School of Engineering and Digital Sciences
Chemical and Materials Engineering Department

NAZARBAYEV
UNIVERSITY

ENG 400 Capstone Project
“Design of Plant for Industrial Production of Butadiene from Butane”

Student Name and ID Number:
Nurzhan Rakhimgaliyev (201946455)
Arsen Musahanov (201965636)
Nurbek Khamidulla (201924017)
Daniyar Amanbayev (202077675)
Bakdaulet Yendibay (202026212)
Ulan Akimov (201975248)

Course Instructor:
Dr. Dhawal Shah

Team Supervisors:
Dr. Boris Golman
Dr. Almagul Mentbayeva

Spring 2025
Astana, Kazakhstan
Submission date: 20.04.2025

Work Allocation of Report 4

Section	Topic	Nurzhan	Arsen	Nurbek	Daniyar	Bakdaulet	Ulan
1. Process introduction							
1.1	General Physical Properties of 1,3-Butadiene				1st		
1.2	The Applications of 1,3-Butadiene				1st		
1.3	Targeted Purity and Production Rate		1st				
1.4	Production Process Selection						1st
2. Process summary							
2.1	Selected kinetics	1st					
2.2	Suitable Catalyst		1st				
2.3	Mass balance			1st			
3. Major equipment design							
3.1	Design of R-101	1st					
3.2	Design of R-102					1st	
3.3	Design of D-101			1st			
3.4	Design of D-103						1st
3.5	Design of D-104				1st		
3.6	Design of H-101		1st				
4. Minor equipment design							
4.1	D-102 Design					1st	
4.2	M-101 Design				1st		
4.3	Design of Valves			1st			
4.4	Design of compressors					1st	
4.5	F-101 Design		1st				
4.6	Storage Tanks		1st				
4.7	Design of heaters and coolers			1st			

5. Plant location and layout							
5.1	Plant Location	1st					
5.2	Plant Layout	1st					
6. Environment and waste streams							
6.1	Reactor	1st					
6.2	Furnace	1st	2nd				
6.3	Flash Drum	1st					
6.4	Extractive Distillation Columns	1st					
7. Total investments and profitability							
7.1	Bare Modulus Cost					1st	
7.2	Initial Total Investments					1st	
7.3	Fixed Cost of Production				1st		
7.4	Variable Cost of Production			1st			
7.5	Revenue of the Production				2nd	1st	
8. Formatting of the paper							
8.1	Format of references						1st
8.2	Format of text						1st
8.3	Format of tables and figures		1st			2nd	
9. Appendix							1st

Table of Contents

1. Process Introduction

Butadiene is one of the most important chemical substances used in the petrochemical industry. It is a building block of most of the synthetic rubbers that are highly used in the automotive industry [1]. Butadiene is a colourless gas in room temperature and atmospheric pressure with a chemical formula C_4H_6 which has two double bonds. Four carbon atoms and two double bonds in the molecule makes it a light and reactive chemical which easily undergoes polymerization reaction. Therefore, 1,3-butadiene monomers are mainly used to make polybutadiene, and other copolymer rubbers by addition of styrene or acrylonitrile to butadiene.

Synthetic rubbers have many applications and one of them is use in the tire production by vulcanization, which is a process of addition of sulfur to polymer chains to produce cross-links that enhance its durability and elasticity [2]. Strong and at the same time elastic rubbers are an essential part of tire production which is a growing industry in Kazakhstan. Therefore, it is important to investigate the production process of butadiene, which is why the main objective of this project is to design a plant for butadiene production to meet 25% of demand for CIS region. To achieve this objective, the report will present the main production routes, final product specifications, relevant kinetic characteristics and catalysts, major and minor equipment designs, plant location selection, economic and market analysis, and future estimates.

1.1. General Physical Properties of 1,3-Butadiene

To be familiar with the general properties of 1,3-butadiene, following Table 1 was constructed.

Table 1. Properties of 1,3-Butadiene (extracted from [3]).

	1,3 - Butadiene
Chemical formula	C_4H_6
Molecular weight [g/mol]	54.0916
Normal boiling point [℃]	-4.41
Freezing point [℃]	-108.91
Liquid density [kg/m^3]	640
Water solubility [mg/litre]	735
Critical pressure [bar]	43.2
Critical temperature [℃]	151.85
Critical volume [cc/mol]	221
Critical compressibility factor	0.270

Also, properties such as liquid viscosity and liquid thermal conductivity are shown in the following Figure 1 and Figure 2 below. Furthermore, these properties were compared with the results obtained from Aspen Plus V14 to check the validity of data given in the software.

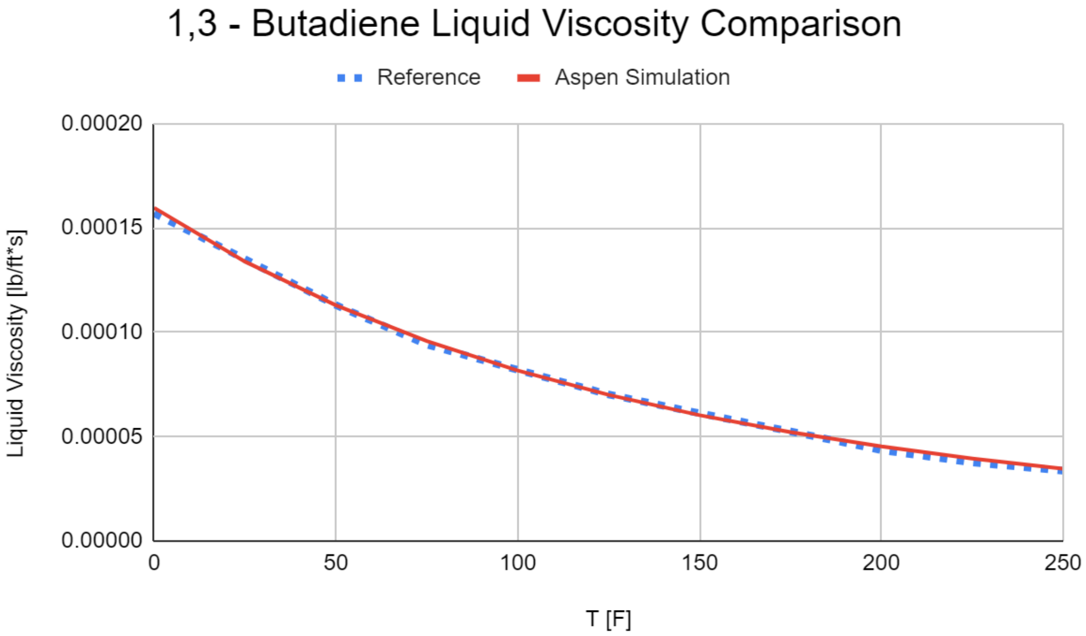


Figure 1. 1,3-butadiene liquid viscosity comparison [4].

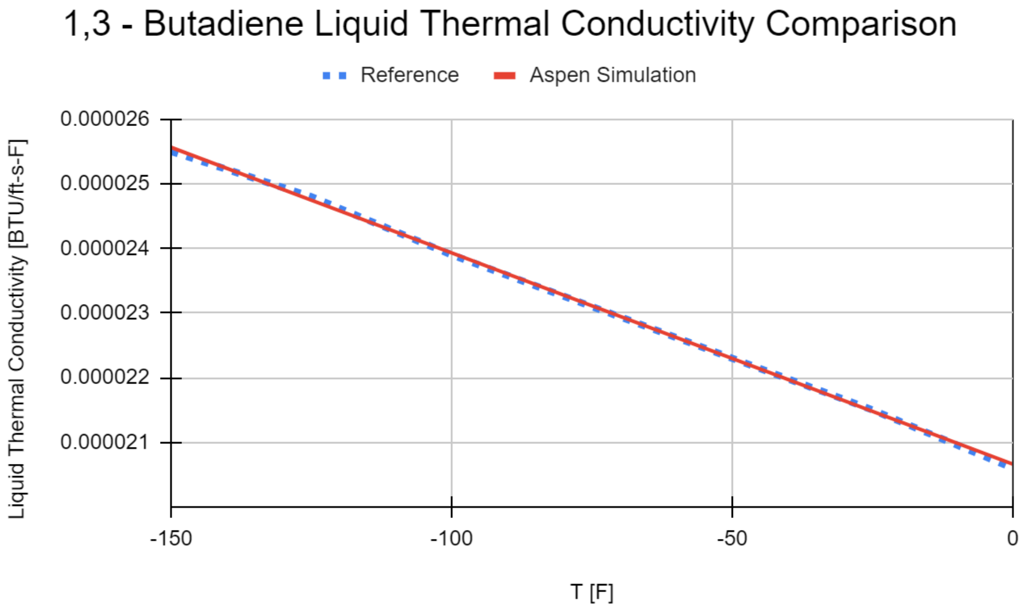


Figure 2. 1,3-butadiene liquid thermal conductivity comparison [4].

In addition to these properties, some other properties of 1,3-butadiene can be found in the Appendix section of this report.

1.2. The Applications of 1,3-Butadiene

1.2.1. Polybutadiene synthesis

The double bonds in 1,3-butadiene makes it easy to undergo polymerization to synthesise polybutadiene which accounts for almost quarter of all butadiene consumption [4]. This type of polymerization is called addition polymerization, where the monomers of 1,3-butadiene form cis- or trans-isomer rich type of polybutadiene depending on the catalyst used. For example, using the Ziegler-Natta-type catalyst system results in high (97%) cis-1,4-polybutadiene which has more bend and curved polymer structure. This gives elasticity to the polymer which is the necessary quality of a rubber. On the other hand, using alkyl lithium initiator in the process results in low cis-1,4-butadiene content (40%) which has mostly linear structure, therefore it is less elastic and brittle [5]. The general addition polymerization for 1,3-butadiene has the following reaction in the presence of a catalyst.

$$H_2C = CH - CH = CH_2 \rightarrow (- H_2C - CH = CH - CH_2 -)_n$$

1.2.2. Styrene-butadiene rubber

Another highly used polymer which uses around 23% of produced butadiene is styrene-butadiene rubbers that are made of styrene and butadiene monomers [4]. The main source of SBR is through emulsion polymerization where surfactant is used to form a stable mixture of styrene and butadiene monomers, and free radicals to initiate the reaction [6]. The double bonds in both of the monomers break down to form long carbon chains the same way as in addition polymerization. SBR synthesised via emulsion polymerization is also largely used in tire industry, conveyor belt production and other mechanical goods.

$$C_6H_6 - CH = CH_2 + H_2C = CH - CH = CH_2 \rightarrow$$
$$\left[\left(- H_2C - CH = CH - CH_2 -\right)_n - CH(C_6H_6) - CH_2 -\right]_n$$

1.2.3. Adiponitrile

Another polymer which has industrial importance is nylon, which is used in textile industry and plastic production. Even though butadiene is not primarily used to make nylon, it is used to synthesise intermediate adiponitrile which is then used to make hexamethylenediamine. The latter reacts with adipic acid to release water and then formed dimer reacts further elongating the nylon polymer. This type of reaction is called condensation polymerization [7]. The synthesis of adiponitrile could be done by directly adding hydrogen cyanide to the butadiene or by first chlorination of butadiene, then addition of sodium cyanide followed by hydrogenation [8].

$$H_2C = CHCH = CH_2 \rightarrow ClCH_2CH = CHCH_2Cl \rightarrow NCCH_2CH = CHCH_2CN \rightarrow$$
$$\rightarrow NCCH_2CH_2CH_2CH_2CN \text{ (adiponitrile)}$$

1.3. Targeted Purity and Production Rate

Butadiene is a colorless flammable gas under standard conditions which has two isomers: 1,3-butadiene and 1,2-butadiene. The latter has no industrial significance, however it is also present in butadiene mixture. Therefore, there are some typical specifications for the butadiene in the market. The butadiene most of the companies are producing has 99.5% pure 1,3-butadiene and the rest are impurities. For example, German chemical company BASF produces 99.5% pure butadiene, which is stabilised by 4-tert-butylcatechol to prevent butadiene from polymerization [9]. The same purity has TPC Group - the largest butadiene producer in North America [10]. However, Lummus Technology for butadiene extraction yields higher purity of 99.7%, but they also use feedstock of crude C_4 cuts consisting of butadiene, butane, butene and a small amount of acetylenes [11]. Therefore, such high pure butadiene is not a common occurrence in the butadiene market.

