SLOVAK UNIVERSITY OF TECHNOLOGY
IN BRATISLAVA

FACULTY OF CHEMICAL AND FOOD TECHNOLOGY

Reg. No.: FCHPT-16584-97284

Modelling and Optimal Operation of an Alkylation Unit

MASTER PROJECT

2024 **Bc. Martin Bíreš**

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Study programme:	Automation and Information Engineering in Chemistry and Food Industry
Study field:	Cybernetics
Training workspace:	Institute of Information Engineering, Automation and Mathematics
Thesis supervisor:	doc. Ing. Radoslav Paulen, PhD.
Consultant:	Ing. Rastislav Fáber, Ing. Karol Ľubušký

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Slovak University of Technology in Bratislava
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Faculty of Chemical and Food Technology
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Selected bibliography:

1. ŠVISTUN, Ladislav; VARINY, Miroslav. *Prevádzková optimalizácia a možnosť uplatnenia nových technológií pri výrobe alkylátu.* Diplomová práca. 2021.
2. SPEIGHT, James G. The refinery of the future. Gulf Professional Publishing, Elsevier. 2020. ISBN 978-0-8155-2041-2

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Abstract

The alkylation unit is a key part of an oil refinery. The energy intensity of this process plays an important role in the economy of the company. The goal of this project is to create a mathematical model of the alkylation unit process, verify the correctness of the designed model based on consultation with industry, and propose an economically optimal operation.

Key words: alkylate, sulphuric acid, mathematical model, AVEVA process simulation

Abstrakt

Alkylačná jednotka je kľúčovou súčasťou ropnej rafinérie. Energetická náročnosť tohto procesu zohráva dôležitú úlohu v hospodárení spoločnosti. Cieľom tohto projektu je vytvoriť matematický model procesu alkylačnej jednotky, overiť správnosť navrhnutého modelu na základe konzultácií s priemyselným odvetvím a navrhnúť ekonomicky optimálnu prevádzku.

Key words: alkylát, kyselina sírová, matematický model, AVEVA process simulation

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CHAPTER 1

Introduction

The petrochemical industry is a large consumer of energy and accounts for around 10% of global demand. The industry relies heavily on fossil fuels, mainly oil and natural gas, as feedstock and energy sources [2]. The optimization of chemical processes is crucial for the industry. It provides the following benefits. Increased efficiency and productivity lead to higher yields, improved overall efficiency, and reduced energy consumption [6]. Optimization enables the reduction of raw material and energy consumption and minimizes waste treatment and disposal costs [8]. Fine-tuning process parameters can help ensure an increase in product quality [6] [4]. Reducing the load on the environment through the efficient use of energy leads to a reduction in waste and emissions, making the process more sustainable and environmentally friendly [8]. Applying advanced optimization techniques, simulations, or statistical tools, allows companies to stay ahead of the competition [7] [4].

The alkylation process produces alkylated naphtha from C_4 unsaturated hydrocarbons, which is very valuable high-octane component for automotive gasoline. The great advantage is that alkylate contains only paraffinic hydrocarbons which, when burned in engines, produce fewer harmful emissions than when burned aromatics and olefins. Olefins are hydrocarbon compounds that contain one or more carbon pairs connected by a double bond. In alkylation reactions, light olefins (C_3, C_4 and C_5) react with isobutane in the presence of strongly acidic catalyst. Although alkylation can take place at high temperatures without the presence of a catalyst, the only commercially important processes are low-temperature alkylations using sulphuric or hydrofluoric acid catalysts. Proper selection of operating conditions can ensure that the product will be in the desired distillation range of motor gasoline with a motor octane number (MON) 88 to 95 units and research octane number (RON) 93 to 98 units. STRATCO alkylation process with reaction mixture cooling and reaction equipment (contactor) is designed to promote alkylation reactions and suppress competing reactions such as polymerization. These competing reactions increase acid consumption and result in a product with a low octane number [9].

A suitable mathematical model provides a good source of information about the behavior of the process when the operating parameters are changed, whether it is the feed variability, temperature, or pressure change [3]. Simulating the model in different modes reveals how the inputs affect the outputs concerning the quantity processed and the energy used, without the need to interfere with the real process. This work aims to improve the energy efficiency of alkylation unit operation by using a mathematical model in the AVEVA Process Simulation environment.

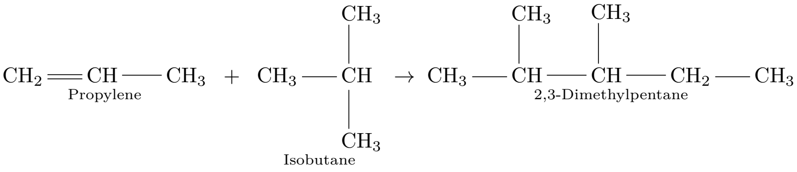
Chapter 2

Theoretical Part

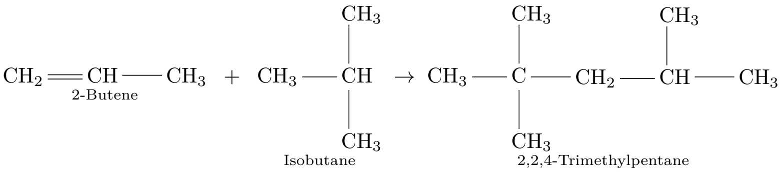
2.1 Alkylation Unit Description

In this chapter, we will get acquainted with the alkylation unit, the main chemical reactions that occur in it, and also with the optimization tool Data Reconciliation, which is used to modify the obtained data. The last part of this chapter will be a description of the AVEVA Process Simulation modeling program and the main blocks that make up the mathematical model.

