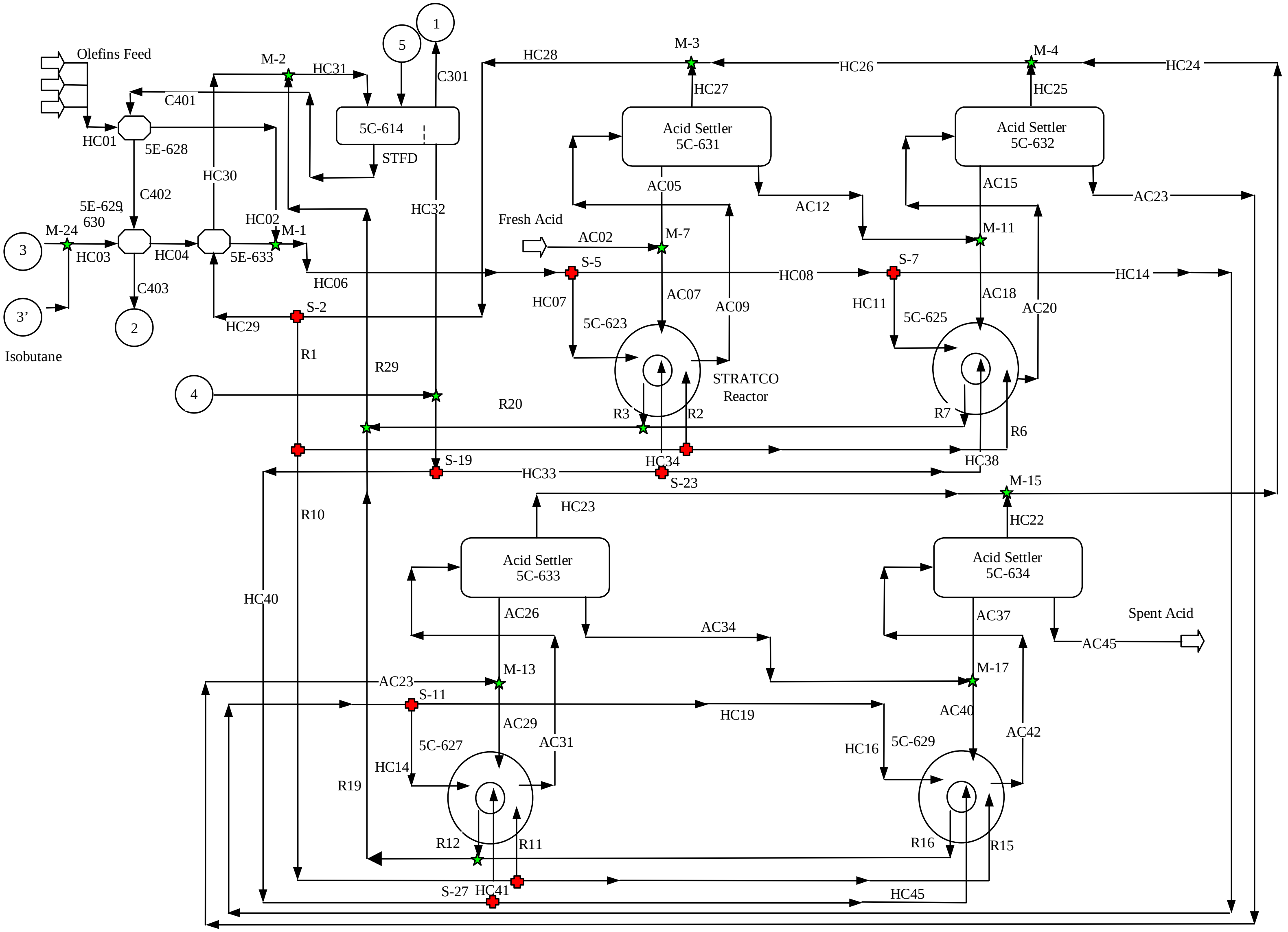


Figure 4.1. Reactor Section of the Alkylation Process

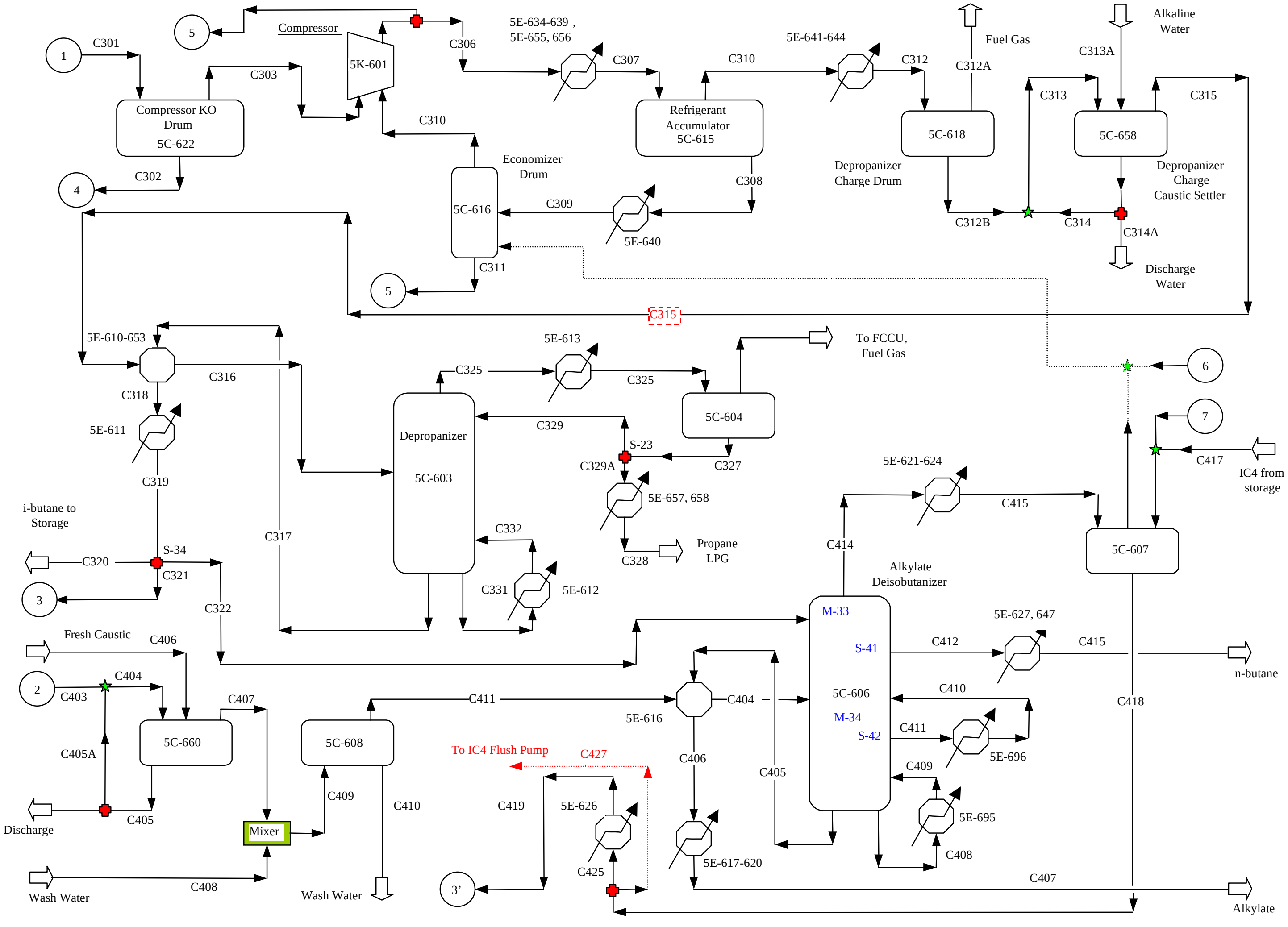


Figure 4.2. Refrigeration, Depropanizer and Deisobutanizer Sections of the Alkylation process

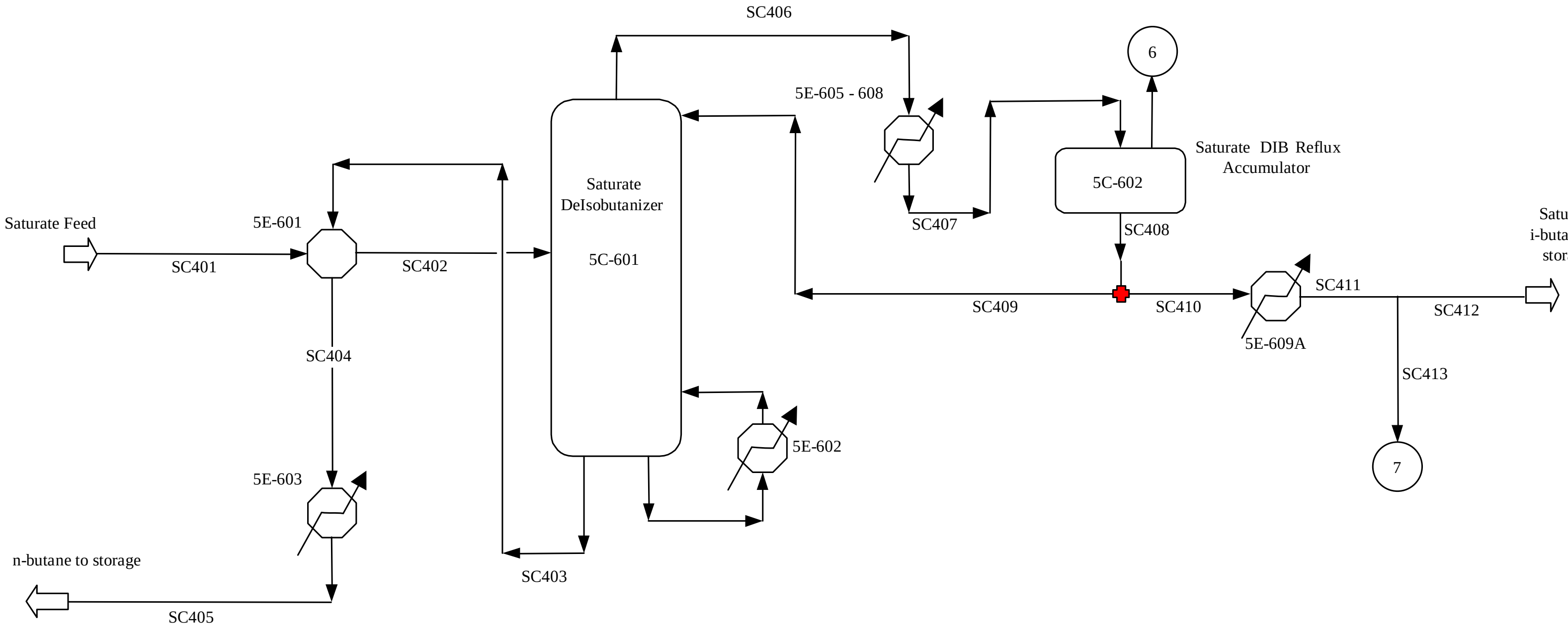


Figure 4.3. Saturate Deisobutanizer Section of the Alkylation Process

In order to maintain the desired spent acid strength (89.0 wt% H_2SO_4) in the last two of the eight Contactors, fresh acid (98.5 wt% H_2SO_4) is continuously charged to the first two Contactors, and an equivalent amount of 89.0 wt% spent acid is withdrawn from the acid settler.

