MODELING ACETIC ANHYDRIDE PRODUCTION FROM ACETONE WITH ASPEN PLUS

A MASTER'S THESIS
in
Chemical Engineering and Applied Chemistry
Atilim University

by

BASAM ISSA SALEM M ABOGHALIA

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MODELING ACETIC ANHYDRIDE PRODUCTION FROM ACETONE WITH ASPEN PLUS

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BASAM ISSA SALEM M ABOGHALIA

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FEBRUARY 2018

Approval of the Graduate School of Natural and Applied Sciences, Atilim University.

Prof. Dr. Ali Kara

Director

I certify that thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Atilla Cihaner
Head of Department

This is to certify that we have read the thesis "Modeling Acetic Anhydride production from Acetone with Aspen plus" submitted by "Basam Issa Salem M Aboghalia" and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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Name Last Name: Basam Issa Salem M Aboghalia

Signature:

ABSTRACT

MODELING ACETIC ANHYDRIDE PRODUCTION FROM ACETONE WITH ASPEN PLUS

Basam Issa Salem M Aboghalia
M.S., Chemical Engineering and Applied Chemistry
Supervisor: Asst. Prof. Dr. Enver Güler
February 2018, 91 pages

This study investigates the modeling of production of acetic anhydride from acetone with Aspen Plus software. The purpose of this study is to simplify the design of the suitable system to produce acetic anhydride at a high degree of purity as well as to study the operational variables such as temperature, pressure and their effects on the products. In the design, acetone initially decomposes to ketene and methane; then ketene reacts with acetic acid to produce acetic anhydride at high purity. All these steps are to be modeled with Aspen Plus software at specific conditions. First, to produce ketene, suitable conditions are determined for the cracking reaction of acetone. Second, suitable conditions are chosen to produce acetic anhydride by the reaction of ketene and acetic acid. Then, the effects of operational variables on the products by sensitivity analysis are studied. Finally, the sensitivity analysis has been studied to find out the effects of the variables on the mole fractions of products providing the optimum conditions.

Keywords: Acetic anhydride, acetone, Aspen Plus, ketene, acetic acid.

ÖZ

ASPEN PLUS İLE ASETONDAN ASETİK ANHİDRİT ÜRETİMİNİN MODELLEMESİ

Basam. Issa Salem M Aboghalia
Yüksek Lisans, Kimya Mühendisi ve Uygulamalı Kimya
Tez Yöneticisi: Yrd. Doç. Dr. Enver Güler
Şubat 2018, 91 sayfa

Bu çalışma asetondan, Aspen Plus yazılımıyla, asetik anhidrit üretimini incelemiştir. Bu çalışmanın amacı yüksek saflık seviyesinde asetik anhidriti üretmek için uygun bir sistem tasarımını basitleştirmek ve aynı zamanda ürünler üzerindeki etkileri ve basınç gibi operasyonal değişiklikleri incelemektir. Tasarımda, aseton ilk adımda ketine ve metana ayrışır, ardından ketin yüksek saflıkta asetik anhidrit üretmek üzere asetik asit ile reaksiyona girer. Bütün bu adımlar Aspen Plus yazılımı ile özel koşullar altında yapılmıştır. İlk olarak, spesifik ketin üretmek asetonun kraking reaksiyonu için uygun şartlar seçilmiştir. Ardından, ketin ve asetik asit arasında tepkimeyle asetik anhidrit üretmek için uygun şartlar seçilmiştir. Daha sonra, hassasiyet analiziyle ürünler üzerinden operasyonal değişikliklerin etkileri incelenmiştir. Son olarak, değişkenlerin üretimin mol fraksiyonu üzerindeki etkileri bulunmuş ve en iyi şartları seçmek için de hassasiyet analizi gerçekleştirilmiştir.

Anahtar kelimeler: Asetik anhidrit, aseton, Aspen Plus, ketin, asetik asit

To My Parents

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my thesis supervisor Asst. Prof. Dr. Enver Güler for his kind support, guidance, understanding, encouraging advices, constructive criticism and valuable discussions throughout my thesis.

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LIST OF ABBREVATIONS

PFR - Plug Flow Reactor

CSTR - Continuous Stirred Tank Reactor

RECT - Rectifying column

UNIFAC - Universal Functional Activity Coefficient

PPM - Part Per Million

hr - Hour

CHAPTER I

INTRODUCTION

1.1 Research Background

In research and industry, acetic anhydride is one of the most important organic intermediates [1]. Acetic anhydride, which is also named as Ethanoic anhydride or methyl carboxylic anhydride, has some features similarity with acetic acid in its pungent and acrid odour, a colorless liquid, viscosity, density and refractive index. C. F. Gerhardt was the first to synthesize acetic anhydride in 1852 by the reaction of benzoyl chloride and molten potassium acetate, as it does not occur naturally. About 40% of the acetic anhydride was produced globally by utilizing the Vinyl production process.

Acetic anhydride has a lot of applications, where the most important one is manufacturing the Aspirin, which is a highly important medicine. As same as Aspirin, acetic anhydride is used in production of acetanilide, which is used as a starting material in the manufacture of some sulpha drugs. Acetic anhydride is also used in manufacture of perfumes, herbicides, acetyl peroxide bleach and plasticizers. All those application are directly affected by chemical and physical properties of acetic anhydride.

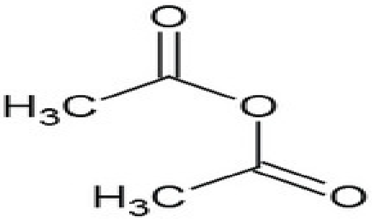


Figure 1.1: Molecular structure of acetic anhydride.

Generally, two manufacturing processes are used to produce acetic anhydride. The ketene acetic acid technology is the most common production process, which includes thermal cracking acetic acid to ketene. Then the subsequent reaction of the ketene with additional acetic acid to form acetic anhydride. The second method is the methyl acetate carbonylation process, where acetic acid is produced as a co-product [2]. The French chemist Charles Frederic Gerhardt (1816–1856) was the first to synthesize acetic anhydride by heating potassium acetate with benzoyl chloride [3]. Due to the increase in the demand for acetic anhydride to producing cellulose acetate, in 1922, Wacker Chemie developed acetic anhydride production from acetic acid and ketene [2, 4].

The research aim is to model, design and simulate a suitable system to produce acetic anhydride at high degree of purity, where the acetone is decomposed to ketene and methane as the first step. In the second step, the ketene reacts with acetic acid to produce acetic anhydride at high purity. All these steps are simulated by Aspen plus software and under a specific condition.

1. Specific and suitable condition to produce ketene is chosen at a high mole fraction from acetone.

2. Find out suitable condition to produce acetic anhydride by reaction between ketene and acetic acid.

1.1.1 Research Objectives

The research objectives can be classified as follows:

- To understand and study the production process of acetic anhydride.
- To simulate the production process with Aspen Plus software.
- To design a system with the smallest number of units.
- To study the operational variables and their effects on the product to get the product at high purity.
- Approximately acetic anhydride production is 26600 tons/year with a purity at least 99.4%.

1.1.2 Research methodology and content

This research focuses on modeling acetic anhydride production from acetone with Aspen Plus. The study involves five chapters,

1. Chapter one includes the introduction, research objectives, methodology, acetic anhydride properties, applications and acetic anhydride reactions.
2. Chapter two involves acetic anhydride productions, including acetaldehyde oxidation, then methyl acetate carbonylation, dehydration of acetic acid and acetone cracking. In addition, research theory and introduction to the Aspen plus.

3. Chapter three, named as modeling, is divided into two parts. The first part is production model, which includes setup, properties, components, method and simulation with three steps. The second part includes sensitivity analysis, this part studying the effect of process parameters such as temperature and pressure of stream flow rate to plug flow reactor. As well as sensitivity of step 2 temperature and mass flow of condenser, and finally sensitivity of step 3, which are reactor temperature and pressure.
4. Chapter 4, which is results and discussions of research. In this chapter, modelling results, data and graphs are presented. Acetic anhydride production process was discussed in term of sensitivity.
5. Chapter five includes research conclusions and recommendations.

1.2 Properties of Acetic Anhydride

Acetic anhydride is known as a colorless liquid that has a highly offensive smell. The molecular weight of acetic anhydride is 102.1 g/mol. It boils at a temperature 139 C° and melts at a temperature of -73 C°. The density of acetic anhydride is 1.08 g/cm^3. Regarding reactivity, acetic anhydride likes to react with water and alcohol. It can react with water, which is known as a hydrolysis reaction, which leads to the formation of acetic acid, also known as vinegar. Besides being reactive, it is also characterized as a combustible compound. This simply means that under specific conditions, acetic anhydride can become ignitable and create a fire risk. It is worth noting that acetic anhydride does have toxic properties. This must be considered prior to the handling and utilize of this compound. Chemical and physical properties of acetic anhydride [1, 5]. Are as follows:

- Molecular Formula: $C_4H_6O_3$
- Structural Formula: $(CH_3CO)_2O$
- Molecular Weight: 102.09
- Boiling point (760 mmHg): 138.6 C° (282 F°)
- Freezing point: -73C° (-100 F°)
- Vapor pressure: 4 mm Hg at 20 C°; 100 mm Hg at 36 C°
- Odor Threshold: 0.14 ppm
- Flammable limits in air,
- Flash point: 52.5-53 C° (closed cup); 124-130 F°
- Autoignition Temperature: 315-331 C° (629 F°)
- Specific gravity: 1.082 - 1.083 (at 20 C°)
- Vapor density: 3.5 (air = 1)
- Solubility in water: 2.6 wt% at 20C°
- Evaporation Rate: 0.46
- Stability: Stable in dry air

1.3 Applications of Acetic Anhydride

Acetic anhydride reactivity of the acetyl group is utilized to synthesize product and intermediates in the chemical industry [6]. Acetic anhydride is commonly used in industrially for its acetylating and dehydrating properties [6-8]. The main utilizing is acetylation of cellulose to produce acetate fibers, coatings, plastics and films. In addition, where acetic acid can not be used, acetic anhydride is especially valuable for the direct esterification of alcohols. A more common use of acetic anhydride is in medical manufacture, such as; acetylsalicylic acid (aspirin), sulfa drugs, as well as acetylcholine hydrochloride, sulfonamides, cortisone, theophylline, acetanilide, certain vitamins and hormones.

In plasticizers industry, acetic anhydride is used in production of acetyl ricinoleates, acetyl tributyl citrate and triacetin. Moreover, the tri acetic glycerol esters is used in plastics and paint industry. In addition, in perfumery, it is used as fixatives and as solvents for fungicides and basic dyes [9, 10]. In addition, acetic anhydride can be used as solvent for electric current producing cell systems [11]. Furthermore, the acetic anhydride is used in the agro-industries and food [12-15].

CHAPTER 2

PRODUCTIONS METHODS OF ACETIC ANHYDRIDE

2.1 Production of Acetic Anhydride

This part introduces the most common acetic anhydride productions processes in industry:

2.1.1 Acetaldehyde oxidation

Acetic anhydride can be produced by the acetaldehyde oxidation process as well as co-produces acetic acid. The conditions of production reaction are 60º C at 1 atm pressure, also 70º C at 6 atm. The air or oxygen is used for the oxidation purpose. In fact, cobalt acetate catalyst is promoted by copper acetate, where production reaction is through the oxidation of acetaldehyde to produce acetic acid, then another reaction for acetic acid with acetic acid to produce acetic anhydride as showing in 2.2. In addition, to maintain at 95-98 % purity, the overall selectivity of acetaldehyde requires the addition of acetic acid. In order to produce higher ratios, vapor should promptly be produced from the reactor to get rid of catalyst from the product mixture. Some isotropic solvents like ethyl acetate can also enhance water vaporization from the reaction zone [16].

$$CH_3CHO + O_2 \rightarrow CH_3COOOH \qquad 2.1$$

$$CH_3COOOH + CH_3CHO \rightarrow (CH_3CO)_2O + H_2O \qquad 2.2$$

When acetic anhydride reaches, water is immediately transferred to acetic acid again, as showing in reaction 3.3:

$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$ 2.3

The heat reaction can be adequately be to used vaporize the product and reconvert acetaldehyde as well. Because of the low vapor pressure of the reaction products, there is a need for high recycling of low oxygen content off-gas for stripping.

2.1.2 Methyl Acetate Carbonylation

Similar to acetaldehyde oxidation, acetic anhydride can be produced by methyl acetate carbonylation [17-19], as well as, by oxidation of methanol [20]. The first reaction is methanol acetylation, which is essential in anhydride manufacture by carbonylation. This step has been performed by the reaction between acetic acid and methanol to produce methyl acetate as shown in equation 2.4. After that, methyl acetate is reacted with CO. Acetic anhydride resulted from reaction as shown in equation 2.5:

$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$ 2.4

$CH_3COOCH_3 + CO \rightarrow (CH_3CO)_2O$ 2.5

Some components such as rhodium chloride tri-hydrate, methyl iodide, chromium metal powder and alumina support or nickel carbonyl complex with tri-phenyl phosphine, methyl iodide and chromium hexa-carbonyl can be involved in the catalyst stream for the methyl acetate carbonylation process. In methyl acetate carbonylation, the main operating problem catalyst is recovery, where rhodium is highly expensive metal. In addition, every trace should be recovered, otherwise it may lead to high economic losses. In that case, additional process might be required for the recovery of the catalyst, which makes the production process costly. In the World, only about 15% of the acetic anhydride is produced by methyl acetate carbonylation. Moreover, this production process is still in a developing phase [21-23].

2.1.3 Dehydration of Acetic Acid

By the thermal decomposition of acetic acid, acetic anhydride can be produced. Acetic acid dehydration at 15-20 kpa pressures and temperature nearly 700 ºC can produce the ketene, as shown in equation 2.6. Then in equation 2.7 shows the reaction of acetic acid with ketene at a temperature of nearly 50ºC, the acetic anhydride formed [23-25]:

$$CH_3COOH \rightarrow CH_2{=}CO + H_2O \qquad 2.6$$

$$CH_2{=}CO + CH_3COOH \rightarrow (CH_3CO)_2 \qquad 2.7$$

In the first step, dehydration catalyst tri-ethyl phosphate is commonly used, where water was formed in this reaction, ammonia is produced as an exit gas, and the water is neutralized. In the second step, about 30% aqueous ammonia is utilized as a solvent and water makes the reaction smooth. Overall, the small amount of water that is introduced is not significant. Nickel reacts with carbon monoxide yielding a highly toxic metal carbonyl. In this process, the acetic acid pyrolysis tubes are required to be made from nickel-free alloys, such as; ferrochrome alloy and chrome-aluminium steel. The acetic acid process is the one most common production process, which is generally used to produce acetic anhydride. In fact, acetic acid process is being selected as a production process due to its advantages that are not available with the other processes of manufacturing. Moreover, ketene easily reacts with acetic acid to produce acetic anhydride. About 85% of the acetic anhydride produced in the world is being manufactured by dehydration of acetic acid, hence production process is economically and practically more feasible.

2.1.4 Acetone cracking (Research theory)

Acetone cracking is one of the production processes that can produce acetic anhydride. Acetone cracking involves some steps, such as; cracking acetone to ketene and methane as first step, which is done in a pyrolysis heater at about 700 ºC and 1.5 atm pressure as shown in equation 2.8. In next step, as shown in reaction 2.9, ketene reacts with acetic acid to produce acetic anhydride. This reaction achieves 20-25% of acetone. These reactions taking place is:

$$CH_3\text{-}CO\text{-}CH_3 \rightarrow CH_2{=}CO + CH_4 \qquad 2.8$$

$$CH_2{=}CO + CH_3COOH \rightarrow (CH_3CO)_2O \qquad 2.9$$

This study model tries to deal with some process problems, where acetone is relatively expensive, and methane is produced through a process, which is very harmful and extra measures needs to be taken to remove it. Moreover, during acetic acid dehydration process, coke formation at the severe process conditions is a serious issue. The low conversion that demands more heater duty for the ketene produced is considered one of disadvantages as well.

2.2 Aspen Plus

Aspen Plus can be defined as process flow sheet simulator. The flow sheet simulator known as computer software, which is used to quantitatively model a chemical processing plant [26]. Generally, the reactor unit and several additional unit operations are chemical processing plants, which are form of the pre- and post-treatment steps [27, 28]. Moreover, Aspen Plus is considered as very powerful tool, which is utilized for the following:

1. Simulation
2. Optimization
3. Data regression
4. Design specifications
5. Sensitivity analysis
6. Operation system that based on calculation tasks
7. Solids handling, dynamics and control
8. Safety compliance
9. Process economic analysis

As an acronym, ASPEN stands for Advanced System for Process ENgineering. The flow sheet simulation is the main base of ASPEN. In latest versions Aspen was replaced by Aspen Plus. The entire chemical process starts from the raw material to the final finished product, which is the mechanism of this simulation. There are several icons provided with a symbolic representation, where each one of them stands for a unit operation, chemical process, input or output material stream, input or output energy stream, or input/output electric.

Process modeling and simulation describes a given real physical process by a set of linearly independent algebraic/differential equations, such that the number of written equations is be equal to the number of variables, such as; kinetic [29, 30]. Generally, writing such equations stems from:

- Extensive thermodynamic properties (balance equations) like mass, mole, and energy.
- Thermodynamic relationships for reacting and non-reacting medium like phase and chemical equilibrium.
- Rate correlations for momentum and heat
- Mass transfer
- Reaction stoichiometry
- Kinetic data
- Physical constraints imposed on the process.

2.3 Research Theory

The research theory is modeling, simulating and designing acetic anhydride production from acetone with Aspen Plus software. This process contains some sub-processes preparations and reactions.

2.3.1 Process discretion

This section briefly describes the acetic anhydride production process that follows in this study and defines the suitable operational variables and their effects on the production process. Due to the acetone produced, the research production process of acetic anhydride is not a direct method. For that reason, the production processes modeling involves three consecutive steps.

- **First step:**

Cracking reaction of acetone to methane and ketene.

- **Second step:**

Separation process (separate ketene from other products).

- **Third step:**

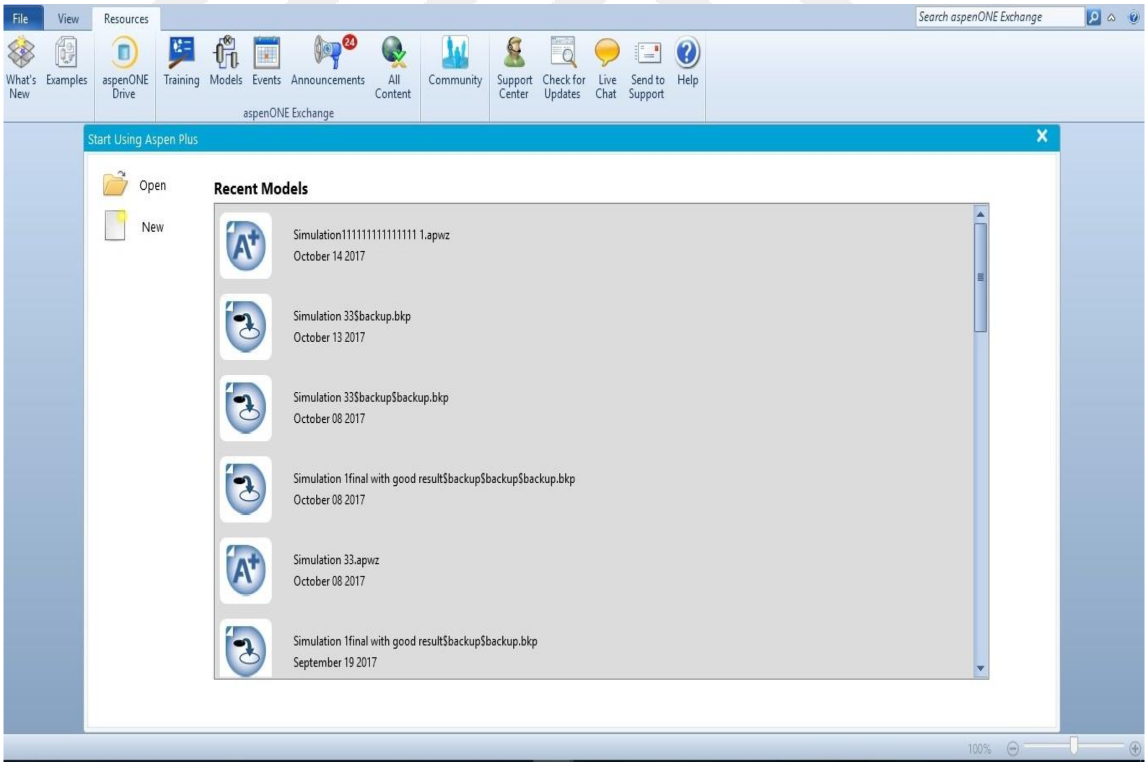
Acetic anhydride production (Reaction of ketene with Acetic acid).

CHAPTER 3

MODELING ACETIC ANHYDRIDE PRODUCTION FROM ACETONE WITH ASPEN PLUS

3.1 Entering Components and Property Method.

The aspen plus software is run as an administrator through opening its folder from the start menus and right-clicking for additional options. Based on that, the program is opened through a new window as shown in Figure 3.1.



Recent Models

Simulation111111111111111 1.apwz
October 14 2017

Simulation 33$backup.bkp
October 13 2017

Simulation 33$backup$backup.bkp
October 08 2017

Simulation 1final with good result$backup$backup$backup.bkp
October 08 2017

Simulation 33.apwz
October 08 2017

Simulation 1final with good result$backup$backup.bkp
September 19 2017

Figure 3.1: Selection of new simulation

Two main options are provided, which is opening an old model or starting a new model, which opens subsequent windows that guide the user towards constructing the required model, as shown in Figure 3.2.

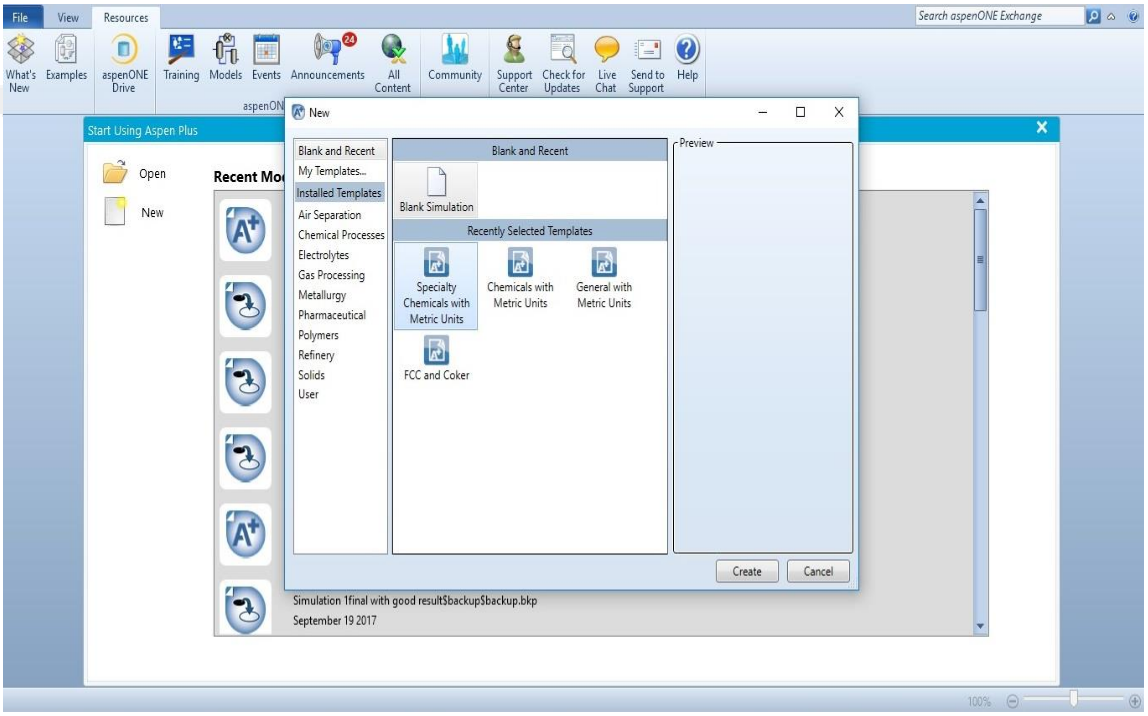
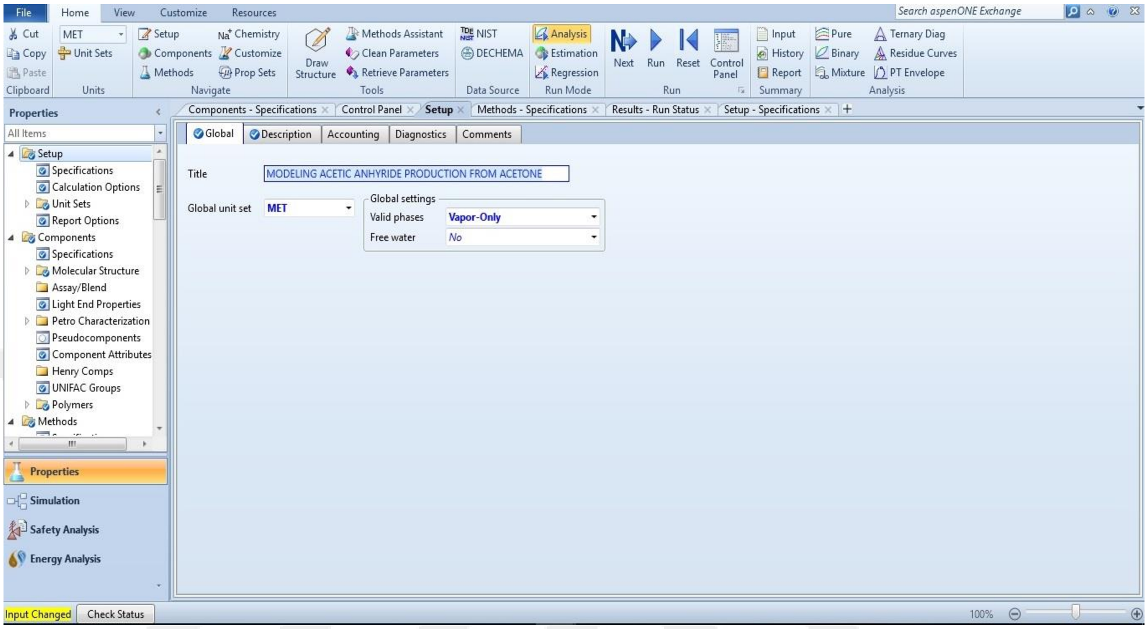


Figure 3.2: Creating specialty chemicals with metric units templates.

By clicking on “New”, clicking “specialty chemicals with metric units” template, and clicking “create” at the right bottom of the window, the new model is set up. From “Navigation” pane and under “Properties” environment, the title of the project is specified as “Modeling Acetic Anhydride production from Acetone” under the “setup” then “Global” options, as shown in Figure 3.3.



Title: MODELING ACETIC ANHYDRIDE PRODUCTION FROM ACETONE

Global unit set: MET

Global settings

Valid phases: Vapor-Only

Free water: No

Figure3.3: Entering the title, global units and the valid phases

The valid phases is set as “vapor only” and the global units are chosen as metric units “MET”. In the “Navigation” pane, the folder “Components” then “Specification” is selected, which views the “Selection” window in order to define the components used in the model according to their chemical name and formula. The “Find” button at the bottom of the tab is another option that could be used to search for predefined components and formulas, as shown in Figure 3.4. The components are added as follows:

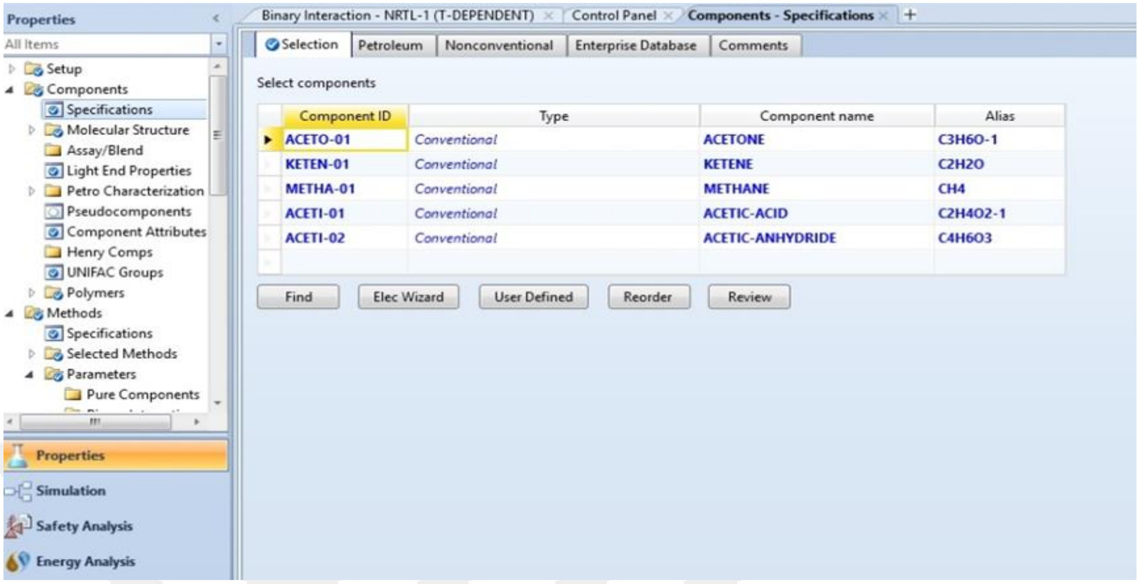
ACETO-01 for Acetone.