Table 2. Typical butadiene specifications. Adapted from [12].

Chemical	Specifications
1,3-butadiene, wt%	$\geq 99.5\%$
1,2-butadiene, ppm	< 20
4-tert-butylcatechol, ppm	$< 50 - 150$
Propadiene, ppm	< 10
Dimers, ppm	< 500
Isoprene, ppm	< 10
C_5 compounds, ppm	< 500
Sulfur, ppm	< 5
Acetylenes, ppm	< 20
Water, ppm	< 300

Table 2. shows typical specification for a butadiene. Even though some companies offer high purity butadiene, it is not that commonly distributed in the industry, therefore the desired purity of 1,3-butadiene will be 99.5% or higher.

Butadiene is one of the most essential materials utilised in order to be used in production of automobile tires, toys, turf, and other different products of polymerization [13]. In terms of production capacity butadiene takes 36th place in the chemical industry [13]. According to Duan et al [14] the necessity for butadiene in 2012 was around 10 million metric tons, and it was reported that this value is going to rise annually by 1-2 percent [14]. Furthermore based on Figure 3, it can be seen that production capacity of butadiene in 2020 was approximately 14 million tons and it is predicted that by 2025 this amount is going to be around 16 million tons [13]. Also according to some other data, it was reported that the market size of butadiene in 2022 was almost 11 billion US dollars with compound annual growth rate (CAGR) of 9.4% till 2032 [15]. In comparison with another report, it was revealed that market size value in 2022 was 10.5 billion US dollars and 9.3% CAGR value is almost the same as the previous reported number [16].

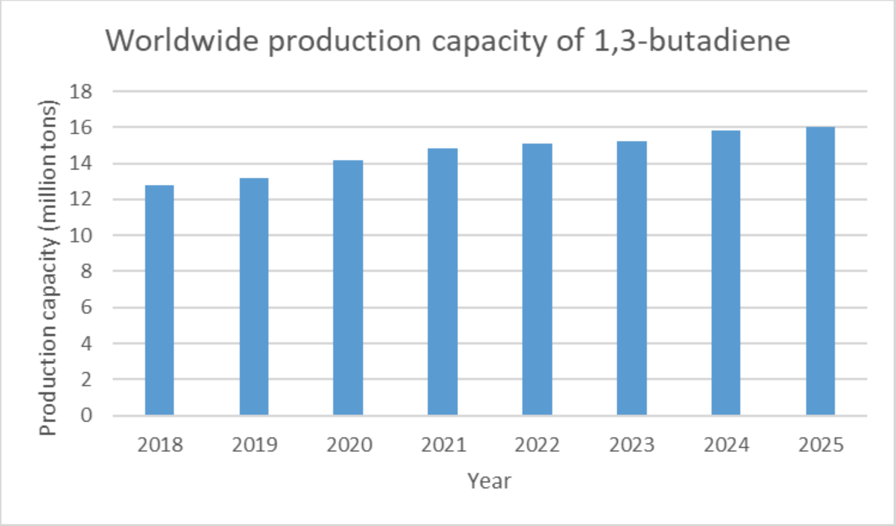


Figure 3. Trend present in production capacity of 1,3-butadiene. Adapted from [13].

The main companies present in the butadiene industry market are Shell, LyondellBasell Industries, Evonik Industries, China National Petroleum Corporation (CNPC), INEOS and some other companies [15]. Regarding their production rate, in 2021 LyondellBasell reported that in both North and South America annual capacity of butadiene was 400 kilotons (kT) [17]. Moreover in 2010, Shell Eastern Petrochemical Complex in Singapore reported that they started to produce butadiene at the rate of 155 kT per year [18]. In addition, INEOS reports the value of 350 kT which is produced in three different countries such as Germany, France and the UK [19].

Butadiene market in CIS region is quite poorly developed even though there are few large high quality tire producers. Only Armenia, Belarus, Kazakhstan, Kyrgyzstan, Moldova, Tajikistan and Uzbekistan are considered as CIS region. None of these countries have butadiene production plants and they import the most common product of butadiene - synthetic rubber from other countries. However, Samruk-Kazyna Foundation is planning to open butadiene production plant in Atyrau, Kazakhstan by 2026 in partnership with Russian oil company “Tatneft (Татнефть)” [20]. The annual production rate of this plant will be 45,000 tons of butadiene and 60,000 tons of synthetic rubber some of which later will be sent to “KamaTyresKz” tire production plant in Kazakhstan and exported to other countries [21]. This tire producing plant is one of three large plants of the same company. Another one is located in Russia and the third one is in Uzbekistan with a total annual production rate of 23.5 million tires [22]. Belarus also has one of the largest tire production plants “Belshina” which has around 300 different tire products that are being exported to nearly 70 countries worldwide [23]. Its production rate is approximately 4 million tires per year [24]. This shows the importance of having a domestic butadiene production plant to facilitate the growth of the tire industry within the CIS region. By analysing the CIS market, the yearly production of 60 kilotons (kT) of 1,3-butadiene is enough to satisfy the 25% demand of CIS region.

1.4. Production Process Selection

In the petrochemical sector, butadiene is an essential component that is used to make synthetic rubber, polymers, and other high-value compounds. Butadiene can be produced using a variety of techniques, each with benefits and uses of its own. The main ways that butadiene is produced are steam cracking (naphtha cracking), catalytic dehydrogenation of n-butane and n-butene (the Houdry process),and oxidative dehydrogenation of n-butane and n-butene (Oxo-D or O-X-D process). Each of these processes were analyzed based on the literature review and compared via real life implementations by large companies. Important criteria for the selection of the process were adequate conversion and selectivity for butadiene, with butane used as feedstock. The commercial processes used by large companies are demonstrated in Table 3.

Table 3. Processes, implied by large companies.

Company name	**Process**	**Feedstock**	**Operating conditions**	**Catalysts**	**Conversion**	**BD selectivity**	**Source**
Phillips	O-X-D (ODH)	n-butene	480-600°C (adiabatic)	unknown	~75-80%	88-92%	[25]
Lummus Technology	Catadiene (catalytic dehydrogenation)	butane	600-620°C at 0.2-0.4 bar	Cr-oxide and Al-oxide	30-40%	Up to 63%	[25]
Dow Chemical	Catalytic dehydrogenation	butane	600-675°C at 1 bar	Ca-Ni-phosphate stabilized with Cr_2O_3	~50%	~90%	[25]
Petro-Tex	Oxo-D (ODH)	butene	550-600°C (adiabatic)	probably ferrite-Zn-Mn-Mg	65%	Up to 93%	[25]
Mitsubishi Chemicals	BTcB (ODH)	butene	300~400°C at ambient pressure	unknown	unknown	Crude butadiene	[26]

The process selected for the production of butadiene from butane is based on the technology developed by Lumus Technologies, namely the CATADIENE process with the BASF NMP separation unit. This choice was supported by the process's remarkable efficiency, scalability, and conformity to industry standards. This method provides a reliable and profitable way to produce 1,3-butadiene under carefully regulated conditions. The CATADIENE process uses cyclic dehydrogenation of n-butane with chromium-alumina catalysts. Integration with BASF NMP extraction units allows 1,3-butadiene to be efficiently separated and purified from other C4 hydrocarbons and reaction byproducts, which further improves process performance. NMP's strong selectivity for butadiene and low energy consumption make it especially effective at extracting high-purity butadiene [27-28]. By recycling unreacted butanes and butenes back to the dehydrogenation step, this combined approach improves feedstock utilisation while guaranteeing high-purity product [29].

2. Process Summary

The production of butadiene consists of 3 main stages: dehydrogenation of n-butane to butadiene and butenes, separation of reaction products from hydrogen, and then separation of butadiene from butane and butenes mixture by using extractive distillation. The process flow diagram is shown in the Figure 4 where the butadiene with the purity of higher than 99.5%

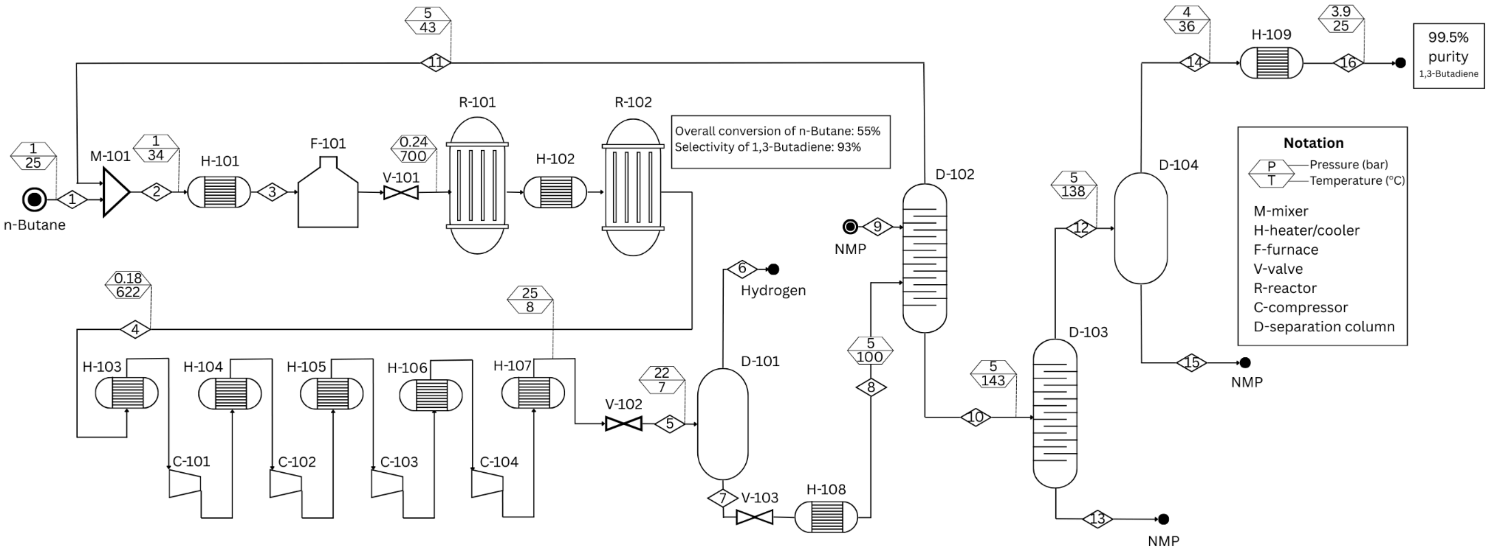


Figure 4. Process flow diagram

Fresh feed of n-butane (stream 1) is mixed with a recycle stream 11 which consists of unreacted n-butane, butenes and fraction of butadiene. Mixed stream 2 is then heated in H-101 heat exchanger from 34ºC to 150ºC, which is then transferred into furnace F-101 to heat it further to 700ºC. After that, it gets expanded by V-101 from 0.8 bars to 0.24 bars to meet the operating conditions of the reactor R-101 which are 700°C and 0.24 bars. After the first reactor, the stream goes into heater H-102, where it gets reheated, because inside the reactor temperature drops due to the endothermic dehydrogenation reaction. Temperature drop does not allow further efficient conversion of n-butane into butadiene, so it heats up again until 700ºC, then enters the second reactor R-102. Inside the reactors n-butane is converted into butenes, which then get converted into 1,3-butadiene. During the dehydrogenation step hydrogen is also produced as a byproduct. As a result, the output stream 4 of the reactor has n-butane, butenes, butadiene and hydrogen. In order to remove hydrogen the stream should be compressed by a series of compressors and cooled by a series of coolers to get the conditions of 8°C and 25 bar. At these conditions flash drum D-101 operates to get hydrogen as an overhead stream 6 and liquid hydrocarbons from the downstream 7.

