ON-LINE OPTIMIZATION, ENERGY ANALYSIS AND ENVIRONMENTAL IMPACT ASSESSMENT OF SULFURIC ACID CATALYZED ALKYLATION PROCESS

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Abstract

An 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 System (Telang et al., 1999) a significant increase in profit and energy savings were projected through reduced steam usage in the distillation columns. A small decrease in sulfuric acid consumption potentially could be obtained.

1. Introduction

Alkylation process is one of the most important refinery processes for producing conventional gasoline. 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. 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.

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 1990, Cupit et al. 1961).

In this study a commercial sulfuric acid catalyzed alkylation process is analyzed using an integrated approach to process analysis provided by the Advanced Process Analysis System (Telang *et al*., 1999).

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). The System uses a chemical reactor analysis program, 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 Microsoft Access database.

The advanced process analysis methodology identifies sources of excess energy use and of pollutant generation and was based on the framework shown in Figure 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 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 off-line studies using reactor analysis, pinch analysis and pollution assessment, and to achieve process improvements that reduce pollution and energy consumption.

The Advanced Process Analysis System has been already applied to two contact processes at the IMC Agrico Company's agricultural chemical complex and the details of these results were given in (Telang *et al.*, 1999).
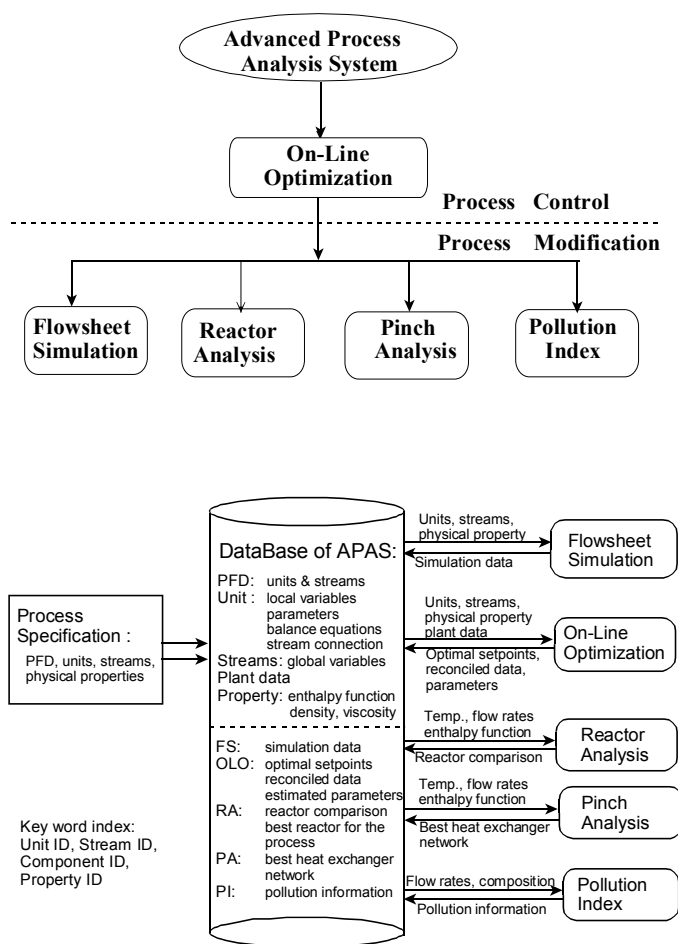

Figure 1. Framework of Advanced Process Analysis System

2. **Motiva Alkylation Process**

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.

Motiva alkylation process is divided into three sections to facilitate detailed modeling, namely the reaction section, the refrigeration, depropanizer and deisobutanizer section and the saturate deisobutanizer section.

The process has four reactor pairs and four acid settlers. In the reaction section there are three feed streams, the olefin feed, the isobutane feed and the recycled olefin/isobutane mixture. 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.

3. Results

The alkylation process model developed using the Flowsheet Simulation program is summarized in Table 1. The degree of the freedom in the model is 55.

Table 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

3.1 On-Line Optimization

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.

3.1.1 Gross Error Detection and Data Reconciliation

Combined gross error detection and data reconciliation is the first step in conducting on-line optimization. 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 (Brook *et al.*, 1998). 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. 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.

3.1.2 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. The performance for the other five steady state operation points was similar. 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.

3.1.3 Economic Optimization

Maximizing profit was used as the objective of economic optimization of the alkylation process model. 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 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 (by increasing the separation in the saturate deisobutanizer column rather than using isobutene from the raw material storage tank), 7.2% reduction in saturate feed to the Saturate Deisobutanizer column and 2.2% increase in the alkylate. The alkylate quality didn't change at the economically optimal operation.

The results for all of the six cases show an increase in profit 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.

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.

3.2 Heat Exchanger Network Optimization

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.

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.

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 Grand Composite Curve (GCC) can be seen in Figure 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 is achieved by these additional heat exchangers.
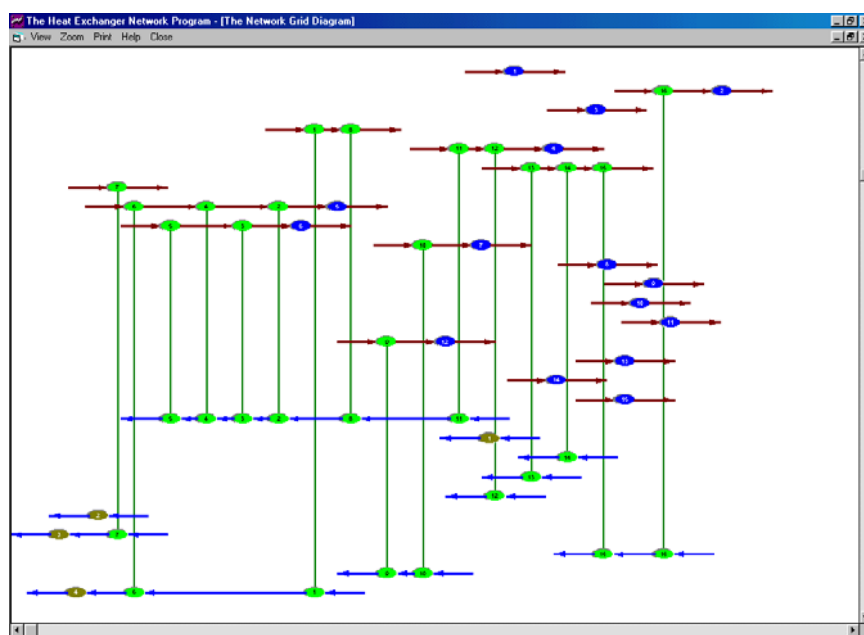

Figure 2. Network Grid Diagram for Alkylation Process

Heat integration above the pinch involves streams such as the flow to Saturate Deisobutanizer reboiler, the charge to Depropanizer column and the sidestream to inter-reboiler of Deisobutanizer column, which are heated up by streams such as Deisobutanizer bottoms, Depropanizer bottoms and the side stream from Desiobutanizer. This integration eliminates some of the heat exchangers existing in the current plant configuration. 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 analysis 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 Saturate Deisobutanizer column (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 Depropanizer and Saturate Deisobutanizer columns can reduce the separation energy requirements by 650 MJ/min. 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.