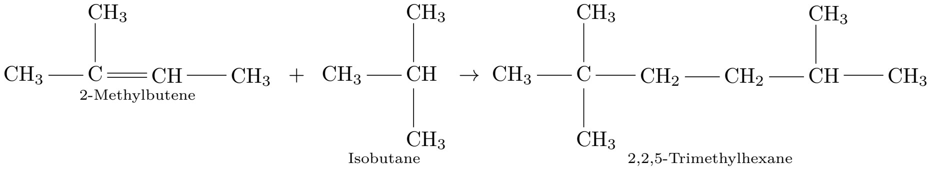
In the STRATCO alkylation process, olefins are alkylated with isobutane in the presence of a sulfuric acid catalyst to form an alkylate. The following reactions are simplified alkylation reactions for C_3, C_4 and C_5 olefins [9]:



$$\underset{\text{Propylene}}{CH_2{=}CH-CH_3} + \underset{\text{Isobutane}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}}} \rightarrow \underset{\text{2,3-Dimethylpentane}}{CH_3-\overset{\displaystyle CH_3}{CH}-\overset{\displaystyle CH_3}{CH}-CH_2-CH_3}$$



$$\underset{\text{2-Butene}}{CH_2{=}CH-CH_3} + \underset{\text{Isobutane}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}}} \rightarrow \underset{\text{2,2,4-Trimethylpentane}}{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{\displaystyle CH_3}{CH}-CH_3}$$



$$\underset{\text{2-Methylbutene}}{CH_3-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_3} + \underset{\text{Isobutane}}{CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{CH}}} \rightarrow \underset{\text{2,2,5-Trimethylhexane}}{CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2-CH_2-\overset{\overset{\textstyle CH_3}{|}}{CH}-CH_3}$$

The actual reactions taking place are much more complex. These reactions take place in the acidic emulsion phase, where olefins get in contact with isobutane. The acid-hydrocarbon emulsion is maintained by vigorous mixing of the acid and hydrocarbons in the STRATCO contactor. By definition, the catalyst participates in and promotes the chemical reaction without being consumed in the alkylation process. In the H_2SO_4 alkylation process, however, the acid is continuously added to the process. The addition of fresh acid is necessary because there is a decrease in concentration due to side reactions and the presence of impurities in the feed. A typical side reaction is polymerization, which is a competing reaction to alkylation. In polymerization reactions, olefin molecules react with each other to produce a low-octane product with a high distillation end and an increasing consumption of acid. Polymerization reactions can be prevented by ensuring a low reaction temperature, the desired ratio of isobutane to olefins, and the use of concentrated sulfuric acid. [9].

2.1.1 Brief description of the technological stages

1. Reaction section - contact of reacting hydrocarbons and sulfuric acid (catalyst) occurs under controlled conditions.

2. Cooling section - reaction heat and light hydrocarbons are removed from the unit.

3. Reaction product processing section - removes free acid, alkyl sulfates and dialkyl sulfates from the reaction mixture to prevent corrosion and precipitation.

4. Fractionation section - removes isobutane from the reaction products, returns it to the reaction section and the remaining hydrocarbons are separated into individual products.

5. Effluent, and acid slurry section - effluent and recovered acid are degassed, the pH of the effluent is adjusted and the acid effluent streams are neutralized before they leave the production unit.

The olefin feedstock (hydrogenated or non-hydrogenated C_4 raffinate) enters the eaction section where it is cooled by the reaction product, which passes to the reaction product processing section where the free water is separated. The olefin feedstock is joined to the isobutane recycle from the deisobutanizer and split in parallel into three branches. Before entering the contactors, a recycle of refrigerant is added to each branch of the feedstock-isobutane mixture. In the contactors, the hydrocarbons are intensively mixed with the acid while alkylation reactions take place and heat is generated. The reaction mixture is cooled in the intertube space of the contactors and discharged to the acid settlers above the contactors. Here the hydrocarbon and acid phases are separated. The acid phase is in the form of an emulsion, the residence time is such that the hydrocarbons are not completely separated from acid. The emulsion recirculates back to the contactor. The acid flows from the first through the second to the third contactor. To maintain the desired acid concentration, a small amount of fresh concentrated acid is continuously added to the first contactor and an approximately equal amount of used acid is withdrawn from the third contactor. The hydrocarbon phase from the settling tanks is cooled by reducing the pressure, passing through the contactor tubes removing the reaction heat and evolving a vapour-liquid mixture. The steam is led to the cooling section where it is compressed, cooled and condensed. A portion of the liquid refrigerant is vented from the unit through a lye scrubber as a propane vent. The remaining liquid as refrigerant is pumped back to the contactors. The reaction product from the reaction section contains acid, alkyl sulfates and dialkyl sulfates which must be removed. These compounds are extracted in an acid wash tank with fresh acid and further washed with hot water to get rid of the remaining alkyl sulfates. Waste caustic water is degassed, neutralized and pumped to the wastewater treatment plant. The purified reaction product is fed to the fractionation section, the deisobutanizer (DIB). To DIB is injected with fresh isobutane mixture from storage. Through the head of the DIB, the isobutane goes back to the reaction section. At the bottom of the column, the n-butane and alkylate leave the column to the debutaniser, where this mixture is split into products. The n-butane leaves through the debutaniser head. The alkylate, the product which, after heat transfer in the heat exchangers, leaves through the bottom of the column is pumped to the Motor Fuels Expedition [9].

For a better understanding, a simplified sketch of the process with a single contactor is shown in Figure 2.1. In this work, we will mainly focus on equipment such as chemical reactors and deisobitizer.

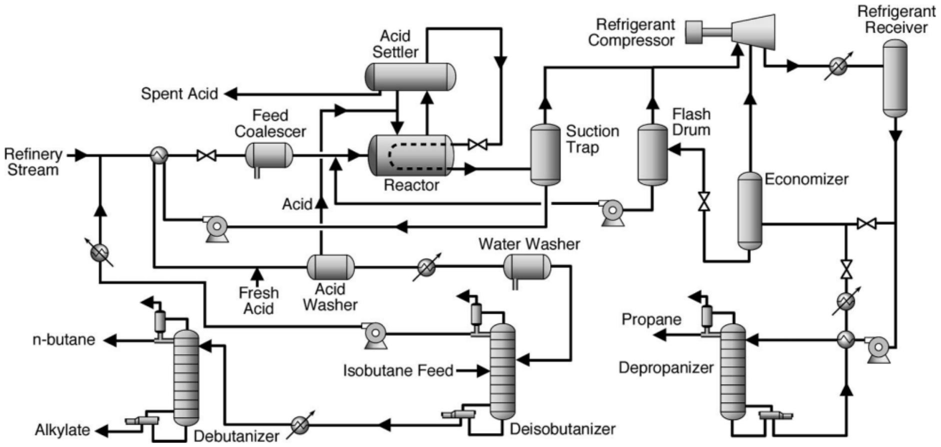


Figure 2.1: Simplified scheme of the alkylation unit [5].

