

# A design for producing ethyl tert-butyl ether (ETBE) from petroleum sourced LPG and renewably sourced ethanol

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## Executive Summary

The objective to adapt the supply of petroleum products in South Africa through a more renewable manner was considered in the production of ethyl tert-butyl ether (ETBE) from petroleum sourced LPG and sustainably sourced ethanol (bioethanol). Not only does the addition of ETBE to petroleum products enhance the octane rating and allow for cleaner, more efficient combustion; but the ETBE additive is also more environmentally friendly than the traditionally used additives, namely lead and methyl tert-butyl ether (MTBE) (De Menezes *et al*, 2006).

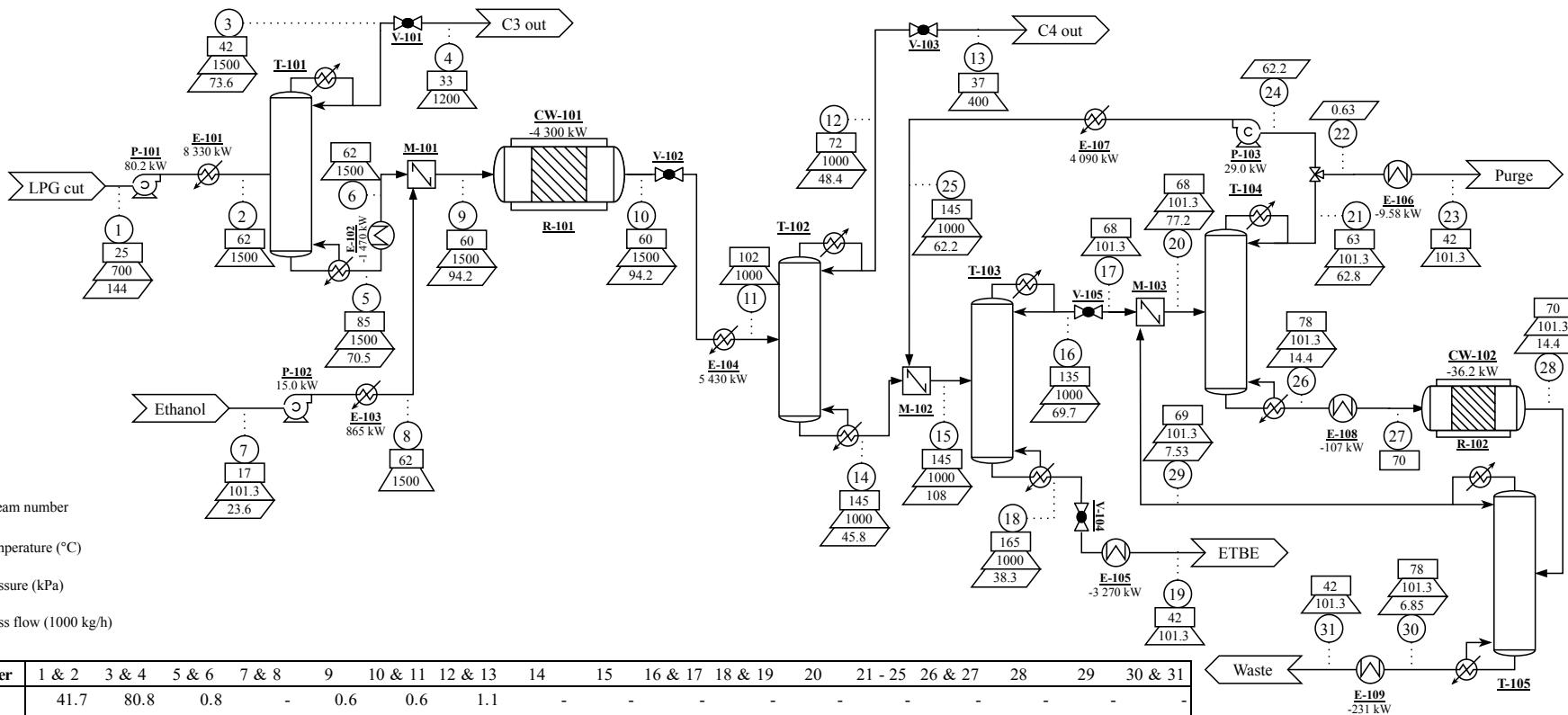
A process plant was designed for the production of ethyl tert-butyl ether (ETBE) at a rate of 38 tonne h<sup>-1</sup>. Ethanol and isobutene were the primary reactants in liquid phase and Amberlyst-15 was used as catalyst in the primary reactor. A secondary reactor was added to the system to further react the excess ethanol and a byproduct formed in the primary reactor, TBA, to form ETBE; with all reactants in the liquid phase. The catalyst used in this reactor was S-54. The conversion of isobutene to ETBE in the primary reactor was 75 % and the conversion of isobutene to TBA in the primary reactor was 13.88 %. Hence the overall conversion of isobutene was 88 %. The selectivity of ETBE in the primary reactor was 84.38 %. The addition of the second reactor accounted for 1.6 tonne h<sup>-1</sup> of the total ETBE produced, increasing the total ETBE yield by 4.22 %.

The process design included the initial separation and preparation of the LPG feed by removing inert C<sub>3</sub> hydrocarbons to form a purely C<sub>4</sub> product stream to fed into the primary reactor. The primary reactor inlet stream consisted of bioethanol (95 wt%) in a stoichiometric excess of 10 %. Thus the composition of the feed stream consisted of 26.95 % ethanol, 3.63 % water, 40.79 % isobutene and the remainder C<sub>4</sub> inerts. Thus the unreacted reactants, byproducts, inerts and wanted products were separated with a separation train using pressure swing distillation to achieve the separations where necessary and to form a pure ETBE product. Furthermore, the separation train played a role in purifying outlet streams from the primary reactor such that TBA and ethanol could be fed to a secondary reactor to further maximise the yield of ETBE. A purge stream of 1 % was included in the simulation to prevent the excessive build-up of inert hydrocarbons.

The finalised process was simulated using DWSim and the simulation was used to verify the mass and energy balances as well as to size utilities and other equipment such as distillation columns, reactors and the remaining peripheral equipment. The finalised process was decided upon after careful consideration of process recycles, stream waste reduction and reuse as well as other optimisation parameters. The final PFD is given in Figure 1, while the DWSim simulation is given by Figures 18, 19 and 20 under Section 12. Tables 1, 2, 4, 3, 4, 5, 6, 7 summarise the simulation results.

A HAZOP study was performed over the primary reactor. Possible hazards and operational issues were identified and feasible safeguards were suggested. The HAZOP study revealed the dangers related to a runaway exothermic reaction; triggering the need for control of the flow into the reactor, the reactor temperature as well as the control of a water coil cooling system to maintain the reactor at isothermal operation. The implementation of a temperature, flow and pressure control system was highly recommended to reduce the risks and hazards that could arise in their absence. These control systems would be used to regulate the temperature, pressure and flow through the reactor vessel. Given that the process encounters high pressures and highly flammable and explosive materials, a pressure relief valve was also suggested as an additional safety measure. Furthermore, appropriate training of operators and the enforcement of strict safety protocols would further mitigate any human errors.

Upon economic analysis, the plant FCI was calculated as R610 million. A net present value of R3.48 billion was calculated at an interest rate of 12 %. The IRR was calculated as 68 %. The payback period for this plant was found to be four years.



Stream number	1 & 2	3 & 4	5 & 6	7 & 8	9	10 & 11	12 & 13	14	15	16 & 17	18 & 19	20	21 - 25	26 & 27	28	29	30 & 31
Components mass fraction (%)																	
Propane	41.7	80.8	0.8	-	0.6	0.6	1.1	-	-	-	-	-	-	-	-	-	-
Propylene	8.3	16.3	Trace	-	Trace	Trace	Trace	-	-	-	-	-	-	-	-	-	-
1-Butene	16.5	1.3	32.5	-	24.3	24.3	47.3	-	Trace	Trace	-	Trace	Trace	-	-	-	-
2-Butene	10.7	Trace	21.8	-	16.3	16.3	31.7	-	0.5	0.7	-	0.7	1.1	-	-	-	-
Isobutene	17.9	1.3	35.3	-	26.5	2.9	5.7	-	-	-	-	-	Trace	-	-	-	-
n-Butane	3.9	Trace	8.0	-	6.0	6.0	11.6	-	Trace	Trace	-	Trace	0.1	-	-	-	-
Isobutane	0.9	Trace	1.6	-	1.2	1.2	2.4	-	-	-	-	-	-	-	-	-	-
ETBE	-	-	-	-	-	36.1	-	74.3	73.9	60.0	99.3	60.6	56.2	4.0	36.1	66.7	2.5
Ethanol	-	-	-	95.0	23.9	7.6	-	15.5	20.5	31.8	Trace	31.4	41.0	63.0	48.5	28.1	70.9
TBA	-	-	-	-	-	4.9	-	10.0	4.9	7.2	Trace	6.8	1.3	31.1	7.8	2.4	13.6
Water	-	-	-	5.0	1.3	Trace	-	0.2	Trace	0.1	-	0.4	0.2	2.0	7.6	2.8	12.9

Figure 1: Process flow diagram (PFD) for the production of ETBE

**Table 1:** Simulation results characterising the inlet to reactor 1 (R-101).

Compound	Composition (wt %)	Flow rate (kg h <sup>-1</sup> )
C <sub>3</sub> trace	0.62	26.63
Isobutane	1.23	1162.31
Isobutene	26.47	24 925.95
1-Butene	24.30	22 893.93
n-Butane	5.96	5610.17
<i>trans</i> -2-butene	12.82	12 070.70
<i>cis</i> -2-butene	3.49	3291.84
Ethanol	23.85	22 461.97
Water	1.26	1182.21
ETBE	0.00	0.00
TBA	0.00	0.00
Total flow rate (kg h <sup>-1</sup> )		94 179.50

**Table 2:** Simulation results characterising the outlet of reactor 1 (R-101).

Compound	Composition (wt %)	Flow rate (kg h <sup>-1</sup> )
C <sub>3</sub> trace	0.61	580.41
Isobutane	1.23	1162.31
Isobutene	2.94	2770.56
1-Butene	24.31	22 893.93
n-Butane	5.96	5610.17
<i>trans</i> -2-butene	12.82	12 070.70
<i>cis</i> -2-butene	3.50	3291.84
Ethanol	7.55	7112.10
Water	0.08	70.93
ETBE	36.15	34 044.34
TBA	4.85	4572.21
Total flow rate (kg h <sup>-1</sup> )		94 179.50

**Table 3:** Simulation results characterising the inlet of reactor 2 (R-102).

Compound	Composition (wt %)	Flow rate (kg h <sup>-1</sup> )
C <sub>3</sub> trace	trace	trace
C <sub>4</sub> trace	trace	trace
Ethanol	63.00	9059.33
Water	1.96	282.47
ETBE	3.95	568.67
TBA	31.09	4470.47
Total flow rate (kg h <sup>-1</sup> )		14 380.70

**Table 4:** Simulation results characterising the outlet of reactor 2 (R-102)

Compound	Composition (wt %)	Flow rate (kg h <sup>-1</sup> )
C <sub>3</sub> trace	trace	trace
C <sub>4</sub> trace	trace	trace
Ethanol	48.51	6976.55
Water	7.63	1097.34
ETBE	36.10	5190.26
TBA	7.77	1117.56
Total flow rate (kg h <sup>-1</sup> )		14 380.70

**Table 5:** LPG and ethanol feed composition

Compound	Composition out (wt %)	Flow rate out (kg h <sup>-1</sup> )
LPG flow rate (kg h <sup>-1</sup> )		144175.00
Propene	8.30	12 014.60
Propane	41.70	60 071.31
Isobutane	0.90	1259.52
Isobutene	17.90	25 877.62
1-Butene	16.50	23 856.70
n-Butane	3.90	5650.83
<i>trans</i> -2-butene	8.42	12 141.94
<i>cis</i> -2-butene	2.29	3302.48
Ethanol flow rate (kg h <sup>-1</sup> )		23 644.20
Ethanol	95.00	22 461.98
Water	5.00	1182.22
Total flow rate in (kg h <sup>-1</sup> )		167 819.20

**Table 6:** Simulation results for the process outlet streams

Compound	Composition out (wt %)	Flow rate out (kg h <sup>-1</sup> )
ETBE product stream flow rate (kg h <sup>-1</sup> )		38 309.80
C <sub>3</sub> & C <sub>4</sub> trace	trace	trace
Ethanol	0.02	6.79
Water	trace	trace
ETBE	99.25	38 024.21
TBA	0.73	278.78
Purge stream (kg h <sup>-1</sup> )		628.99
C <sub>3</sub> & and C <sub>4</sub> trace	0.96	5.99
Ethanol	24.20	152.23
Water	0.05	0.31
ETBE	73.59	462.90
TBA	1.20	7.56
Waste stream (kg h <sup>-1</sup> )		6853.66
C <sub>3</sub> & C <sub>4</sub> trace	trace	trace
Ethanol	70.94	4862.30
Water	12.92	885.45
ETBE	2.51	172.66
TBA	13.62	933.25

**Table 7:** Simulation results for the process outlet streams (continued)

Compound	Composition out (wt %)	Flow rate out (kg h <sup>-1</sup> )
C <sub>4</sub> stream (kg h <sup>-1</sup> )		48 371.60
Propane	1.14	553.74
Propene	0.06	26.63
1-Butene	47.32	22 891.64
<i>trans</i> -2-butene	24.94	12 065.49
<i>cis</i> -2-butene	6.80	3288.48
Isobutene	5.72	2770.28
n-Butane	11.60	5609.09
Isobutane	2.40	1162.22
Ethanol	trace	3.97
TBA	trace	0.01
ETBE	trace	trace
C <sub>3</sub> stream (kg h <sup>-1</sup> )		73 640.90
Propane	80.80	59 518.49
Propene	16.30	11 988.17
1-Butene	1.30	962.78
Isobutene	1.30	951.69
n-Butane	0.06	trace
Isobutane	0.13	trace
<i>trans</i> -2-butene	0.10	trace
<i>cis</i> -2-butene	0.01	trace
Total flow rate out (kg h <sup>-1</sup> )		167 804.95

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# 1 Introduction

South Africa is a country whose fuel source is heavily based on the use of liquid fuels such as petrol or diesel (Sasol Oil (Pty) Ltd, 2020). The National Refinery of South Africa (Natref) is one of South Africa's crude oil refineries and is a collective enterprise between Sasol Oil (Pty) Ltd and Total South Africa (Pty) Ltd (Sasol Oil (Pty) Ltd, 2020). Natref produces products such as refined oil, petrol, diesel and LPG (liquid petroleum gas) (Sasol Oil (Pty) Ltd, 2020).

Global warming as a result of the impact of excessive greenhouse gas release, is an ever-increasing threat and leading cause of climate change (Chiroma *et al*, 2015). Given that greenhouse gas emissions are responsible for above 90 % of global warming as a result of human operations (Chiroma *et al*, 2015), methods to reduce harmful emissions are actively being sought. One such field where this is prevalent, is that of fuels (Umar, Saleemi & Qaiser, 2008). Fossil fuel burning is a leading cause of the greenhouse effect (Chiroma *et al*, 2015), as a result of harmful carbon emissions (Chiroma *et al*, 2015). Thus, a cleaner fuel burning would result in reduced harmful combustion products, and hence less emissions (Yuan & Jonsson, 2006).

Octane additives are incorporated into gasoline to improve the efficiency of the combustion process and to prevent knocking (Norkobilov, Gorri & Ortiz, 2017a; Gonzalez-Olmos & Iglesias, 2007; Yuan & Jonsson, 2006). However, traditional additives such as lead octane additives, are harmful to the environment (Yuan & Jonsson, 2006). A replacement was sought in the use of methyl tert-butyl ether (MTBE). Currently, MTBE (methyl tert-butyl ether) is the most commonly used oxygenate, but its detrimental effects on the environment are making ETBE (ethyl tert-butyl ether) a more promising and attractive alternative (Sneesby *et al*, 1997a). Ethyl tert-butyl ether (ETBE) has various advantages over MTBE, but most notable, it has a higher octane rating, is far more environmentally friendly and is considered as semi-renewable because it can be produced from renewable ethanol (Menezes & Cataluna, 2008) whereas MTBE is produced from natural gas (Francoisse & Thyrion, 1991). However, conventional production processes of ETBE have high energy demands which makes the oxygenate costly (Norkobilov *et al*, 2017a; Francoisse & Thyrion, 1991).

In order to generate a more renewable petrol supply in South Africa, the production of ethyl tert-butyl ether (ETBE) from petroleum sourced LPG, and renewably sourced ethanol is to be considered. Thus, the reaction that will be investigated involves reacting isobutene with ethanol to produce ETBE over an ion-exchange catalyst (Menezes & Cataluna, 2008).

Through liquid-phase reaction of excess ethanol with isobutene obtained from a fluid catalytic cracker (FCC), and acid-ion exchange resin, Amberlyst-15; ETBE is synthesised under high pressure (1.5 MPa) and temperatures of around 60 °C; in a packed bed reactor. The products are separated using a separation train of 4 ordinary distillation columns, and a second reactor is utilised to optimise the production of ETBE by reacting a by-product of the primary reactor, tert-butyl alcohol (TBA) with the remaining ethanol.

The plant design was centralised on meeting the industrial, local demands of necessary supply of ETBE in South Africa, such that all of the fuel produced by Natref could be treated with this oxygenate additive. Further considerations include, energy efficiency, economic viability, environmental effects, plant hazards as well as plant safety and operability.

## 2 Literature Survey

### 2.1 Petroleum production in South Africa

Petroleum products such as petrol and diesel are widely consumed in South Africa, with an annual consumption of petrol and diesel of 11 142 and 12 539 million litres respectively (SAPIA, 2018).

The production capacities of South African refineries are shown in Table 8:

**Table 8:** Capacity of South African refineries as of 2018 (SAPIA, 2018).

Refinery	Sapref	Enref	Chevref	Natref	Sasol	PetroSA
Capacity (bbl day <sup>-1</sup> )	180 000	135 000	100 000	108 000	150 000	45 000

The South African standards for petroleum production, as published by the South African Department of Energy, have been determined such that they parallel the European emission standards (Euro 2) which limit the allowable carbon monoxide emissions (Ratshomo & Nembahé, 2017).

The legal maximum for MTBE and ETBE volume concentration as an additive to gasoline is 15 % and 17 %, respectively (Yuan, 2006). As previously experimented and studied by Yuan (2006) and Collignon & Poncelet (2001), a reasonable and realisable ETBE additive

volume content is between 10–15 % in gasoline. According to the South African National Standard (SANS), leaded or unleaded gasoline can be blended with 1–10 % volume of anhydrous denatured fuel ethanol (Standard *et al*, 2010).

## 2.2 Reactant and product properties

### 2.2.1 Ethyl tert-butyl ether as an oxygenate additive

Fuels blended with oxygenated additives have lower exhaust and carbon monoxide emissions (Fran oisse & Thyrion, 1991). Tertiary ethers, such as MTBE and ETBE, are widely used oxygenates as they ensure more efficient combustion of gasoline and thus reduce the amount of harmful air pollutants that are released into the atmosphere through incomplete combustion (Yuan & Jonsson, 2006). MTBE has been more widely utilised as an oxygenate additive for gasoline (Yuan & Jonsson, 2006). Although the production of MTBE is cheaper than ETBE (Fran oisse & Thyrion, 1991; Sneesby *et al*, 1997a), MTBE is more harmful to groundwater systems than ETBE (Yuan & Jonsson, 2006), and is produced from natural gas (Fran oisse & Thyrion, 1991).

Consequently, there has been gained interest in ETBE as a more environmentally friendly oxygenate additive (Yuan & Jonsson, 2006). Compared to MTBE, ETBE has a higher octane rating (Yee, Mohamed & Tan, 2013), a lower solubility in water, a higher boiling point (Hamid & Ali, 2004), and a lower vapour pressure (Yuan & Jonsson, 2006) which implies that ETBE will be more easily incorporated into a gasoline mixture and is also easily carried through pipelines (Yuan & Jonsson, 2006).

ETBE is considered semi-renewable as it can be produced from renewable ethanol (Sneesby *et al*, 1997a). Furthermore, the rise in ETBE utilisation for gasoline will stimulate the demand for bioethanol production, which positively impacts agricultural sectors (Hamid & Ali, 2004), and lessens the dependency on methanol from natural gas (Fran oisse & Thyrion, 1991). The physical properties and environmental advantages of ETBE compared to MTBE make the ether an attractive alternative as an oxygenate additive (Yee *et al*, 2013).

### 2.2.2 LPG: liquid petroleum gas

The synthesis of ETBE requires the reaction of ethanol with isobutene. The isobutene is sourced from LPG, liquid petroleum gas, which is composed of a mixture of saturated and unsaturated C<sub>3</sub> and C<sub>4</sub> molecules (McKinsey, 2020).

The LPG can be sourced from a fluid catalytic cracker (FCC) (McKinsey, 2020). The fluid catalytic cracker produces a product which includes saturated propane and butane as well as unsaturated propene and butenes (McKinsey, 2020). The butene fraction is made up of different isomers of the butene molecule. Unsaturated alkenes are useful in the production of ETBE and other gasoline oxygenating additives. Therefore, the alkenes, specifically the butenes need to be separated from the FCC product. The feed for ETBE production is the product from a FCC with a Vacuum Oil Gas (VGO) feed (Behera, Ray & Singh, 2008).

Rigutto, van Veen & Huve (2017) alludes to the fact that an FCC is able to withstand feed rates of VGO of between 2 000 and 10 000 tons per day. With an LPG yield in the region of 12 % to 15 % with a composition given in Table 9 adapted from Rigutto *et al* (2017).

**Table 9:** LPG composition as a product from an FCC, adapted from Rigutto, van Veen & Huve (2017).

Component	Composition (wt %)
Propane	5.6
Propene	30.6
n-Butane	4.0
i-Butane	16.3
n-Butenes	30.8
i-Butene	12.7

Further, Gilbert *et al* (2011) supports the findings by Rigutto *et al* (2017); these findings showed a 12.4 % LPG yield from a VGO feed using the standard FCC catalyst. This yielded LPG product indicated to contain around 12 % C<sub>4</sub>'s.

In order to get a clear idea of the composition of the FCC product stream, multiple sources were reviewed and the results reported in Table 10.

**Table 10:** FCC product stream composition from different sources.

Component	Yield (wt % in FCC product stream)						
	Reference	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\sigma$
Dry gas		5.4	4.7	5.3	3.5	4.0	3.4
C <sub>3</sub> 's		6.3	6.9	8.5	17.6	26.8	7.1
C <sub>4</sub> 's		10.7	11.9	12.2	17.6	26.8	10.9
Gasoline		45.9	48.7	43.4	55.1	48.1	41.2
LCO		17.8	10.5	15.0	10.2	12.4	19.6
HCO		-	2.0	14.3	9.3	-	-
Bottoms		8.8	10.3	-	-	-	14.4
Coke		5.1	5.0	1.3	4.3	8.2	5.0
Propene in C <sub>3</sub> 's		-	-	7.5	4.9	8.8	5.9
Butenes in C <sub>4</sub> 's		-	-	8.8	8.1	7.3	7.0

<sup>a</sup> Akpa & Dagde (2014)

<sup>b</sup> Shishkova, Stratiev & Pechlivanov (2011)

<sup>c</sup> Aitani, Yoshikawa & Ino (2000)

<sup>d</sup> Letzsch (2014)

<sup>e</sup> Qiu, Lu & Li (2004)

<sup>f</sup> Dath, Vermeiren & Noiret (2007)

This literature information provides sufficient insight into making an informed decision and reasonable assumption for the composition of the petroleum based LPG feed to the ETBE production process. The review of FCC product information provided in this section is further supported by Ravishankar, Rao & Choudary (2018), who suggests a total isobutene content in the FCC product of *c.a.* 10 %.

Investigation into the possibilities and methods for separation of the LPG and butene was conducted. Su *et al* (2015) suggested a means to separate the isobutene using the following steps: adsorption of the LPG where ion exchange treatment is performed in a Y-shaped molecular sieve (this assists with impurity removal). This is then followed by another adsorption column with this use of a modified molecular sieve to adsorb the n-butane and separate isobutene (Su *et al*, 2015). The final step includes desorption and separation of the n-butane. This process is suggested to yield a pure isobutene product which can then be reacted to form oxygen additives in gasoline. Drennan (1947) provides a novel process which separates isobutene from a FCC product.

### **2.2.3 Bioethanol**

Bioethanol is ethanol produced from a renewable resource (M Balat & H Balat, 2009). Bioethanol is the most widely used bio-fuel for transportation and mitigates the emission of greenhouse gases (M Balat & H Balat, 2009).

Bioethanol production involves the conversion of biomass through fermentation followed by distillation (European Biomass Industry Association, 2020). Typical biomass feedstocks include, wheat, sugar cane, corn straw, and wood (M Balat & H Balat, 2009); however, any feedstock that contains sugars or carbohydrates can be used in the bioethanol production (Halder *et al*, 2019).

According to Freeman, Yampolskii & Pinna (2006), the water content in the bioethanol needs to be less than 1 % on a volume basis in order for the bioethanol to be a component mixed into gasoline.

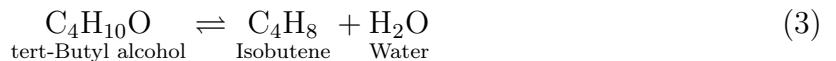
Despite bioethanol and ethanol in general having a lower HHV than gasoline, the addition of bioethanol to gasoline increases the performance of the gasoline, owing to bioethanol's high octane number (Halder *et al*, 2019). When compared to fossil fuels, the bioethanol significantly reduces the life cycle of CO<sub>2</sub>, implying a significant reduction in greenhouse gas emissions (Chen *et al*, 2019). Despite this advantage, it should be kept in mind that bioethanol is miscible with water and has the ability to form hydrogen through steam reforming processes (Vita, Italiano & Pino, 2017).

Bioethanol is obtainable in a range of purities (Kiss & Ignat, 2012). As a result of the presence of water, ethanol and water form an azeotropic mixture (Kiss & Ignat, 2012) making their separation complex. Although many methods are available to separate ethanol from water, namely: pervaporation, adsorption, pressure-swing distillation, extractive distillation, azeotropic distillation, as well as hybrid methods (Kiss & Ignat, 2012); they have proven to not be economical for industrial scale applications (Kiss & Ignat, 2012). Furthermore, even upon obtaining high purity ethanol (over 99.9 %), due to ethanol's hygroscopic nature (Torres-Jimenez *et al*, 2011), the ethanol is diluted unless stored under very specific and expensive conditions. It is thus not economical to purchase high purity ethanol (above 99 %) as one will inevitably end up with a diluted product nonetheless. An alternative is to consider the cost of purifying a lower grade ethanol.

## 2.3 Synthesis of ETBE

### 2.3.1 Overview of reactions & operating conditions

The production of ETBE is achieved through etherification, where an alcohol is converted to an ether (Yee *et al*, 2013). Ethanol is reacted with either isobutene (IB) or tert-butyl alcohol (TBA) to form ETBE in the presence of a catalyst (Yee *et al*, 2013; Jensen & Datta, 1995; Menezes & Cataluna, 2008). The reaction can be carried out in either liquid or gas phase (Larsen *et al*, 1995a). The reaction involving TBA as a reactant can either be reacted via an indirect (Equation 3 followed by Equation 1) or direct method (Equation 2 (Assabumrungrat *et al*, 2004)). The production of ETBE from a renewable ethanol source reacted with a petroleum based LPG was particularly of interest. Consequently, the main reactions that are considered are shown in Equation 1 through Equation 3:



While Reaction 1 is the more researched and better documented reaction, the reactions involving TBA are considered more of an emerging study, with very little research on the reactions documented. The synthesis of ETBE is an exothermic reversible reaction (Norkobilov *et al*, 2017a). Thus, higher operating temperatures favour the reverse reaction (Menezes & Cataluna, 2008). Consequently, two side reactions can take place in Reaction 1: the dimerisation of isobutene to form isobutanol and the hydration of isobutene (IB) to form di-isobutene (DIB) (Yu-Chu & Tade, 2000; Bisowarno, Tian & Tadé, 2004).



The hydration of isobutene, Equation 5, can be prevented by ensuring the absence of water (Bisowarno *et al*, 2004); however, depending on the purity of the ethanol used, this may prove challenging (Kiss & Ignat, 2012).

The Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism has been widely used in literature to model the rate of ETBE production (Domingues, Pinheiro & Oliveira, 2014). The LHMW model describes that using an excess of at least 4 % ethanol causes ethanol to adsorb and cover the surface of the catalyst (Amberlyst-15) which prevents the occurrence of the dimerisation (Equation 4) and oligomerisation of isobutene (Sneesby *et al*, 1997a; Bisowarno *et al*, 2004). However, an inordinate excess of ethanol in the feed hinders the ability of isobutene to diffuse into the catalyst; thus, an increase in the ethanol feed concentration causes a reduction in the reaction rate (Yee *et al*, 2013).

The reaction is followed by a sequence of separations to achieve a higher conversion and purity of the desired product, ETBE (Yee *et al*, 2013). The excess ethanol is then recycled to the reactor (Yee *et al*, 2013).

Section 2.3.4 investigates the affects on catalyst selection and the performance of the catalysts and influencing catalyst variables and parameters. Many papers use cation exchange resins as the catalyst of choice when using TBA as a reactant; however, BL Yang, Yang & Yao (2000) illustrated that the D-72 and S-54 catalyst resulted in the best selectivity and an optimum water inhibition coefficient. These catalysts are used for MTBE production and are readily available. Additionally, Degirmenci, Oktar & Dogu (2009a) reports that Amberlyst-15 illustrated high activity.

Given that isobutene is available from a petroleum LPG source and despite the advantages of reacting TBA with ethanol at atmospheric pressure; very little research papers illustrate the hydration of isobutene to form TBA as a primary production method for ETBE. Therefore, a conservative assumption was made: given the privileged availability of isobutene as a raw material, the favoured reaction to produce ETBE is chosen as Reaction 1, neglecting TBA as a primary reactant in the ETBE production.

### 2.3.2 Liquid phase reactions

The liquid phase synthesis of ETBE with reactants, IB and ethanol, requires higher pressures than the gas-phase synthesis method; the gas phase reaction can be carried out at atmospheric pressures (Yee *et al*, 2013). Furthermore, the reaction between ethanol and isobutene to form ETBE has certain restrictions to ensure profitability and maximised conversion. The reaction in the liquid phase must take place in the absence of water as

water prompts the development of unwanted side reactions which ultimately decrease the yield and selectivity of the process (Yee *et al*, 2013). Furthermore, the presence of water deactivates the catalyst (Degirmenci, Oktar & Dogu, 2009b). Thus, anhydrous ethanol is required for synthesis (Degirmenci *et al*, 2009b).

However, the use of TBA as a reactant invites the possibility of a liquid phase reaction occurring at atmospheric pressures as a result of its higher boiling point (82°C) as compared to isobutene (-6.9°C) (Yee *et al*, 2013). The reactions involving TBA occur at atmospheric pressure of 1 atm and a temperature range of 50°C to 65°C (BL Yang *et al*, 2000) (Yee *et al*, 2013). These reaction temperatures are supported by Degirmenci *et al* (2009a) who suggests that ethanol dehydration occurs at temperatures above 95°C as well as the fact that IB and ETBE conversion increases up to this temperature. Further, according to numerous sources, reacting at atmospheric pressure implies that the isobutene formed as a result of the dehydration of TBA exists in its gas phase (Yee *et al*, 2013). Therefore, isobutene exists in small concentrations and will not influence the production of ETBE (Assabumrungrat *et al*, 2004).

BL Yang *et al* (2000) elaborate on the reaction involving TBA with ethanol. Indicating that since Reaction 2 produces water, the water content in the ethanol becomes unimportant in terms of preventing side reactions and hindering the ETBE production rates. However, Degirmenci *et al* (2009a); Assabumrungrat *et al* (2004); Degirmenci *et al* (2009a) as well as BL Yang *et al* (2000) illustrate the influence of the presence of water on the rate of reaction and performance of catalyst.