To separate butadiene from butane and butenes, an extractive distillation method is used because of the similar volatility of these compounds. It is impossible to separate them by conventional distillation process. Firstly, stream 7 is expanded by V-102, and NMP solvent (stream 9) diluted with water at ratio 4:1 (by mass) is added to the distillation column D-102 at ambient conditions. Flow rate of NMP is 9.5 times of the feed to the distillation column. Distillation column (D-102) operates at 5 bar which separates most of the n-butane and butenes from the butadiene which is dissolved in NMP. Top product stream 11 of the column is recycled back to be mixed with fresh feed, while the bottom stream 10 is sent to another distillation column D-103 to separate butadiene from NMP. Stream 12 is the top product from this column containing butadiene with some impurities and stream 13 is the separated NMP which then can be reused to separate butadiene from hydrocarbons mixture. After that stream 12 goes to another flash drum D-104, to separate butadiene from NMP. Stream 15 is the used NMP and stream 14 is the butadiene product with 99.5% purity. However, it is in the gas form which cools down in the cooler to condense the product into the liquid form.

All the equipment used in this process are listed in Table 4.

Table 4. Equipment used in the butadiene production.

Code	Equipment	Comments
Butadiene production units		
M-101	Mixer	Mixing fresh butane with recycle stream
H-101	Heat exchanger	Preheats the feed stream before the reactor
F-101	Furnace	Heats up the stream to the required reaction temperature
V-101	Valve	Expands and decreases the pressure of the reagents before the reaction
R-101	Reactor	First fixed bed reactor
H-102	Heater	Heater between two reactors, required to re-heat the stream to required temperature
R-102	Reactor	Second fixed bed reactor
Product stream compressing units		
H-103	Cooler	Cools down the products
C-101	Compressor	Compresses the stream

H-104	Cooler	Cools down the compressed products
C-102	Compressor	Compresses the stream
H-105	Cooler	Cools down the compressed products
C-103	Compressor	Compresses the stream
H-106	Cooler	Cools down the compressed products
C-104	Compressor	Compresses the stream
H-107	Cooler	Cools down the compressed products
Butadiene separation units		
V-102	Valve	Rapidly expands the stream
D-101	Flash drum	Separates hydrogen from product stream
V-103	Valve	Expands the stream after the flash drum
H-108	Heater	Heats up the stream, preparing it for the extractive distillation
D-102	Extractive distillation column	Uses NMP as a solvent to separate the butadiene from mixture of hydrocarbons
D-103	Distillation column	Separates the NMP from butadiene
D-104	Flash drum	Separates remaining NMP from the butadiene, yielding 95.5% pure product
H-109	Cooler	Condenses the product for convenient transportation

2.1. Mass balance

In this process there are several sources that are being added into the system and outlets that are removing materials from the overall systems. In the Table below it can be seen that mass flow of all inlet and outlet streams are the same.

Table 5. Mass balance of inlet and outlet streams (kg/hr).

	Inlet streams		Outlet streams			
Components	Feed	NMP	H2rich stream	Stream 13 (NMP exit)	Stream 15	Butadiene
N-butane	10850	0	212.44	0	0	0.08
1-butene	0	0	705.28	0	0	1.27
Butadiene	0	0	798.04	505.22	30.08	7885.09
Hydrogen	0	0	712.42	0	0	0
NMP	0	492302.28	0	492056.13	246.12	0.03
Water	0	123072.01	3.56	121208.7	1831.88	31.43
Total	626227.85		626227.78			

Table 6. Mass balance of inlet and outlet streams in ASPEN (kg/hr).

Inlet streams		Outlet streams			
Feed	NMP	H2 rich stream	Stream 13	Stream 15	Butadiene
10850	615088	2431.13	613481	2107.31	7918.4
625938		625937.84			

There is around 290 kg/hr difference between Aspen material balance and the one calculated by hand. This difference is accumulated due to rounding and multiplication with few significant figures.

The main part of the process is a reactor which consists of two reactors connected in series with a heater between them to provide enough temperature required for the reaction.

Table 7. Mole balance for the first reactor (kmol/hr).

Components	Inlet stream	Moles consumed	Outlet stream	Moles produced
N-butane	333.16	111.81	221.35	0
1-butene	455.41	98.64	468.58	111.81
Butadiene	406.13	0	504.77	98.64
Hydrogen	14.04	0	224.49	210.45
Total moles	1225.13	210.45	1435.57	420.9

Table 8. Mole balance for the second reactor (kmol/hr).

Components	Inlet stream	Moles consumed	Outlet stream	Moles produced
N-butane	221.35	71.21	150.14	0
1-butene	468.58	71.8	468	71.21
Butadiene	504.77	0	576.57	71.8
Hydrogen	224.49	0	367.49	143.01
Total moles	1435.57	210.45	1578.57	286.02

From Tables 7 and 8 it may appear that there is no balance, however it is a mole balance inside the reactor. This means that after the reaction one mole of feed can produce two moles of products. Therefore, after the reactor materials by mole appear to be higher. Which is not the case during mass balance which is given in Table 9.

Table 9. Mass balance for the reactors (kg/hr).

	Inlet of 1st reactor	Inlet of 2nd reactor	Outlet of 2nd reactor
N-butane	19365.39	12867.53	8727.92
1-butene	25550.95	26289.39	26257.50
Butadiene	21967.17	27302.39	31185.60
Hydrogen	28.30	452.45	740.71
Total	67208.42	67208.38	67208.35

Butadiene purification requires several distillation columns and flash drums. Table 10 shows material balance for the first flash drum (D-101) which is mainly used to separate hydrogen from the hydrocarbons. As a result, at least 96% of all the hydrogen is removed from the system.

Table 10. Mass balance for D-101 (kg/hr)

Components	Inlet of D-101	Top stream	Bottom stream
N-butane	8727.92	212.44	8515.48
1-butene	26257.50	705.28	25552.22
Butadiene	31185.60	798.04	30387.56
Hydrogen	740.71	712.42	28.30
Water	296.61	3.56	293.05
Total	67208.35	2431.73	64776.62
ASPEN	67177.3	2131.13	64746.1

Table 11 shows a mass balance for the D-102, an extractive distillation column which uses NMP to extract most of the butadiene from the butane and butene that have similar volatility. Due to higher affinity of NMP to the butadiene, mostly butadiene is dissolved in NMP.

Table 11. Mass balance for D-102

Components	Inlet of D-102	NMP in	Top stream	Bottom stream
N-butane	8515.48	0	8515.39	0.09
1-butene	25552.22	0	25550.95	1.28
Butadiene	30387.56	0	21967.17	8420.39
Hydrogen	28.30	0	28.30	0
NMP	0	492302.28	0	492302.28
Water	293.05	123075.57	296.61	123072.01
Total	64776.62	615377.85	56358.42	623796.05
	680154.47		680154.47	
ASPEN	679834.1		679834.1	

To separate butadiene from the solvent it is heated in the next distillation column (D-103) and condensed again at the top of the column. However, due to volatility of butadiene it remains gas phase and moves into the final column - D-104. In which it separates butadiene from other impurities to give 99.5% pure butadiene as a product. The mass for these columns are given in Table 12 and 13.

Table 12. Mass balance for D-103

Components	Inlet of D-103	Top stream	Bottom stream
N-butane	0.09	0.09	0
1-butene	1.28	1.27	0.01
Butadiene	8420.39	7915.17	505.22
Hydrogen	0	0	0
NMP	492302.28	246.15	492056.13
Water	123072.01	1863.31	121208.70
Total	623796.05	10025.99	613770.06
	623796.05	623796.05	
ASPEN	623507	623506.7	

Table 13. Mass balance for D-104

Components	Inlet of D-104	Top stream	Bottom stream
N-butane	0.09	0.08	0.01
1-butene	1.27	1.27	0
Butadiene	7915.17	7885.09	30.08
Hydrogen	0	0	0
NMP	246.15	0.03	246.12
Water	1863.31	31.43	1831.88
Total	10025.99	7917.91	2108.08
	10025.99	10025.99	
ASPEN	10025.7	10025.7	

2.2. Selected kinetics

All the reactions are endothermic and require additional energy in the form of heat. For the kinetics of the reaction, Happel et. al. [30] was chosen, as they are studying the n-Butane and Butenes dehydrogenation over the chromia-alumina catalyst, which is the catalyst of our project. The composition of the catalyst is 20% Cr_2O_3 and 80% Al_2O_3. They have done laboratory scale experiments to determine the kinetics of n-butane and butenes dehydrogenation. Different reaction conditions were checked and the reaction rate law was determined from experimental data. The Langmuir-Hinshelwood mechanism of adsorption was used in the reaction rate law. The kinetics of two reactions could be seen there with the appropriate units [30]:

$$C_4H_{10} \rightarrow C_4H_8 + H_2$$

$$r_{net,b} = c_f \phi_b [p_{butane}^{1/2} - (\frac{p_{butenes} p_{H_2}}{K_{eq,b}})^{1/2}] \quad \text{(mole/g}_{\text{cat}}\text{*hr) (2.1.1)}$$

$$c_f = 1.878 * 10^6 exp[\frac{-31,400}{RT}] \quad \text{(mole/g}_{\text{cat}}\text{*hr*atm}^{1/2}\text{) (2.1.2)}$$

$$K_{eq,b} = 1.642 * 10^7 exp[\frac{-29,570}{RT}] \quad \text{(atm) (2.1.3)}$$

$$\phi_b = \frac{1}{[1 + 0.0055\, p_{hydrogen}^{1/2} + 1.499\, p_{butene}^{1/2}]^2} \quad \text{(2.1.4)}$$

$$C_4H_8 \rightarrow C_4H_6 + H_2$$

$$r_{net,d} = k_f \phi_d [p_{butenes}^{1/2} - (\frac{p_{diene} p_{H_2}}{K_{eq,d}})^{1/2}] \quad \text{(mole/g}_{\text{cat}}\text{*hr) (2.1.5)}$$

$$k_f = 7.763 * 10^3 exp[\frac{-20,330}{RT}] \quad \text{(mole/g}_{\text{cat}}\text{*hr*atm}^{1/2}\text{) (2.1.6)}$$

$$K_{eq,d} = 1.94 * 10^6 exp[\frac{-30,260}{RT}] \quad \text{(atm) (2.1.7)}$$

$$\phi_d = \frac{1}{[1 + 1.210\, p_{butenes}^{1/2} + 1.263\, p_{diene}^{1/2}]^2} \quad \text{(2.1.8)}$$

Where, $r_{net,b}$ is a reaction rate of butane consumption, $r_{net,d}$ is a reaction rate of butenes consumption, c_f and k_f are the pre-exponential factors, $K_{eq,b}$ and $K_{eq,d}$ are the constants of equilibrium of adsorption on catalyst surface, ϕ_b and ϕ_d are the absorption expressions. The activation energies are given in cal/mol and R = 1.987 cal/mol*K.

For the sake of simplicity, 1-butene, cis-2-butene and trans-2-butene were simplified as butenes. Units in the paper and the input units in aspen are different and there is a need to make conversions before inputting different coefficients into aspen. To validate the units of the paper, python was used to check the values in the paper. Two reactions were observed in the kinetic model. The first reaction n-Butane→Butenes + H_2 was denoted as R1, the second reaction Butenes→1,3-Butadiene + H_2 was denoted as R2.

Table 14. Units of paper and aspen.

Parameters	Paper units	Aspen units
Reaction rate	mole/g_{cat}*hr	kmol/kg_{cat}*s
Pre-exponential factor	mole/g_{cat}*hr*$atm^{1/2}$	kmol/kg_{cat}*s*$Pa^{1/2}$
Equilibrium constant	atm	$Pa^{1/2}$

Here, it is seen that dimensions for the reaction rate and pre-exponential factor are the same, however we see that the Equilibrium constant is different. The paper has the units in the power of 1, while in Aspen we have the units in the power of ½. This is because the paper uses K_{eq} inside the brackets that have the power of ½. So, it means that the K_{eq} of paper has the dimensions of power 1, but it is followed by the change of the power to ½. In Aspen, we do not have the same option of inputting K values, so we need to follow the way Aspen is working. It multiplies the constants to partial pressures immediately, without the brackets, which means that the units for it already have the power of ½. This is a small difference which does not affect the overall results of Aspen.