KETEN-01 for Ketene.

METHAN-01 for Methane.

ACETI-01 for Acetic Acid.

ACETI-02 for Acetic Anhydride.

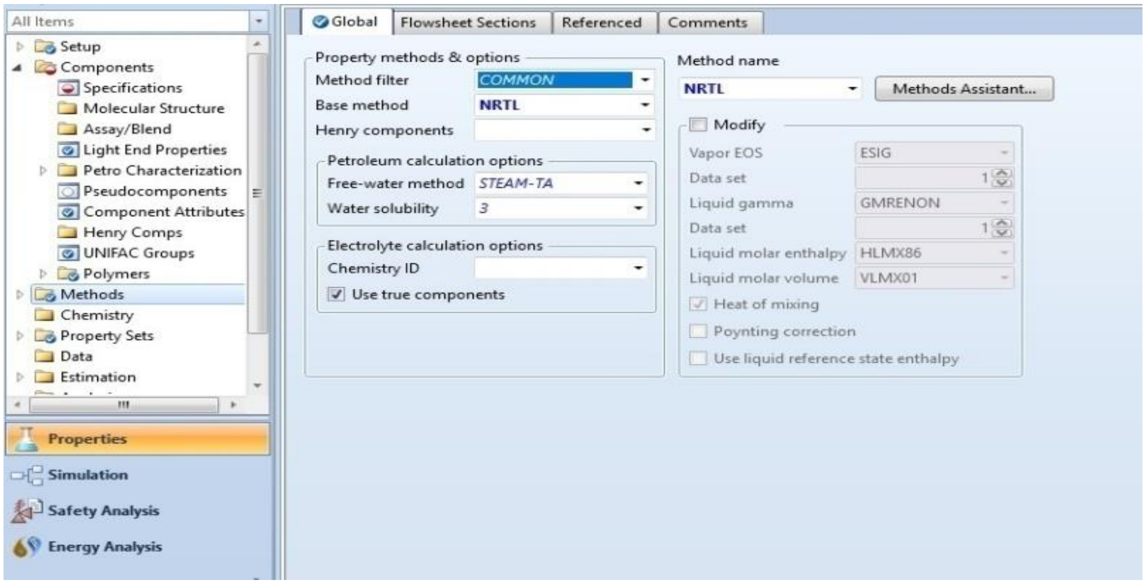


Select components

Component ID	Type	Component name	Alias
ACETO-01	Conventional	ACETONE	C3H6O-1
KETEN-01	Conventional	KETENE	C2H2O
METHA-01	Conventional	METHANE	CH4
ACETI-01	Conventional	ACETIC-ACID	C2H4O2-1
ACETI-02	Conventional	ACETIC-ANHYDRIDE	C4H6O3

Figure3.4. Entering the components of the reactions in the production of process.

Under “Properties” environment, In “Navigation” folder, the “Methods” folder is selected, followed by a clicking on “Specification”, which produces the “Global” sheet as shown in Figure 3.5.

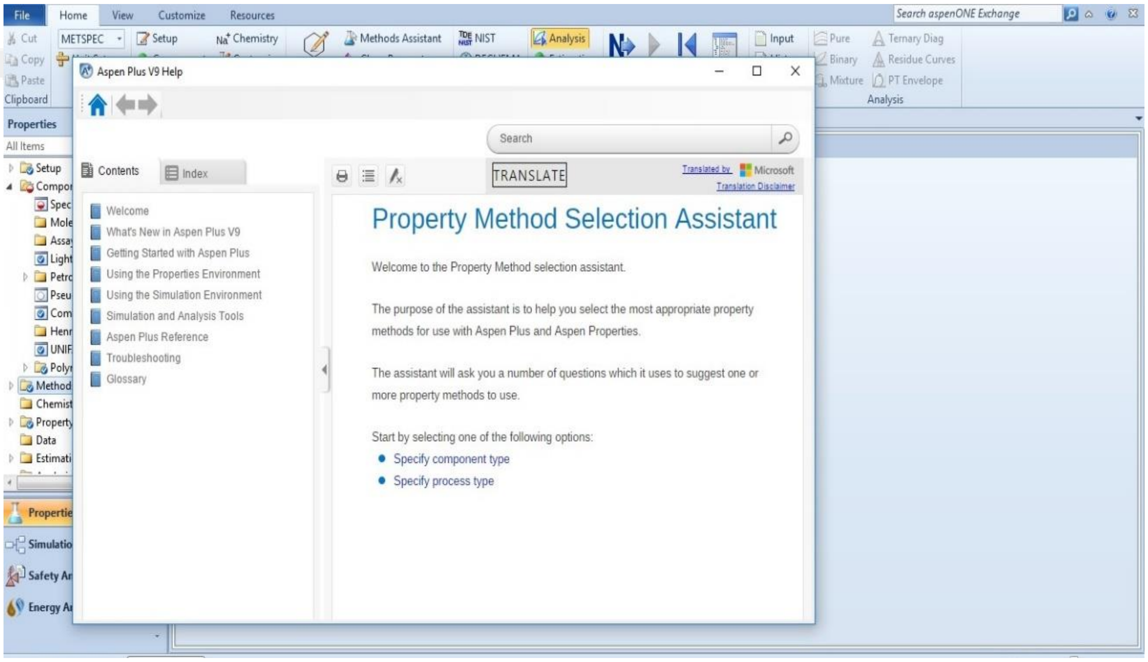


Property methods & options
Method filter: COMMON
Base method: NRTL
Henry components:
Petroleum calculation options
Free-water method: STEAM-TA
Water solubility: 3
Electrolyte calculation options
Chemistry ID:
☑ Use true components

Method name: NRTL
☐ Modify
Vapor EOS: ESIG
Data set: 1
Liquid gamma: GMRENON
Data set: 1
Liquid molar enthalpy: HLMX86
Liquid molar volume: VLMX01
☑ Heat of mixing
☐ Poynting correction
☐ Use liquid reference state enthalpy

Figure 3.5: Entering the method filter and the base method.

In the Global sheet, the method filter is selected as chemical and the base method as “WILS-NTH” or “NRTL-HOC”. In case of the undefined methods in the model problem, the “Property Method Selection Assistant” can be used by clicking on the “Methods Assistant” button as shown in Figure 3.6.



Property Method Selection Assistant

Welcome to the Property Method selection assistant.

The purpose of the assistant is to help you select the most appropriate property methods for use with Aspen Plus and Aspen Properties.

The assistant will ask you a number of questions which it uses to suggest one or more property methods to use.

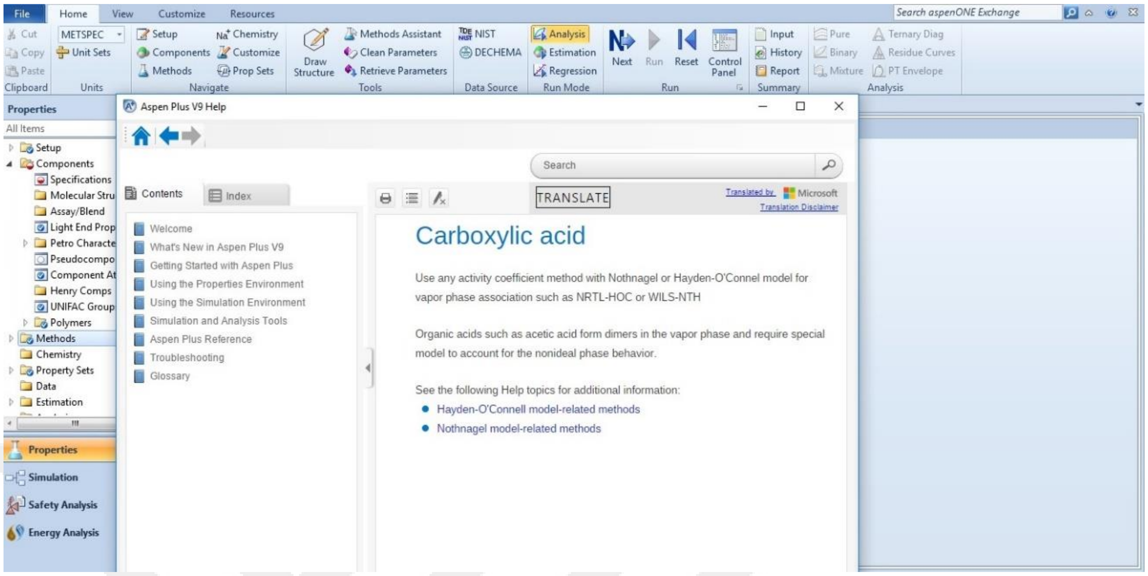
Start by selecting one of the following options:

- Specify component type
- Specify process type

Figure3.6: The selection assistant of property method

Several questions are asked by the assistant, which can define and suggest more property methods to use. The process starts by selecting “Specify component type” or “Specify process type”.

The type of process to be chemical is selected by clicking on “Carboxylic acids” as a subset of “Chemical” process. The assistant provides guidance to select either “NRTL-HOC” or “WILS-NTH” as shown in Figure 3.7.



Carboxylic acid

Use any activity coefficient method with Nothnagel or Hayden-O'Connel model for vapor phase association such as NRTL-HOC or WILS-NTH

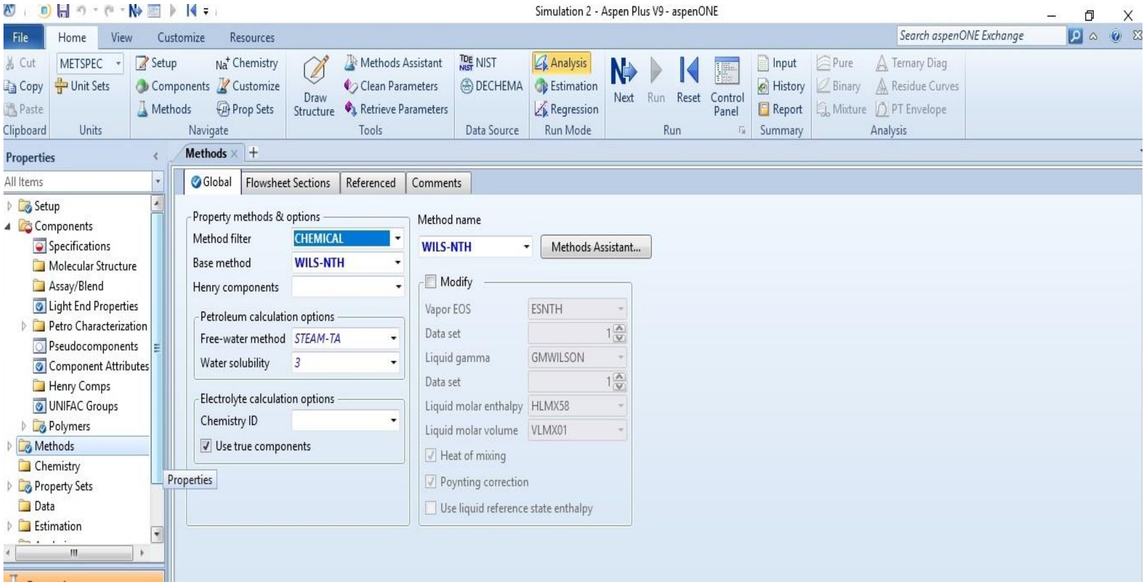
Organic acids such as acetic acid form dimers in the vapor phase and require special model to account for the nonideal phase behavior.

See the following Help topics for additional information:

- Hayden-O'Connell model-related methods
- Nothnagel model-related methods

Figure 3.7: The selection assistant of property method

By going back to the “Global” tab window from the “Method” folder, the method as “WILS-NTH” can be selected, as shown in Figure 3.8.



Property methods & options

Method filter: CHEMICAL

Base method: WILS-NTH

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true components

Method name: WILS-NTH

☐ Modify

Vapor EOS: ESNTH

Data set: 1

Liquid gamma: GMWILSON

Data set: 1

Liquid molar enthalpy: HLMX58

Liquid molar volume: VLMX01

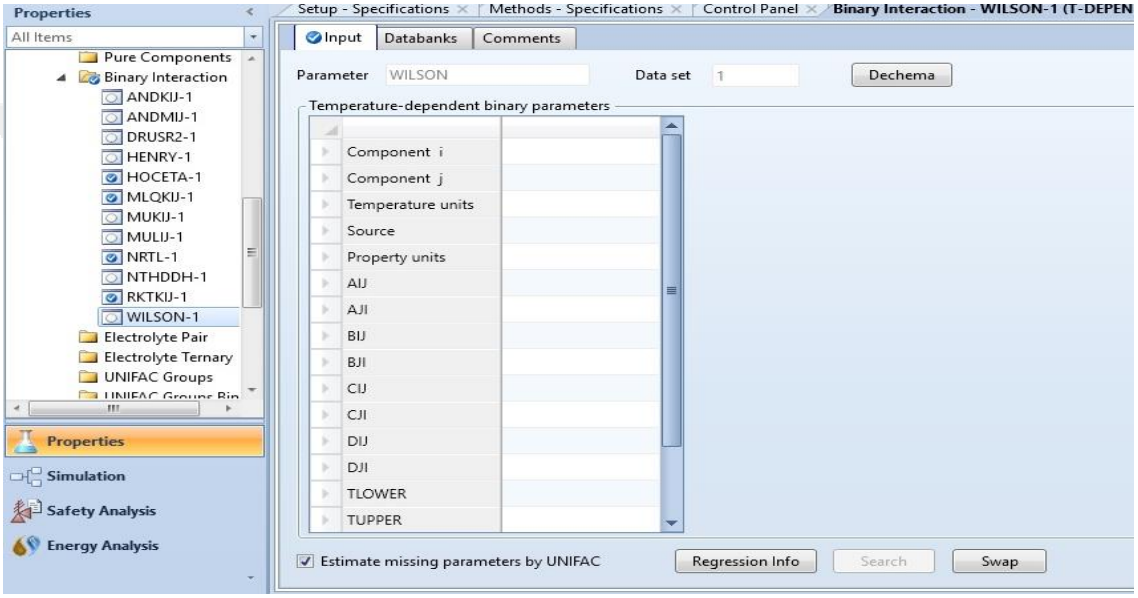
☑ Heat of mixing

☑ Poynting correction

☐ Use liquid reference state enthalpy

Figure 3.8: The recommendation by the “Property Method Selection Assistant” wizard the property method is set to “WLIS-NTH”

In the “Navigation” pane, it is important to ensure that the “Estimate missing parameters by UNIFAC” option is checked as shown in Figure 3.9, through clicking on “Methods” – “Parameters” – “Binary Interaction” – “WILS-1” sheet.



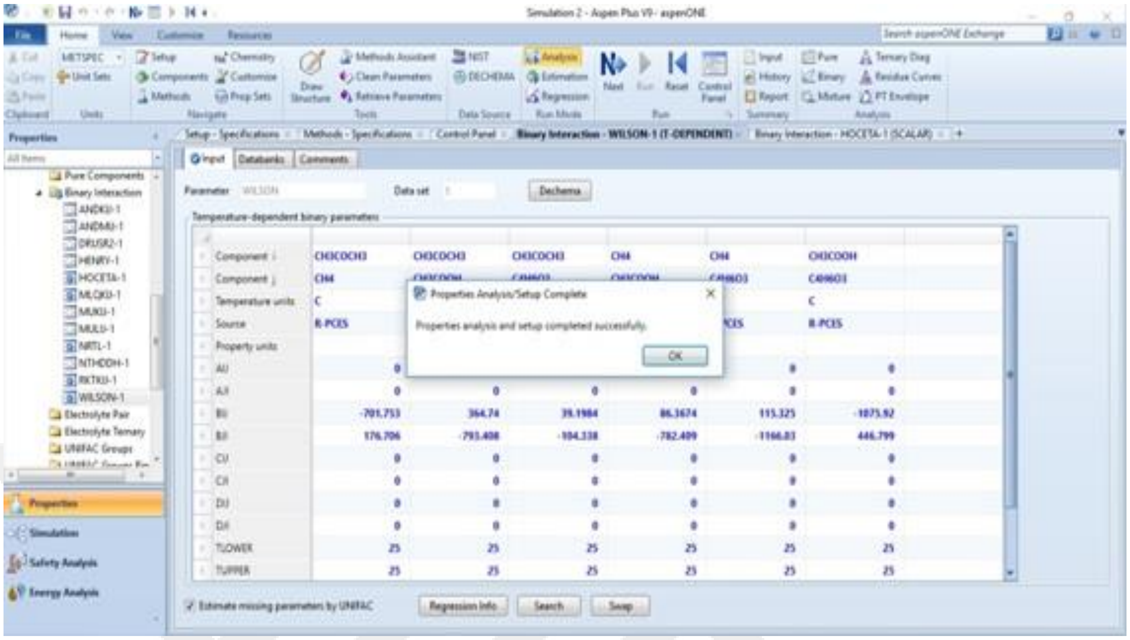
Parameter WILSON

Data set 1

☑ Estimate missing parameters by UNIFAC

Figure3.9: The estimate missing parameters by UNIFAC

The model can be run for simulation by clicking on “Reset” then “Next” buttons, which produces a message confirming the successful completion of the operation as shown in Figure 3.10.


Binary Interaction - WILSON-1 (T-DEPENDENT)

Parameter: WILSON Data set: 1

Temperature-dependent binary parameters

Component i	CH3COCH3	CH3COCH3	CH3COCH3	CH4	CH4	CH3COOH
Component j	CH4	CH3COOH	C4H6O3	CH3COOH	C4H6O3	C4H6O3
Temperature units	C	[illegible]	[illegible]	[illegible]	[illegible]	C
Source	R-PCES	[illegible]	[illegible]	[illegible]	R-PCES	R-PCES
Property units						
AIJ	0	[illegible]	[illegible]	[illegible]	0	0
AJI	0	0	0	0	0	0
BIJ	-701.753	364.74	39.1984	86.3674	115.325	-1075.92
BJI	176.706	-793.408	-104.338	-782.409	-1166.83	446.799
CIJ	0	0	0	0	0	0
CJI	0	0	0	0	0	0
DIJ	0	0	0	0	0	0
DJI	0	0	0	0	0	0
TLOWER	25	25	25	25	25	25
TUPPER	25	25	25	25	25	25

Properties Analysis/Setup Complete

Properties analysis and setup completed successfully.

☑ Estimate missing parameters by UNIFAC

Figure3.10: Model simulation completion message

By clicking on the “Next” button, another message appears that leads to the simulation sheet, which confirms the process by clicking on “Ok”. The simulation tab window is shown in Figure 3.11.

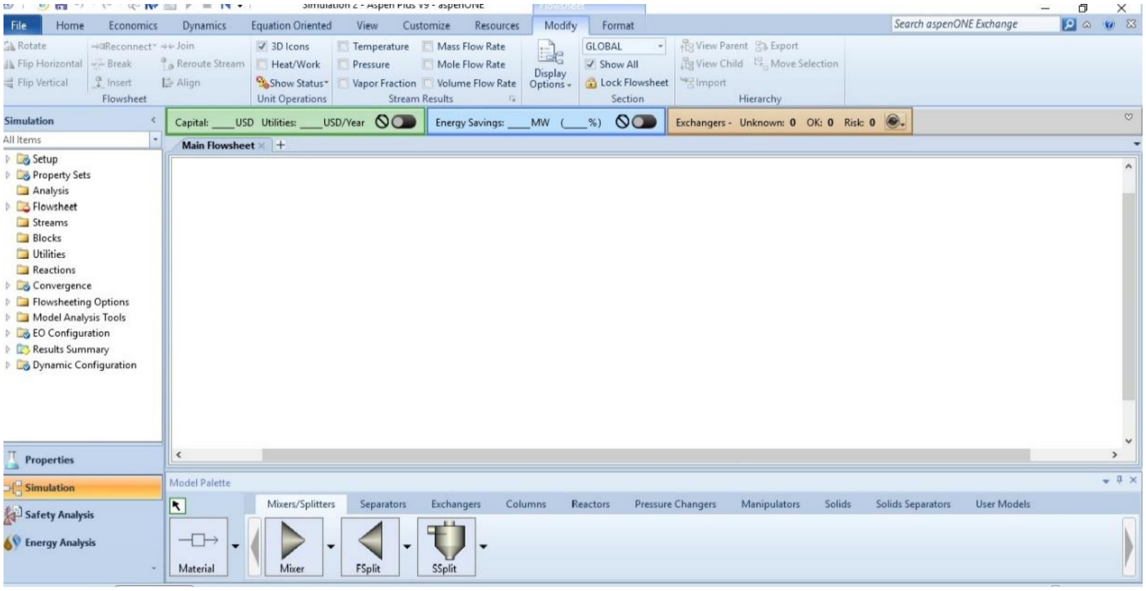


Figure3.11: The simulation sheet

3.2 The Rigorous “PFR” Plug-Flow Reactor.

The plug-flow reactor is added from the “Reactors” tab in “Model Palette” in the bottom of simulation tab window to the flow sheet. The flow sheet consists of one inlet stream, plug-flow reactor and one product stream, as shown in Figure 3.12.

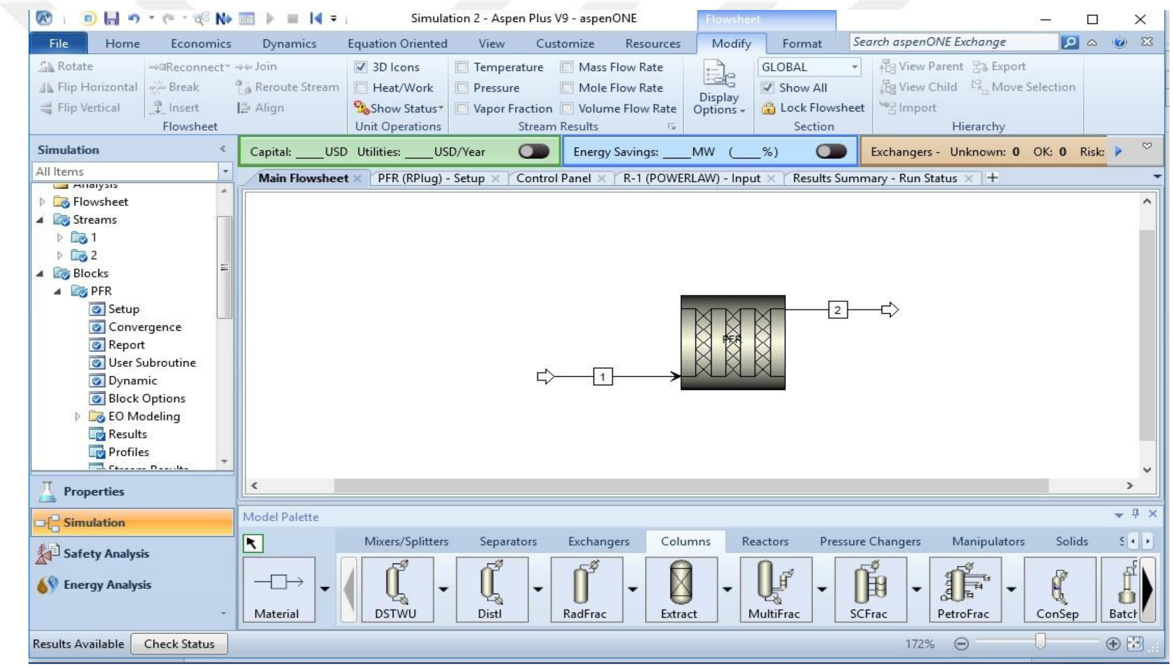


Figure3.12: The addition of “plug-flow reactor” to the flow sheet

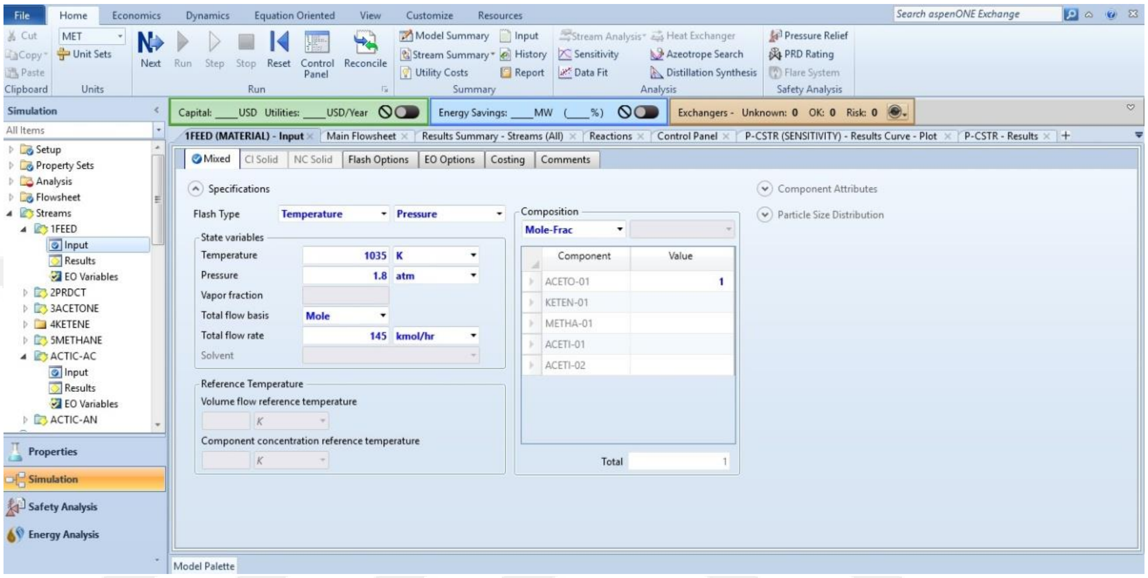
By clicking the “Next” button, Aspen plus opens the properties tab of the feed stream in order to enter the properties for this stream. The properties are entered as following:

Temperature: 1035 ºK

Pressure : 1.8 atm.

Total flow : 145 kmol/hr.

In the “composition” menu, as Figure 3.13, the “mass fraction” option is used to enter the mass fraction of Acetone to be 1.0, while leaving the mass fractions of ketene and methane as zero.



1FEED (MATERIAL) - Input

Flash Type: Temperature, Pressure

State variables

Temperature: 1035 K

Pressure: 1.8 atm

Vapor fraction:

Total flow basis: Mole

Total flow rate: 145 kmol/hr

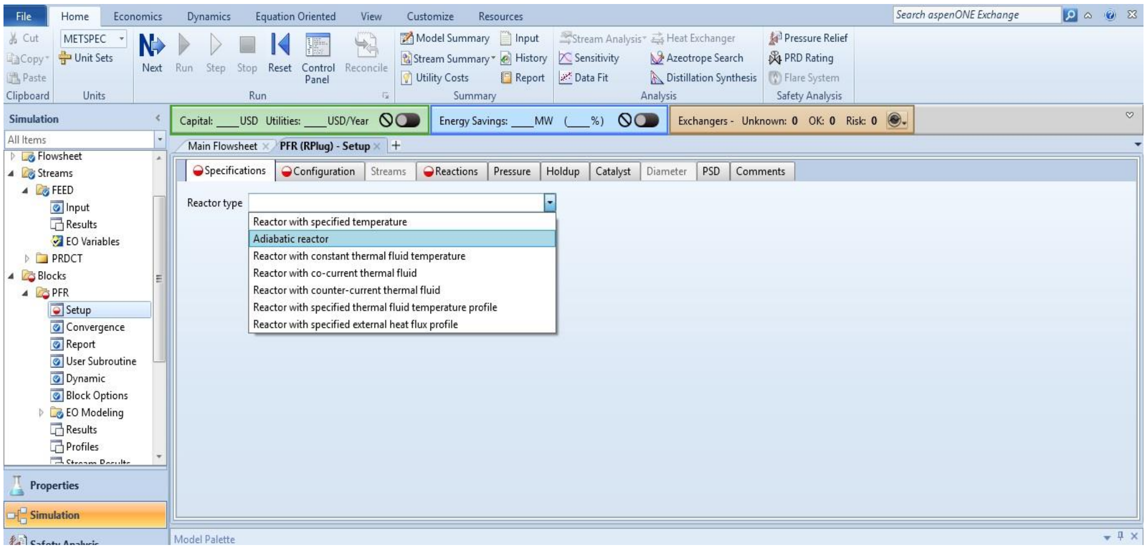
Composition: Mole-Frac

Component	Value
ACETO-01	1
KETEN-01	
METHA-01	
ACETI-01	
ACETI-02	

Total: 1

Figure 3.13: The properties of feed stream

After completing the entry of the mass fraction, clicking the “Next” button opens the “setup” window of plug flow reactor tab window. From “Specification” of this window, the “Reactor type” is selected to be “Adiabatic reactor” as in Figure 3.14.