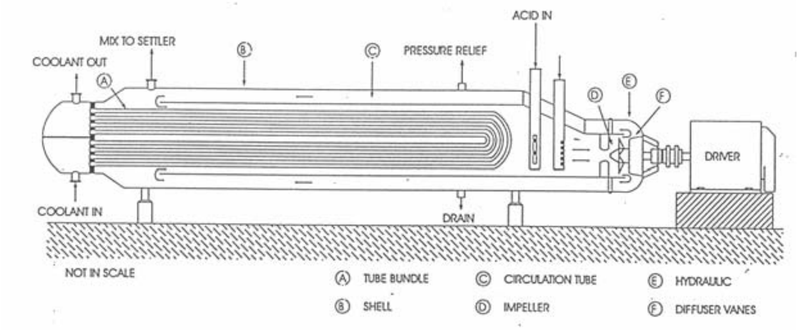


Figure 4.4. STRATCO Effluent Refrigeration Reactor (Yongkeat, 1996)

The hydrocarbon and acid are separated in four settlers 5C-631 to 5C-634 and the acid-free hydrocarbon phase (HC22, HC23, HC25, HC27) flows from the top of the acid settler through a backpressure control valve. Part of it goes into the tube side of the contactor tube bundle (R1). The backpressure control valve is set at a pressure (60.0 psig) to maintain the contents of the settler in the liquid phase. As the hydrocarbon stream passes through the control valve, its pressure is reduced to about 5.0 psig, flashing a portion of the stream's lighter components, thereby, cooling the stream to a temperature of about 30 °F. When the two-phase stream passes through the tube bundle, additional vapor is generated as a result of absorbing heat generated by the alkylation reaction.

4.1.2 Refrigeration Section

As shown in Figure 4.1, the second portion (HC29) of the hydrocarbon effluent from the settler goes to the isobutane chiller (5E-633) and is used to reduce the temperature of the isobutane feed stream. It then combines with the Contactor effluent stream leaving the tube bundle and flows into the suction trap side of the suction trap/flash drum (5C-614), where the liquid and vapor portions of this stream are separated. The suction trap/flash drum is a two-compartment vessel with a common vapor space. The net Contactor effluent is accumulated on one side of a separation baffle and is pumped to the effluent treating section. The cold refrigerant condensate is accumulated on the other side of the baffle. This effluent recycle stream consists mostly of isobutane and is returned to the Contactor by the effluent recycle pump. The vapor portions of both of these streams combine and flow to the suction of the refrigeration compressor (5K-601) shown in Figure 4.2.

The compressor driven by an electric motor, increases the pressure of the refrigerant vapor to allow condensing by cooling water. The vapor is condensed in two steps to provide a higher concentration of propane in the depropanizer feed.

Liquid generated by the first bank of condensers (e.g. 5E-634-639) is separated from the propane-rich vapor in the refrigerant accumulator (5C-615), further cooled by the refrigerant cooler, and then flashed across a control valve. Vapor and liquid are separated in an economizer (5C-616). The economizer vapor returns to an intermediate stage of the compressor (5K-601) to be recompressed, while the liquid is returned to the suction trap/flash drum (5C-614).

The remaining vapor portion of the compressor discharge stream (C310) flows from the separator to the "total condenser" (5E-641-644). Liquid from the total condenser is accumulated in the Depropanizer Charge Drum (5C-618), and ultimately fed to the Depropanizer (5C-603) for stripping of propane before being sent to the Alkylate Deisobutanizer (5C-606).

4.1.3 Depropanizer (5C-603)

The depropanizer feed stream is pumped from the charge drum to the depropanizer feed caustic wash (5C-658) to neutralize acidic components. The neutralized stream then flows to the depropanizer feed/bottoms exchanger (5E-610-5E-653) before entering the tower, as shown in Figure 4.2.

The overhead propane vapor from the depropanizer (C325) is totally condensed by cooling water and collected in the depropanizer reflux accumulator drum (5C-604). A part of the liquid is refluxed to the column's top tray (C329), and the rest is further cooled and sent to the LPG section (C328). The depropanizer bottoms product (C317) temperature is reduced in the feed/bottoms exchanger (5E610-653). The stream then enters a water-cooled exchanger (5E-611) before it is split into three portions, one each for the Alkylate Deisobutanizer, the Contactor (③) and storage.

4.1.4 Alkylate Deisobutanizer (5C-606)

The net effluent from the suction trap/flash drum (5C-614) is heated in the feed/effluent exchangers (5E-628; 5E-629, 5E-630) as shown in Figure 4.1 and then treated with caustic to remove any traces of acid (5C-660 and 5C-608 in Figure 4.2). The treated net effluent is fed to the alkylate deisobutanizer (DIB) tower (5C-606) to strip isobutane from alkylate as shown in Figure 4.2. Two steam-fired thermosiphon reboilers (5E-695, 5E-696) supply the majority of the heat to the lower portion of the column by vaporizing liquid side draws (C411) from the column as well as the DIB bottoms liquid (C408). A portion of the depropanizer bottoms is fed to the column as the reflux (C322).

Normal butane is removed as a vapor side-draw (C412). The vapor is condensed and cooled by cooling water (5E-627, 5E-647). The normal butane product (C415) can be used for vapor pressure blending or sold. The rate of the normal butane product will vary depending on the desired deisobutanizer alkylate product Reid Vapor Pressure (RVP).

The overhead isobutane vapor is condensed by cooling water and accumulated in the isobutane accumulator pot (5C-607). Make-up isobutane (C417) from storage is added to the pot and the combined stream (C418) is sent to the Contactors to react with the olefins (③’).

The deisobutanizer bottoms (C405) is the alkylate product. It is cooled by the deisobutanizer feed/effluent exchanger (5E-616) and also a heat exchanger with cooling water (5E-617-5E-620). The cooled alkylate (C407) is removed as a product and sent to storage.

4.1.5 Saturate Deisobutanizer (5C-601)

Another source for isobutane is the saturate deisobutanizer (SatDIB) column (Figure 4.3), which strips isobutane from saturate feed coming from reformer unit of the refinery (SC401). The saturate feed, containing mainly C_4’s, flows to the SatDIB feed/bottoms exchanger (5E-601) before entering the tower, as shown in Figure 4.3. The overhead isobutane vapor is condensed by cooling water and a fraction of it (stream SC413) is accumulated in the isobutane accumulator pot (5C-607, Figure 4.2). The saturate deisobutanizer bottoms (SC403) are mainly n-butane product. It is cooled by the SatDIB feed/bottoms exchanger (5E-601) and also by a heat exchanger with cooling water (5E-603). The cooled n-butane (SC405) is sent to storage.

4.2 Process Simulation

This section describes the models of the various process equipments in the alkylation process. The process flow diagram, as developed with Flowsim, the flowsheet simulation tool of Advanced Process Analysis System, is shown in Figure 4.5.

The equipment in the plant can be categorized according to their functions as follows:

Reaction Zone:

- STRATCO Contactor
- Acid settler

Separation Zone:

- Depropanizer
- Alkylate Deisobutanizer
- Saturate Deisobutanizer
- Suction Trap Flash Drum
- Economizer
- Compressor

Heat Transfer Zone:

- Heat Exchangers
- Condensers
- Reboilers

Miscellaneous:

- Mixers
- Splitters
- Reflux Accumulators

The models are developed for each of these units and are given in this chapter.

The alkylation process involves mixtures of a variety of components. The components and compositions of streams vary widely from one section to the other. For record keeping, all the hydrocarbon streams in the plant are composed of the following components:

1.	C_3-	Propane and lower
2.	C_4=	Butenes
3.	iC_4	iso-butane
4.	nC_4	normal-butane
5.	iC_5	iso-pentane
6.	nC_5	normal-pentane
7.	iC_6	iso-hexane
8.	iC_7	iso-heptane
9.	iC_8	iso-octane
10.	iC_9+	iso-nonane and higher

All the sulfuric acid streams in the plant are composed of:

11.	H_2SO_4	sulfuric acid
12.		Water and impurities

The streams carrying the reaction products from the contactors to the acid settlers contain all of the twelve components.

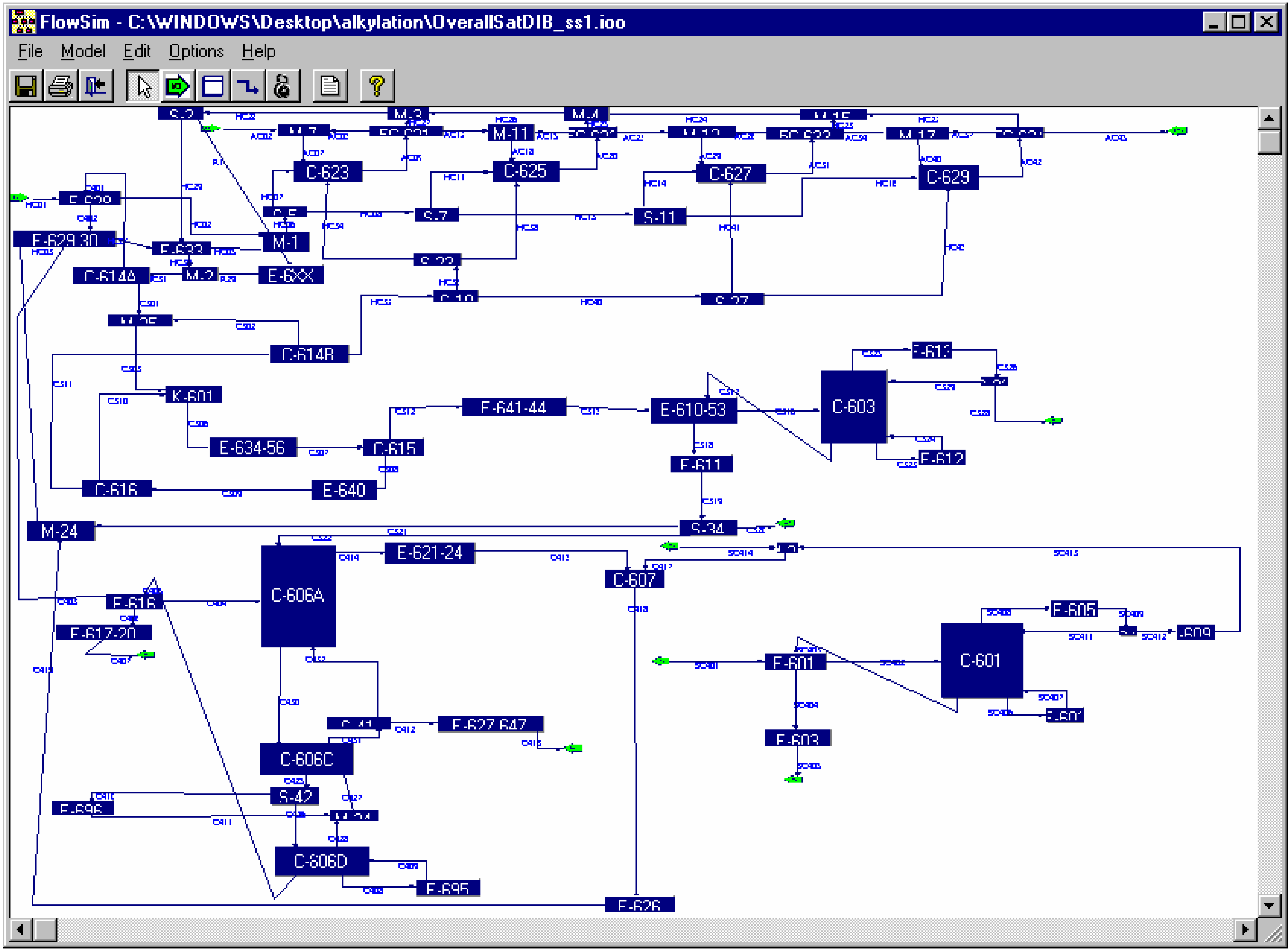


Figure 4.5. Process flow diagram, as developed with the Flowsheet Simulation tool of Advanced Process Analysis System

4.2.1 STRATCO Contactor (5C-623)

The sulfuric acid alkylation reaction mechanism for pure propylene and pure butylene feeds were shown in Tables 2.2 and 2.3. These are based on the Schmering carbonium ion mechanism with modification introduced to account for iC_9 and iC_{10} formation. The material balance on reactants and the product formation equations are shown in the same tables. The parameters that affect the performance of the contactor are:

1. Operating Temperature
2. Acid Strength
3. Isobutane Concentration
4. Olefin Space Velocity

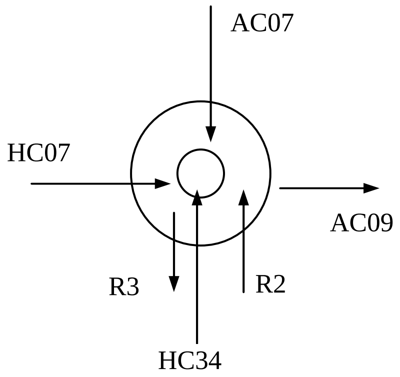


Figure 4.6: Contactor 5C-623

The contactor was modeled as of a Continuously Stirred Tank Reactor (CSTR) with heat exchange. The intense mixing provided by the propellers ensures that there is no spatial variation in concentration, temperature, or reaction rate throughout the vessel. The composition and temperature of the exit stream were the same as those inside the reactor.