3.3 Pollution Assessment
The alkylation process has 10 input and output streams relevant to the pollution assessment. The output streams are classified as product and non-product. For example, spent acid is a non-product whereas alkylate 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.

Pollution impact is calculated using specific environmental impact potentials (SEIP) of the components in the streams. 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 2, 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.

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 increased, although specific component's consumption might be less (e.g. sulfuric acid consumption is reduced by 2.2%).

Table 2. 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

Conclusions

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 didn't change at the economically optimal operation. 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%. The cooling requirement can be reduced as much as 7.4% 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.

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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Telang, K. S. F. C. Knopf, J. R. Hopper, J. Saleh, S. Waghchoure, S. C. Hedge and T. A. Hertwig, 1999, *An Advanced Process Analysis System for Improving Chemical and Refinery Processes*, Computers Chem. Engng., Vol. 23, p. S727-730.

On-Line Optimization, Energy Analysis and Environmental Impact Assessment of Sulfuric Acid Catalyzed Alkylation Process

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Overview of Presentation

Advanced Process Analysis System

Alkylation Process

Results

Mineral Processing Research Institute

Louisiana State University

Program and Users Manual (267 pages)

www.mpri.lsu.edu
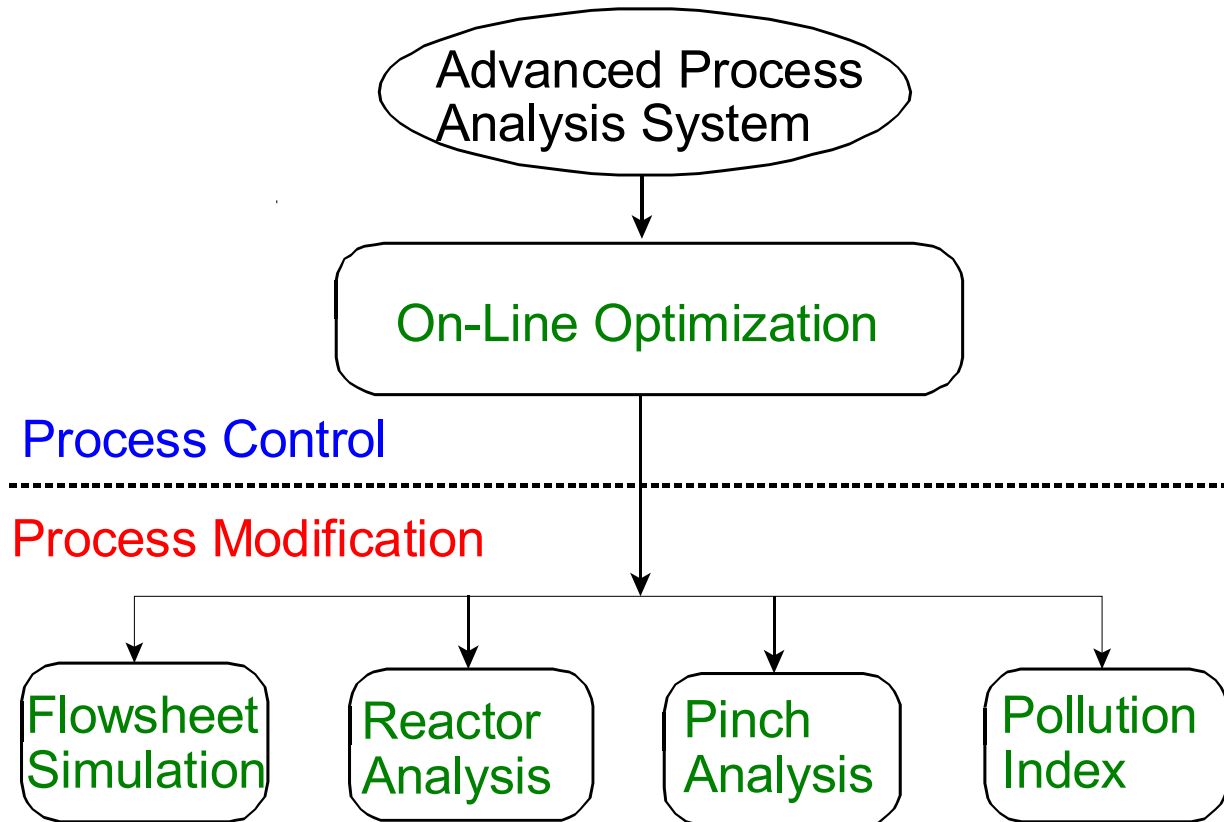
Advanced Process Analysis System

Fig. 1 Overview of Advanced Process Analysis System
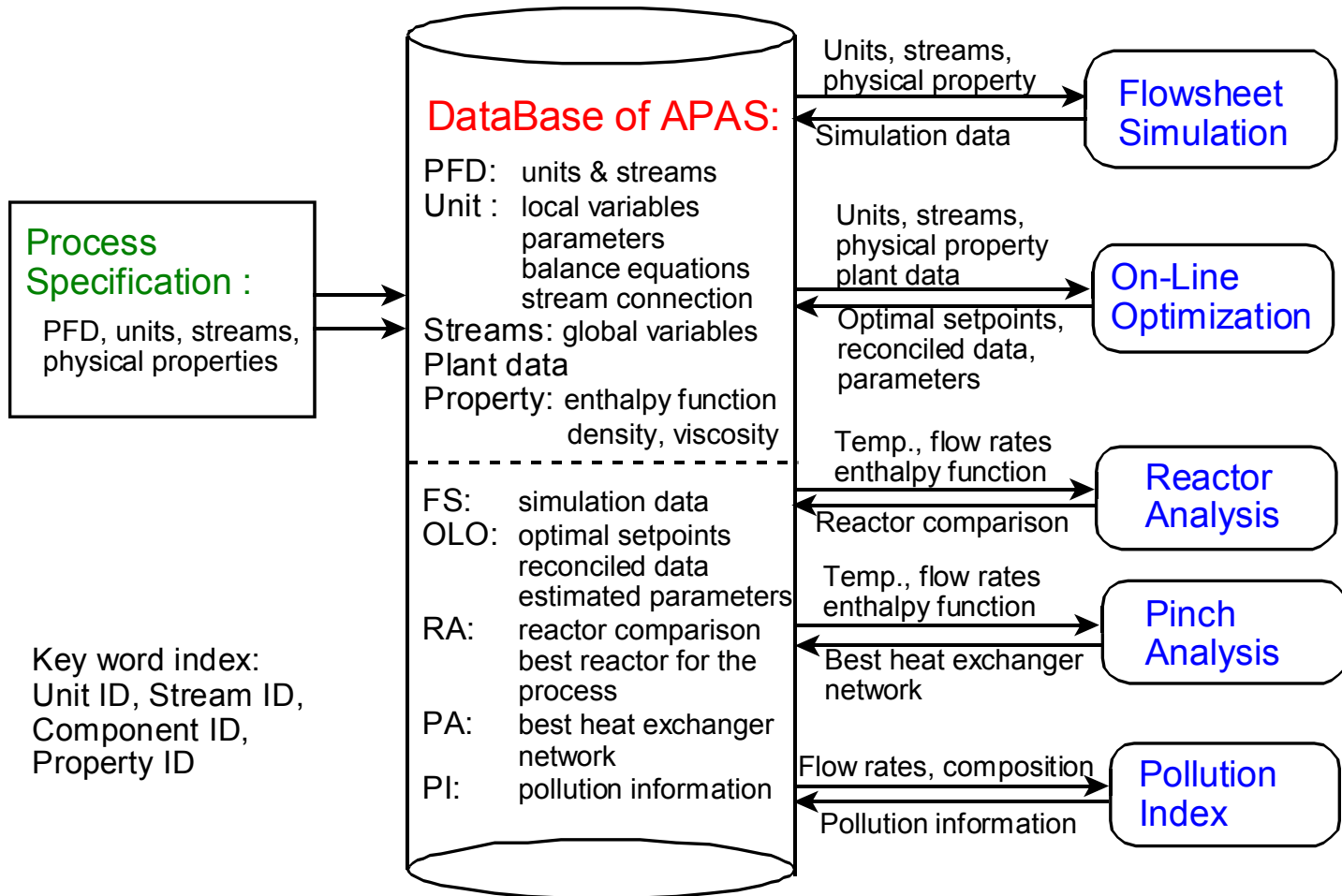
Advanced Process Analysis System Structure