For the liquid phase reaction, temperatures below 80°C are employed to avoid favouring the reverse reaction (Yu-Chu & Tade, 2000); however, the reaction rates become slow at temperatures below 80°C (Sneesby *et al*, 1997b). High operating pressures (about 0.6-1.0 MPa) are utilised to ensure the light hydrocarbons remain in the liquid phase (Norkobilov *et al*, 2017a; Yu-Chu & Tade, 2000).

At temperatures above 368 K, limitations in terms of the equilibrium of the reaction become substantial (Degirmenci *et al*, 2009b).

When heteropolyacid catalysts were used, di-ethyl ether (DEE) begins to form in a side reaction, ultimately reducing the overall conversion of ETBE (Degirmenci *et al*, 2009b). Similarly, when temperatures exceed 423 K, ethylene formation is found and peaks at a temperature of 523 K (Degirmenci *et al*, 2009b).

Furthermore, the ETBE reaction itself is heavily dependent on the activity of the catalyst in use, which is susceptible to both deactivation and poisoning (Sneesby *et al*, 1997a).

Although some issues arise with the liquid phase reaction of these reactants, this type of reaction is generally preferred over the gas phase reaction as the gas phase reaction lends itself to complexities such as the strict control and measures required to make it successful (Yee *et al*, 2013).

### 2.3.3 Gas phase reactions

ETBE can also be synthesised through gas phase reactions at lower operating pressures (atmospheric pressure) (Larsen *et al*, 1995a) and at temperatures between 313 and 363 K (Larsen *et al*, 1995a). Poźniczek, Lubańska, *et al*, 2006 found solid Wells Dawson type catalyst was both active and selective for ether synthesis at the relatively low temperature of 40 °C; with an optimal conversion at temperatures between 50 and 60 °C. Gas phase synthesis of ETBE requires specific partial pressures of the various reactants to ensure a high conversion (Larsen *et al*, 1995a). In order to manipulate the partial pressures of reactants, nitrogen gas is mixed with the reactant mixture before it is fed to the reactor (Larsen *et al*, 1995a).

As this etherification reaction is exothermic (Norkobilov *et al*, 2017a), the additional stream of nitrogen gas as an inert also assists in controlling the increasing temperature of the exothermic reaction (Alcántara *et al*, 2000) and hence aids in thermal stability (Alcántara *et al*, 2000). However, with increasing the nitrogen stream and reducing the isobutene in the mixture, the ETBE production is reduced (Larsen *et al*, 1995a). This behaviour was observed when the H-mordenite catalyst was tested (Larsen *et al*, 1995a).

Beta-zeolites displayed a maximum yield of ETBE (34 %) at a temperature of 50 °C (Collignon & Poncelet, 2001). At temperatures above 50 °C, by-products begin to form (Collignon & Poncelet, 2001). Additionally, Collignon & Poncelet, 2001 suggests the pre-treatment of the beta-zeolite catalyst by calcining to further improve its efficiency. In comparison to other catalysts used for vapour-phase synthesis, beta-zeolites prevent the over absorption of ethanol onto their surface, allowing the adsorption of IB (Collignon & Poncelet, 2001).

Alcántara *et al*, 2000 studied ETBE synthesis in both a fluidized bed and fixed bed. Alcántara *et al*, 2000 used anhydrous ethanol with 99 % pure IB and additional nitrogen gas (99 % pure) to fluidise the bed. In order to obtain the reactants, ethanol and IB as vapours for the gas phase synthesis, the reactants are sent to a vaporiser prior to feeding them to the reactor and vaporised at 125 °C (Alcántara *et al*, 2000). The reactors were run at atmospheric pressure and operated at 100 °C (Alcántara *et al*, 2000). Alcántara *et al*, 2000 utilised the H-ZSM-5 catalyst for vapour phase synthesis and found an intermediate

adduct formed when this catalyst was used (Alcántara *et al*, 2000). A maximum yield for ETBE was noted at 115 °C and 100 °C for fixed-bed and fluidised bed respectively (Alcántara *et al*, 2000). Ultimately, fluidised beds proved to be less effective in the synthesis of ETBE due to the phenomenon of "attrition" (Alcántara *et al*, 2000).

Iborra *et al*, 1989 conducted the gas phase reaction at a temperature of 85 °C and with an IB:ethanol ratio of 1.7:1. Again, nitrogen can be utilised to manipulate the partial pressures of the reactants as well as a transportation medium of the reactants (Iborra *et al*, 1989).

#### 2.3.4 Catalysts

A catalyst is a necessary addition in this synthesis process as it drives the reaction towards a higher yield and conversion (Yee *et al*, 2013). Factors that are considered when selecting a catalyst for this process include the rate of mass transfer, as well as the adsorption-desorption dynamics (Yee *et al*, 2013) of the reactants and products on the catalyst. Furthermore, acid site location played a vital role in the effectiveness of the catalyst along with the volume of the acid in the catalyst (Yee *et al*, 2013).

Sulphuric acid, zeolites, heteropoly and mineral acids as well as ion-exchange resins have been considered for use in the liquid-phase synthesis of ETBE (Yee *et al*, 2013). Dilute sulphuric acid was found to be the originally preferred catalyst but its damage to the environment was unfavourable (Yee *et al*, 2013).

Amberlyst-15 (A-15) and Amberlyst-35 (A-35) are two acidic ion-exchange resin catalysts which displayed good catalytic activity and selectivity (Yee *et al*, 2013) as a result of the location of their acid sites on the catalyst surface. Conversion of IB to ETBE using Amberlyst 15 as a catalyst displayed a reduced conversion with an increase in temperature (Degirmenci *et al*, 2009b). This was notably due to an equilibrium limitation the reaction faces at temperatures higher than 80 °C (Degirmenci *et al*, 2009b). Furthermore, the catalytic activity of the ion-exchange resin is reduced by the presence of water (Françisse & Thyrion, 1991; Degirmenci *et al*, 2009b). When Amberlyst 15 was used as a catalyst with IB and ethanol as reactants to form ETBE, a reduced activity was observed when water was present (Degirmenci *et al*, 2009b); this reduction was especially significant at lower temperatures (Degirmenci *et al*, 2009b). This behaviour is as a result of the greater chance of water adsorbing onto the acidic catalyst's surface over ethanol; thus obstructing active sites which otherwise would have been occupied by reactants (IB and ethanol) (Degirmenci *et al*, 2009b).

Contrary to these limitations, Amberlyst 15 displayed the highest yield of ETBE (35 %) when compared to other ion-exchange resins in liquid phase synthesis (Degirmenci *et al*, 2009b). Additionally, the hindered activity of A-15 in the presence of water was still greater than the activities of Amberlyst 16 and 35 in the presence of anhydrous ethanol (Degirmenci *et al*, 2009b). Given these conclusions, Amberlyst 15 displayed promising characteristics for use as a catalyst in a liquid-phase synthesis process with diluted ethanol, decreasing the overall costs of the ETBE synthesis production (Degirmenci *et al*, 2009b).

However, ion-exchange resins exhibit low mass transfer rates (Yee *et al*, 2013) and poor thermal stability and hence should not be used in temperatures above 120 °C (Domingues, Pinheiro, Oliveira, *et al*, 2012). Furthermore, ion-exchange resins are pressure sensitive, where the mass transfer rates are severely affected under the high pressure conditions required for the liquid-phase reaction of IB and ethanol (Yee *et al*, 2013). Yee *et al* (2013) suggests zeolites as a promising alternative to conquer the above-mentioned issues. Zeolites offer improved selectivity compared to A-15 but yields remained similar (Yee *et al*, 2013). This was also seen in gas-phase reactions (Collignon & Poncelet, 2001).

Many catalysts have been studied for use in the gas-phase synthesis of ETBE (Micek-Ilnicka, 2006). These include but are not limited to: Wells Dawson type catalysts, beta-zeolites, H-ZSM-5 and ion exchange resins such as Amberlyst 15 (Larsen *et al*, 1995b).

Zeolites such as  $\beta$ -zeolite, H-ZSM-5 and H-mordenite exhibit thermal stability and can be used with the reaction of IB and ethanol in the gas phase, under atmospheric pressure (Larsen *et al*, 1995b), as mentioned in more detail under Section 2.3.3. These are common catalysts for use in the petrochemical sector, specifically for use in ether synthesis (Hamid & Ali, 2004).

However, Larsen *et al* (1995b) also found that this method of reaction requires ethanol protection to prevent unwanted isobutene oligomerisation of the products. Additionally, this method was shown to have high concentrations of ethanol collecting in the pores of the zeolite which contributed to an impedance of the reaction (Larsen *et al*, 1995b). Ultimately zeolites have been shown to be thermally stable and have no acid effluent making them viable catalysts for use in this process (Larsen *et al*, 1995b).

Amberlyst-15 is commonly used in the liquid phase synthesis of ETBE (Yee *et al*, 2013). However, this catalyst can also be used in the gas phase synthesis of the ether (Iborra *et al*, 1989) at atmospheric pressure in a flow reactor (Iborra *et al*, 1989). Similar to other gas phase methods with alternate catalysts, anhydrous ethanol with a purity of at least 99.5 % must be used to prevent the deactivation of the catalyst (Iborra *et al*, 1989). Iborra *et al*, 1989 conducted the gas phase reaction at a temperature of 85 °C and with

an IB:ethanol ratio of 1.7:1. Again, nitrogen can be utilised to manipulate the partial pressures of the reactants as well as a transportation medium of the reactants (Iborra *et al*, 1989).

Heteropolyacid catalysts have been studied for the ETBE synthesis process in gas phase, specifically diphosphooctadecatungstic acid was shown to be suitable for use as a catalyst in the production of ETBE in a gas phase synthesis at temperatures as low as 40 °C (Poźniczek, Micek-Ilnicka, *et al*, 2005). Another heteropolyacid used was silicotungstic acid (STA) and Keggin-type tungstophosphoric acid (TPA-K) (Degirmenci, Oktar & Dogu, 2010). TPA-K and STA are both efficient for use in the etherification process under gas-phase reaction but prove to be less active at high temperatures above 200 °C. As a result, these catalysts begin to lose their acidity and this in turn makes them less effective (Degirmenci, Oktar & Dogu, 2011). When STA is supported by activated carbon a higher conversion of IB and ethanol to ETBE is observed in a gas-phase reaction (Degirmenci *et al*, 2011) as compared to pure STA catalyst.

Ultimately the gas phase reaction to create ETBE with H-mordenite as a catalyst promoted the benefit of the sole formation of ETBE as a product when absolute ethanol was used as a reactant (Larsen *et al*, 1995a). Although this catalyst showed a decreased activity in comparison to A-15 (Larsen *et al*, 1995a); it showed the most promising results with favourable conditions of ETBE formation (Larsen *et al*, 1995a), in that it featured an adequate pore size and strong acidity (Larsen *et al*, 1995a).

### 2.3.5 Azeotropes & thermodynamic models

The liquid phase synthesis of ETBE is subject to non-idealities, resulting in the presence of azeotropes between ETBE, ethanol and isobutene (Sneesby *et al*, 1997a). The UNIFAC model predicts the presence of the ethanol-ETBE azeotrope which occurs at low and high pressures, as well as the presence of an azeotrope between ETBE and butenes which occurs only at high pressures (Norkobilov *et al*, 2017a; Sneesby *et al*, 1997a; Domingues, Pinheiro & Oliveira, 2014; Françoisse & Thyrion, 1991). The compositions of the azeotropes at two different pressures are shown in Table 11

**Table 11:** Azeotropes between ethanol and ETBE, and ETBE and butenes at high pressures predicted by the UNIFAC model (Sneesby *et al*, 1997a)

Compounds	EtOH composition at 0.95 MPa	EtOH composition at 1.4 MPa
EtOH-iBut	no azeotrope	1.25 %
EtOH-nBut	no azeotrope	1.45 %
EtOH-ETBE	59 %	66 %

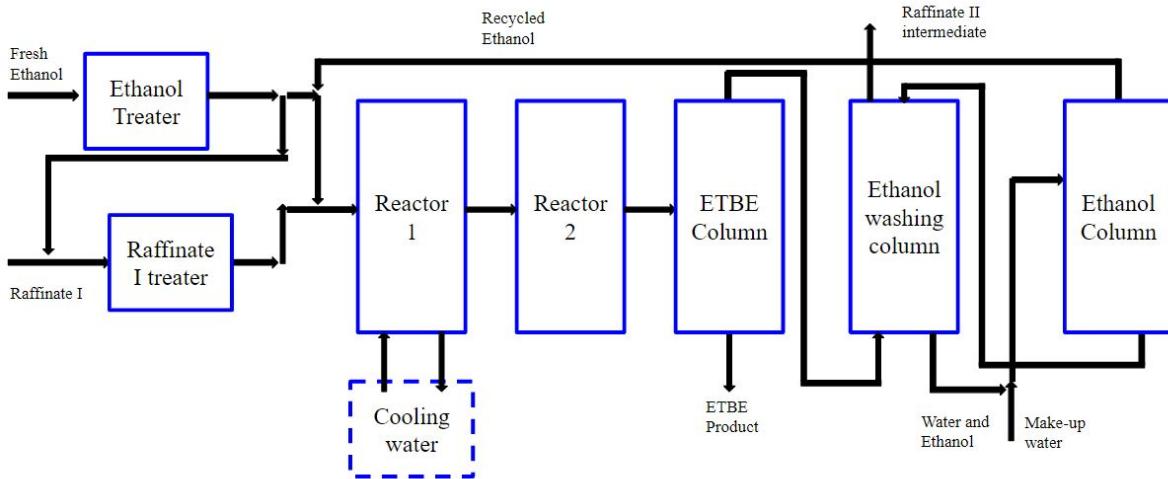
The UNIFAC model appears to be popular for the prediction of the liquid-phase activities (Bumbac *et al*, 2009; Kaur & Sangal, 2017), however, both the Wilson and UNIQUAC model can be used for ether reactions (Bisowarno *et al*, 2004). Both the Soave-Redlich-Kwon (SRK) and Peng-Robinson thermodynamic models can be used to predict the properties of the ETBE system (Bisowarno *et al*, 2004; Sneesby *et al*, 1997b; Kaur & Sangal, 2017).

The ETBE-EtOH azeotrope prevents the possibility of recycling ethanol back into the reactor (Menezes & Cataluna, 2008). In order to separate azeotropic ETBE-EtOH, multiple separation units would be required, as described in Section 2.4.3.

## 2.4 Conventional unit operations

### 2.4.1 Overview

Traditionally, ETBE is produced through a multi-step process (Yee *et al*, 2013). Domingues, Pinheiro, Oliveira, *et al* (2012) employed conventional methods for the reaction and purification of ETBE production from isobutene and ethanol. The process is shown schematically in Figure 2 below:



**Figure 2:** Block diagram of a conventional industrial ETBE production process as adapted from Domingues, Pinheiro & Oliveira (2014) and Domingues, Pinheiro, Oliveira, *et al* (2012)

Industrial production of ethers, such as ETBE, for fuel addition have been commercialised through a number of processes namely: The Hüls process (which makes use of ethanol and  $C_4$  cuts produced from FCC or SC processes) (Badia Córcoles, 2016), the Phillips process and the Texaco process (Badia Córcoles, 2016). Industrially, these processes make use of catalysts such as acid-ion exchange and zeolite catalysts as discussed in more detail under Section 2.3.4.

A sufficient conversion encountered in industrial plants with liquid phase synthesis is between 94 and 97 %; depending on whether or not the plant desires the  $C_4$  to be recycled into the cracker again or otherwise combusted (Domingues, Pinheiro, Oliveira, *et al*, 2012).

#### 2.4.2 Feed pre-treatment & reactors

The process begins with a preliminary treatment of the liquid reactant feed to eliminate any potential impurities (such as metal ions, butadiene, and compounds containing nitrogen) which may have adverse effects on the catalyst activity in the reactor (Domingues, Pinheiro & Oliveira, 2014; Domingues, Pinheiro & Oliveira, 2017). This step is followed by the reaction stage where two reactors are operated in series (Domingues, Pinheiro & Oliveira, 2014), as shown in Figure 2. Most of the feed is converted in the first multitubular reactor (Domingues, Pinheiro & Oliveira, 2017). As discussed previously, the etherification reaction to form ETBE is exothermic and equilibrium limited (Sneesby *et al*, 1997a; Norkobilov *et al*, 2017a). Consequently, cooling water is utilised to prevent

an excessive increase in the reactor temperature (Domingues, Pinheiro & Oliveira, 2017), which impacts the equilibrium of the reaction and hence negatively impacts the desired conversion as well as the catalytic activity (Fran oisse & Thyrion, 1991; Norkobilov *et al*, 2017a). The second reactor is intended to maximise the overall conversion (Domingues, Pinheiro & Oliveira, 2014). Higher temperatures are encountered in reactor one (where most of the feed is converted); subsequently, the catalyst requires more frequent replacement in reactor one as compared to the catalyst in reactor 2 (Domingues, Pinheiro & Oliveira, 2014). The catalyst used in the conventional process is an acid ion-exchange resin such as Amberlyst-15 or Lewatit K-2629 (Domingues, Pinheiro, Oliveira, *et al*, 2012).

Following the reaction, separation techniques are required to obtain the desired, pure, products (Domingues, Pinheiro, Oliveira, *et al*, 2012). These techniques are described in more detail in the following Section: 2.4.3.

#### **2.4.3 Separation techniques**

Large-scale production of ETBE is produced through the reaction of IB with excess ethanol and as a result the ethanol is recovered along with the product, ETBE (Menezes & Cataluna, 2008; Yee *et al*, 2013). Depending on the process conditions, azeotropic mixtures may form between ethanol, ETBE and the C<sub>4</sub>-hydrocarbons, (Sneesby *et al*, 1997a; Yee *et al*, 2013), as discussed in Section 2.3.5. In order to acquire a highly pure product of ETBE, special separation techniques are required (Yee *et al*, 2013).

#### **2.4.4 Distillation**

As shown in Figure 2, the products from the second reactor are carried to a separation step involving two distillation columns and an "ethanol washing column" (Domingues, Pinheiro & Oliveira, 2014). The first distillation column separates ETBE as the bottoms product, while the remaining products and unreacted compounds are removed as the distillate (Domingues, Pinheiro & Oliveira, 2017). This distillate is fed to a second column under which liquid-liquid extraction can be performed owing to ethanol's higher affinity to water as compared to the organic phase (Domingues, Pinheiro & Oliveira, 2014). Thus a liquid-liquid extraction with water is done in an "ethanol washing column" (Menezes & Cataluna, 2008). Finally, this mixture is then fed to a third and final column where the ethanol is dehydrated and recycled to the entry of the first reactor (Domingues, Pinheiro & Oliveira, 2014).

#### **2.4.5 Liquid-liquid extraction**

Liquid-liquid extraction employed in the ethanol washing column produces ETBE of high purity, however, an azeotropic mixture of water and ethanol is encountered which hinders the ability to recycle pure ethanol back into the reactor (Menezes & Cataluna, 2008). Furthermore, the implementation of a liquid-liquid extraction (or "ethanol washing column" (Menezes & Cataluna, 2008)) increases the capital and running costs. Subsequently, it may be more viable to utilise the azeotropic ETBE/EtOH product as a unique additive for gasoline products (Menezes & Cataluna, 2008).

It is known that ethanol can be utilised as a combustion fuel (Kohse-Höinghaus *et al*, 2010), consequently the use of an ETBE and ethanol mixture as a gasoline additive should also be considered (Menezes & Cataluna, 2008). De Menezes *et al* (2006) and Menezes & Cataluna (2008) suggest that an azeotropic mixture of ETBE and ethanol as a direct additive to gasolines may hold possible advantages over pure ethanol or pure ETBE additives. The mixture of ETBE and ethanol presents advantages such as reduced Reid vapor pressures (RVP) as compared to fuels containing pure ethanol; therefore these mixture additives demonstrate smaller levels of volatile organic compounds (De Menezes *et al*, 2006). Furthermore, De Menezes *et al*, 2006 found the azeotropic blend of ethanol and ETBE displayed octane ratings similar and slightly higher to that of pure ETBE additives. This mixture was shown to be adequate for use as a gasoline additive in terms of enhancing the efficiency of the gasoline and overall- reducing the emission of volatile organic compounds (De Menezes *et al*, 2006). Thus, utilising the ETBE-ethanol azeotropic mixture may be a more environmentally friendly, and cost effective alternative compared to separating and purifying ETBE from ethanol through multiple operations (De Menezes *et al*, 2006; Menezes & Cataluna, 2008).

Alternatively, other extraction solvents have been studied such as ionic liquids and hyperbranched polymers in order to separate the ETBE-ethanol azeotropic mixture (Yee *et al*, 2013). These solvents have shown to be environmentally friendly alternatives (Yee *et al*, 2013) with advantages such as their complete recovery and excellent operation in terms of efficient extraction (Yee *et al*, 2013). This is especially helpful since the utilisation of water as a liquid solvent to achieve a high purity ETBE product results in the formation of a water-EtOH azeotrope that hinders the ability to recycle anhydrous ethanol (Menezes & Cataluna, 2008).

## 2.5 Other synthesis techniques

### 2.5.1 Pervaporation

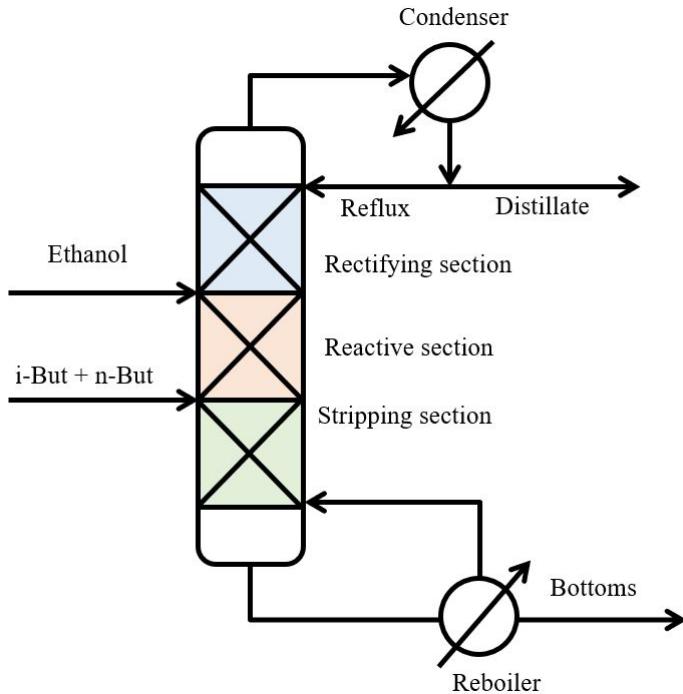
Pervaporation is a method that employs a membrane under vacuum, which does not contain pores and is highly selective in terms of separating liquid blends which are homogeneous (Yee *et al*, 2013). An inert sweeping gas is passed downwards through the membrane (Yee *et al*, 2013) on the permeate side of it. The permeate is then recovered on the alternate side of the membrane (Yee *et al*, 2013). The membranes can be synthesised by different materials and the choice of material influences the performance of the separation process (Yee *et al*, 2013). Ultimately, this process is complex and many variations can be employed to manipulate the outcomes of the operation (Yee *et al*, 2013).

### 2.5.2 Hybrid Processes

A hybrid process is designed such that unit operations which work well together are united such that they perform in a superior manner when combined as opposed to on their own (Norkobilov, Gorri & Ortiz, 2017b).

### 2.5.3 Reactive distillation

Reactive distillation (RD) is a popular hybrid process for the synthesis and purification of ETBE (Bisowarno *et al*, 2004; Domingues, Pinheiro & Oliveira, 2014; Domingues, Pinheiro & Oliveira, 2017). Reactive distillation combines the reaction and separation operations into a single unit, which reduces capital and running costs as the number of equipment required is reduced (Sneesby *et al*, 1997b). A diagram of a reactive distillation unit is shown in Figure 3:



**Figure 3:** Reactive distillation column. The figure has been adapted from Yee, Mohamed & Tan (2013) and Bisowarno, Tian & Tadé (2004)

Reactive distillation can potentially improve the equilibrium reaction limitation by the continuous separation of products which increases conversion (Malone & Doherty, 2000). The RD process for synthesis of ETBE displays increased income in terms of ETBE in comparison to the traditional process (Domingues, Pinheiro & Oliveira, 2017). Furthermore, the RD process requires lower capital investment (Domingues, Pinheiro & Oliveira, 2017), and reactant costs, in terms of ethanol and steam, are lower when compared to the conventional process (Domingues, Pinheiro & Oliveira, 2017). Overall, the economic earnings of the RD process in comparison to the traditional method are small, but Domingues, Pinheiro & Oliveira (2017) states that small differences in earnings lead to substantial benefits both in terms of the environment and economically. In summary, the RD process amounts to higher product formation, at a cheaper cost in comparison to conventional techniques of synthesising ETBE (Domingues, Pinheiro & Oliveira, 2017).

Contrary to these many advantages, the design and optimisation of a reactive-distillation hybrid process is complex due to interactions of the rate of reaction, and the vapour-liquid equilibrium encountered in the column (Domingues, Pinheiro & Oliveira, 2017). The issue of multiplicity implies that multiple operating conditions can achieve the same conversion (Bisowarno *et al*, 2004). Consequently, the product purity cannot be compared based on a conversion (Bisowarno *et al*, 2004). Furthermore, the issue of multiplicity becomes more problematic with an increases in the number of separation stages (which is contradictory to conventional distillation theory); which requires more complex control

and design considerations (Bisowarno *et al*, 2004).

#### 2.5.4 Pervaporation distillation

Pervaporation distillation is a promising hybrid process in that it increases the obtainable purity of ETBE synthesised to values as high as 95.2 wt % (Norkobilov *et al*, 2017b; Yee *et al*, 2013), with lower energy consumption as compared to conventional ETBE synthesis (Norkobilov *et al*, 2017b; Yee *et al*, 2013). Furthermore, the permeate stream produced contains a large amount of ethanol which can be recycled back to the reactor (Norkobilov *et al*, 2017b). This is achieved through the use of an alcohol-selective membrane (Yee *et al*, 2013), Norkobilov *et al*, 2017b states a cellulose acetate membrane has shown to be selective towards ethanol; this is promising, as organic-organic mixtures have proven to be difficult to separate (Norkobilov *et al*, 2017b). Another advantage of pervaporation distillation is its tailorabile and "compact" design (Norkobilov *et al*, 2017b).

Norkobilov *et al*, 2017b studied feeds comprising of ethanol (10 % excess), ETBE as well as multi component C<sub>4</sub> mixtures; as most studies only consider ETBE-ethanol feeds to the membrane. In comparison to conventional ETBE synthesis and product separation methods which may require pressure swing distillation (Norkobilov *et al*, 2017b), pervaporation distillation showed enhanced separation and overall purification process performance (Norkobilov *et al*, 2017b). The process is tailorabile in that the pervaporation unit can be placed in more than one location (Norkobilov *et al*, 2017b). (Norkobilov *et al*, 2017b) reported the placement of the pervaporation units on side streams that are removed from the distillation column resulted in a more energy efficient design with less ethanol in the distillate flow as compared to other placements; such as before the debutanizer column. This column is typically operated at pressures between 7 and 9 bar, with feed temperature at 70 °C and feed pressure at 4.8 bar to ensure the stream is in liquid phase (Norkobilov *et al*, 2017b). The membrane pressure is kept constant at 2.7 kPa (20 mm Hg) (Norkobilov *et al*, 2017b); another study by (Ortiz, Alonso & Urtiaga, 2002) tested feed temperatures between 50-70 °C and with membrane pressures constant at 3 mm Hg when the Pervap2256 commercial membrane was used. With these conditions Norkobilov *et al*, 2017b reported an isobutene conversion of 94.3 % and an ETBE product purity of 95.2 %, with a 99.9 % ETBE recovery from what is produced in the reactor.

Norkobilov *et al*, 2017b considered the additional energy consumption of the heating and cooling of product and feed streams in order to compare the energy efficiency of the pervaporation distillation process with the conventional ETBE synthesis method as well as reactive distillation. Final temperatures and phases of products are an essential consideration in terms of storage and transport of the commodity produced and influence

costing of the entire process. Streams that need to be considered are: the ETBE product stream from the distillation column which needs to be cooled to a temperature suitable to store (Norkobilov *et al*, 2017b). Additionally, the streams that are withdrawn from the distillation column to feed to the pervaporation column need to be at the required feed temperature and would need to be cooled (Norkobilov *et al*, 2017b). A large amount of energy required for distillation can be provided by heat exchange between the reactors (due to the exothermic nature of the etherification reaction (Norkobilov *et al*, 2017b)) and thus the energy produced and required in the process can be optimised such that less power needs to be supplied by external utilities (Norkobilov *et al*, 2017b). An additional area to consider in terms of energy requirements is maintaining adiabatic conditions for the pervaporative membrane (Norkobilov *et al*, 2017b).

Norkobilov *et al*, 2017b reported that the pervaporation distillation hybrid process to synthesise ETBE resulted in the most energy efficient process out of the three options (PV, conventional synthesis and RD) and additionally had the most enhanced yield of ETBE. It is thus a promising method for use in synthesis of ETBE and should be considered and compared alongside conventional distillation with possible modifications. It suggests an advantage in that it can also be applied to existing conventional systems after a few modifications are made (Norkobilov *et al*, 2017b).

## 2.6 Conclusion

ETBE is a more environmentally suitable oxygenate additive than the traditionally used alternatives (Alcántara *et al*, 2000). Its synthesis through the reaction of bioethanol with isobutene is readily carried out in either liquid or gas phase (Collignon & Poncelet, 2001). Various catalysts exist that can be used to promote the production of ETBE including zeolites, acid-resins and various heteropolyacids (Yee *et al*, 2013). In order to ensure a high conversion and selectivity for the desired product, ETBE, an excess of ethanol is reacted with isobutene to inhibit any undesired side-reactions from the hydrocarbon (Degirmenci *et al*, 2009b). Furthermore, the reactants fed should be anhydrous such that the activity of the catalysts is preserved and the hydration of IB to TBA is inhibited (Bisowarno *et al*, 2004). The reactions are carried out at temperatures between 40–100 °C and at pressures ranging from atmospheric to 1 MPa; depending on whether or not the reaction takes place in the liquid or gas phase (Collignon & Poncelet, 2001). ETBE and ethanol can be separated by liquid-liquid extraction or their azeotropic mixture utilised as is as an oxygenate additive (Yee *et al*, 2013). The synthesis process ultimately is not too complex and requires attention in terms of separation techniques depending on what the desired output product is.

### 3 Process selection & creation

#### 3.1 Tonnage

According to von Gruenewaldt *et al* (2018), the actual consumption rate of crude oil at Natref is  $650 \text{ m}^3 \text{ h}^{-1}$ . Scaling this parameter to a yearly consumption rate correlates with a report published by SAPIA (2018) which indicates that Natref's capacity is  $108000 \text{ bbl day}^{-1}$ .

The mass yield of petroleum at Natref was reported as 35 % (von Gruenewaldt *et al*, 2018). Thus, the production of petrol was calculated to be  $260.43 \text{ m}^3 \text{ h}^{-1}$ , as shown below:

$$\text{Mass petrol} = 0.35(650)(870) = 1979.25 \text{ kg h}^{-1}$$

$$\text{Volume petrol} = \frac{760}{1979.25} = 260.43 \text{ m}^3 \text{ h}^{-1}$$

where the density of crude oil and petrol was taken as  $870 \text{ kg m}^{-3}$  and  $760 \text{ kg m}^{-3}$  respectively (WEBBOOK, 2011). ETBE is intended to be blended with Natref's current petroleum to produce a commercially available fuel with an oxygenate additive. The legal maximum of ETBE that can be blended with petroleum is 17 %, and for MTBE it is 15 % (Yuan, 2006). Subsequently, the amount of ETBE that is targetted is based on a blending composition of 15 %–17 % (v/v) of ETBE in petrol — which is based on Natref's petroleum production rate, shown below:

$$\text{Mass ETBE lower limit} = (736)(260.43) \frac{0.15}{0.85} = 33825 \text{ kg h}^{-1}$$

$$\text{Mass ETBE upper limit} = (736)(260.43) \frac{0.17}{0.83} = 39259 \text{ kg h}^{-1}$$

where the density of ETBE is  $736 \text{ kg m}^{-3}$  (WEBBOOK, 2011). Thus, the production rate of ETBE will be designed as  $33.83 \text{ tonne h}^{-1}$ – $39.26 \text{ tonne h}^{-1}$ .