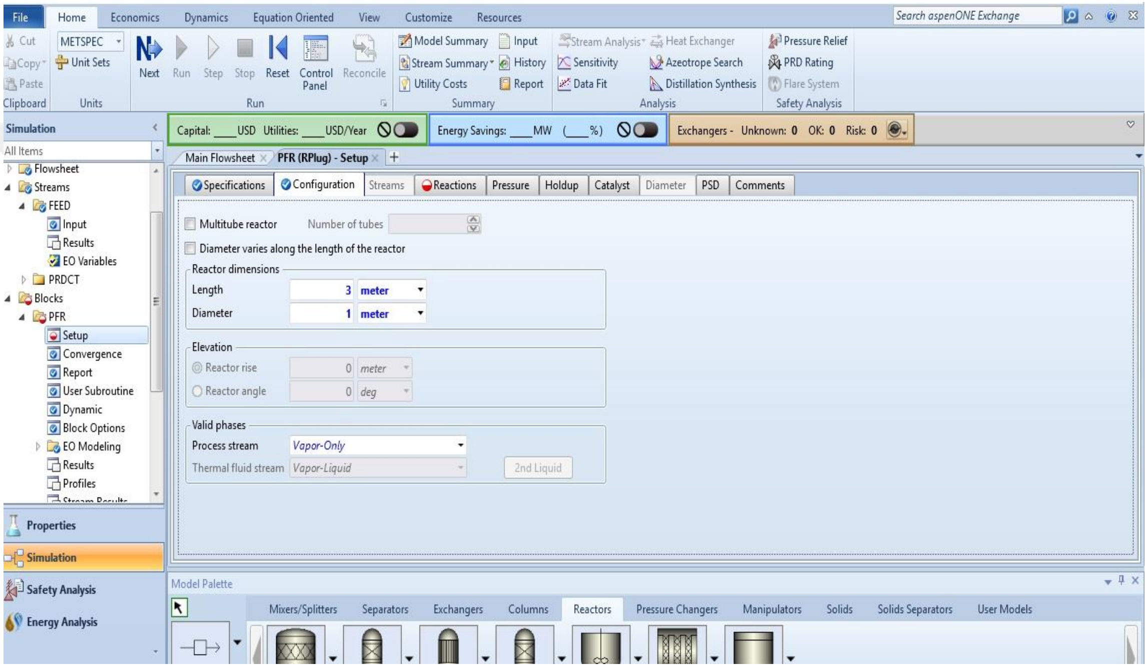


PFR (RPlug) - Setup

Reactor type: Adiabatic reactor

Figure 3.14: Choosing the type of reactor in the specification tab window

Clicking the “Next” button moves to the “configuration” tab in “plug flow reactor setup” tab window. From this window, the length in “Reactor dimensions” is entered to be 3 meters and the diameter 1 meter. Under the valid phase, “vapor only” is selected for process stream as shown in Figure 3.15.



☐ Multitube reactor Number of tubes

☐ Diameter varies along the length of the reactor

Reactor dimensions

Length 3 meter

Diameter 1 meter

Elevation

○ Reactor rise 0 meter

○ Reactor angle 0 deg

Valid phases

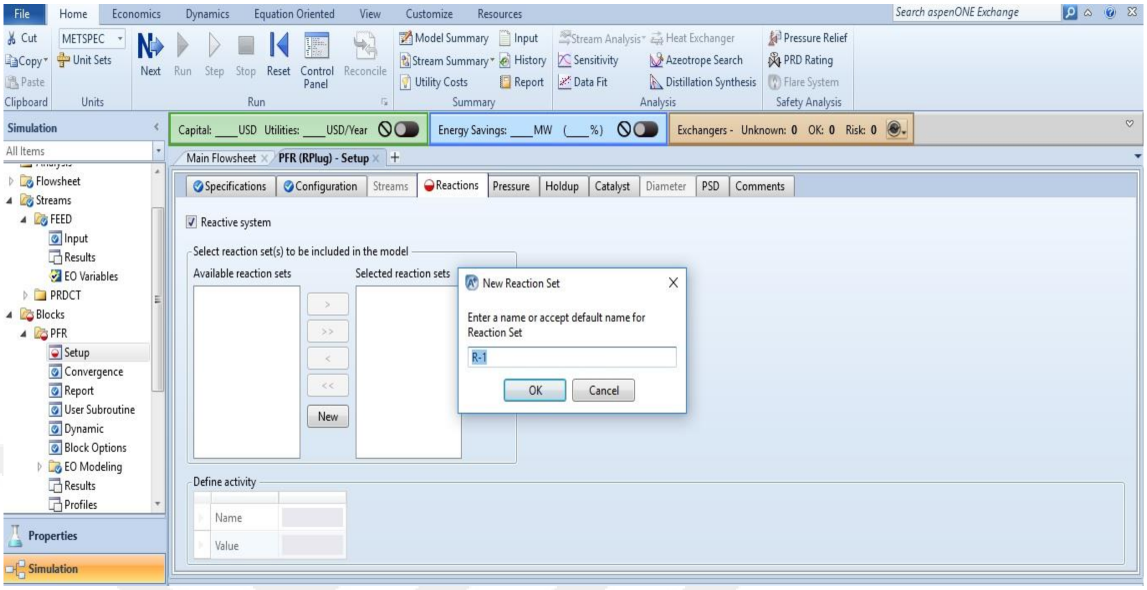
Process stream Vapor-Only

Thermal fluid stream Vapor-Liquid

Figure3.15: PFR configuration as a single-tube reactor

It is important to note that if the inlet pressure value is left “0”, then Aspen plus is instructed to let the inlet pressure equal to the feed stream pressure [31].

In order to create the reaction set “Reactions” tab in “plug flow reactor setup” tab window, the “next” button is clicked, then the “New” button is clicked to select new reaction, which starts another window to select the name of reaction as shown in Figure 3.16.



☑ Reactive system

Select reaction set(s) to be included in the model

Available reaction sets

Selected reaction sets

New Reaction Set

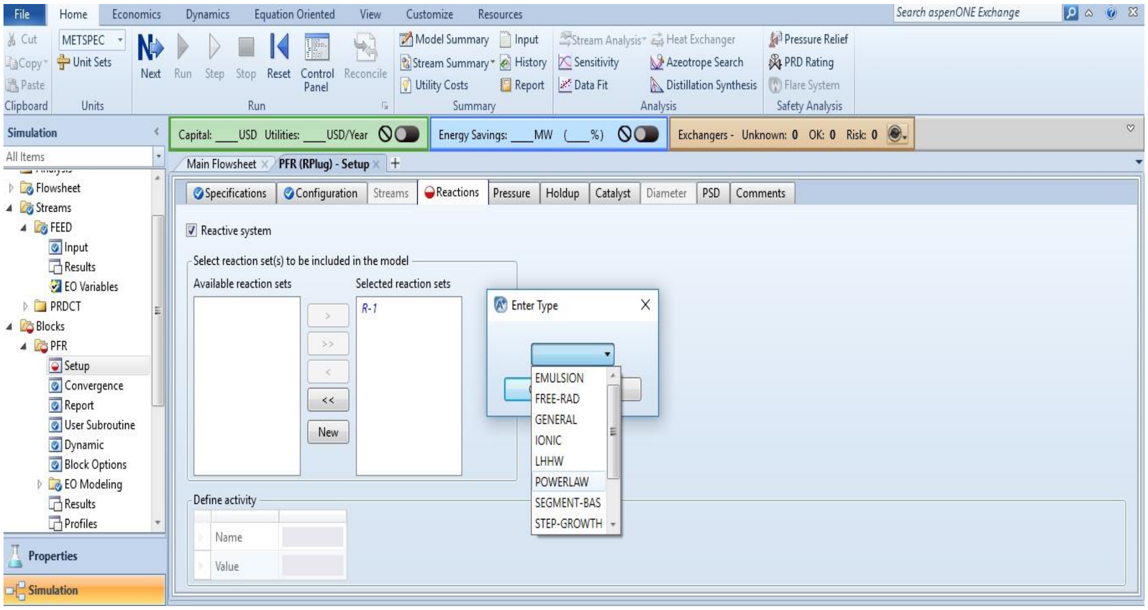
Enter a name or accept default name for Reaction Set

R-1

OK Cancel

Figure 3.16: Selection the name of reaction

By clicking “Ok”, Aspen plus requests the selection of the type of the reaction, which is selected for this research as “POWERLAW” and confirmed by clicking on the “Ok” button, as shown in Figure 3.17.



☑ Reactive system

Select reaction set(s) to be included in the model

Available reaction sets

Selected reaction sets

R-1

Enter Type

EMULSION
FREE-RAD
GENERAL
IONIC
LHHW
POWERLAW
SEGMENT-BAS
STEP-GROWTH

Figure 3.17: Selection the type of reaction

Through clicking on the “Next” button, the “Stoichiometry” tab opens in the “Reactions” tab window under “simulation” tab in “Navigation” pane as shown in Figure 3.18.

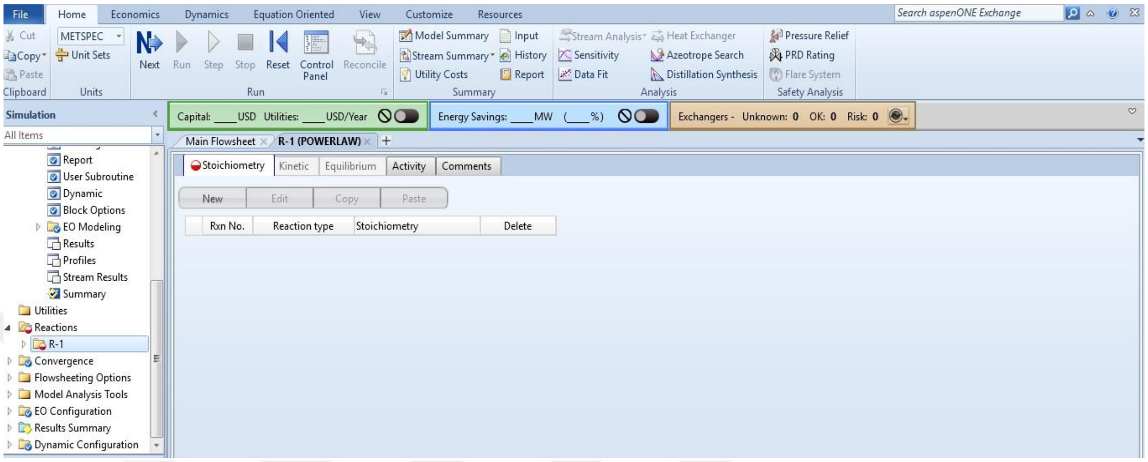
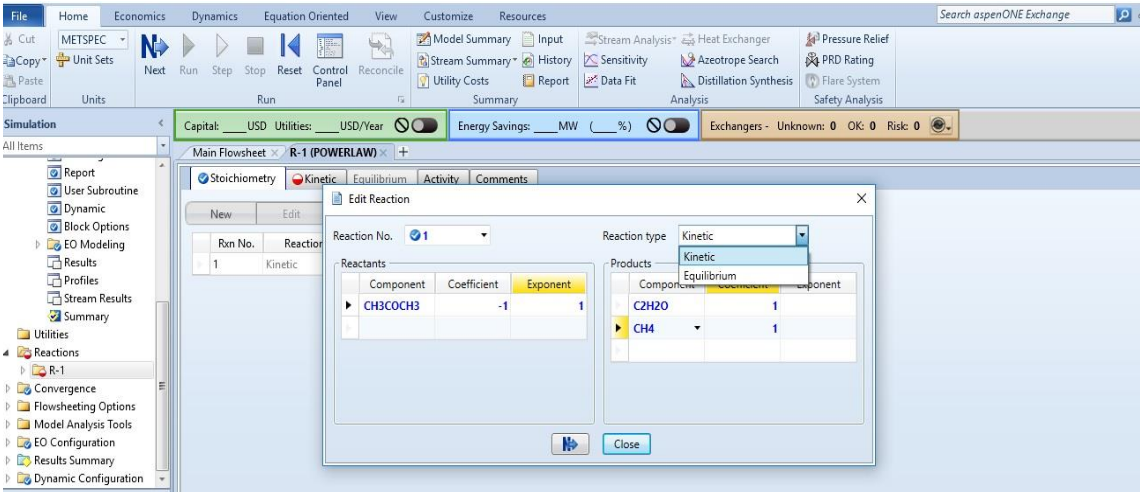


Figure 3.18: Stoichiometry tab in the “Reactions” tab window

After the completion of the previous operation, clicking the “New” button in the “Stoichiometry” tab window opens the “Edit Reaction” window, where the reaction equation, the stoichiometry, the order of reaction and its type kinetic or equilibrium are defined. The reaction order is selected as first-order, the type of reaction as kinetic and the others as shown in Figure 3.19



Reaction No. 1

Reaction type Kinetic

Reactants

Component	Coefficient	Exponent
CH3COCH3	-1	1

Products

Component	Coefficient	Exponent
C2H2O	1	
CH4	1	

Figure 3.19: Selection the equation, order, stoichiometry and type of reaction

The last step in this stage is the calculation of activation energy and reaction rate constant. The key of this calculation is taken from Chemical Engineering Application book (REFERENCE) and Elements of Chemical Reaction Engineering book, Fourth Edition (REFERENCE). The key of an acetic anhydride-manufacturing is the acetone vapor-phase cracking to ketene and methane. In addition, this reaction is first-order with respect to acetone and the specific reaction rate can be expressed by the formula below [31-33]:

$$ln\, k = 34.34 - \frac{34222}{T} \tag{3.2}$$

Where: k is in reciprocal seconds, and T is in Kelvin.

In this simulation step, the reaction rate constant and activation energy can be calculated by two ways according to equation 3.2.

1. The first method does not contain the reference temperature T_{0}:

$$ln\, k = 34.34 - \frac{34222}{T}$$

$$k = e^{34.34 - \frac{34222}{T}}$$

$$k = e^{34.34} \times e^{-\frac{34222}{T}} \tag{3.3}$$

$$k = 8.1973X10^{14} \times -\frac{34222 * R}{T}$$

$$\ln k = A \times e^{\frac{-E}{RT}}$$

$$k = 8.1973X10^{14} \times e^{\frac{-284522}{RT}}$$

So,

A = 8.1973×10^{14}

E = 284521.7 kJ/mol or J/mol.

2. The second method contains the reference temperature T_{0},

Let T_0= 1000 K

$$k = A \times e^{\frac{-E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}$$

$$k = A \times e^{\frac{-E}{R}(\frac{1}{T}-\frac{1}{1000})}$$

$$k = A \times e^{-\frac{E}{R}\left(\frac{1}{T}\right)} \times e^{-\frac{E}{R}(\frac{1}{1000})} \tag{3.4}$$

$$k = e^{34.34} \times e^{\frac{-34222}{T}}$$

Equal both equation 3.3 and 3.4 to become:

$$k = e^{34.34} \times e^{-\frac{34222}{T}} = A \times e^{-\frac{E}{R}\left(\frac{1}{T}\right)} \times e^{\frac{E}{R}(\frac{1}{1000})} \tag{3.5}$$

Equal the exponent terms on both sides, that contain 1/T to calculate E:

$$e^{\frac{34222}{T}} = e^{-\frac{E}{R}\left(\frac{1}{T}\right)} = \frac{-34222}{T} = -\frac{E}{R}\left(\frac{1}{T}\right)$$

$$E = R \times 34222 \tag{3.6}$$

E = 8.314 × 34222 = 284522 l kJ/kmol

Equal the constant of both sides of equation 3.4,

$$e^{34.34} = A \times e^{\frac{E}{R}(\frac{1}{1000})}$$

Value of E is substituted, which is calculated in equation 3.6,

$$e^{34.34} = A \times e^{\frac{284522}{8.314}\left(\frac{1}{1000}\right)}$$

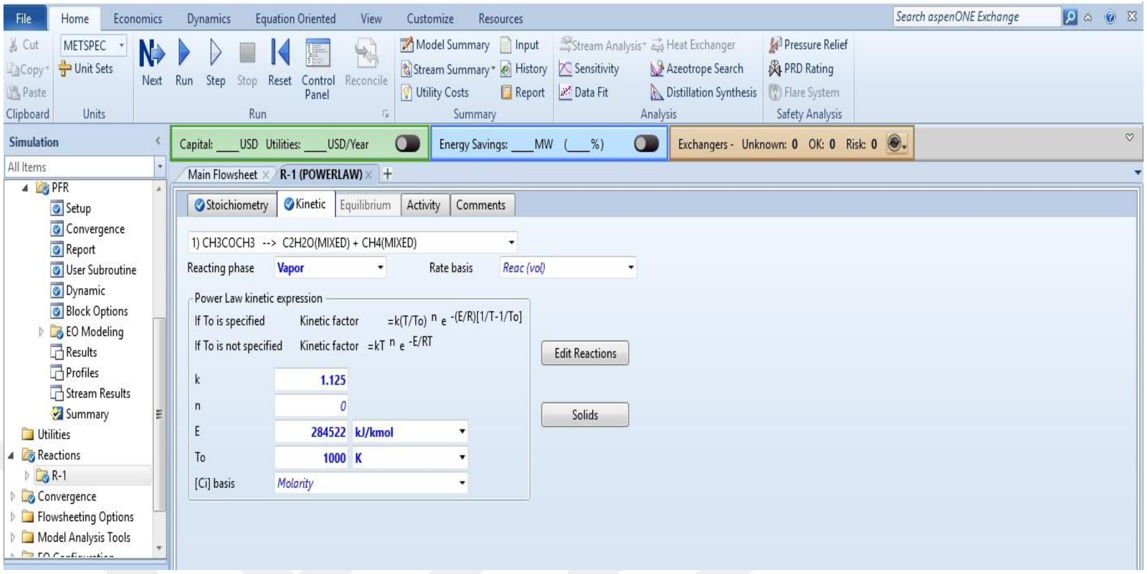
$$A = \frac{e^{34.34}}{e^{34222}} = e^{34.34-34222} = 1.125\ s^{-1}$$

By clicking the “Next” button to move to the “Kinetic” tab in the same tab window, the kinetic parameters are defined and the input data in this window are shown below:

The reaction constant is 1.125 or 8.19733e+14 for k.

The activation energy is 284,521.7 kJ/kmol for E.

The reference temperature T_o is 1000 K.



1) CH3COCH3 --> C2H2O(MIXED) + CH4(MIXED)

Reacting phase: Vapor

Rate basis: Reac (vol)

Power Law kinetic expression

If To is specified: Kinetic factor $=k(T/T_o)^n e^{-(E/R)[1/T-1/T_o]}$

If To is not specified: Kinetic factor $=kT^n e^{-E/RT}$

k: 1.125

n: 0

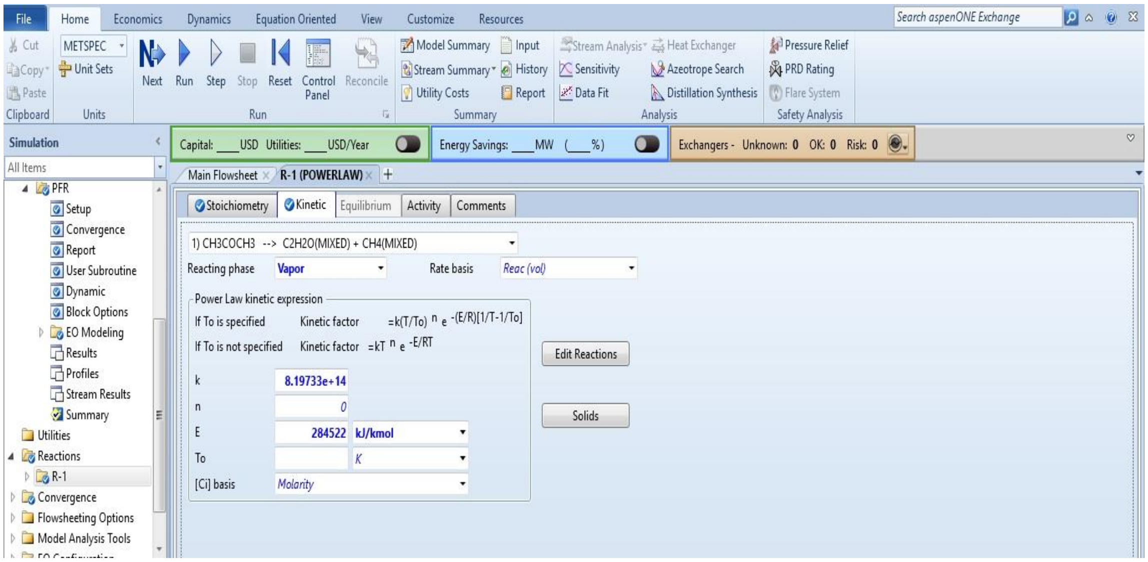
E: 284522 kJ/kmol

To: 1000 K

[Ci] basis: Molarity

Figure 3.20: Entering the kinetic parameters

It is important to note that if the value of k is entered as $8.19733e^{+14}$, the value for the reference temperature must be left empty in the space for T_o, and if the value of k is entered as 1.125, the reference temperature must be entered as 1000 K [22]. Figure 3.21 shows the details for the kinetic parameters.



1) CH3COCH3 --> C2H2O(MIXED) + CH4(MIXED)

Reacting phase: Vapor

Rate basis: Reac (vol)

Power Law kinetic expression

If To is specified: Kinetic factor $=k(T/T_o)^n e^{-(E/R)[1/T-1/T_o]}$

If To is not specified: Kinetic factor $=kT^n e^{-E/RT}$

k: 8.19733e+14

n: 0

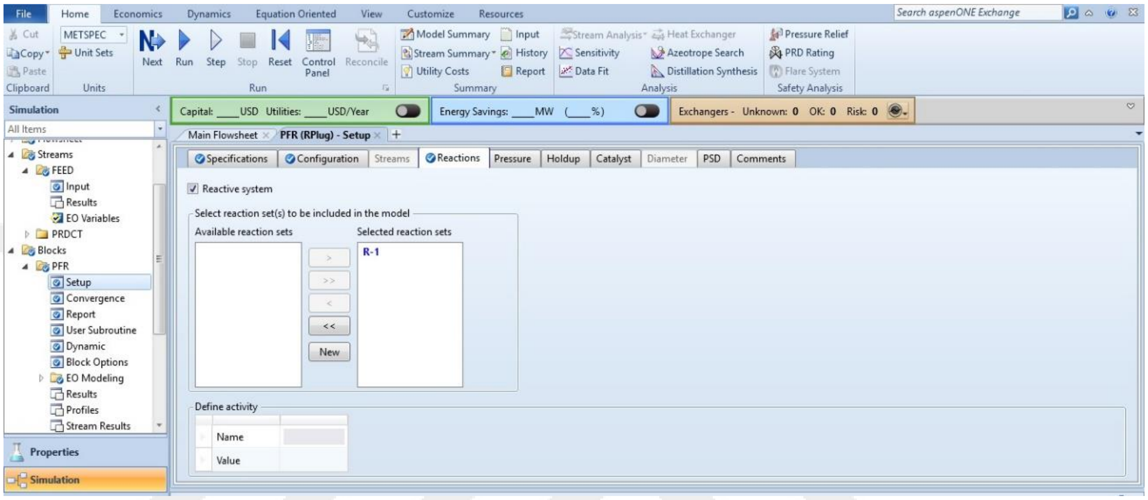
E: 284522 kJ/kmol

To: K

[Ci] basis: Molarity

Figure 3.21: Entering different kinetic parameters

After the completion of the kinetic parameters, clicking the “Next” button leads to the “Reactions” tab in the “Reaction” window of plug flow reactor setup tab window. In this window, the reaction that is named before as “R1” must be moved from the “Available reaction sets” to “Selected reaction sets” to activate this reaction, as shown in Figure 3.22.



☑ Reactive system

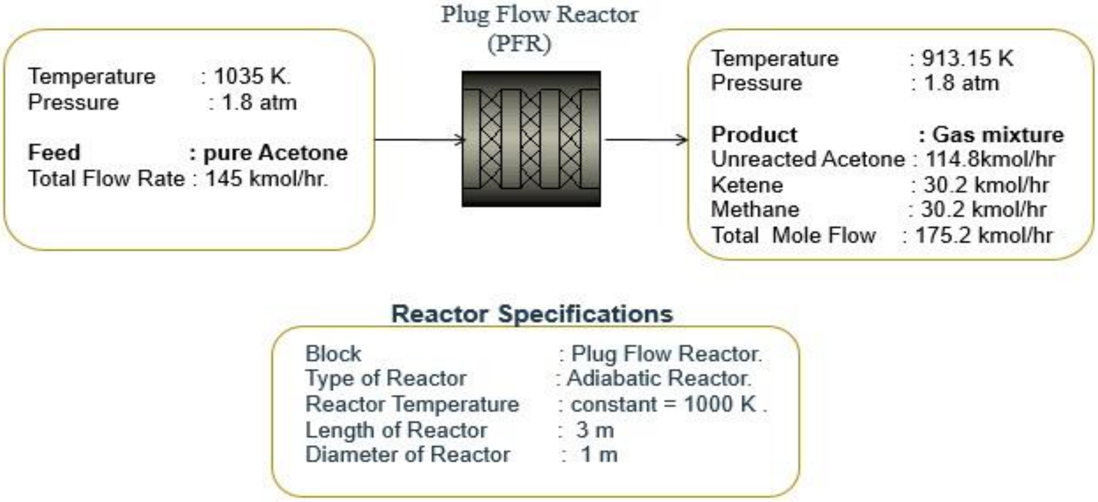
Select reaction set(s) to be included in the model

Available reaction sets	Selected reaction sets
	R-1

Figure3.22: The reaction activation

3.3 Running the Simulation for Plug Reactor (PFR).

After the completion of all the required data, clicking the “Next” button provides an account to start the calculation in this simulation. The window error appears in case of missing data or error. All the results of this process are shown in the chapter 4. Figure 3.23 shows the details of Plug Flow Reactor result.



Temperature : 1035 K.
Pressure : 1.8 atm

Feed : pure Acetone
Total Flow Rate : 145 kmol/hr.

Temperature : 913.15 K
Pressure : 1.8 atm

Product : Gas mixture
Unreacted Acetone : 114.8kmol/hr
Ketene : 30.2 kmol/hr
Methane : 30.2 kmol/hr
Total Mole Flow : 175.2 kmol/hr

Block : Plug Flow Reactor.
Type of Reactor : Adiabatic Reactor.
Reactor Temperature : constant = 1000 K .
Length of Reactor : 3 m
Diameter of Reactor : 1 m

Figure3.23: Plug Flow Reactor details

3.4 The addition and specification of RadFrac Rectifying Column (RECTIF).

As discussed in chapter 2, the outlet stream of plug flow reactor PFR consists of ketene, methane and unreacted acetone as a mixture. Therefore, the purpose of the addition of (RECT) is to separate ketene from the other components. In this part of the chapter the addition of rectifying column RECT in flow sheet as follows:

The rectifying column is added from the “Column” tab in “Model Palette” in the bottom of simulation tab window of the flow sheet, which consists of one inlet stream, rectifying column and three product streams, as shown in Figure 3.23.

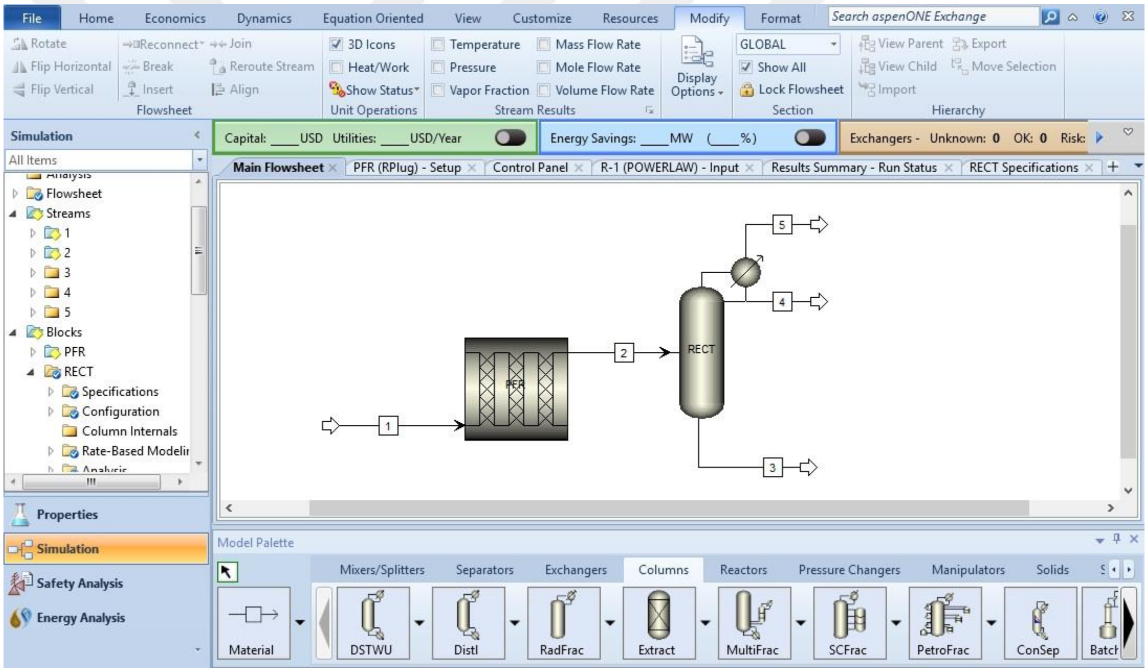
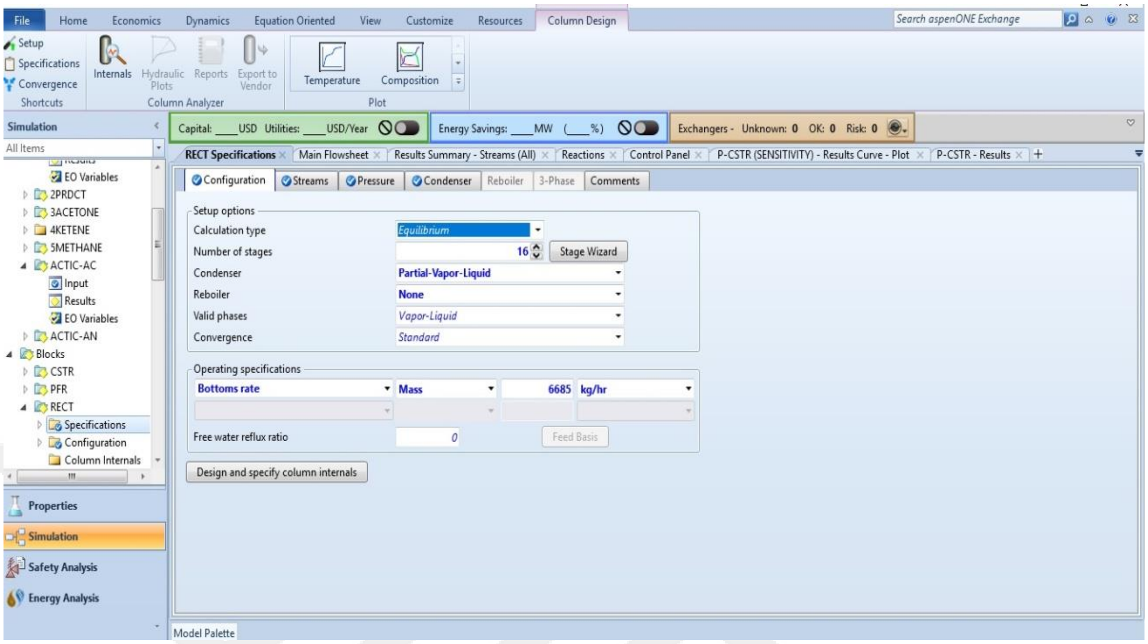


Figure3.24: The addition of Rectifying Column type (RECT)

By clicking the “Next” button, Aspen plus opens the “Configuration” tab of the specifications tab of rectifying column, in order to enter the properties for this column. The calculation type is selected as “Equilibrium”, the number of stage equal to 16, the condenser is “Partial-vapor-liquid” and, none re-boiler and the valid phase as “vapor-liquid”. The changing of the “Operating specifications” to “Bottoms flow rate” is the last step in this window. Figure 3.24 shows the configuration tab window.