2.2 Data Reconciliation

In general, an optimization problem consists of two main parts namely the objective function and the corresponding constraints. In finding the optimal process parameters, the value of the objective function will be maximized if our goal is, for example, to achieve higher product purity or the value of the objective function will be minimized if our goal is to reduce energy consumption with respect to the constraints.

The measurement of process streams provides important information on how much raw material is processed, its composition, temperature, and pressure. By running continuous processes for long periods, these meters can lose accuracy. Calibration of the instrument requires dismantling which could affect the operation of the process. If this problem is not so serious, the solution may be to use the Data Reconciliation method.

The principle of data matching is to minimize the sum of squared deviations between the measured value and its optimized value, taking into account equality constraints, which can be expressed, for example, as material or enthalpy balances, and inequality constraints, such as technological constraints. The optimization problem is shown in Equation 2.1.

$$\begin{aligned} &\min_{\overline{x}} (x-\overline{x})^T \sigma^{-1} (x-\overline{x}) \\ s.t.\ \ &F(\overline{x}) = 0 \\ &G(\overline{x}) \leq 0 \end{aligned} \tag{2.1}$$

where $\overline{x}$ is the vector of matched data, σ is the covariance matrix of measurement errors, F represents the process model used as equality constraints in the optimization problem, and G denotes the inequality constraints indicating the boundaries of the variables [10].

To approximate the Data Reconciliation method, use the following example. We consider a process that has two inputs and one output, where F_i represents the mass flow rate of a given stream. Figure 2.2 shows that the inputs are not equal to the output. The notation of the optimization problem will be the same as given in Equation 2.1, x represents the lying vector of measurements F. The equilibrium constraint will be written in the form of a mass balance. The inequality constraint will be used if the value of the flow rate needs to be kept within a specific interval. The full notation of the optimization problem for the example is written in Equation 2.2.

$$\begin{aligned} &\min_{\overline{x}} (x-\overline{x})^T \sigma^{-1} (x-\overline{x}) \\ s.t.\ \ &F_1 + F_2 - F_3 = 0 \\ &F_{min} \leq F_i \leq F_{max} \end{aligned} \tag{2.2}$$

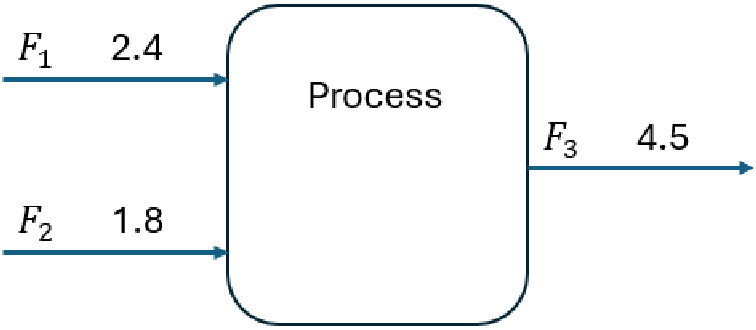


Figure 2.2: The process outline for the above example explains the Data Reconciliation method.

The result of the optimization is a vector $\overline{x}$ of optimized parameters F_i whose material balance is matched so that the input equals the output.

2.3 Aveva Process Simulation Environment

AVEVA Process Simulation is an innovative, integrated platform that helps develop the process side of the digital twin to explore all design potentials and quantify the impact on sustainability, feasibility and profitability. With legacy tools, even small projects require multiple, dedicated simulators. Engineers waste time learning interfaces and transferring data, and errors can occur. This modeling environment improves the user experience, IT availability, and unifies many use cases into a single integrated platform for designing and optimizing process equipment. Aveva process simulation can be used in the following areas [1]:

Chemical processes: It allows the simulation of complex systems with many recycles where conventional simulators perform poorly. It includes a library with Distillation columns, reactors, heat exchangers and many other devices. Provides many thermodynamic methods and interfaces with an administrator thermodynamic data interface for defining custom components. It allows the user to simulate the process in a dynamic or steady state [1].

Renewables and sustainability: It is suitable for the design of renewable energy networks for solar panels, wind turbines, electricity distribution and hydrogen electrolysis. It allows design alternatives for the electricity network to enable better decision-making in conceptual design [1].

Process utility: Process utility engineers can use one simulation on cooling water or steam and then change the mode to perform the analysis piping network. These options include libraries with boilers, steam turbines, chilled water, steam, and others [1].

Flare networks: The flare library provides an easy way to evaluate multiple offloading scenarios and instantly view back pressure predictions. Field burner networks are evaluated in the same software environment as chemical processes for easy coordination of engineering changes. The library further includes flare stacks, tailpipes, relief valves and robust flare network solutions, especially with multiple stacks [1].

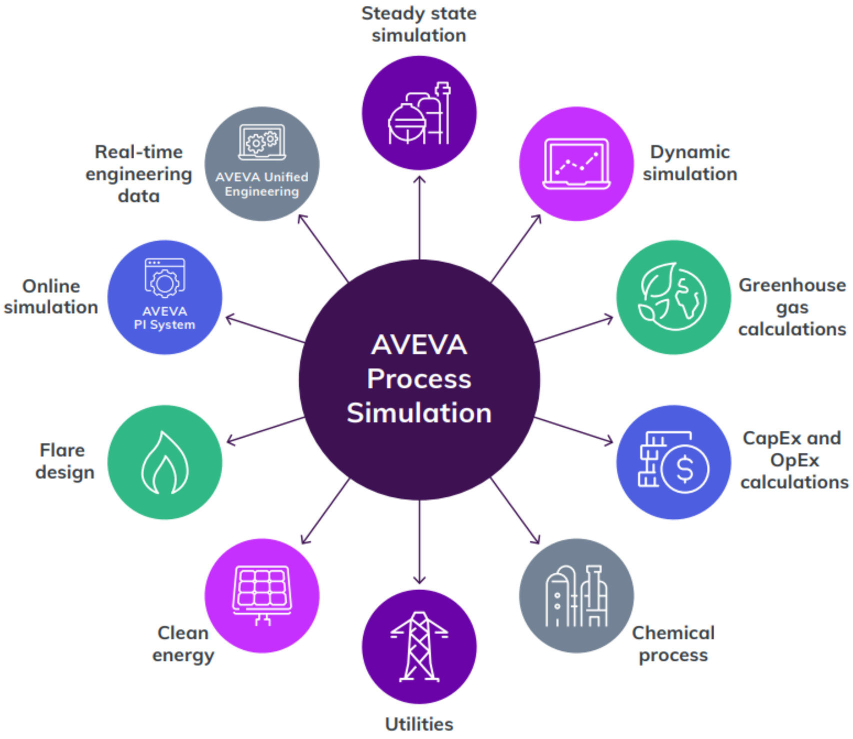


Figure 2.3: Graphical representation of the options provided by Aveva Process Simulation [1].