### 3.2 Composition of LPG feed

The source of isobutene comes from the LPG stream, which is produced from the fluid catalytic cracker (FCC) (McKinsey, 2020). The LPG contains both saturated and unsaturated C<sub>4</sub> and C<sub>3</sub> hydrocarbons (Rigutto *et al*, 2017). Although the product from the FCC contains other species (such as coke, dry gas and gasoline), for the sake of simplicity the product from the FCC will be assumed to only consist of C<sub>3</sub> and C<sub>4</sub> hydrocarbons.

Table 13 indicates the relative composition of the C<sub>3</sub> and C<sub>4</sub> species in the LPG. Both Letzsch (2014) and Qiu, Lu & Li (2004) reported that the C<sub>3</sub> and C<sub>4</sub> hydrocarbons are present in a 1:1 mass ratio. Furthermore, Table 13 indicates that propane and propene are the only two C<sub>3</sub> hydrocarbons present in the LPG. The mass of propane in the C<sub>3</sub> component is 5 times more than that of the propene (Qiu *et al*, 2004).

As shown in Table 12, the mass fraction of isobutene in the C<sub>4</sub> hydrocarbons is about 20 %. Table 12 indicates various compositions of the C<sub>4</sub> hydrocarbon fraction in the LPG stream, however, the composition of the C<sub>4</sub> stream will be taken from (Menezes & Cataluna, 2008), where the C<sub>4</sub> species have the following composition:

**Table 12:** The assumed composition of the C<sub>4</sub> hydrocarbons in the LPG, as reported by (Menezes & Cataluna, 2008)

Species	Composition (mol %)
Isobutene	36.0
<i>cis</i> -2-Butene	4.6
<i>trans</i> -2-Butene	16.9
1-Butene	33.2
Isobutane	1.7
n-Butane	7.6

The composition was based on Menezes & Cataluna (2008) due to the fact that the study published by this author utilised this LPG stream for the production of ETBE. Subsequently, a more reliable conversion could be assumed for the reaction, which was mainly based on this study.

The composition of the LPG stream was calculated based on the assumption that the mass ratio of C<sub>4</sub>:C<sub>3</sub> is 1:1, as well as the composition of the C<sub>4</sub> and C<sub>3</sub> composition respectively. The LPG composition is shown in Table 13:

**Table 13:** LPG Composition

Compound	Composition (wt %)	Composition (molar %)
Propene	8.33	9.75
Propane	41.67	46.52
Isobutane	0.87	0.74
Isobutene	17.95	15.75
1-Butene	16.55	14.52
n-Butane	3.92	3.32
<i>trans</i> -2-Butene	8.42	7.39
<i>cis</i> -2-butene	2.39	2.01

The LPG feed is shown to have a large amount of C<sub>3</sub> hydrocarbons. An excessive amount of inerts into the reactor feed will result in an increase in reactor volume required. Therefore, increasing the amount of isobutene in the hydrocarbon feed into the reactor was investigated.

### 3.3 Separation train of LPG feed

As shown in Table 13, isobutene only consists of 15.75 % (mol %) of the LPG feed. It was desired to increase the concentration of isobutene in the LPG feed to the reactor. The separation of the hydrocarbons was investigated.

The C<sub>3</sub> hydrocarbons contribute 56.25 % (mol %) of the LPG feed. Therefore, separating the C<sub>3</sub> and C<sub>4</sub> hydrocarbons, to increase the composition of isobutene fed into the reactor, is justifiable. The viability of separating the components in the LPG was investigated to determine the degree to which the isobutene composition in the LPG can be increased. A separation train sequence was developed.

The vapour pressure of each component in the LPG was calculated at 40 ° C using the Antoine equation and the Antoine constants from WEBBOOK (2011). The components were arranged in order of volatility, and the relative volatility's were calculated using Equation 6

$$\alpha_{AB} = \frac{P_A^*}{P_B^*} \quad (6)$$

where  $\alpha_{AB}$  is the volatility of species A relative to species B, and  $P_A^*$  and  $P_B^*$  are the vapour pressures of species A and B respectively. The results are shown in Table 14.

**Table 14:** Vapour pressure of the LPG individual components at 40 °C, arranged in decreasing volatility.

Component	mol %	$P^*$ (kPa)	$\alpha$
Propene	9.750	1637	1.195
Propane	46.52	1370	2.591
Isobutane	0.740	529.0	1.187
Isobutene	15.75	445.8	1.017
1-Butene	14.52	438.3	1.162
n-Butane	3.320	377.3	1.026
<i>trans</i> -2-butene	7.390	367.6	1.090
<i>cis</i> -2-butene	2.010	337.3	

It is evident that separating the C<sub>3</sub> and C<sub>4</sub> hydrocarbons is the best first separation. The relative volatility,  $\alpha_{propane-isobutane}$ , is the highest relative volatility encountered which indicates that it is the easiest separation. Furthermore, separating between propane and isobutane results in near equimolar amounts in the distillate and bottoms products. Complete separation is assumed for the sake of simplicity. In reality, the simulated separation account for about 1 % of the light and heavy keys in the bottoms and distillate respectively. The distillate and bottoms compositions were calculated.

A distillation column should be designed such that the distillate temperature is at least 40 °C, so that cooling water can be used at 30 °C to allow a temperature difference of at least 10 °C. However, it should be noted that the actual  $\Delta T_{min}$  of the process is not 10 °C, as described in Section 7. To determine the minimum pressure of the column, the distillate temperature was specified as 40 °C, and the vapour pressure of each component in the distillate was calculated using the Antoine equation. Subsequently, the total pressure of the column was calculated using Raoult's law; described by Equation 7.

$$P_{tot} = \sum_{n=1}^n x_n P_n^* \quad (7)$$

where  $P_{tot}$  is the column pressure,  $x_n$  is the molar fraction of the  $n^{\text{th}}$  component, and  $P_n^*$  is the vapour pressure of the  $n^{\text{th}}$  component. For the column pressure, the  $n^{\text{th}}$  component refers to the  $n^{\text{th}}$  component in the distillate. The total column pressure was determined to be 1416 kPa. Therefore a minimum pressure of 1416 kPa should be used for column where the C<sub>3</sub>'s and C<sub>4</sub>'s are separated.

The separation of the LPG feed stream resulted in an increase of the isobutene composition from 15.75 %–36 % (mol %). However, as shown in Table 14, the relative volatilities of the C<sub>4</sub> hydrocarbons are very similar. Further separating off some of the inert C<sub>4</sub>'s would require a distillation column of many stages, or a sequence of separation where furfural is used as a mass separating agent. A separation was investigated where isobutane, isobutene and 1-butene were separated from n-Butane, *trans*-2-butene and *cis*-2-butene. The resulting column could be operated at about 500 kPa, however the simulation indicated that the column would require a minimum number of stages of 73. Extractive distillation was also simulated using furfural for this separation, however, the minimum number of stages decreased to only 43. Therefore, it was determined that it would be more economically viable to only separate the C<sub>3</sub> hydrocarbons before the reactor. The C<sub>3</sub> hydrocarbons which constitute the distillate are sold as an LPG, and a C<sub>4</sub> mixture consisting of 36 % isobutene is fed into the reactor.

Kaur & Sangal (2017) stated that at the operating conditions of the liquid phase synthesis of ETBE, 1-butane, n-butene, isobutane, *cis*-2-butene and *trans*-2-butene are inert. Therefore, the other C<sub>4</sub>'s will not react under the operating conditions. It would not be viable or economically feasible to separate the LPG feed to produce pure isobutene—maintaining inerts with isobutene is an important consideration for highly exothermic reversible reactions. Norkobilov *et al* (2017a) stated that a 94 % conversion of isobutene to ETBE can be expected when 19 % isobutene is present in the feed and a 10 % excess ethanol is fed to the reactor. Menezes & Cataluna (2008) utilised a 36 % isobutene LPG feed and achieved conversions of isobutene up to 92 %. Therefore, it is assumed that maintaining a concentration of 36 % (mol) in the LPG feed will not hinder the rate of the reaction.

Only one distillation column will be implemented before the reactor. The column will operate at 1.5 MPa as this will increase the temperature of the distillate to slightly more than 40 °C. Furthermore, the reactor will be maintained at 1.5 MPa. The bottoms product from the column therefore does not need to undergo another increase in pressure to be fed into the reactor.

### 3.4 Reaction pathway

As detailed in Section 2, the production of ETBE can follow two major reaction pathways: the reaction of ethanol with isobutene (IB) or the reaction of ethanol with tert-butyl alcohol (TBA) both in the presence of a catalyst (Yee *et al*, 2013). Both bioethanol and a petroleum based LPG constitute the reactants available for the synthesis of ETBE. The petroleum based LPG is comprised of C<sub>3</sub> and C<sub>4</sub> hydrocarbons, where isobutene is one of the components. Therefore, the major synthesis of ETBE will be produced from bioethanol and isobutene, as described in Equation 1.

The isobutene feed is sourced from a petroleum based LPG that is referred to as an FCC cut (Ravishankar *et al*, 2018). The composition of this FCC cut is provided in Table 13. It was decided to separate this cut prior to feeding it to the reactor. This selection was made to increase the amount of valuable reactant (isobutene) as well as eliminate potential undesired reactions between bioethanol and C<sub>3</sub> hydrocarbons (Sneesby *et al*, 1997a). However, the feed is not high purity isobutene. Due to the reaction being highly exothermic, inert species, in the form of C<sub>4</sub>'s, are used to absorb unwanted energy produced by the reaction (Degirmenci *et al*, 2009b). Thus, satisfying another design heuristic which declares that inert species should not be removed before the reactor if the reaction is highly exothermic (Seider, Seader & Lewin, 2009). Hence, the inert species additionally aid in preventing the formation of reactor hot spots. Additionally, separating the C<sub>3</sub>'s from the feed is achieved through cost effective and economic ordinary distillation. The decision to increase the isobutene fraction in the reactor feed has been elaborated on in Section 3.3.

Bioethanol is reacted in excess to satisfy a common design heuristic which declares that the valuable reactant (isobutene) should be completely consumed by using the other reactant (ethanol) in excess (Seider *et al*, 2009). In doing this, the valuable reactant, isobutene, is then the limiting reagent, reducing the amount of isobutene that is wasted or unreacted. However, feeding bioethanol in excess runs on a trade off: the bioethanol being fed in excess may promote the production of unwanted byproducts (Yee *et al*, 2013) through side reactions under specific temperatures and pressures as detailed in Section 2. Furthermore, excess ethanol hinders the kinetics by reducing the rate of reaction (Yee *et al*, 2013). However, although the catalytic adsorption kinetics are slowed by excess ethanol, the conversion of isobutene increases with an increase in ethanol excess (Menezes & Cataluna, 2008). For this reason, careful attention had to be given when selecting reaction temperature and pressure.

The bioethanol that is fed is not anhydrous. Although various studies have been conducted where anhydrous ethanol is used for ETBE synthesis, for large scale industry this was determined to be impractical. Ethanol is hygroscopic implying that even the storage

of anhydrous ethanol would result in the absorption of water (Kiss & Ignat, 2012). If ethanol is fed with a composition of water of more than 1 %, the hydration of isobutene should be considered (Kiss & Ignat, 2012; Umar, Saleemi, *et al*, 2008). To maintain anhydrous ethanol before it is fed into the reactor, the stored ethanol would have to be pre-treated using molecular sieves or distillation to maintain a very low water content (Patil, 2016). Consequently, 95 % bioethanol was utilised as the feed, which is also less expensive than purchasing anhydrous ethanol.

### 3.5 Phase of reaction

The reaction between isobutene and bioethanol can occur in either the gas or liquid phase (Larsen *et al*, 1995a). For the purpose of design the liquid reaction is selected. The liquid phase reaction is preferred based on the commonly cited design heuristic which states that it is easier to pump a liquid than it is to compress a gas (Seider *et al*, 2009). Additionally, liquids are safer to handle than gasses (Seider *et al*, 2009). The LPG feed is stored at high pressure in the liquid phase. Therefore, various stages of compression and expansion would have to be utilised to cycle between the liquid and gas phase of the light hydrocarbons.

Furthermore, the use of the liquid phase, also satisfies another design heuristic which states that raw materials should be selected such that the storage of hazardous materials is avoided (Seider *et al*, 2009); this heuristic applies as the storage of these compounds in the vapour phase is an explosive threat due to their high flammability and tendency to explode under pressure and at high temperatures.

The choice for liquid phase is further emphasised by the fact that gas phase reactions are carried out at high temperatures (Larsen *et al*, 1995a). At high temperatures, specifically temperatures above 95°C, the dehydration of ethanol occurs and this implies an increase in water content in the reaction (Collignon & Poncelet, 2001). The presence of excess water hinders the performance of reaction catalysts selected (Degirmenci *et al*, 2009b). Production of ETBE is strongly dependent on the performance of the catalyst (Degirmenci *et al*, 2009b). Additionally, liquid phase reaction eliminates complications (i.e control and manipulation) (Zhang *et al*, 1997) and allows for a simple conversion reactor to be designed for implementation. The reaction conditions were carefully studied with guidance from literature. In the liquid phase, the ether system is non-ideal (Jensen & Datta, 1995). Therefore, the UNIFAC model was used for the modelling of the thermodynamics (Jensen & Datta, 1995).

### 3.6 Operating conditions

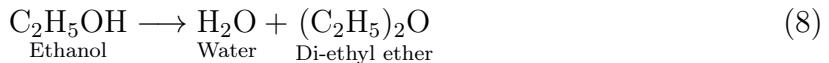
As described in Section 2, temperatures above 80 °C result in the favouring of the reverse reaction due to the fact that ETBE synthesis is a reversible exothermic reaction (Sneesby *et al*, 1997b). Reactor hot spots may provide a platform to support unwanted side reactions (BL Yang *et al*, 2000), which produce water as a product and thus influence the overall yield and reaction to produce ETBE as well as influence reaction kinetics (Fran oisse & Thyrian, 1991). Therefore, to avoid reactor hot spots, reactor and reaction conditions need to be selected to ensure hot spot formation is negligible, additionally feeding inerts into the reactor may help re-mediate these effects (Larsen *et al*, 1995a).

Menezes & Cataluna (2008) showed that the maximum conversion of isobutene with anhydrous ethanol was achieved between 59 °C–63 °C. At these temperatures, the conversion of isobutene achieved varied between 88–92 % depending on the amount of ethanol in excess (Menezes & Cataluna, 2008). Consequently, an operating temperature of 62 °C was chosen and the assumed overall conversion of isobutene will be taken as 89 %. Maintaining a lower temperature of 62 °C also prevents unwanted side reactions from occurring, as discussed in Section 3.7.

High pressures are employed to maintain a liquid phase in the reactor. Pressures of 0.6 MPa–2.0 MPa are usually utilised to ensure the light hydrocarbons remain in the liquid phase (Yu-Chu & Tade, 2000; Norkobilov *et al*, 2017a; Menezes & Cataluna, 2008). Thus, the pressure of the reactor depends on the composition of the reactor feed. The C<sub>3</sub> hydrocarbons are separated from the C<sub>4</sub>'s before the reactor (see Section 3.3). The pressure required to maintain the light C<sub>4</sub>'s in the liquid phase at 62°C was calculated to be about 700 kPa. However, at this pressure the hydrocarbons are close to their bubble point. If the isothermal reactor is not maintained at exactly 62 °C at 700 kPa, and if the temperature were to increase then the hydrocarbons would vaporise which has severe implications on the reactor kinetics, safety and conversion (Yu-Chu & Tade, 2000). Therefore, a safety factor was incorporated to ensure that the hydrocarbons would be maintained in the liquid phase if the reactor temperature had to increase. Utilising an operating pressure of 1.5 MPa ensures that the LPG remains in the liquid phase even if the reactor temperature had to increase to 95 °C.

### 3.7 Side reactions

As discussed in Section 2, the main side reactions that can occur are the hydration of isobutene (Equation 5), the dimerisation of isobutene (Equation 4), and the dehydration of ethanol to form di-ethyl ether (Equation 8).



The dimerisation of isobutene has been found by Cunill *et al*, 1993 to only occur at higher temperatures (70 °C and above) and where isobutene is in excess. Using an excess of at least 4 % ethanol prevents the formation of di-isobutene (Sneesby *et al*, 1997a; Domingues, Pinheiro & Oliveira, 2017). Other research also supports these findings. The rates of the reaction of the dimerisation of isobutene, as well as the formation of diethyl ether have been shown to increase with temperature (Jayadeokar & Sharma, 1992). In low temperature ranges, from 30 °C to 60 °C, the dimerisation of the isobutene and the dehydration of ethanol have been found to be hindered completely (Jayadeokar & Sharma, 1992).

Consequently, around 10 % excess ethanol will be fed into the reactor, with about 5 % (wt %) water in the aqueous ethanol. As a result, the formation of DIB and DEE will be avoided.

The hydration of isobutene to form TBA can be prohibited by using ethanol with 0.5 % water or less (Bisowarno *et al*, 2004). However, as already discussed, it would be unrealistic to assume there is a negligible amount of water in the system. Consequently, the formation of TBA will be considered. Although water is known to have an inhibitory effect on the ion-exchange catalyst, the equilibrium reaction of TBA formation is more rapid than the reaction between isobutene and ethanol to form ETBE (Cunill *et al*, 1993). Subsequently, water is rapidly converted to TBA which reduces the effect on the catalyst (Cunill *et al*, 1993). Thus, it will be assumed that the small fraction of water in the bioethanol feed will not have a profound impact on the performance of the catalyst.

### 3.8 Selectivity of ETBE and conversions

The selectivity of the ETBE and TBA reactions were found to vary linearly with the initial concentration of water in the ethanol feed (Cunill *et al*, 1993). The selectivity of ETBE at equilibrium was found to be about 88 % where 5 % (wt %) water was present in the ethanol feed. Due to the fact that 10 % excess ethanol will be used, a more conservative selectivity of 85 % will be assumed. the overall conversion of isobutene is assumed to be 88 %, the selectivity of ETBE to TBA is 85 %, and 10 % excess ethanol in the reactor is fed where there is 5 % water in the ethanol. Using these parameters, the conversion of isobutene for Reaction 1 is about 75 %, and the conversion of water to form TBA in Reaction 5 is 94 %. This yields a selectivity of ETBE of 85 %. These

results were validated by the simulation, as shown in Section 6.

### 3.9 Simulation of the first reactor

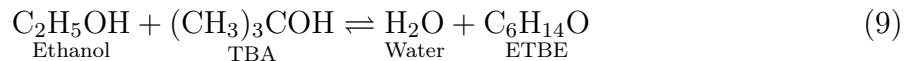
The mass balance, yields and conversions are investigated in more detail in Section 6. The inlet into the first reactor consists of about 27 % (mol %) ethanol, 24.5 % IB, 3.6 % water and the balance hydrocarbons. Based on the selectivity and conversion specified, the outlet of the reactor is composed of about 0.3 % (mol %) water, 11 % ethanol, 4.4 % TBA, 23.6 % ETBE and the balance hydrocarbons.

The hydrocarbons were separated from the reactor product, as discussed in Section 3.12. The polar mixture consisting of ethanol, ETBE, TBA and water was separated, and the side product TBA was then utilised in another reactor to produce ETBE. The entire separation train is discussed in Section 3.12, however, the utilisation of TBA to increase ETBE production is discussed below.

### 3.10 ETBE formation with TBA

Most studies regarding the liquid phase synthesis of ETBE are generally focused on the reaction between isobutene and ethanol (BL Yang *et al*, 2000). However, ETBE can also be synthesised from a reversible and exothermic reaction between TBA and ethanol (Ozbay & Oktar, 2009).

As discussed in Section 3.4, the hydration of isobutene results in the formation of TBA. Ethanol is also fed in an excess of 10 % into the first reactor. Therefore, there will be a considerable amount of TBA and ETBE in the reactor product that can be utilised to maximise the production of TBA. A second reactor has been included in the separation train (see Section 3.12) to produce ETBE from TBA and ethanol. The reaction between TBA and ethanol is shown in Equation 9:



The literature has found that the dehydration of TBA to IB and water may occur as a side reaction:



The IB production from the side-reaction shown in Equation 10 can also react with ethanol to produce ETBE, which is the standard reaction described in Equation 1. This is an indirect synthesis of ETBE (Umar, Patel & Saha, 2009). However, BL Yang *et al* (2000) and Umar, Patel, *et al* (2009) have described that at atmospheric pressure, there were undetectable concentrations of isobutene throughout the liquid phase solution.

The liquid phase synthesis of ETBE from ethanol and TBA is carried out at atmospheric pressure (Ozbay & Oktar, 2009). Ozbay & Oktar (2009) investigated the reaction at various temperatures, and molar ratios of TBA and ethanol. Equation 9 is an equilibrium reaction where water is a product. Accordingly, water should not be allowed to accumulate in the system where it is fed into the reactor. Feeding accumulated water into the reactor would cause the equilibrium reaction to favour the reverse reaction and may also have inhibitory effects on the activity of the catalyst. Therefore, water will be separated from the product stream, as discussed in Section 3.12.

Ozbay & Oktar (2009) found that at a 2:1 molar ratio of ethanol:TBA, the equilibrium conversion of TBA to ETBE was about 84 %. An increase in ethanol concentration was also shown to increase the equilibrium conversion. At a molar ration of 10:1 of ethanol to TBA, the equilibrium conversion increased to about 97 % (Ozbay & Oktar, 2009). For the separation train designed in Section 3.12, the ratio of ethanol:TBA will change slightly depending on the steady state of the separation train. However, it is expected that at least a 2:1 ratio of ethanol to TBA will be encountered in the reactor as the bottoms product of T-104 (refer to Section 3.12). If the ratio of ethanol:TBA increases during the transient response of the system, this would results in a higher conversion of TBA. Therefore, a 2:1 mole ratio is a safe assumption for the determination of the TBA conversion. However, there will be some water fed into the reactor due to the difficult separation of water from TBA and ethanol. Furthermore, reactors are not usually operated to achieve equilibrium conversions, as there is a trade-off between the maximum conversion that can be achieved, as well as the size of the reactor required to achieve an equilibrium conversion of TBA. Therefore, a more conservative conversion of 74 % will be assumed for Equation 9.

The selectivity of ETBE was described by Equation 11 (Umar, Patel, *et al*, 2009):

$$\% \text{ ETBE selectivity} = \frac{C_{ETBE,t}}{C_{TBA,0} - C_{TBA,t}} \quad (11)$$

Where  $C_{ETBE,t}$  and  $C_{TBA,t}$  are the concentrations of ETBE and TBA at time  $t$  respectively, and  $C_{TBA,0}$  is the initial concnetration of TBA. The selectivity of ETBE at atmospheric conditions was found to be is around 90 % (Umar, Patel, *et al*, 2009). Due to the definition of ETBE selectivity, as well as the fact that ETBE and water form in a

1:1 mole ratio, it will be assumed that only Equation 9 occurs. This can be validated by the fact that negligible amounts of IB were detected in the reactor (BL Yang *et al*, 2000; Umar, Patel, *et al*, 2009). In reality, there would be slightly more water formed during the TBA and Ethanol reaction due to the side-reactions, however, for the purposes of simulation, only Equation 9 will be considered for this reactor.

The formation of ETBE from TBA and ethanol is also an equilibrium exothermic reaction (Umar, Saleemi, *et al*, 2008; Umar, Patel, *et al*, 2009). Umar, Patel, *et al* (2009) found that the operating temperature of 343 K achieved the highest conversion of TBA. Consequently, this temperature will be maintained in an isothermal reactor to prevent the inhibition of the exothermic reaction. Umar, Patel, *et al* (2009) observed that A-15 and A-35 were not advantageous for maximising the selectivity of ETBE. BL Yang *et al* (2000) showed that the selectivity of ETBE decreased with an increase in temperature, whereas the rate of the reaction of TBA dehydration increased. The catalyst S-54 showed to obtain the highest selectivity of ETBE compared to A-15 and D-72 BL Yang *et al* (2000). S-54 also showed to have the lowest inhibition by water BL Yang *et al* (2000). Thus, the catalyst S-54 will be used in for the TBA reaction.

### 3.11 Separation techniques

According to a known design heuristic, liquid mixtures should be separated by either distillation, stripping, LLE, crystallisation and or adsorption (Seider *et al*, 2009). Furthermore, another heuristic states that if any streams are vapours they should be condensed with cooling water and then separated using any of the above-mentioned methods (Seider *et al*, 2009). If this is not achievable, the vapor mixtures should be separated by partial condensation, cryogenic distillation, adsorption, absorption and membrane separation (Seider *et al*, 2009).

The initial separation of the reactor outlet C<sub>4</sub> mixture from the ethanol and ETBE can easily be achieved using ordinary distillation - the ease of separation index for this initial separation supports selection of ordinary distillation (Sneesby *et al*, 1997a). This valuable pure C<sub>4</sub> mixture can then be recycled to the reactor feed. While the separation of the azeotropic ETBE and ethanol mixture will be separated using pressure swing distillation (Sneesby *et al*, 1997a).

Based on the chosen desired conversion, and the related process conditions, the product formed can be manipulated such that a pure ETBE product and pure ethanol for recycle are formed along with an azeotropic mixture of ethanol and ETBE- which can be sold off as a product in its own (Menezes & Cataluna, 2008). There is a trade-off between a

higher conversion (which results in more of the ETBE that is produced being trapped in an azeotrope with ethanol) versus a lower conversion which produces some pure ETBE and ethanol (for recycle) along with an azeotropic mixture of the two (Menezes & Cataluna, 2008). Menezes & Cataluna, 2008 suggests maximising the conversion and eradicating the recycle of unreacted ethanol (as it is trapped in the purely azeotropic mixture product) as this product can readily be added to gasoline mixtures as is. Furthermore, Menezes & Cataluna, 2008 suggests this method of ETBE synthesis results in lower synthesis expense.

The ETBE and ethanol azeotropic mixture possibilities are detailed in Section 2.3.5. Pressure swing was preferred to LLE as a result of pressure swing being a cheaper alternative (Menezes & Cataluna, 2008). Additionally, the complications regarding solvent addition are also eliminated (Menezes & Cataluna, 2008). For example, choosing water as an LLE solvent for the separation of ETBE and ethanol, implies pure ETBE product production. However, ethanol and water form an azeotrope. Since the ethanol feed is pure ethanol separation of the water and ethanol azeotrope will need to be achieved. This implies further energy costs, as this separation cannot be achieved through ordinary distillation (Yee *et al*, 2013).

## 3.12 Separation of reactor product

### 3.12.1 Separation of hydrocarbons from polar compounds

The first reactor is maintained at 1.5 MPa, where the production of ETBE as well as TBA (the side product) occurs. The product has a mixture of C<sub>4</sub> hydrocarbons, a trace amount of C<sub>3</sub> hydrocarbons, and a mixture of ETBE, ethanol, water and TBA. The reactor product is composed of about 61 % hydrocarbons. The composition, as well as the relative volatility of the product is shown in Table 15, arranged in decreasing order of relative volatility—calculated at 40 °C:

**Table 15:** Composition and relative volatility calculated at 40 °C, arranged in decreasing volatility

Component	mol %	$\alpha$
C <sub>3</sub> trace	0.94	-
Isobutane	1.41	1.190
Isobutene	3.49	1.020
1-Butene	28.85	1.16
n-Butene	6.83	1.03
<i>trans</i> -2-Butene	15.21	1.09
<i>cis</i> -2-Butene	4.15	20.06
Ethanol	10.92	1.110
ETBE	23.56	1.100
TBA	4.36	1.850
Water	0.280	

In order to produce pure ETBE, the hydrocarbons were first separated from the polar mixture. It is evident that separating the C<sub>4</sub> hydrocarbons from ETBE and ethanol is an easy separation due to the high relative volatility of *cis*-2-Butene and ethanol. Thus, the C<sub>4</sub> stream is separated off in the distillate and the bottoms product consists of mainly ETBE, ethanol, TBA and water — with traces of hydrocarbons. The optimal method of producing pure ethanol was considered.

The first distillation column out of the reactor was not maintained at the reactor pressure of 1.5 MPa. At very high pressures (about 1.2 MPa and above), azeotropes exist between ethanol and some of the C<sub>4</sub> hydrocarbons, as shown in Table 11 (Sneesby *et al*, 1997a). It would be viable to decrease the operating pressure of the column to atmospheric pressure to allow the easy separation of the light hydrocarbons from the polar mixture. However, the pressure would have to then be increased to produce pure ETBE due to the location of the polar mixture on the residue curve of ETBE, ethanol and TBA. Frequently alternating pressures is not desired as it would require multiple pumps and valves which is an unnecessary sink of energy.

Consequently, the first distillation column where the C<sub>4</sub>'s are removed was chosen to be held at a pressure of 1 MPa. This pressure ensures that no azeotropes between ethanol and the hydrocarbons are formed, and the proceeding column can also be maintained at 1 MPa for the optimal pressure swing distillation to produce ETBE. The column pressure of 1 MPa also results in a distillate temperature much higher than 40 °C which allows cooling water at 30 °C to be used for the condenser.

### 3.12.2 Pressure swing distillation for ETBE purification

The bottoms product of the distillation column is a mixture of ethanol, ETBE, TBA and water, where water is present in small amounts. Although this process of separation involves four components, one of the components is present in small amounts in the feed into each distillation column, and hence does not drastically affect the azeotropes between the other three major components. Consequently, for illustrative purposes, the pressure swing distillation was shown for ternary mixtures, where the component in the smallest amount was neglected. Pressure swing distillation was conducted where columns were specified to have a pressure of either 1000 kPa or 101 kPa. The azeotropic composition of ethanol and ETBE at these pressures were calculated using DWSim with the UNIFAC model as shown in Table 16:

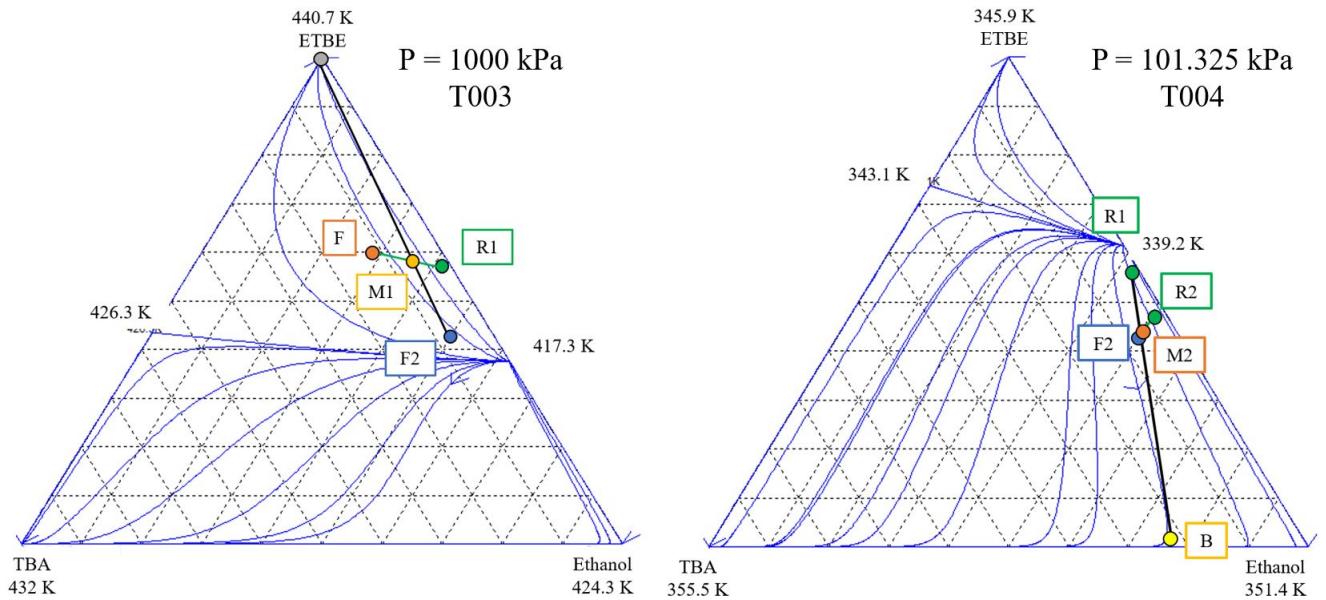
**Table 16:** Azeotropic composition of ETBE-Ethanol at 1 MPa and 101 kPa, as determined using DWSim with the UNIFAC thermodynamic package.