Table 15. Aspen values for pre-exponential factors.

	k	E
c_f	1.639 kmole/kg_{cat}*s*$Pa^{1/2}$	31400 cal/mol
k_f	0.00677 kmole/kg_{cat}*s*$Pa^{1/2}$	20330 cal/mol

From this Table it is seen that the activation energies for both of the reactions are given in cal/mol, so it is important to use according value of R, which is equal to 1.987 cal/mol*K. For the driving force and adsorption terms we have the following convention of inputting values in Aspen.

Table 16. The Driving Force and Adsorption terms.

R1	
Driving force	**Term**
Term 1	$k_1 p_{butane}^{1/2}$
Term 2	$k_2 p_{butene}^{1/2} p_{hydrogen}^{1/2}$
Overall driving force	$k_1 p_{butane}^{1/2} - k_2 p_{butene}^{1/2} p_{hydrogen}^{1/2}$
Adsorption	**Term**

Term 1	k_5
Term 2	$k_6 p_{hydrogen}^{1/2}$
Term 3	$k_7 p_{butenes}^{1/2}$
Overall adsorption	$(k_5 + k_6 p_{hydrogen}^{1/2} + k_7 p_{butenes}^{1/2})^2$
R2	
Driving force	**Term**
Term 1	$k_3 p_{butenes}^{1/2}$
Term 2	$k_4 p_{diene}^{1/2} p_{hydrogen}^{1/2}$
Overall driving force	$k_3 p_{butenes}^{1/2} - k_4 p_{diene}^{1/2} p_{hydrogen}^{1/2}$
Adsorption	**Term**
Term 1	k_8
Term 2	$k_9 p_{butenes}^{1/2}$
Term 3	$k_{10} p_{diene}^{1/2}$
Overall adsorption	$(k_8 + k_9 p_{butenes}^{1/2} + k_{10} p_{diene}^{1/2})^2$

Where,

$$ln(k_i) = A + \frac{B}{T} + C * ln(T) + D * T \qquad (2.1.9)$$

In the table below, A, B, C and D values are given for the according k_i values in appropriate terms.

Table 17. Driving force values for R1.

	Term 1	Term 2
N-butane exponent	0.5	0
Butenes exponent	0	0.5

Hydrogen exponent	0	0.5
A (k_1 and k_2)	0	-14.07
B (k_1 and k_2)	0	7440.87
C (k_1 and k_2)	0	0
D (k_1 and k_2)	0	0

Table 18. Driving force values for R2.

	Term 1	Term 2
Butenes exponent	0.5	0
Butadiene exponent	0	0.5
Hydrogen exponent	0	0.5
A (k_3 and k_4)	0	-13
B (k_3 and k_4)	0	7614.49
C (k_3 and k_4)	0	0
D (k_3 and k_4)	0	0

Table 19. Adsorption values for R1.

	Term 1	Term 2	Term 3
H_2 exponent	0	0.5	0
Butenes exponent	0	0	0.5
A (k_5, k_6 and k_7)	0	-10.96	-5.36
B (k_5, k_6 and k_7)	0	0	0
C (k_5, k_6 and k_7)	0	0	0
D (k_5, k_6 and k_7)	0	0	0

Table 20. Adsorption values for R2.

	Term 1	Term 2	Term 3
Butenes exponent	0	0.5	0
Butadiene exponent	0	0	0.5
A (k_8, k_9 and k_{10})	0	-5.57	-5.53

B (k_8, k_9 and k_{10})	0	0	0
C (k_8, k_9 and k_{10})	0	0	0
D (k_8, k_9 and k_{10})	0	0	0

For the validation of kinetics in the paper, experimental data at different reaction conditions was chosen. In this report Aspen was used to simulate the reaction at different molar flow rates, temperatures and partial pressures of the system. They are given in the table below. The reactor diameter is equal to 1" and the length is 3.5", the catalyst pellet density is equal to 1.42 g/cm^3. In the Aspen model such experimental conditions were applied. In the experiments, authors of the paper have used different amounts of catalysts in their experiments with the values of 0.0045 kg in R1 and 0.004 kg in R2. The kinetic model was simplified as follows: the products of the first dehydrogenation reaction of n-Butane are the mixture of butenes (1-Butene, cis-2-Butene and trans-2-Butene), but in the kinetic model instead of defining each component butenes were simplified as the mixture of butenes. To validate the given kinetics conversions of n-Butane and Butenes were chosen. The graph of conversions at different conditions is given in Figure 5.

Table 21. Reactor dimensions and catalyst properties.

Reactor diameter	1 in
Reactor length	3.5 in
R1 catalyst loading	0.0045 kg
R2 catalyst loading	0.004 kg
Catalyst pellet density	1.42 g/cm^3

Table 22. Reaction conditions for the R1.

Experiment #	F (moles of n-Butane/hr)	T (K)	P_{butane} (atm)
1	27.55	832	0.191
2	26.34	833	0.595
3	26.35	833	0.568
4	26.08	830	0.948
5	29.6	828	1.363
6	32.53	824	1.76
7	32.84	825	1.8

8	41.74	823	2.551
9	44.96	830	3.042
10	51.06	827	3.331
11	20.4	794	1.036
12	17.04	773	0.989
13	16.8	777	0.627
14	16.26	720	1.055

Table 23. Reaction conditions for the R2.

Experiment #	F (moles of Butene/hr)	T (K)	$P_{butenes}$ (atm)
1	18.7	759	0.994
2	23.4	845	0.903
3	20	845	1.268
4	18.02	880	0.231
5	19.45	845	0.248
6	14.55	696	0.625
7	13.55	735	0.491
8	17.8	786	0.52
9	13.8	822	0.641
10	15.32	825	1.109

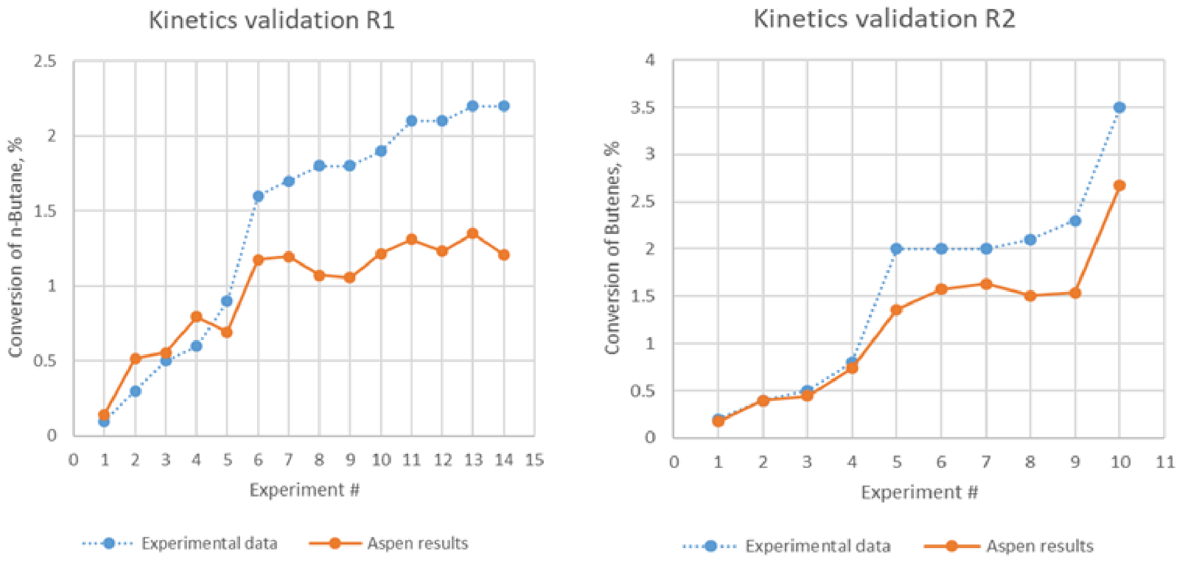


Figure 5. Comparison of conversions in reference paper and Aspen

From Figures below, it is seen that Aspen correlates with the trends in conversion changes at different reaction conditions with the paper. However, there are differences in the absolute values at higher conversions than the lower conversions. From our perspective, the reason for such differences is that we are trying to compare experimental results with the Aspen simulations. Moreover, according to the year of publication, it is seen that the publication year is 1966, which could mean that the equipment accuracy might not be accurate at that time, leading to such errors. Moreover, there is also better correlation between the paper and Aspen in the R2 than R1. The reason for such difference could be due to Aspen simplifications in calculations, such as activity coefficients.

2.3. Suitable Catalyst

Dehydrogenation of alkanes to olefins is a widely used process with different kinds of catalysts. They are divided into different categories and are summarised in Table 25. In industrial applications chromium oxide-based and platinum-based catalysts are used for the dehydrogenation of light alkanes such as propane, butanes and i-butanes. Catalysts are required for the dehydrogenation process as the reactions are happening on the catalyst surface. Generally, catalysts increase the rate of the reaction by altering the chemical pathway in which reaction takes place. So, generally catalysts decrease activation energy but do not affect thermodynamics [31]. The reaction of butane dehydrogenation has the following mechanism: n-Butane firstly is adsorbed on the catalyst surface, by interaction of hydrogen atoms with the metals on the surface. Then, the second hydrogen atom binds to the catalyst, which then leads to H_2 and 1-Butene or 2-Butene (cis and trans). After that, hydrogen atoms in the Butenes molecule bind with the catalyst in a similar way and then it is followed by hydrogen abstraction by forming 1,3-Butadiene and H_2 [31]. The main problem with the catalysts is the catalyst fouling due to the coke formation on the surface. At elevated temperatures, partial cracking is happening, which leads to coke formation on the catalyst surface leading to decrease in the catalyst efficiency. Periodical catalyst regeneration is needed and is done by combustion of coke by air.

Table 25. Dehydrogenation catalyst [33]

Catalyst type	Examples
Platinum-based supported catalyst with promoters (and Group VIII metals)	Pt-Sn supported by alumina
Chromium oxide-based supported catalyst with promoters	Alumina supported CrO_x catalyst Zirconia supported CrO_x catalyst
Vanadium oxide-based catalysts	Vanadium-magnesium mixed oxides V_xO_y supported by alumina
Molybdenum oxide-based catalysts	Unsupported MoO_x Silica supported MoO_x Alumina supported chromium-molybdenum oxide
Gallium supported oxide or included in zeolites	GaO_3 /H-ZSM-5 ZrO_2 supported gallium oxide-based
Carbon-based catalysts	Carbon nanotubes Nitrogen-doped carbon nanotubes Carbon supported metal (platinum/carbon)
Other formulations	20% In_2O_3 and 80% Al_2O_3 Supported iron oxides Zinc supported on H-ZSM-5 zeolites

3. Major Equipment Design

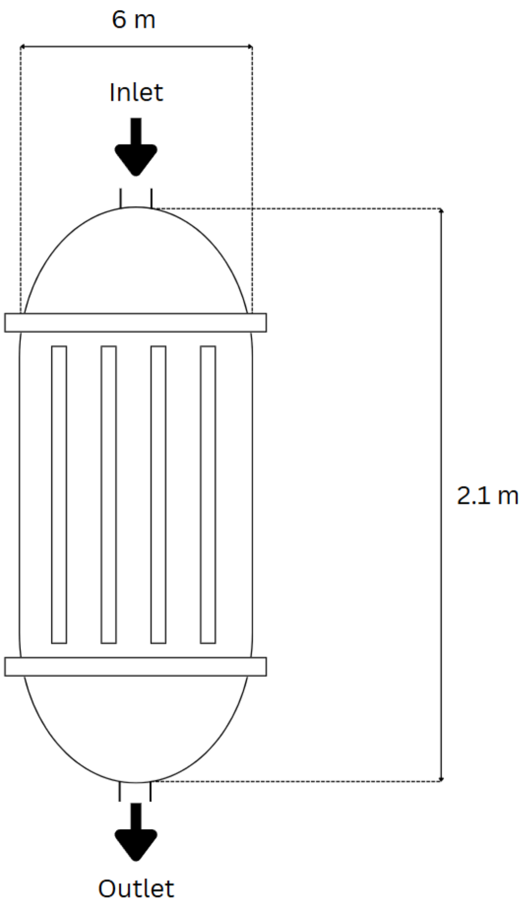
3.1. Design of R-101

The reactor type for this process is a fixed-bed reactor. Many dehydrogenation plants use this type of reactor because of its effectiveness and process control. Because the butane dehydrogenation reaction is thought to be highly endothermic, the reactor's internal temperature must be kept high. Due to this fact, isothermal operation is not suitable in this case. It is costly to maintain a high, steady temperature inside the reactor because doing so would require a significant amount of energy, raising the process's operating expenses. After taking this information into account, it is better to use adiabatic conditions inside the reactor because it is less expensive in terms of reactor parts and energy needs. The intended conversions and production rates can be achieved by improving the process conditions. A reactor system with three reactors connected in series was selected for an optimized process.