This environment allows you to simulate mathematical models in three modes.

Process: Process Mode performs steady-state calculations to create and refine a process design. In this mode, variables such as inlet flow rates and composition are typically specified alongside the placement of each model on the screen. It provides more feedback when creating the simulation and provides an initial solution for Fluid Flow mode.

Fluid Flow: Fluid Flow Mode performs steady-state simulations that are pressure-controlled. This mode is used for piping network analysis. Flow rates are typically not specified, they are calculated based on the specified boundary pressures and pressure-flow relationships.

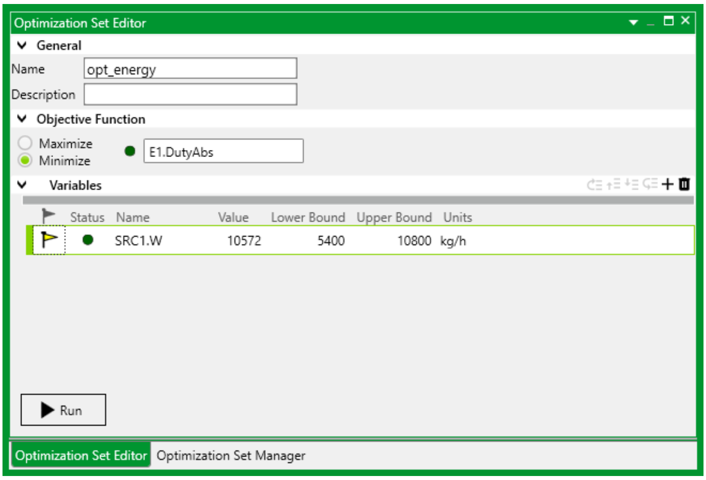
Dynamics: Dynamic mode simulates transient phenomena of the system over time. The simulation speed can be varied (accelerated, slowed down, or directly going to a steady state).

The modeling environment itself consists of three main parts:

The top bar: Shows information in which mode the user is working (Process, Fluid Flow and Dynamics), whether the inputs, model parameters and also Simulation status (successful or unsuccessful). If these identifiers are visualised in green, the model is correctly defined and simulated. Yellow color represents a warning. For example, if a distillation column is used, some of the stages do not contain any liquid, which means that the distillation is not proceeding correctly. Red color represents an error that may have occurred e.g. by defining a low number of parameters. The environment allows snapshots to be created, which when created, store information about the current settings of the model. If there is a need to perform a simulation with different settings, the original ones will be saved and can be returned at any time. In this section, there is also an optimization tool. This bar is shown in Figure 2.5.

The optimization tool provided by AVEVA Process Simulation is very easy to use. An example of an optimization problem setup is shown in Figure 2.4. In the above example, the objective function expresses the amount of energy to be delivered to the stream in the heat exchanger. The objective of this optimization is to minimize this energy. The optimized parameter is the flow rate of the medium at the inlet of the process with the constraints set. The displayed flag if not highlighted, the given optimized parameter is not included in the optimization.

Model Library: The Process tab defines devices such as Heat Exchangers, Distillation Columns, Source or Sink streams, etc. It also contains models that are used for reactors (e.g. chemical kinetics data). As with chemical reactions, the relevant block needs to be defined for liquids. The Fluids tab contains blocks with predefined liquids. If the desired fluid is not present there, it is possible to define a custom block with the desired fluid. The last tab, which bears the name of the created model, contains blocks



Name: opt_energy

Description:

○ Maximize
● Minimize
● E1.DutyAbs

Status	Name	Value	Lower Bound	Upper Bound	Units
●	SRC1.W	10572	5400	10800	kg/h

Figure 2.4: Example of setting up an optimization tool.

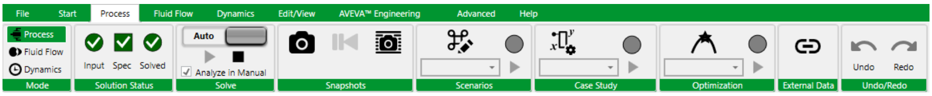


Figure 2.5: Illustration of the top bar.

for chemical kinetics and for the selected fluid. The Model Library contains additional tabs that contain tools e.g. creating graphs, defining equations, control blocks and others.

Canvas: The surface on which the mathematical model is created. The model blocks are inserted here from the Process Library by drag and drop.

Figure 2.8 shows the blocks that were used in the development of the mathematical model. Each device contains a specific location that is displayed when the cursor is moved. Through this location, we connect to the next device. Their designation can be for example liquid outlet, gas outlet, pressure signal for the controller, and others.

CSTR: A continuous stirred tank reactor is used to convert a reactant into a product while it needs to have a defined reaction block that contains the kinetics of the chemical reaction. It contains a jacket through which it can be cooled or heated.

Column: The main parameters of the distillation column include reflux ratio, number of stages, choice of external or internal condenser, and reboiler. Figure 2.8 shows a

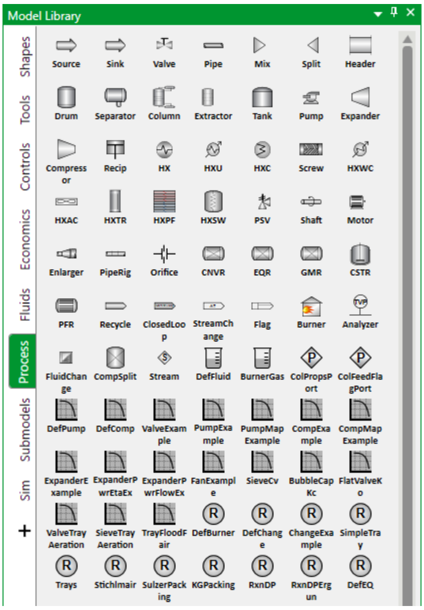


Figure 2.6: Illustration of Model Library.

