

**MODELLING AND STUDY OF CONTROL STRUCTURES OF REACTIVE
DISTILLATION FOR THE PRODUCTION OF METHYL TERT-BUTYL ETHER
(MTBE)**

By

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ABSTRAK

Projek ini melibatkan simulasi penyulingan reaktif metil tersier butil eter menggunakan ASPEN PLUS dan ASPEN Dynamics. Satu model simulasi dipilih daripada artikel berjaya dimodelkan menggunakan ASPEN PLUS. Model simulasi tersebut adalah berdasarkan pada sumber literasi yang dipilih, dengan tambahan maklumat yang digunakan dari sumber literasi lain-lain. Setelah berjaya menjalankan simulasi, model dalam projek ini disahkan dengan sumber asalnya. Setelah mengesahkan bahawa model yang dibuat membawa kepada hasil yang serupa dengan rujukan asal, projek tersebut dipindahkan ke bahagian ASPEN Dynamics. Pengawal dipasang menggunakan ASPEN Dynamics dan tindak balas mereka terhadap ujian gangguan dan ujian perubahan 'setpoint' dinilai. Pengawal FLOWMET, TEMPC dan LEVELTOPS dinilai dengan ujian gangguan. Pengawal ini menunjukkan tindak balas yang agak baik dan dapat memulihkan parameter yang ingin dikawal untuk kembali ke titik asal masing-masing. Oleh itu, dapat disimpulkan bahawa adalah mungkin untuk menggunakan kaedah linear untuk mengawal dinamika lajur penyulingan reaktif. Walaupun begitu, gangguan yang dilaksanakan adalah berskala kecil dan tidak terlalu besar. Oleh itu, penalaan dan perubahan lebih lanjut mungkin harus dilakukan untuk meningkatkan lagi penyesuaian pengawal ini jika sistem kawalan ini akan dilaksanakan pada skala yang lebih besar.

ABSTRACT

This project studies the reactive distillation of methyl tertiary butyl ether (MTBE). A simulation model for this process was selected based on a selected literature source, with additional information utilised from other literature sources. This model was and successfully modelled in the ASPEN PLUS software. After successful running of the simulation, the model in this project was verified with the original source it was based on. After verifying that the model created leads to a result similar to the original reference, the project was moved to the dynamics portion. Controllers were installed using ASPEN Dynamics and their responses to disturbances and set-point changes were evaluated. The controllers FLOWMET, TEMPC and LEVELTOPS were evaluated with step-point changes. These controllers displayed relatively good responses and were able to guide the varying process variables back to the intended set-point. Hence, it is concluded that is possible to utilise linear methods to control the dynamics of a reactive distillation column. Even so, the disturbances implemented were relatively small-scale and not too large. Therefore, further tuning and changes may have to be made to further improve the tuning of these controllers if this control system is to be implemented on a larger scale.

1 INTRODUCTION

1.1 Background

Reactive distillation is a method that combined the procedures of both a chemical reactor and that of a distillation column into a single unit operation. Early conceptions of reactive distillation columns were derived back in the 1920s. (Kiss, 2019) Successful implementation of reactive distillation in processes such as esterification and etherification has sparked interest in further optimizing and improving the process. Reactive distillation is primarily suited for processes in which there are complications in completing the desired reaction without separating the desired and un-desired product. For example, reactive distillation can be used to overcome azeotrope mixtures. (Rameshwar S, 2003)

Moreover, much economical costs can be conserved by its application as we are essentially reducing the downstream processing section of the chemical plant. This enables us to control the operation of our reaction in an easier manner while minimizing the operating resources. However, much research and improvements have been made in an attempt to increase its usage on an industrial scale. (Jana, 2011)

However, the combination of both distillation and reaction operations into one singular unit increases the complexity in creating a well-functioning column. Each column must be designed to match the reaction kinetics of its desired reaction while ensuring that both separation and reaction process share similar operating conditions. Therefore, this leads to most reactive distillation columns exhibiting non-linear behaviours, further complicating the control aspect of the system.

Methyl tertiary butyl ether (MTBE) is an organic compound with a chemical formula of $(\text{CH}_3)_3\text{COCH}_3$. At room conditions, it exists as a volatile, colourless liquid. MTBE is most commonly used as an anti-knocking additive for gasoline. Anti-knocking agents are added into gasoline or other fuels to reduce engine knocking and increase their respective octane numbers. Engine knocking is an incident in which the air/fuel mixture in an engine occurs separately from that ignited by the sparkplug. Octane number is a measure of knock resistance of fuels. (Z. Wang, 2017)

Prior to its usage, most fuels use lead-based compounds such as tetraethyllead (TEL) to reduce engine knocking. However, the combustion of lead-based fuel resulted in the release of lead to the atmosphere which further contributed to air pollution. MTBE was used as a substitute for

TEL as it was considered as a more environmentally-friendly option. (Beatty & Lovell, 1949) It also helps boost the combustion rate of gasoline and reduce the emissions from motor vehicles. Other side uses of MTBE include its usage to dissolve gallstones in the medical field. (Schoenfield & Marks, 1993)

However, its role as a potential water pollutant has regulated its use as an anti-knocking agent in the United States of America and other countries (Japan, Europe, Canada etc.). (*California Reformulated Gasoline Phase 3 (CaRFG3) | California Air Resources Board*, n.d.) These countries have banned the usage of MTBE with concerns of its potential toxic effects on the environment, with Ethyl tert-butyl ether (ETBE) being considered a safer alternative to replace MTBE. However, MTBE still has a large production based in Asia as well as the Middle East.

Saudi Arabia is known as the largest production rate for MTBE in the Middle East, capping at 3.07 million metric ton per year. Over at Asia, China produces approximately 2.47 million metric ton per year of MTBE. This is followed by South Korea and Taiwan, each capping at 994,000 and 680,000 metric ton per year respectively. The production capacities of MTBE in Asian and Middle Eastern countries are slated to increase in response to a greater demand for automobiles and gasoline. (*Saudi Aramco's MTBE Trading Volume Likely to Rise after Sabic Purchase | S&P Global Platts*, n.d.)

In Malaysia, there is one company that produces MTBE being ran by Petronas. Founded in 1989, PETRONAS Chemicals MTBE Sdn Bhd is located in Kuantan, Malaysia. The plant utilizes Oleflex Dual Feed Dual Product process technology incorporated from the United States of America. In addition, another plant is scheduled to be launched in Johor by Pengerang Refining and Petrochemical (PRefChem). The plant is estimated to be produce 750,000 tonnes per year of MTBE. (*PETRONAS Chemicals MTBE Sdn Bhd | NrgEdge*, n.d.)

1.2 Problem Statement

The usage of reactive distillation in the production of MTBE is a well-established process. Even so, it is still a complex and difficult process to control due to its highly-linear characteristics. It is crucial to identify accurate and precise methods to ensure that the operation of the reactive distillation for MTBE. This final year project is aimed to develop a control method to implement on a simulation of a MTBE reactive distillation operation.