This is because the reaction is endothermic, which causes the reaction stream to cool. As a result, the streams between the reactors in series require heaters. While the other two reactors are minor units, the first reactor is a major unit.

Catalyst weights are calculated based on the required stream composition. Through sensitivity analysis, catalyst weights were calculated to achieve optimal results. The reactor details can be seen in Table 26.

Table 26. Reactor schematics.

<table>
<tr><th colspan="2">Technical sketch for R-101</th></tr>
<tr><td colspan="2">
</td></tr>
<tr><td>Reactor type</td><td>Adiabatic</td></tr>
<tr><td>Reactor length (m)</td><td>1.6</td></tr>
<tr><td>Reactor diameter (m)</td><td>6</td></tr>
<tr><td>Wall thickness (mm)</td><td>12</td></tr>
<tr><td>Material</td><td>304 stainless steel</td></tr>
<tr><td>Volume (m^3)</td><td>45.2</td></tr>
</table>

Temperature (°C)	700
Pressure (bar)	0.24
Catalyst bed volume (m^3)	40.5
Pressure drop (bar)	3.3E-2
Bed voidage	0.6

Mass balance of the inlet and outlet of the reactor can be made from the Aspen Plus simulation results, the mass balance for the reactor can be seen on Table 27.

Table 27. Streams mass balance and composition.

Mass balance		
Component	Inlet mass flow (kg/hr)	Outlet mass flow (kg/hr)
C_4H_{10}	19354	12860
C_4H_8	25441	26161
C_4H_6	21969	27318
H_2	28	453
Total	67088	67088

Accordingly, energy balance can be made for the reactor, as our operating condition is adiabatic, total heat change must be equal to 0. For the reactor following expression can be written:

$$\Delta E = Inlet\ Enthalpy - Outlet\ Enthalpy + \Delta H_{reaction} - mC_p \Delta T \quad (3.1.1)$$

Here, $\Delta H_{reaction}$ is an enthalpy change due to reaction, $mC_p\Delta T$ is a heat change due to temperature decrease. The values for the enthalpies are found using Aspen Plus simulations and can be seen on Table 28, heat of reaction is found using RStoic reaction model, heat of temperature change is found by using heater, model can be found in ESI section of this report.

Table 28. Energetic parameters for the reactor.

Inlet enthalpy flow (kW)	33342
Outlet enthalpy flow (kW)	33342
Heat of reaction (kW)	7469.99

Heat from temperature drop (kW)	7473.04

$$\Delta E = 34462.74 - 34462.74 + 7469.99 - 7473.04 \approx 0$$

The reactor inlet stream consists of hot butane gas and the recycled stream at 700°C and 0.24 bar. The hydrocarbons themselves are not corrosive, but LPG can contain trace amounts of corrosive substances, such as sulfur compounds and moisture. It is crucial to build the reactor out of corrosion-resistant materials, like stainless steel, because, for instance, a concentration of 0.4 ppm H_2S [34] is enough to corrode some metals. For this application, 304 stainless steel is sufficient because the reactor environment is not very corrosive.

The stream temperature entering the first reactor was subjected to sensitivity analysis. The Figure 6 shows the outcomes. The required yield for the process after the first reactor is 30%, so the according temperature of 700ºC was chosen for it.

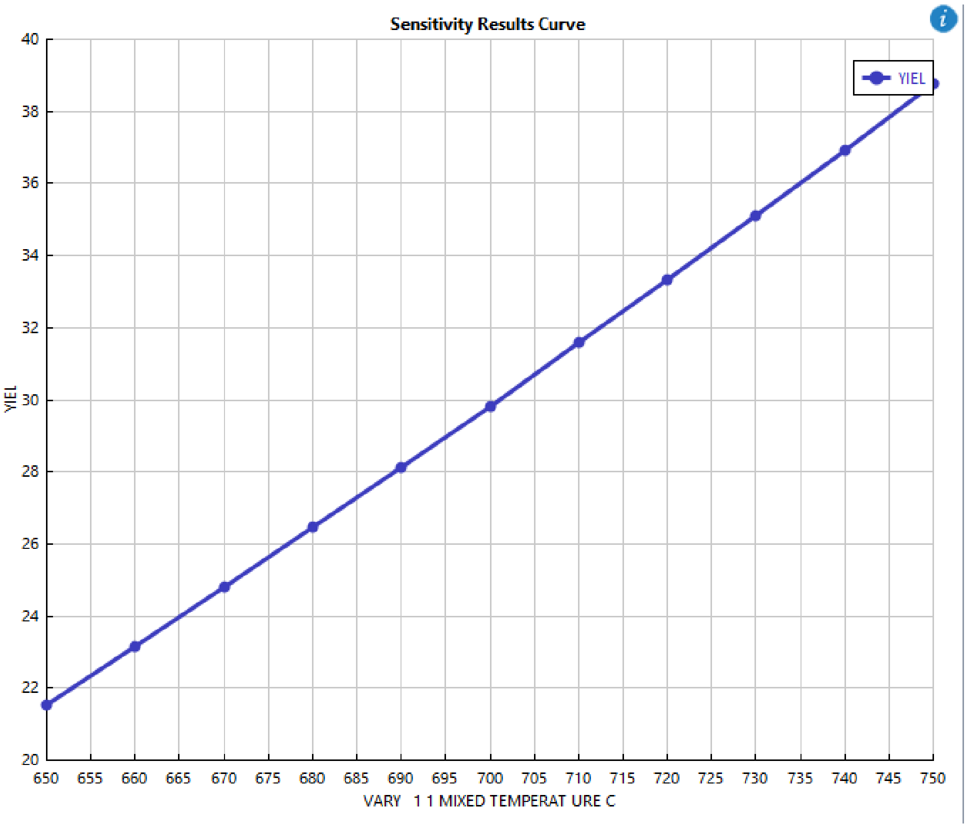


Figure 6. Butadiene yield at the first reactor dependence on the temperature

The catalyst used in the process is Cr_2O_3/Al_2O_3. The properties of the catalyst are provided according to the information given by the supplier from China [35] and can be seen on Table 29:

Table 29. Catalyst parameters.

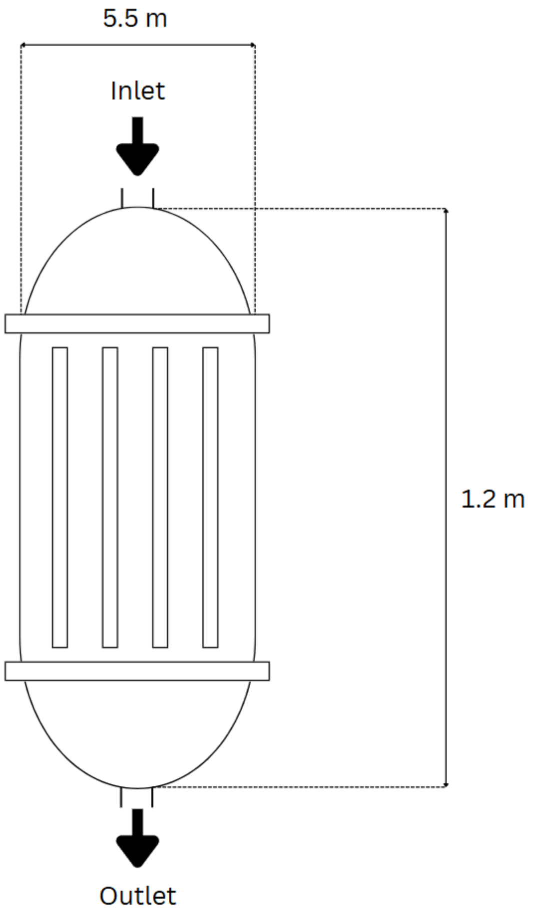
Catalyst	Cr_2O_3/Al_2O_3

Shape	Extrudate
Diameter	3.2±0.2 mm
Bulk density	0.9-1.1g/cm3
Surface area	>100 m^2/g
Price	9 $/kg

3.2. Design of R-102

After the first reactor and a heater, the gas stream goes to the second dehydrogenation reactor. There, butane and butene are dehydrogenated to produce butadiene and hydrogen. The details of the reactor can be seen on Table 30.

Table 30. R-102 Reactor schematics.

Technical sketch for R-102	
 	
Reactor type	Adiabatic

Reactor length (m)	1.2
Reactor diameter (m)	5.5
Wall thickness (mm)	12
Material	304 stainless steel
Volume (m^3)	28.5
Temperature (^oC)	700
Pressure (bar)	0.21
Catalyst bed volume (m^3)	25.4
Pressure drop (bar)	2.7E-2

According to streams mass balance can be estimated through Aspen Plus, and can be found on Table 31. The Aspen file can be found in the ESI section of this report.

Table 31. Mass balance of the R-102.

Mass balance		
Component	Inlet mass flow (kg/hr)	Outlet mass flow (kg/hr)
C_4H_{10}	12860	8717
C_4H_8	26161	26145
C_4H_6	27318	31189
H_2	453	741
Total	67088	67088

As the condition of the reactor is adiabatic, a total heat transfer should be 0. By using Eq. 2.1.1 it is possible to calculate the energy transfer for this reactor, too. The stream enthalpies and heat of reaction can be seen on Table 32.

Table 32. Energetic parameters for the reactor.

Inlet enthalpy flow (kW)	40716
Outlet enthalpy flow (kW)	40716
Heat of reaction (kW)	4161.27
Heat from temperature drop (kW)	4161.26

$$\Delta E = 40298.5 - 40298.5 + 4161.27 - 4161.26 \approx 0$$

The reactor size is found according to the pressure drop inside the reactor. From Aspen Simulatio, it is possible to determine that the length and diameter of the reactor should be equal to 2.9 m and 4.1 m, respectively.

The catalyst weight is found by sensitivity analysis between mass fraction of butadiene in the product stream and catalyst weight in the reactor. The graph can be seen in Figure 7 and the catalyst weight required for obtaining the desired mass fraction is equal to 16000 kg.