Process Specification :

PFD, units, streams, physical properties

DataBase of APAS:

PFD: units & streams
Unit : local variables
        parameters
        balance equations
        stream connection
Streams: global variables
Plant data
Property: enthalpy function
          density, viscosity

FS: simulation data
OLO: optimal setpoints
       reconciled data
       estimated parameters
RA: reactor comparison
       best reactor for the
       process
PA: best heat exchanger
       network
PI: pollution information

Key word index:
Unit ID, Stream ID,
Component ID,
Property ID

Units, streams, physical property

Simulation data

Flowsheet Simulation

Units, streams, physical property plant data

Optimal setpoints, reconciled data, parameters

On-Line Optimization

Temp., flow rates enthalpy function

Reactor comparison

Reactor Analysis

Temp., flow rates enthalpy function

Best heat exchanger network

Pinch Analysis

Flow rates, composition
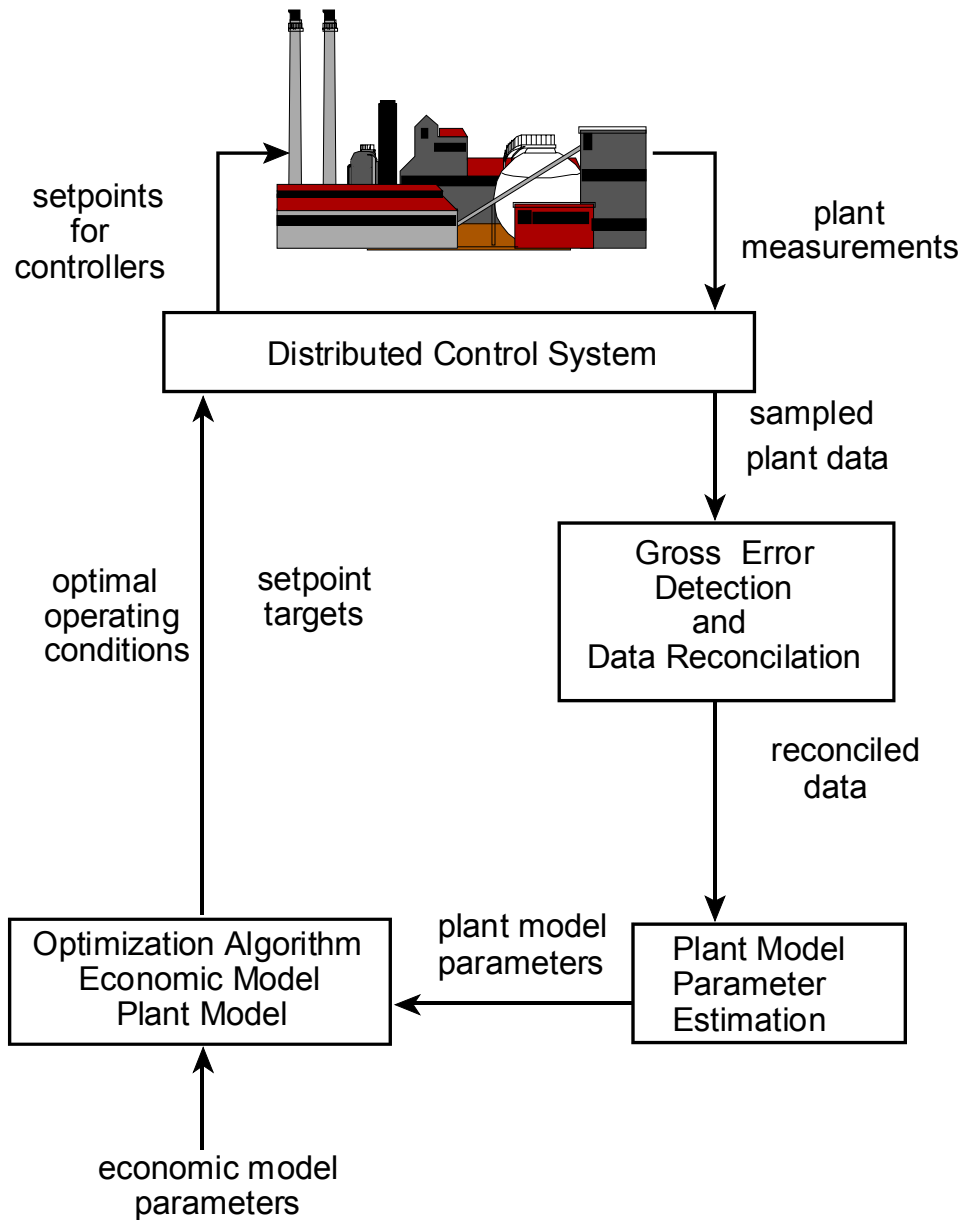
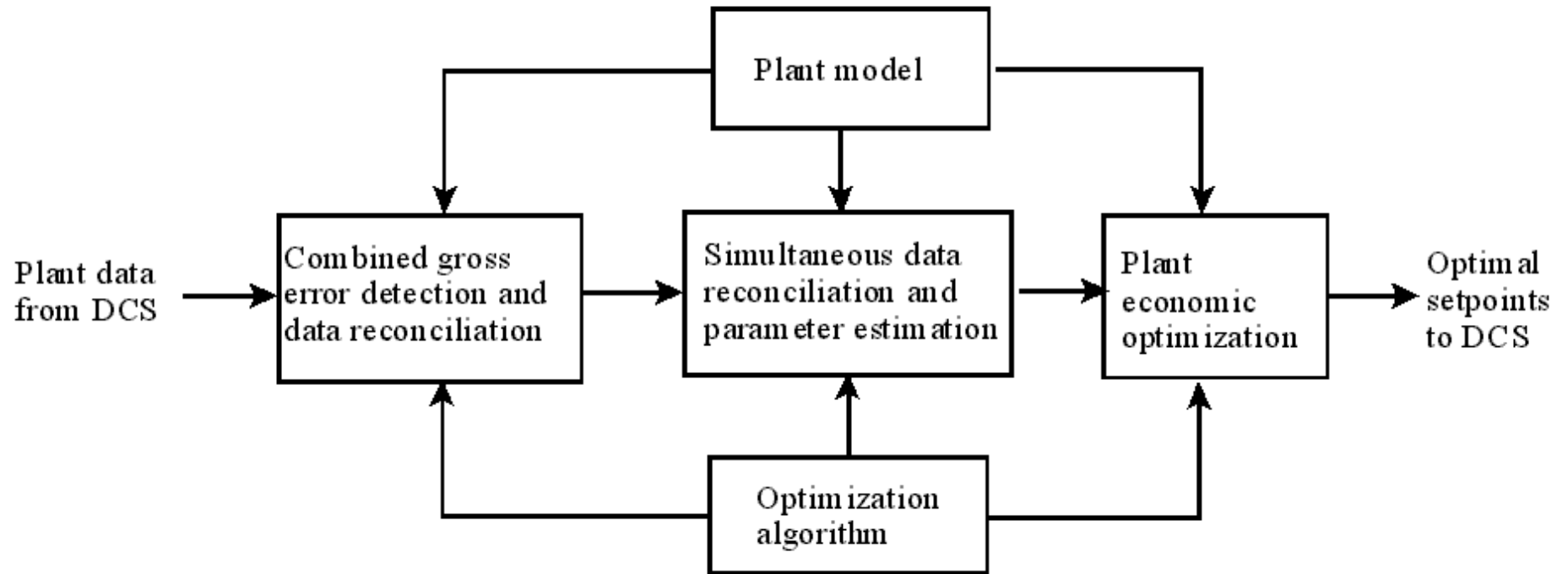Pollution information