1.3 Objectives

- To develop a reactive distillation (RD) model via ASPEN PLUS & perform simulation.
- To verify the model by comparing with the experimental or data from literature.
- To study on control methods for reactive distillation on MTBE process and implement a chosen control strategy on the developed model.

2 LITERATURE REVIEW

2.1 Control Structures

The main objective of control in reactive distillation setups is to obtain a high yield for our desired product while ensuring that we obtain the maximum amount of conversion possible from our reactants simultaneously. The control of reactive distillation includes the fundamental selection of control configurations and control algorithms. These can be dubbed as control structures. Control structures refer to the number of control loops and specific input-output pairings used in said loops.

Reactive distillation shares several input variables as most conventional distillation systems. They include the reflux ratio, reboiler duty, rate of reactant feeds, reflux rate to name a few. These input variables are then paired with output variables. Variables that are chosen as output variables are commonly easier to measure, enabling researchers to adequately gauge the efficiency of the control structure in order to acquire a high product yield. They include outlet stream compositions or temperatures. (Sharma & Singh, 2010)

Control structures generally manage their input variable by monitoring the output variables. After operation, we can check if the output variables meet our desired standards. If they do not, we can change the input variables. Some control structures use composition analyzers to measure a composition of a selected product. Even so, analyzers are generally expensive and require consistent maintenance. Analyzers also introduce dead time into control loops, which is undesired as dead time will affect the effectiveness of the control structure. (Martin G. Sneesby, 1999)

Multiple researches had been conducted by other researchers to develop a control structure for the reactive distillation of MTBE. It is possible to control the highly non-linear process by the use of simple linear control strategies. A linear control strategy was capable of maintaining a high product purity in the bottoms section. (S. J. Wang, 2003)

Moreover, linear models or non-linear models can be used to control the process. They are considered as more advanced control strategies when compared to the conventional PID controllers. Linear model predictive control (LMPC) is able to control the operation of reactive distillation with multiple linear models. (K Nagy, 2007)

Even so, non-linear model predictive control (NMPC) is much more effective than LMPC. This is primarily because as a process becomes more non-linear, a linear model will have greater

difficulty in predicting the outcome. Non-linear models can be developed by using the input-output modelling method, to identify potential non-linear empirical models from plant data. Another method of non-linear modelling is to develop a first-principle model from process data. (Venkateswarlu & Reddy, 2008)

These methods are generally coupled with control structures comprising of several controlled variable pairings. The most common one used are LV, DV and BL configurations, in which they are listed below:

- L – Reflux rate
- V – Reboiler duty
- B & D – Bottoms product draw rate

The LV control structure is considered a direct configuration as we are directly manipulating the internal variables of the distillation column. The other two methods are considered indirect control structures as manipulation is done towards a product flow rate, which is an external variable. (M. G. Sneesby, 2000)

2.2 Chemical Properties of MTBE

Methyl tertiary butyl ether (MTBE) is a part of the chemical compound group known as oxygenates. This group of chemicals are hydrocarbons consisting of at least an oxygen atom, in which the number of oxygen atoms may exceed one. Oxygenates serve a key role when added to vehicle fuels. This is because they increase the octane number of the fuel.

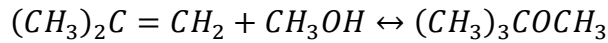
This means that the combustion process occurs in a more complete manner, producing less carbon monoxide. Although its usage has decreased in western nations, it is still an important compound used in Asia and the Middle East. The table below displays several advantages and disadvantages of the use of MTBE.

Table 2.1 Advantages and disadvantages of the use of MTBE

Advantages	Disadvantages
High octane value	Availability of economical isobutylene feedstock is limited.
Low volatility	Potential health hazard
Reduces carbon monoxide and exhaust emissions.	Potential drinking water toxicity

2.3 Reaction Kinetics

The process being studied is the production methyl tertiary butyl ether (MTBE) from isobutylene and methanol as shown in the chemical equation below:



The reaction is considered as a reversible reaction, with forward and backward reactions. To that end, the reaction kinetics are needed to replicate the process when performing modelling in ASPEN PLUS.

This MTBE synthesis process takes place in the liquid phase, commonly occurring at a temperature range between 40 °C and 100 °C. The pressure at which the reaction occurs is approximately 1000 kPa with minor differences. A small quantity of catalyst is often used in this process, more specifically that of an acidic cation exchange resin variant.

The forward reaction rate is as follows:

$$r_{forward} = 3.67 \times 10^{12} \exp\left(-\frac{92440}{RT}\right) \left(\frac{x_{IB}}{x_{MeOH}}\right)$$

The backward reaction rate is as follows:

$$r_{backward} = 2.67 \times 10^{17} \exp\left(-\frac{134454}{RT}\right) \left(\frac{x_{MTBE}}{x_{MeOH}^2}\right)$$

Notes:

- x = liquid phase molar fraction

The catalyst used by the reference source (Jana, 2011), is Amberlyst 15, a strong acidic macroreticular ion exchange resin. The catalyst takes up to eight reactive stages, with 204.1 kg of catalyst being used per stage reported by the source. (Jana, 2011)

2.4 Modelling of system

2.4.1 Modelling software

Before creating a control structure for the MTBE synthesis process, it is a prerequisite to model a MTBE synthesis process. To that end, the reactive distillation process modelled in this project is based on the source, (S. J. Wang, 2003).

From the original source, modelling was done using ChemCad software. For this project, the modelling and simulation was done using the ASPEN PLUS V10 software. ASPEN PLUS is a software in which users are able to conduct modelling and simulation activities without the requirement of excessive calculations.

It has a database of relative size encompassing most of the conventional compounds and processes that are commonly used by present-day industries. They include chemical processes, biofuel-related processes and power related processes, etc.

Moreover, ASPEN PLUS is one of the more easily accessible modelling software that can be utilized at the moment. Use of the software has also been exposed and taught to students on previous occasions as well. The modelling and simulation were done using data obtained from literature review of a specific reference source.

2.4.2 Feed information

In conventional industrial processes, the reactive distillation to produce MTBE is commonly used as an intermediate process. This is primarily because the isobutylene used as one of the feeds is commonly mixed with other compounds belonging to the butane group. Such compounds include 1-butene, isobutene and propylene etc.

Feed streams of such variant are difficult to separate using conventional means. For example, as the compounds share a rough similar range of boiling points, conventional distillation will not separate the mixture. This inadvertently increases the production costs of industries which require the butane group compounds to be separated. Hence, reactive distillation is opted.

The reference reported a use of a double inlet feed reactive distillation column. The first feed is a mixture of n-butene and isobutylene. The n-butene is an inert and will not partake in the reaction process. This will mimic the scenario faced by many of the present-day industries dealing in the MTBE production business.