Referring to Figures 4.1 and 4.6, the material and energy balance equations for the contactor 5C-623 are as follows:

Description

Inlet streams:	HC07 (isobutane- olefin mixture), HC34 (effluent recycle-mainly isobutane), and AC07 (sulfuric acid catalyst)

Outlet streams: AC09

Coolant streams: R2 (in), R3 (out)

Material Balance

Overall:

Mass flowrate in – Mass flowrate out = 0 (4.1)

$$F_{HC07} + F_{HC34} + F_{AC07} - F_{AC09} = 0 \tag{4.2}$$

$$F_{R2} - F_{R3} = 0 \tag{4.3}$$

where, F_X is the total mass flow rate (metric ton/min) of stream X.

Component:

Mass flowrate in – Mass flowrate out + Mass generation rate = 0 (4.4)

$$F^i_{HC07} + F^i_{HC34} - F^i_{AC09} + r^i V^a_{5C623} MW^i = 0 \tag{4.5}$$

for the hydrocarbon components. Here, r^i is the reaction rate of component i, in terms of moles of i produced per unit time, per unit volume of the acid catalyst (metric ton moles/(m^3·min)), and MW^i is the molecular weight of component i. The quantity V^a_{5C623}, shown in the material balance equations, is the volume of acid in the contactor, and is typically 60 % of the total contactor volume.

Considering the degradation of the catalyst, the material balance equation for the acid component can be written as

$$F^i_{AC07} - F^i_{AC09} - R^a_{5C623} = 0 \tag{4.6}$$

where, R^a_{5C623} is the rate of degradation of the acid (metric ton/min). The acid degradation rate can be related to the volumetric flowrate of butylenes into the contactor as follows (Graves 1999),

$$R^{a}_{5C623} = 0.121 Q^{C4=}_{HC07} \tag{4.7}$$

The total mass flow rates are calculated as the sum of the component flow rates.

$$\sum F^{i}_{X} - F_{X} = 0 \tag{4.8}$$

The subscripts to the process variables like mass flow rates, specific enthalpies and stream temperatures indicate the stream names, and their superscripts indicate the component. The subscripts to the process parameters indicate the process unit they represent.

The material in the contactor is a two-phase mixture, consisting of a hydrocarbon phase and an acid phase. Since the reaction model assumes that all the reactions occur in the acid phase, the concentrations shown in the reaction model equations are those in the acid phase.

The olefin feed to the process is composed of about 45% lv butylenes (1-BUT + C2B + T2B) and about 3.5% lv propylene among other paraffins. Because of the low presence of propylene and the non-participation of paraffins in the alkylation reaction, the reaction mechanism of alkylation of isobutane with pure butylene (Table 2.3) was adopted. The reaction rate terms in Equation 4.5 is evaluated using corresponding equations from Table 2.3. Appendix A shows the procedure followed for calculating the concentrations of the contactor components in the acid phase.

Alkylation of isobutane with olefins is an exothermic reaction. The reaction mixture must be maintained in a particular temperature range (0-10 °C) in order to obtain the desired yields. Higher operating temperatures result in oxidation and polymerization reactions, decreasing the yields. Lower temperatures result in decreased effectiveness due to the increase in acid viscosity and decrease in solubility of hydrocarbons in the acid phase. Therefore, the temperature in the contactor is maintained by recycling the cold refrigerant condensate from the Suction Trap Flash Drum, which consists mostly of isobutane, and by circulating a part of the flashed, acid-free effluent from the settlers, through the contactor tube bundle. When the two-phase stream passes through the tube bundle, additional vapor is generated.

The tube bundle in the contactor, is effectively, a partial boiler, which vaporizes a portion of the coolant. This can be modeled by assuming that the two-phases in the coolant mixture are in equilibrium with each other throughout the tube bundle. The component mass balance for the two-phase coolant stream can be written as

$$(F^i_{R2l} + F^i_{R2v}) - (F^i_{R3l} + F^i_{R3v}) = 0 \tag{4.9}$$

$$K_i = \frac{y_i}{x_i} \qquad \text{where,} \quad \sum x_i = 1, \quad \sum y_i = 1 \tag{4.10}$$

In the above equation, y_i is the mole fraction of component i in the vapor phase, and x_i is that in the liquid phase.

The model can be simplified by assuming that all the vapor generation in the tube bundle, due to transfer of heat from the contactor, occurs at a point outside the tube bundle; i.e. after the coolant has passed through it. This is the same as considering the partial boiler to be equivalent to a heater followed by an isothermal flash operation. Then, the mole fractions can be written as

$$y_i = \frac{F^i_{R3v} / MW^i}{\sum F^i_{R3v} / MW^i} \qquad \text{and} \qquad x_i = \frac{F^i_{R3l} / MW^i}{\sum F^i_{R3l} / MW^i} \tag{4.11}$$

Energy Balance

Overall:

Energy in + Energy generated - Energy out = 0 (4.12)

$$h_{HC07} + h_{HC34} + h_{AC07} + h_{R2} + H_{5C623} - h_{AC09} - h_{R3} = 0 \tag{4.13}$$

where, h_X is the enthalpy of stream X in (MJ/min), and H_{5C623} is the heat generated in the contactor by the exothermic reaction (MJ/min).

The stream enthalpies are calculated from the component specific enthalpies, as

$$h_X = \sum F_X^i h_X^i \quad \text{for single phase streams, and} \tag{4.14}$$

$$h_X = \left(\sum F_X^i h_X^i\right)_l + \left(\sum F_X^i h_X^i\right)_v \tag{4.15}$$

for two-phase streams (R2 and R3)

where, h_X^i is the specific enthalpy of the component i in stream X in (MJ/metric ton).

Heat Transfer:

Energy in – Energy out – Energy transferred out = 0 (4.16)

$$h_{R2} - h_{R3} - U_{5C623} A_{5C623} \Delta T_{lm} = 0 \tag{4.17}$$

where, U_{5C623} is the overall heat transfer coefficient (MJ/m^2·°C·min), A_{5C623} is the area of heat transfer (m^2), and ΔT_{lm} is the log mean temperature difference in the contactor 5C-623 (°C).

$$\Delta T_{lm} = \frac{\left(T_{5C623} - T_{R2}\right) - \left(T_{5C623} - T_{R3}\right)}{\ln \dfrac{\left(T_{5C623} - T_{R2}\right)}{\left(T_{5C623} - T_{R3}\right)}} \tag{4.18}$$

The mass and energy balance equations for contactor 5C-623 are summarized in Table 4.1.

Table 4.1. Summary of the contractor model

Material Balances	
Overall	$F_{HC07} + F_{HC34} + F_{AC07} - F_{AC09} = 0$ $F_{R2} - F_{R3} = 0$
Species	$F^{i}_{HC07} + F^{i}_{HC34} - F^{i}_{AC09} + r^{i}V^{a}_{5C623}MW^{i} = 0$ $F^{i'}_{AC07} - F^{i'}_{AC09} - R^{a}_{5C623} = 0$ $R^{a}_{5C623} = 0.121Q^{C4=}_{HC07}$ where, *i*= 1,2,3,4,5,6,7,8,9,10 and *i'*= 11
Energy Balances	
	$h_{HC07} + h_{HC34} + h_{AC07} + h_{R2} + H_{5C623} - h_{AC09} - h_{R3} = 0$ $h_{R2} - h_{R3} - U_{5C623}A_{5C623}\Delta T_{lm} = 0$

The equations given in Table 4.1 describe each of the four pairs of contactors. However, the kinetic model is not a function of the catalyst concentration, and plant data are not available for sulfuric acid concentration in the contactors. Consequently, the model for each of the contactors is the same.

4.2.2 Acid Settler (5C-631)

The acid settler separates the emulsion from the contactor into the acid and hydrocarbon phases. One acid settler is provided to each pair of contactors. The inputs to the settler are the effluents from the contactor pair and the outputs are the separated acid and hydrocarbon streams.

The material and energy balance equations for the acid settler (5C-631) are as shown in Table 4.2. The mass flow rate of each component coming in is equal to the mass flow rate of each component leaving of the settler. Since there is no heat transferred from or into the settler, the temperatures of the various input and output streams can be assumed to be equal. We also assume that the separation of the two phases in the settler is complete, so that there is no acid component in the output hydrocarbon stream and vice-versa.

Table 4.2. Summary of the acid settler model

Material Balances	
	$F^{i}_{AC09} - F^{i}_{HC27} = 0 \qquad i=1,2,3,4,5,7$ $F^{11}_{AC09} + F^{12}_{AC09} - F_{AC05} - F_{AC12} = 0$ $F^{11}_{AC05} - s_{C631} F^{11}_{AC09} = 0$ $F^{12}_{AC05} - s_{C631} F^{12}_{AC09} = 0$ $x^{11}_{AC05} - x^{11}_{AC12} = 0$
Energy Balances	
	$T_{AC09} = T_{HC27}$; $T_{AC09} = T_{AC12}$; $T_{AC09} = T_{AC05}$

4.2.3 Depropanizer (5C-603)

The Depropanizer was modeled using Smith-Brinkley Group method (Smith, 1963; Perry *et al.*, 1984). This method can be applied to absorption, extraction processes and distillation. The equation, which applies to the distillation process, is for each component i,

$$f = \frac{\left(1 + S_{n,i}^{N-M}\right) + R\left(1 - S_n\right)}{\left(1 + S_{n,i}^{N-M}\right) + R\left(1 - S_n\right) + hS_n^{N-M}\left(1 - S_m^{M+1}\right)} \tag{4.19}$$

where R is the external-reflux ratio F_{C329}/F_{C328} and $f = (F^i_{C317}/F^i_{C316})$, is the fraction of i leaving in the bottoms product. The quantity S is the stripping factor (for each component) and is defined for each group of stages in the column by $S_{n,i}=K_iV/L$ and $S_{m,i}=K'_iV'/L'$. K is the equilibrium ratio y/x for each component and V, L are the vapor and liquid molar flow rates in the column. The K_i, V and L values are the effective values for the top column section; K'_i, V' and L' are the effective values for the section below the feed stage. The quantity h depends on whether K or K' is used for the feed stage. If the feed is mostly liquid, the feed stage is grouped with the lower stages and

$$h_i = \frac{K'_i L}{K_i L'}\left(\frac{1 - S_n}{1 - S_m}\right)_i \tag{4.20}$$

If the feed is mostly vapor,

$$h_i = \frac{L}{L'}\left(\frac{1 - S_n}{1 - S_m}\right)_i \tag{4.21}$$

The following four specifications for the column are necessary:

1. N, the total number of equilibrium stages
2. M, the number of stages below the feed stage
3. The reflux rate or the maximum vapor rate at some point in the column

4. The distillate rate D

Specification of D and L (or V), along with specifications of the feed stream variables fixes the assumed phase rates in both sections of the column. Determination of separation factors S_n and S_m then depends upon estimation of individual K values. If ideal solutions are assumed, K values are functions of only temperature and column specified pressure. Estimation of K values and, in turn, S_n and S_m values for each component reduces to estimation of the effective temperature in each column section or group of stages.

The effective temperature is assumed to be the arithmetic average for simplicity.

$$T_n = {(T_N + T_{M+1})}/{2} \tag{4.22}$$

$$T_m = {(T_{M+1} + T_1)}/{2} \tag{4.23}$$

The feed enters the column at the (M+1)th stage. The material and energy balance equations for the depropanizer are shown in Table 4.3. The Saturate Deisobutanizer column is modeled in a similar way.