Pollution Index

Fig. 2 Database Structure of Advanced Process Analysis System
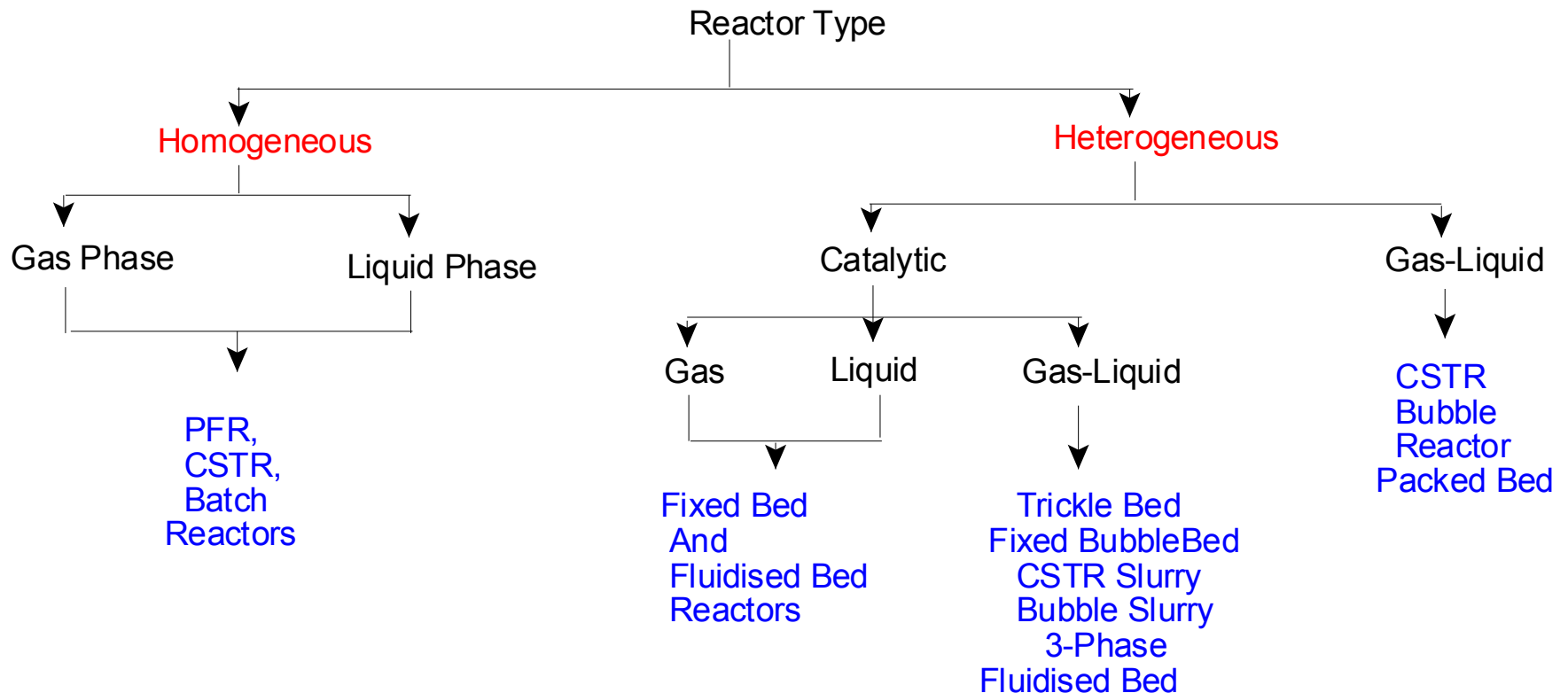
On-Line Optimization