Pressure	ETBE mole %
1 MPa	38
101 kPa	61

The difference in ETBE composition at 1 MPa and 101 kPa is about 23 %. Therefore, utilising a high pressure column far below 1 MPa would decrease the difference between these azeotropes which increases the difficulty of separation. Consequently, it was decided that utilising 1000 kPa and 101 kPa was optimal for efficient pressure swing distillation.

The ternary mixture of ETBE, ethanol and water coming out as the bottoms (F) of the first distillation column (T-102), where the hydrocarbons were separated, has a composition that allows for the production of pure ETBE at 1 MPa, as shown in Figure 4. Pure ETBE (99 mol %) was produced at this 1 MPa column (T-103). An azeotropic mixture

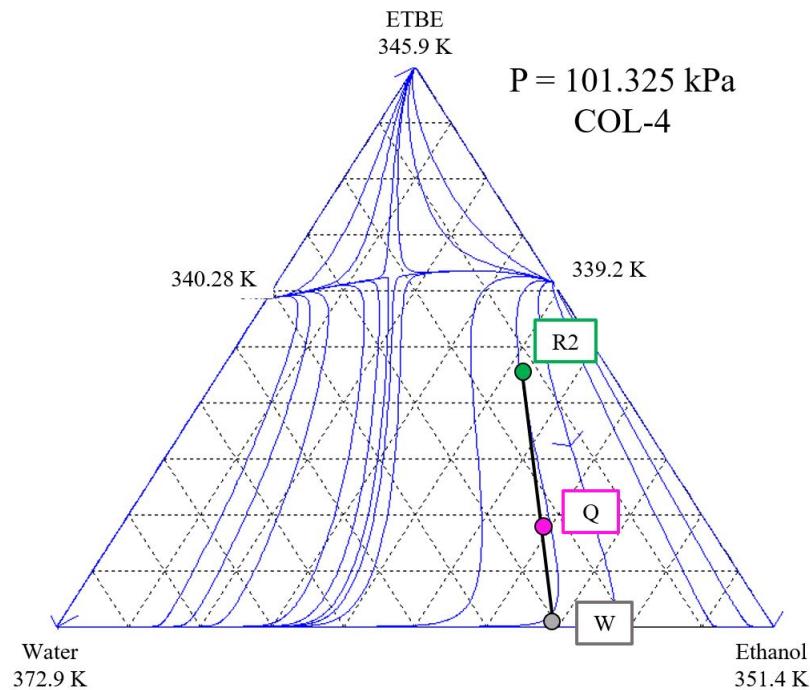
is then produced as a distillate (F2) which is then fed into another distillation column at 101 kPa (T-104). This mixture was then distilled to produce another azeotropic mixture of ETBE and ethanol (R1), and an ethanol, TBA and water mixture as the bottoms product (B). R1 was then recycled back into T-103 that operates at 1 MPa. Azeotropic mixtures of ETBE and ethanol were recycled to maximise the yield of ETBE. The first 2 separations are shown in Figure 4



**Figure 4:** Residue curve of ETBE, ethanol and TBA at 1000 kPa and 101.325 kPa.

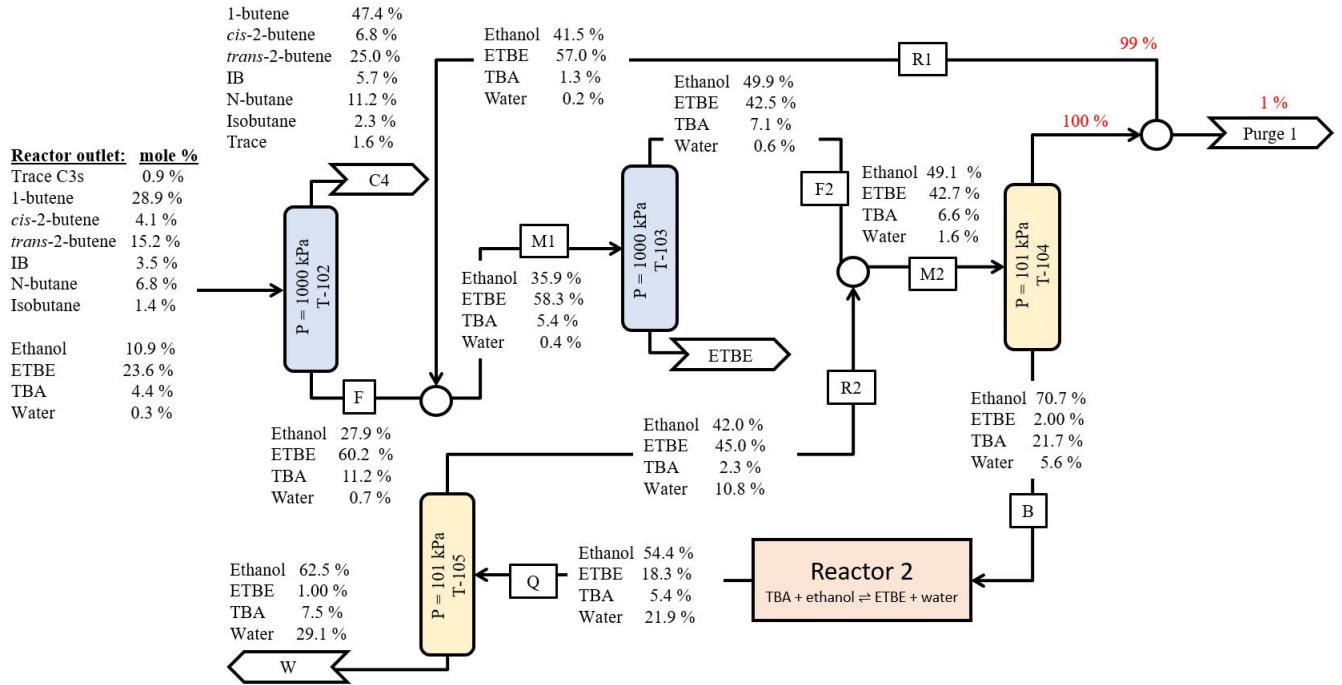
As discussed in Section 3.10, TBA and ethanol were fed into another reactor to produce ETBE and ethanol at atmospheric pressure. The mixture (M2) going into the atmospheric distillation (T-103) column could have been specified to produce pure TBA, and then another distillation could have been performed to produce pure ethanol. However, it is intended to mix ethanol and TBA to feed into another reactor. Therefore, the distillation column was specified to produce a TBA and ethanol mixture (B) that could be fed directly into the reactor which eliminates the unnecessary purification of TBA and ethanol respectively. Furthermore, the excess ethanol produced in the bottoms product (B) is inconsequential. It has been shown that the conversion of TBA increases with an increase in ethanol concentration in the feed (Ozbay & Oktar, 2009). A conservative conversion of TBA to ETBE (75 %) was assumed to account for variations in the ethanol:TBA molar ratio in the feed. As already discussed, the catalyst S-54 will be used for this reaction as it is much less susceptible to the inhibitory effect of water on the catalyst activity when compared to Amberlyst-15 (BL Yang *et al*, 2000). However, the presence of water will result in a shift of the equilibrium of the reaction towards the reverse reaction. For these reasons, the lower conversion of TBA to ETBE was assumed.

The TBA and ethanol mixture (which has about 22 % water) is fed into a secondary reactor. TBA and ethanol react to produce ETBE and water. The product of this reactor (Q) consists of mainly water, ethanol and ETBE, where this ternary residue curve was plotted. A near-complete recovery of ETBE was desired so that an ETBE mixture could then be recycled back into the atmospheric column (T-104). Accordingly, the reactor product (Q) was separated in T-105 to produce an azeotropic mixture (R2) and a bottoms product consisting of ethanol, water and TBA (W). This separation is shown in Figure 5:



**Figure 5:** Residue curve of ETBE, ethanol and water at 101.325 kPa.

A simplified diagram of the separation train is shown in Figure 6. Please note, the compositions shown in Figure 6 were normalised for illustrative purposes so that the composition of the ternary polar mixtures could be analysed.



**Figure 6:** Separation train considering the recycle of the TBA and ethanol reaction products.

The bottoms product of T-105 contains a lot of ethanol that could be utilised as a recycle into the first reactor (where isobutene is reacted with ethanol to form ETBE). However, issues with simulating this recycle arose. Ideally, the ethanol must be utilised to reduce the running costs of operation. This consideration is more thoroughly discussed in Section 4. However, for the sake of completion, the bottoms product (W) is assumed to be sold as a low cost aqueous ethanol mixture.

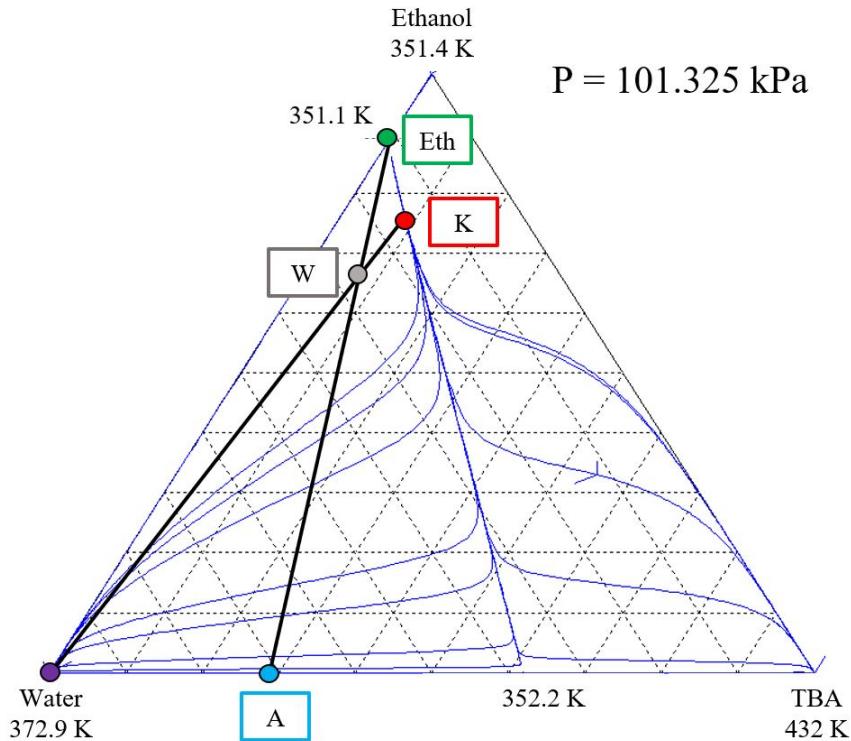
## 4 Remarks & recommendations

### 4.1 Remarks on process creation

The process designed in Section 3 allowed for a high yield of ETBE, which is outlined in more detail in Section 6. The target ETBE production stated in Section 3.1 was achieved. A pure ETBE product (99 % (mol %)) was produced at a rate of 38.31 ton h<sup>-1</sup>. The purge stream introduced into the separation train was only 1 %, as shown in Figure 6. The purge was introduced for control purposes. the hydrocarbons are separated in the first column after the reactor, however, trace amounts remain in the bottoms product. The purge serves to prevent an excessive buildup of hydrocarbons in the separation train. The azeotropic mixtures were recycled back into T-103 and T-104, which increased the ETBE

yield considerably. Pressure swing distillation is advantageous for maximising the ETBE yield from these azeotropes.

However, the main shortfall of the design is the fact that the ethanol mixture (W) was not recycled. The ethanol mixture which constitutes the bottoms of T-105 has about 62.5 % (mol %) ethanol, 7.45 % TBA and the balance water. Ideally, the majority of the water would be separated from this mixture so that a high quality ethanol mixture can be fed back into the primary reactor to reduce the running cost of ethanol. In order to separate the excess water in this mixture, the following separation would have been performed following T-105:



**Figure 7:** Residue curve of ethanol, TBA and water at 101.325 kPa.

Initially, the separation was intended to produce 88 % ethanol and 12 % water as a distillate (Eth), and a water/TBA mixture as the bottoms (A). The distillate (Eth) could then be directly fed back into the first reactor as a recycle. However, this separation was found not to be possible in DWSim. The azeotrope between ethanol and water has a very similar boiling point to that of TBA and water. Therefore, TBA could not be excluded from the distillate, and it would only be possible to produce pure water as a bottoms product and an ethanol, water and TBA mixture as the distillate (K).

This distillate could then be recycled into the primary reactor, where the mixture contains about 76 % ethanol (K). However, the presence of water could cause inhibitory effects on

the Amberlyst-15 catalyst, and the presence of TBA could result in the favouring of the reverse reaction. Therefore, it was decided that the bottoms product (W) could be sold off as a low cost fuel as the ethanol can be used for a source of hot utility.

It should be noted that this simulation was performed in DWSim where the 76 % ethanol (K) was recycled into the primary reactor. However, this recycle would only work where ChemSep columns were used. The simulation programme would not allow this recycle to execute. A recent update did fix this issue, however other issues with the simulation programme arose. Although the authors realise that recycling the ethanol is the most economical option for waste-reduction, this separation could not be performed. It was decided that selling this ethanol mixture as a low cost fuel was an adequate alternative.

## 4.2 Recommendations

### 4.2.1 Production of isobutene from C<sub>4</sub> hydrocarbons

In order to prioritise waste reduction, certain compounds produced throughout the ETBE synthesis process can be further reacted into more useful products. The utilisation of the C<sub>4</sub> hydrocarbons for isobutene production was not implemented in this design, however, can be investigated. A proposed synthesis is that of isobutene from 1-butene (Traiprasertpong & Svang-Ariyaskul, 2012); the isobutene produced can then be recycled to the primary reactor to react with ethanol and form ETBE (Traiprasertpong & Svang-Ariyaskul, 2012). This is an isomerisation reaction (Traiprasertpong & Svang-Ariyaskul, 2012) and is shown in Equation 12.



Traiprasertpong & Svang-Ariyaskul, 2012 suggests the use of fluroinated  $\eta$ -alumina catalyst for this reaction; while SM Yang *et al*, 1999 studied the gas-phase conversion of 1-butene to isobutene over silicoaluminate zeolite catalysts (ZSM-22 and ferrierite) and aluminophosphate molecular sieves (SAPO-11 and MeAPO-11).

The activity of the catalyst, SAPO-11, improves with an increasing temperature (SM Yang *et al*, 1999), but isobutene has improved thermodynamic stability at lower temperatures (SM Yang *et al*, 1999) and so the best temperature to consider is 300 °C (SM Yang *et al*, 1999). Another factor to consider is preventing prolonged contact times as this will lend to the formation of unwanted hydrocarbons (SM Yang *et al*, 1999).

#### 4.2.2 Utilisation of C<sub>4</sub> waste stream

The C<sub>4</sub> distillate product from T-102 has a composition similar to that of the product known as C<sub>4</sub> raffinate II from the FCC process in an ordinary oil refinery (Schulze & Homann, 1989). This distillation stream was sold as raffinate II, as discussed in Section 9. The raffinate product can be fed to an alkylation unit where isobutane and light olefins (mainly the butenes) are converted to high octane petroleum components (Edwards, Stanley & Shreehan, 1998). According to an article published by Shell Chemicals, 2017, this raffinate stream is often used as a chemical building block for the manufacturing of 2-butanol and methyl ethyl ketone (MEK), which are intermediates in the production of industrial cleaning compounds, coatings, inks, oil treating chemicals, and many more. Due to this raffinate stream being dependent on the composition of the crude oil feedstock of a refinery, this crude raffinate stream does not have a set composition. The composition of the distillate stream is compared to the composition of raffinate II streams from different sources as shown in Table 17. From this table it is clear that the composition of the raffinate II stream from refineries vary. It is, therefore, assumed that the distillate stream from T002 can be sold as a by-product due to its composition which closely resembles that of a raffinate II stream.

**Table 17:** Comparison of the compositions of the C<sub>4</sub> distillate stream and raffinate II streams from different sources

Component	T002 distillate composition (%)	Raffinate II composition (%)		
		Edwards <sup>a</sup>	LG Petrochem <sup>b</sup>	HIP-Petrohemija <sup>c</sup>
1-Butene	47.5	45.0 – 60.0	48.6	49.1 – 56.2
2-Butene	31.9	18.0 – 42.0	20.0	23.3 – 35.4
n-Butane	10.9	7.00 – 20.0	22.8	4.10 – 9.40
Isobutane	2.30	0.00– 7.00	7.60	4.40 – 7.80
Isobutene	5.80	0.10	-	1.40 – 2.90

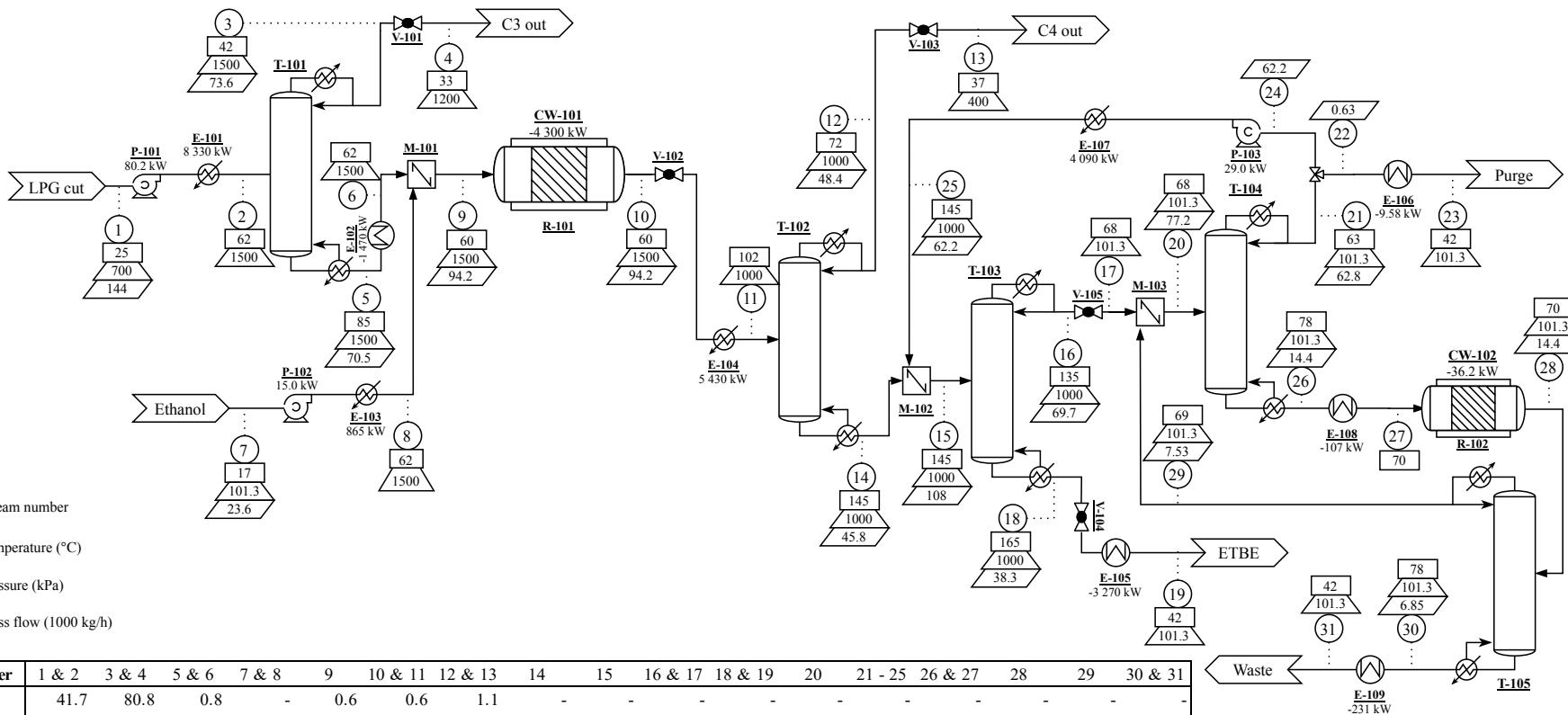
a Edwards, Stanley & Shreehan (1998)

b LG Petrochemical Co. Ltd. (1996)

c HIP-Petrohemija (2015)

## 5 Process Flow Diagram

The process flow diagram for the final design is given in Figure 1 below:



Stream number	1 & 2	3 & 4	5 & 6	7 & 8	9	10 & 11	12 & 13	14	15	16 & 17	18 & 19	20	21 - 25	26 & 27	28	29	30 & 31
Components mass fraction (%)																	
Propane	41.7	80.8	0.8	-	0.6	0.6	1.1	-	-	-	-	-	-	-	-	-	-
Propylene	8.3	16.3	Trace	-	Trace	Trace	Trace	-	-	-	-	-	-	-	-	-	-
1-Butene	16.5	1.3	32.5	-	24.3	24.3	47.3	-	Trace	Trace	-	Trace	Trace	-	-	-	-
2-Butene	10.7	Trace	21.8	-	16.3	16.3	31.7	-	0.5	0.7	-	0.7	1.1	-	-	-	-
Isobutene	17.9	1.3	35.3	-	26.5	2.9	5.7	-	-	-	-	-	Trace	-	-	-	-
n-Butane	3.9	Trace	8.0	-	6.0	6.0	11.6	-	Trace	Trace	-	Trace	0.1	-	-	-	-
Isobutane	0.9	Trace	1.6	-	1.2	1.2	2.4	-	-	-	-	-	-	-	-	-	-
ETBE	-	-	-	-	-	36.1	-	74.3	73.9	60.0	99.3	60.6	56.2	4.0	36.1	66.7	2.5
Ethanol	-	-	-	95.0	23.9	7.6	-	15.5	20.5	31.8	Trace	31.4	41.0	63.0	48.5	28.1	70.9
TBA	-	-	-	-	-	4.9	-	10.0	4.9	7.2	Trace	6.8	1.3	31.1	7.8	2.4	13.6
Water	-	-	-	5.0	1.3	Trace	-	0.2	Trace	0.1	-	0.4	0.2	2.0	7.6	2.8	12.9

**Figure 8:** Process flow diagram (PFD) for the production of ETBE

# 6 Mass and Energy Balances

## 6.1 Columns

The mass balances surrounding the columns were checked to ensure the reliability of the separation processes. Although mass balance can be done for every compound involved in the separation as no reactions occur in the distillation, only the overall mass balance for the columns are shown. The component balances exhibited very similar degrees of inaccuracy as the overall mass balance. Therefore, it is unnecessary to investigate every component. The mass balance for a column is described by Equation 13.

$$F = D + B \quad (13)$$

where F, D and B are the molar flow rates of the feed, distillate and bottoms respectively in  $\text{kmol h}^{-1}$ . The error for each column was calculated using Equation 14:

$$\% \text{ Error columns} = \frac{F - (D + B)}{F} \quad (14)$$

The results are shown in Table 18:

**Table 18:** Mass balance over the columns

Column	F	D	B	Error
	( $\text{kmol h}^{-1}$ )	( $\text{kmol h}^{-1}$ )	( $\text{kmol h}^{-1}$ )	%
T-101	144 175	73 641	70 535	-0.0008
T-102	94 180	48 372	45 804	0.0039
T-103	105 746	67 697	38 053	-0.0036
T-104	75 210	60 915	14 302	-0.008
T-105	14 302	7 544	6 758	-0.0044

As shown, the mass balance around each column is accurate due to the small errors. However, the errors are negative which implies that mass has been created. In reality,

mass would be lost throughout the process. Mass would not be created but rather lost in practical operation. However, the negative error is due to the discrepancy of the simulation.

## 6.2 Reactors

### 6.2.1 R-101

The mass balance over the reactor was investigated and was found to hold a negligible error. However, the conversion over the reactors is more valuable to investigate the yield of ETBE achieved, as well as the selectivity of the reactions involved. For the first reactor, isobutene is the limiting reagent for Reaction 1, and water is the limiting reagent for Reaction 5, as shown in Table 19:

**Table 19:** Reactor 1

Component	Moles in (kmol h <sup>-1</sup> )	Moles out (kmol h <sup>-1</sup> )	Conversion %
Inerts	812	812	
IB	444	49.41	88.9 %
ETBE	0	333	
Ethanol	488	154	68.3 %
TBA	0	61.7	
Water	65.6	3.9	94 %

The total isobutene conversion is shown to be 88 %. However, the conversion of IB in the reaction where ETBE is produced is calculated by Equation 15

$$x_{IB\ main} = \frac{ETBE\ out}{IB\ in} = 75\% \quad (15)$$

The conversion of IB for the hydration of IB to TBA is calculated by Equation 16

$$x_{IB \text{ side}} = \frac{TBA \text{ out}}{IB \text{ in}} = 13.88 \% \quad (16)$$

Finally, the selectivity of ETBE compared for reactor 1 is calculated using Equation 17

$$S_{ETBE} = \frac{ETBE \text{ produced}}{IB \text{ consumed}} = 84.38 \% \quad (17)$$

The selectivity of EBTE for the etherification reaction as well the side reaction of IB hydration is relatively conservative. Therefore, the yield of ETBE simulated can be considered as a realistic indication of what may be expected in practical operation.

### 6.2.2 R-102

The second reactor was also analysed. Only the reaction between TBA and ethanol to produce ETBE was assumed to occur, due to the operating conditions of the reactor. A more conservative conversion of TBA was assumed, 75 %, due to the presence of the reaction products (ETBA and water) that may displace the equilibrium of the reaction towards the reverse reactions. A conversion reactor was employed to model the reaction. Consequently, the use of an equilibrium reactor, where the kinetics may be used to model the reaction will provide a much more reliable conversion that may be achieved. The mole balance around the reactor is shown in Table 20.

**Table 20:** Reactor 2

Component	Moles in (kmol h <sup>-1</sup> )	Moles out (kmol h <sup>-1</sup> )	Conversion %
ETBE	5.7	50.8	
Ethanol	197	151	23 %
TBA	60.3	15.1	75 %
Water	15.7	60.9	

As discussed in Section 3.12 of the unreacted TBA, was not recycled back into R-102 due to the difficulty in separating TBA, water and ethanol. Only 15 % of the unreacted TBA was recycled back into the reactor. The benefits of implementing recycles of unreacted

reactants is in order to ensure the complete conversion of the reagents fed into a process. Thus, recycling all of the unreacted TBA would ensure the complete conversion of the 60.911 kmol h<sup>-1</sup> entering the reactor process. Introducing a recycle stream would ensure an additional ETBE production of 15.679 kmol h<sup>-1</sup>, or 1.601 tonne h<sup>-1</sup>. The total ETBE produced (pure product) is 38.024 tonne h<sup>-1</sup>. Thus, the complete recycle of TBA would increase the total ETBE yield by 4.22 %.

### 6.3 ETBE yield

In order to evaluate the viability of the designed process, the ideal yield was compared to the yield of ETBE that was achieved. In order to utilise all the reagents, the unreacted reactants would be completely recycled to ensure the complete conversion of the limiting reactants into the process. If all of the unreacted IB was recycled back into R-101, then the ETBE that would be produced is

$$\text{Ideal ETBE}_{\text{R-101}} = IB_{in}(S_{ETBE})$$

$$\text{Ideal ETBE}_{\text{R-101}} = 444.26(0.8438) = 375 \text{ kmol h}^{-1}$$

and the TBA that would be produced would be

$$\text{Ideal TBA}_{\text{R-101}} = IB_{in}(1 - S_{ETBE})$$

$$\text{Ideal TBA}_{\text{R-101}} = 444.26(1 - 0.8438) = 69.4 \text{ kmol h}^{-1}$$

Furthermore, if all the unreacted TBA produced from R-101 were recycled back to R-102, then all of the 66.399 kmol h<sup>-1</sup> would be converted to ETBE and water. Thus, the total ideal ETBE produced would be

$$\text{Ideal ETBE}_{\text{total}} = 374.86 + 66.399 = 444 \text{ kmol h}^{-1}$$

$$\text{Ideal ETBE}_{\text{total}} = 45\ 390 \text{ kg h}^{-1}$$

The actual production rate of ETBE is 38 024 kg h<sup>-1</sup>. Accordingly, the yield of ETBE compared to the ideal yield of ETBE is

$$\text{Yield ETBE} = \frac{38\ 024}{45\ 390} = 83.8\ \%$$

Therefore, about 16.23 % of potential ETBE is lost through the failure to perfectly recycle the limiting reagents. However, the purification of isobutene for Reaction 1 and Reaction 2 would require expensive and intricate separation processes. In order to recycle the unreacted IB, it would have to be completely separated from all the other C<sub>4</sub> hydrocarbons which act as inert. If the entire C<sub>4</sub> stream were recycled into R-101, then the inert would build up. The complete separation of IB from the other hydrocarbons of very similar volatility would be very energy intensive. The use of multiple columns, mass separating agents or other intricate processes would have to be employed. The increase in total ETBE yield may not be worth the total economic demand of separating pure IB from the reactor product stream.

Furthermore, TBA would also have to be separated from water to be recycled back into R-102. If too much water is recycled with the TBA, then the reversible reaction would be hindered as the presence of water would drive the reverse reaction. Water would also build up within the system if it were not separated from TBA. The amount of unreacted TBA from R-102 does not justify the number of column that would be needed. However, an important consideration of the waste stream (ST-31) would be to produce aqueous ethanol to recycle back into R-101. Although this obstacle has been discussed in Section (refer to separation train section), a much more thorough investigation of employing membrane technologies to separate ethanol and water from TBA should be investigated.

## 6.4 Overall mass balance

The overall mass balance of the simulation was checked to determine the accuracy of the simulation. For the sake of validation, the same number of significant figures will be used for checking the mass balance as what is given by DWSim.

**Table 21:** Mass balance over the entire process

Stream	Description	Mass in kg h <sup>-1</sup>	Mass out kg h <sup>-1</sup>
ST-1	LPG	144 175	
ST-7	Ethanol	23 644	
ST-4	C <sub>3</sub>		73 641
ST-13	C <sub>4</sub>		48 372
ST-19	ETBE product		38 3107
ST-23	Azeotropic purge		628
ST-31	Polar waste		6 854
		167 819	167 804

As can be seen, the total mass out is slightly less than the mass into the system. It is impossible to create or lose mass. However, this inaccuracy is due to the simulation, and the convergence error that is permitted for the recycles streams to converge. The error was calculated to be 0.00890 %. This positive error indicates that mass has been theoretically created. There is 14.93 kg h<sup>-1</sup> more going into the system than there is going out. This inaccuracy may be due to the simulation, and the error that is permitted for the recycles streams to converge. However, the percentage error indicates that the discrepancy of the simulation is negligible. Thus, the simulated process can be considered as accurate. It should be noted that in practice, the mass balance error would be much larger. This is due to leakages of vapour and liquid that are unavoidable in a real plant, as well as other losses. Furthermore, the error in a real plant would always be positive as mass would be "lost" through leakages in the process.

## 6.5 Energy balance

### 6.5.1 Overview

The energy requirements of the process is an important consideration. The production of ETBE is an energy intensive process. Consequently, the energy requirements largely

contribute to the running costs of the plant. Every utility was checked in order to determine the accuracy of the simulation. The overall energy balance for a steady state process can be described by Equation 18 (RK, 2005):

$$E_{out} = E_{in} + E_{generated} - E_{consumed} \quad (18)$$

The following energy flows have been identified in the process:

- Work done by the pumps
- Work required by the streams to increase pressure
- Enthalpy of the streams entering the system
- Enthalpy of the streams leaving the system
- Energy generated by the exothermic reactions
- Heat required to maintain isothermal reactor conditions
- Energy generated by vaporising streams
- Energy consumed by condensing streams
- Heat required to vaporise and condense the streams

In reality, the energy balance of the system will have large discrepancies due to the non-ideality of energy consumption and production. The efficiency of equipment can not be 100 %. Thus, energy is lost throughout the system through a plethora of mechanisms. Regardless, the simulation of the ETBE plant should be such that the energy requirements of every process has been met.