Table 4.3. Summary of the depropanizer model

Material Balances	
Overall	$F_{C316} + F_{C329} - F_{C317} - F_{C325} = 0$
Species	$F^{i}_{C316} + F^{i}_{C329} - F^{i}_{C317} - F^{i}_{C325} = 0$ where *i*=1,3,4,5
Smith- Brinkley Method Equations	
	$K_i = f(P_{C603}, T_n)$ $K_i^{'} = f(P_{C603}, T_m)$ $S_{n,i} = \frac{K_i F_{C325}}{F_{C329}}$ $S_{m,i} = \frac{K_i^{'} V^{'}}{L^{'}}$ $f_i = \frac{\left(1 + S_{n,i}^{N-M}\right) + R\left(1 - S_{n,i}\right)}{\left(1 + S_{n,i}^{N-M}\right) + R\left(1 - S_{n,i}\right) + h_i S_{n,i}^{N-M}\left(1 - S_{m,i}^{M+1}\right)}$ $f_i = \frac{F^{i}_{C317}}{F^{i}_{C316}}$ $h_i = \frac{K'_i L}{K_i L'}\left(\frac{1 - S_n}{1 - S_m}\right)_i$ where *i*=1,3,4,5,7 $x^{i}_{C317} - x^{i}_{C323} = 0$, where *i*=1,3,4,5 $T_{C317} - T_{C323} = 0$

4.2.4 Alkylate Deisobutanizer (5C-606)

The alkylate deisobutanizer column has two feed streams, two product streams, two side streams and two reboilers, one of which is used as a side reboiler. One of the feed streams is fed to the column, at the top tray, in place of the reflux. There was no readily available short cut method to model such a distillation column as it is, therefore, the column was divided into three reasonable sections (C-606A, C-606C and C-606D) which can be modeled using Smith Brinkley Method and by employing equilibrium stage assumption. General Smith-Brinkley Method is used for a classical distillation column with recycle and reboiler streams, however the model of deisobutanizer requires the derivation of the method for the rectifying and stripping sections separately. Derivations can be found in (Smith, 1963) – Design of Equilibrium Stage Processes. The equations for the alkylation deisobutanizer are given in Table 4.4.

Table 4.4. Summary of the deisobutanizer model

Material Balances	
Overall	$F_{C404} + F_{C432} + F_{C322} - F_{C414} - F_{C430} = 0$ $F_{C430} + F_{C427} - F_{C431} - F_{C425} = 0$ $F_{C426} - F_{C428} - F_{C405} = 0$ $F_{C427} - F_{C431} = 0$ $F_{C425} - F_{C430} = 0$
Species	$F^{i}_{C404} + F^{i}_{C432} + F^{i}_{C322} - F^{i}_{C414} - F^{i}_{C430} = 0$ $F^{i}_{C430} + F^{i}_{C427} - F^{i}_{C431} - F^{i}_{C425} = 0$ $F^{i}_{C426} - F^{i}_{C428} - F^{i}_{C405} = 0$ where i=1,3,4,5
Smith- Brinkley Method Equations	
	$K_{i,C606A} = f(P_{C606A}, T_{n,C606A})$ $K'_{i,C606A} = f(P_{C606A}, T_{m,C606A})$ $K_{i,C606C} = f(P_{C606C}, T_{C425})$ $K'_{i,C606D} = f(P_{C606D}, T_{m,C606D})$ $S_{m,i,C606A} = \frac{K'_{i,C606A} V'_{C606A}}{L'_{C606A}}$ $S_{n,i,C606A} = \frac{K_{i,C606A} F_{C414}}{F_{C322}}$ $S_{m,i,C606D} = \frac{K_{i,C428} F_{C428}}{F_{C426}}$

Table 4.4. Summary of the deisobutanizer model (Cont'd)

Smith- Brinkley Method Equations

$$f_{i,C606A}=\frac{\left(1-S_{n,i,C606A}^{N-M}\right)+q_{i,C606A}^{S}(S_{n,i,C606A}^{N-M}-S_{n,i,C606A})+q_{i,C606A}^{F}h_{i,C606A}S_{n,i,C606A}^{N-M}\left(1-S_{m,i,C606A}^{M}\right)}{\left(1-S_{n,i,C606A}^{N-M}\right)+h_{i,C606A}S_{n,i,C606A}^{N-M}\left(1-S_{m,i,C606A}^{M+1}\right)}$$

$$f_{i,C606A}=\frac{F_{C430}^{i}}{(F_{C404}^{i}+F_{C322}^{i}+F_{C432}^{i})}$$

$$h_{i,C606A}=\frac{F_{C322}}{L_{C606A}^{'}}\left(\frac{1-S_{n,C606A}}{1-S_{m,C606A}}\right)_{i}$$

$$x_{i,C606D}^{M}=\frac{F_{C428}K_{i,C606D}^{'}\left(S_{m,i,C606D}^{M_{D}-1}-1\right)+F_{C426}\left(S_{m,i,C606D}-1\right)}{F_{C426}^{2}\left(S_{m,i,C606D}-1\right)}$$

where *i*=1,3,4,5,7

$xx_{C425}^{i}K_{C606C}^{i}-xx_{C431}^{i}=0$, where *i*=1,3,4,5

$x_{C408}^{i}-x_{C405}^{i}=0$, where *i*=1,3,4,5

$$L_{C606A}^{'}=F_{C322}+q_{C606A}F_{C404}$$

$$V_{C606A}^{'}=F_{C432}$$

$$T_{C431}-T_{C425}=0$$

4.2.5 Suction Trap/Flash Drum (5C-614)

The suction trap/flash drum (STFD) splits the hydrocarbon effluent from the settlers based on volatility. It is a two-compartment vessel, with a common vapor space. The net contactor effluent is accumulated on one side of the baffle and the cold refrigerant condensate on the other. The vapors from the two compartments combine, and flow out from the top.

The STFD is modeled as two separate units – suction trap and flash drum, with the vapor streams from the two units combining in a mixer, as shown in Figure 4.7. The suction trap acts as the separating vessel for the two-phase contactor from the contactor tube bundles and from the isobutane chiller (5E-633). The liquid and vapor streams leave the vessel as two separate streams. In the Flash drum, the cold condensate from the economizer is flashed and separated. This unit is modeled as an equilibrium stage with adiabatic flash. The material and energy balance equations for the two units are as follows:

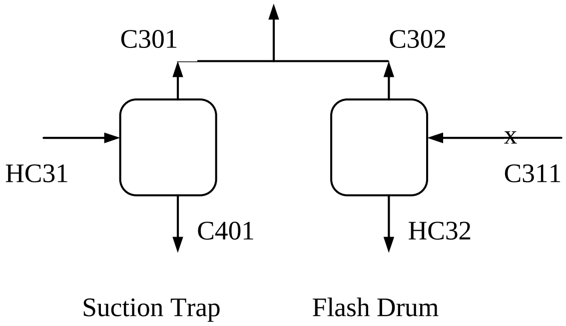


Figure 4.7: STFD 5C-614

Suction Trap:

Overall material balance: $$\left(F_{HC31l} + F_{HC31v}\right) - \left(F_{C401} + F_{C301}\right) = 0 \tag{4.24}$$

$$F_{HC31l} - F_{C401} = 0 \tag{4.25}$$

Component material balance: $$\left(F^{i}_{HC31l} + F^{i}_{HC31v}\right) - \left(F^{i}_{C401} + F^{i}_{C301}\right) = 0 \tag{4.26}$$

$$F^{i}_{HC31l} - F^{i}_{C401} = 0 \tag{4.27}$$

Energy balance: $$T_{HC31} = T_{C301} = T_{C401} \tag{4.28}$$

Flash Drum

Overall material balance: $$F_{C311} - F_{HC32} - F_{C302} = 0 \tag{4.29}$$

Component material balance: $$F^{i}_{C311} - F^{i}_{HC32} - F^{i}_{C302} = 0 \tag{4.30}$$

$$K_i = \frac{y_i}{x_i}, \text{ where, } \sum x_i = 1, \ \sum y_i = 1 \tag{4.31}$$

Energy balance: $$h_{C311} - h_{HC32} - h_{C302} = 0 \tag{4.32}$$

The flash operation has been described, in detail, in the contactor modeling section. The Suction Trap Flash Drum model described above is summarized in Table 4.5.

Table 4.5. Summary of the suction trap/flash drum model

Material Balances	
Overall	$\left(F_{HC31l}+F_{HC31v}\right)-\left(F_{C401}+F_{C301}\right)=0$ $F_{HC31l}-F_{C401}=0$ $F_{C311}-F_{HC32}-F_{C302}=0$
Species	$\left(F^{i}_{HC31l}+F^{i}_{HC31v}\right)-\left(F^{i}_{C401}+F^{i}_{C301}\right)=0$ $F^{i}_{HC31l}-F^{i}_{C401}=0$ $F^{i}_{C311}-F^{i}_{HC32}-F^{i}_{C302}=0$, where i=1,3,4,5,7 $K_i=\frac{y_i}{x_i}$, where, $\sum x_i=1$, $\sum y_i=1$
Energy Balances	
	$T_{HC31}=T_{C301}=T_{C401}$ $h_{C311}-h_{HC32}-h_{C302}=0$

4.2.6 Economizer (5C-616)

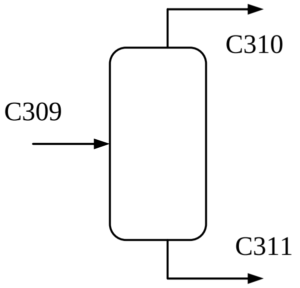


Figure 4.8. Economizer 5C-616

The Economizer separates the vapor and liquid phases generated when the liquid portion of the propane-rich vapor, in the Depropanizer section, is flashed. This unit is modeled the same way as the flash drum of STFD, i.e. assuming an adiabatic flash operation, where the two phases generated are in equilibrium with each other. The mass and enthalpy balances are:

Overall material balance:

$$F_{C309} - F_{C310} - F_{C311} = 0 \tag{4.33}$$

Component material balance:

$$F^{i}_{C309} - F^{i}_{C310} - F^{i}_{C311} = 0 \tag{4.34}$$

$$K_i = \frac{y_i}{x_i}\text{, where, } \sum x_i = 1,\ \sum y_i = 1 \tag{4.35}$$

In the above equation, K_i is the distribution coefficient or the K-factor, y_i is the mole fraction of component i in the vapor phase, and x_i is that in the liquid phase.

Enthalpy balance:

$$h_{C309} - h_{C310} - h_{C311} = 0 \tag{4.36}$$

where, h_X is the enthalpy of stream X.

4.2.7 Compressor (5K-601)

The combined vapor stream from Suction Trap and the Flash Drum is rich in propane, and is sent to the depropanizer section. The vapor is compressed in the

Refrigeration compressor (5K-601), to allow condensing by cooling water. The compressor was assumed to operate under adiabatic conditions, and hence the calculations were based on the following formulas (Perry *et al.*, 1984):

Adiabatic head is expressed as

$$H_{ad} = \frac{k}{k-1} R T_1 \left[\left(\frac{p_2}{p_1} \right)^{\frac{(k-1)}{k}} - 1 \right] \tag{4.37}$$

where H_{ad} = adiabatic head, ft; R = gas constant, (ft·lbf)/(lb·°R) = 1545/molecular weight; T_1 = inlet gas temperature, °R; p_1 = absolute inlet pressure, lbf/in^2; p_2 = Absolute discharge pressure, lbf/in^2, k = ratio of specific heat capacities (c_p / c_v).

The work expended on the gas during compression is equal to the product of the adiabatic head and the weight of the gas handled. Therefore, the adiabatic power is as follows:

$$hp_{ad} = \frac{W H_{ad}}{550} = \frac{k}{k-1} \frac{W R T_1}{550} \left[\left(\frac{p_2}{p_1} \right)^{\frac{(k-1)}{k}} - 1 \right] \tag{4.38}$$

or

$$hp_{ad} = 4.36 \times 10^{-3} \frac{k}{k-1} Q_1 p_1 \left[\left(\frac{p_2}{p_1} \right)^{\frac{(k-1)}{k}} - 1 \right] \tag{4.39}$$

where hp_{ad} = power, hp; W = mass flow, lb/s; and Q_1 = volume rate of gas flow, ft^3/min.