The second inlet is a pure methanol stream. The table below displays the nominal feed conditions of the reactive distillation feed specifications:

Table 2.2 Inlet feed specifications of column

Feed	Methanol	C₄ Mixture
Feed tray	10	11
Temperature (K)	320	350
Pressure (kPa)	1115	1115
Flow rate (mol/s)	198	547

Composition (mol%)	100	36% isobutylene 64% n-butene
---------------------------	-----	---------------------------------

2.4.3 Column Specifications

The reactive distillation column modelled is a 17-stage reactive distillation column. The 17 stages consist of 15 column stages, a total condenser stage and a partial reboiler stage. The reaction process occurs between the 4th and 11th stages of the distillation column.

The desired product MTBE will exit the distillation column at the bottoms portion of the distillation column. The top portion outlet of the column will yield a high composition of n-butene and small traces of unreacted reactants.

The column specifications are shown as follows:

Table 2.3 Reactive Distillation Column Specifications

Rectification stages	3
Reaction stages	8
Stripping stages	6
Overhead pressure (kPa)	1110
Column pressure drop (kPa)	50
Reflux ratio	7
Reflux rate (mol/s)	2725
Reboiler duty (MJ/s)	43.5

2.4.4 Simulation unit

The distillation unit used in this is a RadFrac unit. The RadFrac unit is one of the most used units in ASPEN PLUS to replicate distillation behaviour on a simulation scale. Compared to other units, for example the DSTWU unit, the RadFrac is much more suited for more vigorous distillation simulations.

On the other hand, the DSTWU unit is considered a short-cut method of simulation. RadFrac enables users to complete simulation work, size and rate various types of columns (tray and packed).

Users are able to input various commands and settings onto the column. They include column configurations, feed configurations as well as any information related to by-product streams, if necessary. These inputs generally are reliant on the available degree of freedoms.

The degree of freedom can then be based on several of the operating parameters of the distillation column. They would include the flow rates of the distillate or bottoms, the reflux rate, reflux ratio and the heat duty etc. (Y. Hussain, 2015)

Even so, the RadFrac alone is not a reactive unit. In ASPEN PLUS, reactive units such as RStoic or RPlug are generally used to simulate processes involving reactions. (Y. A. Hussain, 2012) However, it is possible to configure the RadFrac to include reactive elements into the unit. This can be done by manipulating the reaction tab in ASPEN. In this case, a RadFrac unit which has been modified with two reactions (backward and forward) will be used.

2.4.5 Thermodynamic Model

The model used in the original source was the UNIQUAC (universal quasi-chemical) model. This model was then replicated when performing simulation using ASPEN PLUS V10. Even so, adjustments need to be made to obtain a simulation with high product yield. In the end, the UNIQUAC method was selected for the ASPEN PLUS simulation.

The use of UNIQUAC kinetic model with the aid of a modified Redlich-Kwong Equation of State (EOS) enables a high product yield of MTBE. Therefore, UNIQUAC method is used in the final simulation. This shows that it is important to identify an appropriate model to be used for simulation and modelling purposes. This is primarily because it will affect the outcome of the simulation.

2.4.5.1 UNIQUAC Model

In this project, UNIQUAC activity coefficient model is used primarily to imitate the model used by the original source. The model was derived based on the two-fluid theory. Therefore, the model is suitable to be used to describe the phase equilibria (in this case, liquid) for binary mixtures. A pair of adjustable parameters are used to describe the behaviour of the molecules of the components. (Maurer & Prausnitz, 1978) (Abrams & Prausnitz, 1975)

UNIQUAC is a model which serves as an expression for excess Gibbs energy, consisting of enthalpy and entropy terms. The UNIQUAC equation for Gibbs energy is as follows:

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual})$$

$$\frac{g^E(\text{combinatorial})}{RT} = x_1 \ln \left(\frac{\phi_1}{x_1} \right) + x_2 \ln \left(\frac{\phi_2}{x_2} \right) + \left(\frac{z}{2} \right) \left(q_1 x_1 \ln \left(\frac{\theta_1}{\phi_1} \right) + q_2 x_2 \ln \left(\frac{\theta_2}{\phi_2} \right) \right)$$

$$\frac{g^E(\text{residual})}{RT} = -q'_1 x_1 \ln(\theta'_1 + \theta'_2 \tau_{21}) - q'_2 x_2 \ln(\theta'_2 + \theta'_1 \tau_{12})$$

Where: $z = 10 = \text{coordination number}$

Mole fraction = x_i

$$\text{Segment fractions, } \Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$$

$$\text{Area fractions, } \theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \quad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$$

$$\theta'_1 = \frac{x_1 q'_1}{x_1 q'_1 + x_2 q'_2} \quad \theta'_2 = \frac{x_2 q'_2}{x_1 q'_1 + x_2 q'_2}$$

Parameters r , q and q' are pure-component molecular-structure constants which are dependent on the components. They mainly depend on the molecular size and external surface area of the components.

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right)$$

$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right)$$

Where: Δu_{12} & $\Delta u_{21} = \text{characteristics energies of components}$

$R = \text{gas constant}$ (Anderson & Prausnitz, 1978)

In ASPEN PLUS V10, the UNIQUAC model is generally used to calculate the liquid activity coefficients of the selected components. This model is generally recommended for utilization in highly non-ideal chemical systems, such as VLE or LLE.

For our case, the reactive distillation is highly non-ideal to due to the combination of two process into a single process. Therefore, it is suitable to be used. The equation implemented by ASPEN PLUS V10 is as follows:

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} - q'_i \ln t'_i - \frac{q'_i \sum_j \theta'_j \tau_{ij}}{t'_j} + l_i + q'_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j$$

Where:

$$\theta_i = \frac{q_i x_i}{q_T} \quad \theta'_i = \frac{q'_i x_i}{q'_T} \quad \Phi_i = \frac{r_i x_i}{r_T}$$

$$l_i = \frac{z}{2} (r_i - q_i) + 1 - r_i \quad \tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T} + C_{ij} \ln T + d_{ij} T\right)$$

$$z = 10$$

$$\begin{array}{ll}
 a_{ij} \neq a_{ji} & b_{ij} \neq b_{ji} \\
 c_{ij} \neq c_{ji} & d_{ij} \neq d_{ji} \quad (\text{AspenTech, 1999})
 \end{array}$$

2.4.5.2 Binary Properties

The use of UNIQUAC model will require the use of binary properties of the components. Generally, these properties can be determined via the data regression of data obtained from VLE or/and LLE experiments. However, ASPEN PLUS has a relatively large library of in-built parameters for the UNIQUAC model.

Even so, utilization of the readily available data does not result in a high yield of MTBE in the bottoms stream. Therefore, it is possible to self-input the binary properties into ASPEN PLUS provided the user has the appropriate references.

For this project, the binary properties for b_{ij} and b_{ji} were obtained from page 445 of (Seader, 2011). The binary parameters of a_{ij} and a_{ji} were set at 0, following the same original source. The b_{ij} and b_{ji} properties are shown in Table 2.4.