It is not thermodynamically sound to only consider the utilities calculated by the simulation. It should be investigated whether the utilities indicated by DWSim are such that the energy requirements have been met. For example, the energy of the condensers of each column has been calculated by DWSim, however, this utility should be compared to the heat generated through vaporising the rectifying liquid of the column. Accordingly, the energy balance will be checked by comparing the utilities indicated by the simulation with the energy requirements of the streams that undergo a change in enthalpy.

### 6.5.2 Reactors

The heat of reaction of both reactors were checked in order to determine the accuracy of the simulation. Maintaining isothermal conditions in the reactor is important for the thermodynamic equilibrium of the reactions. All of the main and side-reactions involved are reversible and exothermic, thus, if the reactor duty is not adequate, the ETBE yield will be severely affected.

In the first reactor, Reaction 1 and Reaction 5 occur, where IB and water are the limiting reagents respectively. For the second reactor, Reaction 9 occurs where TBA is the limiting reagent. The heat released from all three exothermic reactions were calculated. The molar consumption of the limiting reagents were calculated for each respective reaction in order to calculate the heat generated from the reactions. This is shown in Table 22. This was compared to the cooling water duty required to maintain isothermal conditions for each reactor which was given by the simulation. The comparison is shown in Table

**Table 22:** Heat released by the exothermic reactions compared to the simulated duties to maintain isothermal conditions.

Reactor	Reaction	$\Delta H_{rxn}$ (kJ kmol $^{-1}$ )	Moles consumed (kmol h $^{-1}$ )	$E_{gen}$ (kW)
R-101	Rxn 1	-64450	333.20	-5965.15
	Rxn 5	-53486	61.685	-916.47
R-102	Rxn 9	-10964	45.23	-137.76

Finally, an overall energy balance was conducted around each reactor to determine whether the simulated duty of the reactor is adequate to maintain isothermal conditions. The energy balance over the reactor is described by Equation

$$Q_{CW} = \hat{\Delta H}(\dot{m}) + E_{gen} \quad (19)$$

where  $Q_{CW}$  is the cooling water required to maintain isothermal conditions in kW,  $\hat{\Delta H}$  is the enthalpy change of the stream in kW, and  $E_{gen}$  is the heat generated from the exothermic reaction in kW. The energy balance is shown in Table 23:

**Table 23:** Energy balance of the reactor

Reactor	$E_{gen}$ (kW)	$\hat{\Delta H}$ (kJ kg <sup>-1</sup> )	$\dot{m}$ (kg h <sup>-1</sup> )	$Q_{calculated}$ (kW)	$Q_{simulated}$ (kW)
R-101	-6 812	99	94 180	-4 295.6	-4 295.6
R-102	-137.76	28	12 675	-36.2	-36.2

As can be seen, the calculate duty of the cooling water is the same as the duty simulated by DWSim. The energy balance around the reactor is shown to be accurate where the right amount of duty is specified to maintain isothermal conditions.

### 6.5.3 Column duties

An energy balance over each column can be conducted, where the enthalpy of the feed, distillate and bottoms are taken into account, as well as the duties required for the reboiler and condenser. However, the intention of checking the energy balance is to verify the utilities of the equipment, as described by DWSim. Therefore, only the duties of the reboiler and condensers will be checked in order to verify whether the minimum utility has been met.

It is assumed that the rectifying vapour, and the reboil vapour and are saturated vapours. It is also assumed that the distillate, bottoms and stripping liquid are saturated liquids. Therefore, the energy released from condensing the rectifying vapour will be calculated and compared with the duty of the condenser given by the simulation. Similarly, the energy consumed to reboil part of the stripping liquid will also be calculated and compared with the duty of the reboiler.

The physical properties of the streams given by DWSim were utilised to calculate the heat generated and consumed from vaporisation and condensation respectively. However, the latent heat of vaporisation of the stream is not an obtainable parameter from the DWSim database. Subsequently, the latent heat of vaporisation was found from NIST (ref) and the latent heat of vaporisation of each stream that undergoes a phase change was calculated using Equation

$$\lambda_{mix} = \sum_{n=1}^n \lambda_n x_n \quad (20)$$

where  $\lambda_{mix}$  is the latent heat of vaporisation of the mixture in  $\text{kJ kmol}^{-1}$ ,  $\lambda_n$  is the latent heat of vaporisation of the  $n^{\text{th}}$  component in the stream, and  $x_n$  is the mole fraction of the component in the stream.

To calculate the heat generated by condensation, the rectifying liquid flow rate was used, as the shortcut column utilises a total condenser, as described by Equation 22

$$H_{cond} = \frac{\lambda_{mix}(V)}{3600} \quad (21)$$

where  $H_{cond}$  is the energy released by condensation in  $\text{kW}$ , and  $V$  is the molar flow rate of the rectifying vapour in  $\text{kmol h}^{-1}$ .

To calculate the heat consumed by vaporisation, the stripping vapour was used as a partial reboiler is utilised, as shown in Equation

$$H_{vap} = \frac{\lambda_{mix}(\bar{V})}{3600} \quad (22)$$

where  $H_{vap}$  is the energy consumed by vaporisation in  $\text{kW}$ , and  $\bar{V}$  is the molar flow rate of the stripping vapour in  $\text{kmol h}^{-1}$ .

$H_{cond}$  was calculated for every condenser for every column and compared to the simulated duties, as shown in Table 24:

**Table 24:** Comparison of the calculated and simulated condenser duties required

Condenser from column	$\lambda_{mix}$ ( $\text{kJ kg}^{-1}$ )	Flow rate ( $\text{kg h}^{-1}$ )	$H_{cond}$ ( $\text{kW}$ )	Simulated duty ( $\text{kW}$ )
T-101	19 213	4 181	-22 316	-15 568
T-102	22 099	2 159	-13 252	-10 409
T-103	30 528	2 512	-21 302	-23 322
T-104	35 113	1 733	-16 905	-19 079
T-105	36 560	264	-2 678	-2 653
			-76 453	-71 031

similarly,  $H_{vap}$  was calculated for every reboiler for every column and compared to the simulated duties. The enthalpy change of the stream in and out of the cooler and heaters were calculated and compared to the specified simulated duty, as shown in Table 25:

**Table 25:** Comparison of the calculated and simulated reboilers required

Reboiler from column	$\lambda_{mix}$ (kJ kg <sup>-1</sup> )	Flow rate (kg h <sup>-1</sup> )	$H_{cond}$ (kW)	Simulated duty (kW)
T-101	22 067	3 259	19 975	12 039
T-102	35 054	1 355	13 189	7 062
T-103	30 528	1 481	12 556	19 710
T-104	41 737	1 286	14 912	15 324
T-105	41 435	263.73	2 689	2599
			63 667	56 824

As can be seen, there is a large discrepancy for the simulated duties required by the reboilers and condensers compared to the calculated duties required. A more comprehensive discussion of the error is evaluated in Section 21. However, it can be seen that the largest difference exists for T-101 and T-102. The first 2 distillation columns involve C<sub>3</sub> and C<sub>4</sub> hydrocarbons. Whereas for T-103, T-104 and T-105 only involve trace amounts of C<sub>4</sub> hydrocarbons. Therefore, the latent heat of vaporisation that was used for the calculation may inaccurate compared to the parameters used for the DWSim simulation. In comparison, the simulated duties of the column involving the polar compounds are quite similar to those calculated. This indicates that the  $\lambda$  values obtained for water, ethanol, TBA and ETBE may be more accurate than those obtained for the hydrocarbons.

#### 6.5.4 Heaters and coolers

The same process was followed for the heaters and coolers, as what was done for the condensers and reboilers. The duties of the coolers were checked, as shown in Table 26.

**Table 26:** Comparison of the calculated and simulated cooling duties required

Coolers	$\Delta H$ (kJ kg <sup>-1</sup> )	$\dot{m}$ (kg h <sup>-1</sup> )	Q <sub>calculated</sub> (kW)	Q <sub>simulated</sub> (kW)
E-102	-75.2	70 535	-1 474	-1 474
E-105	-297	38 310	-3 166	-3 274
E-106	-54.8	629	-9.58	-9.58
E-108	-27	14 381	-108	-107
E-109	-133	6 854	-254	-231
			-5 010	-5 096

the calculated error for the coolers is only about 1 %. Similarly, the duties of the heaters were checked, as shown in Table 27.

**Table 27:** Comparison of the calculated and simulated Heating duties required

Heating	$\Delta H$ (kJ kg <sup>-1</sup> )	$\dot{m}$ (kg h <sup>-1</sup> )	Q <sub>calculated</sub> (kW)	Q <sub>simulated</sub> (kW)
E-101	208	144 175	8 325	8 325
E-103	109	23 644	717	865
E-104	264	94 180	6 915	5 432
E-107	321	62 204	5 545	4 088
			21 503	18 710

The total error for the heaters was calculated as 20 %. This is a relatively large error, especially when compared to the cooler calculation. This may be due to the fact that some heaters were utilised to achieve a phase change so that a liquid vapour mixture could be fed into the distillation columns to reduce the number of stages required. However, the latent heat of vaporisation should be accounted for in the specific enthalpy of the outlet stream. There is a large discrepancy for duties that have been used to induce phase changes.

## 6.6 Pumps

The duties of the pumps were also checked. Although the work of a pump can be calculated by evaluating the change in pressure, the enthalpy of the mixture out and in can also provide the duties required. Therefore, the simulated work of the pumps was evaluated as for the coolers and heaters, as shown in Table 28.

**Table 28:** Comparison of the calculated and simulated pump duties required.

Pump	$\Delta H$ (kJ kg <sup>-1</sup> )	$\dot{m}$ (kg h <sup>-1</sup> )	$Q_{\text{calculated}}$ (kW)	$Q_{\text{simulated}}$ (kW)
P-101	2	144 175	80.1	80.2
P-102	2.31	23 644	15.2	15.1
P-103	1.68	62 204	29.0	29.0
				124
				124

The work of the pumps is shown to have a negligible error.

## 6.7 Overall energy balance

An overall energy balance of the process was analysed to determine the reliability of the simulation with regards to the energy requirements of the process. The enthalpy of the streams going into and out of the process were accounted for, as well as the heat generated by the reaction, the pump-work and heat in and out of the process. The overall energy balance is shown in Table 18:

**Table 29:** Overall energy balance over the process

Energy source	Energy in (kW)	Energy out (kW)
Streams		
ST-1	14 004	
ST-7	6 558	
ST-4		5 722
ST-13		3 075
ST-19		3 349
ST-23		75.3
ST-31		1 951
Columns		
Total Condenser		71 031
Total Reboiler	56 824	
Coolers & heaters		
E-102		1 474
E-105		3 274
E-106		9.58
E-108		107
E-109		231
E-101	8 325	
E-103	865	
E-104	5 432	
E-107	4 088	
Pumps		
P-101	60.2	
P-102	11.3	
P-103	21.7	
Reactors		
R-101		4 296
R-102		36.2
E <sub>gen</sub> 1	6 882	
E <sub>gen</sub> 2	138	
	103 076	94 276

The error of the energy balance is calculated using Equation 23

$$\% \text{ Error} = \frac{\text{Energy in} - \text{Energy out}}{\text{Energy in}} \quad (23)$$

The error was calculated to be 8.54 %. the energy into the process is about 8 799 kW more than the energy out. This indicates that that energy requirements of the plant would be slightly less than what is indicated by the simulation. However, the utilities of the equipment have been investigated assuming 100 % efficiency. For example, the pumps are simulated with 75 % efficiency, however, for the energy balance 100 % efficiency was assumed in order to account for the energy that would have been lost from the non-idealities of the pumps. Consequently, it is expected that for a real plant, the efficiencies of the condensers, reboilers, pumps, heaters, coolers and other equipment would be much less than 100 %. Thus, there would be a lot of energy lost and the energy requirements of the process would be much higher than what has been simulated.

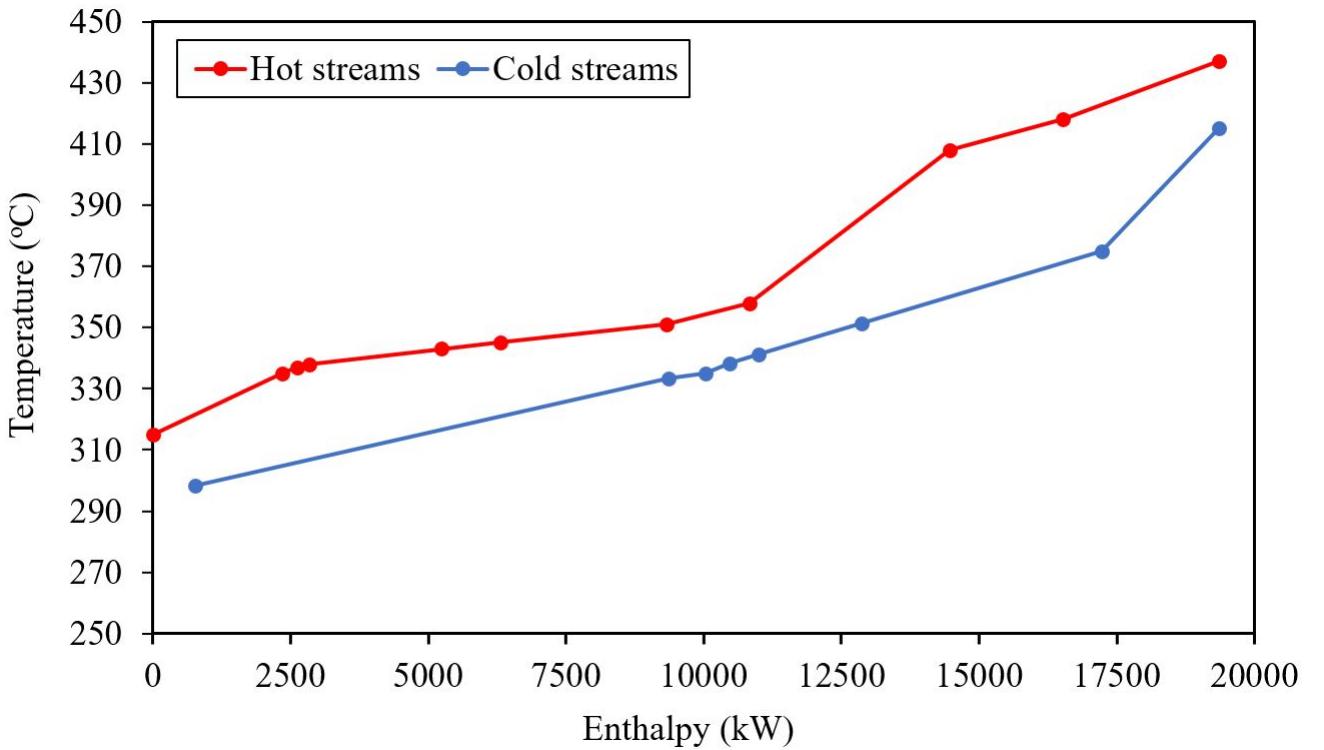
## 7 Thermal Efficiency

### 7.1 Maximum energy recovery

The thermal efficiency of a plant involves the integration of heat in such a manner so as to utilise energy in high temperature streams that need to be cooled and/or condensed to heat and/or vaporise the cold streams whilst ensuring no heat is lost and minimizing on the usage of utilities. When designing an optimal heat exchange network (HEN) the most important factor to consider is the total capital investment that would be needed to develop the proposed HEN (Seider *et al*, 2009). Additionally, the capital investment is dependent on the size of the heat exchanger, the  $\Delta T_{min}$  and the amount of utility being used. The procedure that will be followed in designing an efficient HEN for the ETBE process proposed, includes obtaining a network of heat exchangers with minimum usage of utilities, usually requiring a large number of heat exchangers. The number of heat exchangers is then reduced towards the minimum at the expense of increasing the consumption of utilities (Seider *et al*, 2009). However, since a threshold problem was encountered the energy relaxation proved redundant. Relaxation could be achieved by adding a heat exchanger with an "empty" utility. However, this diverts from the energy relaxation objective which is to *remove* heat exchangers. Furthermore, heat exchanger removal can be achieved through internal/process loops. However, when the internal/process loops were created  $\Delta T_{min}$  violations occurred that would require energy

relaxation. Thus, the idea of removing heat exchangers for the specific HEN designed proved redundant.

The process of designing the HEN with regards to minimizing the use of utilities was tested in two ways initially using composite curves and then verified via the maximum energy requirement (MER) method. The composite curve method is a graphical method in which composite heating and cooling curves are positioned no closer than a distance of  $\Delta T_{min}$  apart. Figure 9 represents all the flows of sensible heats within heat exchangers from our ETBE process.



**Figure 9:** Composite curve of the ETBE process.

The sensible heats shown on the diagram were derived from the following equations:

$$CP = \dot{m}C_p \quad (24)$$

$$H = CP(T_{Out} - T_{In}) \quad (25)$$

Where  $\dot{m}$  is the mass flow rate in  $\text{kg s}^{-1}$ ,  $C_p$  heat capacity of the flowing streams  $\text{J kg}^{-1} \text{K}^{-1}$ .  $T_{In}$  and  $T_{Out}$  represent the temperatures of the flowing streams into and out of the heat

exchangers. It is important to note that the composite curve displayed above does in fact account for phase change. The method that was used is such that a fictitious heat capacity flow rate can be used based on the change in enthalpy flow rate due to all applicable effects (latent heat of phase change, heat of reaction and heat of mixing) divided by the temperature range (Seider *et al*, 2009). This in essence isn't exact and does introduce a degree of error within the design of the MER. The results that were obtained from the composite curve can be seen below:

$\Delta T$	$Q_{Hot}$	$Q_{Cold}$
17 °C	0 kW	668 kW

It is shown that no hot utility is required, and a minimum cold utility of 700 kW was calculated. This implies that the system is a threshold problem. The the pinch point occurs at  $T_H = 358$  °C and  $T_C = 341$  °C, at an enthalpy of 10 838 kW on Figure 9. Thus,  $\Delta T$  of this system was calculated to be 17 °C.

With the collected data the HEN can then be designed following the method mentioned in Seider *et al*, 2009. Firstly, the MER targeting was done as shown by the composite curve and the problem table below. The problem is then decomposed at the pinch as illustrated by the green line in figure 10 yielding two independent HEN's to be designed. The HEN that was designed on the hot side of the pinch was paired such that the  $CP_{Cold} \geq CP_{Hot}$ . However on the cold side of the pinch the streams are paired with  $CP_{Hot} \geq CP_{Cold}$ . Whilst adding heat exchangers, duties need to be added in such a manner so as to retain sufficient temperature driving forces for additional matches. This resulted in the finalised HEN shown by figure 10.

## 7.2 Heat exchanger network

A heat exchanger network was developed in order to meet the MER. The heat exchange network on the cold side was difficult to design. In order to ensure that no  $\Delta T_{min}$  violations occurred, the cold stream C<sub>3</sub> had to be split in a 1.17:1 ratio. This split was done due to the fact that C<sub>3</sub> has a large  $CP_{cold}$  value (130.2 kW °C<sup>-1</sup>). The stream C<sub>3</sub> reaches the cold pinch temperature of 341 °C. All of the hot streams that reach the hot pinch temperature on the cold side (H<sub>2</sub>, H<sub>4</sub> and H<sub>8</sub>) have a C<sub>P</sub> lower than C<sub>3</sub>. Therefore the stream C<sub>3</sub> had to be split so that a hot stream could exchange heat with the a split stream of C<sub>3</sub> with a lower  $CP_{cold}$ .

On the hot side, five heat exchangers were utilised where no hot utility was required. There were fourteen heat exchangers utilised to exchange heat between the hot and cold

streams on the cold side, and three coolers were also used. On the cold size, a minimum cold utility of 668 kW was achieved. As shown in Figure 9, the actual minimum cold utility was calculated to be about 700 kW. An error of about 32 kW between the HEN design and the actual composite curve exists. This error could be due to the number of significant figures used to design the HEN, whereas the composite curve was plotted based on accurate figures.

It should be noted that no heat exchangers were removed and no temperature relaxations were performed. This is due to the fact that a temperature violation occurs as soon as a heat exchanger is removed, and the threshold temperature would have to be decreased in order to remove heat exchangers. The sizing of the heat exchangers (see Section 8) indicated that the heat exchangers would not be extremely costly. Therefore, it was decided that the MER design would be used to maintain an energy efficient plant.

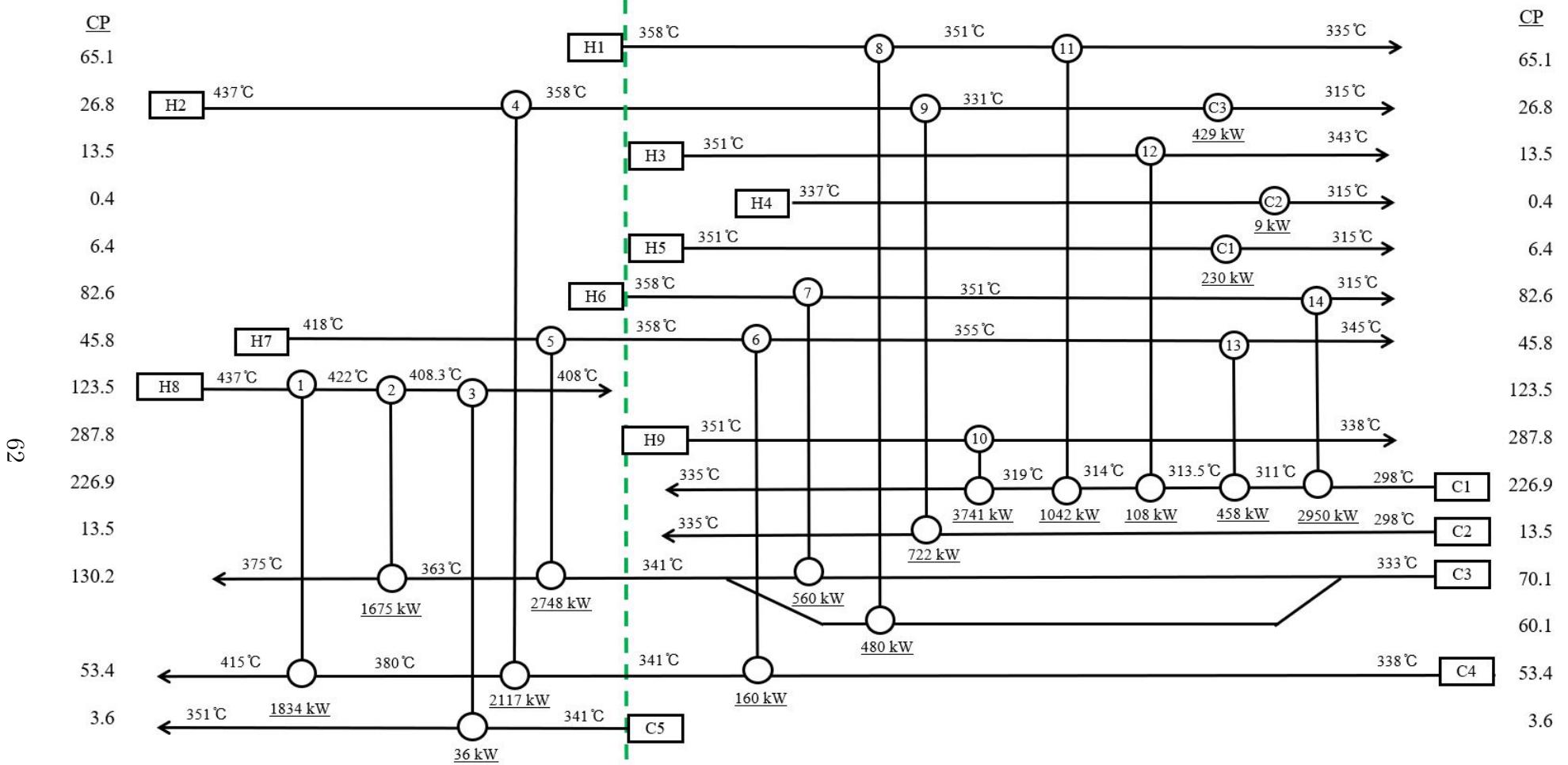


Figure 10: Heat exchanger network to meet the MER.

## 8 Preliminary Equipment Design

### 8.1 Reactors & catalysts

#### 8.1.1 Reactor sizing

Menezes & Cataluna, 2008 used a single space velocity of  $0.52 \text{ h}^{-1}$  for a reactor volume of  $380 \text{ cm}^3$ .

Using this single space velocity as reference and the relevant calculated flow rate from the DWSim simulation,  $Q = 157.589 \text{ m}^3 \text{ h}^{-1}$ , the volume of the reactor can be sized using Equation 26

$$\frac{1}{\tau} = \frac{Q}{V} \quad (26)$$

Therefore, the size of the primary reactor (R-101) required based on the simulation flow rate and the space velocity from literature (Menezes & Cataluna, 2008) is  $303.06 \text{ m}^3$ . In comparison to the literature study by Menezes & Cataluna, 2008 this reactor is much larger in volume. However, the design is based on an industrial-scale project meeting the required production of ETBE in accordance to Natref's production. To reduce the volume of the reactor, several reactors could be operated in series and achieve the same space velocity and overall conversion; however, research was done on large-scale reactors in South Africa and Sasol was found to have constructed reactors with diameters as large as 8 m (Technology, n.d.). Thus it was deemed acceptable to have a reactor of such a large volume for an industrially-scaled project. Further considerations of a reactor of such size is that it would need to be assembled on site.

The second reactor (R-102) was sized in the same manner with a flow rate  $Q = 19.1216 \text{ m}^3 \text{ h}^{-1}$ . Badia *et al* (2013) states that the number and size of reactor units should be decided such that an hourly space time liquid velocity between  $1.8\text{--}2 \text{ h}^{-1}$  is achieved, even if more than one reactor needs to be used in series to reduce the volume required. Using a space time velocity of  $1.8 \text{ h}^{-1}$  a reactor volume of  $10.623 \text{ m}^3$  is achieved.

#### 8.1.2 Catalysts

The mass of the catalyst in each reactor was calculated. The first reactor (R-101) will utilise Amberlyst-15, and the second reactor (R-102) will use S-54. The catalyst S-54 is

a Chinese ion-exchange resin catalyst which is similar to Amberlyst-15 (BL Yang *et al*, 2000). However, S-54 is much less susceptible to water inhibition, which is necessary for the second reactor as water is fed into the second reactor in an amount that cannot be assumed negligible. The mass of the catalysts were calculated from the packing density and reactor volumes, as shown in Table 30.

**Table 30:** Sizing of the reactor and catalyst

Reactor	Catalyst	Packing density (kg m <sup>-3</sup> )	Reactor Volume (m <sup>3</sup> )	Mass of catalyst (kg)
R-101	Amberlyst-15	540	303	163 620
R-102	S-54	10.623	560	5 949

There are no poisons present in the feed that would damage the activity of the catalyst. Water is known to decrease the activity of the catalyst. However, due to the fact that the hydration of isobutene is a fast reaction that consumes almost all of the water in the feed, the inhibition of water is considered negligible. However, if the catalyst activity is impaired over time, the water would have to be removed through continuous dehydration. If there are minimal poisons present, then the catalysts could last up to a year (Moulijn, Van Diepen & Kapteijn, 2001). Therefore, it will be assumed that the catalyst need only be replaced once a year.

## 8.2 Distillation columns

### 8.2.1 Number of trays

An approximate column sizing of the distillation columns will be done. This involves specifying the columns diameter, tray spacing and height of the columns. However, it should be noted that the preliminary column design should be revisited upon the detailed design of the columns.

The minimum number of trays, flow rates and physical properties of the liquid and vapour phases are given as parameters by DWSim. These parameters will be used for the proceeding calculations. The total number of trays can be calculated from the minimum number of stages once a reasonable estimate of the overall efficiency has been determined. The column efficiency can be estimated from the relative volatility and the dynamic

viscosity of the light key component, as shown by the O'Connell correlation which is described by Equation 27 (Wankat, 2006):

$$E_o = 0.52782 - 0.27511 \log_{10}(\alpha_{LK}\mu) + 0.044923[\log_{10}(\alpha_{LK}\mu)]^2 \quad (27)$$

where  $\alpha$  is the relative volatility of light key, and  $\mu$  is the viscosity of the feed (Wankat, 2006). For a multi-component system, the relative volatility of the light key is described by the Fenske equation (Wankat, 2006), as shown in Equation 28:

$$\alpha_{LK} = \left( \frac{F_{LK}}{1 - F_{LK}} \right) \left( \frac{1 - F_{HK}}{F_{HK}} \right) \quad (28)$$

where  $F_{LK}$  and  $F_{HK}$  are the recoveries of the light and heavy keys respectively. For Equation 27, the viscosity of the light key was obtained from the given physical properties of the feed by DWSim at the average column temperature: the sum of the distillate and bottoms temperatures divided by two.

Once the overall efficiency has been calculated the actual number of stages can be found by Equation 29:

$$N_{actual} = \left( \frac{N_{min}}{E_o} \right) \quad (29)$$

The distillation columns with azeotropic mixtures required a different correlation in order to calculate the relative volatility's, overall efficiencies and hence the actual number of stages. Wankat, 2006 makes use of Equation 30 to calculate the relative volatility at the average column temperature.

$$\alpha = \left( \frac{y(1 - x)}{x(1 - y)} \right) \quad (30)$$

The binary phase envelopes were plotted on DWSim at the average column temperature. The corresponding  $y$  composition at  $x = 0.5$  was then found and the relative volatility calculated. Thereafter Equation 27 is used to find the overall efficiency and the actual number of stages calculated as before using Equation 29.

### 8.2.2 Plate spacing

The plate spacing is chosen depending on the diameter of the column. For columns with a diameter greater than 1 m, plate spacing of 0.3 m–0.6 m are used in order to allow maintenance staff to access the larger area of the trays (RK, 2005: 574).

The plate spacing was used as an optimisation parameter in that it was adjusted between 0.3 m and 0.6 m until the lowest diameter for the column was obtained. This optimisation was done for each column and for both the stripping and rectifying sections. Thereafter once both the stripping and rectifying sections were considered with varying plate spacing and effective column diameter, it was found that the optimal plate spacing which gave the lowest column diameter for each instance (stripping and rectifying) was the same for both stripping and rectifying sections. Once the plate spacing was confirmed, the largest column diameter between the stripping and rectifying sections was selected such that a uniform-diameter column is built with an adequate column diameter for proper functioning of the column.

### 8.2.3 Column diameter

The Souders and Brown equation is employed to calculate the maximum superficial vapour velocity, as given by Equation 31:

$$u_v = (-0.171l_t^2 + 0.27l_t - 0.47) \left[ \frac{\rho_L - \rho_v}{\rho_v} \right]^{0.5} \quad (31)$$

where  $u_v$  is the maximum vapour velocity in  $\text{kg s}^{-1}$ ,  $l_t$  is the plate spacing in m,  $\rho_v$  is the density of the vapour in  $\text{kg m}^{-3}$ , and  $\rho_L$  is the liquid density in  $\text{kg m}^{-3}$ .

The column diameter,  $D_c$  can then be calculated:

$$D_c = \sqrt{\frac{4V_w}{\pi \rho_v u_v}} \quad (32)$$

Taking the plate spacing as 0.5 m the maximum allowable vapour velocities of the various columns were calculated, thereafter the column diameter's were found.

#### 8.2.4 Column height

Once the tray spacing had been determined as well as the total number of trays and tray thickness, the column height could be estimated (RK, 2005).

The height of the column accounting for only the number of trays present can be calculated from Equation 33

$$H_{trays} = (N_{trays})(t_{space} + t_{tray}) \quad (33)$$

This height does not account for the accommodation of manholes, and entrainment issues (RK, 2005), hence an additional spacing must be added at both the top and bottom of the column such that the height is adjusted accordingly. Therefore to make provisions, 1.5 m will be added to both the top and bottom of the columns (RK, 2005). Typical plate thicknesses are given as 5 mm for carbon steel and 3 mm for stainless steel (RK, 2005). Thus a more conservative plate thickness of 5mm was used for these calculations.