Adiabatic discharge temperature is:

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{\frac{(k-1)}{k}} \tag{4.40}$$

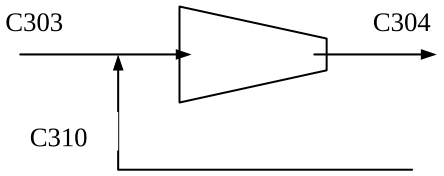


Figure 4.9: Compressor 5K-601

The constraint equations, for the compressor, are developed using the above formulas.

Overall material balance:

$$F_{C303} + F_{C310} - F_{C304} = 0 \tag{4.41}$$

Component material balance:

$$F^i_{C303} + F^i_{C310} - F^i_{C304} = 0 \tag{4.42}$$

Enthalpy balance:

$$h_{C303} + h_{C310} + hp_{ad} - h_{C304} = 0 \tag{4.43}$$

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{\frac{(k-1)}{k}} \tag{4.44}$$

where hp_{ad} is the compressor as given in Equations (4.38, 4.39). The constraints of the compressor are summarized in Table 4.6.

Table 4.6. Summary of the compressor model

Material Balances	
Overall	$F_{C303}+F_{C310}-F_{C304}=0$
Species	$F^{i}_{C303}+F^{i}_{C310}-F^{i}_{C304}=0$ where *i*=1,3,4,5
Energy Balances	
	$h_{C303}+h_{C310}+hp_{ad}-h_{C304}=0$ $T_2=T_1\left(\frac{p_2}{p_1}\right)^{\frac{(k-1)}{k}}$ $hp_{ad}=\frac{k}{k-1}\frac{8.314F_{C306}T_{C303}}{55}\left[\left(\frac{p_2}{p_1}\right)^{\frac{(k-1)}{k}}-1\right]$

4.2.8 Olefin Feed Effluent Exchanger (5E-628)

The olefin feed effluent exchanger cools the olefin feed by exchanging heat with the alkylate effluent stream from the suction trap/flash drum. The material and energy balance equations for this exchanger are shown in Table 4.7. Since no mass transfer is involved in this unit, the masses of the two streams are conserved. The heat transferred between the streams can be accounted for as shown in the energy balance equations.

Table 4.7. Summary of the exchanger model

Material Balances

Overall	$F_{HC01} + F_{HC02} = 0$ $F_{C401} + F_{C402} = 0$
Species	$x^{i}_{HC01} + x^{i}_{HC02} = 0$ $x^{i}_{C401} + x^{i}_{C402} = 0$ where *i*= 1,2,3,4,5
Energy Balances	
	$(h_{HC02} - h_{HC01}) - (h_{C401} - h_{C402}) = 0$ $(h_{HC01} - h_{HC02}) - U_{5E628} A_{5E628} \Delta T_{lm} = 0$ $\Delta T_{lm} = \dfrac{(T_{HC02} - T_{C401}) - (T_{HC01} - T_{C402})}{\ln \dfrac{(T_{HC02} - T_{C401})}{(T_{HC01} - T_{C402})}}$

4.3 Model Validation

The accuracy of the alkylation process model to predict the performance of the plant has to be established. This model validation was performed by solving the data validation problem using a set of plant data (steady state operation point #1) and then comparing the results of the model with the plant data. For the 125 measured plant variables, 88 were within the accuracy of the measurements. The remaining 37 variables are shown in Table 4.8 for the plant data from the DCS, their reconciled value and the standard measurement error $\in_i$ ($\in_i = |y_i - x_i|/\sigma_i$, where is σ_i the standard deviation of the process variable). In consulting with the alkylation plant process engineers, it was concluded that these 37 variables were within the range of possible process values. This includes FC316, FC322, x5C417, xx5C412, xx7C414. The discrepancy in the variable xx1C322 is a result of the model assumption that the propane purge from the drum 5C-618 occurs infrequently. In summary, the model of the process accurately predicts its performance and therefore can be used for on-line optimization.

Table 4.8. Plant vs. Model Data

Variable Name	Plant Data (y_i)	Reconciled Data from Data Validation (x_i)	Standard Measurement Error ($\in_i$)
FAC02	0.1125	0.1600	4.2235
FAC12	0.1259	0.1600	2.7085
FAC23	0.1253	0.1600	2.7653
FAC45	0.1040	0.1600	5.3846
FC308	2.1990	3.1032	4.1120
FC316	0.6581	1.8000	17.3515
FC322	0.4427	1.5619	25.2812
FC328	0.0942	0.0535	2.6399
FC403	3.8766	2.2834	4.1097
FC412	0.0324	0.0418	2.8968
FSC411	2.7287	1.3525	5.0436
FstmE612	0.1425	0.0889	3.7607

x1C417	0.0372	0.0255	3.1309
x2SC402	0.0136	0.0084	3.7929
x2SC408	0.0221	0.0002	9.9048
x3C325	0.0017	0.0000	10.0000
x3SC403	0.0103	0.0212	10.5665
x4C316	0.0580	0.0796	3.7155
x4SC408	0.0331	0.0088	7.3475
x5C316	0.0020	0.0060	19.8000
x5C417	0.0009	0.0295	286.2300
x5HC32	0.0096	0.0306	22.0134
x6SC402	0.0167	0.0666	29.8204
x6SC403	0.0250	0.0950	27.9946
x7HC32	0.0197	0.0497	15.2312
x7SC402	0.0022	0.0032	4.3956
x7SC408	0.0022	0.0000	10.0000
xx1C322	0.0027	0.1167	428.5338
xx1C414	0.0330	0.0800	14.2498
xx2HC01	0.4525	0.1291	7.1481
xx3C407	0.0003	0.0000	7.4194
xx3HC01	0.3558	0.0125	9.6498
xx4C407	0.1124	0.0853	2.4068
xx5C407	0.0803	0.1506	8.7555
xx5C412	0.0022	0.0581	255.6751
xx5C414	0.0021	0.0011	4.8325
xx7C414	0.0015	0.0080	44.4218

4.4 Summary

In this chapter, Motiva alkylation process and the system model for the process was described. Also the validity of the model was demonstrated by comparing plant data with model predictions. The complete model equations can be found in Appendix B. The next chapter describes the results from the Advanced Process Analysis System.

CHAPTER 5

RESULTS

This chapter describes the optimization of Motiva Alkylation process using Advanced Process Analysis System. The methodology of the system, as described in Chapter 4, is to develop process model using Flowsheet Simulation program, obtain optimal setpoints for the distributed control systems using On-Line Optimization program, and then to perform off-line analysis using Pinch Analysis and Pollution Assessment programs. The Reactor Analysis program was used to develop the kinetic model for the alkylation reactions.

5.1 Flowsheet Simulation

Developing a process model using Flowsheet Simulation program involves drawing the process flow diagram, describing the process using constraint equations, and specifying measured and unmeasured variables, constants and parameters. Each of these steps is explained with numerous illustrations in the user manual given in Appendix J.

5.1.1 Process Flow Diagram

Before using the program to enter process details, a model name and description have to be specified. The name ‘Alkyl’ was used for the alkylation process. All the information entered for the process will be associated with this name. The next step in using the program is drawing the process flow diagram, which is a visual representation of the process. The program has an interactive graphical interface to facilitate easy drawing and editing of the flow diagram. It provides a toolbar with buttons to draw units and streams, move and resize them, and change their appearance. Each unit and stream in the flow diagram has a unique name and description.

The process flow diagram for Motiva alkylation process, as drawn in the Flowsheet Simulation program, is shown in Figure 4.5. This is the program equivalent of the flow diagrams shown in Figures 4.1 to 4.3. For each process unit, the material and energy balance equations are added as described in the user's manual in Appendix J. Also, rate equations and equilibrium relations are added as are thermodynamic functions and global data. These make up the constraint equations for on-line optimization. In addition, an economic model of the process is included (See Section 5.2.3).

5.1.2 Constraint equations

As described in Chapter 3, constraints fall into two types: equality constraints and inequality constraints. Equality constraints depict conservation laws (material and energy balances), equilibrium relations and empirical formulas. Inequality constraints include minimum approach temperatures, demand for product, availability of raw materials and capacities of process units. Equality constraints for the alkylation process were developed in Chapter 4. For example, Table 4.1 shows the equality constraints for contactor 5C-623. Constraints can be entered into the program at specific unit or stream level, or at global level. Constraints that pertain to a specific unit or stream, say, isobutane mass balance or temperature limit for contactor 5C-623, are entered by clicking on that unit or stream. Constraints that pertain to multiple units or streams, say, the overall mass balance for the process, are entered at the global level. An optional scaling factor can be specified for equality and inequality constraints. Refer to the program's user manual for a detailed explanation.

The Alkylation Process Model, "Alkyl", has 1,579 equality constraints and 50 inequality constraints (Appendix B) to describe 76 process units and 110 streams. These are stored along with other information of the process, in the central database, which can be accessed by all the programs of Advanced Process Analysis System. The next step in developing the process model using Flowsheet Simulation program is to enter specifications: measured and unmeasured variables, plant parameters, constants and enthalpy information. The following sections describe these specifications for the alkylation process.

5.1.3 Measured Variables

As described in Chapter 3, measured variables are process variables whose values that can be obtained from the plant's distributed control system. For the alkylation process, information from the distributed control system was requested by specifying Tag Ids of measuring devices selected from process and instrumentation diagrams. The data corresponding to the Tag Ids were made available in the form of Microsoft Excel files, which contained plant measurements obtained at intervals of one minute over a period of two consecutive days for five individual dates (11/08-09/98, 11/22-23/98, 12/06-07/98, 12/13-14/98 and 12/27-28/98). These files contained variables such as flow rates, temperatures and pressures. Also, concentrations from laboratory analysis were made available for those dates.

As mentioned in Chapter 3, the On-Line Optimization program inputs plant data at steady states for calculating optimal setpoints. So, the data from distributed control system was analyzed for steady states visually by using MathCAD's graphics capabilities. This information is given in Appendix I. Six (6) ranges are identified where for all of the measured variables the fluctuations are minimal. They are given in Appendix I. The average values for these steady states were entered as plant data in the Flowsheet Simulation program (Appendix C.3). The process model Alkyl has 125 measured variables in the first two, 120 in the third, forth and fifth, and 113 in the last steady state data sets.

For each measured variable, the program stores all the information required to run all the programs of Advanced Process Analysis System. The information that is required for GAMS (General Algebraic Modeling System) to solve the optimization problem is name of the variable, plant data and standard deviation. Other information like initial point, scaling factor, lower and upper bound values are provided by the user. These values entered into Flowsheet Simulation program are given in Appendix C.3.

5.1.4 Unmeasured Variables

As the name suggests, unmeasured variables are those process variables whose values cannot be obtained from the distributed control system. Unmeasured variables pertaining to a specific unit or stream can be specified in the Flowsheet Simulation program opening the window for the unit or stream. Those that pertain to multiple units or streams, or to the entire process, can be specified as global variables. The required information for specifying an unmeasured variable is its name. Optional information, like initial value, bounds and scaling factor, are defaulted by the program. The program's user manual provides a detailed description for this step. The alkylation process model has 1,509 unmeasured variables. Initial values for these unmeasured variables entered into Flowsheet Simulation program are given in Appendix C.4.

5.1.5 Parameters

As mentioned in Chapter 3, parameters are those quantities in a process model, which change slowly with time, and are related to the degradation of performance of equipment. Parameters include coefficients of heat transfer and fouling factors in heat exchangers, and catalyst deactivation parameters. The information required for specifying parameters in the Flowsheet Simulation program include its name, description, initial value, lower and upper bounds, and units. The program's user manual describes this step in detail.

The alkylation process has overall heat transfer coefficients and LMTD correction factors of heat exchangers, reflux ratios of two distillation columns (5C-601 and 5C-603) and pressure drops in two heat exchangers (5E-634 and 5E-640) as parameters. The alkylation process model has 64 parameters and the plant parameter values entered into Flowsheet Simulation program are given in Appendix C.5.