Table 2.4 b_{ij} and b_{ji} properties

Components in Binary Pair, ij	Binary Properties	
	b_{ij} (K)	b_{ji} (K)
MeOH-IB	35.38	-706.34
MeOH-MTBE	88.04	-468.76
IB-MTBE	-52.2	24.63
MeOH-NB	35.38	-706.34
NB-MTBE	-52.2	24.63

2.4.5.3 Redlich-Kwong Equation of State (RK-EOS)

The Redlich-Kwong EOS is an algebraic equation that is used to relate temperature, pressure, and volume of gases in the fields of physics and thermodynamics. Formulated by Otto Redlich and Joseph Neng Shun Kwong in the year 1949, this EOS is generally used to predict the gas-phase properties of multiple compounds.

The EOS is widely considered to be more accurate in doing the aforementioned function in comparison to other equations such as the van der Waals equation or ideal gas equation. This is primarily since the RK-EOS is generally designed to function well at temperatures above the

critical temperature. As time passed, many revisions and modifications has increased the EOS' accuracy, increasing its reliability at lower temperature conditions. (Redlich & Kwong, 1949)

IN ASPEN PLUS V10, the RK-EOS is used to calculate the vapour phase thermodynamic properties in conjunction with several models. For example, NRTL, UNIFAC and UNIQUAC.

The equation of the model is as follows:

$$p = \frac{RT}{V_m - b} - \frac{\frac{a}{T^{0.5}}}{V_m(V_m + b)}$$

Where:

$$\sqrt{a} = \sum_i x_i \sqrt{a_i}$$

$$b = \sum_i x_i b_i$$

$$a_i = \frac{0.42748023R^2T_{ci}^{1.5}}{p_{ci}}$$

$$b_i = \frac{0.08664035RT_{ci}}{p_{ci}} \quad (\text{AspenTech, 1999})$$

2.4.5.4 Conclusion

The combination of UNIQUAC-RK is a suitable thermodynamic model to be used in the project. The UNIQUAC portion of the model enables able estimations of liquid-phase activity components, whereas the RK portion of the model enables good estimations for vapour-phase fugacities. The combination of both methods provides a desirable and high MTBE bottoms yield.

2.4.6 Results from literature source

Based on the selected literature source, the final isobutylene conversion rate was 90% on a molar basis. The source reports a high bottoms MTBE purity of 99.2 mol percent. The distillate flow rate was 389 mol/s while the bottoms flow rate was 178 mol/s. From the source, a final composition of the components present in the column is shown as follows:

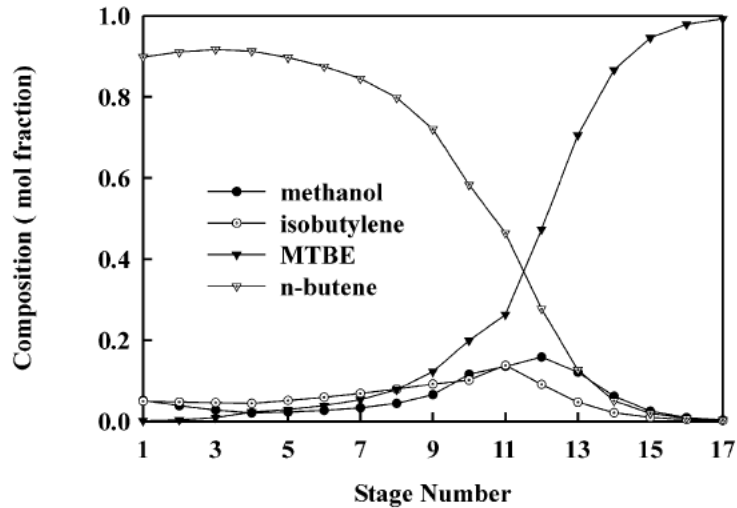


Figure 2.1 Composition (mole fraction) Vs Stage Number from reference source

From the (S. J. Wang et al., 2003), it is shown that the reactive distillation process yields a high MTBE from the bottoms product flow. Moreover, the temperature difference graph as shown in Figure 2.2 was also obtained from the reference source. The figure displays the output temperature of the bottoms flow leaving stage 17 has a temperature of about 420 K. The distillate leaving the top of the column (stage 1) is about 340 K.

In this project, the goal will be to replicate the above result via modelling of a reactive distillation system using ASPEN PLUS. After replicating the result, control elements will be applied to the simulation and subsequently tested with disturbances and step-changes.

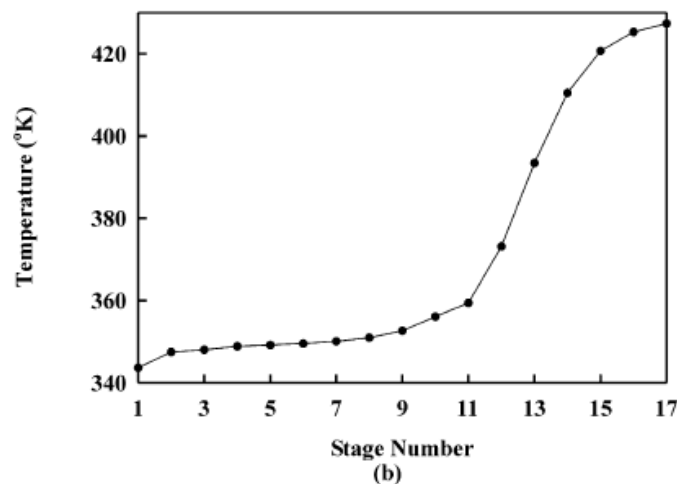


Figure 2.2 Temperature (K) Vs Stage Number from reference source

2.5 Selected Model of Simulation

The model used for this project was chosen from the source (S. J. Wang, 2003) for several reasons.

2.5.1 The Rarity of the Chosen Reaction

Reactive distillation is still considered a relatively advanced and efficient process that can be used to improve the efficiency of the manufacturing sector. At the same time, reducing the number of equipment in the factories.

It has been introduced since the 1920s with one of its earliest produced substances being MTBE. Therefore, there is a lot papers and sources which can be used to replicate the reactive distillation of MTBE. This makes it easier to find reliable information to replicate the process using ASPEN PLUS V10. (Kiss, 2019)

With that being said, the study of implementation of control elements into the reactive distillation of MTBE is always up for further research. This is primarily as the process being naturally non-linear is highly difficult to control. This facilitates a good objective and reason for the project to focus on the chosen process.

2.5.2 The Details of the Chosen Source

The chosen literature provides sufficient details to enable proper replication of the simulation in ASPEN PLUS V10. This provides a suitable baseline for all future decisions or changes that will be made as the model is adapted to obtain an optimum result using ASPEN PLUS V10. Any errors or mistakes can be traced back to the original source article. As the original article utilises the software CHEMCAD to produce the simulation, changes must be made to produce the same desired result in ASPEN PLUS V10.

These changes must be made with information from other sources that are unavailable to the original source. As the original source article (S. J. Wang, 2003) provides relatively sufficient information to run the simulation, a minimal number of other references need to be used to complete the simulation.