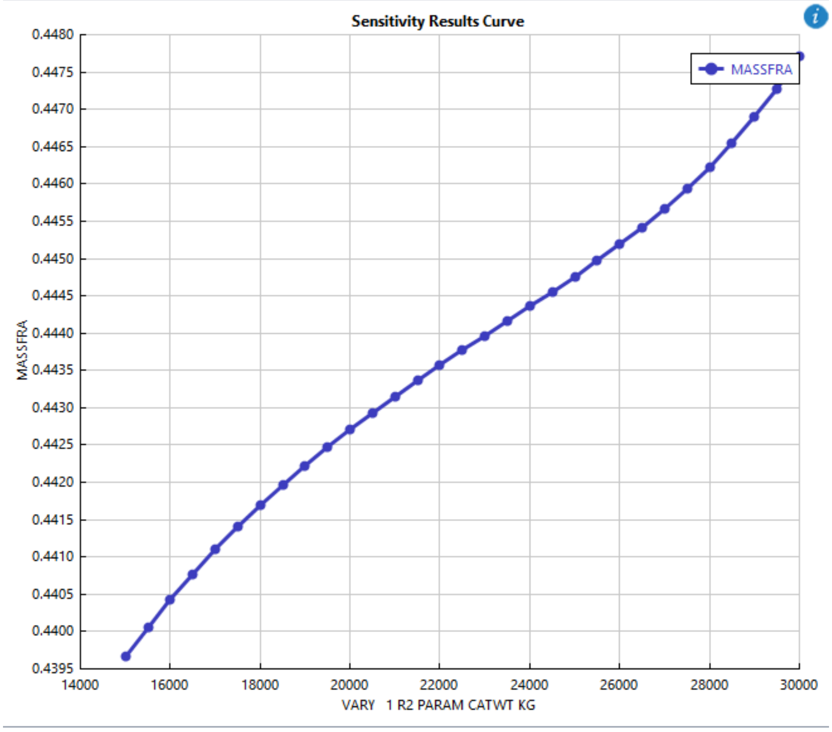


Figure 7. Sensitivity analysis: butadiene mass fraction and catalyst weight

3.2.1. Effectiveness factor and Thiele modulus

The reactor dimensions were selected according to the pressure drop in the fixed bed reactors. As we have a gas flowing through the fixed catalyst bed inside the reactor, we are experiencing the pressure drop due to friction. Firstly, there is a need to evaluate the effectiveness factor and Thiele modulus of our process, because the literature kinetics used for our catalyst have been studied on a laboratory scale. Usually, under such conditions, the catalyst is finely powdered to eliminate mass transfer limitations, ensuring that the reaction is limited solely by reaction kinetics. In industrial processes, however, the catalyst can take various shapes, such as spherical or cylindrical particles, or, as in our case, extrudates. In such cases, it is necessary to evaluate whether mass transfer limitations exist within the catalyst. This can be done by assessing the effectiveness factor and the Thiele modulus.

$$Effectiveness\ factor\ (\eta) = \frac{Real\ reaction\ rate}{Reaction\ rate\ without\ mass\ transfer\ limitations} \tag{3.1.2}$$

To ignore mass transfer limitations, the effectiveness factor must be at least 0.9. The effectiveness factor depends on another parameter called the Thiele modulus.

$$\phi = \frac{d}{2}\sqrt{\frac{v\ k_m\rho_p}{D}} \tag{3.1.3}$$

$$d = \frac{6V}{S} = \frac{6m/\rho}{S_c m} = \frac{6}{S_c \rho} \tag{3.1.4}$$

Where:

- d – mean diameter of a particle,
- v – reaction coefficient,
- k□ – rate constant,
- ρ□ – apparent particle density,
- D – diffusivity constant of butane over chromia-alumina.

So, there is a need to calculate those parameters, accordingly. The diffusivity constant is taken as 0.0472 cm^2/s, as estimated by Uchida et al. (1975) [36]. The apparent particle density was taken as 2.1 g/cm^3, based on alumina-based catalysts reported by Ledakowicz et al. (2013) [37].

With our parameters, $\phi = 0.386$, and the effectiveness factor can be estimated using the following formula:

$$\eta = \frac{tanh(\phi)}{\phi} \tag{3.1.5}$$

This equals 0.95 in our case, meaning that mass transfer limitations can be neglected, and the reaction kinetics depend solely on the chemical reaction kinetics, which is desired.

The next parameter required for reactor design is the pressure drop. The pressure drop inside the reactor can be determined using the Ergun equation.

$$\Delta p = \frac{150\mu L}{D_p^2}\frac{(1-\epsilon)^2}{\epsilon^3}v_s + \frac{1.75L\rho}{D_p}\frac{(1-\epsilon)}{\epsilon^3}v_s^2 \tag{3.1.6}$$

Calculations were made to different reactor diameters with varied void fraction inside the catalyst bed. Moreover, pressure drop was also evaluated using Aspen Plus. The details of the model and calculations can be found in the ESI section of this report. Table 33 presents the reactor parameters in Aspen Plus.

Table 33. Reactor parameters required for the pressure drop calculation.

Mass of catalyst (kg)	34000

Apparent density of catalyst (kg/m^3)	2100
Mean diameter of particles (mm)	4.5

3.3. Design of D-101

D-101 is a flash drum which will be used to separate most of the hydrogen from the system. It operates at elevated pressure (22 bar) and relatively low temperature (7°C) to make sure that most of the hydrocarbons remain in liquid form to save as much butadiene as possible. Flash drum works in a way that pressurized stream enters a tank that has a lower pressure than the feed which results in a flashing and separation of vapor from the liquid [38].

To find optimal operating conditions Sensitivity Analysis tool in Aspen Plus has been used. By varying pressure and temperature it was found that hydrogen separation is higher at lower temperatures and lower pressures. However, at lower pressure butadiene loss is also large as it starts to vaporize. Therefore, 22 bar and 7°C was chosen where butadiene loss is only 2.56% by mass and hydrogen separation is 96% by mass.

To keep the temperature at 7 degrees 124 kW of heat needs to be supplied to prevent temperature drop and no separation.

Operating conditions allow us to run an Aspen simulation and find output streams of flash drum which will help to find dimensions of a drum.

Table 34. Mass balance for a flash drum.

Components	Inlet stream, kg/hr	Top stream, kg/hr	Bottom stream, kg/hr
n-Butane	8727.33	212.45	8514.88
1-Butene	26223.50	704.4	25519.1
1,3-Butadiene	31188.50	798.2	30390.3
Hydrogen	740.81	712.52	28.29
NMP	0.000	0.000	0.000
Water	297.180	3.569	293.611
		2431.139	64745.881
Total	67177.3	67177.3	

From the data in Table 34 and molecular weight of each component and molar density (from Aspen) the density of top stream and bottom stream could be calculated. The densities are given in Table 35.

Table 35. Flash drum top and bottom stream properties.

Top stream average molecular weight, kg/kmol	Top stream molecular density, kmol/m^3	Bottom stream average molecular weight, kg/kmol	Bottom stream molecular density, kmol/m^3
6.32	0.94	54.25	11.375
Top stream density, kg/m^3		Bottom stream density, kg/m^3	
5.94		617.1	

Vessel diameter is calculated by setting vapor velocity less than the terminal velocity of a drop according to following formula:

$$u_t = 0.07\sqrt{\frac{\rho_l-\rho_v}{\rho_v}} \quad (3.2.1)$$

Vessel has no demister, therefore $0.15u_t$ is taken as maximum vapor velocity.

$$u_t = 0.07\sqrt{\frac{617.1-5.94}{5.94}} = 0.71\, m/s \quad (3.2.2)$$

$$u_{vapor} = 0.15 \times 0.686 = 0.107\, m/s \quad (3.2.3)$$

From the mass flow and the density, volumetric flow-rate can be calculated which will help to find the minimum diameter of the vessel.

$$Q = \frac{m_v}{\rho_v} = \frac{2431.139}{5.94} \times \frac{1}{3600} = 0.1137\, \frac{m^3}{s} \quad (3.2.4)$$

$$A = \frac{Q}{u_{vapor}} = \frac{0.1137}{0.107} = 1.06\, m^2 \quad (3.2.5)$$

$$D_{min} = \sqrt{\frac{4\times A}{\pi}} = \sqrt{\frac{4\times1.06}{\pi}} = 1.16m \quad (3.2.6)$$

To find the height of the vessel liquid height should be calculated. In addition, 1 diameter above the feed and 0.6 below the feed should be allowed.

Liquid height can be calculated by its volumetric flow-rate and residence time in a following way:

$$V_v = Q_v * \tau = 0.14 \times 5 = 0.7\, m^3 \quad (3.2.7)$$

$$Q_l = \frac{64745.881}{617.1} \times \frac{1}{3600} = 0.029\, \frac{m^3}{s} \quad (3.2.8)$$

$$V_l = 0.029 \times 300 = 8.686\, m^3 \quad (3.2.9)$$

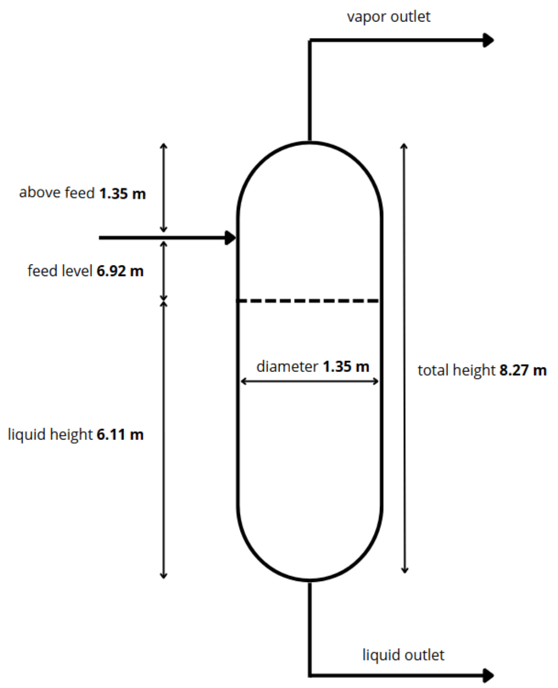
$$H_l = \frac{Q_l * \tau}{A} = \frac{8.686}{1.16} = 7.53\ m \qquad (3.2.10)$$

$$H_{total} = H_l + H_{above\ feed} + H_{below\ feed} = 9.4\ m \qquad (3.2.11)$$

By repeating these calculations for different diameters it was found that the most optimal diameter is 1.35 m. Therefore, the height of the vessel is 8.27 meters.

To choose a material for a flash drum following design conditions are used: 38°C and 23.4 bar. Presence of little amounts of water results in use of stainless steel 304, which is the most popular and economical choice to resist corrosion.

Table 36. The Specification Sheet of D-101.

Sketch	Unit	D-101 (Flash drum)
	**Diameter**	**1.35 m**
	Feed level	6.92 m
	Liquid height	6.11 m
	Above feed	1.35 m
	Below feed	0.81 m
	Total height	**8.27 m**
	Thickness	21 mm
	Operating pressure	22 bar
	Operating temperature	7 ℃
	Material	Stainless steel 304

3.4. Design of D-103

The bottom product of the Extractive Distillation Column D-102 enters the Rectification Column D-103. The unit was modeled in Aspen Plus by using RadFrac column design with NRTL method. The purpose of this unit is to separate the 1,3-butadiene from NMP-water solvent. As both NMP and water are less volatile than 1,3-butadiene, the rectification column was the most suitable design.

A rectification column is a kind of distillation column that uses constant contact between descending liquid reflux and rising vapors to separate components in a mixture with high purity. In order to concentrate the more volatile components at the top of the column and retain the less volatile components at the bottom, the process uses repeated condensation and vaporization [39].

As it can be seen from Table 37, the 98.423% of water and 99.94% of NMP by mass introduced in the feed (NMP-Butadiene) are separated from 1,3-butadiene. The separated NMP-water solvent is almost at the same concentration as the initial 0.8:0.2 by mass composition and is stored for further implementations or recycling.

Table 37. Product Specifications of the Column.

	Mass Flow [kg/hr]		
	NMP-Butadiene	*Crude Butadiene*	*NMP Solvent*
n- Butane	0.129	0.129	0.0005
Butenes	19.45	19.1	0.35
1,3-Butadiene	11804.15	10996.41	807.74
NMP	721214.45	430.764	720783.68
Water	180293.32	2842.881	177450.44
Total	913331.5	14289.28	899042.22

	Mass Fraction		
	NMP-Butadiene	*Crude Butadiene*	*NMP Solvent*
n- Butane	0.0000	0.0000	0.0000
Butenes	0.0000	0.0013	0.0000
1,3-Butadiene	0.0129	0.7696	0.0009
NMP	0.7897	0.0302	0.8017
Water	0.1974	0.1989	0.1974
Total	1	1	1

To begin with the design, the minimum stage number and reflux ratio were calculated by hand using Fenske and Underwood equations:

$$N_{min} = \frac{log[(x_{LK,D}/x_{LK,B})(x_{HK,B}/x_{HK,D})]}{log\,[\alpha_{LK,HK}]} \qquad (3.2.12)$$

$$R_{min} + 1 = \Sigma\frac{\alpha_i(x_{iD})}{\alpha_i - \theta} \tag{3.2.13}$$

where, LK is butadiene, HK is water, because NMP is nonvolatile, and θ can be found using the formula:

$$1 - q = \Sigma\frac{\alpha_i z_{iF}}{\alpha_i - \theta} \tag{3.2.14}$$

The streams that are either entering or leaving the column are in liquid phase with molar liquid fraction of 1. Therefore, q is equal to 1 which means "fully liquid". The findings of hand calculation were compared with the values of the DSTWU column in Aspen Plus. The relative volatility was calculated based on the K-values of the components in the feed stream (NMP-Butadiene) and shown in Table 38.