5.1.6 Constants

Constants are numeric quantities in a process model whose values do not change. For example, area of a heat exchanger and molecular weight of a component are constants. In the Flowsheet Simulation program, constants are entered are stored in logical groups called ‘constant property’. Constant properties can have names and descriptions. For example, areas of the heat exchangers in the model Alkyl are stored together in a constant property called ‘scalar_areas’, with a description of ‘Heat Exchanger Areas’. The program’s user manual describes this in detail, and the constants used for the alkylation process are given in Appendix C.8.

5.1.7 Enthalpy Tables

An enthalpy table in Flowsheet Simulation program can store enthalpy coefficients of the chemical components in the process model. These tables are used in On-Line Optimization and Pinch Analysis programs. The enthalpy formula used here is:

$$\text{Enthalpy} = A_0 + A_1{*}T + A_2{*}T^2 + A_3{*}T^3 + A_4{*}T^4 + A_5{*}T^5$$

where, A_0 to A_5 are enthalpy coefficients and T is the temperature. Any consistent set of units can be used here. The program’s user manual describes entering this information in detail. Enthalpy coefficient values for gas and liquid phases entered into Flowsheet Simulation program are given in Appendices C.6 and C.7.

5.1.8 Flowsheet Simulation Summary

The alkylation process model developed using the Flowsheet Simulation program is summarized in Table 5.1. The degree of the freedom in the model is 55.

Table 5.1. Summary of the Alkylation Process model

Feature	Quantity
Process Units	76
Process Streams	110
Equality Constraints	1579
Inequality Constraints	50
Measured Variables	125
Unmeasured Variables	1509
Parameters	64

5.2 On-Line Optimization

As discussed in Chapters 2 and 3, On-Line Optimization uses the plant model developed in Flowsheet Simulation to calculate optimal setpoints for the distributed control system. This involves rectifying gross errors of plant data sampled from distributed control system using combined gross error detection and data reconciliation, estimating process parameters and reconciling plant data using simultaneous data reconciliation and parameter estimation, and optimizing the operating setpoints using the updating process and economic models. These three steps were shown in Figure 1.2.

5.2.1 Gross Error Detection and Data Reconciliation

Combined gross error detection and data reconciliation is the first step in conducting on-line optimization. As mentioned in Chapters 2 and 3, On-Line Optimization solves this step by creating a non-linear optimization problem, where the process model serves as the set of constraints, and the objective function is one of the available methods specified by the user. The program solves the optimization problem by using GAMS. The program's user manual describes this procedure in detail. In this step the data is reconciled and gross errors are detected and removed. Their values are replaced by reconciled values, and this gives a set of data with only random errors for use in data reconciliation and parameter estimation.

For the alkylation process model, Robust Function method was selected as the objective function and CONOPT2 was set as the default solver for GAMS. The program gave an optimal solution of 78.8 after 1,192 iterations for the operation point #1 of the six steady sate operation points. The others had comparable values. The reconciled data and the optimal setpoint for the measured variables are given in the Table 5.2 for operation point #1. For a confidence level of 95% the critical value is calculated as 3.53, i.e. if the standard measurement error ($\in_i = |y_i - x_i|/\sigma_i$) is greater than 3.53 a gross error is declared. Using this test criterion 31 measurements are identified as having gross errors as shown in Table 5.2. Appendix D.1 and D.2 document the reconciled values from data validation for measured and unmeasured variables for the alkylation process model. Appendix H.1 documents the complete GAMS output for the Data Validation step.

Table 5.2. Measured Variables for operation point #1

Variable Name	Plant Data	Optimal Set Point	Reconciled Data From Parameter Estimation	Reconciled Data From Data Validation	Gross Error $|y_i - x_i|/\sigma_i$
FAC02	0.1125	0.1600	0.1600	0.1600	4.2235
FAC12	0.1259	0.1600	0.1600	0.1600	
FAC23	0.1253	0.1600	0.1600	0.1600	
FAC34	0.1389	0.1600	0.1600	0.1600	
FAC45	0.1040	0.1600	0.1600	0.1600	5.3846
FC308	2.1990	3.1197	3.0606	3.1032	4.1120
FC316	0.6581	1.7518	1.8000	1.8000	17.3515
FC320	0.1468	0.0459	0.1490	0.1497	
FC322	0.4427	1.5684	1.5644	1.5619	25.2812
FC328	0.0942	0.0545	0.0547	0.0535	
FC329	0.7724	0.7635	0.7655	0.7491	

FC403	3.8766	2.3677	2.3223	2.2834	4.1097
FC407	1.1070	0.9348	0.9205	0.9145	
FC412	0.0324	0.0420	0.0421	0.0418	
FC417	0.2799	0.1439	0.2754	0.2748	
FHC01	1.0155	0.8980	0.8569	0.8513	
FHC32	1.8596	1.9569	1.8455	1.8690	
FSC402	0.5223	0.4587	0.4916	0.4943	
FSC405	0.3344	0.3148	0.3452	0.3463	
FSC411	2.7287	1.3267	1.3499	1.3525	5.0436
FSC413	0.1445	0.1439	0.1464	0.1480	
FstmE612	0.1425	0.0888	0.0889	0.0889	3.7607
PC302	102.3615	101.0000	102.8996	102.1638	
PC310	264.5339	260.0000	264.1366	264.5758	
PC601	618.4222	625.0000	625.0000	625.0000	
PC603	1635.3720	1691.3731	1694.5308	1694.5255	
QHC07	2.2343	1.9469	1.7391	1.8842	
QHC11	1.8496	1.7391	1.7761	1.7391	
QHC14	2.0061	1.7391	1.9149	1.7391	
QHC16	2.0344	1.7391	1.7391	1.7391	
QHC34	0.9205	1.1464	0.9354	0.9505	
QHC38	0.5705	0.5352	0.5761	0.5791	
QHC41	0.8344	0.8699	0.8465	0.8489	
QHC45	0.8392	0.8518	0.8515	0.8720	
TAC09	284.1800	280.0000	281.6669	282.0713	
TAC12	284.5783	280.0000	281.6669	282.0713	
TAC23	284.7406	280.0000	280.0000	281.4793	
TAC31	282.9628	280.0000	281.1345	281.4267	
TAC34	284.9250	280.0000	281.1345	281.4267	
TAC42	287.1733	280.0000	283.3783	284.2594	
TAC45	284.9372	280.0000	283.3783	284.2594	
TC303	264.0644	280.6862	280.6987	281.4996	
TC306	341.9278	349.4271	349.7839	349.8897	
TC307	315.5806	328.4033	329.3628	328.9195	
TC308	315.8461	328.4033	329.3628	328.9195	
TC315	308.2378	307.3612	308.2378	308.6556	
TC316	344.0172	345.2250	345.1410	345.1528	
TC317	363.4556	359.0690	359.0000	359.0000	
TC321	301.0450	300.0000	301.0948	301.1193	
TC324	365.0522	359.0690	359.0000	359.0000	
TC325	319.6617	322.5997	322.6861	322.6859	
TC404	318.6700	305.2492	306.2880	307.0948	
TC405	426.1200	410.0000	411.1033	410.0000	
TC407	302.9500	303.5753	302.9500	302.9500	
TC408	426.1200	405.0000	405.0000	405.0000	
TC410	356.2411	363.3260	363.3927	363.0366	
TC414	324.4561	337.0859	336.7854	336.7774	

TC418	305.9128	307.1433	307.4867	308.4341	
TC419	301.6367	304.5245	305.1181	305.9727	
THC32	263.4350	261.9077	256.5978	256.4405	
TSC402	314.6989	322.8886	324.6526	324.6567	
TSC403	337.5928	336.6046	335.7424	335.7490	
TSC405	301.2561	300.0000	301.2561	301.2561	
TSC408	319.2900	318.7440	317.9076	317.9181	
TSC413	298.6917	300.0000	300.0000	300.0000	
x11AC12	0.9670	0.9687	0.9718	0.9695	
x11AC23	0.9380	0.9424	0.9451	0.9432	
x11AC34	0.9220	0.9162	0.9162	0.9169	
x11AC45	0.9060	0.8900	0.8900	0.8906	
x1C316	0.1408	0.1166	0.1184	0.1178	
x1C325	0.9720	1.0000	1.0000	1.0000	
x1C417	0.0372	0.0200	0.0253	0.0255	
x1HC32	0.0258	0.0228	0.0235	0.0233	
x1SC402	0.0143	0.0063	0.0142	0.0142	
x1SC403	0.0001	0.0000	0.0000	0.0000	
x1SC408	0.0475	0.0200	0.0477	0.0474	
x2SC402	0.0136	0.0000	0.0084	0.0084	3.7929
x2SC403	0.0119	0.0000	0.0119	0.0119	
x2SC408	0.0221	0.0000	0.0002	0.0002	9.9048
x3C316	0.7790	0.7851	0.7880	0.7886	
x3C325	0.0017	0.0000	0.0000	0.0000	10.0000
x3C417	0.8699	0.9738	0.8137	0.8141	
x3HC32	0.8187	0.7604	0.7708	0.7708	
x3SC402	0.2910	0.3216	0.2959	0.2973	
x3SC403	0.0103	0.0234	0.0212	0.0212	10.5665
x3SC408	0.8761	0.9739	0.9435	0.9436	
x4C316	0.0580	0.0894	0.0795	0.0796	3.7155
x4C417	0.0609	0.0061	0.0514	0.0509	
x4HC32	0.1054	0.1401	0.1255	0.1257	
x4SC402	0.5934	0.5280	0.5601	0.5587	
x4SC403	0.8540	0.7666	0.7940	0.7936	
x4SC408	0.0331	0.0061	0.0086	0.0088	7.3475
x5C316	0.0020	0.0056	0.0060	0.0060	19.8000
x5C417	0.0009	0.0000	0.0295	0.0295	286.2300
x5HC32	0.0096	0.0288	0.0306	0.0306	22.0134
x5SC402	0.0503	0.0686	0.0516	0.0516	
x5SC403	0.0758	0.1000	0.0734	0.0736	
x5SC408	0.0001	0.0000	0.0000	0.0000	
x6SC402	0.0167	0.0686	0.0666	0.0666	29.8204
x6SC403	0.0250	0.1000	0.0949	0.0950	27.9946
x6SC408	0.0001	0.0000	0.0000	0.0000	
x7HC32	0.0197	0.0479	0.0496	0.0497	15.2312
x7SC402	0.0022	0.0069	0.0032	0.0032	4.3956

x7SC403	0.0046	0.0100	0.0046	0.0046	
x7SC408	0.0022	0.0000	0.0000	0.0000	10.0000
xx1C322	0.0027	0.1133	0.1167	0.1167	428.5338
xx1C414	0.0330	0.0762	0.0798	0.0800	14.2498
xx1HC01	0.1088	0.0976	0.1111	0.1099	
xx2HC01	0.4525	0.1296	0.1290	0.1291	7.1481
xx3C317	0.9430	0.7900	0.7930	0.7930	
xx3C322	0.9430	0.7900	0.7930	0.7930	
xx3C407	0.0003	0.0000	0.0000	0.0000	7.4194
xx3C412	0.0027	0.0021	0.0027	0.0027	
xx3C414	0.8772	0.8081	0.8196	0.8196	
xx3HC01	0.3558	0.0125	0.0125	0.0125	9.6498
xx4C317	0.0671	0.0899	0.0800	0.0800	
xx4C322	0.0671	0.0899	0.0800	0.0800	
xx4C407	0.1124	0.0851	0.0850	0.0853	
xx4C412	0.9004	0.8771	0.8668	0.8549	
xx4C414	0.0860	0.1067	0.0916	0.0914	
xx4HC01	0.1085	0.1108	0.1064	0.1067	
xx5C407	0.0803	0.1512	0.1514	0.1506	8.7555
xx5C412	0.0022	0.0568	0.0581	0.0581	255.6751
xx5C414	0.0021	0.0010	0.0011	0.0011	4.8325
xx7C414	0.0015	0.0080	0.0080	0.0080	44.4218

5.2.2 Parameter Estimation and Data Reconciliation

In this step the data is reconciled and parameter estimates are updated by solving the nonlinear programming problem using the measured variable values from the previous step. The program gave an optimal solution of 113.8 after 1,490 iterations for the operation point #1 of the six steady states, and these results are shown in Table 5.2 for the measured variables. The performance for the other five steady state operation points were similar. The updated values of the parameters for the first steady state solution are listed in Table 5.3. The values of 36 of the 64 parameters remained the same whereas the adjustments for the rest during parameter estimation are minimal. These values along with the error free, reconciled measured variables represent the current specifications of the process plant, which can be used to calculate the optimal operating setpoints. Appendix H.2 documents the complete GAMS output for the Parameter Estimation step.