setpoints
for
controllers

plant
measurements

Distributed Control System

sampled
plant data

optimal
operating
conditions

setpoint
targets

Gross Error
Detection
and
Data Reconcilation

reconciled
data

Optimization Algorithm
Economic Model
Plant Model

plant model
parameters

Plant Model
Parameter
Estimation
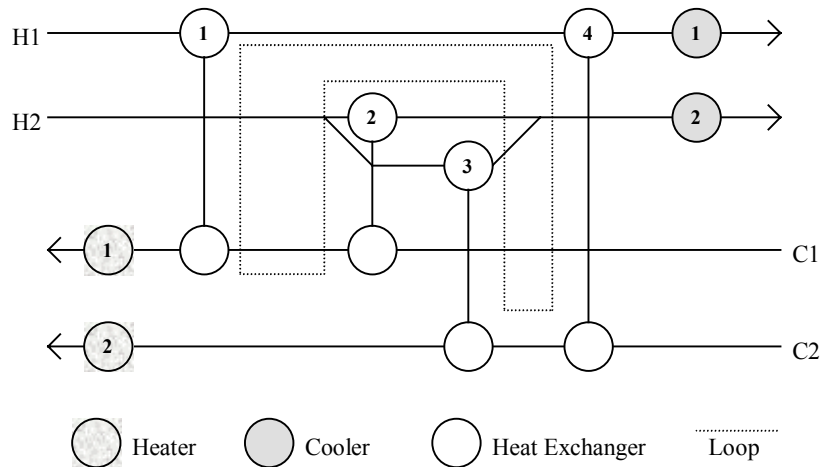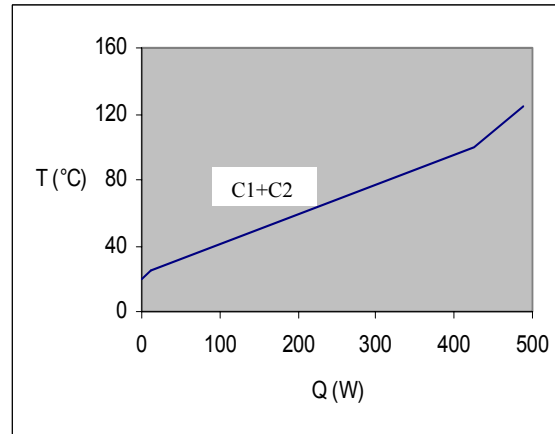
economic model
parameters

Key Elements of On-Line Optimization

Reactor Analysis

Energy Integration – Pinch Analysis
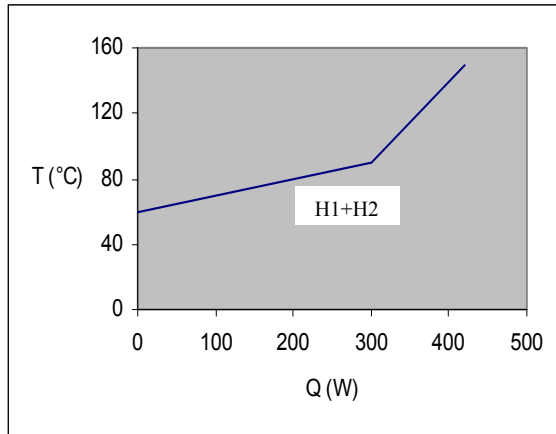
Pollution Assessment

Waste Reduction Algorithm (WAR) and
Environmental Impact Theory

Pollution Index

I = wastes/products = - (ΣOut + ΣFugitive) / ΣP_n

Potential Environmental Impact

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

α_l relative weighting factor

$\Psi_{k,l}^s$ units of potential environmental impact/mass of chemical k

$\Psi^s_{k,l}$ 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

Alkylation

Isoparaffin-olefin alkylation produces branched paraffins in the gasoline range

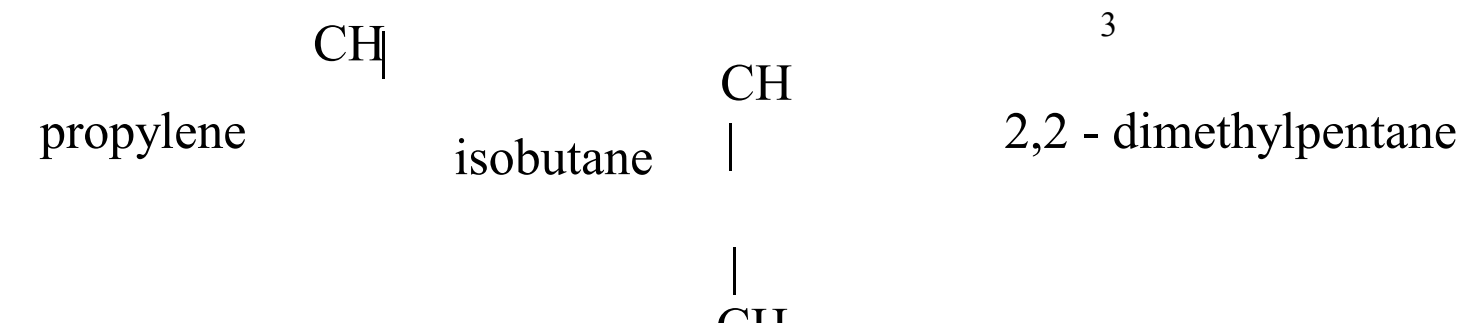Refineries use C_3 C_4 and C_5 hydrocarbon streams

Sulfuric acid catalyst concentration maintained above 88% to prevent polymerization

Reactor temperatures in the range of 10-20 ^{o}C

Alkylation is a two-phase system

      - low solubility of isobutane in the catalyst phase

      - intimate contact of the reactant and the catalyst

      - efficient mixing with fine subdivision

Main Alkylation Reactions

$$CH_3 - C = CH_2 + \ CH_3 - CH - CH_3 \ \rightarrow \ CH_3 - C - CH_2 - CH - CH_3$$

isobutylene   isobutane   2,2,4 - trimethylpentane

(isooctane)

$$CH_2 = CH - CH_3 + \ CH_3 - CH - CH_3 \ \rightarrow \ CH_3 - CH - CH_2 - CH_2 - CH_3$$

propylene   isobutane   2,2 - dimethylpentane
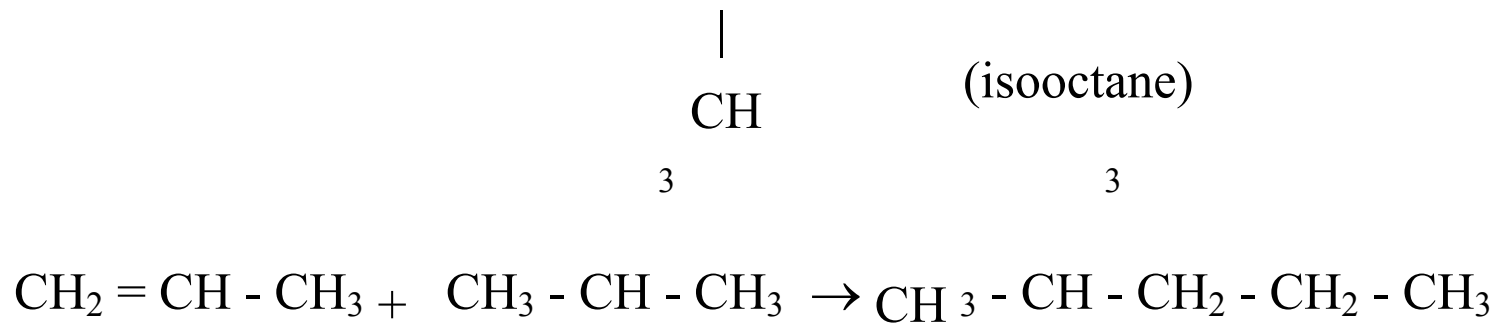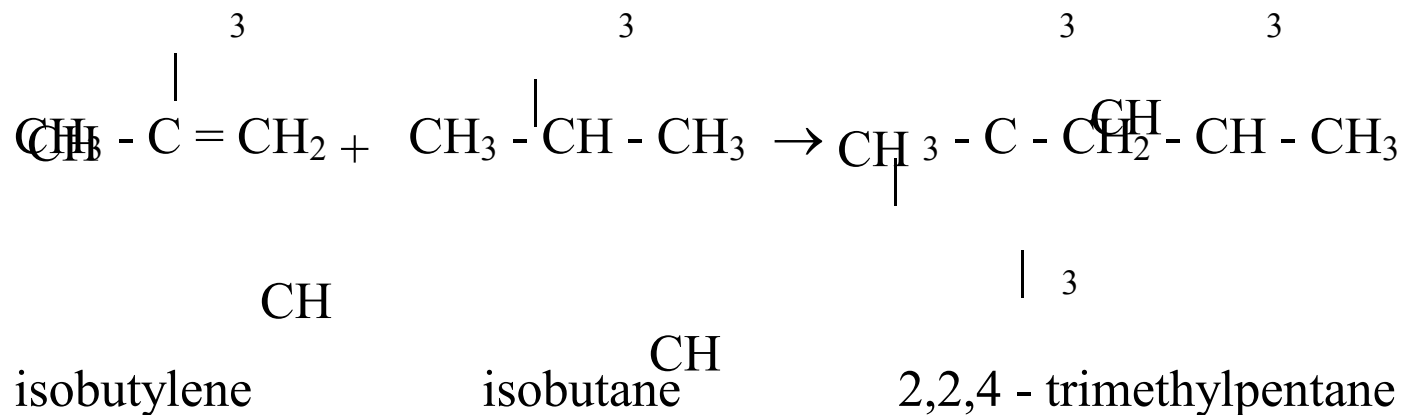
Mechanism and Other Reactions