Table 38. The feed stream parameters at 142.763°C and 5 bar.

Component	Molar Flow rate (kmol/hr)	Molar compositions	K values, vapor/liquid (Final Aspen Plus file)	Volatility of component relative to Water
N-butane	0.001	$1.2735*10^{-7}$	68.776	77.470
1-butene	0.023	$1.981*10^{-5}$	49.922	56.232
1,3-butadiene	155.684	0.0131	37.359	42.081
NMP	4963.919	0.4154	0.035	0.040
Water	6828.535	0.5715	0.888	1
Total flow rate (kmol/hr)	11948.162			

Table 39. The values of hand calculations and Aspen Plus

	Hand calculation	**Aspen Plus**
Nmin	1.714	1.797
Rmin	0.1893	4.1094
Relative volatility, $\alpha_{LK,HK}$	42.081	-
θ	22.4336	-

The parameters obtained from hand calculations and Aspen Plus were derived from a shortcut method using RadFrac as the initial values found from hand calculations were not suitable as the mass flows and fraction were not similar. Parameters like actual stage number, reflux ratio, distillate to feed ratio, feed stage were changed to acquire similar mass fractions and flows as in the mass balance.

The height of the column is based on the spacing between trays. The tray spacing in both sections is equal to 0.762 m. So, the height of the stages without condenser and reboiler stages are 7.62 m. According to the rule of the thumb, height of 1.5 m to 3 m has to be added to the top and bottom stages of the column [40]. Therefore, the overall height of the column was approximated to be 11.5 m.

The feed stage was calculated by using Kirkbride equation of:

$$log(\frac{N_r}{N_s}) = 0.206 * log(\frac{B}{D} * \frac{x_{HK,f}}{x_{LK,f}} * (\frac{x_{LK,b}}{x_{HK,d}})^2) \tag{3.2.15}$$

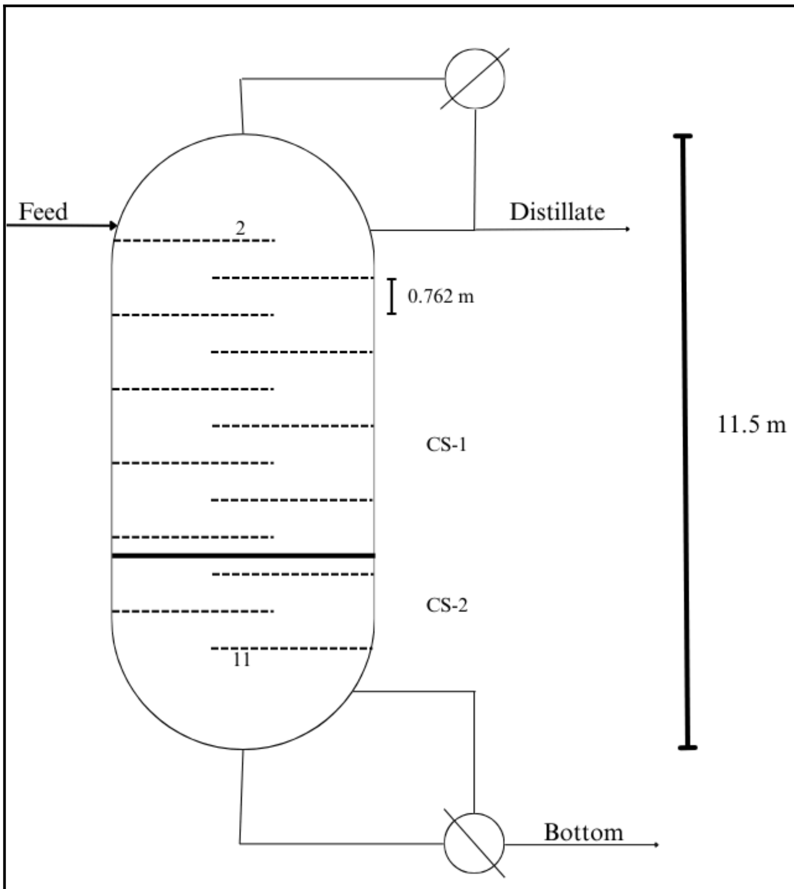
where, N_r is the stages above the feed, N_s is the stages located below feed, B and D are the flow rates of the bottom products and distillate, respectively, $x_{HK,f,}$ and $x_{LK,f}$ are the molar fractions of light key and heavy key in the feed, $x_{LK,b}$ is the molar fraction of light key in the bottom products, $x_{HK,d}$ is the molar fraction of heavy key in the distillate.

All the calculations can be seen in the Excel file located in *ESI* of the Report. The calculated feed stage is 3rd stage; however, in the design it was changed to the 2nd stage, because the total liquid flow rate in the 2nd stage was not enough for the column to work.

The internal column parameters were also derived using the shortcut method to obtain hydraulic plot without errors and warnings. The Table 39 indicates the shell and internal parameters of the column at rate-based modeling and this design works well for both sieve and bubble cap trays.

Table 40. The Rectification Column Specification Sheet.

Sketch	Unit	D-103 (Rectifier)
	Design	Trayed
	Phase	Liquid
	Tray material	Stainless Steel 304
	Total height	11.5 m
	Total number of stages	12
	Reflux ratio (molar)	1.7
	Distillate to feed ratio (mole)	0.0209
	Inlet Stream Conditions	
	Pressure, bar	5
	Temperature, ℃	142.763



Condenser Properties	
Type	Total
Temperature, ℃	36.7408
Pressure, bar	4.95

Reboiler Properties	
Type	Kettle
Temperature, ℃	163.913
Pressure, bar	4.961

Internal Design

From Stage 2 to Stage 9		From Stage 10 to Stage 11	
Tray Type	SIEVE	Tray Type	SIEVE
Tray Spacing	0.762 m	Tray Spacing	0.762 m
Column Diameter	3.6 m	Column Diameter	4 m
Section Height	6.096 m	Section Height	1.524 m
Number of Holes	500	Number of Holes	1000
Hole Diameter	12.7 mm	Hole Diameter	12.7 mm
Number of passes	4	Number of passes	4

3.5. Design of D-104

As the result of the stream, which was produced from D-103, in order to obtain the purity value of 99.5 wt% for 1,3-butadiene, flash drum D-104 was added to the production as one of the major equipment. The following Table 41 is introducing the feed properties entering the flash drum.

Table 41. Feed data at 35.4°C and 4.95 bar taken from overall Aspen file.

Component	Molar Flow rate (kmol/hr)	Molar fractions	K values, vapor/liquid (Final Aspen Plus file)
N-butane	0.001	$5.80*10^{-6}$	235
1-butene	0.023	$8.98*10^{-5}$	234
1,3-butadiene	146.0	0.580	137
NMP	2.48	0.010	$9.64*10^{-5}$
Water	103.0	0.410	0.012
Total flow rate (kmol/hr)	252.0		

Then to design the flash drum, calculations are started from defining operating conditions such as temperature and pressure. These values were obtained by applying sensitivity analysis in Aspen Plus, so the defined values are 30°C and 3.5 bar.

Next, in case of the settling velocity, data from Table 42 and formula 3.2.1 were used.

Table 42. Properties of inlet and outlet streams

	Feed product	Vapor product	Liquid product
Molar flow rate ($kmol/hr$)	252.0	147.0	105.0
Mixture density ($kmol/m^3$)	0.326	0.139	48.7
Volumetric flow rate (m^3/s)	0.215	0.294	$6.00 *10^{-4}$

So, the estimated velocity is equal to 1.31 m/s. Next task was to determine the diameter of the vessel, so the following formula was used [41].

$$D_{min} = \sqrt{\frac{4\times Q_{vapor}}{\pi * u_{settling}}} = \sqrt{\frac{4\times 0.294\ m^3/s}{\pi * 1.31\ m/s}} = 0.535\ m \tag{3.2.16}$$

Further, by applying the same approach described in the 3.2.1 section, the height of liquid level in the flash drum was identified as 0.8 m. In order to find the overall height of the flash drum, heuristic assumptions were used since diameter value is low. So, based on these assumptions, the height between liquid level and inlet stream should be equal to half of the diameter or 0.6 m, so 0.6 m was taken [41]. The distance between demister pad and feed steam should be at least equal to 1 m [41]. It should be noted that the demister pad is used to increase the purity of vapor product by removing some liquid droplets [42]. The size of the demister pad itself was taken as 0.4 m by minimum [41]. And for the safety considerations, the overall length was increased to 20% [43].

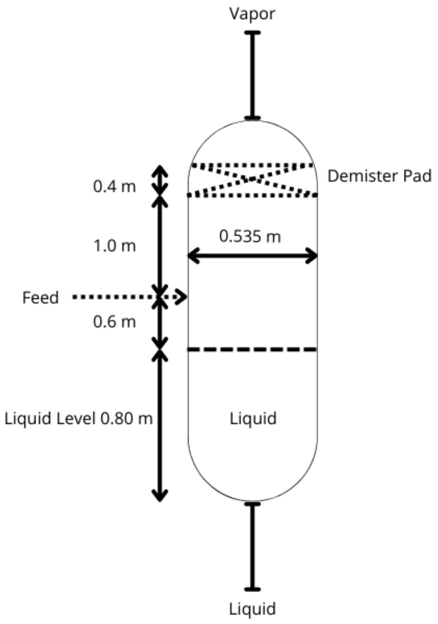
L = (0.8 m + 0.6 m + 1 m + 0.4 m) * 1.2 = 3.36 m

The thickness of the flash drum was obtained by applying the following formula, where P_i is 10% excess of operating pressure, D_i is the diameter of the vessel, S is maximum allowable stress of the material, and E is joint efficiency taken as 0.9 [41]. For the design of this flash drum stainless steel 316 was chosen as the main material in order to avoid corrosion.

$$t = \frac{P_i * D_i}{2 * S * E - 1.2 * P_i} \tag{3.2.17}$$

Estimated value for thickness with the allowed corrosion value of 2 mm for stainless steel was 3.16 mm, so the overall thickness value can be taken as 4 mm.

Table 43. The Specification Sheet of D-104

Sketch	Unit	D-101 (Flash drum)
	Diameter	0.54 m
	Feed level	1.40 m
	Liquid height	0.80 m
	Above feed	1.96 m
	Below feed	1.40 m
	Total height	3.36 m
	Thickness	4 mm
	Operating pressure, bar	3.5
	Operating temperature (℃)	30
	Material	Stainless steel 304

3.6. Heat exchanger (H-101)

To produce 1,3-butadiene, the feed—primarily composed of n-butane/light hydrocarbons—must be heated to 700°C before entering the reactor. Since no heat exchanger can achieve temperatures beyond 500°C, a two-stage heating process is employed. First, a shell-and-tube heat exchanger preheats the feed from 34.1°C to nearly 150°C, after which a furnace raises the temperature to the required level.