2.5.3 The Accessibility of the Chosen Source

Another good reason as to why the simulation was chosen to be modelled from (S. J. Wang, 2003) is that it is easily accessible. As a good portion of research papers and articles reside behind a paywall, it is not easy to access the information within these papers. The prices are relatively expensive and there is a risk of not obtaining the needed information even after paying and reading the article.

Moreover, the clearance provided by the university does not encompass all the articles which are available online. There are papers which are still not accessible even with clearance from the university. Therefore, it is essential to find an article that can be accessed free of charge and provides as much valuable information as possible to facilitate a smoother simulation process.

The chosen article by (S. J. Wang, 2003) is free to access with the aid of clearance from the university and was one of the first few articles found during the literature review process. Moreover, it is highly informative, providing valuable information to conduct the simulation process albeit only lacking in several areas of information. Therefore, this article was chosen to be replicated in ASPEN PLUS V10 for this project.

3 METHODOLOGY

3.1 Research Methodology

Overall, this final year project will be focused on the simulation of reactive distillation of methanol and a butene mixture to produce MTBE. Figure 3.1 displays the activity procedure of the project.

ASPEN PLUS is used to simulate the reaction and separation processes and verify the model from the reference source. After successful verification and replication of the model, the model is brought to ASPEN Dynamics to implement control elements.

After successful implementation of controllers, the model is tested with step changes and disturbances to test the effectiveness of the controllers. Tuning procedures are conducted to improve the robustness of the controllers if necessary. Data for the model are used from the source literature review and implemented.

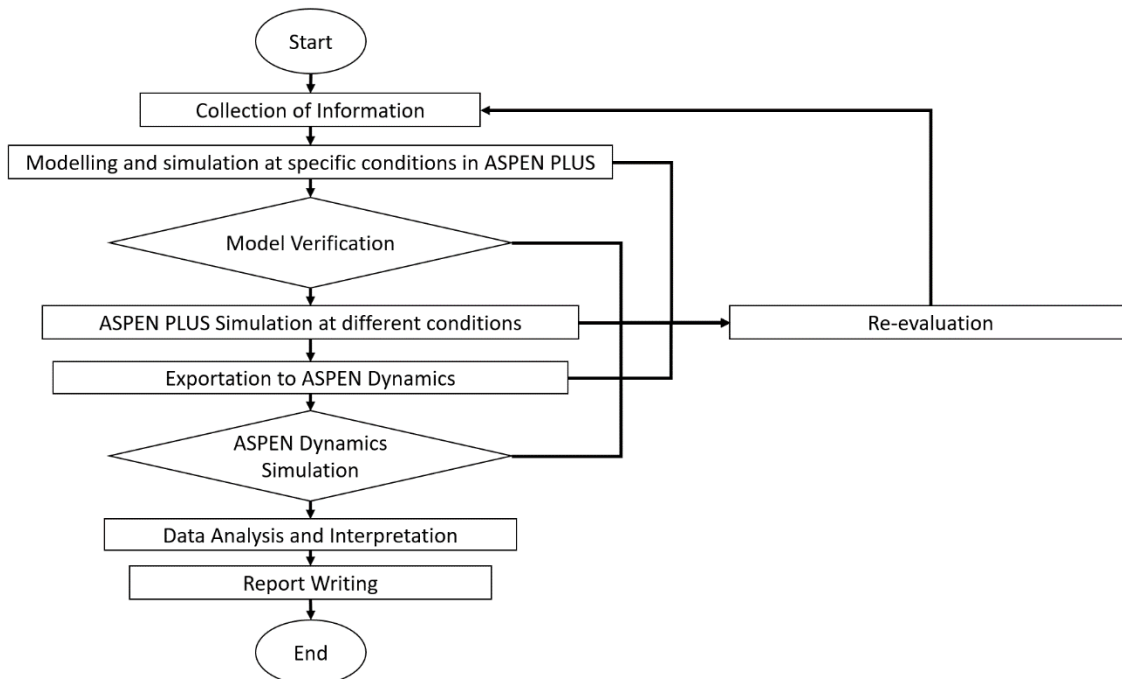


Figure 3.1 Activity flow diagram of research project

3.2 ASPEN PLUS SIMULATION

3.2.1 Model Setup

3.2.1.1 Reactants and thermodynamic model

A model simulating the reactive distillation of methanol and butenes to produce MTBE was created successfully on the ASPEN PLUS software. To begin the modelling process, the reactants were specified and selected. Next, a thermodynamic model was selected for the simulation. The choice for model selection was UNIQ-RK. Figure 3.2 and Figure 3.3 display this action, with Figure 3.4 displaying the flowsheet of the system created.