Setup options

Calculation type: Equilibrium

Number of stages: 16

Condenser: Partial-Vapor-Liquid

Reboiler: None

Valid phases: Vapor-Liquid

Convergence: Standard

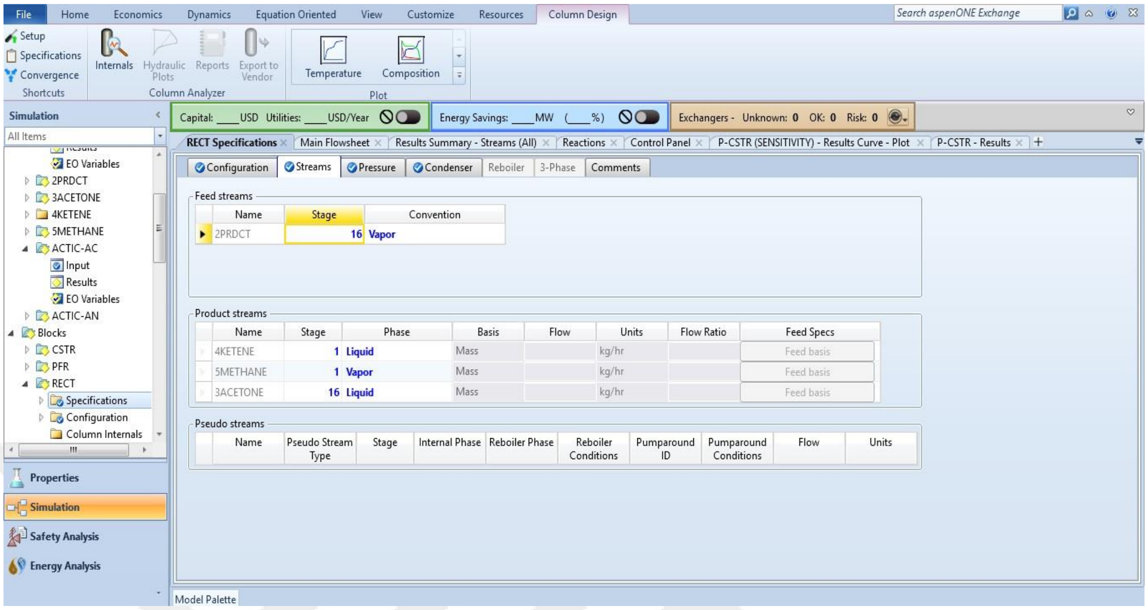
Operating specifications

Bottoms rate — Mass — 6685 — kg/hr

Free water reflux ratio: 0

Figure 3.25: Entering the configuration for Radfrac column

After the completion of configuration of the rectifying column, clicking the "Next" button leads to the "streams" tab in "specifications" window of rectifying column setup tab window. Here the location of the feed stream must be defined with respect to the top tray. Due to the lack of need of the re-boiler, the feed stream is introduced as a vapor at the bottom of the column, where the feed stream becomes available as the vapor phase throughout the entire rectifying column. The number of stages is 16. Figure 3.25 shows the number of stages, the location and the phase of the feed stream.



Feed streams

Name	Stage	Convention
2PRDCT	16	Vapor

Product streams

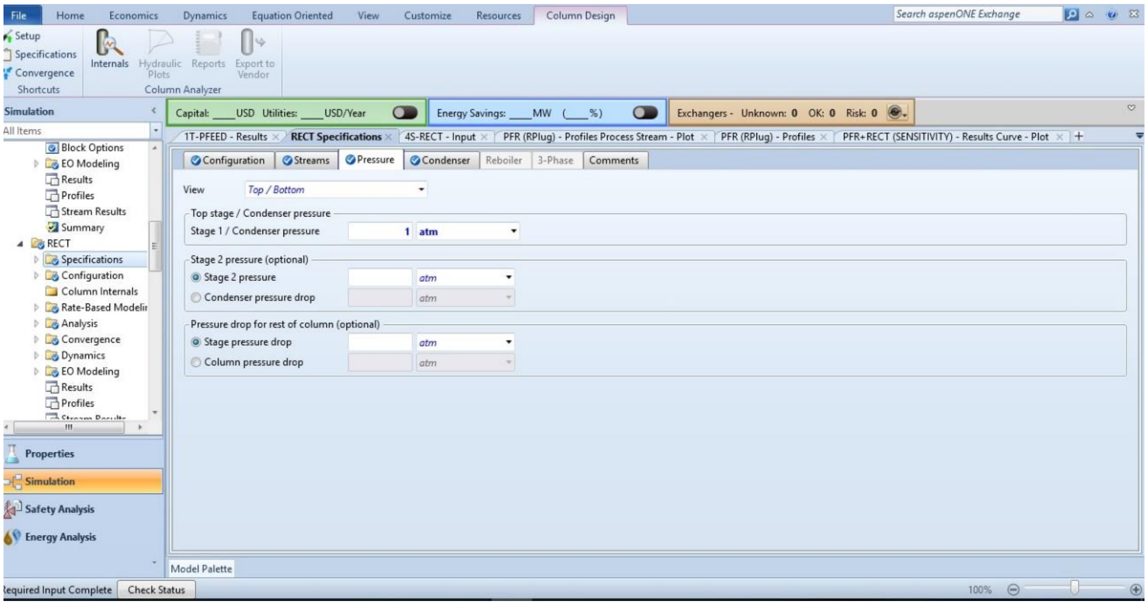
Name	Stage	Phase	Basis	Flow	Units	Flow Ratio	Feed Specs
4KETENE	1	Liquid	Mass		kg/hr		Feed basis
5METHANE	1	Vapor	Mass		kg/hr		Feed basis
3ACETONE	16	Liquid	Mass		kg/hr		Feed basis

Pseudo streams

Name	Pseudo Stream Type	Stage	Internal Phase	Reboiler Phase	Reboiler Conditions	Pumparound ID	Pumparound Conditions	Flow	Units

Figure 3.26: Entering the number of stage, the location and the phase of feed stream

By clicking the “Next” button, the “Pressure” tab window appears, where the pressure at the condenser stage (top stage) is 1 atm as shown in Figure 3.26.



View: Top / Bottom

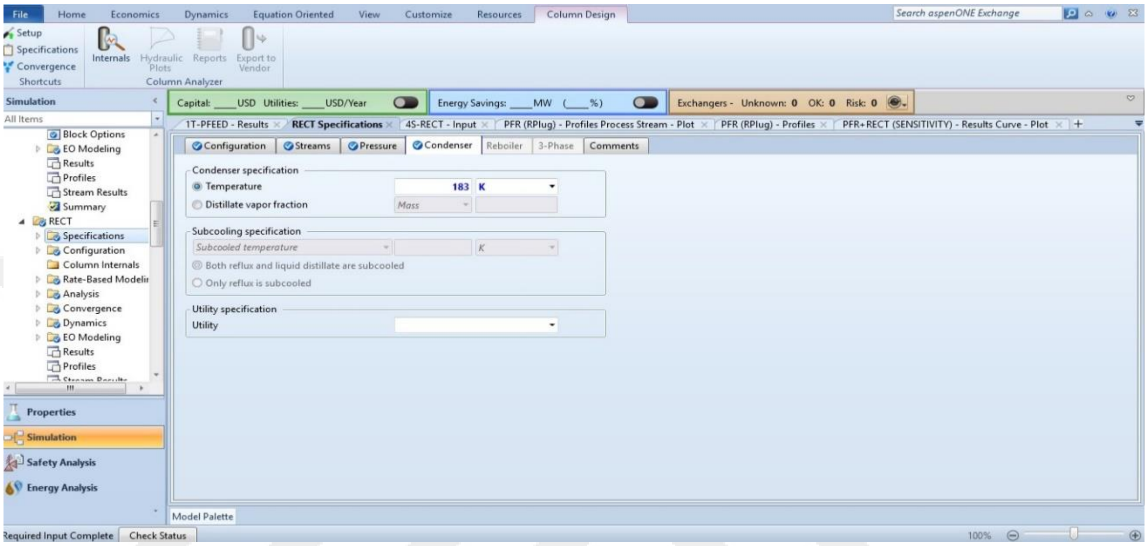
Top stage / Condenser pressure
Stage 1 / Condenser pressure: 1 atm

Stage 2 pressure (optional)
● Stage 2 pressure: atm
○ Condenser pressure drop: atm

Pressure drop for rest of column (optional)
● Stage pressure drop: atm
○ Column pressure drop: atm

Figure 3.27: Entering the pressure condenser or top stage

By clicking the “Next” button, the software moves to the “Condenser” tab window, where the condenser temperature must be entered. The temperature condenser is equal to 183Kº, as shown in Figure 3.27.



Condenser specification

● Temperature 183 K

○ Distillate vapor fraction Mass

Subcooling specification

Subcooled temperature K

○ Both reflux and liquid distillate are subcooled

○ Only reflux is subcooled

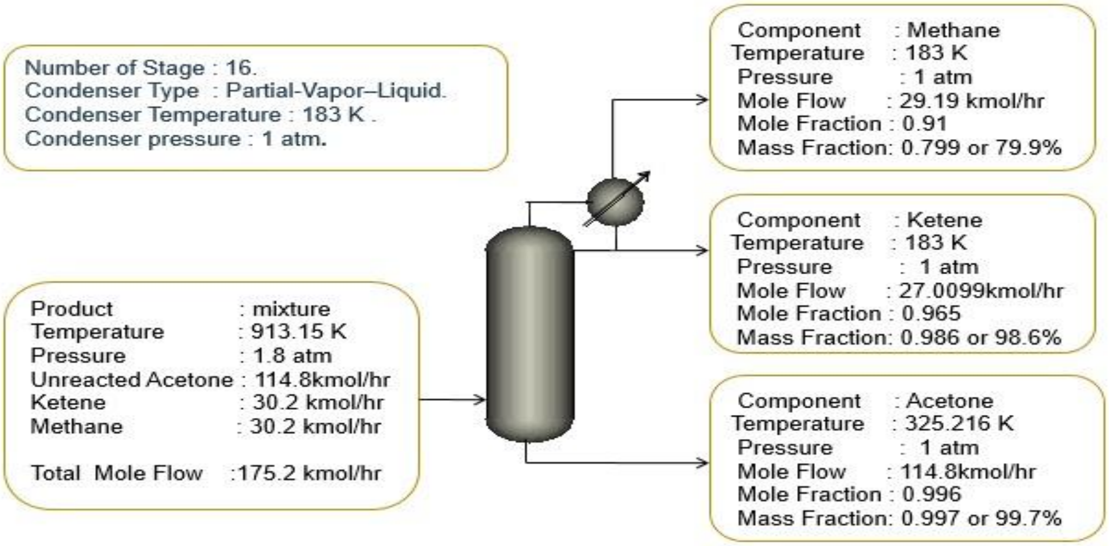
Utility specification

Utility

Figure 3.28: Entering the temperature for condenser

3.5 Running the Simulation for [PFR+RECT].

After the completion of all the required data. Clicking the “Reset “button followed by the “Next” button, the software reinitializes the last calculations and starts the new calculations. Figure 3.29 bellow shows simple details of rectifying column results.



Number of Stage : 16.
Condenser Type : Partial-Vapor–Liquid.
Condenser Temperature : 183 K .
Condenser pressure : 1 atm.

Product : mixture
Temperature : 913.15 K
Pressure : 1.8 atm
Unreacted Acetone : 114.8kmol/hr
Ketene : 30.2 kmol/hr
Methane : 30.2 kmol/hr

Total Mole Flow :175.2 kmol/hr

Component : Methane
Temperature : 183 K
Pressure : 1 atm
Mole Flow : 29.19 kmol/hr
Mole Fraction : 0.91
Mass Fraction: 0.799 or 79.9%

Component : Ketene
Temperature : 183 K
Pressure : 1 atm
Mole Flow : 27.0099kmol/hr
Mole Fraction : 0.965
Mass Fraction: 0.986 or 98.6%

Component : Acetone
Temperature : 325.216 K
Pressure : 1 atm
Mole Flow : 114.8kmol/hr
Mole Fraction : 0.996
Mass Fraction: 0.997 or 99.7%

Figure3.29: Rectifying Column details

3.6 The Addition of Continuous Stirred Tank Reactor.

The third step is the reaction of ketene that was separated from methane and unreacted acetone in rectifying column with acetic acid to produce acetic anhydride. This reaction is carried out in the Continuous Stirred Tank Reactor. The specifications of a CSTR reactor are as follows:

Reactor temperature: 298 K.

Reactor pressure: 0.01 atm.

The reaction taking place is:

$$CH_3COOH + C_2H_2O \rightarrow C_4H_6O_3 \qquad 3.2$$

In the simulation process, there are two inlet streams; ketene and acetic acid stream, and only one outlet stream; acetic anhydride stream. The stream temperature and pressure are entered. The flow rate of acetic acid should be equal to the flow rate of ketene stream that is produced from Radfrac, rectifying column. The acetic acid feed stream properties are entered in" mixed" tap in the Setup window under CSTR folder. In addition, the second reaction is added and named as R2. The type of reaction is selected as "POWERLAW". Under editor reaction window, the stoichiometry for this reaction must be defined, which are -1 for both reactants ketene and acetic acid, and 1 for acetic anhydride. The type of reaction is set as Equilibrium. Figure 3.28 below shows the addition of Continuous Stirred Tank Reactor.

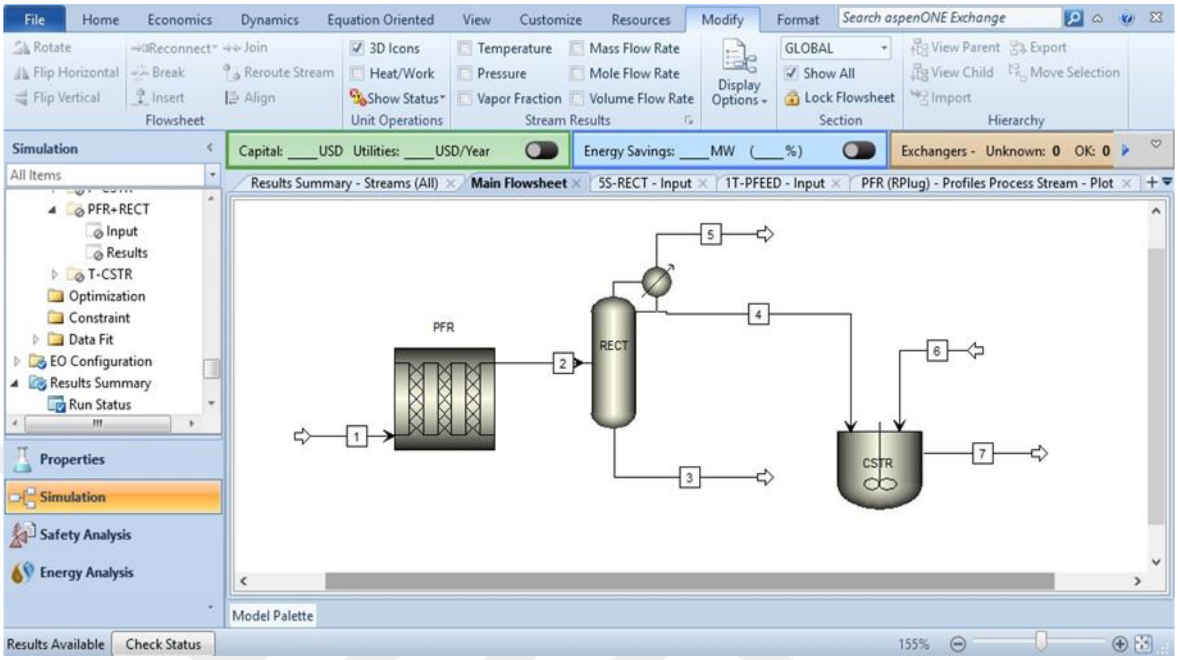
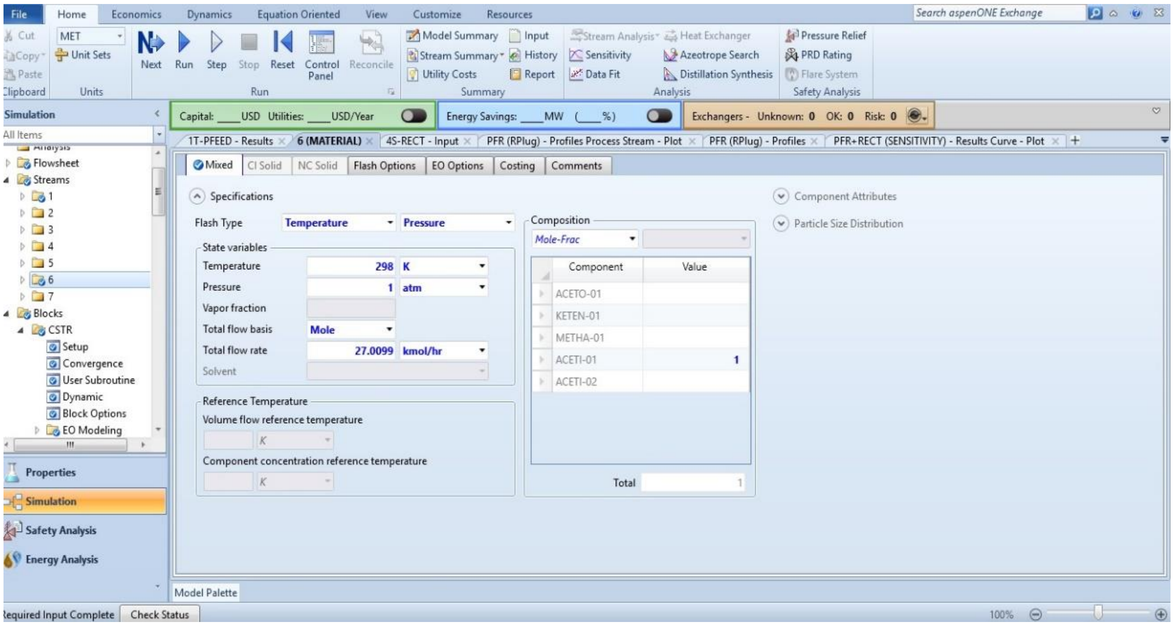


Figure 3.30: The addition of CSTR to production model.

Figure 3.29 below shows the properties of acetic acid stream.



Specifications

Flash Type: Temperature, Pressure

State variables

Temperature: 298 K

Pressure: 1 atm

Vapor fraction:

Total flow basis: Mole

Total flow rate: 27.0099 kmol/hr

Solvent:

Reference Temperature

Volume flow reference temperature: K

Component concentration reference temperature: K

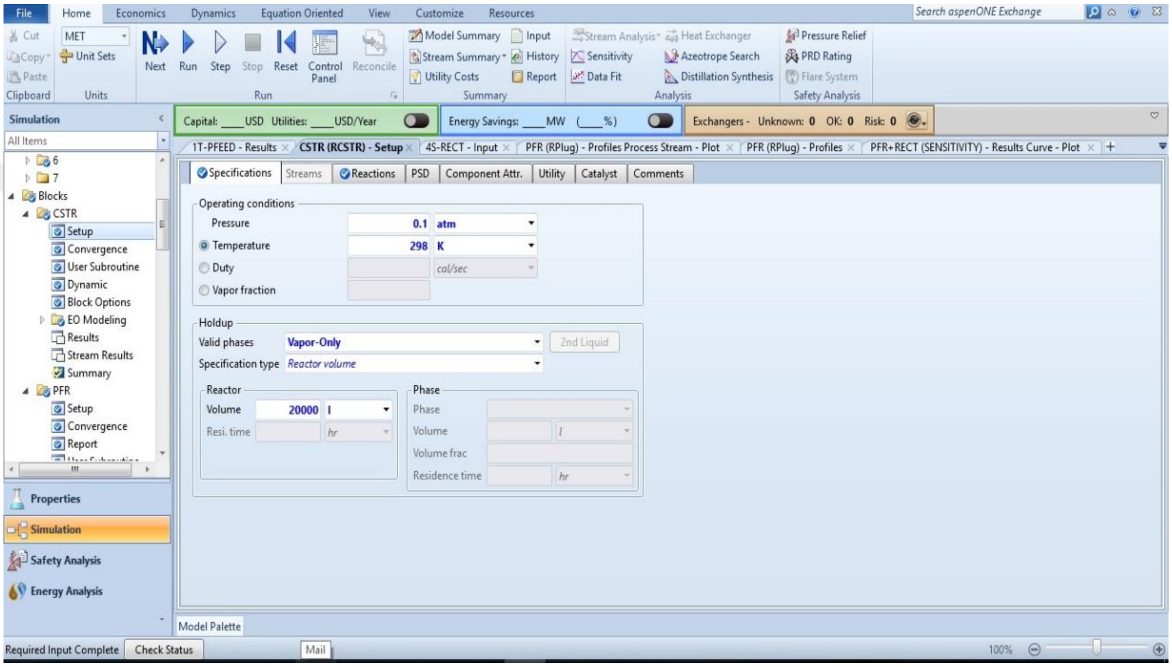
Composition: Mole-Frac

Component	Value
ACETO-01	
KETEN-01	
METHA-01	
ACETI-01	1
ACETI-02	

Total: 1

Figure 3.31: Entering the acetic acid feed stream properties in “mixed” tab window

The specifications of the reactor are added as below in Figure 3.30. The pressure is 0.1 and the temperature is 298 K. The valid phase is selected as vapor only. Figure 3.30 shows more details.



Pressure 0.1 atm

● Temperature 298 K

○ Duty cal/sec

○ Vapor fraction

Valid phases Vapor-Only

Specification type Reactor volume

Volume 20000 l

Resi. time hr

Phase

Volume l

Volume frac

Residence time hr

Figure 3.32: Entering the specifications and conditions for CSTR

3.7 Running the Simulation of the Final Design [PFR+RECT+CSTR].

The final design with Aspen plus is ready to run now, by clicking the “Reset “bottom followed by the “Next” button and the simulation can be solved.. Figure 3.31 shows the reactor specifications and the inlets and outlets streams final results. However, the result of this design are shown in details in chapter 4.

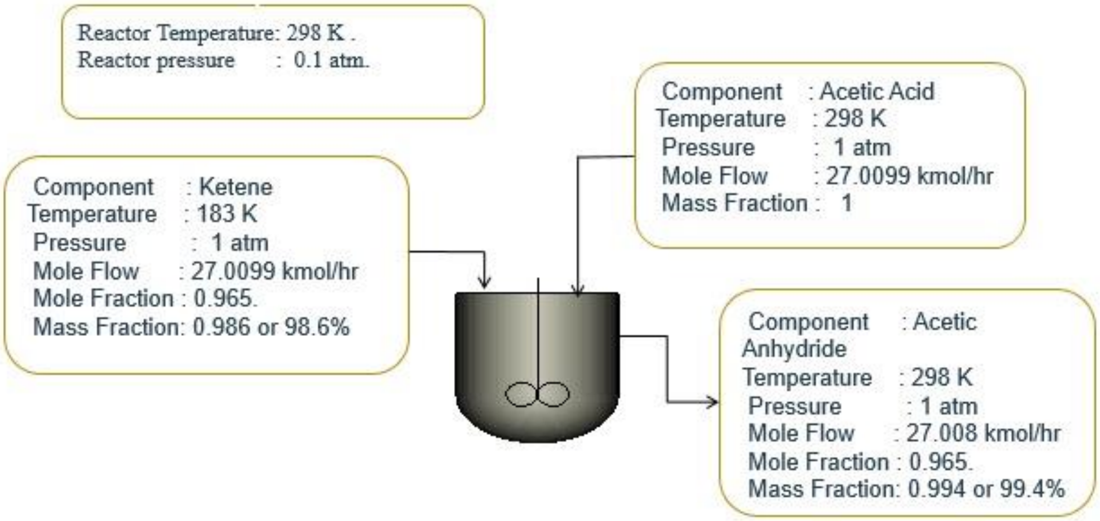


Figure3.33: Continuous Stirred Tank Reactor details

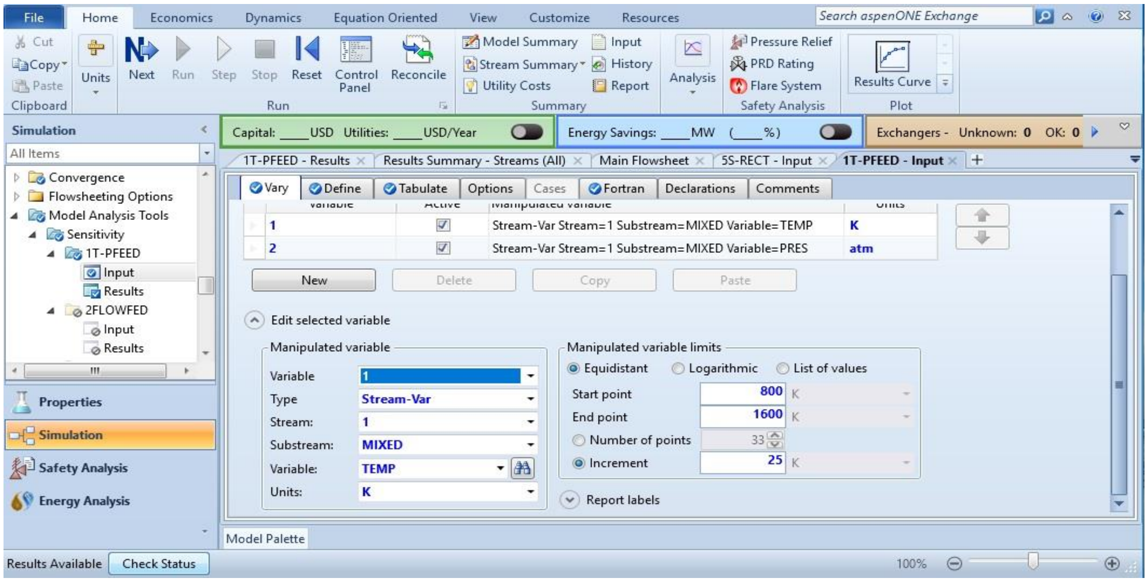
3.2 Sensitivity Analysis

3.2.1 Sensitivity of Plug Flow Reactor PFR.

3.2.1.1 Temperature and Pressure of Stream.

The sensitivity analysis of the temperature, pressure of the feed stream has been performed to observe the effect of the temperature and pressure stream on the results of Plug Flow Reactor, such as; mole fraction and mole flow of ketene, methane and unreacted acetone.

The temperature of outlet stream was analyzed by utilizing the model analysis tools. In the setup option, two variables are selected; temperature and pressure. The temperature is selected as the first variable, and pressure as the second. The range of temperature is set between 800 k and 1600 K, and the increment is 25 K. Similar to the temperature, the pressure variable type is selected as Stream-Var, and the stream as Stream 1, where the start point of the range is 0.5 atm and the end point is 3 atm as shown in Figure 3.32 and 3.33 below.