Carbonium Ion Mechanism in Sulfuric Acid Catalyst

First step is the addition of proton to olefin molecule to form a tertiary butyl cation – initiation reaction

Tertiary butyl cation reacts with an olefin to form C_8 carbonium ion – primary reaction

Tertiary butyl cation regenerated by hydride transfer to isobutane

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

Other Reactions
  polymerization
  disproportionation
  cracking
  self-alkylation

Kinetic Model for Butene Alkylation

Total Reactions - 19

    Initiation – 2

    Primary – 2

    Self-Alkylation 3

    Destructive alkylation – 10

    Regenerate tertiary butyl ion - 2

Values for rate constants and related parameters are given in the users manual

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

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

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

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.

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

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

(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

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

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

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

(d) Carbonium ion rate equations.

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

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

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

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

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

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

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

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

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

Motiva Alkylation Process

15,000 BPD STRATCO Effluent Refrigerated Alkylation Plant

STRATCO reactor contacts the reactants in a high velocity propeller stream and removes heat from the exothermic reaction

Process flow diagrams

  prepared from P&ID's of the plant

  reaction section

  refrigeration, depropanizer and alkylate deisobutanizer sections

  saturate deisobutanizer section

Reactor Section

Four reactors

and acid settlers

Three feed
streams

 Olefin feed
(HC01)

 Isobutane feed
(HC03)

 Recycled
olefin/isobutane

(HC32)

Refrigeration, Depropanizer and Alkylate Deisobutanizer Section

Compressor

5K-601

Compressor KO Drum 5C-622

5E-634-639, 5E-655, 656

Refrigerant Accumulator 5C-615

Economizer Drum 5C-616

5E-640

Depropanizer Charge Drum 5C-618

Fuel Gas

Alkaline Water

5C-658

Depropanizer Charge Caustic Settler

Discharge Water

C301, C302, C303, C306, C307, C310, C312, C312A, C313A, C313, C315, C308, C309, C311, C312B, C314, C314A

5E-610-653

5E-611

i-butane to Storage

5E-613

To FCCU, Fuel Gas

5C-604

Depropanizer 5C-603

S-23

5E-657, 658

Propane LPG

Alkylate Deisobutanizer

5E-621-624

5C-607

IC4 from storage

5E-627, 647

n-butane

5E-612

M-33

S-41

5C-606

M-34

S-42

5E-696

5E-695

Fresh Caustic

5C-660

5C-608

To IC4 Flush Pump

5E-616

5E-626

Mixer

5E-617-620

Wash Water

Discharge

Wash Water

Alkylate

Saturate Deisobutanizer (5C-601)

Another source for isobutane is the saturate deisobutanizer (SatDIB) column. It strips isobutane from saturate feed coming from reformer unit of the refinery (SC401)

Process Simulation

Models of the various process units categorized by function

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

Models developed for each of these units are given in the users manual

Alkylation Process Mixtures of Components

Hydrocarbon streams 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

Sulfuric acid streams 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.

Constraint Equations for the Reactor

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	$F^i_{HC07} + F^i_{HC34} - F^i_{AC09} + r^i V^a_{5C623} MW^i = 0$
	$F^{i'}_{AC07} - F^{i'}_{AC09} - R^a_{5C623} = 0$
	$R^a_{5C623} = 0.121 Q^{C4=}_{HC07}$
	$i = 1,2,3,4,5,6,7,8,9,10$ and $i' = 11$

Energy Balances

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

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

r^i is the reaction rate of component i

where V^a_{5C623}, is the volume of acid in the contactor, typically 60 % of the contactor volume

R^a_{5C623} is the rate of degradation of the acid (metric ton/min).

Constraint Equations for the Depropanizer

Modeled using Smith-Brinkley Group method

Details given in the users manual

Table 4.3. Summary of the depropanizer model

Material Balances	
Overall	$F_{C316} + F_{C329} - F_{C317} - F_{C325} = 0$
Species	$F_{C316}^i + F_{C329}^i - F_{C317}^i - F_{C325}^i = 0$ where i=1,3,4,5

Smith- Brinkley Method Equations

$$K_i = f(P_{C603}, T_n)$$

$$K_i^{'} = f(P_{C603}, T_m)$$

$$S_{n,i} = \frac{K_i F_{C325}}{F_{C329}}$$

$$S_{m,i} = \frac{K_i^{'} V^{'}}{L^{'}}$$

$$f_i = \frac{\left(1 + S_{n,i}^{N-M}\right) + R\left(1 - S_{n,i}\right)}{\left(1 + S_{n,i}^{N-M}\right) + R\left(1 - S_{n,i}\right) + h_i S_{n,i}^{N-M}\left(1 - S_{m,i}^{M+1}\right)}$$

$$f_i = \frac{F_{C317}^i}{F_{C316}^i}$$

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

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

$x_{C317}^i - x_{C323}^i = 0$, where i=1,3,4,5

$T_{C317} - T_{C323} = 0$

Constraint Equations for the Alkylate Deisobutanizer

Table 4.4. Summary of the deisobutanizer model

Alkylate Deisobutanizer Column

- two feed streams

- two product streams

- two side streams

- two reboilers

- one is a side reboiler

The column was divided into three reasonable sections (C-606A, C-606C and C-606D) and modeled using Smith Brinkley Method.