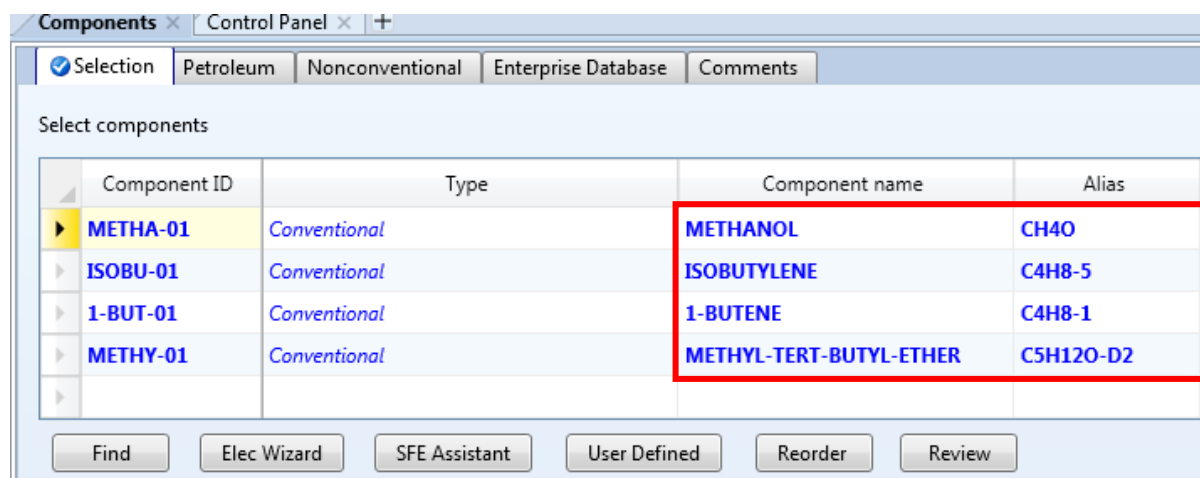


Figure 3.2 Reactant selection in ASPEN PLUS V10

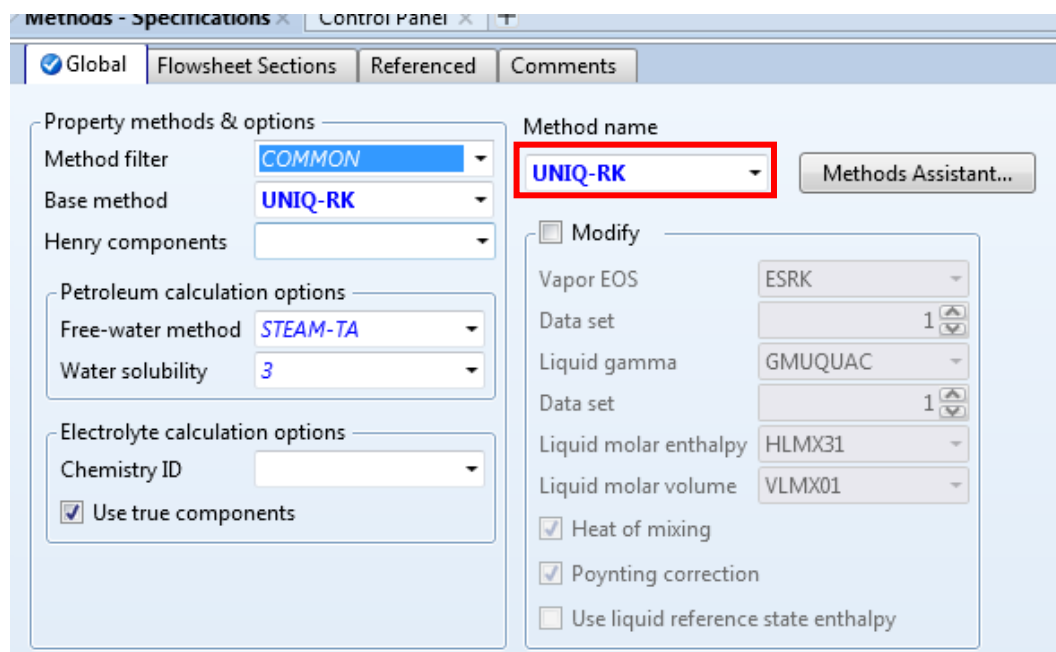


Figure 3.3 Thermodynamic model selection in ASPEN PLUS V10

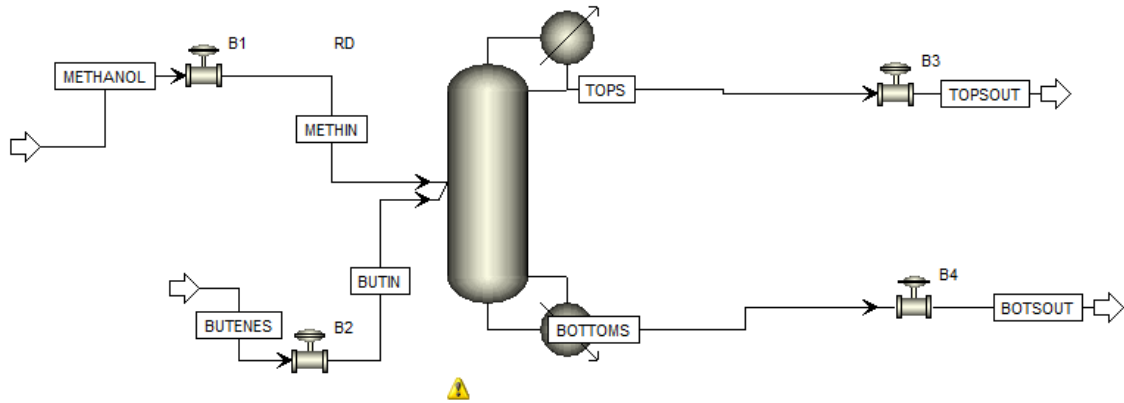


Figure 3.4 Flowsheet created in ASPEN PLUS V10

3.2.1.2 Feed Specification

After setting up the flowsheet, the information from the literature review were used as the input for the feed and column specifications. The following series of figures will depict the aforementioned actions. Figure 3.5 and Figure 3.6 depict the ASPEN PLUS inputs for both feeds into the RadFrac model.

Main Flowsheet x Control Panel x RD (RadFrac) - Profiles x BUTENES (MATERIAL) x RD (RadFrac) - Composition -

Mixed CI Solid NC Solid Flash Options EO Options Costing Comments

Specifications

Flash Type: Temperature Pressure

State variables:

Temperature	350 K
Pressure	1200 kPa
Vapor fraction	
Total flow basis	Mole
Total flow rate	547 mol/sec
Solvent	

Reference Temperature

Volume flow reference temperature: C

Component concentration reference temperature: C

Composition: Mole-Frac

Component	Value
METHA-01	
ISOBU-01	0.36
1-BUT-01	0.64
METHY-01	
Total	1

Figure 3.5 Iso-butylene feed specifications in ASPEN PLUS V10

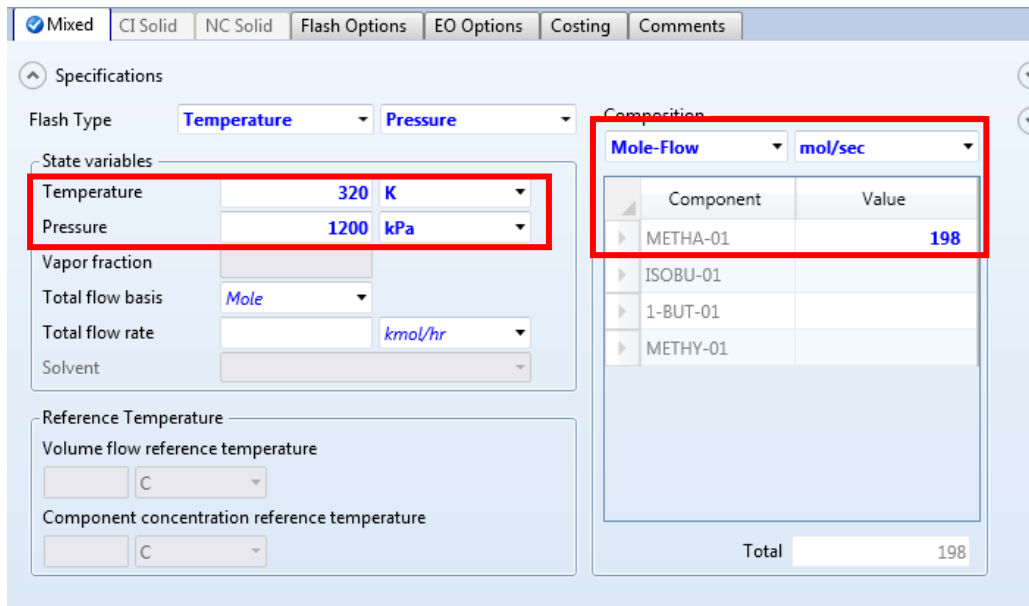


Figure 3.6 Methanol feed specifications in ASPEN PLUS V10

3.2.1.3 Control Valves

To further improve the ease of which to control certain parameters in the subsequent ASPEN DYNAMICS section of the project, a control valve was installed into each of the reactant and product stream. This leads to a total of four control valves installed in the unit operation. Table 3.1 Summary of control valves below details a summary of the control valves installed:

Table 3.1 Summary of control valves

Control Valve	Inlet	Outlet	Pressure of Outlet (kPa)
B1	METHANOL	METHIN	1115
B2	BUTENES	BUTIN	1115
B3	TOPS	TOPSOUT	100
B4	BOTTOMS	BOTSOUT	100

The following list of figures detail the configurations of the control valves B1 to B4 in the ASPEN PLUS interface:

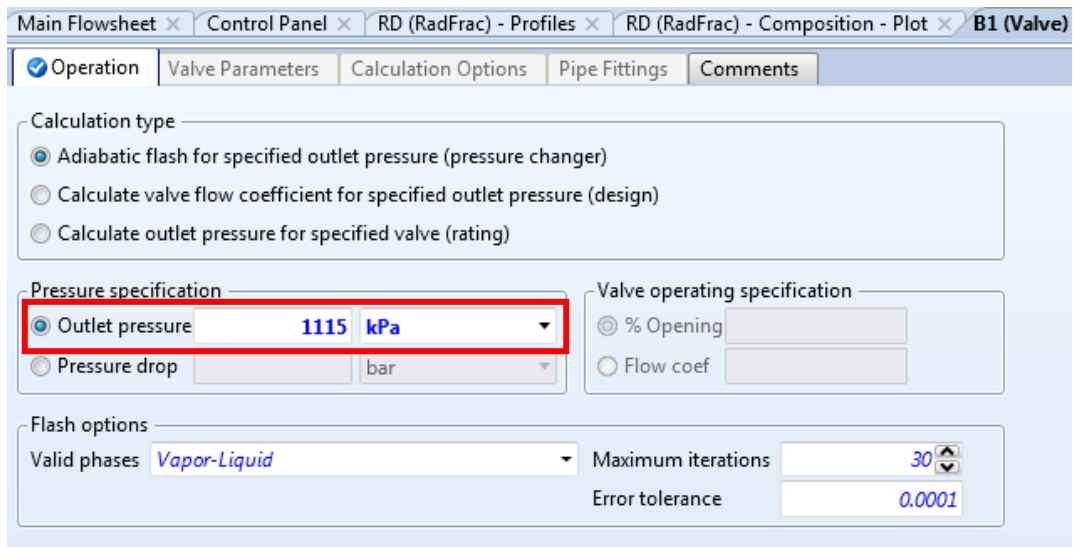


Figure 3.7 Configuration of valve B1 in ASPEN PLUS interface

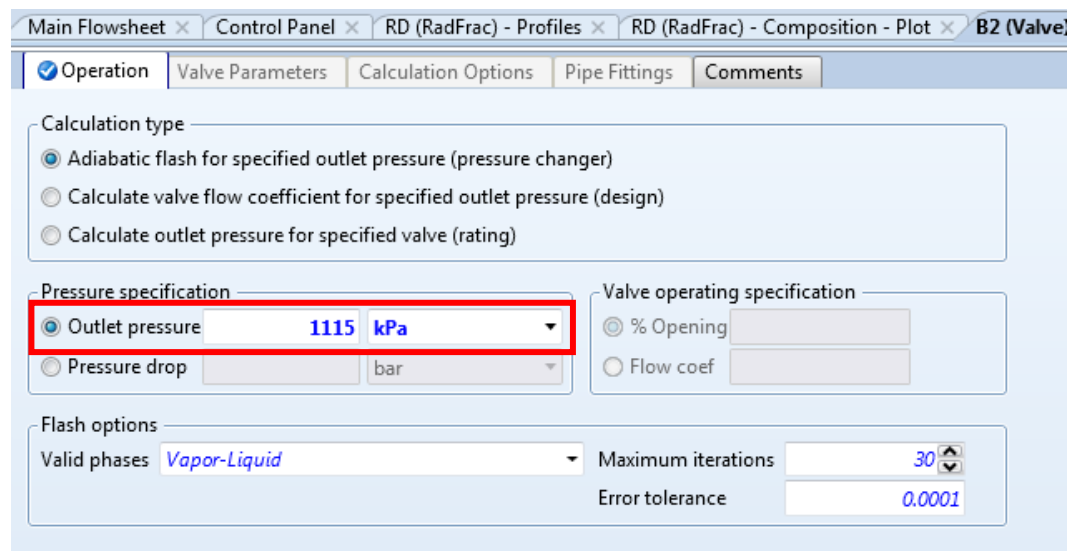


Figure 3.8 Configuration of valve B2 in ASPEN PLUS interface

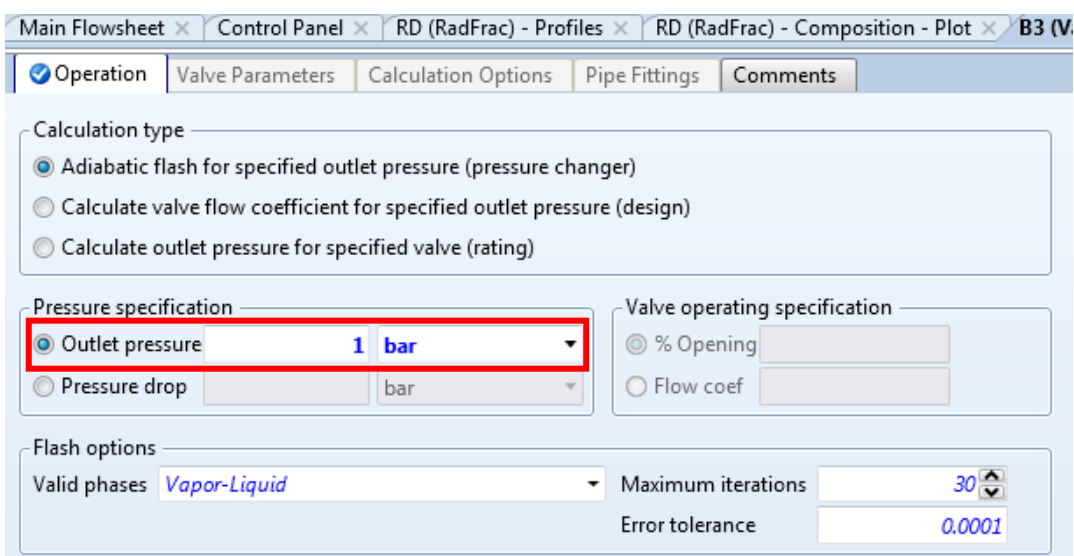


Figure 3.9 Configuration of valve B3 in ASPEN PLUS interface

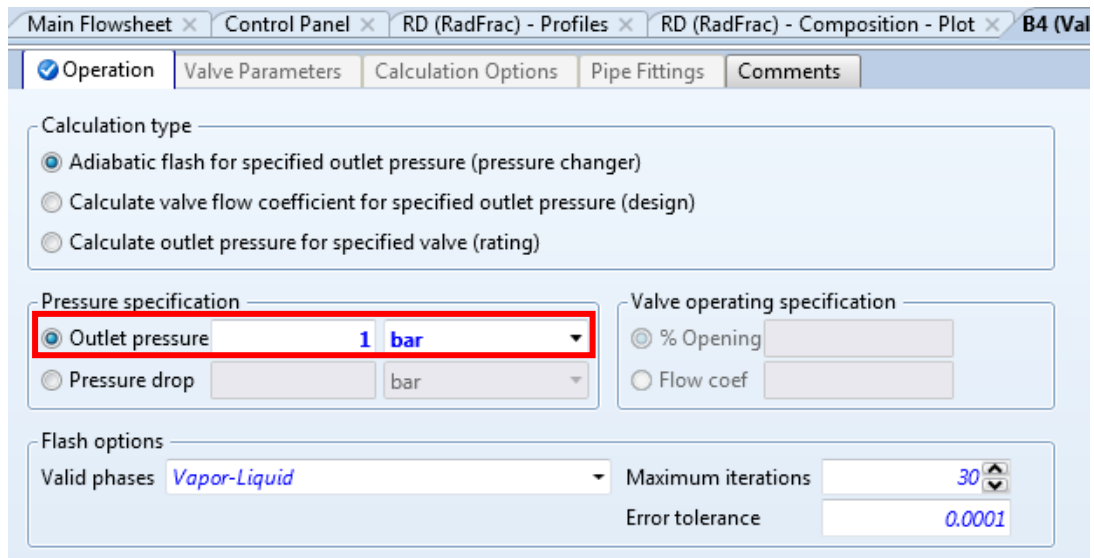


Figure 3.10 Configuration of valve B4 in ASPEN PLUS interface

3.2.1.4 Column Specifications

Figure 3.11 to Figure 3.13 the specifications of the RadFrac model in ASPEN PLUS.

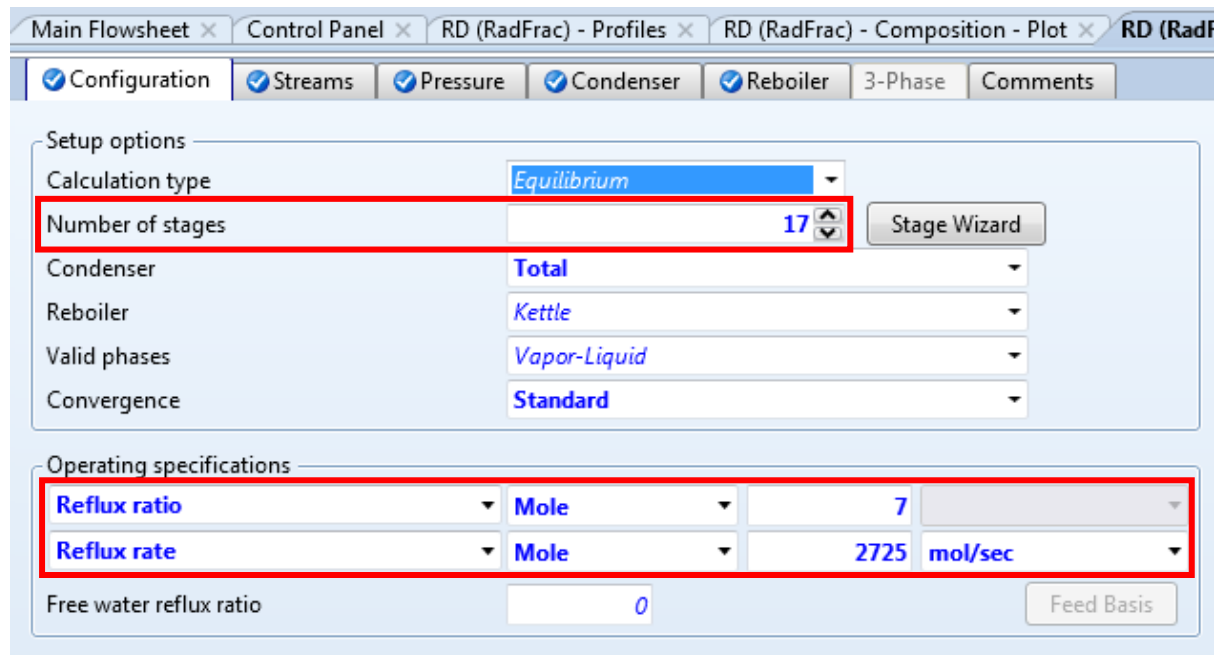


Figure 3.11 Operating specifications of RadFrac in ASPEN PLUS V10

The screenshot shows the 'Configuration' tab for a RadFrac column. The 'Feed streams' table lists two feeds: METHIN at Stage 10 and BUTIN at Stage 11, both with an 'Above-Stage' convention. The 'Product streams' table lists two products: TOPS at Stage 1 (Liquid phase) and BOTTOMS at Stage 17 (Liquid phase), both on a 'Mole' basis.

Feed streams		
Name	Stage	Convention
METHIN	10	Above-Stage
BUTIN	11	Above-Stage

Product streams								
Name	Stage	Phase	Basis	Flow	Units	Flow Ratio	Feed Specs	