Variable	Active	Manipulated variable	Units
1	☑	Stream-Var Stream=1 Substream=MIXED Variable=TEMP	K
2	☑	Stream-Var Stream=1 Substream=MIXED Variable=PRES	atm

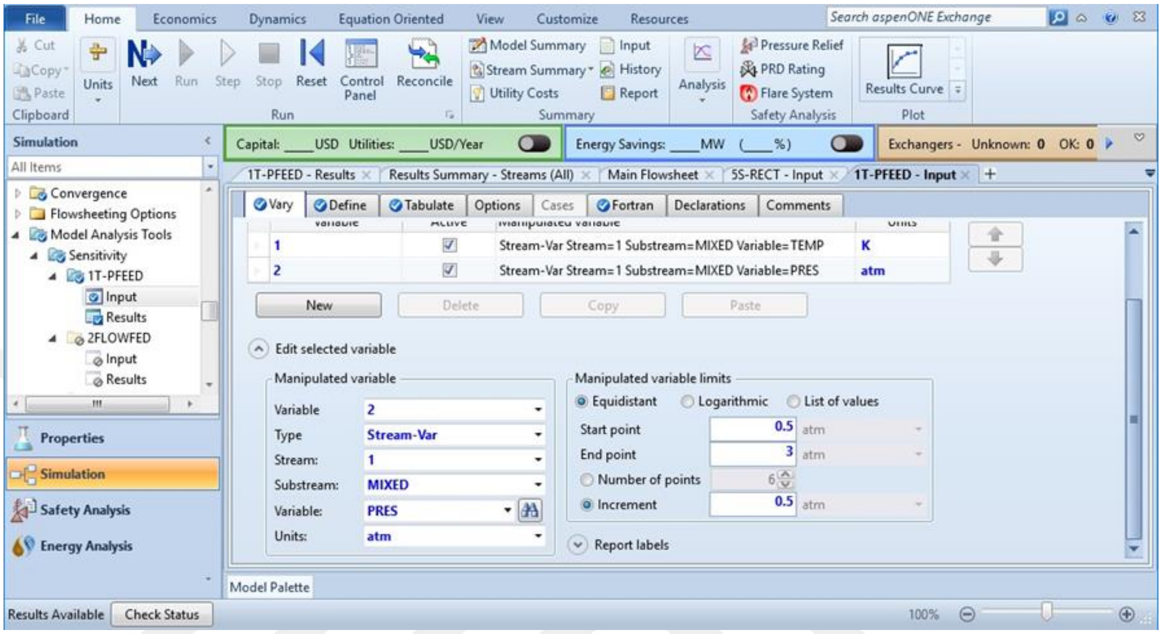
Manipulated variable

Variable: 1
Type: Stream-Var
Stream: 1
Substream: MIXED
Variable: TEMP
Units: K

Manipulated variable limits

● Equidistant ○ Logarithmic ○ List of values
Start point: 800 K
End point: 1600 K
○ Number of points: 33
● Increment: 25 K

Figure 3.34: Temperature setup and its effect on the reaction performance.



Variable	Active	Manipulated variable	Units
1	☑	Stream-Var Stream=1 Substream=MIXED Variable=TEMP	K
2	☑	Stream-Var Stream=1 Substream=MIXED Variable=PRES	atm

Manipulated variable
Variable: 2
Type: Stream-Var
Stream: 1
Substream: MIXED
Variable: PRES
Units: atm

Manipulated variable limits
● Equidistant ○ Logarithmic ○ List of values
Start point: 0.5 atm
End point: 3 atm
○ Number of points: 6
● Increment: 0.5 atm

Figure 3.35: Pressure setup and its effect on the reaction performance.

Stream-Var means the difference in streams, and not the conditions of equipment.

In sensitivity analysis, the sensitivity variables are defined as mole fraction of ketene, methane and acetone, such that:

- Mole fraction Ketene is YKETENEP
- Mole fraction Methane is YMETHANP
- Mole fraction Acetone is YACTONEP

For the product stream, defined Y refers to the vapor mole fraction, and P means the product.

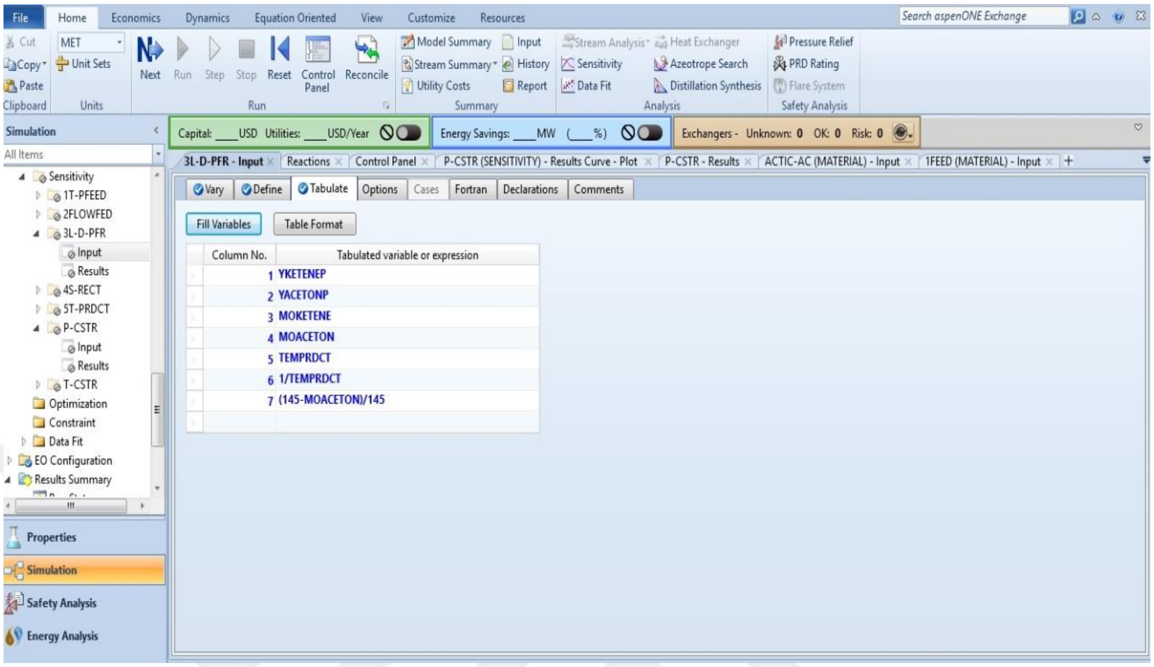
3.2.1.3 The Dimensions of Plug Flow Reactor.

The sensitivity analysis for the length and diameter of Plug Flow Reactor PFR has been analyzed in this part, which has been conducted to study the effects of Plug Flow Reactor specifications, such; as the length and diameter on the outlet stream products. Sensitivity model of Plug Flow Reactor specifications was made in the following steps. New sensitivity analysis model named as S-3 was added, and the length and diameter as variables were selected.

- The length variable Block-Var is selected as a type of variable, which means the change will occur in the length of Plug Flow Reactor, the start point was selected as 3, and the end point as 5 and the increment 1.
- The diameter variable was selected the as diameter DIAM variable and the start point was selected as 1 m, the endpoint as 4m and the increment 0.5.

Figure 3.34 shows the five variables as follows:

1. YKETENEP: the mole fraction of ketene in the product stream.
2. YACETONP: the mole fraction of acetone in the product stream.
3. MOKETENE: the mole flow of ketene in the product stream.
4. MOAECTON: the mole flow of acetone in the product stream.
5. TEMPRDCT: the outlet temperature stream.



Column No.	Tabulated variable or expression
1	YKETENEP
2	YACETONP
3	MOKETENE
4	MOACETON
5	TEMPRDCT
6	1/TEMPRDCT
7	(145-MOACETON)/145

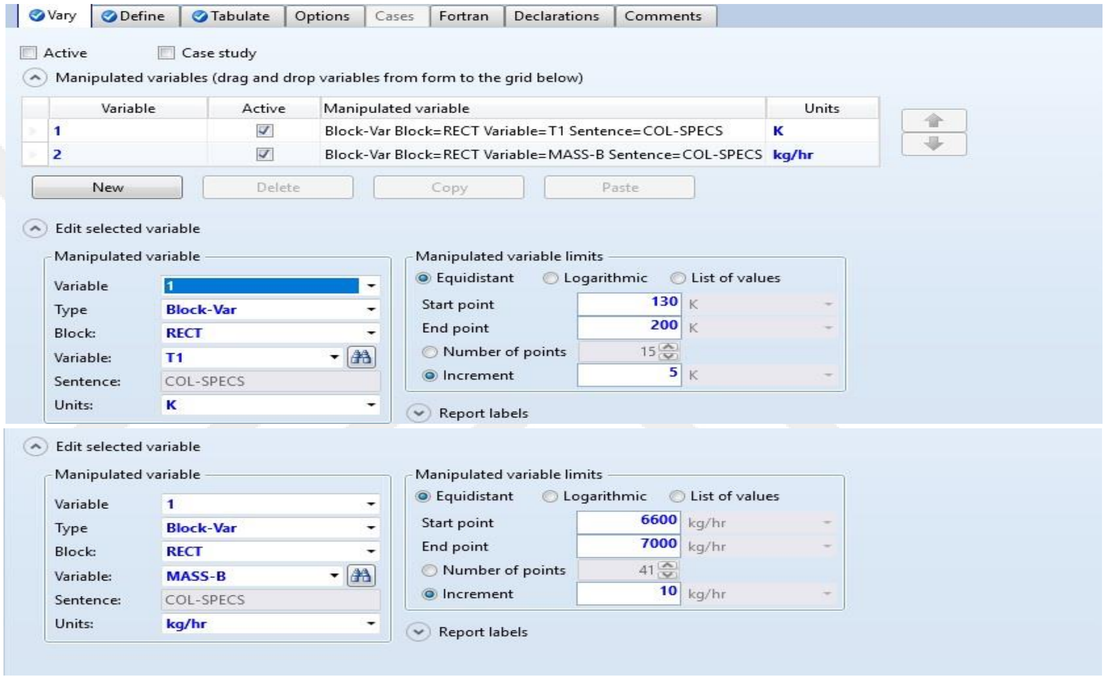
Figure 3.36: Entering variables in Plug flow of reactor.

3.2.2 Sensitivity analysis of rectifying column RECT.

3.2.2.1 Condenser temperature and bottoms mass flow rate of RECT.

The sensitivity analysis for the condenser temperature and bottoms mass flow rate of Radfrac column RECT are highly important. In this simulation part, the sensitivity analysis for the variables have been analyzed to observe the effect of the condenser temperature and bottoms mass flow rate of RECT on the product streams, which shows their effects on the mole fraction of ketene, methane and acetone in stream 3, 4 and 5. The sensitivity has been added and named as sensitivity S-RECT, then two variables were selected under this sensitivity analysis window. The first variable is the condenser temperature T1, and the second variable is the bottoms mass flow rate MASS-B:

- The temperature of condenser start point is 130 k^0, the end point is 190 k and the increment is 5.
- The start point of bottoms mass flow rate is 6600 kg/hr, the end point as 6700 kg/hr and the increment is 1, more details are shown in Figure 3.35:



☐ Active ☐ Case study

Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Units
1	☑	Block-Var Block=RECT Variable=T1 Sentence=COL-SPECS	K
2	☑	Block-Var Block=RECT Variable=MASS-B Sentence=COL-SPECS	kg/hr

Edit selected variable

Manipulated variable
Variable 1
Type Block-Var
Block: RECT
Variable: T1
Sentence: COL-SPECS
Units: K

Manipulated variable limits
● Equidistant ○ Logarithmic ○ List of values
Start point 130 K
End point 200 K
○ Number of points 15
● Increment 5 K

Edit selected variable

Manipulated variable
Variable 1
Type Block-Var
Block: RECT
Variable: MASS-B
Sentence: COL-SPECS
Units: kg/hr

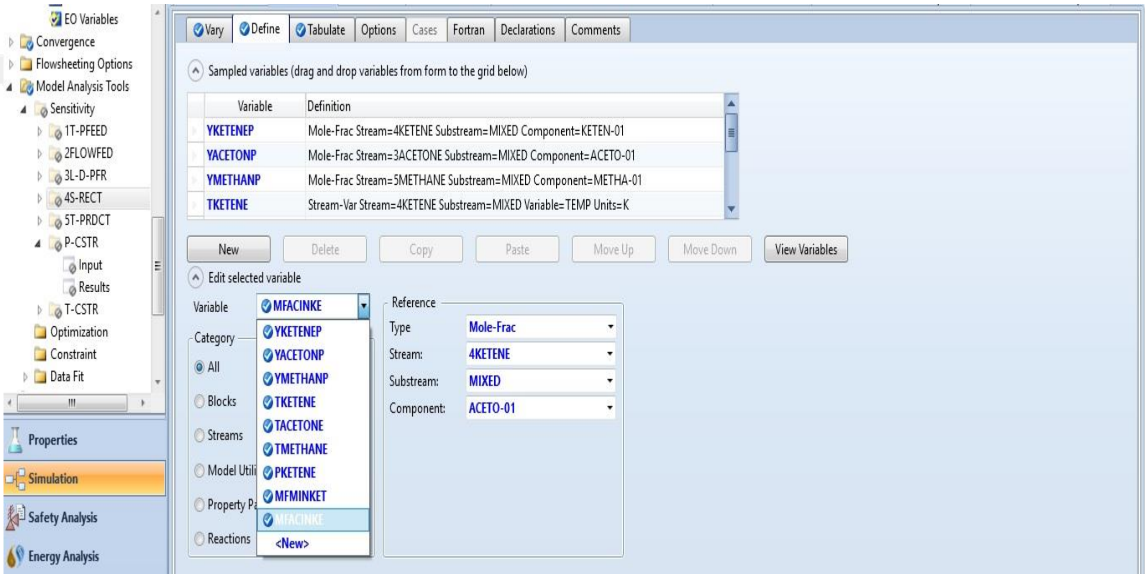
Manipulated variable limits
● Equidistant ○ Logarithmic ○ List of values
Start point 6600 kg/hr
End point 7000 kg/hr
○ Number of points 41
● Increment 10 kg/hr

Figure 3.37: The condenser variable setup.

The simulation process needs some definition of the variables in the product stream that are utilized to find out the effect of the feed variables. Figure 3.36 shows the most important variables, which are defined as follows:

1. YKETENEP: the mole fraction of ketene in the ketene stream “Stream 4”.
2. YACETONP: the mole fraction of acetone in the acetone stream “Stream 3”.
3. YMETHANP: the mole fraction of methane in the methane stream “Stream 5”.

4. TKETENE: the temperature of ketene in the ketene stream “Stream 4”.
5. TACETONE: the temperature of acetone in the acetone stream “Stream 3”.
6. TMETHANE: the temperature of methane in the methane stream” Stream 5”.
7. MFMINKET: the mole fraction of methane in the ketene stream “Stream 4”.
8. MFACINKE: the mole fraction of acetone in the ketene stream “Stream 4”.



Sampled variables (drag and drop variables from form to the grid below)

Variable	Definition
YKETENEP	Mole-Frac Stream=4KETENE Substream=MIXED Component=KETEN-01
YACETONP	Mole-Frac Stream=3ACETONE Substream=MIXED Component=ACETO-01
YMETHANP	Mole-Frac Stream=5METHANE Substream=MIXED Component=METHA-01
TKETENE	Stream-Var Stream=4KETENE Substream=MIXED Variable=TEMP Units=K

Edit selected variable

Variable: MFACINKE

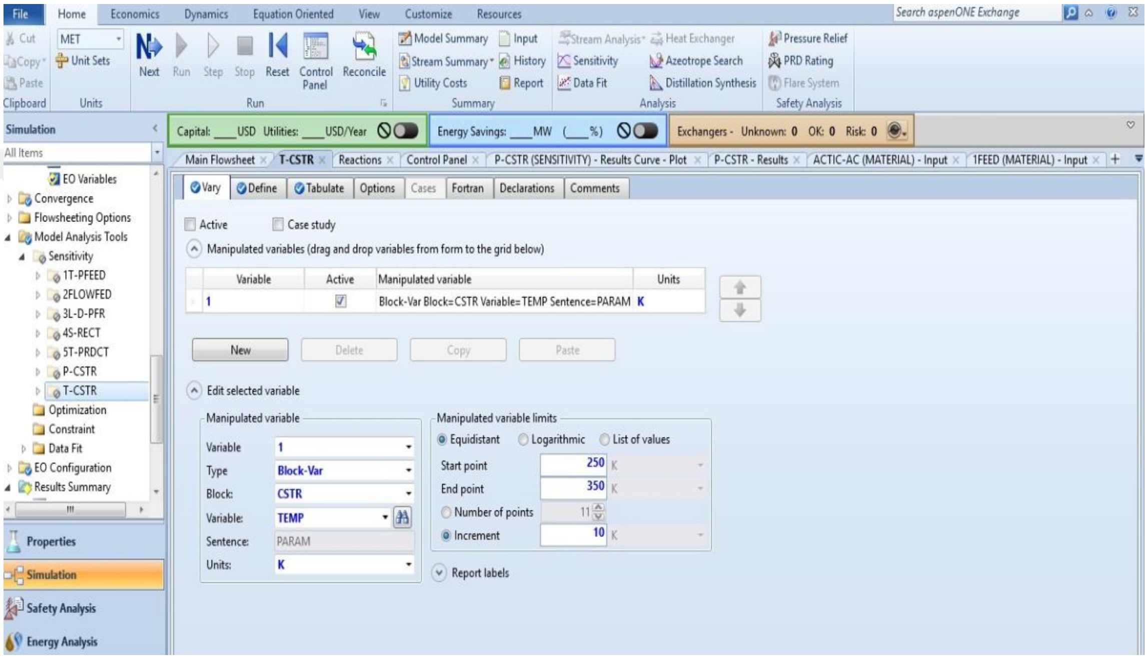
Reference
Type: Mole-Frac
Stream: 4KETENE
Substream: MIXED
Component: ACETO-01

Figure 3.38: Important variables definitions.

3.2.3 Sensitivity analysis of Continuous Stirred Tank Reactor CSTR.

3.2.2.1 Reactor Temperature

The sensitivity analysis for temperature as one of the operational variables of CSTR is as important as other variables. In fact, the sensitivity analysis for the temperature of Continuous Stirred Tank Reactor CSTR has been analyzed to observe the effect of the reactor temperature on the acetic anhydride as products stream. In a simulation model, the sensitivity in model analysis tools has been selected and named as T-CSTR. In addition, the variable is the temperature. The start point of temperature is selected as 250 K, and the endpoint as 350 K. The increment is specified as 10 K, which means that the data is collected for each 10 point of temperature. Figure 3.37 shows selection of the variable as following:



☐ Active ☐ Case study

Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Units
1	☑	Block-Var Block=CSTR Variable=TEMP Sentence=PARAM	K

Edit selected variable

Manipulated variable

Variable	1
Type	Block-Var
Block:	CSTR
Variable:	TEMP
Sentence:	PARAM
Units:	K

Manipulated variable limits

● Equidistant ○ Logarithmic ○ List of values

Start point	250	K
End point	350	K
○ Number of points	11	
● Increment	10	K

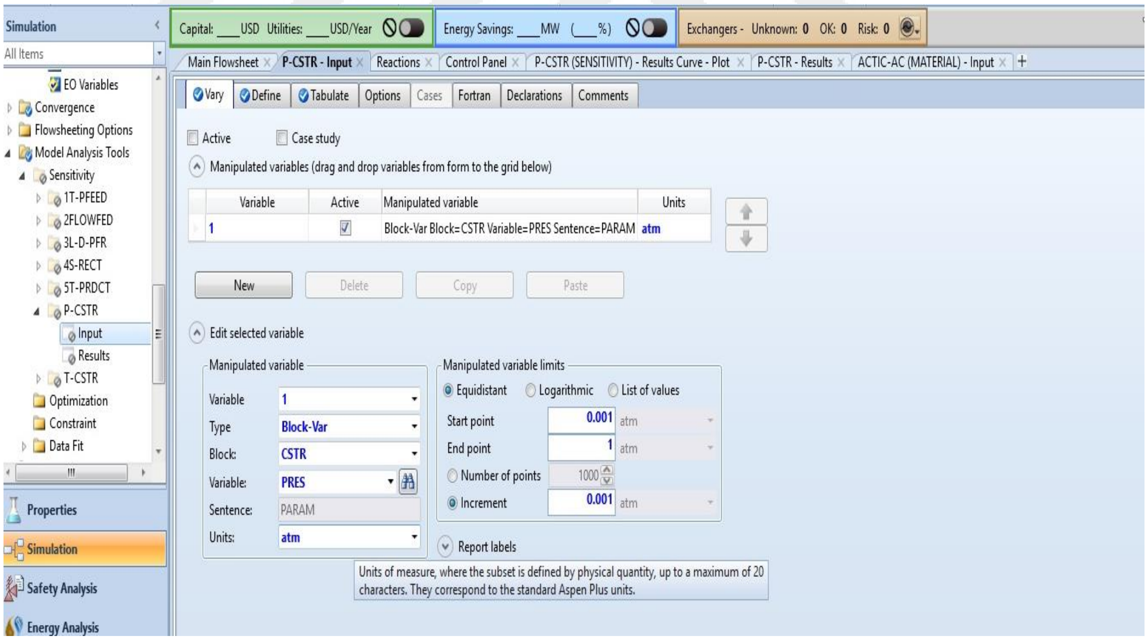
Figure 3.39. The temperature variable definition in CSTR reactor.

Four variables have been defined as following:

1. YACTICAN: the mole fraction of acetic anhydride in the product stream.
2. YKETENEP: the mole fraction of ketene in the product stream.
3. YACTICAC: the mole fraction of acetic acid in the product stream.
4. TACTICAN: the product stream temperature.

3.2.2.2 Reactor Pressure.

The sensitivity analysis of the reactor pressure is highly important, similar to other operational variables of CSTR reactor. This sensitivity has been analyzed to study the effect of the reactor pressure on the product stream. In addition, a simulation model of this sensitivity analysis is named as P-CSTR. The start point of pressure is selected as 0.001 atm, the endpoint as 1 atm and the increment as 0.001 atm, which means that the increase in the pressure is set to be every 0.001 point of pressure. Figure 3.38 shows the selection of variable.



☐ Active ☐ Case study

Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Units
1	☑	Block-Var Block=CSTR Variable=PRES Sentence=PARAM	atm

Edit selected variable

Manipulated variable

Variable: 1
Type: Block-Var
Block: CSTR
Variable: PRES
Sentence: PARAM
Units: atm

Manipulated variable limits

● Equidistant ○ Logarithmic ○ List of values

Start point: 0.001 atm
End point: 1 atm
○ Number of points: 1000
● Increment: 0.001 atm

Units of measure, where the subset is defined by physical quantity, up to a maximum of 20 characters. They correspond to the standard Aspen Plus units.

Figure 3.40: The selection of pressure variable of CSTR reactor.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 The Overall Results

4.1.1 The Results of Plug-Flow Reactor

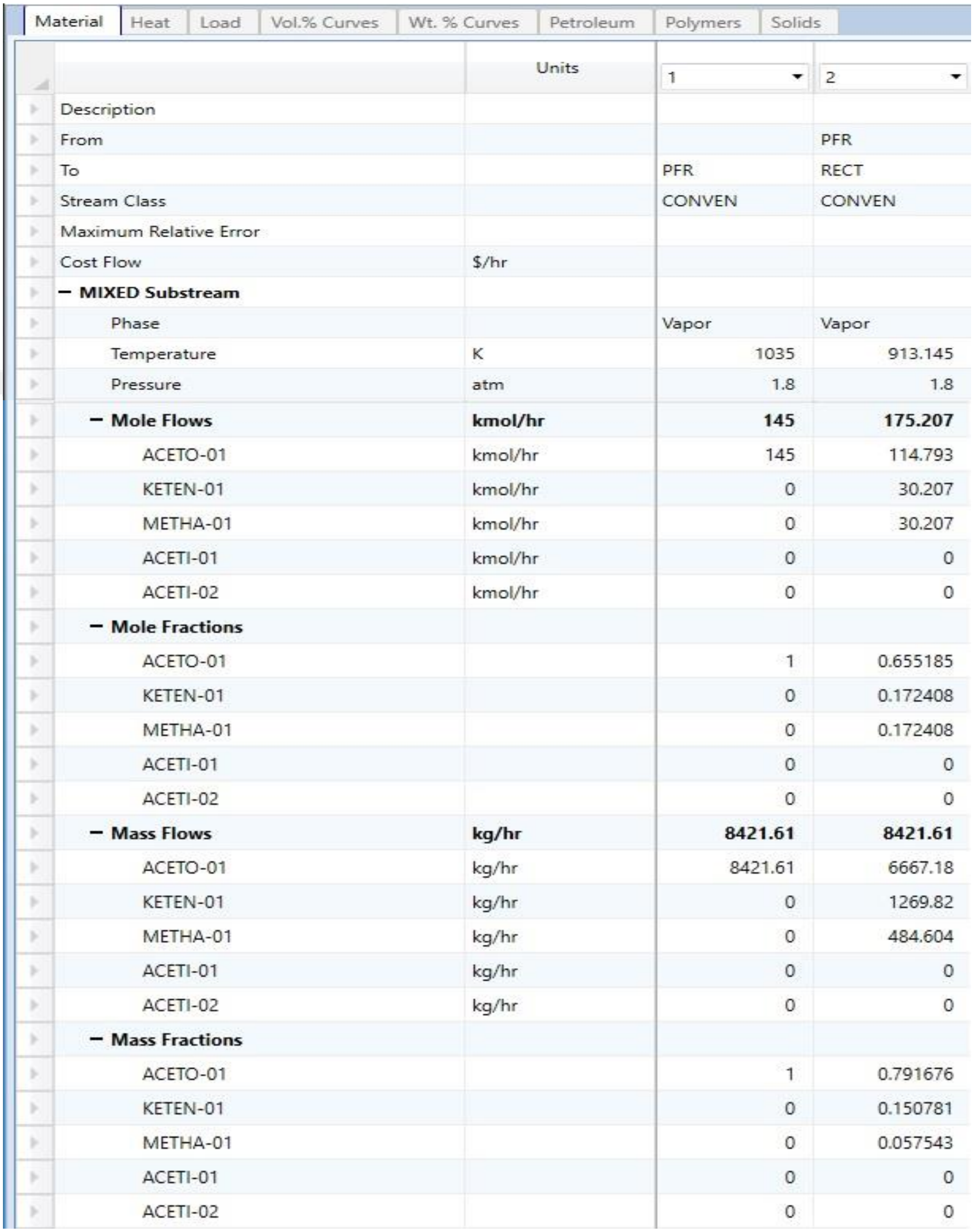
Figure 4.1 shows the overall results of plug flow reactor, where the total mole flow of feed is 145 kmol/hr and the conversion about 20.8%. That means the 20.8% of the feed 145 kmol/hr is converted to produce ketene and methane. The conversion of acetone can be obtained as following:

The conversion X = mole of acetone reacted / mole of acetone fed.

X = (145 – 114.793) / 145

So, X = 0.208 = 20.8%.

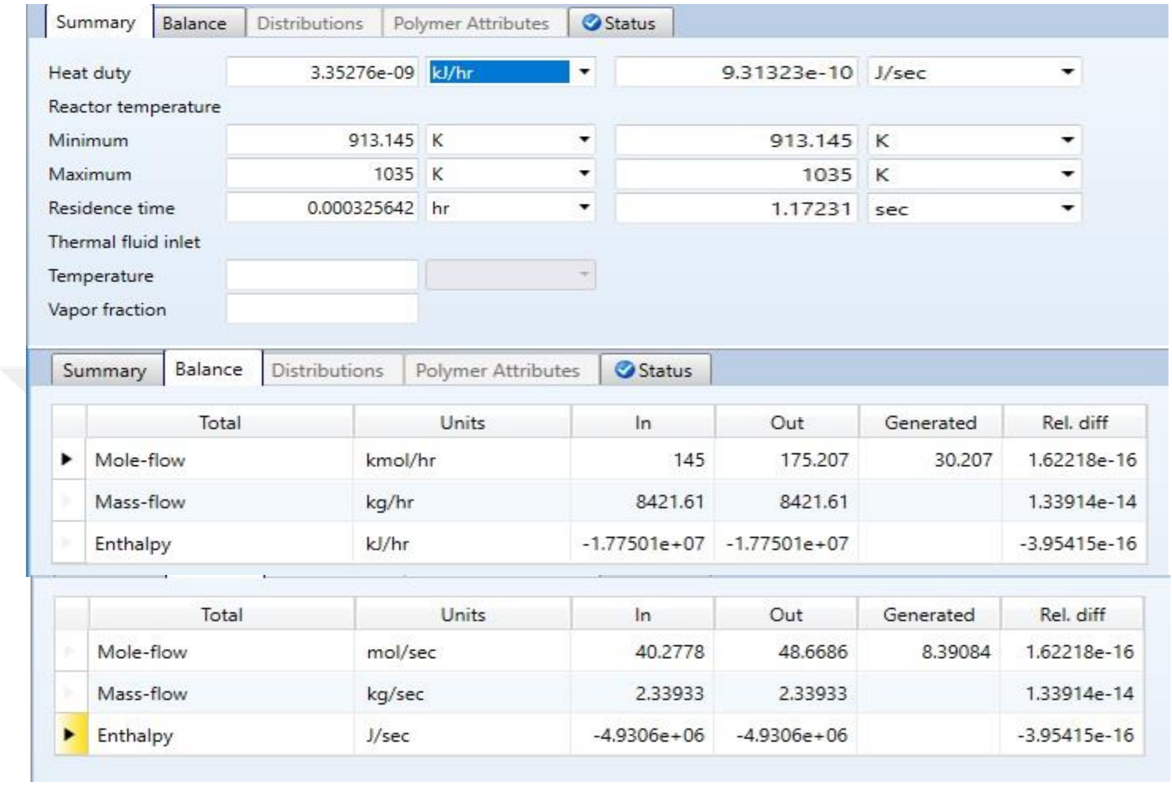
The reaction has been carried out in adiabatic reactor and the value of Q = Zero in adiabatic process. As shown in figure 4.1, the total mole flow of acetone fed is 145 kmol/hr and the total mole flow outlets as a stream product is 175.207 Kmol/hr. The mole flow of ketene in outlet stream is 30.207 kmol/hr with the same mole flow of methane and the mole flow of unreacted acetone is 114.793 in the product stream that means the conversion of acetone is 20.8 %. The conversion is calculated by divided the mole flow of acetone reacted on the total mole flow of acetone fed. The mole flow of acetone reacted can be calculated as the total mole flow fed mins the mole flow of acetone in the product stream.