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	$F_{C404}^{i} + F_{C432}^{i} + F_{C322}^{i} - F_{C414}^{i} - F_{C430}^{i} = 0$
	$F_{C430}^{i} + F_{C427}^{i} - F_{C431}^{i} - F_{C425}^{i} = 0$
	$F_{C426}^{i} - F_{C428}^{i} - F_{C405}^{i} = 0$
	where i=1,3,4,5

Smith- Brinkley Method Equations
$K_{i,C606A} = f(P_{C606A}, T_{n,C606A})$
$K'_{i,C606A} = f(P_{C606A}, T_{m,C606A})$
$K_{i,C606C} = f(P_{C606C}, T_{C425})$
$K'_{i,C606D} = f(P_{C606D}, T_{m,C606D})$
$S_{m,i,C606A} = \dfrac{K'_{i,C606A} V'_{C606A}}{L'_{C606A}}$
$S_{n,i,C606A} = \dfrac{K_{i,C606A} F_{C414}}{F_{C322}}$
$S_{m,i,C606D} = \dfrac{K_{i,C428} F_{C428}}{F_{C426}}$

Suction Trap/Flash Drum (5C-614)

Suction Trap/Flash Drum

splits the hydrocarbon effluent from the settlers based on volatility

two-compartment vessel, with a common vapor space

net contactor effluent is accumulated on one side of the baffle and the cold refrigerant condensate on the other

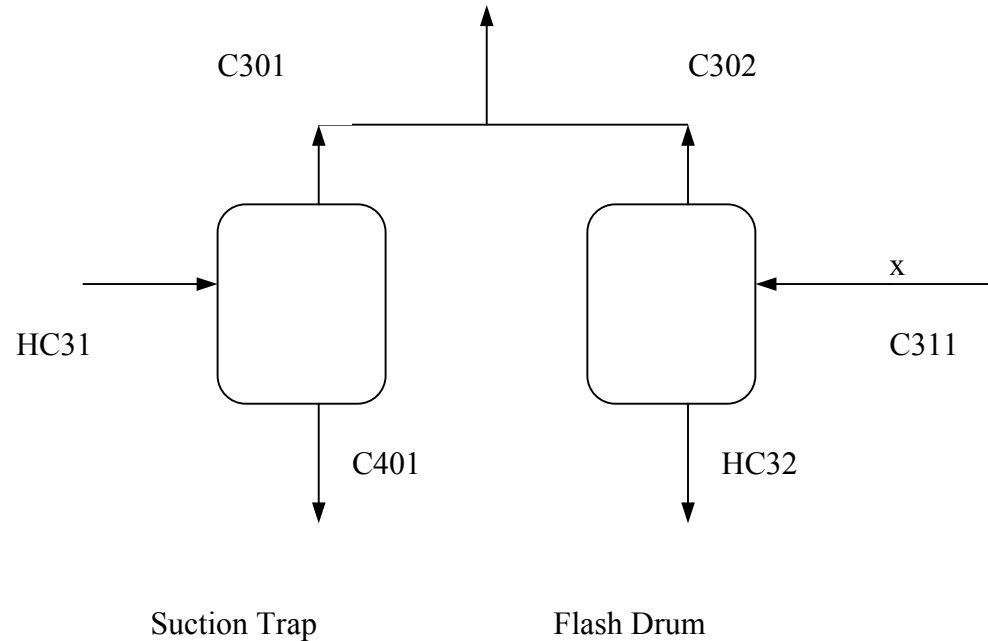vapors from the two compartments combine, and flow out from the top.

C301

C302

x

HC31

C311

C401

HC32

Suction Trap

Flash Drum

Figure 4.7: STFD 5C-614

Constraint Equations for Suction Trap/Flash Drum

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
	$K_i = \dfrac{y_i}{x_i}$, where, $\sum x_i = 1$, $\sum y_i = 1$
Energy Balances	
	$T_{HC31} = T_{C301} = T_{C401}$
	$h_{C311} - h_{HC32} - h_{C302} = 0$

Model Validation

Establish accuracy of model to predict performance of plant

Used data validation

125 measured plant variables, 88 were within the accuracy of the measurements

Remaining 37 variables shown here with standard measurement error

$\in_i$ ($\in_i = |y_i - x_i|/\sigma_I$

Process engineers concluded that these 37 variables were within the range of possible process values

Model of the process accurately predicted its performance and 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

Model Summary

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

Economic Model

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

Alkylation Plant Raw Material/Utility Costs and Product Prices

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	C407	26.34	24.19
Alkylate			

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

On-Line Optimization

Process Data from Distributed Control System

Plant measurement at 1.0 minute intervals over a two day period

Six steady state periods identified using time series with MathCAD graphics

Data Reconciliation and Gross Error Detection

Robust Lorentzian function method and CONOPT2

Optimal solution obtained in 1,200 iterations

Reconciled measurements reported and about 30 gross errors identified

Parameter Estimation and Data Reconciliation

Optimal solution obtained in 1,500 iterations

Small adjustments in values of parameters

On-Line Optimization Results Economic Optimization

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

Improvement in profit

8.5% reduction in costs and 2.2% increase in sales

5.5% more olefin charge

98% reduction in isobutane purchase cost (because of reduced isobutane flow rate)

7.2% reduction in saturate feed to the Saturate Deisobutanizer column

2.2% increase in the alkylate (alkylate quality did not change at optimal operation)

Average of 9.4×10^9 BTU/yr in energy savings from steam usage in the distillation columns
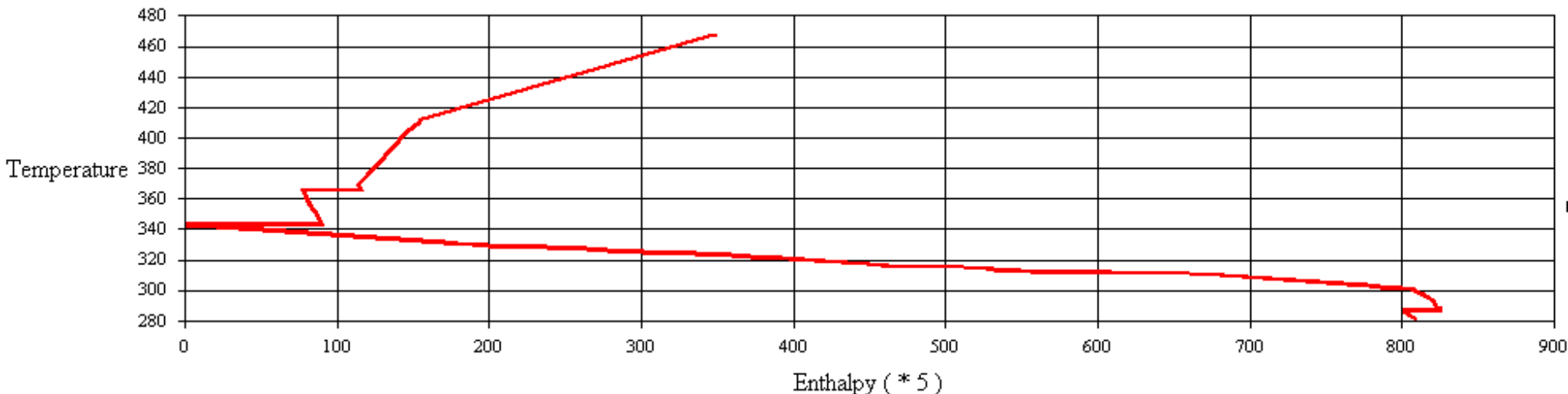
Energy Integration – Pinch Analysis