TOPS	1	Liquid	Mole		kmol/hr		Feed basis	
BOTTOMS	17	Liquid	Mole		kmol/hr		Feed basis	

Figure 3.12 Feed stages of RadFrac in ASPEN PLUS V10

The screenshot shows the 'Pressure' configuration panel for a RadFrac column. The 'View' is set to 'Top / Bottom'. The 'Stage 1 / Condenser pressure' is set to 1110 kPa. Under 'Stage 2 pressure (optional)', 'Stage 2 pressure' is selected. Under 'Pressure drop for rest of column (optional)', 'Column pressure drop' is selected and set to 50 kPa.

Figure 3.13 Pressure drop of RadFrac in ASPEN PLUS V10

3.2.1.5 Reaction Specifications

Figure 3.14 to Figure 3.17 depicts the reaction configurations in the ASPEN PLUS V10 interface.

The screenshot shows the 'Edit Reaction' dialog box. The reaction list at the top shows two kinetic reactions. Reaction 1 is highlighted, showing the stoichiometry: METHA-01 + ISOBU-01 --> METHY-01. The 'Edit Reaction' dialog shows the reaction type as 'Kinetic' and the reactants as METHA-01 (coefficient -1, exponent -1) and ISOBU-01 (coefficient -1, exponent 1). The product is METHY-01 (coefficient 1, exponent 1).

Rxn No.	Reaction type	Stoichiometry	Delete
1	KINETIC	METHA-01 + ISOBU-01 --> METHY-01	X
2	KINETIC	METHY-01 --> METHA-01 + ISOBU-01	X

Reactants				Products			
Component	Coefficient	Exponent		Component	Coefficient	Exponent	
METHA-01	-1	-1		METHY-01	1		
ISOBU-01	-1	1					

Figure 3.14 Forward reaction stoichiometry of RadFrac in ASPEN PLUS V10