	Units	1	2
Description			
From			PFR
To		PFR	RECT
Stream Class		CONVEN	CONVEN
Maximum Relative Error			
Cost Flow	$/hr		
− MIXED Substream			
Phase		Vapor	Vapor
Temperature	K	1035	913.145
Pressure	atm	1.8	1.8
− Mole Flows	**kmol/hr**	**145**	**175.207**
ACETO-01	kmol/hr	145	114.793
KETEN-01	kmol/hr	0	30.207
METHA-01	kmol/hr	0	30.207
ACETI-01	kmol/hr	0	0
ACETI-02	kmol/hr	0	0
− Mole Fractions			
ACETO-01		1	0.655185
KETEN-01		0	0.172408
METHA-01		0	0.172408
ACETI-01		0	0
ACETI-02		0	0
− Mass Flows	**kg/hr**	**8421.61**	**8421.61**
ACETO-01	kg/hr	8421.61	6667.18
KETEN-01	kg/hr	0	1269.82
METHA-01	kg/hr	0	484.604
ACETI-01	kg/hr	0	0
ACETI-02	kg/hr	0	0
− Mass Fractions			
ACETO-01		1	0.791676
KETEN-01		0	0.150781
METHA-01		0	0.057543
ACETI-01		0	0
ACETI-02		0	0

Figure 4.1: Results of first reaction in plug flow reactor.

The summary, mass and enthalpy balance of plug flow reactor are as in Figure 4.2.



Heat duty	3.35276e-09	kJ/hr	9.31323e-10	J/sec
Reactor temperature				
Minimum	913.145	K	913.145	K
Maximum	1035	K	1035	K
Residence time	0.000325642	hr	1.17231	sec
Thermal fluid inlet				
Temperature				
Vapor fraction				

Total	Units	In	Out	Generated	Rel. diff
Mole-flow	kmol/hr	145	175.207	30.207	1.62218e-16
Mass-flow	kg/hr	8421.61	8421.61		1.33914e-14
Enthalpy	kJ/hr	-1.77501e+07	-1.77501e+07		-3.95415e-16

Total	Units	In	Out	Generated	Rel. diff
Mole-flow	mol/sec	40.2778	48.6686	8.39084	1.62218e-16
Mass-flow	kg/sec	2.33933	2.33933		1.33914e-14
Enthalpy	J/sec	-4.9306e+06	-4.9306e+06		-3.95415e-16

Figure 4.2: The summary and process balance of plug flow reactor.

The feed stream temperature of Plug Flow Reactor is 1035K and the outlet temperature is approximately 913K. This difference between the inlet and outlet temperature with the value of the heat of reaction that is calculated in Appendix A refers to the energy or heat that is absorbed by this reaction. Consequently, the cracking reaction of acetone to ketene and methane is an endothermic reaction [32, 33]. The heat of reaction is calculated as shown in the appendix of this project by two different ways:

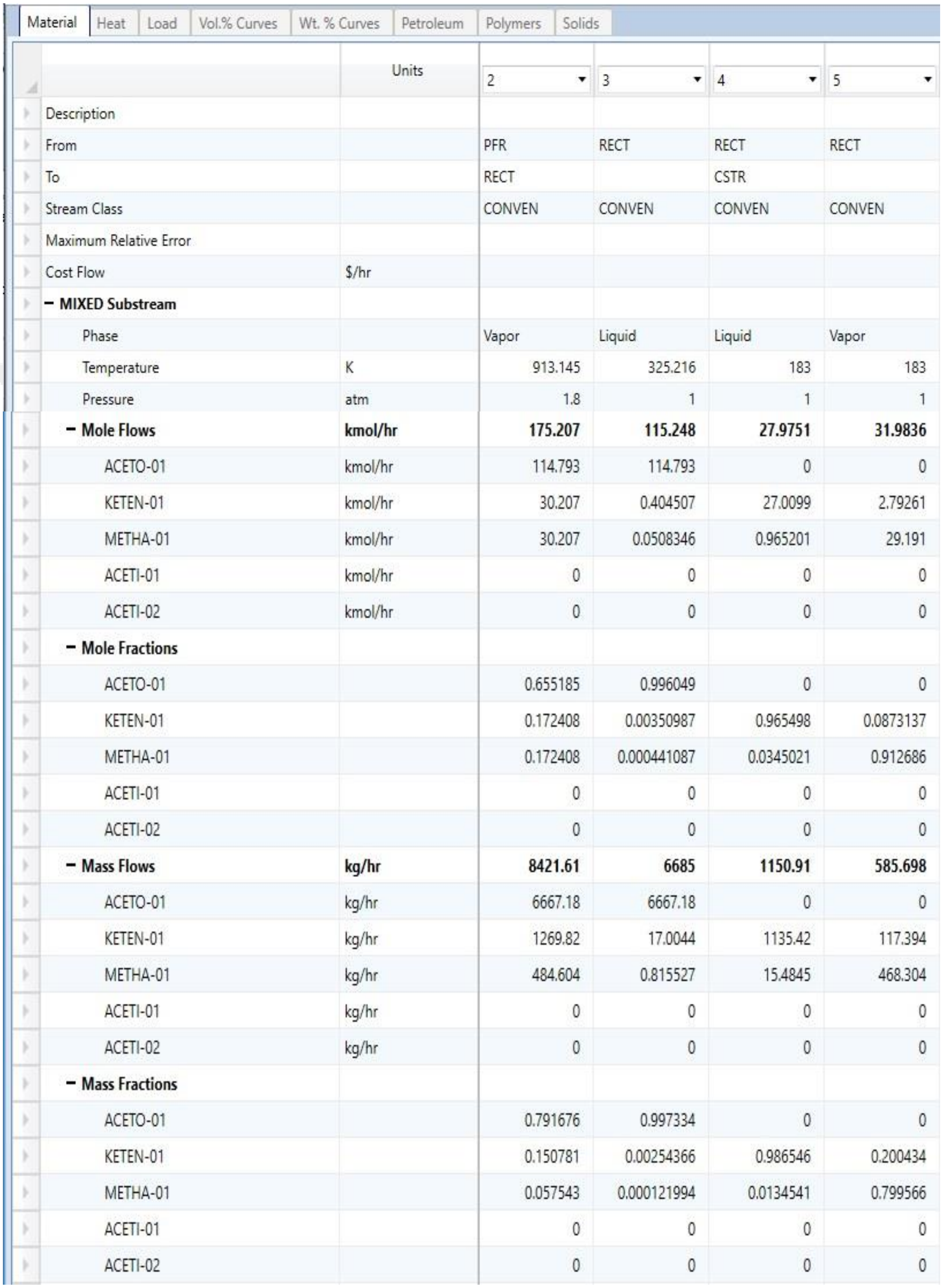
- From the heat of formation of the components.
- From the heat capacity of the components.

However, the inlet enthalpy in Figure 4.2 is equal to outlet enthalpy, which is due to this reaction being performed adiabatically, and it is known that, in adiabatic case heat transfer is zero or Q = 0 [33].

4.1.2 The Results of Rectifying Column RECT.

The second stage is Rectifying Column RCET. Figure 4.3, shows the overall result stream of RCET, where the overall result stream shows the temperature and pressure of feed and production in details. The total mole flow rate of feed is 175.2 kmol/hr and the mole flow rate of acetone in stream 3 or bottom stream is 114.79 kmol/hr, the ketene in stream 4 middle stream of distillation column is 27.0099 kmol/hr and methane in the top stream is 29.19 kmol/hr. The table displays the details of mole fraction, mass flow rate and mass fraction, as well as feed and production. The total mass flow rate of feed is 8421.6 kg/hr, and the mole flow rate of acetone is 6667.17 kg/hr, ketene is about 1269.82 kg/hr and methane is 484.604 kg/hr. Moreover, the total mass flow rate in the bottom stream is 6685 kg/hr with the mass fraction of acetone 0.997, ketene 0.0025 and methane 0.00012.

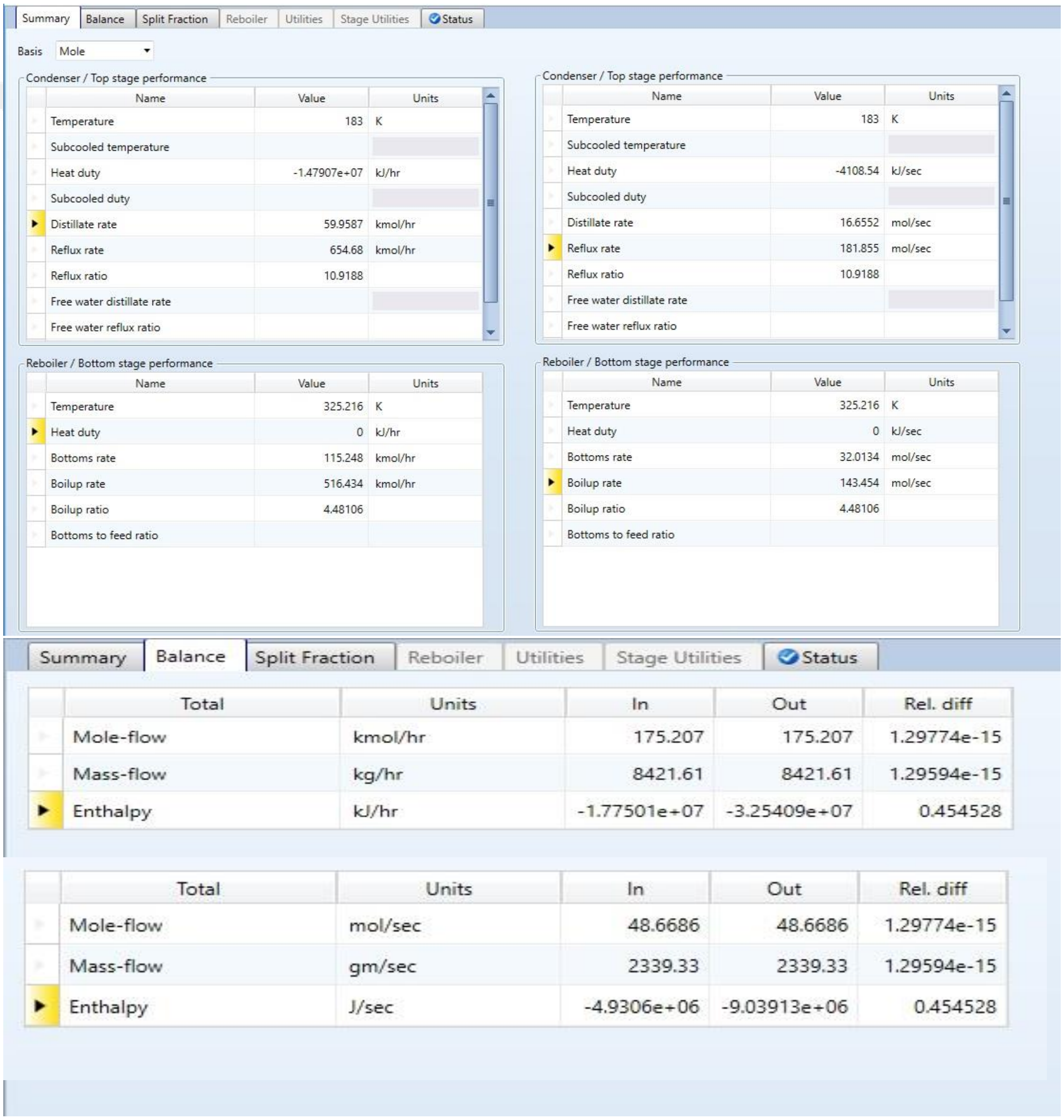
The total flow rate in stream 4 is 1150.91 kg/hr and the mass fraction of ketene has received the largest mass fraction in this stream with the mass flow of 1135.42 kg/hr. The mass flow rate and mass fraction of acetone in this stream are zero and the mass flow of methane is 15.48 kg/hr with mass fraction is about 0.01. The largest mass fraction of methane is 0.79 in stream 5, top stream with a mass fraction of ketene is about 0.2 and trace mass fraction of acetone. The mass flow rate of methane in this stream is 468.30 kg/hr and the mass flow rate of ketene is 117.39 kg/hr. Figure 4.3 below shows the results of rectifying column.



	Units	2	3	4	5
Description					
From		PFR	RECT	RECT	RECT
To		RECT		CSTR	
Stream Class		CONVEN	CONVEN	CONVEN	CONVEN
Maximum Relative Error					
Cost Flow	$/hr				
− MIXED Substream					
Phase		Vapor	Liquid	Liquid	Vapor
Temperature	K	913.145	325.216	183	183
Pressure	atm	1.8	1	1	1
− Mole Flows	**kmol/hr**	**175.207**	**115.248**	**27.9751**	**31.9836**
ACETO-01	kmol/hr	114.793	114.793	0	0
KETEN-01	kmol/hr	30.207	0.404507	27.0099	2.79261
METHA-01	kmol/hr	30.207	0.0508346	0.965201	29.191
ACETI-01	kmol/hr	0	0	0	0
ACETI-02	kmol/hr	0	0	0	0
− Mole Fractions					
ACETO-01		0.655185	0.996049	0	0
KETEN-01		0.172408	0.00350987	0.965498	0.0873137
METHA-01		0.172408	0.000441087	0.0345021	0.912686
ACETI-01		0	0	0	0
ACETI-02		0	0	0	0
− Mass Flows	**kg/hr**	**8421.61**	**6685**	**1150.91**	**585.698**
ACETO-01	kg/hr	6667.18	6667.18	0	0
KETEN-01	kg/hr	1269.82	17.0044	1135.42	117.394
METHA-01	kg/hr	484.604	0.815527	15.4845	468.304
ACETI-01	kg/hr	0	0	0	0
ACETI-02	kg/hr	0	0	0	0
− Mass Fractions					
ACETO-01		0.791676	0.997334	0	0
KETEN-01		0.150781	0.00254366	0.986546	0.200434
METHA-01		0.057543	0.000121994	0.0134541	0.799566
ACETI-01		0	0	0	0
ACETI-02		0	0	0	0

Figure 4.3: Rectifying column RCET results.

Figure 4.4 shows the summary of mass and enthalpy balance of rectifying column RCET. The temperature in condenser top stage is 183 k and the temperature in the bottom is 325.216 k. Moreover, the total mole flow rate is balanced with 175.207 kmol/hr, as well as the mass flow rate is balanced with 8421.61 kg/hr. The appendix contains more details about mass and material balance.



Basis Mole

Condenser / Top stage performance

Name	Value	Units
Temperature	183	K
Subcooled temperature		
Heat duty	-1.47907e+07	kJ/hr
Subcooled duty		
Distillate rate	59.9587	kmol/hr
Reflux rate	654.68	kmol/hr
Reflux ratio	10.9188	
Free water distillate rate		
Free water reflux ratio		

Reboiler / Bottom stage performance

Name	Value	Units
Temperature	325.216	K
Heat duty	0	kJ/hr
Bottoms rate	115.248	kmol/hr
Boilup rate	516.434	kmol/hr
Boilup ratio	4.48106	
Bottoms to feed ratio		

Condenser / Top stage performance

Name	Value	Units
Temperature	183	K
Subcooled temperature		
Heat duty	-4108.54	kJ/sec
Subcooled duty		
Distillate rate	16.6552	mol/sec
Reflux rate	181.855	mol/sec
Reflux ratio	10.9188	
Free water distillate rate		
Free water reflux ratio		

Reboiler / Bottom stage performance

Name	Value	Units
Temperature	325.216	K
Heat duty	0	kJ/sec
Bottoms rate	32.0134	mol/sec
Boilup rate	143.454	mol/sec
Boilup ratio	4.48106	
Bottoms to feed ratio		

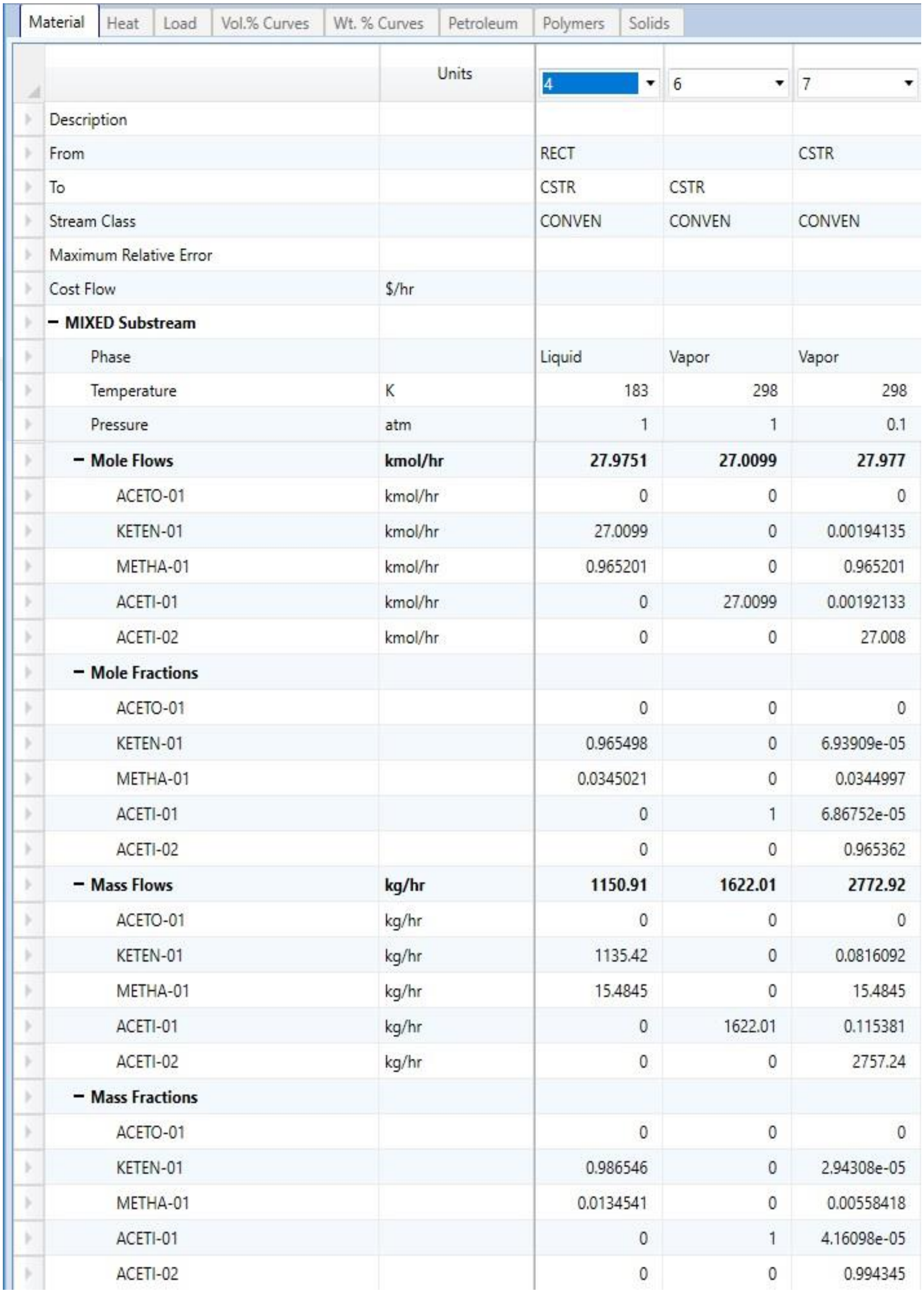
Total	Units	In	Out	Rel. diff
Mole-flow	kmol/hr	175.207	175.207	1.29774e-15
Mass-flow	kg/hr	8421.61	8421.61	1.29594e-15
Enthalpy	kJ/hr	-1.77501e+07	-3.25409e+07	0.454528

Total	Units	In	Out	Rel. diff
Mole-flow	mol/sec	48.6686	48.6686	1.29774e-15
Mass-flow	gm/sec	2339.33	2339.33	1.29594e-15
Enthalpy	J/sec	-4.9306e+06	-9.03913e+06	0.454528

Figure 4.4: The summary and material balance of RCET.

4.1.3 The Results of Continuous Stirred Tank Reactor CSTR.

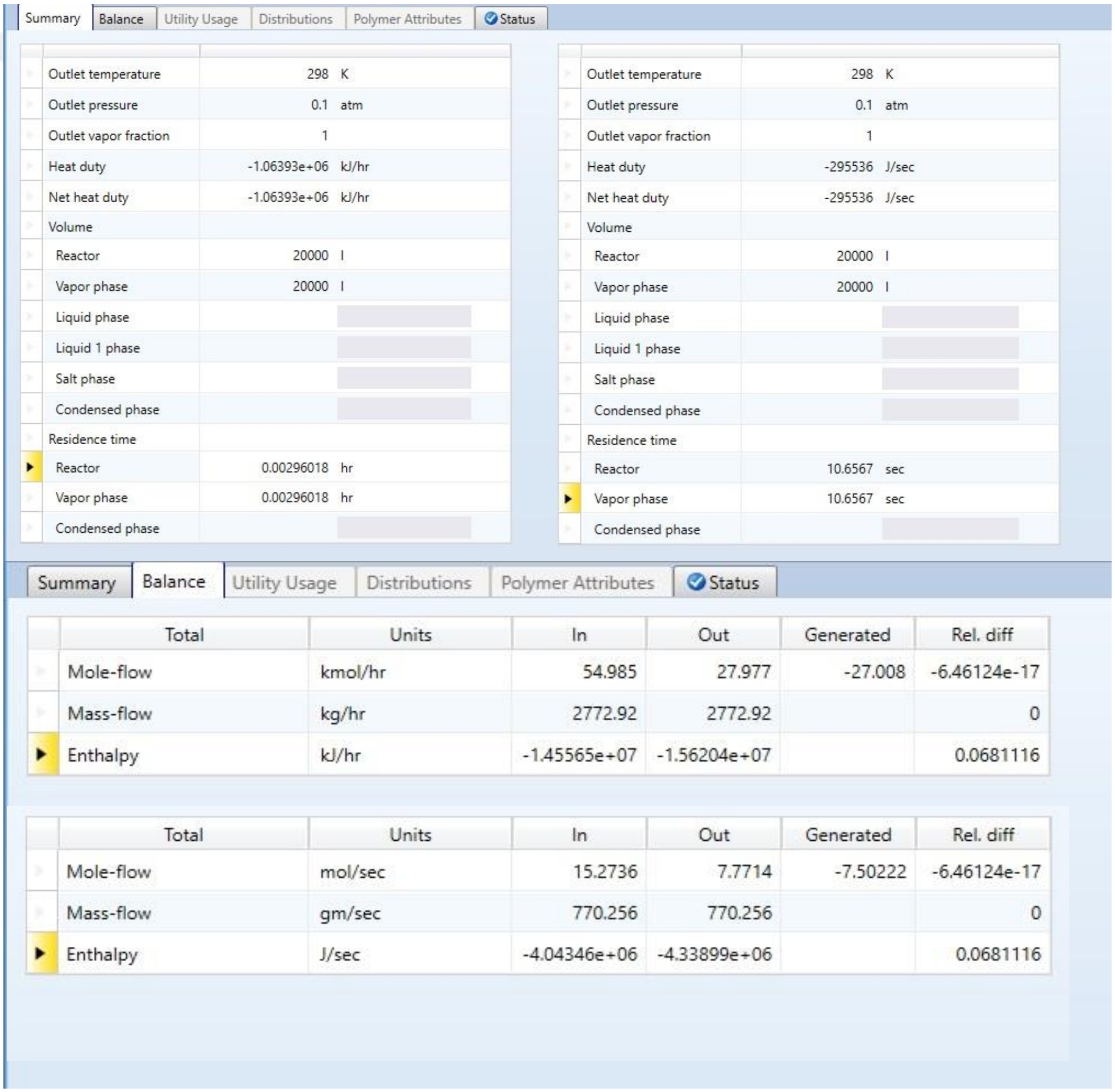
The third stage is the reaction of ketene with acetic acid in Continuous Stirred Tank Reactor CSTR, and overall results are shown in figure 4.5. The table shows the details of temperature and pressure of inlets and outlets streams. The total mole flow rate of stream 4, outlet middle stream of the distillation column, is 27.975 kmol/hr and the mole flow rate of stream 6, an acetic acid feed stream of Continuous Stirred Tank Reactor, is 27.0099 kmol/hr. The mole flow of acetic anhydride in stream 7, outlet stream of Continuous Stirred Tank Reactor, is 27.008 kmol/hr. In addition, the table displays the details of mole fraction, mass flow rate and the mass fraction, as well as feed and production. The total mass flow rate of stream 4 is 1150.9 kg/hr, the mass flow rate in stream 6 is 1622.01 kg/hr, and for the stream 7 is 2772.92 kg/hr.



	Units	4	6	7
Description				
From		RECT		CSTR
To		CSTR	CSTR	
Stream Class		CONVEN	CONVEN	CONVEN
Maximum Relative Error				
Cost Flow	$/hr			
− MIXED Substream				
Phase		Liquid	Vapor	Vapor
Temperature	K	183	298	298
Pressure	atm	1	1	0.1
− Mole Flows	**kmol/hr**	**27.9751**	**27.0099**	**27.977**
ACETO-01	kmol/hr	0	0	0
KETEN-01	kmol/hr	27.0099	0	0.00194135
METHA-01	kmol/hr	0.965201	0	0.965201
ACETI-01	kmol/hr	0	27.0099	0.00192133
ACETI-02	kmol/hr	0	0	27.008
− Mole Fractions				
ACETO-01		0	0	0
KETEN-01		0.965498	0	6.93909e-05
METHA-01		0.0345021	0	0.0344997
ACETI-01		0	1	6.86752e-05
ACETI-02		0	0	0.965362
− Mass Flows	**kg/hr**	**1150.91**	**1622.01**	**2772.92**
ACETO-01	kg/hr	0	0	0
KETEN-01	kg/hr	1135.42	0	0.0816092
METHA-01	kg/hr	15.4845	0	15.4845
ACETI-01	kg/hr	0	1622.01	0.115381
ACETI-02	kg/hr	0	0	2757.24
− Mass Fractions				
ACETO-01		0	0	0
KETEN-01		0.986546	0	2.94308e-05
METHA-01		0.0134541	0	0.00558418
ACETI-01		0	1	4.16098e-05
ACETI-02		0	0	0.994345

Figure 4.5: The results of CSTR reactor.

Figure 4.6 shows a summary of mass and enthalpy balance of Continuous Stirred Tank Reactor. The outlet temperature is 298 K. Moreover, the second part is the mass and enthalpy balance, where it is shown that the balance of total mass flow rate is 2719.84 kg/hr.



Outlet temperature	298	K
Outlet pressure	0.1	atm
Outlet vapor fraction	1	
Heat duty	-1.06393e+06	kJ/hr
Net heat duty	-1.06393e+06	kJ/hr
Volume		
Reactor	20000	l
Vapor phase	20000	l
Liquid phase		
Liquid 1 phase		
Salt phase		
Condensed phase		
Residence time		
Reactor	0.00296018	hr
Vapor phase	0.00296018	hr
Condensed phase		

Outlet temperature	298	K
Outlet pressure	0.1	atm
Outlet vapor fraction	1	
Heat duty	-295536	J/sec
Net heat duty	-295536	J/sec
Volume		
Reactor	20000	l
Vapor phase	20000	l
Liquid phase		
Liquid 1 phase		
Salt phase		
Condensed phase		
Residence time		
Reactor	10.6567	sec
Vapor phase	10.6567	sec
Condensed phase		

Total	Units	In	Out	Generated	Rel. diff
Mole-flow	kmol/hr	54.985	27.977	-27.008	-6.46124e-17
Mass-flow	kg/hr	2772.92	2772.92		0
Enthalpy	kJ/hr	-1.45565e+07	-1.56204e+07		0.0681116

Total	Units	In	Out	Generated	Rel. diff
Mole-flow	mol/sec	15.2736	7.7714	-7.50222	-6.46124e-17
Mass-flow	gm/sec	770.256	770.256		0
Enthalpy	J/sec	-4.04346e+06	-4.33899e+06		0.0681116

Figure 4.6: The summary, mass and enthalpy balance of CSTR reactor.

4.2 Results of Sensitivity Analysis

4.2.1 Plug Flow Reactor

4.2.1.1 The Effect of Temperature of Feed Stream in Plug Flow Reactor.

The effect of feed stream temperature on the conversion of acetone is shown in Figure 4.7. The conversion can be defined as:

Conversion X = (mole of acetone feed - mole of acetone in production)/mole of acetone [33].

Figure 4.7 explains that increasing the feed temperature increases the conversion. However, if temperature raises more than 1035 K, ketene decomposes. For this reason, the feed temperature is kept constant at 1035 K. Consequently, it is important to keep the conversion low because the ketene is unstable and tends to decompose, which is an important reason to keep the temperature low.