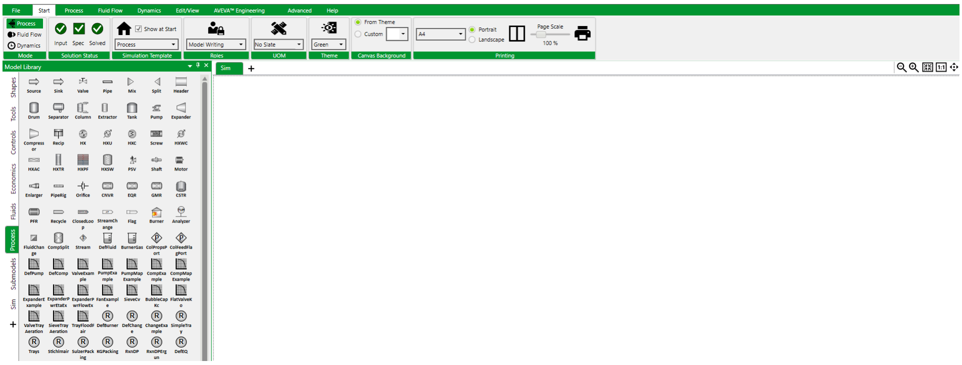


Figure 2.7: Illustration of the AVEVA process simulation environment of a new blank canvas project.

column with internal wiring. The condenser allows the condensate to be set up as a vapor-liquid mixture, liquid, or supercooled liquid.

Drum: It is used to separate the liquid and gaseous phases and can also be used as a collection vessel.

HX: The heat exchanger allows setting the desired temperature of the output stream or can also be operated with an external heating/cooling medium.

Source: It contains a Fluid Block in which the chemicals used in the process are defined. Allows to specify temperature, pressure, and composition of the input stream to the mathematical model.

Sink: Both the input and the output must be defined for chemical substances. It contains information about the flow and composition of the liquid, gas, and the overall composition of the stream.

Mix: It is used for coupling multiple streams.

Split: It can branch a single stream with the ability to adjust the flow ratio for individual branches.

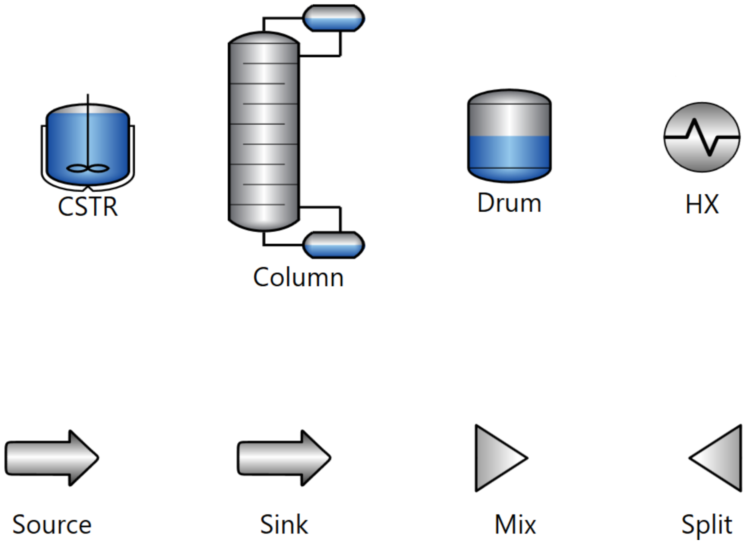


Figure 2.8: Building blocks of the mathematical model of the alkylation unit.

Chapter 3

Practical Part

3.1 Data Reconciliation

Before the application of the data reconciliation method, it is necessary to select suitable measured data from the process, we have chosen the consequent balance boundaries. The considered process contains a reaction section, a cooling section and a reaction product processing section. The input to the process is a stream of olefins and a stream of isobutane from the deisobutanizer. The output is the alkylate mixed with isobutane and inert substances such as n-butane, the mixture is fed to the deisobutanizer. This setup of balance boundaries is satisfactory because of the location of the measuring devices on the individual streams.

The data obtained from the measuring devices are shown in Figure 3.1. The graph on the left represents the data for the olefin stream, in the middle for the isobutane stream, and on the right for the alkylate-isobutane stream. The data shown represent a time interval of seventeen days with a sampling period of one minute.

From the graph on the right, we can see that the measurement is affected by high levels of noise. This noise can be reduced using the data reconciliation method. The computation of the optimization problem was done in a Matlab environment using the Yalmip toolbox. The sum of squares of deviations was minimized according to equation 2.1 given an equality constraint of the form:

$$\dot{m}_{1,j} + \dot{m}_{2,j} - \dot{m}_{4,j} = 0 \tag{3.1}$$

where $\dot{m}_{1,j}$, $\dot{m}_{2,j}$, and $\dot{m}_{4,j}$ represent the mass flow rates of olefin, isobutane, and alkylate-isobutane, respectively, for the j^{th} measurement at local steady state.

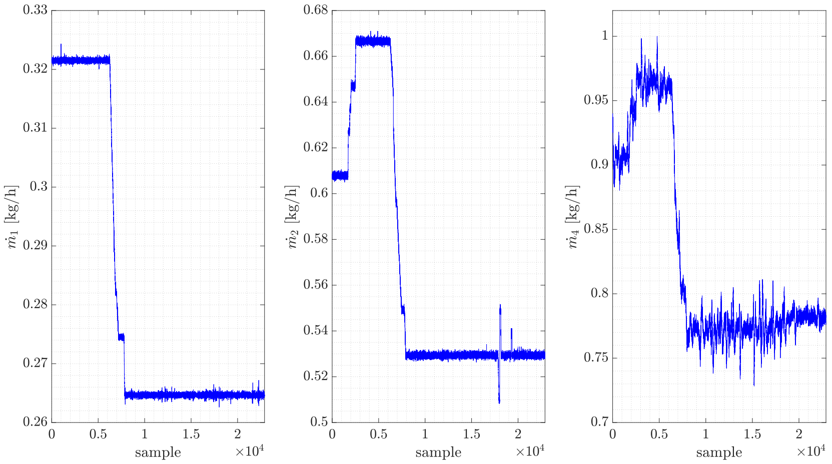


Figure 3.1: Normalized data concerning mass flow rate $\dot{m}_4$ from three measuring devices.

3.1.1 Results and Applications

The result from the data reconciliation method is shown in Figure 3.2. From the first two plots, the optimized and measured data are identical, while the third plot already shows significantly this difference is significant. The difference between the optimized and measured data may have arisen from the assumption of the considered system of two inputs and one output, while the other streams were neglected. Another cause could be gauge error or a combination of the two.