Table 5.3. Plant Parameters for operation point #1

Plant Parameter	Initial Value	Estimated Value
deltaPE634	70.0000	70.0000
deltaPE640	20.0000	20.0000
FE601	0.5000	0.5000
FE603	1.0000	1.0000
FE609A	0.5000	0.5000
FE610	1.0000	0.9340
FE611	0.5000	0.5218
FE616	0.5000	0.5000
FE617	1.0000	1.0000
FE621A	0.7220	0.7397
FE621B	1.0000	1.0000
FE626	0.5000	0.5000
FE627A	0.5000	0.5016
FE627B	0.5000	0.5257
FE628	0.5000	0.5000
FE629	0.5000	0.5000
FE634	1.0000	1.0000
FE640	0.5000	0.7569
FE641	0.5000	0.5000
hstmE602	2145.0000	2145.0000
hstmE612	2145.0000	2145.0000
hstmE695	1920.0000	1920.0000
hstmE696	2145.0000	2145.0000
PC606A	900.0000	900.0000
PC606C	890.0000	890.0000
PC606D	900.0000	900.0000
PE633	145.0000	145.0000
qC601	1.0000	1.0000
qC603	1.0000	0.9904
qC606A	0.5000	0.5000
RC601	9.1410	9.2210
RC603	14.0000	14.0000
sfC631	0.9770	0.9774
sfC632	0.9820	0.9815
sfC633	0.9910	0.9913
sfC634	0.9900	0.9893
Tcwin	290.0000	290.0000
UE601	0.0080	0.0080
UE602	0.0160	0.0160
UE603	0.0250	0.0251
UE605	0.0450	0.0498
UE609A	0.0400	0.0400
UE610	0.0830	0.0898

UE611	0.0990	0.1000
UE612	0.0130	0.0130
UE613	0.0200	0.0256
UE616	0.0100	0.0100
UE617	0.0520	0.0526
UE621A	0.1140	0.1140
UE621B	0.0780	0.0759
UE626	0.0100	0.0100
UE627A	0.0100	0.0100
UE627B	0.0100	0.0100
UE628	0.0100	0.0144
UE629	0.0100	0.0100
UE633	0.0160	0.0177
UE634	0.0210	0.0206
UE640	0.0100	0.0100
UE641	0.0840	0.0874
UE695A	0.0330	0.0329
UE695B	0.0390	0.0388
UE696A	0.0120	0.0122
UE696B	0.0100	0.0100
UE6XX	0.0310	0.0286

5.2.3 Economic Optimization

Maximizing profit was used as the objective of economic optimization of the alkylation process model. The alkylation unit costs and prices for summer and winter conditions are as shown in Table 5.4. The objective function was based on the winter data since the plant data available was measured in winter.

The economic model was developed as follows:

Profit = Sales - Cost - Utilities

Sales = Alkylate (C_3, C_4 and C_4 Raffinate) produced * Price of alkylate

Cost = Σ Input * Cost

Utilities = Σ Input * Utility Cost

where the Input for Cost includes olefins (propylene and butylene), C_4's from the reformer (feed to the Saturate Deisobutanizer column), isobutane and sulfuric acid and the Input for the Utilities includes steam, water and electricity.

This economic model was used with operation point #1 in Appendix I, and the program gave an optimal solution after 63 iterations. The profit for the process was calculated to be \$29.11/min, which is an increase of 144% over the operating condition (#1). The profit from the current operating condition was evaluated using the reconciled data prior to economic optimization. This improvement in the profit is caused by 8.5% reduction in costs and 2.2% increase in sales. The economically optimum solution had 5.5% more olefin charge, almost 100% reduction in isobutane purchase cost (because of reduced isobutane flow rate), 7.2% reduction in saturate feed to the Saturate Deisobutanizer column and 2.2% increase in the alkylate. The alkylate quality did not change at the economically optimal operation. Energy savings attained through reduced steam usage in the distillation columns total an average of 9.4×10^9 BTU/yr. This amount corresponds to 0.16% reduction in the utility cost and results in a saving of \$5600 /yr.

The results for all of the six cases are shown in Table 5.5 where the increase was from 25% to 216%. This wide range of increase in the optimal profit for six different operation points is observed because of even wider ranges existing in the plant data. The flow measurements differ as much as 300% and mass fraction measurements as much as 4000%, between operation points. Appendices D.1 and D.2 document the optimal values for measured and unmeasured variables for the alkylation model. Appendix H.3 documents the complete GAMS output for this step.

Collectively, these results show that by applying on-line optimization to the alkylation process with reconciled data and estimated parameters, the profit of the plant can be improved significantly.

Table 5.4. Alkylation Plant Raw Material/Utility Costs and Product Prices

Feed and Product	Stream Number	Cost and Price ($/bbl) Summer	Winter
Feeds			
Propylene	HC01	11.79	10.44
Butylene	HC01	18.00	16.56
Iso-butane	SC414	16.88	17.39
Products			
N-butane	SC405, C413	13.29	12.71
C_3 Alkylate	C407	24.49	22.30
C_4 Alkylate	C407	26.32	24.06
C_4 Raffinate Alkylate	C407	26.34	24.19

Catalyst and Utilities		Cost
H_2SO_4	(Stream AC02)	$110/Ton
Electricity		$0.04/KWH
50# Steam		$2.50/M-Lbs
250# Steam		$3.60/M-Lbs
600# Steam		$4.40/M-Lbs

Table 5.5. Calculated Profit after Data Validation (D.V.), Parameter Estimation (P.E.) and Economic Optimization (E.O.) Steps for six Different Operation Points (Steady States)

Operation points	**D.V.**	**P.E.**	**E.O**	**% Increase**
#1	11.9	12.1	29.1	144
#2	7.4	7.4	21.4	189
#3	21.4	22.1	26.9	26
#4	7.0	7.0	22.1	216
#5	10.1	23.3	26.3	160
#6	22.0	23.6	27.6	25
		Average % increase		127

5.3 Heat Exchanger Network Optimization

The Heat Exchanger Network Optimization (THEN) program integrates networks of heat exchangers, boilers and condensers. It uses pinch analysis as the basis for designing an optimum network. The Pinch Analysis program of Advanced Process Analysis System is used to perform off-line analysis of processes to achieve better energy integration. This section describes the use of the program for the alkylation process.

Alkylation process is very energy intensive. The alkylation reactions occurring in the contactors are exothermic, and the heat generated is removed by effluent refrigeration. The process requires proper control of temperature, which is done by feed-effluent heat exchanging and also by external utilities. Also, energy is required in the separation units of the process. The alkylation process model has 28 heat exchangers, plus four pair of contactors. The heat exchange within the contactors using the cold refrigerant condensate through the tube bundle is not included in the pinch analysis since any new arrangement for the contactors will be impractical.

As discussed in Chapter 3, the first step in using THEN is the identification of streams important for heat integration. These streams are the input and output streams to heat exchanging units. Appendix E contains the list of streams from the model used for heat integration.

The second step is retrieving the required information for the selected stream, from the optimization results. The data retrieved are temperature and flowrate as shown in the user's manual, Appendix J. Energy calculations can be done either using constant heat capacities or specifying enthalpy coefficients for variable heat capacities. To obtain average values for constant heat capacities, enthalpy of the streams should be used and this calculation is executed in the program as illustrated in the user's manual. For variable heat capacities, Appendices C.6 and C.7 contain the coefficients of the equations used to evaluate the enthalpy for the components in the process for gas and liquid phases. The temperature-dependent enthalpy equation used is as follows:

$$H = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + A_4 T^4 + A_5 T^5 \quad \text{MJ/min} \tag{5.1}$$

From the enthalpy coefficients and stream compositions, average enthalpy coefficients for streams are calculated as:

$$A_{avg} = \Sigma A_I x_I \tag{5.2}$$

where, A_I and x_I are the enthalpy coefficient and mole fraction of component I.

The third step is classifying the streams as hot or cold streams. As mentioned in Chapter 3, a hot stream is a stream that needs to be cooled, and a cold stream is a stream that needs to be heated. These are designated in the program as shown in the user's manual. Finally, the minimum approach temperature for the network is chosen to be 13 K (See user's manual). This is to ensure sufficient driving force between the streams in the network. The program uses this information to conduct pinch analysis for the alkylation process by using the FORTRAN program THEN.

One of the results of the program is the Grand Composite Curve (GCC) shown in Figure 5.1. This diagram shows the temperature as a function of enthalpy for a composite of the streams. The region of the GCC with a positive slope shows the process segment that requires energy, whereas the region that has negative slope shows the segment that rejects heat. The end points of the curve gives the minimum values of external heating and cooling required by the process.

According to the Pinch Analysis the alkylation process requires a minimum of 1742 MJ/min external heat and 4043 MJ/min of external cooling. From the data validation results, the current external utility requirements are 1907 MJ/min of heat and 4300 MJ/min of cooling. The economic optimization decreases the heating requirement by 1% to 1888 MJ/min whereas the initial pinch analysis reduces it another 7.7%. The cooling requirement can be reduced as much as 7.4% by using pinch analysis from 4367 MJ/min after economic optimization. This is because the economic optimization results in a 1.6% higher cooling requirement than the current value of 4300 MJ/min.

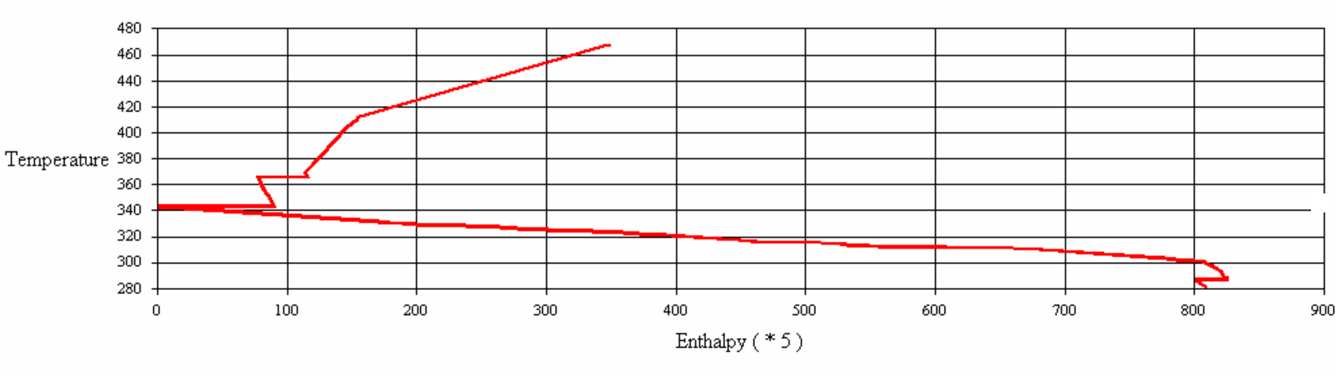


Figure 5.1 Grand Composite Curve for Alkylation Process

Pinch Analysis program also has the ability to design a Maximum Energy Recovery (MER) network for the process under consideration. The network grid diagram that makes use of the external utilities calculated in the GCC can be seen in Figure 5.2. The network found by pinch analysis consists of 16 heat exchangers, 4 heaters and 15 coolers, whereas the process has only 6 heat exchangers, 4 heaters and 12 coolers. This suggests that the improvement in the energy requirements are achieved by these additional heat exchangers.

Heat integration above the pinch involves streams such as SC406 (to Saturate Deisobutanizer reboiler), C315 (charge to Depropanizer column) and C410 (sidestream to inter-reboiler of Deisobutanizer column) which are heated up by streams C405, C406 (Deisobutanizer bottoms), C317 (Depropanizer bottoms) and C412 (side stream from Desiobutanizer). This integration eliminates some of the heat exchangers existing in the current plant configuration (e.g. E-616). However, the configuration from the analysis may result in operational difficulties because of a more intense interaction between input and output streams of the three distillation columns. Moreover, these three distillation columns are placed across the pinch, which is not an appropriate placement of distillation columns for energy integration.