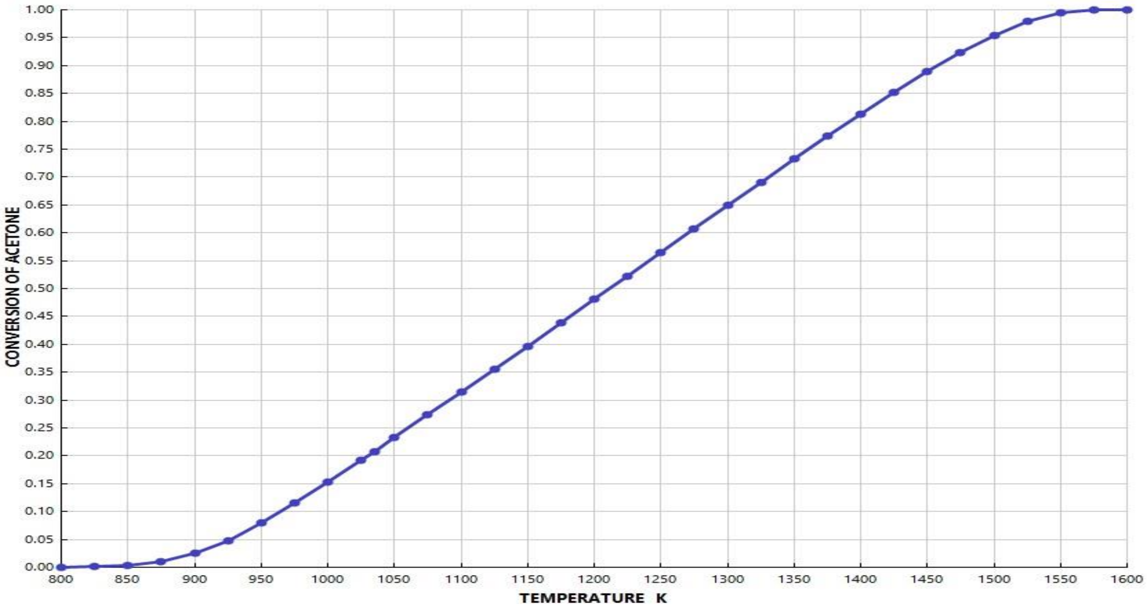


Figure 4.7: The effect of feed stream temperature on the conversion of acetone.

The effect of temperature on the mole fraction is shown in Figure 4.8. The increasing of feed temperature increases mole fraction of ketene, however, decreases acetone mole fraction, due to this reaction being an endothermic reaction.

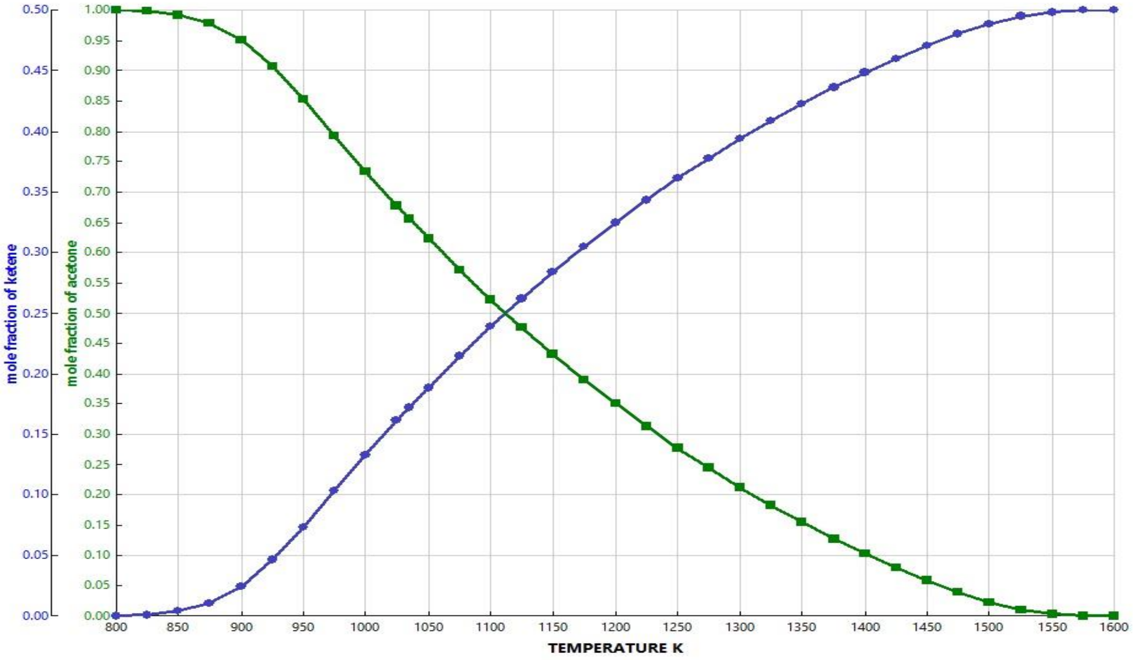


Figure 4.8: The effect of stream temperature on the mole fraction of ketene and acetone.

Figure 4.9 displays the relationship between the feed stream temperature and the outlet temperature, where production temperature is less than feed stream temperature. If the temperature is between 800 K and 875 K does not affect production, this means:

Feed temperature = production temperature

This is attributed to the reaction not starting at this range of temperature. After this range of the feed temperature, the outlet temperature is less than the temperature of feed stream and the difference increases with the increase of the feed stream temperature, as the reaction is an endothermic reaction.

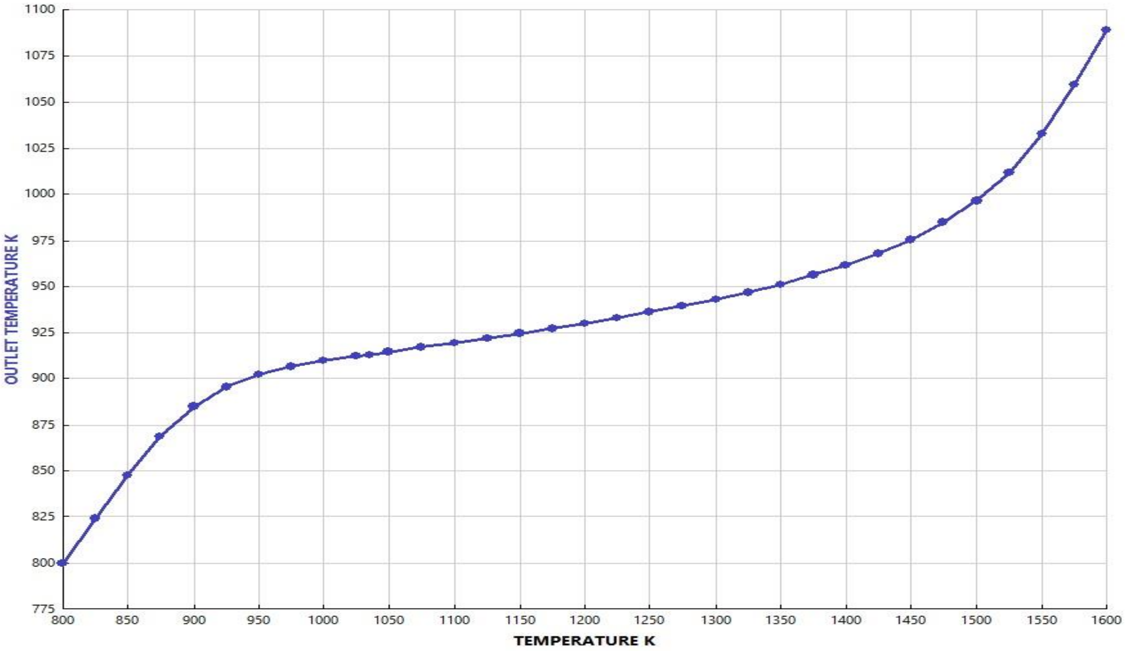


Figure 4.9: The effect of feed stream temperature on the outlet temperature.

4.2.1.2 The Effect of Pressure of Feed Stream in Plug Flow Reactor.

The effect of feed stream pressure of plug flow reactor on conversion of acetone is shown in Figure 4.10. It is clear that the pressure has less effect on the conversion than the temperature of the feed stream. A pressure of 1.8 atm is selected for the feed stream to facilitate using additional equipment that provides pressure, such as; compressors before the second stage, the rectifying column RCET. On the other hand, the pressure is important as well because it has a significant effect on the residence time of the reactants inside the reactor.

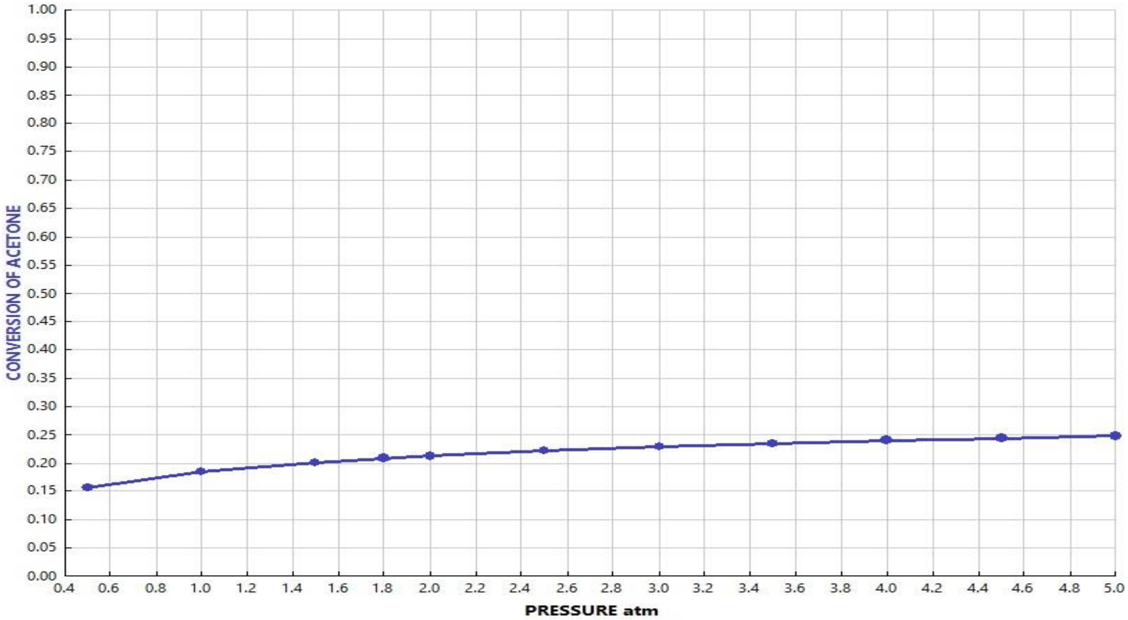


Figure 4.10: The effect of feed stream pressure on conversion of acetone.

The effect of feed stream pressure on the product stream temperature is shown in Figure 4.11. It is seen that the product stream temperature decreases with increasing the feed stream pressure. Generally, when pressure increases the temperature decreases.

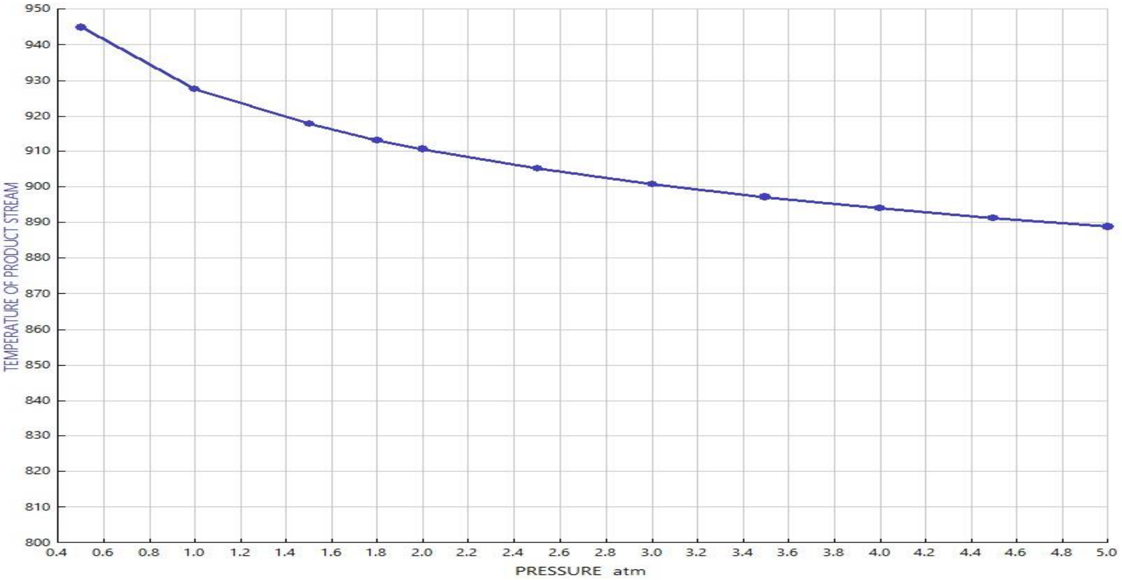


Figure 4.11: The effect of feed stream pressure on the product stream temperature

4.2.1.3 Effect of the Dimensions of Plug Flow Reactor.

Figure 4.12 shows the effect of tube length at different tube diameters of Plug Flow Reactor on the outlet stream temperature. It is observed that the increase in the tube length at different tube diameters decreases the outlet stream temperature, due to the nature of this reaction. This reaction is an endothermic reaction, where increasing of Plug Flow Reactor PFR dimensions increases the residence time of the reactants, which leads to a reduction in the outlet stream temperature. On the other hand, increasing the tube diameters increases the volume of the reactor, which leads to the reduction of the outlet temperature as shown in Figure 4.12. Moreover, decreasing the outlet temperature, the reaction virtually dies out, and this leads to decreasing the conversion as well.

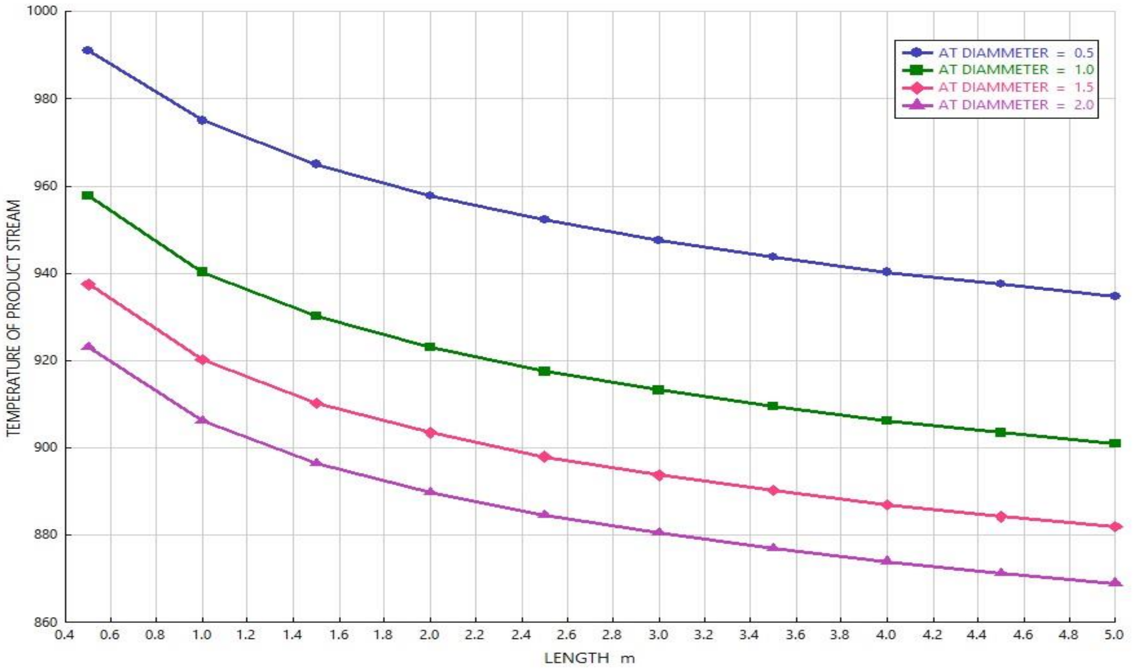


Figure 4.12 the effect of tube length at different tube diameters on the production stream temperature.

4.2.2 RadFrac Rectifying Column RECT.

4.2.2.1 The Effect of Bottoms Mass Flow Rate kg/hr.

Figure 4.14 shows the effect of bottom mass flow rate on the mole fraction of ketene in stream 4 and the mole fraction of acetone in stream 3. The intersection point is shown in Figure 4.14 the mole fraction of both components. The value of bottom mass flow rate is 6685 kg/hr and the mole fraction of ketene is 0.965 kmol/hr, and 0.996 kmol/hr for acetone. The rate of bottom mass flow is little higher than the mass flow of acetone in the feed stream of rectifying column, stream 2. Instead of the reboiler in this column, the feed enters to the bottom of the column and the temperature of the feed stream is used as reboiler. In addition, the bottom mass flow is higher than the mass flow of acetone in the feed stream, due to the small amount of ketene backing down with acetone after they condense to the bottom of the column. Thereafter, the temperature of ketene rises again due to the temperature at the bottom of the column and goes up to the top of the column. In short, the temperature of the feed with the bottom mass flow rate works as a reboiler.

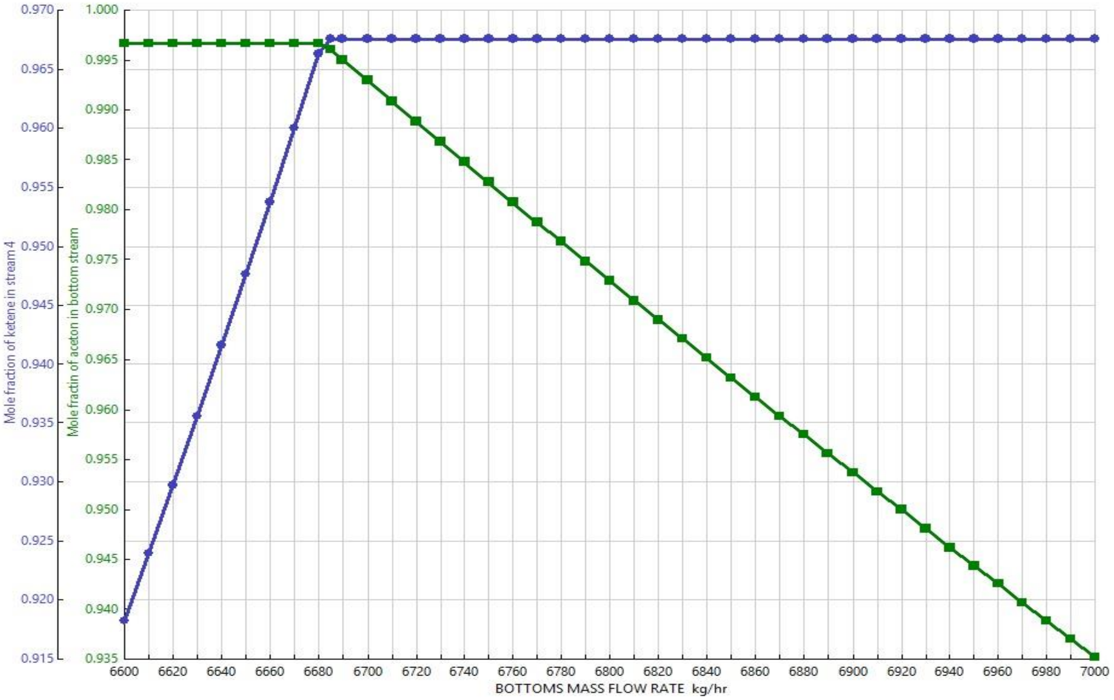


Figure 4.13. The effect of bottoms mass flow rate on the mole fraction.

Figure 4.15 shows the effect of bottom mass flow rate on the mole fraction of all components in stream 4. Ketene has the highest mole fraction at 6685 kg/hr bottoms mass flow rate, where acetone has a mole fraction of zero and methane has a mole fraction of 0.03 kg/hr,

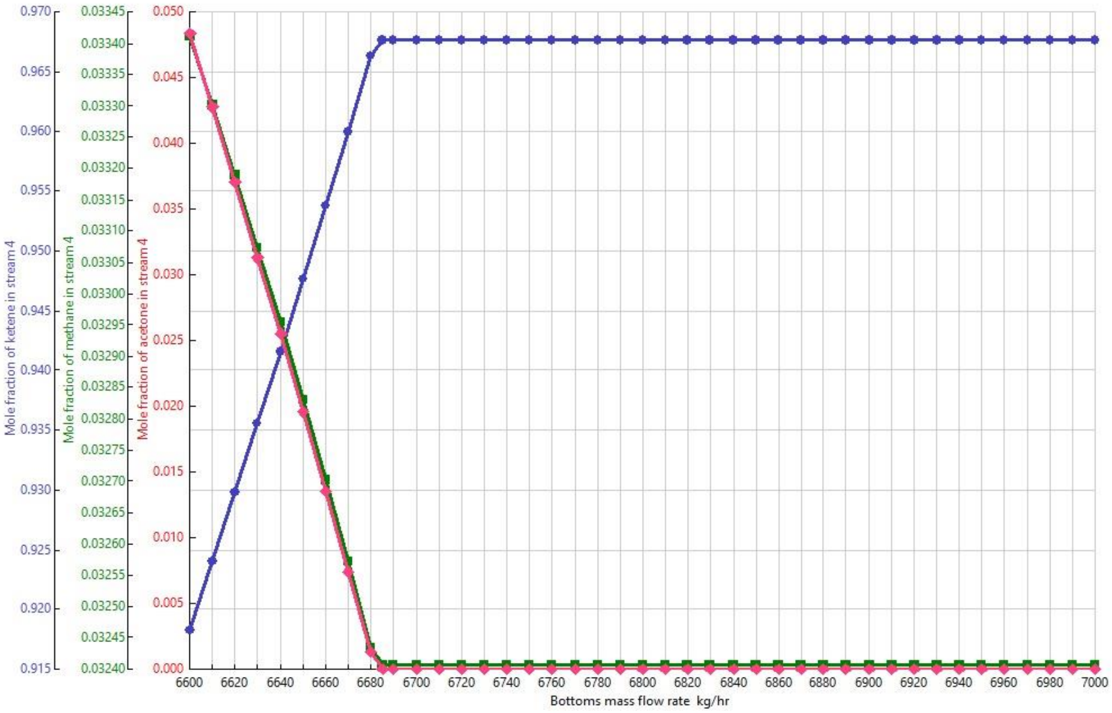


Figure 4.14. The effect of bottoms mass flow rate.

4.2.2.2 The Effect of Condenser Temperature

The effect of condenser temperature has been studied on the mole fraction of ketene, methane, and acetone in streams 3, 4 and 5, as shown in Figure 4.16. The highest mole fraction of ketene is in stream 4. There is no effect of condenser temperature on acetone mole fraction in stream 3, where the focus is to separate ketene and methane as shown in the figure below, and the intersection point is good to get mole fraction to all component at a suitable value. The production target is to produce the ketene with high mole fraction and purity to utilize it in acetic anhydride production at high purity. This operation has been performed at 183 K and mole fraction of ketene was 0.965. Moreover, with this temperature small amount of ketene goes up to stream 5, due to the vapor pressure of ketene at this temperature, which leads to a decrease in methane mole fraction. The vapor pressure of ketene at 183 K is higher than the vapor pressure at other temperature less than 183 K and decreases if the temperature decreases as well.

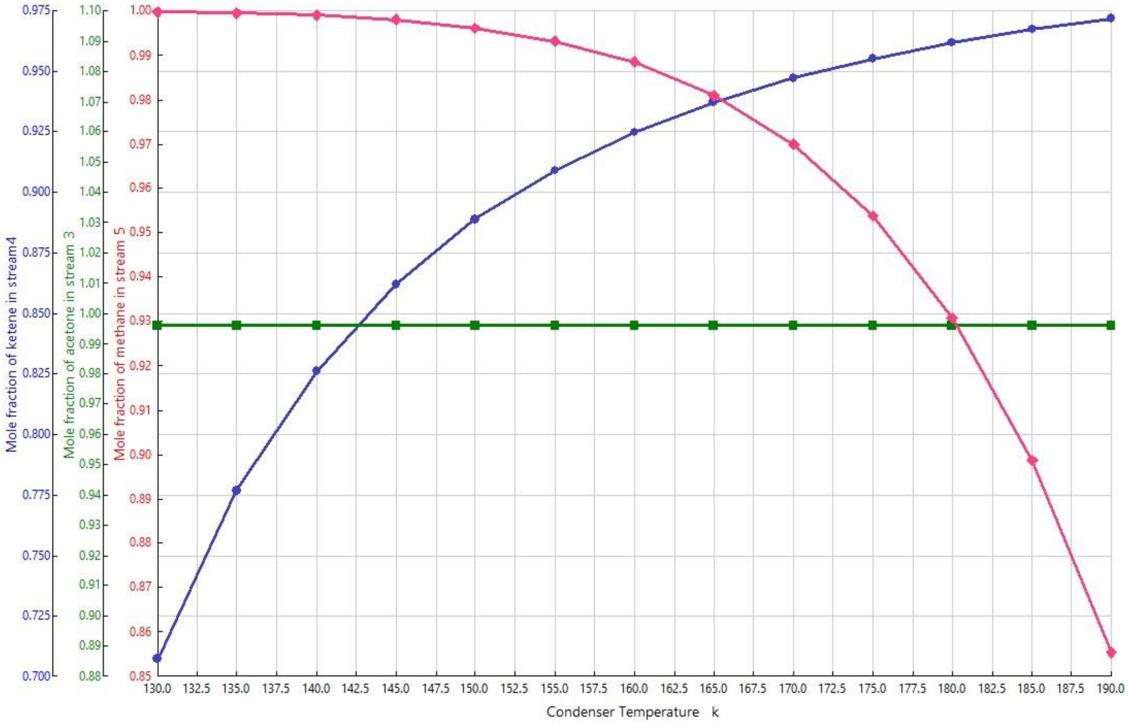


Figure 4.15. The effect of condenser temperature on the mole fraction of ketene, methane and acetone.

4.2.2.3 The Effect of Condenser Pressure

Figure 4.17 shows the effect of condenser pressure on the mole fractions of components in streams 3, 4 and 5. As shown in Figure 415, the mole fraction of acetone in stream 3 is constant, which means there is no effect of condenser pressure on the mole fraction of acetone at this rang of pressure. Therefore, the aim of this design is to separate ketene and methane and bring the mole fraction of ketene at the highest value. In addition, the figure below shows that the mole fraction of ketene is at highest point 0.985 at 0.5 atm condenser pressure, the resulted mole fraction of methane is 0.79 kg/hr. In this case, about 12 kmol/hr of ketene is lost from the total flow rate of ketene in the feed stream due to the vapor pressure of ketene. In this case, the number of moles that loss of ketene at 0.5 atm condenser pressure goes up to stream 5. Therefore, the mole fraction of methane decreases in stream 5. Subsequently, the condenser pressure is 1 atm in order to avoid losing 12 kmol/hr of ketene.

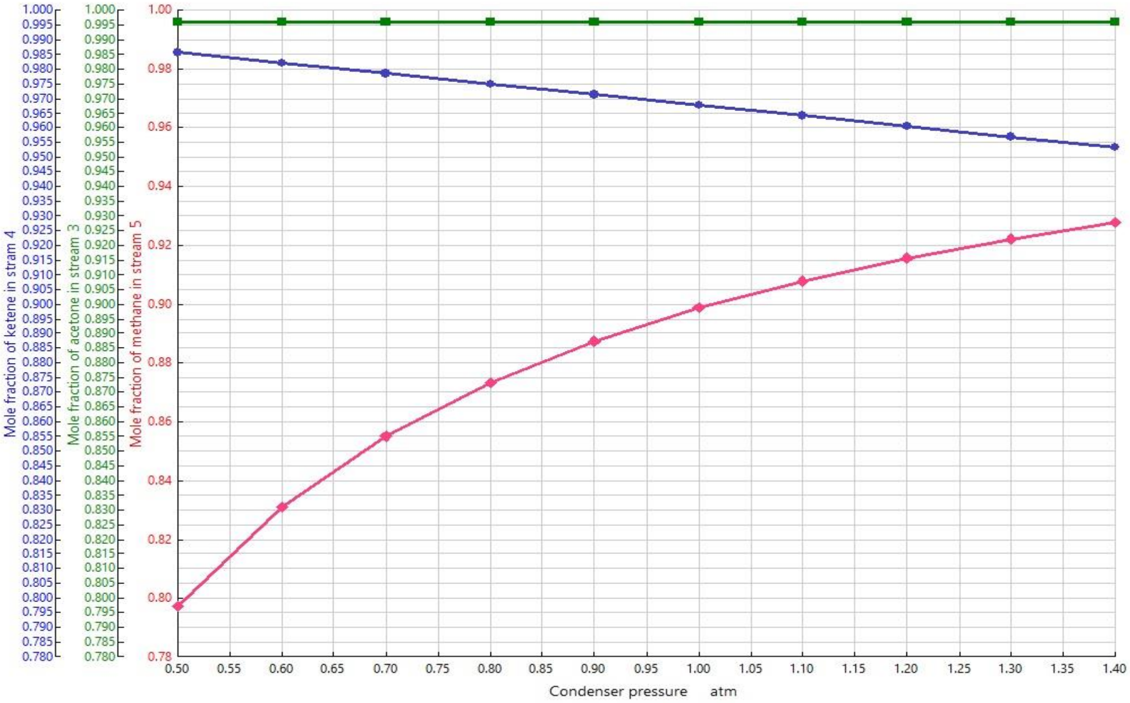


Figure 4.16. The effect of condenser pressure on the mole fractions of products.