The advantage of this method is that there is a significant reduction of noise. Since we considered material balance as a constraint on the optimization. The sum of the inputs will be equal to the output.

The data obtained through optimization can be used as an indicator of poor gauge performance. Noise reduction can improve process control. Also, the use of this data affects the quality of the simulation results of the model.

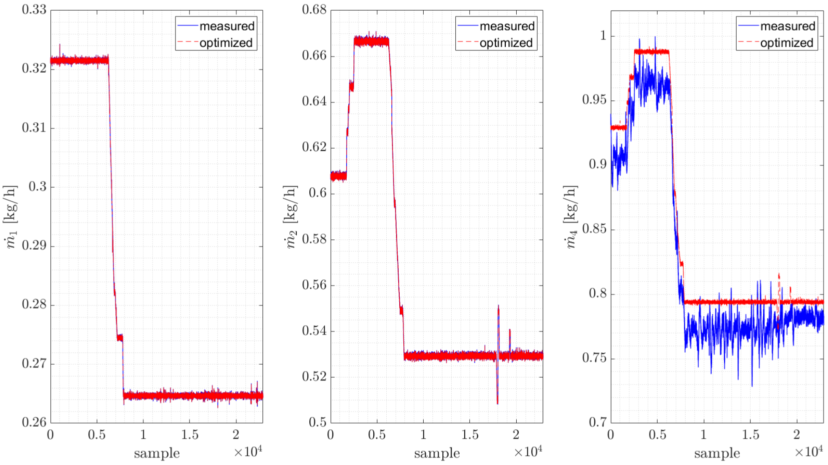


Figure 3.2: Normalized data from three measuring devices and optimized data from the data reconciliation method.

3.2 Model Building

3.2.1 Model Descriptions

Creating an accurate mathematical model of a production unit is very difficult, so we have accepted some simplifications:

- Neglecting the cooling section - all material streams are in the liquid state (except for the streams in the distillation column block), the influence of the cooling section can be replaced by external heat exchangers located on selected streams of the mathematical model, the temperature of the reaction mixture in the contactors is constant, excess heat is dissipated by the internal heat exchanger of the reactor block model
- Simplification of chemical reactions - we consider only one chemical reaction, that of propylene with isobutane to form 2,3-Dimethylpentane
- Neglect of sulfuric acid - in contactors, isobutane with olefins is in one liquid phase, the rate of the chemical reaction is determined only by its chemical kinetics

Since is a chemical process, it is necessary to define which chemicals the model will work with. This setup is done in the Fluid Block, where the desired chemicals are selected from the chemical library. In our case, these are Propylene, Isobutane, and 2,3-dimethylpentane. This mixture will behave according to the thermodynamic properties of the Non-Random Two-Liquid equilibrium system.

In the Chemical Model block, we need to define a chemical reaction. The rate of the chemical reaction is determined by the Arrhenius equation

$$k = Ae^{-\frac{E}{RT}} \tag{3.2}$$

where: k - rate constant, A - Arrhenius factor, E - activation energy, R - universal Gas Constant and T - thermodynamic temperature. The concentration of the i^{th} component at each time can be expressed using differential equations of the form:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \nu k \prod_{i=1}^{m} C_i \tag{3.3}$$

where C is the Concentration of the i^{th} component where the concentrations appearing on the right-hand side of the equation are the reactants, ν is the stoichiometric coefficient, for the reactants it is negative (the concentration of the reactants decreases), and for the products, it is positive (the concentration of the products increases)

When creating complex mathematical models, it is important to start with simpler models and gradually progress towards more complex ones. This approach helps to avoid potential errors and makes debugging easier. Similarly, we constructed the mathematical model for the alkylation unit by beginning with the simplest possible option and building upon it. The model contained a single contactor in which only one chemical reaction took place. The temperatures of the streams entering the devices were not adjusted by heat exchangers. The distillation column contained a low number of stages. After a functional simple version of the model was created, heat exchangers were gradually added, the number of contactors was increased, and the model parameters were adjusted according to the real ones so that the model was as close as possible to the actual operation. In the real process, the cooling of contactors by the reaction of mixtures is used. First, a reducing valve is used to reduce its pressure which causes a temperature drop due to the Joule-Thomson effect. For simplicity, the mathematical model takes advantage of the possibility of adjusting the temperature by using an internal heat exchanger in the reactor block. The created mathematical model is shown in Figure 3.3.

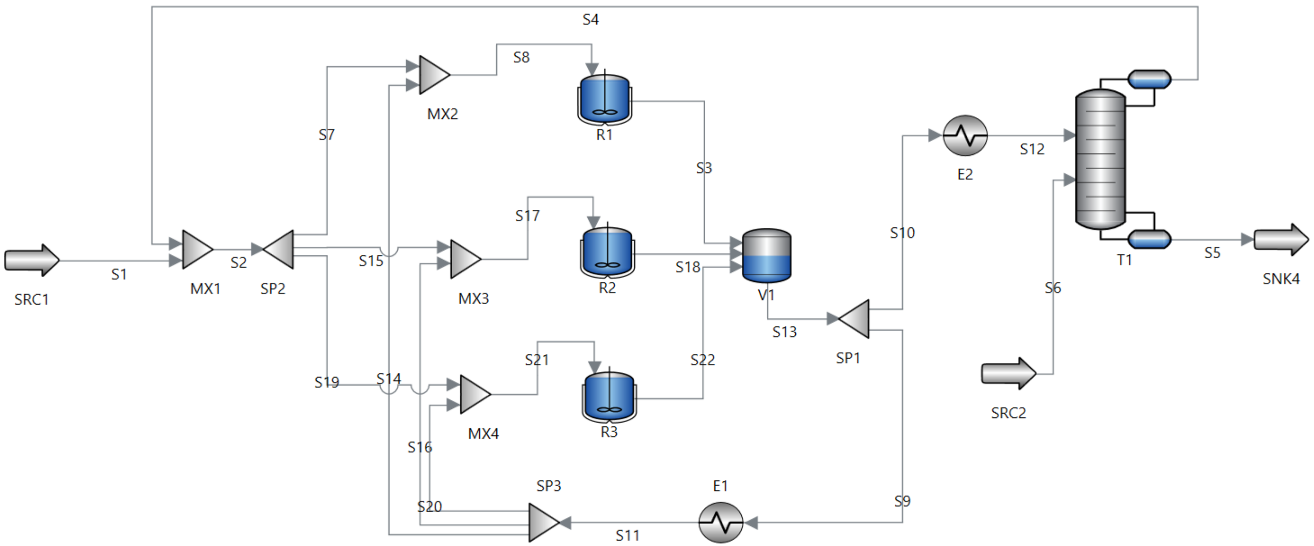


Figure 3.3: Created mathematical model in AVEVA process simulation environment

The constructed mathematical model is shown in Figure 3.3. It can be divided into three main parts.