#### 8.2.5 Wall thickness

RK, 2005 suggests a minimum thickness requirement (which allows for a 2 mm corrosion tolerance) for specific vessel diameters. The table only gives minimum thickness values for column diameters up to 3.5 m. However, upon plotting the correlations a linear relationship was observed and the minimum wall thickness for the large diameter column (4.44 m) was extrapolated and found to be 14.13 mm.

Once the wall thickness had been computed the outer column diameter was found using Equation 34.

$$D_{outer} = D_c + 2t_{wall} \quad (34)$$

#### 8.2.6 Column sizing specifications

The final column sizing specifications are given in Table 31:

**Table 31:** Distillation column sizing specifications

	T-101	T-102	T-103	T-104	T-105
Property					
N <sub>min</sub>	8.070	13.49	15.57	7.100	4.630
E <sub>o</sub>	0.540	0.850	0.760	0.610	0.610
N <sub>actual</sub>	14.91	15.91	20.48	11.60	7.620
D <sub>col</sub> (m)	3.220	2.690	3.450	4.440	1.540
t <sub>tray</sub> (mm)	5.000	5.000	5.000	5.000	5.000
t <sub>spacing</sub> (m)	0.800	0.800	0.800	0.800	0.800
H <sub>trays</sub> (m)	12.08	12.88	16.91	9.660	6.440
H <sub>actual</sub> (m)	15.08	15.88	19.91	12.66	9.440
t <sub>wall</sub> (mm)	10.00	10.00	12.00	14.13	5.000
D <sub>outer</sub> (m)	3.240	2.710	3.470	4.470	1.550

### 8.3 Pumps

The pumps in the system will be required to increase the pressure of the liquid streams to the required pressures. It is important to pick the right type of pump for the application. Centrifugal pumps are common in the industry and are ideal for low viscosity fluids and pressure boosting. These pumps can manage high flow rates and more often than not, they are less expensive than other pumps with the same capacity (Kirk, 2018). Centrifugal pumps have two configurations, namely horizontal or vertical. The two types of centrifugal pumps have similar prices and operate with impeller utilising centrifugal force to move the fluids (Peters, 2019). The vertical configuration is also known as an inline pump. The suction and discharge nozzle of the inline pump are in a straight line, which allows for a lower NPSH<sub>R</sub> (net positive suction head required). Peters (2019) mentioned that the inline centrifugal pump is advantageous in terms of higher operating temperatures and pressures owing to its ability to handle thermal expansion. Vertical inline centrifugal pumps will be used for this design. The pumps should be over-designed in order to ensure that the pumps won't fail under possible operational irregularities. Therefore, the power requirement and volumetric flow rate is multiplied by 1.5. The

design requirements of the pumps are listed in Table 32.

**Table 32:** Design requirements for the pumps

	P-101	P-102	P-103
Volumetric flowrate ( $\text{m}^3 \text{ h}^{-1}$ )	400	45	130
Density ( $\text{kg m}^{-3}$ )	532.6	814.1	715.1
$\Delta P$ (kPa)	800	1400	900
Operating temperature ( $^{\circ}\text{C}$ )	25	25	64
NPSH <sub>A</sub> (m)	2.9	12.1	0.5
NPSH <sub>R</sub> (m)	2.4	11.0	0.02
Efficiency ( %)	75	75	75
Pump power (kW)	120	25	45
Anti-corrosive coating/Stainless Steel	No	Yes	Yes

The values of the pump requirements listed in Table 32 were taken from the DWSIM simulation and the NPSH<sub>R</sub> was determined using the following criteria from Greeff & Skinner (2000):

- $\text{NPSH}_A \geq \text{NPSH}_R + 0.5 \text{ m}$
- For hydrocarbons:  $\text{NPSH}_A \geq 1.1 \text{ NPSH}_R$

The smallest NPSH<sub>R</sub> value from the two criteria is taken as the NPSH<sub>R</sub> of the pump required. The power requirement of the pump given in the simulation was confirmed using the following equation

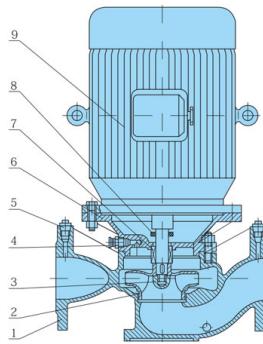
$$P = \frac{\Delta P \cdot W}{3600 \cdot \rho \cdot \eta} \quad (35)$$

Where  $\eta$  is the efficiency of the pump,  $\rho$  is the density of the fluid in  $\text{kg m}^{-3}$ ,  $\Delta P$  is the pressure differential in kPa, and  $W$  is the mass flow rate in  $\text{kg h}^{-1}$ .

The 'High Pressure Inline Circulation Pump Vertical Inline Centrifugal Pump' from Alibaba.com is chosen for the pumps. This particular pump is available in different sizes, power requirements, and flow rates. The costing of the pumps will depend on the size of the pump and will be covered under Section 9. Ethanol and water are very corrosive to carbon steel. Therefore, it is important to ensure that the pumps exposed to streams



**Figure 11:** Example of a vertical inline pump (Pumps, 2020)



**Figure 12:** Cross section of vertical inline pump (YNS Pumps, 2020)

containing these components are made of stainless steel or have a protective coating to ensure that corrosion of the pumps is limited. The pumps chosen have stainless steel shafts and impellers and an anti-corrosive coating. The pumps are also custom to the buyer's requirements with a large range of power requirements available (0.75 kW – 250 kW), making this the ideal choice of pump for the plant. The parameters of the pumps are shown in Table 33. The prices for these pumps will depend on the specific outlet size and power requirement. Figure 11 shows an example of a vertical inline pump; Figure 12 shows a cross section of the vertical inline pump.

**Table 33:** Chosen pump operating ranges and parameters

Pump parameters	
Product name	High Pressure Inline Circulation Pump
Source	Alibaba.com
Max. permissible flow rate	1200 m <sup>3</sup> h <sup>-1</sup>
Max. head	150 m
Impeller and shaft material	Stainless steel 304
Outlet size	25 – 350 mm
Operating temperature range	-10 – 120 °C
Anti-corrosive coating	Yes
Output power	0.75 – 250 kW

## 8.4 Storage tank selection and sizing

The feeds to the plant and the products produced need to be stored at the plant. The LPG feed to the ETBE plant needs to be stored in pressurised vessels in order to keep it in the liquid phase. The ethanol is delivered per truck/rail load to the ETBE plant and pumped into storage vessels. From there it is pumped to the mixer to mix the feed to the reactor. The storage vessels need to be large enough to supply the plant with the required feed flow rate for as long as the plant waits on new feed product deliveries. There also needs to be a backup for unexpected problems with the delivery of feed products, whether it is delivered by rail car or tank car.

For each of the feed and product streams, storage vessels need to be sized. The number of storage vessels depend on the size of the storage vessels used, the feed/production rate of the material and the frequency of collection/delivery of the specific material.

### 8.4.1 LPG feed storage tank

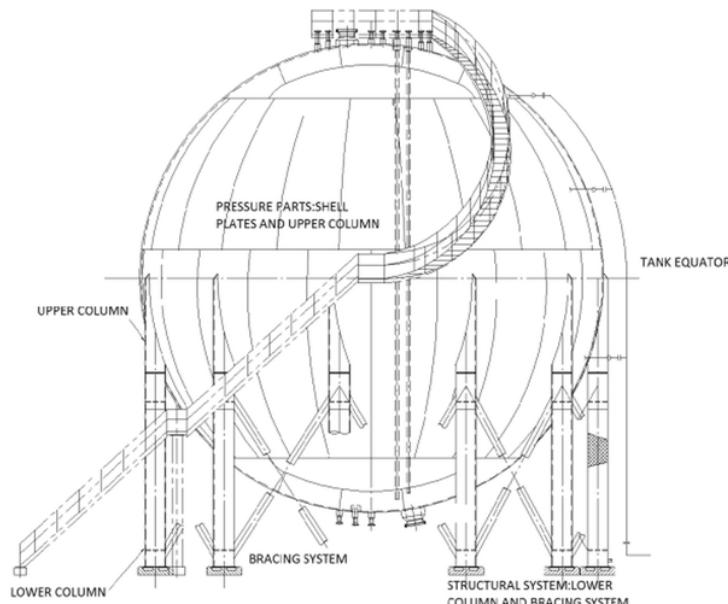
The LPG cut used in the ETBE production needs to be stored at 700 kPa at 25 °C to keep it in the liquid phase. The feed rate of the LPG cut to the system is 144 175 kg h<sup>-1</sup>. The volumetric feed rate is about 271 m<sup>3</sup> h<sup>-1</sup>, meaning that the plant requires about 6500 m<sup>3</sup> of the LPG feed per day. Transport and storage of these large volumes of LPG is unrealistic. Therefore, it is assumed that the LPG feed material is supplied *via* pipeline from the supplier at a specified pressure. The design of this pipeline is beyond the scope of this design. However, the storage tanks that receives the feed from this pipeline will be discussed. The LPG storage tanks need to hold about two days worth of LPG feed material. This ensures ample time to take the necessary safety measures and execute the correct protocols once warning systems notify plant staff of a problem with the LPG feed. It also ensures that there is enough of the LPG feed for two days in the case where the supplier has some issues with their production or there is a problem with the transport pipeline. The plant will, therefore, still be able to run for two days wherein the supply problem can be fixed. The system needs to be designed in such a way that the feed from the supplier occurs at the same rate as the feed requirement to the plant so that the storage tanks remain at a constant level under normal operating conditions. The tanks will not be filled. Therefore, a total of 16 000 m<sup>3</sup> LPG feed material storage capacity was chosen to allow a safety net for any irregularities that might occur during operation.

Spherical tanks with a capacity of 4 000 m<sup>3</sup> each were sourced from Alibaba.com and 4 of these will be uses to store the incoming LPG feed material from the pipeline. These spherical tanks are known as Hortonspheres. These storage spheres are cheaper and safer

when it comes to the storage of gases under high pressure (to keep them in liquid phase), due to the smaller surface area compared to cylindrical tanks with the same capacity (less construction material is required) and the distribution of pressure across the entire surface area of the sphere. The chosen tanks can operate under pressure of up to 1.77 MPa and temperatures of up to 50 °C. Considering the LPG feed needs to be stored at a pressure of 700 kPa at 25 °C to keep it a liquid, these storage tanks will be sufficient for most common irregularities that might occur during operation. The tank is sold as an LPG storage tank. The parameters of these spherical tanks are shown in Table 34. A diagram of the spherical tanks is shown in Figure 13.

**Table 34:** LPG storage tank parameters

Parameter	Value
Product name	4000 m <sup>3</sup> LPG Spherical Tank
Source	Alibaba.com
Storage capacity	4 000 m <sup>3</sup>
Tank diameter	19.6 m
Maximum working pressure	1.7 MPa
Design pressure	1.8 MPa
Operating temperature	-15 – 40 °C
Shell material	SA537 CL.2



**Figure 13:** Diagram of the spherical tanks used for liquefied gas storage (Arabzadeh, Niaki & Arabzadeh, 2018)

#### **8.4.2 C<sub>3</sub> product stream storage tanks**

The distillate from T-101 is mainly propane and propylene. The production rate is 73 641 kg h<sup>-1</sup> or about 3 600 m<sup>3</sup> per day. This gas is produced in such a large volume that it would be infeasible to store and transport it *via* truck or rail. Therefore, it is assumed that the C<sub>3</sub> product stream will be partially stored and continuously transported *via* pipeline to a client that will use the gas to make other products such as salable household or industrial LPG.

There needs to be intermediate storage tanks for the storage of the produced C<sub>3</sub> gas stream. The operating pressure of the storage tanks are 1 200 kPa. This ensure that the C<sub>3</sub> product stream remains a liquid. The C<sub>3</sub> product stream will be pumped into these tanks and transported out of these tanks simultaneously at the same rate *via* the pipeline to the client. This will ensure that the tanks are not overfilled or run empty during normal operating conditions. Extra storage space is necessary to ensure that the tanks do not overfill in case of irregularities during plant operation, whether it be on the plants side or on the client's side. Due to the high pressure and large volumes, the storage tanks chosen for the LPG feed will also be chosen for the C<sub>3</sub> product stream storage. Two of the 4 000 m<sup>3</sup> spherical tanks should be sufficient storage for this purpose. The parameters of these particular tanks can be seen in Table 34. The operating pressures of these tanks are high enough for the high pressure required to keep the C<sub>3</sub> streams a liquid. However, sufficient pressure and level control systems with warning signals need to be implemented to monitor the tanks pressure and level.

#### **8.4.3 C<sub>4</sub> product stream storage tank**

The C<sub>4</sub> product stream (distillate of T-102) needs to be stored at 400 kPa in order to remain in liquid form. The components of this stream are also found in LPG streams. Therefore, this product can be stored in LPG storage tanks. The C<sub>4</sub> product stream is produced at a rate of 48 522 kg h<sup>-1</sup> or about 2 000 m<sup>3</sup> per day. The same assumption will be made as for the C<sub>3</sub> product stream. This product will be transported to a buyer at a specific pressure *via* a pipeline. A similar storage vessel will be used. However, for this purpose two 3000 m<sup>3</sup> spherical tanks will be used. This will ensure sufficient storage space for the C<sub>4</sub> product stream in case of any plant operation irregularities. If possible, the spherical tanks can be designed to have a lower operating pressure than that of the C<sub>3</sub> product stream storage tanks due to the C<sub>4</sub> product stream being stored at only 400 kPa (800 kPa should be more than enough). This will reduce the cost of the tanks. The properties of these tanks can be found in Table 35.

**Table 35:** C<sub>4</sub> storage tank parameters

Parameter	Value
Product name	3000 m <sup>3</sup> LPG Spherical Tank
Source	Alibaba.com
Storage capacity	3 000 m <sup>3</sup>
Tank diameter	19.6 m
Maximum working pressure	1.57 MPa
Design pressure	1.77 MPa
Operating temperature	-15 – 40 °C
Shell material	SA537 CL.1

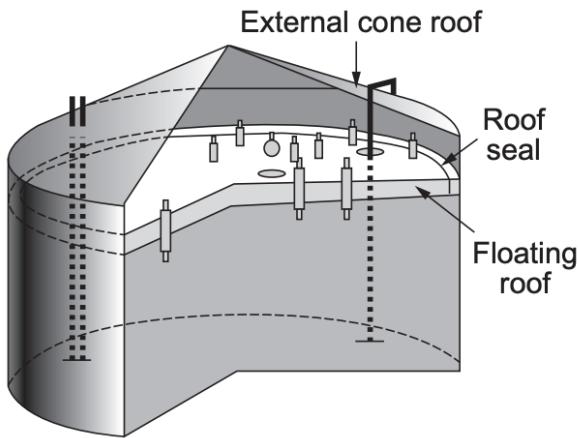
#### 8.4.4 Ethanol feed storage tank

The ethanol used for this ETBE production plant contains water. Water is corrosive to carbon steel and the added ethanol accelerates this corrosion process. Stainless steel storage tanks need to be used for the ethanol feed product. The feed requirement of ethanol is about 5 000 m<sup>3</sup> per week. Assuming the ethanol is transported to the plant *via* railroad transport and delivery occurs every three days, storage for about five days are required. This will ensure that there is always a back-up supply of ethanol should there be a problem with delivery. It also ensures that if the plant has to shutdown due to a problem with the delivery of the products, there will be a long enough warning period to do so before the ethanol feed tanks run empty.

Floating roof storage tanks will be used for the storage of ethanol. The tanks will be at atmospheric pressure. Ethanol and especially ethanol vapours are extremely flammable. It is, therefore, of utmost importance that the safety of the ethanol storage tanks farm is carefully planned out according to the standards of flammable liquid storage tanks and tank farms. Four 1 000 m<sup>3</sup> tanks will be used to store the ethanol feed. The tank design will be an internal floating roof storage tank which will limit the formation of ethanol vapours that could create a big fire hazard when the tanks is relatively empty. The tanks also have a dome roof to ensure that the ethanol vapours don't escape at rapid rates and cause external fire hazards. The tanks also need to be covered in an anti-flammable coating to minimise the fire hazard associated with the ethanol tanks. The tanks will be made of stainless steel in order to prevent crack corrosion of carbon steel tanks with hydrous ethanol. The properties and characteristics of the tanks are stated in Table 36. The fire-resistant layer needs to be painted on after the tanks has been set up on the site. Figure 14 shows a diagram of an internal floating roof tank.

**Table 36:** Ethanol storage tanks parameters

Parameter	Value
Product name	Chemical ethanol gasoline floating roof storage tank
Source	Alibaba.com
Construction material	Carbon steel/stainless steel
Anti-corrosive	Yes
Capacity (m <sup>3</sup> )	1 000
Diameter (m)	11.63
Height (m)	11.96



**Figure 14:** Diagram of an internal floating roof tank (Baker, 2018)

#### 8.4.5 ETBE product stream storage tank

The ETBE is produced at a rate of 38 310 kg h<sup>-1</sup> and 1 250 m<sup>3</sup> per day. ETBE is not corrosive and the storage vessel can be made from carbon steel. ETBE undergoes a peroxidation reaction in the presence of oxygen or other oxidative compounds which occurs relatively slowly in normal storage conditions, but is enhanced by the presence of UV light (Association, 2006). ETBE is chemically stable and highly flammable. Association (2006) suggested the use of internal floating roof tanks for ETBE storage. The same tanks used for the ethanol and purge streams storage will be used for the ETBE, with the exception of construction material of the ETBE tanks being regular carbon steel.

On the basis of having enough storage space for a week's worth of ETBE production, a minimum of 8 750 m<sup>3</sup> is required. However, it will be assumed that the product will be removed from the plant daily *via* truck or railway. If the refinery is in a nearby proximity of the plant (1 km or less), a fraction or all of the ETBE can be transported *via* pipeline to be added to the petroleum products produced at the refinery. It is assumed that the

product is removed daily with a pipeline or every few days *via* road or rail transport. Therefore it was assumed that four days' worth of storage space would be sufficient for the storage of the ETBE product. In case of irregularities occurring during plant operation, extra storage will be included. A total of 6 000 m<sup>3</sup> of storage space will be allocated to the storage of ETBE. Due to the high flammability of ETBE, three internal floating roof tanks of 2 000 m<sup>3</sup> each will be used. The properties of these tanks can be found in Table 37. These tanks also need to be painted with a fire-resistant layer as a safety precaution.

**Table 37:** ETBE storage tanks parameters

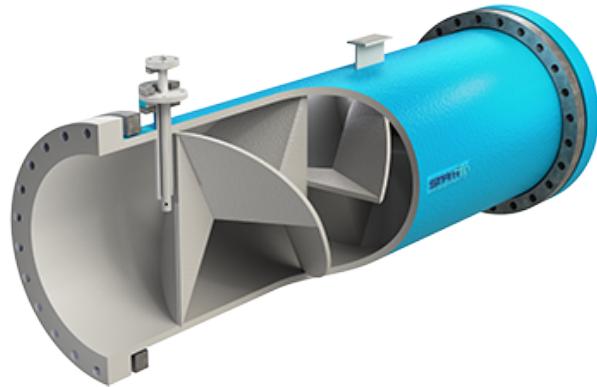
Parameter	Value
Product name	Chemical ethanol gasoline floating roof storage tank
Source	Alibaba.com
Construction material	Carbon steel/Stainless steel
Anti-corrosive	Yes
Capacity (m <sup>3</sup> )	2 000
Diameter (m)	12.84
Height (m)	15.92

#### 8.4.6 Purge and waste stream storage and disposal

Under normal operating conditions of the plant, the purge and waste streams amount to about 20 m<sup>3</sup> per day and 200 m<sup>3</sup> per day, respectively. These two streams contain different amounts of ETBE, ethanol, TBA and water. Due to these streams having the same components, it is assumed that these two streams can be stored in the same storage vessel. The contents of these two streams are considered to be hazardous waste and need to be removed *via* tank car or rail car. The waste product of these two streams is flammable and highly volatile. Therefore, it is of utmost importance that the waste product is stored appropriately. The waste product is also corrosive and needs to be stored in stainless steel storage vessels. It is assumed that the waste is removed from the plant every 3 – 5 days. Therefore, enough storage space for a week's worth of waste product will be allocated to ensure that there is enough storage space for the waste product during operational irregularities. Three 1 000 m<sup>3</sup> stainless steel internal floating roof storage tanks will be allocated to the storage of the waste product. The same tanks will be used for the waste product as is used for the ethanol feed storage tanks. The parameters of these tanks can be seen in Table 36.

## 8.5 Mixer selection and sizing

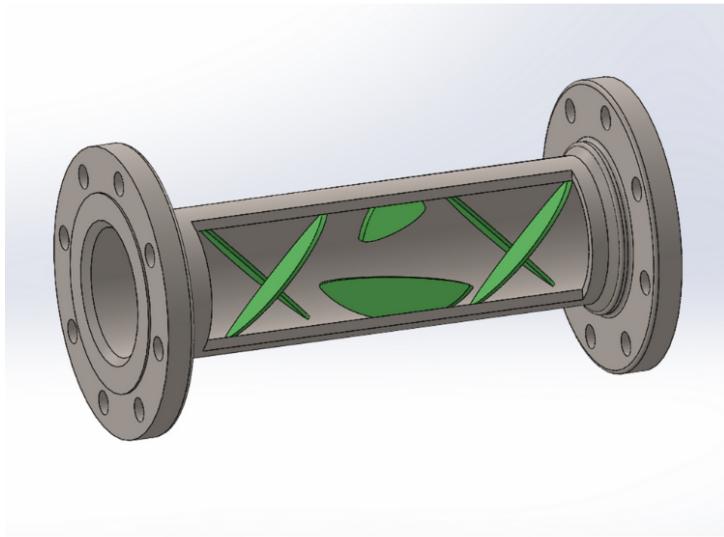
The mixers for this design will be static inline mixers. These mixers have no moving parts and form part of the pipeline through which the fluid travels. This allows for space saving and efficient mixing throughout the process. Static inline mixers rely on the fluid flow for mixing purposes. The static inline mixers are installed in the pipeline and normally has the same diameter as the process pipeline. The degree of mixing required in the streams determine the number and diameter of elements within the mixer. Static inline mixers can be made of stainless steel or carbon steel for industrial purposes. For this plant stainless steel static inline mixers will be used due to the corrosivity of ethanol and water. The mixers need to be designed based on the flow rates and the pipeline diameter. Static inline mixers are ideal for the high volumetric flowrates occurring in the production process of ETBE, due to its simplicity of design and customisable build. The use of static inline mixers result in a pressure drop over the mixer. However, the pressure drop through the mixer is determined by the process stream parameters and mixer diameter and length (Charles Ross & Son Company, 2018) and can therefore be accounted for when designing the piping and control valve system. Figure 15 shows an example of a conventional static inline mixer.



**Figure 15:** Example of a static inline mixer (Statiflo, 2020)

Low pressure drop static mixers are also an option. The low pressure drop static inline mixer from MXR (MXR Technologies, 2017) provides a 65 % lower pressure drop compared to conventional static inline mixers owing to its short mixing length. It is ideal for liquid-liquid and liquid-gas mixing and is reported as high performance mixer for the chemical and petrochemical industry. The pressure drop over the mixers need to be as low as possible to avoid the need for pumps in the system. The low pressure drop over

this mixer makes it an attractive option for mixing in this particular plant, due the elevated and precise high pressure operating conditions of this plant. The mixing elements of the low pressure drop static inline mixer is shown in Figure 16. These mixers will be used for the mixers in the plant and the sizing of the mixers is done with the design of the piping system due to the mixers being in the pipeline and the diameter and length of the mixers are dependent on the flow rates and process pipeline diameter.



**Figure 16:** Diagram of the MXR low pressure drop static mixer (MXR Technologies, 2017)

## 8.6 Valve selection

Most of the valves in the system are used to reduce the downstream pressure of the stream. Pressure reducing valves are typically used for this purpose, with their prime function being to reduce the pressure of the incoming stream to a set outlet pressure. These valves can be butterfly valves, globe valves, or any other type of valve that allows for the varying of flow through the valve (Stoneleigh Engineering Services, 2012). The globe type valves are a popular choice for the regulation of liquid and gas streams at high pressures and volumes. They are also ideal for systems where large pressure drops are required due to the large pressure drop occurring when the liquid passes through the non-linear path in the valve. Globe valves are also ideal for liquids with low viscosity's and can be manual or actuated (Projectmaterials, 2017).

Globe type pressure reducing valves are chosen for the process stream valves, because

they will mainly be used for the reduction of pressure (flow regulation). This decision was based on the viscosity's of the fluids being very low, and the high pressures and flow rates that need to be throttled. There are different types of body patterns/designs for globe valves. The standard or T-pattern has the highest pressure drop of all the patterns and is ideal for cases where throttling is the main focus of the valve. The angle pattern is used for streams that undergo pulsating flow and is ideal for pipe bends as it redirects the flow at a 90°angle. The oblique or Y-pattern reduces flow resistance of the globe valve, minimising the high pressure drops generally associated with globe valves. The seat and stem of the Y-pattern globe valve is at a 45°angle and is ideal for severe flow regulation applications.

The list of valves required in the system are listed below in Table 38. These will probably not be all the valves used in the process as a whole due to some valves being added during the process control aspect of the design. However, these are the main valves required for the process flow.

**Table 38:** Valve parameters

	V-101	V-102	V-103	V-104	V-105
Volumetric flow rate ( $\text{m}^3 \text{ h}^{-1}$ )	157.4	156.6	92.53	51.66	106.5
Pressure drop required (kPa)	300	500.0	600.0	899.0	899.0
Corrosive stream	No	Yes	No	No	Yes

The valves were sized according to a supplier's website Automation, n.d. which sized (and costed) automated globe valves depending on the flow rate and pressure drop experienced by each valve. Using this the valve relative sizes were found and summarised in Table 40 below.

**Table 39:** Valve sizes.

Valve	Size (inch)
V-101	4
V-102	4
V-103	8
V-104	8
V-105	8

## 8.7 Heat exchangers

For the heat exchangers, shell and tube heat exchangers were selected. This is due to the economic efficiency that shell and tube heat exchangers bring in comparison to alternative heat exchanger types (Yunus, 2019). The sizing for the heat exchangers followed procedure giving in (RK, 2005) and (Yunus, 2019).

The heat exchange area was calculated from Equation 36, using the log mean temperature difference method.

$$Q = U \times A_s \times \Delta T_{lm} \quad (36)$$

The log mean temperature is calculated from Equation 37 below:

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln(\frac{\Delta T_1}{\Delta T_2})} \quad (37)$$

where  $\Delta T_1 = T_{h,in} - T_{c,out}$  and  $\Delta T_2 = T_{h,out} - T_{c,in}$ , since cross-flow is assumed for the shell and tube heat exchanger. Following on from this, the calculation of  $U$  proceeds as shown in Equation 38, assuming the thermal resistance of the tube is negligible. This allows for the overall heat transfer coefficient to be calculated from the inner and outer thermal conductivity's respectively; considering fouling does not occur.

$$U \approx (\frac{1}{h_i} + \frac{1}{h_o})^{-1} \quad (38)$$

The Nusselt, Prandtl , Reynolds numbers and the heat transfer coefficient can then be calculated as shown in Equation 39, Equation 40, Equation 41 and Equation 42 with kinematic viscosity  $\mu$  in Pa s, linear velocity  $V$  in m s  $^{-1}$  and hydraulic diameter  $D_c$  in m.

$$Re = \frac{VD_c}{\nu} \quad (39)$$

with dynamic viscosity  $\mu$  in m $^2$  s  $^{-1}$ , heat capacity in W kg $^{-1}$  K  $^{-1}$  and  $k$  is the thermal conductivity W m $^{-1}$  K  $^{-1}$ .

$$Pr = \frac{\mu C_p}{k} \quad (40)$$

where  $n = 0.4$  for heating and  $n = 0.3$  for cooling of fluid

$$Nu = 0.023Re^{0.8}Pr^n \quad (41)$$

$$h = \frac{Nuk}{D_c} \quad (42)$$

**Table 40:** Heat exchanger sizing.

Heat exchanger	Area ( $m^2$ )
H <sub>1</sub>	232.0
H <sub>2</sub>	95.00
H <sub>3</sub>	7.000
H <sub>4</sub>	124.0
H <sub>5</sub>	264.0
H <sub>6</sub>	28.00
H <sub>7</sub>	87.00
H <sub>8</sub>	75.00
H <sub>9</sub>	3981
H <sub>10</sub>	309.0
H <sub>11</sub>	60.00
H <sub>12</sub>	5.00
H <sub>13</sub>	18.00
H <sub>14</sub>	224.0
C <sub>1</sub>	57.00
C <sub>2</sub>	22.00
C <sub>3</sub>	57.00

## 9 Process Costing, Economic Evaluation

Prior to equipment costing being carried out, the cost analysis for a bioethanol feedstock purity was done. This bioethanol feed selection made was based on a cost comparison and realisability of the feed. Comparison was made on purchasing highly pure ethanol (95 %) and relatively low purity ethanol (75 %). Since the production of ETBE involves side reactions using water as a reactant, increasing the water content in the ethanol increased the selectivity of the side reactions (Cunill *et al*, 1993). Therefore, to reduce this side

reaction selectivity (in the case of low purity ethanol) a cost would be considered for the separation to obtain a feed of at least 95 % bioethanol - the purer the ethanol feed implies the reduction in selectivity of side reactions involving water (Cunill *et al*, 1993). In the case of purchasing low purity bioethanol (75 %) the bioethanol will require purification, this was studied in depth by Bastidas & Gil (2010), with plant design taken for the year 2010. Therefore, 2010 and 2019 CEPCI values are 550.8 and 607.5, respectively (du Plessis, 2020b).

The cheapest purification method was evaluated by Bastidas & Gil (2010) to be extractive distillation using ethyleneglycol, which yielded a capital equipment cost of approximately \$2 000 000. Alternative purification involves implementation of molecular sieves, this comes at an estimated capital equipment cost of \$2 376 816. Furthermore, purification via LLE using cyclohexane is too possible and is estimated to have a capital equipment cost of \$3 000 000 (Bastidas & Gil, 2010). However, the feed to this separation process was 88.5 % bioethanol at  $300 \text{ m}^3 \text{ day}^{-1}$ . These separation methods are considered based on the fact that this is the method implemented to produce anhydrous ethanol in the USA and Brazil, the two largest ethanol producers (Bastidas & Gil, 2010). Therefore, prorating to  $452.13 \text{ m}^3 \text{ day}^{-1}$ , provides a rough capital equipment cost estimate of R40 000 000 for extractive distillation using ethyleneglycol and R47 000 000 for molecular sieve adsorption. Lastly, for cyclohexane LLE purification the equipment capital cost is approximated to be R60 000 000. For comparison purposes, it is assumed that this capital equipment cost will be an acceptably similar order of magnitude for a feed composition of 75 %.

The trade-off between the purchasing cost of 95 % bioethanol and the operating, maintenance and equipment cost of purifying a less pure bioethanol feed (75 %) is clear, based on calculated unacosts expected over the estimated plant life. It was decided that it would make more economical sense to opt to purchase a purified bioethanol feed.

## 9.1 Equipment cost

The total equipment cost was calculated in order to calculate the Fixed Capital Investment (FCI) using the Guthrie Method. The pieces of equipment that were considered to constitute the majority of the equipment cost are:

- Distillation columns
- Reactors

- Heat exchangers
- Storage vessels and tanks
- Valves
- Cooling towers
- Mixers
- Pumps

Costing for each piece of equipment was obtained from literature (Garrett, 2012; Loh, Lyons & White, 2002) where the capacity and year of the reference correlating to a cost, was noted. Scale up factors were used to account for the difference in capacity, year and exchange rate. The capacity of the piece of equipment was adjusted using Equation 43

$$P_1 = P_{ref} \left( \frac{C_1}{C_{ref}} \right)^a \quad (43)$$

where  $C_{ref}$  and  $C_1$  are the reference and required capacities respectively,  $P_{ref}$  and  $P_1$  are the prices of the equipment at the reference capacity and adjusted capacity respectively, and  $a$  is a size exponent that is specific to each piece of equipment. However, a fair assumption would be to use the *sixth tenths rule* (du Plessis, 2020a) for all size exponents, applicable in the chemical industry.