To integrate the columns with the remainder of the process, one can remove the columns from the process and then try to use as much energy as possible from the process for the energy requirements of the columns by pressure-shift (Douglas, 1988). A pressure shift applied to column 5C-601 (a decrease in the operation temperature by 7 K) can reduce the heating and cooling requirements by 550 MJ/min. Pressure shifts resulting in 25 K and 9 K decrease in operation temperature for 5C-603 and 5C-601 can reduce the separation energy requirements by 650 MJ/min (Figure 5.3). These changes should be considered if it is feasible with the other operating conditions in the plant.

From the Pinch Analysis, three loops and one path in the heat exchanger network can be located. These provide additional degrees of freedom for further optimization of the system by eliminating some of the exchangers within the loops or on the path.

In summary, Pinch Analysis provided an extensive insight for the optimization of the energy consumption in the alkylation plant and showcased the benefits of heat integration for the process.

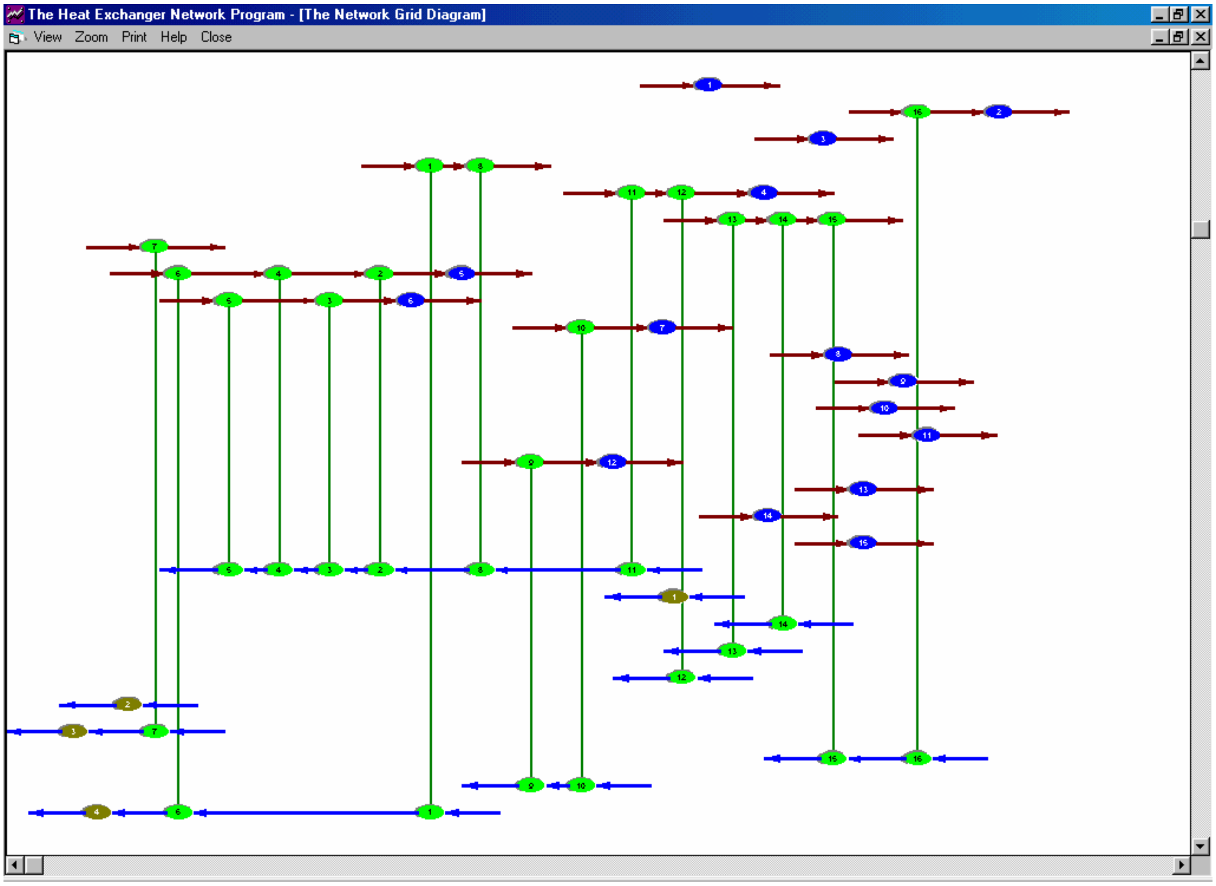


Figure 5.2. Network Grid Diagram for Alkylation Process

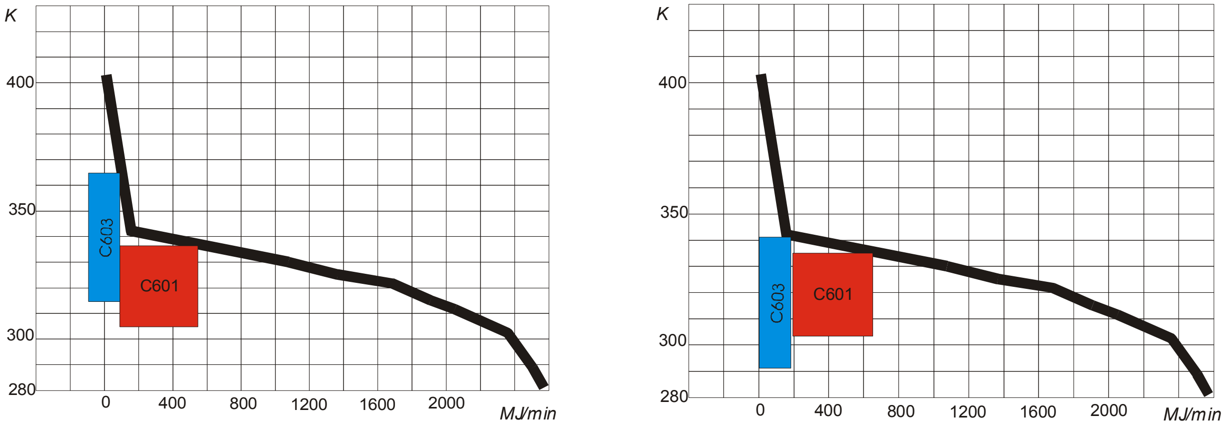


Figure 5.3. Integrating columns (5C-601 and 5C-603) with the process: Pressure shift for column 5C-601 only (left), for both columns (right).

5.4 Pollution Assessment

Pollution Assessment program is used to assess the pollutants generated in the process and determine the location where they are generated. This information is used to modify the process for waste minimization. Also, a pollution index is evaluated for comparison of different processes. In the first step of the program, input and output streams of the process are specified as shown in the user's manual, Appendix J.

The alkylation process has 10 input and output streams as listed in Table 5.6. These streams are selected from Flowsheet Simulation. The output streams are classified as product and non-product. For example, spent acid (AC45) is a non-product whereas alkylate (C407) is a product stream. The components present in each of these streams are specified and the flow rates and compositions of streams are obtained from the results of On-Line Optimization program. The program's user manual describes these steps in detail.

Table 5.6. Input and Output Streams in Alkylation Process.

Stream	Description	Type	Pollution Index
AC02	Fresh Acid Feed	Input	0.808
HC01	Olefin Feed	Input	1.622
SC414	Make-up Isobutane	Input	1.611
SC401	Sat-Deisobutanizer Feed	Input	1.789
AC45	Spent Acid	Non-Product	1.034
C320	To LPG Storage	Product	0
C328	To Fuel Gas	Product	0
C407	To Alkylate Storage	Product	0
C413	To N-butane Storage	Product	0
SC405	To N-butane Storage	Product	0

As discussed in Chapter 3, pollution impact is calculated using specific environmental impact potentials (SEIP) of the components in the streams. SEIP values of the components in alkylation process are listed in Appendix G. Relative weighting factors for the nine categories of impact were all assumed to be one in the absence of actual values. Using the SEIP values and relative weighting factors the program calculates pollution indices for each input, product and non-product stream in the process, scaling the effect of the stream to the environment. These values are used to calculate the six pollution indices for the process, which are listed in Table 5.7, before (BEO) and after (AEO) the economic optimization of the process. Negative values mean that the input streams are actually more harmful to the environment than the non-products if they are not processed through the alkylation process.

Table 5.7. Pollution Assessment Values for Alkylation Process before (BEO) and after (AEO) the economic optimization.

Index Type	Value		
	(BEO)	(AEO)	
Total rate of impact generation	-4.9120	-4.7966	impact/time
Specific impact generation	-3.2860	-3.4584	impact/product
Pollution generation per unit product	-0.9777	-0.9742	mass of pollutant/mass of product
Total rate of impact emission	1.0325	1.0337	impact/time
Specific impact emission	0.6897	0.7453	impact/product
Pollutant emission per unit product	0.1069	0.1154	mass of pollutant/mass of product

Pollution Assessment results show that the economic improvement that is achieved by the economic optimization doesn’t come with a reduced environmental impact. The plant operating at the optimal set point emits more pollutants since the rate of impact generation is reduced, although specific component’s consumption might be less (e.g. sulfuric acid consumption is reduced by 2.2%).

5.5 Summary

Advanced Process Analysis System was applied to the Motiva alkylation plant. The process model was developed using Flowsheet Simulation program. On-Line Optimization was used to generate optimal set points for the distributed control system. Pinch Analysis program was used for energy integration and to determine the minimum heating and cooling requirements. A pollution assessment of the plant was made to determine the source of the pollution generation.

CHAPTER 6

CONCLUSIONS

Alklation process is one of the most important refinery processes for producing conventional gasoline. This project demonstrates process control and modification improvements to this process with Advanced Process Analysis System that employs process flowsheeting, on-line optimization, pinch analysis and pollution assessment. Also, the chemical reaction analysis part of the System was used to determine the best alkylation reaction kinetics.

Using the flowsheeting capability of the Advanced Process Analysis System a simulation of the alkylation process was developed that consist of 76 process units, 110 process streams, 1579 equality and 50 inequality constraints with 1634 variables. The simulation was validated using plant data and data reconciliation to show that the simulation predicted the performance of the plant within the accuracy of the data.

The analysis of the plant data resulted in detecting six steady state operation points. For each operation point gross errors were detected, data were reconciled, parameters were updated and economically optimum setpoints are determined for the distributed control system.

The economic optimization of the process for six operation points resulted in 25.4% to 215.4% increase in the profit. As an example; the profit for the process was calculated to be $29.11/min, which is an increase of 144.6% over the operating condition (#1). This improvement in the profit is caused by 8.5% reduction in costs and 2.2% increase in sales. The economically optimum solution results in 5.5% more olefin charge, almost 100% reduction in isobutane purchase cost, 7.2% reduction in saturate feed to the Saturate Deisobutanizer column and 2.2% increase in the alkylate. The alkylate quality did not change at the economically optimal operation. Energy savings total an average of $9.4x10^9$ BTU/yr. This amount corresponds to 0.16% reduction in the utility cost and results in a saving of $5600 /yr. Another result obtained from the economic optimization of the alkylation process is a 2.2% reduction in the sulfuric acid consumption.

According to the Pinch Analysis the alkylation process requires a minimum of 1742 MJ/min external heat and 4043 MJ/min of external cooling. From the data validation results, the current external utility requirements are 1907 MJ/min of heat and 4300 MJ/min of cooling. The economic optimization decreases the heating requirement by 1% to 1888 MJ/min whereas the initial pinch analysis reduces it another 7.7% (a total of $67x10^9$ BTU/yr). The cooling requirement can be reduced as much as 6% (a total of $106x10^9$ BTU/yr). by using pinch analysis . A further reduction in the energy requirements can be achieved by an appropriate pressure shift applied to distillation columns accounting a maximum reduction of 650 MJ/min ($268x10^9$ BTU/yr).

Pollution assessment of the alkylation plant revealed the extent and location of the pollutant emissions of the process. It has also shown that the economically optimal solution can result in higher overall pollution levels even if the consumption of the sulfuric acid is reduced.

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