Mixing part: The incoming olefins are mixed with the recirculating isobutam from the distillation column. The blended mixture is split into three branches to which the refrigerant recycle is added.

Reaction part: The mixed reactants enter the contactors to form the alkylate product. The product stream is led from all reactors to a collection tank and then divided into two parts. The first part is cooled and mixed with the feedstock as a refrigerant recycle. The second part is heated and led to the deisobutanizer.

Separation part: The product stream from the reaction section leads into the distillation column and fresh isobutane is added too because part of it has reacted. The distillate is mixed with the feedstock as isobutane recycling. The distillation residue contains the desired product, alkylate.

3.2.2 Model Validation

After constructing the mathematical model, it is crucial to evaluate its accuracy and determine the level of deviation from the actual process. To measure the accuracy, we have used the quantity of isobutane present in the refrigerant stream which is fed back to the contactors. We selected this stream because it contains a measurement for flow rate and composition. It is important in terms of controlling the amount of isobutane in the system. In Figure 3.3, this stream is identified as S9. Verification of the model was carried out in one simulation where the parameters and inputs of the model were adjusted according to the average value of the operational data that were collected over one day. The simulation result showed that the amount of isobutane in this stream differs from the real value by 15.3%.

3.3 Process Optimization

Process optimization is an important part of any operation to obtain the highest purity and quantity of product at the lowest possible operating cost. Since alkylate production takes place in chemical reactors, it is important to optimize their parameters. Among the most important are:

Spatial velocity of olefins: The Spatial velocity of olefins is defined as the volume of olefins in the feedstock per hour divided by the volume of acid in the contactor. This term is a measure of the concentration of olefins in the acid phase of the contactor. Reducing the space velocity of olefins increases the probability of isobutane reacting with olefins to produce a higher-quality product [9].

Temperature: Lowering the reaction temperatures increases the ratio of alkylation reactions relative to polymerization reactions. The temperature in the contactor for sulphuric acid alkylation should be maintained between 5°C and 13°C. Contactors can also be operated at temperatures above 18°C, the side effects of this high temperature are excessive polymerization, oxidation of olefins, acid dilution, and formation of alkyl sulfates [9].

Mixing: Isobutane is poorly soluble in sulfuric acid and therefore requires vigorous stirring to maximize surface area, which is crucial for better transfer of isobutane to the acid catalyst. Stirring ensures even temperature distribution along the entire contactor. [9].

Acid concentration: The concentration of the acid affects the quality of the alkylate. The best quality alkylate and the highest yields are obtained with an acid concentration of 93 to 96 weight percentages, 0.5 to 1.0 weight percentages water, and the remainder are acid-soluble hydrocarbons. In most cases, the octane loss results from operating at lower acid concentrations. However, there is a minimum concentration at which it is possible to operate (about 86 to 88 weight percentages of H_2SO_4). At concentrations below this limit, polymerization reactions begin to predominate [9].

Concentration of isobutane: Isobutane is only slightly soluble in acid, and olefins are well soluble, a high concentration of isobutane is needed to suppress the polymerization of olefins. Ratios of isobutane to olefins in the mixed feedstock are commonly in the range of 7:1 to 10:1. Critical ratios are below 5:1, when an uncontrollable decrease in acid concentration can occur. Under these conditions, undesirable polymerization reactions begin to predominate. [9].

When creating the model, we considered simplifications that must be taken into account in the optimization. Since we have neglected the catalyst, one of the most important parameters listed for the optimization, we can only use the high concentration of isobutane. In the comparison of the amount of isobutane to the other substances, it is in predominance and therefore influences not only the material but also the energy balance of the process. Therefore, it is the best candidate for optimization. The result of the optimization confirmed the assumption that by reducing the ratio of isobutane to olefins, energy is saved. The optimum ratio even with the considered limits is 7:1.

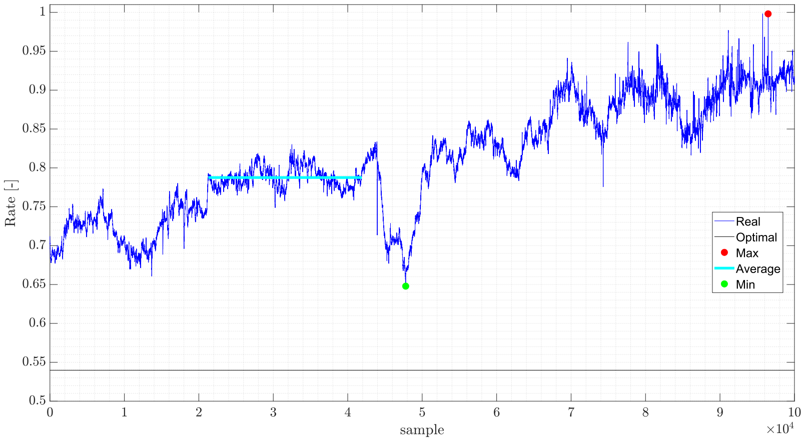


Figure 3.4: Normalized values of the ratio between isobutane and olefins.

In addition to the normalized isobutane to olefin ratio values, the regions labeled max, min, and mean are shown in Figure 3.4. We will examine these three regions in the context of the energy efficiency of the process operation. The premise of reducing the isobutane to olefins ratio is to achieve energy savings.

ΔE[kW]	E1	E2	Condenser	Reboiler
min	-59.0	176.5	-1129.6	941.9
max	-165.2	502.6	-3218.1	2712.9
average	-120.2	365.5	-2340.7	1767.8

Table 3.1: Energy consumption difference between real and optimal isobutane to olefins ratio.

The values in Table 3.1 express the amount of excess energy that needs to be supplied compared to the process if it were operated at the optimum isobutane to olefin ratio. E1 and E2 are the heat exchangers shown in Figure 3.3. The condenser and reboiler are part of the distillation column block.