The Marshall and Stevens index was used to account for the inflation of the equipment which was cited at a certain year. The price was then adjusted using Equation 44.

$$P_2 = P_1 \left( \frac{CEPCI_2}{CEPCI_1} \right) \quad (44)$$

where  $CEPCI_2$  and  $CEPCI_1$  are the cost indices at the original year and current year respectively, and  $P_2$  is the price adjusted for capacity and year. The indices required for the proceeding calculations are shown in Table 41.

**Table 41:** Cost indices utilised for the adjustment of equipment cost to the current year

Year	Cost index
1989	391
2002	395.6
2019	607.5

Finally, the exchange rate of the equipment was also accounted for at the current year (2019). The exchange rate of the South African Rand to the United States Dollar was taken as 14.5 ZAR to 1 USD. This exchange rate was dated December 2019 due to unprecedented and unreliable fluctuations caused by the pandemic of COVID-19 (Pound-Sterling Live, 2019). All reference costs taken from Garrett (2012) and Loh *et al* (2002) where equipment was priced based on a carbon steel only equipment cost. The addition of stainless steel, for specific equipment, was accounted for in the latter part of this section.

The first equipment that was costed was the storage tanks, once knowing an estimate for the capacity of the storage tanks as well as specification of the type, pressure and temperature for the storage tank. Table 42 describes the adjusted price for the storage tanks, taking into account the number of storage tanks as well as the capacity, provided in Section 8. Important to note is that the C<sub>4</sub> and LPG storage tanks were priced directly from the manufacturer of the specific tanks ([alibaba.com](http://alibaba.com)).

**Table 42:** The equipment cost for the product and feed storage tanks for carbon steel only construction

Tank	Pressure kPa	Capacity Gallons	Price
Reference	101.325		\$200 000
Ethanol storage	101.325	264 200	R28 885 000
ETBE storage	101.325	528 400	R431 350
LPG storage	1500	1 056 800	R51 151 800
C <sub>4</sub> storage	1500	792 600	R17 050 600
Total			R115 851 000

The static inline mixers were sized and selected. The equipment cost for the mixers was taken directly from the manufacturer of the static inline mixers (indiamart, 2020). Table 43 shows the detailed adjusted equipment costing for carbon steel static inline mixers. There is a total of 3 mixers (M-101, M-102 and M-103).

**Table 43:** Equipment cost for the 3 static inline mixers constructed out of carbon steel only

Mixer	Price
Reference	R4 286
Total	R12 850

The adjusted price of the pumps were determined from a reference price and capacity, as shown in Table 44.

**Table 44:** The equipment cost for the pumps based on only carbon steel construction based on pump efficiency and capacity of the pump

Pump	Capacity (GMP)	Year	Price
Reference	700	2002	\$10 000
P-101	400	2019	R387 300
P-102	45	2019	R104 400
P-103	105	2019	R173 600
Total			R665 300

Similarly, the adjusted price was determined for the reactors, as shown in Table 45. The reactor costing was based of available literature equipment costing data (Garrett, 2012).

**Table 45:** The equipment cost for reactors based on carbon steel construction, based on reactor volume

Reactor	Capacity (L)	Year	Price
Reference	22 710	1989	\$24 000
R-101	303 000	2019	R2 559 000
R-102	10 623	2019	R342 700
Total			R2 901 800

The cost of the cooling tower was also calculated in Table 46.

**Table 46:** The cost of the cooling tower based on the flow rate of water through the tower for carbon steel construction

Tower	Capacity (GMP)	Year	Price
Reference	3000	2002	\$50 000
Cooling Tower	1265	2019	R663 200
Total			R663 200

The cost of the distillation column were obtained based on the operating pressure, number of stages, diameter and height, as described in Section 8. The reference price of the columns were obtained from Loh *et al* (2002) in the year 2002. The total cost of the distillation columns are shown in Table 47. A pressure factor of 1.631 was used to determine the cost of T-101 which operates at a pressure of 1 500 kPa (Garrett, 2012). This T-101 was the only column which needed a pressure factor adjustment as the other columns run at pressures that align with literature pressures given in Loh *et al* (2002). The type of distillation column chosen was the sieve tray column as this was determined to best fit the petroleum separations required for the design.

**Table 47:** The distillation column equipment cost for of carbon steel construction, based of the number of trays and column diameter

Column	Pressure (psig)	Plates	Diameter (m)	Adjusted price
T-101	150	15	3.22	R7 263 400
T-102	15	16	2.69	R2 783 350
T-103	150	21	3.45	R6 234 700
T-104	15	12	4.44	R5 566 700
T-105	15	8	1.54	R1 319 700
Total				R20 430 000

The valves were sized in Section 8. A supplier (Automation, n.d.) was contacted and the necessary parameters to size the valves communicated. Upon evaluation, the valves were

sized and the related costs calculated on the supplier's website. The valves obtained were fully automated and could be controlled electronically.

**Table 48:** Costing of valves

Valve	Size (inch)	Price
V-101	4	R221 000
V-102	4	R221 000
V-103	8	R300 000
V-104	8	R300 000
V-105	8	R300 000
Total		R1 342 000

Finally, the heat exchangers were costed. The detailed cost breakdown of the heat exchangers is provided in Table 49. The heat exchanger costing was based off the HEN developed in Section 7 and the sizing calculated for the heat exchangers in Section 8.

**Table 49:** Cost for the heat exchangers based on the area of heat exchange

Heat exchanger	Area m <sup>2</sup>	Adjusted price
1	232	R45 000
2	95	R26 000
3	7	R5 240
4	124	R30 640
5	264	R48 120
6	21	R10 670
7	87	R24 740
8	75	R22 560
9	3981	R245 200
10	309	R52 880
11	60	R19 770
12	5	R4 300
13	18	R9 500
14	16224	R43 630
15	57	R19 200
16	22	R10 720
17	57	R19 130
Total		R636 960

The equipment costs calculated above were based on equipment constructed from carbon steel. Most of the process equipment is subject to corrosion due to the components involved in the process. Thus, stainless steel is required for a majority of the equipment. Cost factors were used to calculate the cost of the equipment where stainless steel would be used as the material of construction. The factors used to determine the additional cost for the stainless steel used to manufacture the equipment containing corrosive compounds

is shown in Table 50.

**Table 50:** Factors used to determine the additional cost of the stainless steel (du Plessis, 2020a; Garrett, 2012)

Equipment	Factor
Pumps	1.7
Heat exchangers	2.86
Reactors	1.7
Other	2.8

It is important to note that not all the equipment needs to be constructed from stainless steel. The following pieces of equipment would, therefore, need to be constructed out of stainless steel 304:

- The seven ethanol storage tanks
- All of the heat exchangers
- All of the columns excluding T-101
- The cooling tower
- All of the pumps excluding P-101
- Valves V-102 and V-103
- Both reactors (R-101 and R-102)
- All mixers

Once the carbon steel equipment cost was obtained, the stainless steel factors provided in Table 50 were used to determine the cost of construction if the plant was built entirely out of stainless steel 304. The additional cost, therefore, was then calculated by taking the stainless steel cost for plant construction minus the cost of carbon steel plant construction. The total equipment cost is shown in Table 52 where the additional cost of stainless steel was calculated:

**Table 51:** Total equipment cost for carbon steel

Equipment	Cost for CS	Additional for SS
Distillation columns	R23 239 800	R28 757 600
Heat exchangers	R636 960	R1 184 750
Reactors	R2 901 800	R1 934 550
Pumps	R665 340	R194 600
Storage vessels & tanks	R115 851 040	R53 726 200
Valves	R1 342 000	R364 700
Cooling towers	R663 200	R1 193 750
Mixers	R12 850	R23 140
Total	R145 313 100	R87 379 400

## 9.2 Total fixed capital investment

The fixed capital investment was determined using the Guthrie method for a chemical processing plant (du Plessis, 2020a). This is shown in Table 52.

**Table 52:** Calculation of FCI using the Guthrie method

Equipment	E	100	R145	313	100
Additional material		62.2	R90	384	700
Pipework	32				
Concrete	8.9				
Steel	1.7	m			
Instrumentation	7.3				
Electricity	8.3				
Insulation	3.4				
Paint	0.6				
Total material costs	E + m	M	162.2	R235	697 800
Labour	0.36(M)	L	58.4	R84	851 200
	M + L		220.6	R320	550 000
Indirect costs	0.34(M+L)		75	R108	987 000
Sub total			265.6	R429	535 750
Additional					
	Stainless Steel		87 379	400	
Total			R516	915	100
Contingency allowance + contractors fee (18 %)	53.2		R93	045	000
Total		348.8	R609	959	800

### 9.3 Miscellaneous costs

As described in Section 8, mass of catalyst required per year is 169 600 kg. Amberlyst-15 and S-54 are used for reactor 1 and reactor 2 respectively. Amberlyst-15 and S-54 are used in a mass of 163 620 kg and 5 949 kg respectively. Amberlyst 15 constitutes the majority of the catalyst, and S-54 is a similar catalyst to Amberlyst-15 which is a product

of China. Therefore, the price of Amberlyst-15 will be used for the total catalyst mass required. The price of Amberlyst-15 is taken as \$5 per kg. Therefore, the cost of the catalysts is \$848 000 or R11 872 000.

The plant would be run throughout the year with a downtime of 10 days, thus 350 days a year. Based on this time frame of operation, the total plant production was calculated. Table 53 details how the total plant production on a yearly basis was calculated. Following this, the selling and feedstock was normalised against the annual production rate provided in Table 53. This therefore allowed the selling price to be normalised as provided in Table 55. The unit price for ETBE was taken from Zacharakis & Glystra (2020), while a price for the C<sub>3</sub> LPG product was inferred from Fuel Retailers Association (2020). Additionally, the C<sub>4</sub> separated product was estimated to have a market price similar to that of the price for a general C<sub>4</sub> mixture (Salem, 2017). Given the composition of the C<sub>4</sub> product stream (Section 3), this value for the C<sub>4</sub> mixture is a fair estimate. Finally the 71 % wt ethanol fuel mixture will be dissolved into the fuel market at reasonable prices detailed by Insider (2019).

**Table 53:** Total plant production rate per annum.

Product	Production rate (ton per hour)	Total production (ton per annum)
ETBE	38.3	321 720
71 wt % ethanol fuel mixture	6.85	57 540
C <sub>3</sub> LPG	73.6	318 240
Total		1 404 240

**Table 54:** Product compounds with the market price of the individual product and amount of compound produced

Product	Unit cost (Rton <sup>-1</sup> )
ETBE	13 900
71 wt % ethanol fuel mixture	7000
C <sub>4</sub> Raffinate-2	6670
C <sub>3</sub> LPG	360

Additional to the product costing is the feed costing. It was assumed that the feedstock cost would only consist of the cost of bioethanol. The isobutene feedstock is assumed to originate from a FCC cut produced in an upstream plant operation. Therefore, the cost of the isobutene feed is assumed negligible. The cost of bioethanol (95 %) was taken from alibaba.com as R17 400 per ton of bioethanol. The feed rate of the bioethanol was established in Section 6 as 23.6 ton hr<sup>-1</sup>. Knowing this, the total annual bioethanol requirement was calculated knowing that the plant has a down time of 10 days. The total tonnage of bioethanol requirement (198 240 ton per annum) was then used to calculate an annual cost of the bioethanol. This annual cost was then normalised using the annual production tonnage of 1 404 278. Table 55 details the final feedstock cost as well as the selling price of product based on the plant production tonnage.

**Table 55:** The feedstock cost and product selling price normalised per ton production

Product	Price (Rtonne <sup>-1</sup> )
Product	5562
Feedstock	2461

The utilities were calculated based on the cooling water utilities of the plant. As discussed in Section 7, the cooling water utility is 668 kW. Furthermore, the cooling water requirements of both reactors is 4336 kW in total. Therefore, the total cooling utility is

5004 kW. As shown in the heat exchanger network design, there is no steam utility for the plant as the maximum energy recovery was met. The cost of electricity is taken as 107 c per kW h (Writer, n.d.). Therefore, the total utility cost is R39 285 000 per year.

## 9.4 Running costs

The fixed and variable costs were calculated using heuristics from du Plessis (2020a). This method is used to calculate the production cost which is used to determine the total fixed cost, expressed as a price per annum, and a variable cost expressed as a price per tonne. The proceeding calculations were based on the calculated FCI and selling price per tonne as determined in Table 55. The utilities and catalyst costs have also already been calculated.

The production cost expressed as a price per tonne will be assumed to be a variable X. The direct production cost was calculated based on appropriate fractions of the FCI or production cost (X). The fixed production cost was calculated using Table 56, Table 57, and Table 58:

**Table 56:** Direct production cost

Type	Category	Description	Cost f(X)	Cost
Var	Feedstock material	R2461 tonne <sup>-1</sup>		R3 455 836 000
Fix	Operating labour	15 % of production	0.15(X)	
Fix	Direct supervision	15 % of labour	0.15(0.15)(X)	
Var	Utilities	18 % of production		R39 285 000
Fix	Maintenance	6 % of FCI		R36 600 000
Fix	Consumables	15 % of maintenance		R5 490 000
Fix	Lab fees	10 % of labour	0.10(0.15)(X)	
Var	Patents & Royalties	4 % of production	0.04(X)	
Var	Catalysts & solvents			R12 290 000
Subtotal			0.2275(X)	R3 550 000 000

**Table 57:** Fixed production cost

Type	Category	Description	Cost
Fix	Depreciation		R60 996 000
Fix	Local tax	2 % of FCI	R12 200 000
Fix	Insurance	1 % of FCI	R7 625 000
Subtotal			R80 820 000

The plant overhead costs are based on the cost of labour, supervision and maintenance. The plant overhead costs are assumed to constitute 50 % of the totals of these 3 costs (du Plessis, 2020a). The total was used to calculate the production cost, as shown in Table 58

**Table 58:** Plant overhead costs

Type	Category	Cost f(X)	Cost
	Labour	0.15(X)	
	Supervision	0.0225(X)	
	Maintenance		R36 600 000
	Sub total	0.1725(X)	R36 600 000
Fix	Overhead cost	0.08625(X)	R18 300 000
Total		0.31375(X)	R3 650 000 000

Accordingly, the production cost is calculated using Equation 45 below:

$$X = 0.31375(X) + 3727708000 \quad (45)$$

The production cost X was calculated to be R5 315 945 000 tonne<sup>-1</sup>. The general costs were calculated based on the cost of labour and the sales income. The sales income was

calculated based on the annual production rate in tonnes per annum and the selling price per tonne, as discussed in Section 9.3. The general costs are shown in Table 59

**Table 59:** General costs

Type	Category	Description	Cost
Fix	Administration	5 % of labour	R398 750 000
Var	Local tax	7 % of sales	R546 750 000
Var	Research & development	2 % of sales	R156 213 000
	Sub Total		R110 170 000
	Production + general		R6 418 500 000
Fix	Contingency allowance	5 % of Production + general	R320 900 000

Finally, the total fixed running costs were calculated based on the production costs ( $X$ ) and the remaining fixed costs, as shown in Table 60.

**Table 60:** Total fixed costs

Category	Cost
Operating labour	R797 513 000
Direct supervision	R119 630 000
Maintenance	R36 600 000
Consumables	R5 490 000
Lab fees	R79 750 000
Depreciation	R60 996 000
Local tax	R12 200 000
Insurance	R7 625 000
Plant overhead costs	R18 300 000
Administration cost	R398 750 000
Research & development	R156 213 000
Contingency allowance	R320 900 000
Total	R3 650 000 000

Similarly, the total variable costs were calculated, as shown in Table 61.

**Table 61:** Total variable costs

Category	Cost
Feedstock material	R3 455 836 000
Utilities	R39 285 000
Patents & royalties	R212 267 000
Catalyst & solvents	R12 290 000
Distribution & marketing	R546 747 000
Total	R4 254 540 000

The total variable costs should be expressed as a price per tonne. The variable cost was calculated to be R3030 per tonne.

The variable and fixed costs were utilised to develop a cash flow table for the plant in Section 9.5.

## 9.5 Cash flow

A construction time for the plant was estimated as two years. This was decided upon based on a 15 month construction period of a similarly sized power plant at Sasol (Technology, n.d.). The lifetime of the plant will be assumed to be 10 years. After a period of 10–15 years, even if a plant continues with production, chemical processing plants undergo renovation due to developments in technology (du Plessis, 2020a). Therefore, the time of erection the plant will be taken as 2 years, and the total time of production as 10 years.

The working capital for a chemical plant can be estimated based on 10 %–20 % of the fixed capital investment. Consequently, the working capital will be calculated based on 15 % of the FCI and then expressed as price per tonne, as shown below:

$$WC = 0.15(R607 567 000) = R3 846 699 \text{ per year}$$

$$WC = R \frac{3\ 847\ 000/year}{319200tonne/year} = R91\ 135\ 000 per tonne$$

The production rate will reach maximum capacity in the third year of production. In the first and second year of production it will be assumed that the plant can achieve 50 % and 75 % respectively of the total production capacity. The plant will maintain a maximum production rate until the end of its lifetime. It is assumed that Natref will continue production after this theoretical lifetime, and will undergo renovation instead of selling the plant.

It is assumed that there will be no salvage value at the end of the plant lifetime. It is expected that Natref will only undergo renovation. The depreciation was calculated using the straight line method as this is more conservative. Furthermore, depreciation rates for a fixed percentage method would vary depending on the entity and finance organisation. Therefore the depreciation was calculated using Equation

$$\text{Depreciation} = \frac{FCI - \text{salvage}}{\text{lifetime}} \quad (46)$$

The depreciation was calculated as R60 756 700 per year. In South Africa, corporate income tax is 28 % which will be used for the calculation of the cash flow (SARS, 2020). SASOL's financial statement, published on June 30<sup>th</sup> 2019 reported that their interest rates range from 2 % to 12 %. Therefore, the upper bound of 12 % will be used. The cash flow of the ETBE plant was calculated using the following parameters, reported in Rmillion. It is assumed that half the FCI will be spent in the first year of construction, and the balance at the end of the second year. It is assumed that Natref will operate at 60 % of the maximum capacity in the first year, 80 % of the maximum production in the second year and at total capacity for the remaining 8 years. The cash flow table is shown in Table 62. The values in Table 62 and Table 63 are given in units of R1 000 000 (million rands). The table headings provided are abbreviated for convenience. However, below is a list of the heading associated with the abbreviation:

- Fixed – Fixed cost
- Variable – Variable cost
- Dep. – Depreciation
- PbT – Profit before tax
- PaT – Profit after tax

- WC – Working capital
- FCI – Fixed capital investment
- CF – Cash flow
- CCF - Cumulative cash flow
- DCF – Discounted cash flow
- DCCF – Discounted cumulative cash flow

Therefore, from Table 62 it can be seen that the payback period for the plant will be 4 years. This is the period it takes for the cumulative cash flow to go from making a loss to making a profit. Once the cash flow table as shown above is complete further cost analysis can begin. The important parameter when performing costs analyses is the Internal Rate of Return (IRR). Table 63 shows a cost analysis for the design. Where the CDCF at each specific IRR percentage has the net present value (NPV) given in the last value of the column, corresponding to the specific IRR. Table 63 shows that at an IRR of 68 % the NPV for the design is zero. Additionally, using SASOL's 12 % provides an  $NPV = R3\ 478\ 000\ 000$ .

**Table 62:** Cash flow table

Year	Production	Income	Fixed	Variable	Dep.	PbT	Tax	PaT	WC	FCI	CF	CCF
1										304.98	-304.98	-304.98
2										304.98	-304.98	-609.96
3	842567	4686.4	2013.99	2552.72	61.00	58.69	16.43	103.25	54.90		48.36	-561.60
4	1123422	6248.53	2013.99	3403.63	61.00	769.92	215.58	615.34	18.30		597.04	35.43
5	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	18.30		1109.12	1144.55
6	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	0.00		1127.42	2271.97
7	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	0.00		1127.42	3399.39
8	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	0.00		1127.42	4526.80
9	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	0.00		1127.42	5654.22
10	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	0.00		1127.42	6781.64
11	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	0.00		1127.42	7909.06
12	1404278	7810.67	2013.99	4254.54	61.00	1481.14	414.72	1127.42	-91.49	0	1218.91	9127.97

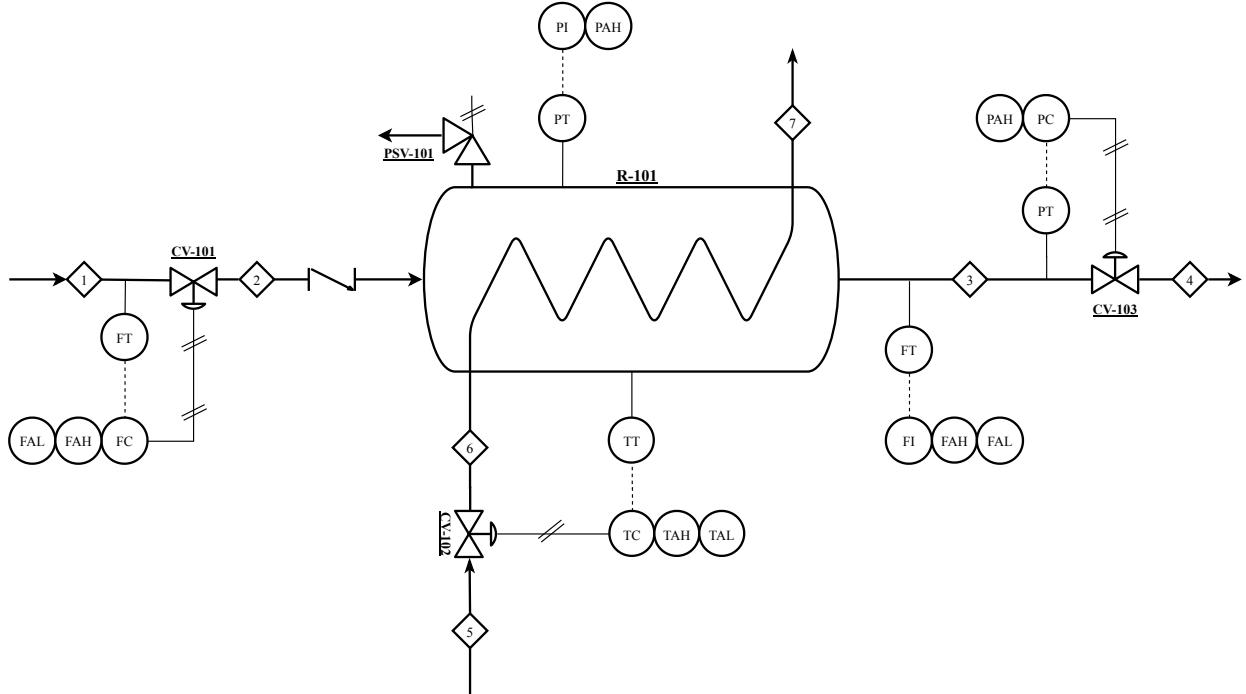
**Table 63:** The cash flow based on a sensitivity analysis of the IRR

Year	CF	CCF	DCF@12 %	CDCF@12 %	DCF@40 %	CDCF@40 %	DCF@68 %	CDCF@68 %
1	-304.98	-304.98	-272.30	-272.30	-217.84	-217.84	-181.65	-181.65
2	-304.98	-609.96	-243.13	-515.43	-155.60	-373.44	-108.19	-289.84
3	48.3566	-561.603	34.42	-481.01	17.62	-355.82	10.22	-279.63
4	597.036	35.4332	379.43	-101.58	155.41	-200.41	75.14	-204.49
5	1109.12	1144.55	629.34	527.76	206.22	5.81	83.14	-121.35
6	1127.42	2271.97	571.18	1098.94	149.73	155.55	50.34	-71.01
7	1127.42	3399.39	509.99	1608.93	106.95	262.50	29.98	-41.03
8	1127.42	4526.8	455.35	2064.27	76.39	338.89	17.86	-23.17
9	1127.42	5654.22	406.56	2470.83	54.57	393.46	10.64	-12.54
10	1127.42	6781.64	363.00	2833.83	38.98	432.44	6.33	-6.20
11	1127.42	7909.06	324.11	3157.94	27.84	460.28	3.77	-2.43
12	1218.91	9127.97	312.86	3470.80	21.50	481.78	2.43	0.00

## 10 HAZOP

A hazard and operability study (HAZOP) is a method used to acutely dissect the manageability of a selected process; while identifying possible hazards or operational issues that may originate from the specified process (Sinnott & Towler, 2019).

A HAZOP study was conducted on a selected section of the process, the primary reactor, its inlet and outlet streams and the cooling water system as shown by the Figure 17.



**Figure 17:** P&ID over the primary reactor

Given that the reactions required in this process are exothermic, a cooling system is required to keep the reactor isothermal and prevent the excess energy energy of the reaction to build up. This is essential in that should the reactor temperature increase, the rate of reaction will increase along with the heat generation rate which could result in a runaway reaction (Seider *et al*, 2009). Furthermore, this runaway reaction could lead to an increase in the pressure of the reactor vessel which may lead to ruptures (Crowl & Louvar, 2001). The addition of a control valve to regulate the flow of cooling water such that the temperature of the reactor is controlled is vital (Crowl & Louvar, 2001).

The HAZOP was conducted over the cooling water system applied to the reactor, see Tables 64, 65, 66, 67, 68.

From this HAZOP section possible process modifications which were found to be necessary included:

- The fitting of high temperature alarms to warn of possible runaway reactions occurring in the event of a failed cooling operation.
- The fitting of check valves required for basic flow control in the cooling lines such that reverse flow is prevented (Crowl & Louvar, 2001).
- The installation of a high temperature alert shutdown system to shutdown the process in the case of a high temperature in the reactor. This temperature would ideally be set higher than the temperature set for the alarm system such that the operator is able to attempt to restore the required cooling before having to shutdown the process (Crowl & Louvar, 2001).
- Regular examination of the condition of the cooling coils.
- Fitting of a flow meter for the cooling water as well as an alarm system for low levels of flow in the cooling water. This is essential for an early indication of reduced cooling.
- Inspection of the source of the cooling water to ensure no contamination is present as well as no interruptions have occurred.

**Table 64:** HAZOP study on the primary reactor cooling water system

Study title:		Primary reactor			Page:	1 of 21
Part considered:		Reactor cooling water coil system			Date:	13/09/2020
Design intent:		A cooling water system to keep the reactor isothermal				
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
5,6	NO	Flow	No flow	<ul style="list-style-type: none"> <li>Control valve fails closed.</li> <li>Control valve is closed.</li> </ul>	<ul style="list-style-type: none"> <li>Loss of cooling, possible runaway reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Select valve to fail open.</li> <li>Install cooling water flow meter and low flow level alarm.</li> </ul>
5,6				<ul style="list-style-type: none"> <li>Plugged cooling coils.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install high temperature alarm to alert operator.</li> </ul>
5,6				<ul style="list-style-type: none"> <li>Cooling water service failure.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Review the water service and its reliability.</li> </ul>
5,6				<ul style="list-style-type: none"> <li>Controller fails and closes valve.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure this controller is listed on the critical instrumentation list.</li> </ul>
5,6				<ul style="list-style-type: none"> <li>Air pressure fails resulting in a closed valve.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Select valve to fail open.</li> </ul>

**Table 65:** HAZOP study on the primary reactor cooling water system continued

					Page:	2 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
5,6	HIGH	Flow	High Flow	<ul style="list-style-type: none"> <li>Control valve fails open.</li> </ul>	<ul style="list-style-type: none"> <li>Cooled reactor, concentration of the reactant would build up and hence a runaway scenario is possible.</li> </ul>	<ul style="list-style-type: none"> <li>Instruct operators and update procedures.</li> </ul>
5,6				<ul style="list-style-type: none"> <li>Controller fails - and control valve is opened.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure this controller is listed on the critical instrumentation list.</li> </ul>
5,6	LOW	Flow	Low Flow	<ul style="list-style-type: none"> <li>Cooling line partial blockage.</li> </ul>	<ul style="list-style-type: none"> <li>Cooling in reactor reduced, possible runaway exothermic reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Install cooling water flow meter and low flow level alarm.</li> </ul>
5,6				<ul style="list-style-type: none"> <li>Water source partial failure.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install cooling water flow meter and low flow level alarm.</li> </ul>
5,6				<ul style="list-style-type: none"> <li>Control valve fails to respond.</li> </ul>	<ul style="list-style-type: none"> <li>Cooling reduced, runaway reaction possible.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure valve is placed on crucial instrumentation list.</li> </ul>

**Table 66:** HAZOP study on the primary reactor cooling water system continued

					Page:	3 of 21
Design intent:		A cooling water system to keep the reactor isothermal				
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
5,6, 7	AS WELL AS	Flow	Other flow	• Contamination of the water supply.	• Reduced cooling ability.	• Routine checks on cooling water system.
5,6				• Cooling water leaks, reactor pressure lower than the coil pressure.	• Reactants and products diluted in reactor. • Ruined products. • More volume taken up in reactor.	• Install high level flow and pressure alarm. • Ensure proper relief valves are installed. • Check maintenance procedure and schedule.
5,6,7				• Reactor product leaks into coils: reactor pressure greater than coil pressure.	• Product will be lost to the coils. • Lower product yield. • Cooling ability of cooling water system reduced. • Possible contamination of cooling water supply.	• Verify maintenance procedures and schedule. • Include an upstream check valve in the cooling water source.
5,6	PART OF	Flow	Covered under Low flow			

**Table 67:** HAZOP study on the primary reactor cooling water system continued

					Page:	4 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
5,6,7	REVERSE	Flow	Reverse flow	<ul style="list-style-type: none"> <li>Water flow failure which would lead to backflow.</li> </ul>	<ul style="list-style-type: none"> <li>Loss of cooling. Possible runaway exothermic reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Install cooling water flow meter and low flow level alarm.</li> </ul>
				<ul style="list-style-type: none"> <li>High back-pressure resulting in backflow.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install a check valve.</li> </ul>
5,6,7	OTHER THAN	Flow	Flow from other source.	<ul style="list-style-type: none"> <li>Another material other than cooling water or reactor contaminant is found.</li> </ul>	<ul style="list-style-type: none"> <li>Reduced cooling, possible runaway reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Isolate the cooling water source from other contaminants.</li> </ul>
			Flow from other source	<ul style="list-style-type: none"> <li>Backflow from sewer.</li> </ul>	<ul style="list-style-type: none"> <li>As above</li> </ul>	<ul style="list-style-type: none"> <li>Install a check valve to prevent backflow.</li> </ul>
5,6	SOONER THAN	Flow	Flow occurs sooner than planned	<ul style="list-style-type: none"> <li>Cooling may begin earlier than planned.</li> </ul>	<ul style="list-style-type: none"> <li>None</li> </ul>	
5,6	LATER THAN	Flow	Flow occurs later than expected.	<ul style="list-style-type: none"> <li>Operator error.</li> </ul>	<ul style="list-style-type: none"> <li>Rise in temperature resulting in a possible runaway reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure an interlock between the cooling flow and the feed of the reactor.</li> </ul>

**Table 68:** HAZOP study on the primary reactor cooling water system continued

					Page:	5 of 21
Design intent:		A cooling water system to keep the reactor isothermal				
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
TEMPERATURE						
6	LOW	Temperature	Decreased temperature.	<ul style="list-style-type: none"> <li>Low temperature of cooling water supply.</li> </ul>	<ul style="list-style-type: none"> <li>None - handled by controller.</li> </ul>	<ul style="list-style-type: none"> <li>None</li> </ul>
6	HIGH	Temperature	Increased temperature.	<ul style="list-style-type: none"> <li>Water supplied has high temperature.</li> </ul>	<ul style="list-style-type: none"> <li>The capacity of the cooling system is restricted resulting in a rise in temperature.</li> </ul>	<ul style="list-style-type: none"> <li>Install a high temperature alarm and or a high flow alarm.</li> </ul>
PRESSURE						
5,6	HIGH	Pressure	High pressure of cooling water in coils.	<ul style="list-style-type: none"> <li>Flow rate and size of piping as well as a possible pump required to pump the cooling water may lead to increased pressure.</li> </ul>	<ul style="list-style-type: none"> <li>May cause ruptures in the coils, damage the pump, pipelines and coils.</li> </ul>	<ul style="list-style-type: none"> <li>Monitor pressure of reactor with control system, have emergency shutdown plans available.</li> </ul>
5,6	LOW	Pressure	Low pressure of cooling water in coils.	<ul style="list-style-type: none"> <li>Pump supplying the cooling water is doing so under too low a pressure.</li> </ul>	<ul style="list-style-type: none"> <li>Reduced flow of cooling water, slower flow, may lead to reduced cooling efficiency and possible runaway reaction.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>

Another section considered was the reactor inlet stream and reactor itself. Tables 69,70, 71, 72, 73, 74, 75, 76, 77, 78, 79 cover the HAZOP for the reactor and its inlet stream.