Alkylation process is very energy intensive

Alkylation process model has 28 heat exchangers, plus four contactors. Heat exchange in contactors not included in the pinch analysis

Grand Composite Curve

End points of the curve gives the minimum values of external heating and cooling required by the process

Pinch Analysis – Minimum Utilities

Minimum Utilities

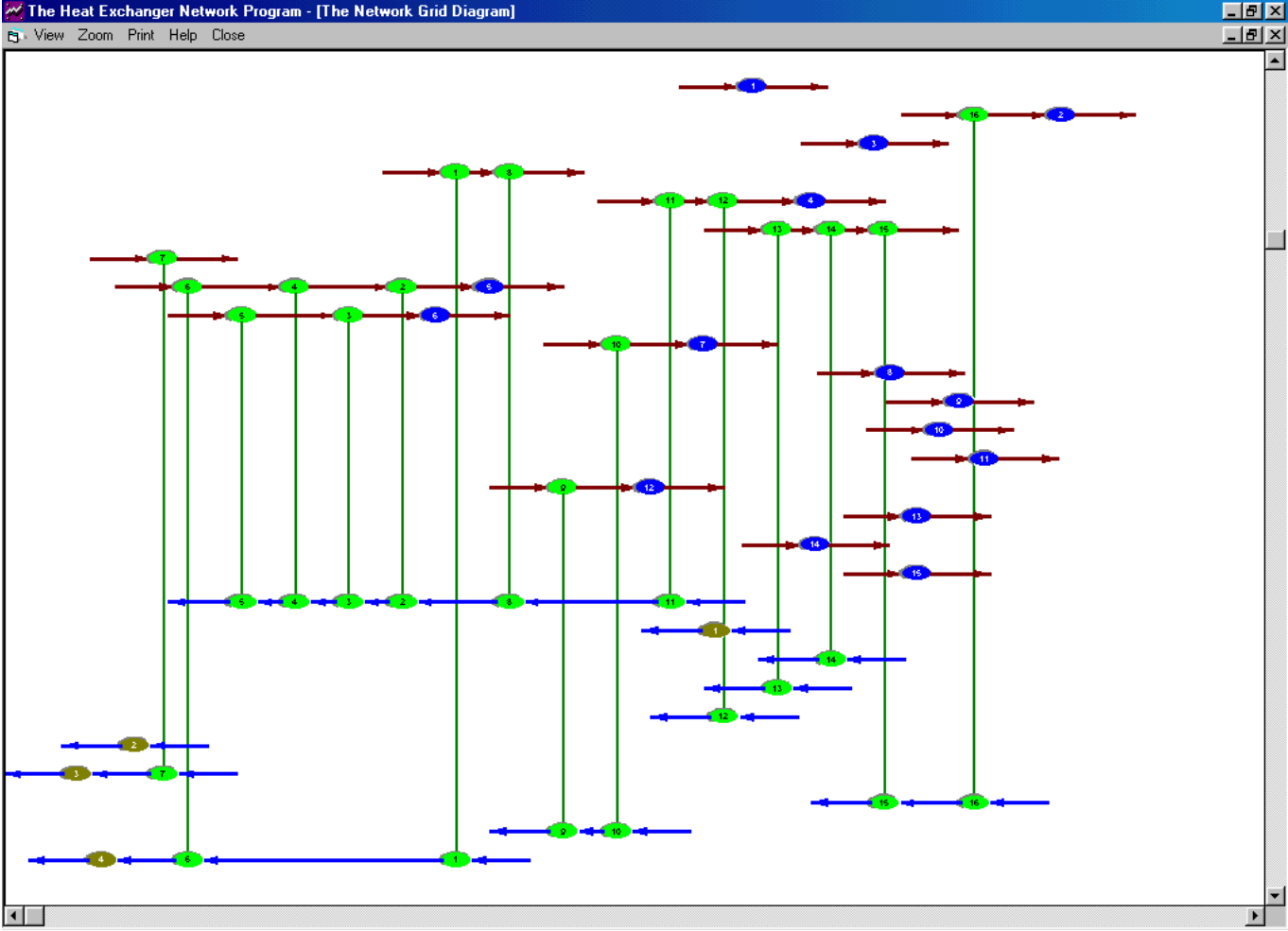1742 MJ/min steam (external heat)

4043 MJ/min of cooling water (external cooling)

Current Operations

1907 MJ/min steam (external heat)

4300 MJ/min of cooling water (external cooling)

Pinch Analysis – Maximum Energy Recovery Network Diagram

Pinch Analysis – Optimum Heat Exchanger Configuration

Current Configuration

6 heat exchangers, 4 heaters and 12 coolers

Optimal Configuration

16 heat exchangers, 4 heaters and 15 coolers

Additional heat exchangers reduce energy requirements

May result in operational difficulties

See report for pressure shift applied to distillation columns

Pollution Assessment

Assess the pollutants generated in the process
Determine location of generation
Modify process for waste minimization

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

Pollution Assessment before and after Economic Optimization

Program calculates pollution indices for each input, produce and non-product stream in the process

These values are used to calculate the six pollution indices for 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 (BEO) and after (AEO)

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

Conclusions – Flowsheeting

Demonstrated Capability of Advanced Process Analysis System
  - process flowsheeting
  - on-line optimization
  - pinch analysis
  - pollution assessment
  - chemical reaction analysis determined
    best alkylation reaction kinetics

Process Flowsheeting
    76 process units, 110 process streams
1,579 equality, 50 inequality constraints, 1,634 variables
Simulation validated using plant data and data reconciliation
Simulation predicted the performance of the plant
    within the accuracy of the data

Conclusions – Economic Optimization

Evaluated six operating points

25% to 215% increase in the profit

Increase of 145% included
    8.5% reduction in costs and 2.2% increase in sales
    5.5% more olefin charge
    98% reduction in isobutane purchase cost
    7.2% reduction in feed to the Sat Deisobutanizer
    2.2% increase in the alkylate
    2.2% reduction in the sulfuric acid consumption.
    1.0% reduction in energy to 1888 MJ/min

Conclusions – Pinch Analysis and Pollution Assessment

Pinch Analysis
 7.7% reduction in steam to 67×10^9 BTU/yr
 6.0% reduction in cooling water to 106×10^9 BTU/yr

Pollution Assessment
Demonstrated ability to locate and estimate the severity pollutant emissions from the process.

Conclusions - Summary

Development and validation of process simulation
      most difficult and time consuming part
      of applying the System

Applicable to small plants

Typical improvements
      5% for on-line optimization
      5 –35% for pinch analysis

Detailed understanding of process
      - most valuable result
      - difficult to measure value

Program and users manual downloaded from
      'www.mpri.lsu.edu - no charge