With a higher ratio of isobutane to olefins, there is more substance in the streams that must be preheated or cooled. As the ratio decreases, the energy cost of thermal pre-treatment also decreases. If the process were operated at the maximum ratio shown in Figure 3.4. The amount of energy required to heat the medium is 277.8 GJ/day and the amount of energy to be removed is 292.3 GJ/day.

CHAPTER 4

Conclusion

This work aimed to improve the energy efficiency of the operation of the alkylation unit by optimizing a mathematical model. The mathematical model was built in the AVEVA Process Simulation environment without a detailed study of the process schematics and some simplifications such as neglecting the cooling section, sulphuric acid, or the use of only one chemical reaction were made which could have reduced the accuracy of the model. The optimization method Data Reconciliation was applied to the process data. Its task was to adjust the mass balance of a selected part of the process and to remove the high influence of noise from the measurements. The validity of the simulation was verified by comparing the simulation data with process data obtained from a real production unit. Using the model, we investigated the energy efficiency of the process, which was related to the ratio of isobutane to olefins at the contactor inlet. By optimizing the ratio, we have reached a lower limit at which it is recommended to operate this process. We then compared the simulation results between the optimal ratio and three selected samples, denoted as min, max, and average. In the future, it can be used as the basis for a more accurate mathematical model that allows the simulation to be performed in dynamic mode and the process to be optimized with data collect in real-time.

Resumé

V alkylačnom procese sa vyrába z C4 nenasýtených uhľovodíkov alkylátový benzín, ktorý je veľmi cennou vysokooktánovou zložkou do automobilových benzínov. Veľkou výhodou je, že alkylát obsahuje iba parafinické uhľovodíky, ktoré pri spaľovaní v motoroch tvoria menej škodlivých emisií ako je to pri spaľovaní aromátov a olefínov. STRATCO alkylačný proces s chladením reakčnou zmesou a reakčné zariadenie (kontaktor) sú projektované tak, aby podporovali alkylačné reakcie a potláčali konkurenčné reakcie ako polymerizácia.

Cieľom tejto práce je vytvoriť matematický model v prostredí Aveva Process Simulation a zistiť ako pomer izobutánu ku olefínom vplýva na energetickú efektivitu procesu.

V STRATCO alkylačnom procese prebieha alkylácia olefínov s izobutánom v prítomnosti katalyzátora kyseliny sírovej za vzniku alkylátu. Chemické reakcie prebiehajú v kyselinovej emulznej fáze, kde sa olefíny kontaktujú s izobutánom. Kyselinovo-uhľovodíková emulzia sa udržiava intenzívnym miešaním kyseliny a uhľovodíkov v kontaktoroch.

Alkylačná jednotka sa v skratke skladá z niekoľký technologických stupňov ktoré sú:

- Reakčná sekcia - dochádza ku kontaktu reagujúcich uhľovodíkov a kyseliny sírovej (katalizátor) pri riadených podmienkach.
- Chladiaca sekcia - z jednotky sa odvádza reakčné teplo a ľahké uhľovodíky.
- Sekcia spracovania reakčného produktu - odstraňuje sa z reakčnej zmesi voľná kyselina, alkylsulfáty a dialkylsulfáty, aby sa zamedzilo korózii a úsadám.
- Frakcionačná sekcia - z reakčných produktov odstraňuje izobután, vracia sa naspäť do reakčnej sekcie a zostávajúce uhľovodíky sa rozdeľujú na jednotlivé produkty.
- Sekcia odplynového systému, odpadovej vody a kyselinového slopu - odplyňuje sa odpadová voda a využitá kyselina, upravuje sa pH odpadovej vody a neutralizujú sa kyslé odplynové prúdy pred tým, ako opustia výrobnú jednotku.

Aveva Process Simulation je inovatívne prostedie ktoré pomáha vyvíjať procesnú stránku digitálneho dvojčaťa za účelom preskúmať všetky potenciáli návrhu a kvantifikovať vplyv na udržateľnosť, realizovateľnosť a ziskovosť. Toto modelovacie prostredie zlepšuje používateľské skúsenosti, dostupnosť IT, zjednocuje mnohé spôsoby použitia do jedinej integrovanej platformy na navrhovanie a optimalizáciu procesného zariadenia.

Vytvorenie presného matematického modelu výrobnej jednotky je veľmi náročné, preto sme prijali isté zjednodušenia:

- Zjednodušenie výrobnej jednotky - uvažujeme systém, len s reaktormi a destilačnou kolónou deizobutanizérom
- Zanedbanie chladiacej sekcie - všetky materialové prúdy sú v kvapalnom skupenstve (okrem tokov v bloku destilačnej kolóny), teplota prúdov na vstupe do zariadení sa upravuje pomocou výmenníkov tepla, reakcia v reaktoroch prebieha pri izotermických podmienkach
- Ziejdnodušenie chemických reakcií - uvažujeme len jednu chemickú reakciu a to propylénu s izobutánom za vzniku 2,3-Dimethylpentane
- Zanedbanie kyseliny sírovej - v kontaktoroch je izobután s olefínmi v jednej kvapalnej fáze, rýchlosť chemickej reakcie je daná len jej chemickou kinetikou

Ak by sa matematický model vytvoril naraz, nemusel by fungovať a odstránovanie chýb by bolo komplikované. Preto pri vytváraní zložitých matematických modelov je dôležité postupovať od jednoduchším modelov k zložitejším.

Po zostrojení matematického modelu je potrebné zistiť do akej miery je presný a o koľko sa lýši od skutočného procesu. Pre ukazovateľ presnosti sme si zvolili množstvo izobutánu v prúde chladiva, ktorý je späť vedený do kontaktoroch. Verifikácia modelu prebehla v rámci jednej simulácii, kde sa parametre a vstupy modelu nastavili podľa priemernej hodnoty prevádzkových údajov v priebehu jedného dňa. Množstvo izobutánu medzi reálnou hodnotou a hodnotou zo simulácie sa lýši približne o 15.3%

Optimalizácia procesu je dôležitou súčasťou každej prevádzy z dôvodu získania produktu o čo navyšej čistote, množstve a pri použití čo najnišších prevádzkových nákladoch. Keďže produkcia alkylátu prebieha v chemickýchkých reaktorok je dôležité optymalizovať ich parametre. Konkrétne sme sledovali vply pomeru medzi izobutánom a olefínmi. Výsledky pozorovanie energetickej úspory medzi optimálnym a prevádzkovým pomerom je vyjadrený v tabuľke 3.1.

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