4.2.3 Continuous Stirred Tank Reactor, CSTR.

4.2.3.1 The Effect of CSTR Reactor Temperature.

Figure 4.18 shows the effect of CSTR reactor temperature on the mole fraction of acetic anhydride. As shown in this figure, when reactor temperature decreases the mole fraction of acetic anhydride increases, since this reaction is exothermic reaction.

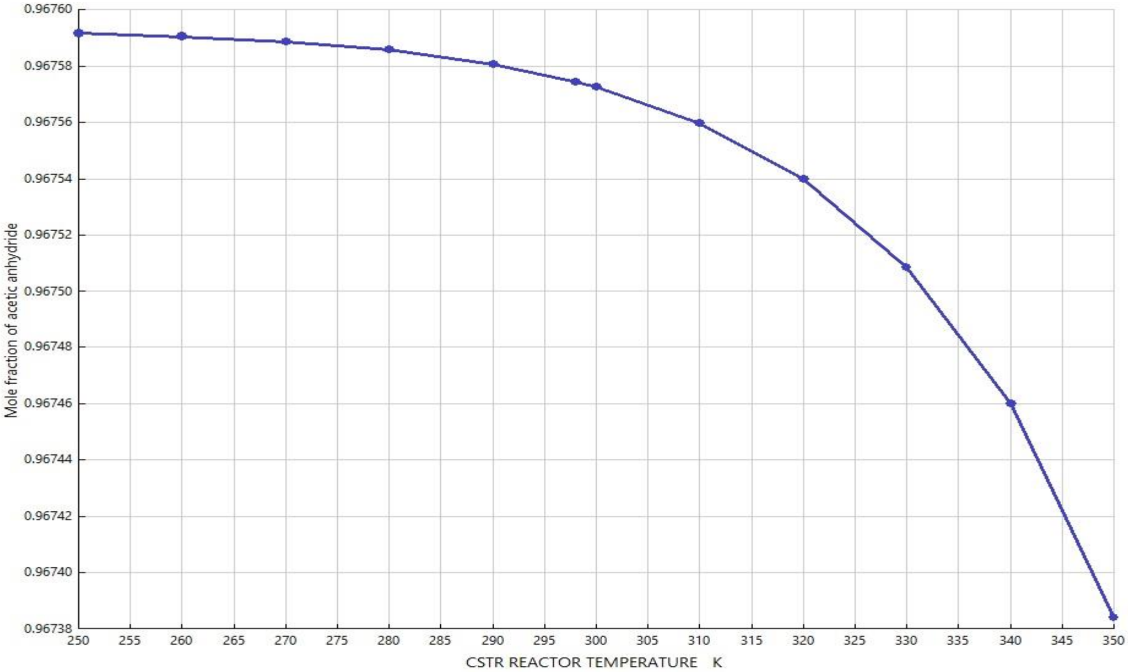


Figure 4.17. The effect of reactor temperature on the mole fraction of acetic anhydride.

4.2.3.2 The Effect of CSTR Reactor Pressure

Figure 4.19 shows the effect of reactor pressure on the mole fraction of acetic anhydride. As shown in this figure, the mole fraction increases with increase the reactor pressure but the range of increase is too small (0.967548 to 0.96757).

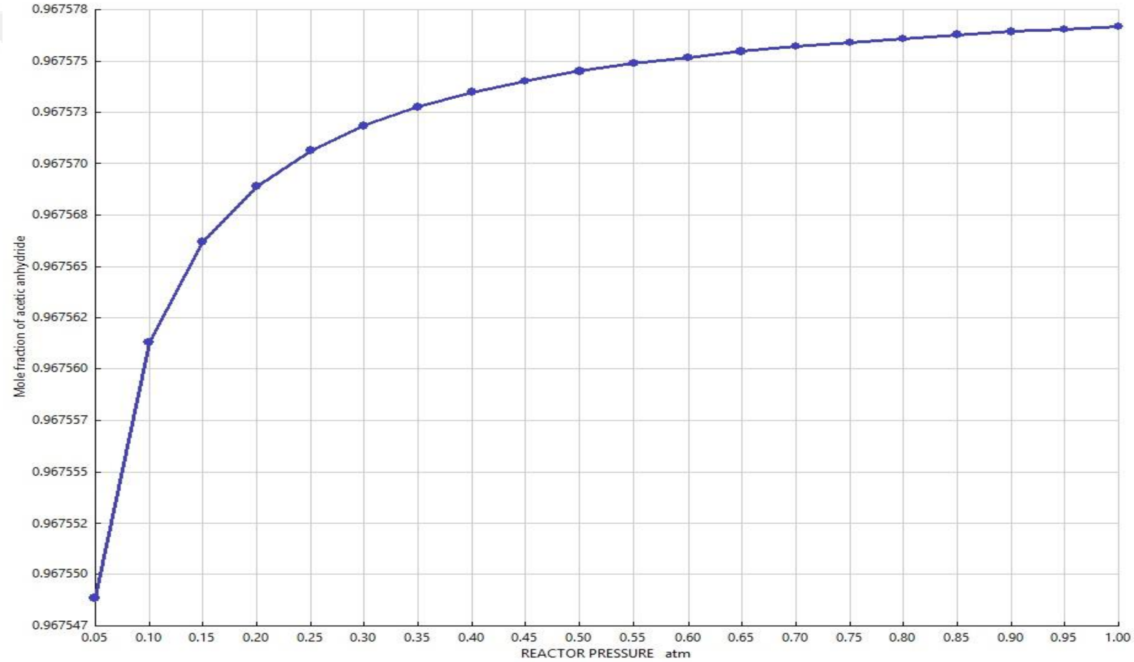


Figure 4.18. The effect of reactor pressure on the mole fraction of Acetic Anhydride.

CHAPTER 5

CONCLUSIONS

This research is modeling acetic anhydride production from acetone with Aspen Plus and aims to understand and study the production process of acetic anhydride as well as simulating the production process with Aspen Plus software and study the operational variables and their effects on the production to get the products at high purity. From the simulation, the main conclusions are drawn from the simulation design as following:

- Since the cracking reaction of acetone is the endothermic reaction and the value of the heat of reaction is positive, the conversion increases with increasing of feed temperature.
- The temperature is the most dominant variable that effects on the conversion of acetone. On the other hand, the pressure has less effect, but it is important also because it has a significant effect on the residence time of the reactants inside the reactor. Consequently, it is important to keep the conversion low because the ketene is unstable and tends to decompose, which is an important reason to keep the temperature low.
- The conversion of acetone at reactor length 3m and diameter 1m of plug flow reactor is 20.8%. When the length of the tube is more than 3.5 m, the reaction virtually dies out due to a large drop in the temperature.

- To avoid adding a compressor before the distillation column, a pressure of 1.8 atm for the feed stream of plug flow reactor is selected. At the same time, this is performed to reduce the residence time of reactants inside the plug flow reactor to avoid cracking of ketene to carbon monoxide and ethylene.
- At a condenser temperature of 183 K, 1 atm condenser pressure and 6885 kg/hr as bottom mass flow rate is suitable. In these conditions, the mole fraction of ketene is at the desired level with purity of 98.7%. In addition, the mole fraction of unreacted acetone at the bottom stream is 0.996 with purity of 99.7%.
- According to the results of sensitivity analysis, the increase in condenser temperature increases the mole fraction of ketene and decreases the mole flow of ketene in stream 4 or middle stream of distillation column. Moreover, the mole fraction of methane at top stream decreases due to the transfer of small amount of ketene to top stream. The mole fraction of acetone at the bottom stream is not affected by increase the condenser temperature.
- The mole fraction of ketene at middle stream increases with the increase in the condenser temperature, because the vapor pressure of ketene increases and small number of mole of ketene is transferred to the top stream, resulting into a decrease in the mole fraction of methane.
- Increasing condenser pressure more than 1 atm decreases the mole fraction of ketene at ketene stream (middle stream of rectifier column). The condenser pressure is higher than the vapor pressure of ketene.
- The reaction of ketene with acetic acid is exothermic, because the heat of reaction is negative, which means that there is energy or heat released from this reaction,

and the mole fraction of acetic anhydride increases with decreasing the temperature of a reactor as shown in sensitivity analysis.

- The production of acetic anhydride is about 26640 tons/year with a purity about 99.4%. This amount corresponds to 16950 tons of acetone and 15673 tons of acetic acid per year.

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APPENDICES

APPENDIX A

- **PROCESS THERMODYNAMICS**

Thermodynamics properties of the material are given in below standard tables:

Table 2.1: Heat of formation.

	A	**B**	**C**	**D**	ΔH_f at 298k
Acetone	-199.175	-7.148×10^{-2}	3.2534×10^{-5}	---	-217.5
Ketene	-44.988	-0.00983	2.46×10^{-6}	---	-47.5
Methane	-63.425	-4.3355×10^{-2}	1.722×10^{-5}	---	-74.85
Acetic acid	-422.584	-4.865×10^{-2}	2.3337×10^{-5}	---	-434.84
Acetic anhydride	-554.715	-8.412×10^{-2}	4.362×10^{-5}	---	-575.72

Table 2.2: The standard heat capacities.

	A	**B**	**C**	**D**	ΔC_p at 298k
Acetone	26.2	0.183	-45.86×10^{-6}	---	-153.05
Ketene	20.04	0.0945	-30.95×10^{-6}	---	-47.47
Methane	13.39	0.077	-18.91×10^{-6}	---	-50.84
Acetic acid	-18.95	1.0971	2.892×10^{-3}	2.928×10^{-6}	-376.69
Acetic anhydride	71.83	8.888×10^{-1}	-2.654×10^{-3}	3.350×10^{-6}	-476.68

Table 2.3: Gibbs energy of formation.

	A	**B**	**C**	$\Delta \boldsymbol{G_f}$ at 298K
Acetone	-218.77	2.118×10^{-1}	2.662×10^{-5}	-153.05
Ketene	-47.916	---	5.04×10^{-6}	-47.47
Methane	-75.262	7.593×10^{-2}	1.87×10^{-5}	-50.84
Acetic acid	-435.963	1.935×10^{-1}	1.636×10^{-5}	-376.69
Acetic anhydride	-578.076	3.316×10^{-1}	2.5188×10^{-5}	-476.68

The heat reaction calculation of first reaction

There are two methods to calculate heat of reaction at 1000K, where the reaction is:

$CH_3COCH_3 \rightarrow C_2H_2O + \quad CH_4$ 2.10

1) The heat of reaction is calculated through the heat of formation of each component at 298 K and 1000 K and then the heat of reaction at these two temperatures are calculated through:

$$\Delta H_f = A + BT + CT^2 \qquad 2.11$$

$$\Delta H_r = H_{fketene} + H_{fmethane} - H_{facetone}$$

2) The heat of reaction is calculated at 298 K then using the heat of capacities of component to calculate the heat of reaction at 1000 K:

$$\Delta H_{r\ at1000k} = \Delta H_1 + \Delta H_{298} + \Delta H_3 \qquad 2.12$$

1) **First, the heat at reaction is calculated by calculating the heat formation of the component at 298 and 1000k.**

1. Acetone

$$\Delta H_f = A + BT + CT^2 + DT^3$$

$$\Delta H_{f298} = [-199.175] + [-7.1484 \times 10^{-2}]T + [3.2534 \times 10^{-5}]T^2$$

$$= [-199.175] + [-7.1484 \times 10^{-2}] \times [298] + [3.2534 \times 10^{-5}] \times [298]^2$$

$$= -217.5\ kJ/mol$$

$$\Delta H_{f1000} = [-199.175] + [-7.1484 \times 10^{-2}] \times [1000] + [3.2534 \times 10^{-5}] \times [1000]^2$$

$$= -237.5\ kJ/mol$$

2. Ketene

$$\Delta H_{f298} = [-44.988] + [-0.00983] \times [298] + [2.46 \times 10^{-6}] \times [298]^2$$

$$= -47.9\ kJ/mol$$

$$\Delta H_{f1000} = [-44.988] + [-0.00983] \times [1000] + [2.46 \times 10^{-6}] \times [1000]^2$$

$$= -52.5\ kJ/mol$$

3. Methane

$$\Delta H_{f298} = [-63.425] + [-4.3355 \times 10^{-2}] \times [298] + [1.7220 \times 10^{-5}] \times [298]^2$$

$$= -74.81\ kJ/mol$$

$$\Delta H_{f1000} = [-63.425] + [-4.3355 \times 10^{-2}] \times [1000] + [1.7220 \times 10^{-5}] \times [1000]^2$$

$$= -90\ kJ/mol$$

$$\Delta Hr\ _{298} = (-47.9) + (-74.81) - (-217.5)$$

$$= 94.9 kJ/mol$$

The heat at reaction at 1000 K

$$\Delta H_{r1000} = [-52.5] + [-90] - [-237.5]$$

$$= 95\ kJ/mol$$

2) **The heat of reaction is calculated from the heat capacity for each component.**

$$\begin{tikzcd}
CH_3COCH_3 \arrow[r, "\mathbf{1000\ K=?}"] \arrow[d, "\Delta H_1"'] & C_2H_2O + CH_4 \\
CH_3COCH_3 \arrow[r, "\Delta H_{298}"'] & C_2H_2O + CH_4 \arrow[u, "\Delta H_2"']
\end{tikzcd}$$

$$\Delta H_1 = \int_{1000}^{298} [Cp_{Aceton}]\ dT \tag{2.13}$$

$$= \int_{1000}^{298} [26.2 + 0.183T + (-45.86 \times 10^{-6}\, T^2]\ dT$$

$$= 26.2\, T \int_{1000}^{298} \quad + \frac{0.183\, T^2}{2} \int_{1000}^{298} \quad - \frac{45.86 \times 10^{-6}\, T^3}{3} \int_{1000}^{298}$$

$$= 26.2\ \times\ (-702) + 0.0915\ \times\ [-911196] - 15.287\ \times\ 10^{-6}\, [-973536408]$$

$$= 18392 - 82918.8 + 14882$$

$$= -86.2 kJ/mol$$

$$\Delta H_{298} = (-47.7) + (-74.81) - (-217.5)$$

$$= 94.9 kJ/mol$$

$$\Delta H_3 = \int_{298}^{1000} [Cp_{ketene+} Cp_{Methane}]\ dT$$

$$= \int_{298}^{1000} [33.43\, T + \frac{0.1715\, T^2}{2} \int_{298}^{1000} \quad - \frac{49.86\ \times\ 10^{-6}\, T^3}{3} \int_{298}^{1000}$$

$$= 86\ kJ/mol$$

$$\Delta H_{1000} = \Delta H_1 + \Delta H_{298} + \Delta H_3$$

$$= -86.2 + 94.9 + 86$$

$$= 94.7\ kJ/mol$$

- **Gibbs Energy of Formation**

$$\Delta G^o = A + BT + CT^2 \qquad 2.14$$

1. **Acetone**

$$\Delta G^{o}_{298} = [-218.77] + [2.1177 \times 10^{-1}]T + [2.6619 \times 10^{-5}]T^{2}$$

$$= [-218.77] + [2.1177 \times 10^{-1}] \times [298] + [2.6619 \times 10^{-5}] \times [298]^{2}$$

$$= -153.05\, J/kmol$$

$$\Delta G^{o}_{1000} = [-218.77] + [2.1177 \times 10^{-1}] \times [1000] + [2.6619 \times 10^{-5}] \times [1000]^{2}$$

$$= 19.619\, J/kmol$$

2. **Ketene**

$$\Delta G^{o}_{298} = [-47.916] + 0 \times T + [5.04 \times 10^{-6}]T^{2}$$

$$= [-47.916] + [5.04 \times 10^{-6} \times (298)^{2}]$$

$$= -47.47\, J/kmol$$

$$\Delta G^{o}_{1000} = [-47.916] + 0 \times [1000] + [5.04 \times 10^{-6}] \times [1000]^{2}$$

$$= 42.9\, J/kmol$$

3. **Methane**

$$\Delta G^{o}_{298} = [-75.262] + 7.5925 \times 10^{-2} \times T + [1.8700 \times 10^{-5}]T^{2}$$

$$= [-75.262] + 22.62 + 1.66063$$

$$= -50.84\, J/kmol$$

$$\Delta G^{o}_{1000} = [-75.262] + 7.5925 \times 10^{-2} \times +[1.8700 \times 10^{-5}] \times [1000]^{2}$$

$$= [-75.262] + 75.925 + 18.7$$

$$= 19.363\ J/kmol$$

Now calculate ΔG_r for the reaction at both temperature.

$$\Delta G_r = \sum \Delta_{G\ products} - \sum \Delta_{G\ reactents}$$

$$\Delta G_{r298} = \Delta G_{ketene} + \Delta G_{Methane} - \Delta G_{Aceton}$$

$$= [-47.47 + (-50.84)] - [153.05]$$

$$= 54.74\ J/kmol$$

So the reaction is not feasible at 298k because ΔG_{298} is positive

$$\Delta G_{r1000} = \Delta G_{ketene} + \Delta G_{Methane} - \Delta G_{Aceton}$$

$$= -42.9 + 19.363 - 19.16$$

$$= -48.172\ J/kmol$$

So this reaction is feasible at 1000k because ΔG_{1000} for reaction is negative.

- **Reaction 2**

1. **The second reaction calculate of the heat of reaction for**

$$C_2H_2O + CH_3COOH \rightarrow C_4H_6O_3 \qquad 2.15$$

Because this reaction is performed at normal temperature 25 C° or 298 K, the heat of the reaction is calculated at this temperature only.

- **Ketene**

$$\Delta H_{f298} = -44.988-[0.00983\times298] +2.46\times10^{-6} \times (298)^2$$

$$= -47.9\ kJ/mol$$

- **Acetic Acid**

$$\Delta H_{f298} = -422.584 - 4.8354 \times 10^{-2} \times (298) + 2.3337 \times 10^{-5} \times (298)^2$$

$$= -434.9\ kJ/mol$$

- **Acetic anhydride**

$$\Delta H_{f298} = -554.715 - 8.4124 \times 10^{-2} \times (298) + 4.3618 \times 10^{-5} \times (298)^2$$

$$= -575.79\ kJ/mol$$

$$\Delta H_r = \Delta H_{f\,Acetic\ Anhydride} - [\Delta H_{f\,Acetic\ Acid} + \Delta H_{f\,ketene}]$$

$$= -575.79 - [-434.9 + (-47.9)]$$

$$= -92.96\ kJ/mol$$

- **Gibbs Energy of Formation**

$$\Delta G^{o} = A + BT + CT^{2} \qquad 2.16$$

- **Ketene**

$$\Delta G \quad = -47.916 + 0 \times T + 5.04 \times 10^{-6}\, T^{2}$$

$$= -47.916 + 0.44757216$$

$$= -47.47 J/kmol$$

- **Acetic Acid**

$$\Delta G \quad = -435.963 + 1.934 \times 10^{-1} \times (298) + 1.6362 \times 10^{-5} \times\ (298)^{2}$$

$$= -435.963 + 57.65 + 1.45301$$

$$= -376.69 J/kmol$$

- **Acetic Anhydride**

$$\Delta G \quad = -578.076 + 3.3162 \times 10^{-1} \times (298) + 2.5188 \times 10^{-5} \times\ (298)^{2}$$

$$= -578.076 + 98.823 + 2.2368$$

$$= -476.68\, J/kmol$$

$$\Delta G_{reaction} = \sum \Delta_{G\ products}\ - \sum \Delta_{G\ reactents}$$

$$= \Delta G_{Acetic\ Acid} + [\Delta G_{Ketene} - \Delta G_{acetic\ acid}$$

$$= -476.68 - [-47.47 + (376.69)]$$

$$= -52.52\, J/kmol$$

So, the reaction is feasible at 298 K because ΔG_{298} of the reaction is negative.

Material Balance.

1. **For first reaction in plug flow reactor.**

The table 3.1 shows the inlet and outlet streams of plug flow reactor for the first reaction:

Components	Inlets, stream 1 kmol/hr	Outlets, stream 2 kmol/hr	Molecular weight Mwt.
Acetone	145	114.793	58.08
Ketene	-	30.207	42.037
Methane	-	30.207	16.04

Table 3.1 the inlets and outlets streams of plug flow reactor.

The mass balance can be calculated from this information in the table or by knowing the mole fraction of each component and total mole flow of both sides of the reactor, stream 1 and 2.

The mass balance is calculated from the information in the table. Since only the acetone is fed as feed stream, the mass can be obtained for acetone only for feed stream and the mass in outlet stream can be obtained for ketene, methane and unreacted acetone.

First, calculate the mass for feed stream:

Where:

Number of moles = the mass / molecular weight

So,

The mass of acetone in feed stream = the total mole flow of acetone in feed × molecular weight of acetone

The mass of acetone = 145 kmol × 58.08 g/mol.

= (145 × 1000 mol) × 58.08 g/mol.

= 8421600 g = 8421.6 kg.

Second, calculate the mass in product stream.

The mass of acetone in product stream = the moles of unreacted acetone × Mwt.

= (114.793 × 1000) mol × 58.08 g/mol

= 6667177.44 g = 6667.177 kg.

The mass of ketene in product stream = the moles of ketene × Mwt of ketene.

= (30.207 × 1000) mol × 42.037 g/mol.

= 1269821.659 g = 1269.82 kg.

The mass of methane in product stream = (30.207 × 1000) mol × 16.04 g/mol.

= 484520.28 g = 484.60 kg.

The total mass in product stream = 6667.177 + 1269.82 + 484.60

= 8421.6 kg.

So, this process in mass balance because the total mass inlet equal to the total mass outlet.

2. **For rectifying column.**

	Inlet kmol	Outlet kmol	Outlet kmol	Outlet kmol	g/mol
Components	Stream 2	Stream 3	Stream 4	Stream5	Mwt
Acetone	114.793	114.793	-	-	58.08
Ketene	30.207	0.4045	27.0099	2.7926	42.037
Methane	30.207	0.0508	0.9652	29.191	16.04

Table 3.2 the inlets and outlets streams of rectifying column.

The mass for stream 2, product stream of plug flow reactor was calculated in last step = 8421.6 kg.

- The masses for each component in stream 3 are calculated, the bottom stream of rectifying column.

1. The mass of acetone in bottom stream, stream 3 is the same with the mass of acetone in stream 2, feed stream of rectifying column or the product stream of plug flow reactor. So, the mass of acetone in stream 3 = 6667.177 kg.
2. The mass of ketene in stream 3 = (0.4045 × 1000) mol × 42.037g/mol.

   = 17003.96 g = 17.004 kg.
3. The mass of methane in stream 3 = (0.0508 × 1000) mol × 16.04 g/mol.

   = 814.83 g = 0.815 kg.

   The total mass in stream 3 = 6667.17 + 17.004 + 0.815

   = 6684.989 kg = 6685 kg.

- The total mass in stream 4 is calculated, middle stream of rectifying column.
    1. The mass flow of acetone in this stream = 0, because the mole flow of acetone in this stream = 0.
    2. The mass of ketene in stream 4 = (27.0099 × 1000) mol × 42.037
       = 1135415.166 g = 1135.42 kg.
    3. The mass of methane in stream 4 = (0.9652 × 1000) mol × 16.04
       = 15481.808 g = 15.48 kg.

       So, the total mass in stream 4 = 1135.42 + 15.48
       = 1150.9 kg.
- The total mass in stream 5 is calculated, Top stream of rectifying column.
    1. The mass of acetone in stream 5 = 0 kg.
    2. The mass of ketene in stream 5 = (2.7926 × 1000) mol × 42.037
       = 117392.52 g = 117.39 kg.
    3. The mass of methane in stream 5 = (29.191 × 1000) mol × 16.04 g/mol
       = 468323.64 g = 468.30 kg.

       So, the total mass in stream 5 = 117.39 + 468.30

       = 585.69 kg.

The total mass of product streams of rectifying column = 6685 + 1150.9 + 585.69

= 8421.6 kg.

So the mass in balance because the inlets mass equal to the outlets mass of rectifying column.

3. **For second reaction in Continuous Stirred Tank Reactor.**

The table 3.3 shows the inlets and outlet streams of Continuous Stirred Tank Reactor.

	Inlets streams kmol		Outlet stream kmol	
Components	Stream 4	Stream6	Stream 7	Mwt
Methane	0.965	-	0.965	16.04
Ketene	27.0099	-	0.00194	42.037
Acetic acid	-	27.0099	0.00192	60.052
Acetic anhydride	-	-	27.008	102.09

Table 3.3 the inlets and outlets streams of Continuous Stirred Tank Reactor.

- The mass in stream 4 is calculated, the inlet stream of Continuous Stirred Tank Reactor and outlet stream, middle stream of rectifying column.

The mass of stream 4 was calculated in last step = 1150.9 kg.

- The mass of stream 6 is calculated, mass of acetic acid = (27.009 × 1000) mol × 60.052 g/mol = 1621998.515 g = 1622.01 kg
- The total mass in stream 7 is calculated, the outlet stream of Continuous Stirred Tank Reactor.

  1. The mass of acetic anhydride in stream 7 = (27.008 × 1000) mol ×102.09 g/mol

     = 2757246.72 g = 2757.24kg.

  2. The mass of acetic acid in stream 7 = (0.00192 ×1000) mol ×60.052 g/mol

     = 115.299 g = 0.115 kg.

3. The mass of ketene in stream 7 = (0.00194 ×1000) mol × 42.037 g/mol.

= 81.64178 g = 0.0816 kg.

4. The mass of methane in stream 7 = (0.965 ×1000)mol ×16.04 g/mol

= 15481.808 g = 15.48 kg.

Where the total mass of inlets streams = mass of stream 4 + mass of stream 6

= 1150.9 + 1622.0

= 2772.92 kg.

And the total mass of outlet stream = the total mass in stream 7

= 2757.24 + 0.115 + 0.0816 + 15.48

= 2772.92 kg.

Consequently, the mass balance is satisfied because the inlets mass equals to the outlets mass of continuous stirred tank reactor.

APPENDIX B

- WILS-NTH equation [31]:

$$P = \frac{PT}{V_m - b}$$

Where:

  - $b = \sum_{i=1}^{nc} y_i b_i + \sum_{i=1}^{nc} \sum_{j=1}^{i} y_{ij} b_{ij}$
  - $b_{ij} = \frac{(bi^{\frac{1}{3}} + bj^{\frac{1}{3}})^3}{8}$
  - nc is the number of component

The question of Wilson model is:

$$ln\gamma_i = 1 - \ln(\sum_j A_{ij}X_j) - \sum_j \frac{A_{ij}X_j}{\sum_k A_{ik}X_k}$$

Where:

- $ln\, A_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} lnT + d_{ij}T$
- $a_{ij} = a_{ji}$
- $b_{ij} = b_{ji}$
- $c_{ij} = c_{ji}$
- $d_{ij} = d_{ji}$

Plug Flow Reactor Calculation

The reaction taking place as follows:

$$CH_3COCH_3 \rightarrow C_2H_2O + \quad CH_4$$

Since only Acetone inters and the reaction has been done in an adiabatic operation which means Q= 0, for no work on the system done W= 0 and U ≡ 0. So the main equation in terms of conversion becomes:

$$\frac{dT}{dV} = \frac{-(rA)[-\Delta H_r(TR)+\Delta Cp(T-TR)]}{FA_{\circ}\,(CpA+X\Delta Cp)}$$

Mole Balance:

$$FA_{\circ} = \frac{8421.6 \times 1000g}{50.08g/mol} = 40.2778 \text{ mol/s}$$

$$CA_{\circ} = \frac{PA_{\circ}}{RT} = \frac{182\ kpa}{8.31\,\frac{kpa.m^3}{kmol.K}\,(\,1035\ K)} = 0.02115 \text{kmol/m}^3 = 21.15 \text{ mol/m}^3.$$

$$\upsilon_{\circ} = \frac{FA_{\infty}}{CA_{\circ}} = \frac{40.2778\ mol/s}{21.15\ mol/m^3} = 1.904 \text{ m}^3\text{/s.}$$

$$\text{V} = \frac{\pi D^2}{4} \times \text{length} = \frac{\pi(1)^2}{4} \times 3 = 2.356 \text{ m}^3.$$

Energy Balance:

The heat of reaction of heats formation at 298 K was calculated above:

Where

$H_{r\ acetone} = -\ 217.5\ kJ/mol$

$H_{r\ ketene} = -\ 47.9\ \ kJ/mol$

$H_{r\ methane} = -\ 74.81\ kJ/mol$

$\Delta H_{r298} = H_{r\ methane} \quad + H_{r\ methane} - \ H_{r\ acetone}$

$\Delta H_{r298} = 94.9\ kJ/mol$

The heat capacities ΔCp are:

Cp acetone = 26.2 + (0.183 × 1000) – (45.86×10-6 × (1000)²) = 163.3 J/mol.K.

Cp ketene = 20.04 + (0.0945 × 1000) – (30.95×10-6 × (1000)²) = 83.6 J/mol.K.

Cp acetone = 13.39 + (0.077 × 1000) – (18.91×10^{-6} × (1000)²) = 71.5 J/mol.K.

ΔCp = -8.2 J/mol.K.