From this study the primary process modifications to consider included:

- The fitting of high temperature alarms to warn of possible runaway reactions occurring in the event of a failed cooling operation or increased feed temperature.
- The fitting of check valves required for basic flow control in the cooling lines such that reverse flow is prevented (Crowl & Louvar, 2001) and no runaway reaction takes place.
- Controllers and control valves in place to prevent the excessive flow of reactant and hence the potential of a runaway reaction occurring.
- Flow meters for the reactant feed to monitor and prevent the above-mentioned scenario.
- The installation of relevant thermocouples and temperature transmitters to prevent the excessive heat generation of a runaway exothermic reaction. Furthermore, to prevent the damage and deactivation of the catalyst.
- The fitting of low temperature, level and pressure alarms to warn of unwanted reaction conditions that favour side reactions.
- Similarly, the fitting of high pressure, level and temperature alarms which is necessary to prevent runaway reactions and explosions.
- Routine checks on cooling water system and catalyst activity.

**Table 69:** HAZOP study on the primary reactor and feed stream

Study title:		Primary reactor			Page:	6 of 21
Part considered:		Reactor, reactant inlet feed streams			Date:	13/09/2020
Design intent:		To ensure safe and efficient operation of the primary reactor				
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
2	NO	Flow	No flow of reactant feed.	<ul style="list-style-type: none"> <li>Control valve fails closed.</li> <li>Control valve is closed.</li> </ul>	<ul style="list-style-type: none"> <li>No reactant fed to reactor, no product produced.</li> </ul>	<ul style="list-style-type: none"> <li>Select valve to fail open.</li> <li>Install low flow meter alarm for the feed stream.</li> </ul>
1,2				<ul style="list-style-type: none"> <li>Blockage in feed pipelines.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install low flow meter alarm for the feed stream.</li> </ul>
2				<ul style="list-style-type: none"> <li>Controller fails and closes valve.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure this controller is listed on the critical instrumentation list.</li> </ul>
2				<ul style="list-style-type: none"> <li>Air pressure fails resulting in a closed valve.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Select valve to fail open.</li> </ul>

**Table 70:** HAZOP study on the primary reactor and feed stream continued

					Page:	7 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
1,2	HIGH	Flow	High Flow	<ul style="list-style-type: none"> <li>Control valve fails open.</li> </ul>	<ul style="list-style-type: none"> <li>Excessive flow of reactant into the reactor, may result in spike in temperature and runaway reaction if the cooling water is unable to control it.</li> </ul>	<ul style="list-style-type: none"> <li>Instruct operators and update procedures. May need to shutdown process.</li> </ul>
1,2				<ul style="list-style-type: none"> <li>Controller fails - and control valve is opened.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure this controller is listed on the critical instrumentation list.</li> </ul>
1,2	LOW	Flow	Low Flow	<ul style="list-style-type: none"> <li>Feed delivery line partial blockage.</li> </ul>	<ul style="list-style-type: none"> <li>Feed to reactor reduced and hence formation of product reduced.</li> </ul>	<ul style="list-style-type: none"> <li>Install flow meter and low flow level alarm in feed stream.</li> </ul>
1				<ul style="list-style-type: none"> <li>Ethanol source failure.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install flow meter and low flow level alarm.</li> </ul>
1				<ul style="list-style-type: none"> <li>Isobutene source failure.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>
1,2				<ul style="list-style-type: none"> <li>Control valve partially shut or fails to respond.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>

**Table 71:** HAZOP study on the primary reactor and feed stream continued

					Page:	8 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
2	LOW	Flow	Low flow of reactant feed into reactor.	<ul style="list-style-type: none"> <li>Control valve fails to respond.</li> </ul>	<ul style="list-style-type: none"> <li>Feed to reactor reduced and hence formation of product reduced.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure valve is placed on critical instrumentation list.</li> </ul>
1,2	AS WELL AS	Flow		<ul style="list-style-type: none"> <li>Other streams contaminate the flow of the reactant.</li> </ul>	<ul style="list-style-type: none"> <li>Not applicable.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>
1,2	PART OF	Flow	Covered under low flow.			
1,2	REVERSE	Flow	Reverse flow.	<ul style="list-style-type: none"> <li>Feed stream flow failure resulting in backflow.</li> </ul>	<ul style="list-style-type: none"> <li>Loss of reactant fed to reactor hence no formation of desired product.</li> </ul>	<ul style="list-style-type: none"> <li>Install flow meter and low flow level alarm.</li> </ul>
1,2				<ul style="list-style-type: none"> <li>High back-pressure of feed stream resulting in backflow.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install a check valve.</li> </ul>

**Table 72:** HAZOP study on the primary reactor and feed stream continued

					Page:	9 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
1,2	OTHER THAN	Flow	N/A			
1,2	SOONER THAN	Flow	Flow of reactant occurs sooner than planned.	<ul style="list-style-type: none"> <li>Reactant is fed earlier than planned.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>
1,2	LATER THAN	Flow	Flow of reactant occurs later than expected.	<ul style="list-style-type: none"> <li>Operator error.</li> </ul>	<ul style="list-style-type: none"> <li>Delayed production of required product.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure an interlock between the cooling flow and the feed of the reactor.</li> </ul>
VOLUME						
R-101	LESS THAN	Volume	Not enough volume in reactor.	<ul style="list-style-type: none"> <li>Build up of materials in reactor would result in decreased reactor volume.</li> </ul>	<ul style="list-style-type: none"> <li>Reaction kinetics are affected, making the reaction outcomes unpredictable.</li> <li>Change in reactor pressure.</li> </ul>	<ul style="list-style-type: none"> <li>Clean reactor often and check for build up.</li> <li>Monitor the pressure of the reactor have emergency shutdown procedure set up.</li> </ul>
R-101	MORE THAN	Volume	More volume than required.	<ul style="list-style-type: none"> <li>Not applicable.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>

**Table 73:** HAZOP study on the primary reactor and feed stream continued

					Page:	10 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
TEMPERATURE						
6	LOW	Temperature	Decreased temperature	<ul style="list-style-type: none"> <li>Low temperature of cooling water supply.</li> </ul>	<ul style="list-style-type: none"> <li>None - handled by controller.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>
2				<ul style="list-style-type: none"> <li>Reactant feed stream temperature too low.</li> </ul>	<ul style="list-style-type: none"> <li>Reaction kinetics are affected making the reaction unpredictable.</li> <li>Reactor pressure may also change.</li> <li>Catalyst activity may be reduced.</li> </ul>	<ul style="list-style-type: none"> <li>Add thermal control jacket to reactor.</li> <li>Monitor reactor temperature, have emergency shutdown procedure in place.</li> <li>Same for pressure.</li> </ul>
6	HIGH	Temperature	Increased temperature	<ul style="list-style-type: none"> <li>Water supplied has high temperature.</li> </ul>	<ul style="list-style-type: none"> <li>The capacity of the cooling system is restricted resulting in a rise in temperature.</li> </ul>	<ul style="list-style-type: none"> <li>Install a high temperature alarm and or a high flow alarm.</li> </ul>
2				<ul style="list-style-type: none"> <li>Incoming reactant feed stream temperature too high.</li> </ul>	<ul style="list-style-type: none"> <li>Reactor could overheat, other side reactions could be favoured.</li> <li>Materials could decompose.</li> <li>Catalyst could be degraded and damaged.</li> <li>Reactor pressure could increase.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> <li>Add emergency shutdown procedures.</li> <li>Monitor reactor pressure and temperature.</li> </ul>

**Table 74:** HAZOP study on the primary reactor and feed stream continued

					Page:	11 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
COMPOSITION						
1,2	LESS THAN	Composition	Lower composition in feed stream of certain product than expected.	<ul style="list-style-type: none"> <li>Changes in the composition of the feed streams supplied. Ethanol composition lower than stoichiometrically specified amount.</li> </ul>	<ul style="list-style-type: none"> <li>Unwanted side reactions may occur under different stoichiometric reactant feeds. Thus desired product yield and conversion is reduced.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure no contamination of the feed streams.</li> </ul>
1,2				<ul style="list-style-type: none"> <li>Not enough ethanol in storage tank.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Check level of storage tanks periodically, include level transmitters.</li> </ul>
1,2				<ul style="list-style-type: none"> <li>Hydrocarbon reactant (isobutene) in lower composition than stoichiometrically required.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure no contamination of the feed streams.</li> </ul>
1,2				<ul style="list-style-type: none"> <li>Not enough hydrocarbons from storage.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Check level of storage tanks periodically, include level transmitters.</li> </ul>

**Table 75:** HAZOP study on the primary reactor and feed stream continued

					Page:	12 of 21
No.	Guide word	Element	Deviation	Possible causes	Consequences	Safeguards
COMPOSITION						
1,2	MORE THAN	Composition	Higher composition in feed stream of certain product than expected.	<ul style="list-style-type: none"> <li>Changes in the composition of the feed streams supplied. Ethanol composition higher than stoichiometrically specified/required amount.</li> </ul>	<ul style="list-style-type: none"> <li>Unwanted side reactions may occur under different stoichiometric reactant feeds. Thus desired product yield and conversion is reduced.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure no contamination of the feed streams.</li> </ul>
				<ul style="list-style-type: none"> <li>Hydrocarbon reactant (isobutene) in higher composition than stoichiometrically required.</li> </ul>	<ul style="list-style-type: none"> <li>As above</li> </ul>	<ul style="list-style-type: none"> <li>As above</li> </ul>

**Table 76:** HAZOP study on the primary reactor and feed stream continued

					Page:	13 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
PRESSURE						
R-101, 2	HIGH	Pressure	Higher pressure in reactor	<ul style="list-style-type: none"> <li>Feed stream entering at higher pressure than required.</li> </ul>	<ul style="list-style-type: none"> <li>Could lead to an explosion as most of the reactants are highly volatile, flammable and explosive under pressures.</li> <li>Uncontrolled reaction could occur.</li> <li>Dramatic temperature increase, runaway.</li> </ul>	<ul style="list-style-type: none"> <li>Monitor pressure of the reactor and feed stream, add shutdown mechanisms.</li> <li>Add valve controls onto reactant and product lines to control flow and pressure build up.</li> <li>Monitor reactor temperature as this will in turn affect the pressure. Have emergency shutdown available as mentioned in temperature section.</li> </ul>
R-101, 3	LOW	Pressure	Low pressure in reactor	<ul style="list-style-type: none"> <li>Too much product flow out of reactor.</li> <li>Lower temperature s in reactor.</li> </ul>	<ul style="list-style-type: none"> <li>Reactants may turn into liquids if not at high enough pressure and the gas phase reaction will then not be possible.</li> </ul>	<ul style="list-style-type: none"> <li>Monitor reactor pressure, have emergency shutdown procedure available.</li> <li>Add valve controls onto product and reactant feed lines.</li> <li>Monitor temperature of reactor simultaneously.</li> </ul>
R-101	REVERSE	Pressure	Vacuum forming	<ul style="list-style-type: none"> <li>Non applicable.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>

Table 77: HAZOP study on the primary reactor and feed stream continued

					Page:	14 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
REACTION						
R-101	NONE	Reaction	No reaction occurs	<ul style="list-style-type: none"> <li>Temperature and pressure conditions not adequate for reaction to occur.</li> </ul>	<ul style="list-style-type: none"> <li>No product formed as no reaction takes place.</li> </ul>	<ul style="list-style-type: none"> <li>Monitor reactor pressure and temperature, have emergency shutdown procedures in place.</li> </ul>
R-101				<ul style="list-style-type: none"> <li>Catalyst fouling or deactivation.</li> </ul>	<ul style="list-style-type: none"> <li>No product formed as no reaction takes place.</li> </ul>	<ul style="list-style-type: none"> <li>Do routine checks on catalyst effectiveness, replace catalyst when required. Can also re-activate catalyst with thermal treatment.</li> </ul>
R-101	HIGHER	Reaction	Higher conversion than expected	<ul style="list-style-type: none"> <li>Kinetics proceed uncontrollably - temperature too high.</li> </ul>	<ul style="list-style-type: none"> <li>Possible runaway reaction.</li> <li>Pressure and temperature build up.</li> </ul>	<ul style="list-style-type: none"> <li>Control temperature and check temperature with thermocouples.</li> <li>Monitor the concentration of ETBE in the product stream for an indication of the conversion.</li> </ul>
R-101	LOWER	Reaction	Lower conversion than expected	<ul style="list-style-type: none"> <li>Temperature too low.</li> <li>Kinetics proceed uncontrollably.</li> </ul>	<ul style="list-style-type: none"> <li>Ratio of reactants may not be consistent.</li> <li>Desired product formation lower than required.</li> <li>Side reactions may occur at lower temperatures.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>

**Table 78:** HAZOP study on the primary reactor and feed stream continued

					Page:	15 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
REACTION						
R-101, 2	AS WELL AS	Reaction	Side reactions occur along with the desired reactions.	<ul style="list-style-type: none"> <li>Undesirable process conditions (temperature, pressure, ratio of feed reactants) can lead to the occurrence of side reactions.</li> </ul>	<ul style="list-style-type: none"> <li>Uncontrollable side reactions may result in unwanted products and increases in temperature and pressure.</li> </ul>	<ul style="list-style-type: none"> <li>Purify reactants as much as possible with separations.</li> <li>Monitor the concentration of ETBE in the outlet stream.</li> </ul>
2				<ul style="list-style-type: none"> <li>Impurities in the feed streams.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>
2, R-101	OTHER THAN	Reaction	Reactions other than the ones expected occur.	<ul style="list-style-type: none"> <li>Impurities in the feed.</li> <li>Other reactions of the reactants that are not expected.</li> </ul>	<ul style="list-style-type: none"> <li>Uncontrollable side reactions may result in unwanted products and increases in temperature and pressure.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>

**Table 79:** HAZOP study on the primary reactor and feed stream continued

					Page:	16 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
REACTION						
R-101	FASTER	Reaction	Reaction occurs faster than expected.	<ul style="list-style-type: none"> <li>• Temperature too high.</li> <li>• Kinetics unpredictable.</li> </ul>	<ul style="list-style-type: none"> <li>• Possible runaway reaction (exothermic).</li> <li>• Build up of temperature and pressure can lead to explosions and reactor vessel rupture.</li> </ul>	<ul style="list-style-type: none"> <li>• Ensure temperature is controlled through temperature control systems and have emergency plant shutdown procedure planned out.</li> <li>• Same procedure for pressures.</li> <li>• Monitor the concentration of ETBE in the product stream.</li> </ul>
R-101	SLOWER	Reaction	Reaction occurs slower than expected.	<ul style="list-style-type: none"> <li>• Temperature too low.</li> <li>• Kinetics unpredictable.</li> </ul>	<ul style="list-style-type: none"> <li>• Ratio of reactants may not be consistent.</li> <li>• Desired product formation lower than required.</li> <li>• Side reactions may occur at lower temperatures/reaction rates.</li> </ul>	<ul style="list-style-type: none"> <li>• As above.</li> </ul>

Finally, the outlet stream of the reactor containing the desired product, ETBE, was also studied. Tables 80, 81, 82, 83, 84 cover the HAZOP study of the reactor outlet.

The primary findings and considerations for this section include:

- The fitting of high temperature alarms to warn of a high temperature outlet stream which is flammable and possibly explosive.
- The fitting of check valves required for basic flow control to prevent back flow of the product stream.
- The fitting of a flow meter to monitor the amount of the product/outlet stream formed.
- The fitting of low temperature, level and pressure alarms to warn of an outlet stream at undesirable conditions.
- Similarly, the fitting of high pressure, level and temperature alarms to warn of an outlet stream at undesirable conditions.
- Monitoring the composition of outlet streams to ensure desired conversion is obtained.

Table 80: HAZOP study on the primary reactor outlet stream

Study title:		Primary reactor			Page:	17 of 21
Part considered:		Primary reactor outlet			Date:	13/09/2020
Design intent:		To ensure safe and efficient operation of the primary reactor outlet stream				
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
3,4	NO	Flow	No flow of reactor outlet product stream	<ul style="list-style-type: none"> <li>Control valve fails closed.</li> <li>Control valve is closed.</li> </ul>	<ul style="list-style-type: none"> <li>No flow of product stream out of reactor.</li> </ul>	<ul style="list-style-type: none"> <li>Select valve to fail open.</li> <li>Install low flow meter alarm for the product stream.</li> </ul>
3,4				<ul style="list-style-type: none"> <li>Blockage in outlet stream in pipelines.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install low flow meter alarm for the outlet stream.</li> </ul>
3,4				<ul style="list-style-type: none"> <li>Controller fails and closes valve.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure this controller is listed on the critical instrumentation list.</li> </ul>
3,4				<ul style="list-style-type: none"> <li>Air pressure fails resulting in a closed valve.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Select valve to fail open.</li> </ul>

**Table 81:** HAZOP study on the primary reactor outlet stream continued

					Page:	18 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
4	HIGH	Flow	High Flow	• Control valve fails open.	• Excessive flow of reactor outlet stream. • May affect downstream operations.	• Install flow meter and high flow level alarm in outlet stream.
				• Controller fails - and control valve is opened.	• As above.	• Ensure this controller is listed on the critical instrumentation list.
3,4	LOW	Flow	Low Flow	• Reactor outlet delivery line partial blockage.	• May affect downstream operations. Less product available.	• Install flow meter and low flow level alarm in feed stream.
				• Control valve partially shut.	• As above.	• As above.
3,4	LATER THAN	Flow	Flow of product stream occurs later than expected.	• Operator error.	• Delayed production of required product.	• Ensure an interlock between the cooling flow and the feed of the reactor.

**Table 82:** HAZOP study on the primary reactor outlet stream continued

					Page:	19 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
FLOW						
3,4	LOW	Flow	Low flow of reactor outlet stream.	<ul style="list-style-type: none"> <li>Control valve fails to respond.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure valve is placed on crucial instrumentation list.</li> </ul>
3,4	AS WELL AS	Flow	N/A.	<ul style="list-style-type: none"> <li>Not applicable.</li> </ul>	<ul style="list-style-type: none"> <li>Not applicable.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>
3,4	PART OF	Flow	Covered under Low flow.			
3	REVERSE	Flow	Reverse flow.	<ul style="list-style-type: none"> <li>Reactor outlet stream flow failure resulting in backflow.</li> </ul>	<ul style="list-style-type: none"> <li>Loss of product stream out of reactor.</li> <li>Same as no flow.</li> </ul>	<ul style="list-style-type: none"> <li>Install flow meter and low flow level alarm.</li> </ul>
3				<ul style="list-style-type: none"> <li>High back-pressure of outlet stream resulting in backflow.</li> </ul>	<ul style="list-style-type: none"> <li>As above.</li> </ul>	<ul style="list-style-type: none"> <li>Install a check valve.</li> </ul>
3,4	OTHER THAN	Flow	N/A			
3,4	SOONER THAN	Flow	Flow of product occurs sooner than planned.	<ul style="list-style-type: none"> <li>Reactant is fed earlier than planned.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>	<ul style="list-style-type: none"> <li>None.</li> </ul>

**Table 83:** HAZOP study on the primary reactor outlet stream continued

					Page:	20 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
TEMPERATURE						
3	LOW	Temperature	Decreased temperature of outlet stream.	<ul style="list-style-type: none"> <li>Low temperature of reactor.</li> </ul>	<ul style="list-style-type: none"> <li>Other side-reaction by-products may be present.</li> </ul>	<ul style="list-style-type: none"> <li>Monitor reactor vessel temperature.</li> </ul>
3	HIGH	Temperature	Increased temperature.	<ul style="list-style-type: none"> <li>Water supplied has high temperature, not cooling adequately.</li> </ul>	<ul style="list-style-type: none"> <li>The capacity of the cooling system is restricted resulting in a rise in temperature. Other unwanted byproducts may form, decreasing the yield of wanted product in outlet stream.</li> </ul>	<ul style="list-style-type: none"> <li>Install a high temperature alarm and or a high flow alarm in the reactor.</li> </ul>
PRESSURE						
3	HIGH	Pressure	High pressure of outlet stream.	<ul style="list-style-type: none"> <li>Valve fails to reduce the pressure of the outlet stream from the reactor.</li> <li>Valve fails closed.</li> <li>Controller fails to open valve.</li> </ul>	<ul style="list-style-type: none"> <li>May cause damage in the pipelines.</li> <li>Product contains explosive compounds.</li> </ul>	<ul style="list-style-type: none"> <li>Monitor pressure of outlet stream with control system, have emergency shutdown plans available.</li> </ul>
3	LOW	Pressure	Low pressure of outlet stream	<ul style="list-style-type: none"> <li>Valve fails open.</li> </ul>	<ul style="list-style-type: none"> <li>Products may experience a phase change. They will vaporise if not under enough pressure.</li> <li>Reduced flow rate.</li> </ul>	<ul style="list-style-type: none"> <li>As above</li> </ul>

**Table 84:** HAZOP study on the primary reactor outlet stream continued

					Page:	21 of 21
No.	Guideword	Element	Deviation	Possible causes	Consequences	Safeguards
COMPOSITION						
3	LESS THAN	Composition	Lower composition of product in outlet stream.	<ul style="list-style-type: none"> <li>Changes in the composition of the feed streams supplied.</li> <li>Incomplete conversion due to catalyst deactivation.</li> </ul>	<ul style="list-style-type: none"> <li>Unwanted side reactions may occur under different stoichiometric reactant feeds. Thus desired product yield and conversion is reduced.</li> <li>Reduced product yield with deactivated catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure no contamination of the feed streams.</li> </ul>
3	MORE THAN	Composition	Higher composition in feed stream of certain product than expected.	<ul style="list-style-type: none"> <li>Changes in the composition of the feed streams supplied.</li> <li>More ethanol or isobutene than required for desired reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Unwanted side reactions may occur under different stoichiometric reactant feeds. Thus desired product yield and conversion is reduced.</li> <li>More reactant leads to more product unless other side reactions are favoured under different reactant compositions.</li> </ul>	<ul style="list-style-type: none"> <li>Ensure no contamination of the feed streams.</li> </ul>

## 11 Conclusion

ETBE is a more environmentally suitable oxygenate additive than the traditionally used alternatives (Alcántara *et al*, 2000). Its synthesis through the reaction of bioethanol with isobutene is readily carried out in the liquid phase (Collignon & Poncelet, 2001). Excess ethanol and the byproduct formed in the primary reactor, TBA, are further reacted in a second reactor to maximise the ETBE production while preventing the waste of the excess ethanol reactant. The total ETBE produced using this design is 38.31 tonne h<sup>-1</sup>, with an ETBE yield of 83.77 % and a conversion of isobutene to ETBE of 75 %. The conversion of isobutene for its hydration to TBA is 13.88 %. The conversion of the TBA to ETBE in the second reactor (R-102) is 75 %, with an ethanol conversion of 23%. The TBA recycled to the second reactor was only 15 % of the unreacted TBA out of the reactor due to the difficulties in separation of the TBA-water-ethanol mixture.

The process plant will be built over a period of two years as an addition to an existing plant at Natref. The lifetime of the plant is taken as 10 years, where the payback period for this plant is 4 years. The fixed capital investment of this plant is R610 000 000 with a net present value of R3 480 000 000 at an interest rate of 12 %. The IRR was calculated to be 68 %.

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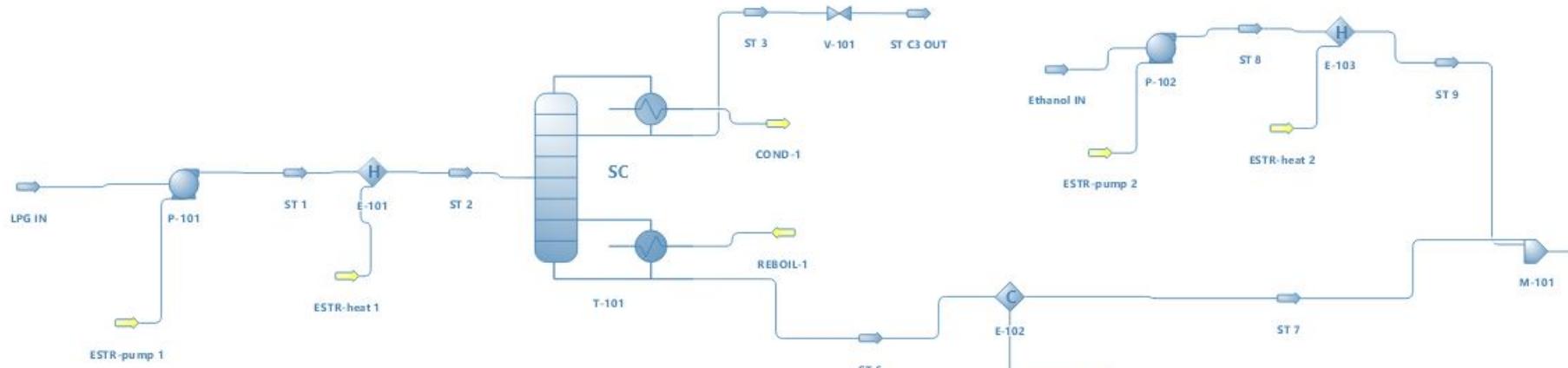
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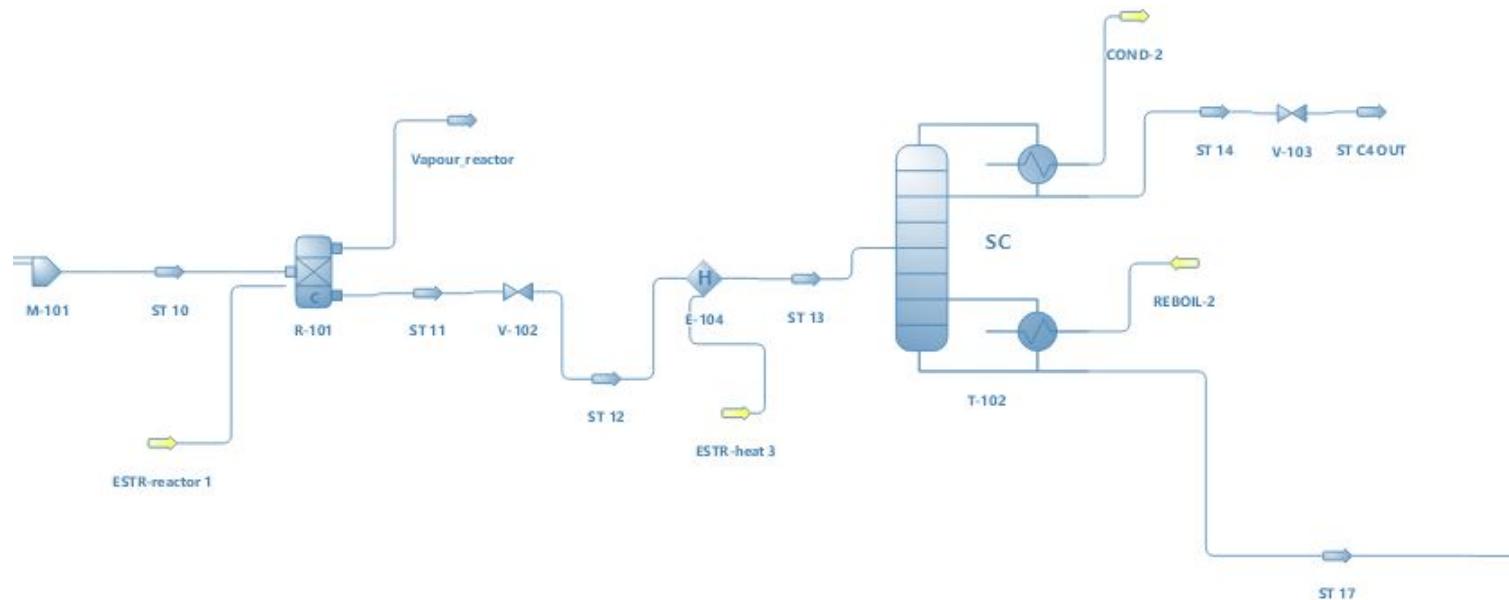
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## Appendix A



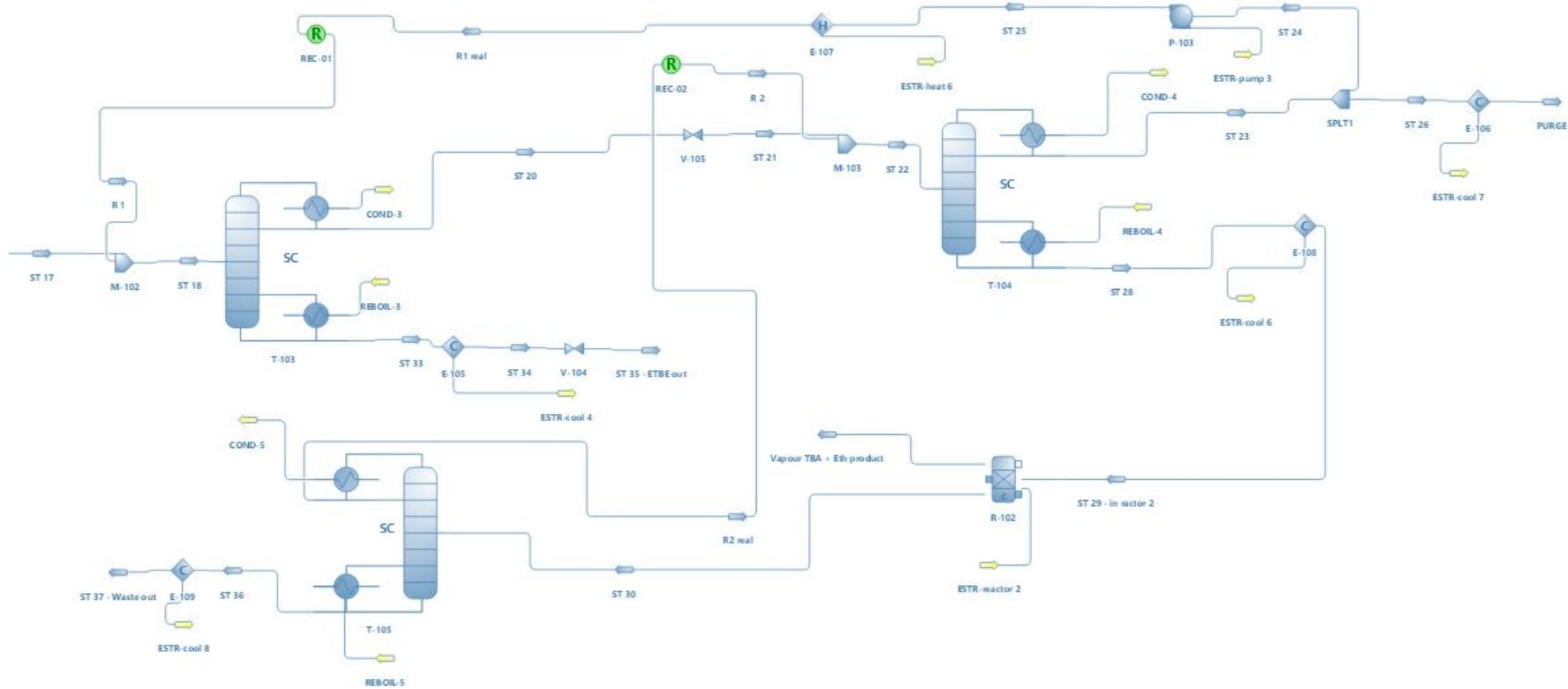
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**Figure 18:** DWSim simulation flow sheet: LPG separation and primary reactor feed preparation



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**Figure 19:** DWSim simulation flow sheet: primary reactor



**Figure 20:** DWSim simulation flow sheet: continuation of separation train and second reactor