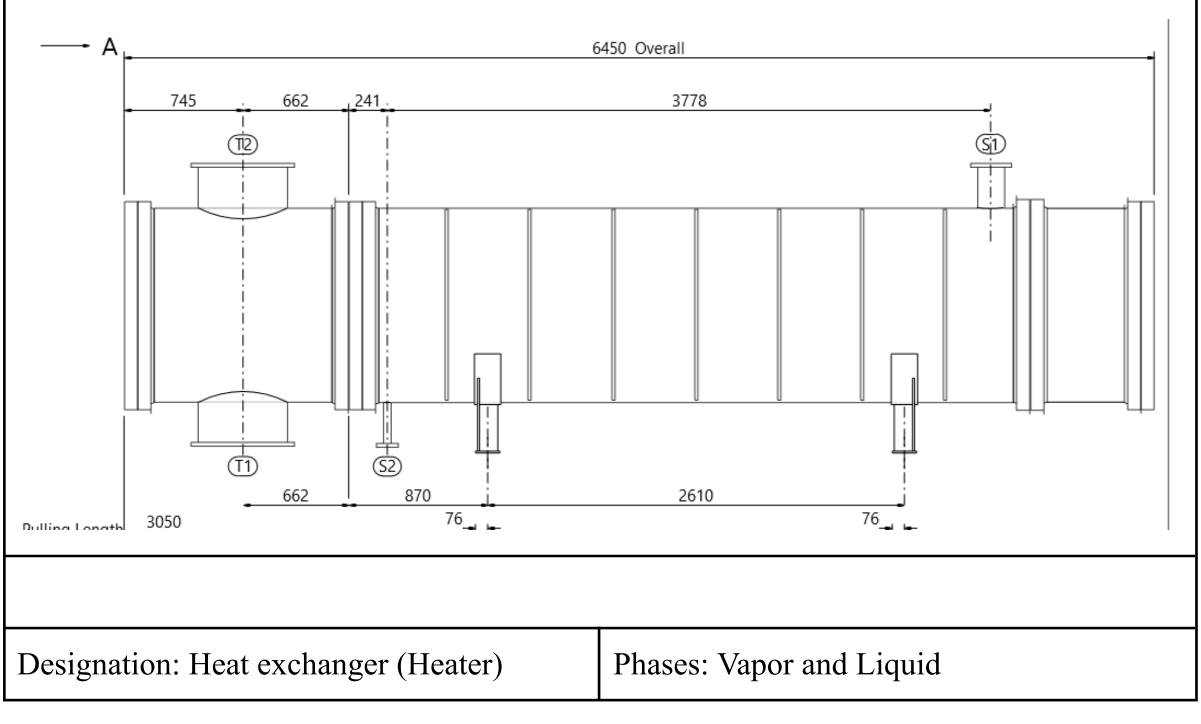
The shell-and-tube exchanger is designed to operate as a condenser. The configuration used in this case is horizontal, with condensation in the shell, and the cooling medium in the tubes. The hot stream consists of steam at 198.3°C and 15 bar is fully condenses in the shell side with the velocity 7103 kg/hr. The cold fluid entering the heat exchanger (consists of n-butane, 1-butene, 1,3-butadiene, and small fractions of hydrogen, water, and NMP) with a total mass flow rate of 67179.6 kg/hr at 34.1 °C and 1 bar goes into the tube side.

This stream allocation was made based on considerations such as stream flow rate, pressure drop, corrosion, fouling, temperatures, and operating pressure [44]. Hydrocarbons, with their higher flow rate, lower pressure, and corrosion potential, are better suited for the tube side to facilitate maintenance and minimize operational issues.

Following this allocation, the exchanger geometry, heat duty, velocity profiles, and pressure drops were found. The hand calculations are presented in excel and the Aspen simulation results are presented in Table 44.

The stainless steel 316 was selected as the construction material due to its excellent high-temperature durability, oxidation resistance, and cost-effectiveness compared to more advanced alloys.

Table 44. Equipment specification sheet for Heat Exchanger.

<table>
<tr><td colspan="2">Technical sketch for Heat Exchanger (Heater)</td></tr>
<tr><td colspan="2">Exchanger type: AEW floating head</td></tr>
<tr><td colspan="2">
</td></tr>
<tr><td colspan="2"></td></tr>
<tr><td>Designation: Heat exchanger (Heater)</td><td>Phases: Vapor and Liquid</td></tr>
</table>

<table>
<tr><td>Tube material: SS 316
Internal diameter of tube: 34.6 mm
Outer diameter of tube: 38 mm
Length of tube: 4.35 m
Number of tubes: 450</td><td colspan="2">U = 256 W/m^2-K
Baffle cut: 30%
Number of baffles: 7
Tube pattern: 90-square
Number of tube passes: 2</td></tr>
<tr><td colspan="3">Process Data (from Aspen simulation)</td></tr>
<tr><td>Component</td><td>Tube side</td><td>Shell side</td></tr>
<tr><td>Phase</td><td>Vapor</td><td>Vapor Liquid</td></tr>
<tr><td>Temperature in, C</td><td>34.1</td><td>198.3</td></tr>
<tr><td>Temperature out, C</td><td>150.3</td><td>197.9</td></tr>
<tr><td>Pressure in, bar</td><td>1</td><td>15</td></tr>
<tr><td>Pressure out, bar</td><td>0.8</td><td>14.9</td></tr>
<tr><td>Pressure drop, bar</td><td>0.2</td><td>0.1</td></tr>
<tr><td>Mass flow rate, kg/hr</td><td>67179.6</td><td>7102.8</td></tr>
</table>

4. Minor Equipment Design

4.1. D-102 Design

After Dehydrogenation by D-101, the crude mixture is flowed into the RadFrac Extractive Distillation Column D-102. In this column, the crude feed is separated from the n-Butane, increasing purity of the 1,3-Butadiene for further distillation. During the process the feed is introduced by the mixture of n-methyl-2-pyrrolidone (NMP) and water. NMP is considered as a difficult non-volatile component, so, incomplete calculation of relative volatility of the components, it is decided to assume this column as a minor component, so in the final design of a plant, this distillation column is projected as a Sep2 column, however, it is important to demonstrate preliminary design of this distillation column. All further results of the specifications and design are based on the Aspen Plus simulation.

D-102 works on the principle of partial-vapor condenser and equilibrium condition. The crude feed is entering into the column with a temperature of 100℃ and pressure of 5 bar, while the mixture of NMP and water is entering with temperature of 25℃ and pressure of 5 bar. Due to the difficulty of relative volatility calculation of the components, it is decided to use other readings as references for determining the Reflux Ratio and number of stages for Aspen Simulation [45-46]. As a result, the operating Reflux Ratio for the column was found as 5.5, with a total of 40 stages.

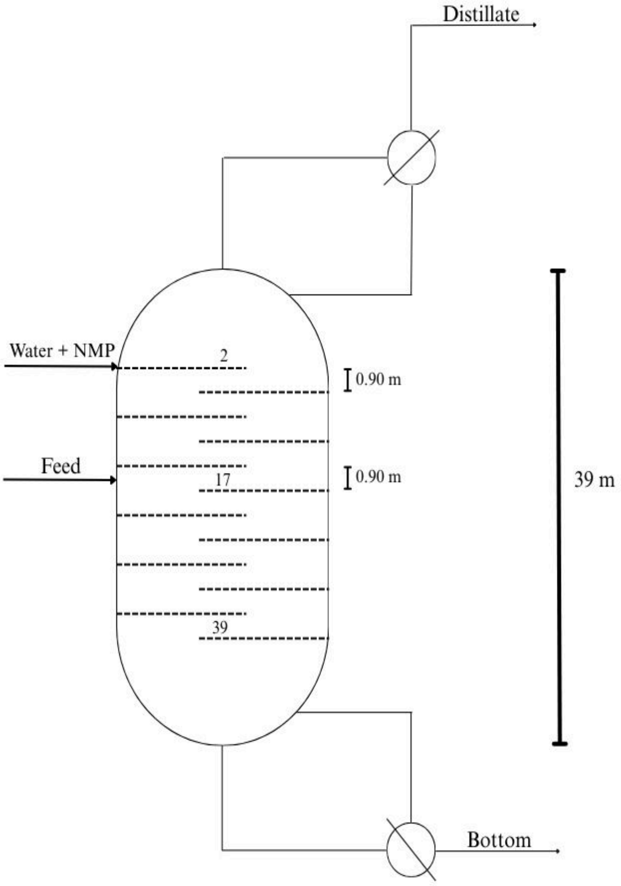
For internal design, both of the packed and trayed columns can be used for this process. However, as the distillation column is operating under high pressure for the separation of C4 mixtures, the tray columns are more preferable [47]. In the simulation by Kim et al, authors used a total number of trays of 85 stages and feed tray of 37 [45]. However, they used other compositions of mixture components and different methods were used during the simulation. By modifying it, our model has 40 trays in total, with feed entering into the system at tray number 17. Each tray has a type of SIEVE model, with spacing of 0.9 m and diameters of 5.21851 m and 4.79407 m for Stages 2-16 and 17-39, respectively. Further details of the column are introduced in Table 45.

Table 45. Product Specifications of D-102.

	Mass Flow [kg/hr]			
	Feed 1	*Feed 2*	*Raffinate*	*NMP-Butadiene*
n- Butane	8042.39	0	8042.31	0.08
Butenes	26654.52	0	26634.52	13.19
1,3-Butadiene	29793.24	0	21537.53	8255.71
Hydrogen	23.57	0	23.57	0
NMP	0.01	492567.73	0.01	492467.73
Water	291.46	123116.93	296.71	123111.68
Total	64798.39	615584.66	56534.66	623848.39

	Mass Fraction			
	Feed 1	*Feed 2*	*Raffinate*	*NMP-Butadiene*
n- Butane	0.1241	0	0.1423	0
Butenes	0.4112	0	0.4711	0
1,3-Butadiene	0.4598	0	0.3810	0.0132
Hydrogen	0.0004	0	0.0004	0
NMP	0	0.80	0	0.7894
Water	0.0045	0.20	0.0052	0.1973

Table 46. Schematics of D-102.

Sketch	Unit	D-102
	Design	Trayed
	Tray Type	SIEVE
	Total height	39 m
	Operating pressure	5 bar
	Condenser temperature (℃)	43.3958
	Reboiler temperature (℃)	142.763
	Total number of stages	40
	Reflux ratio (molar)	5.5
	Distillate to feed ratio (mole)	0.08
	Condenser	Partial-Vapor
	Material	Stainless Steel
	From Stage 2 to Stage 16	
	Tray Spacing	0.9 m
	Column Diameter	5.21851 m
	Section Height	13.5 m
	Number of Holes	12672
	Hole Diameter	12.7 mm
	Tray Material	Stainless Steel
	From Stage 17 to Stage 39	
	Tray Spacing	0.9 m
	Column Diameter	4.79407 m

	Section Height	20.7 m
	Number of Holes	9000
	Hole Diameter	12.7 mm
	Tray Material	Stainless Steel

4.2. M-101 Design

The feed of pure n-butane at 25℃, 1 bar and the distillate of D-102 at 43.4 and 5 bar which is being recycled back to the reactor are mixed in the mixer (M-101). The mixed stream comes out at 41.46℃ and 1 bar. The pressure of the mixed stream remains the same as the smallest pressure out of two streams.

Table 47. The characteristics of M-101.

Outlet temperature, ℃	41.46	
Outlet pressure, bar	1	
Vapor fraction	1	
Pressure drop, bar	0	
	In	Out
Total mole flow, kmol/hr	1237.54	1237.54
Total mass flow, kg/hr	68048.1	68048.1
Total enthalpy, kW	-395.785	-395.785

4.3. Design of Valves

The valves are introduced to drop the pressure of the streams. The valve V-101 placed before the heater and reactor to change pressure of the stream came out of the mixer from 1 bar to 0.24 bar. The second valve V-102 is placed after the flash drum to drop the pressure from 19.5 bar to 5 bar as the stream enters the D-102 column. The change in temperature occurs due to the expansion of gases.

Table 48. The characteristics of the valves.

	V-101	V-102
Outlet pressure, bar	0.24	5

Pressure drop, bar	0.76	14.5
Outlet temperature, ℃	40.1738	13.8185
Outlet vapor fraction	1	0.0136152

4.4. Design of compressors

The compressors were used to increase the pressure of the cooled stream exiting the reactor. They were arranged in series with the coolers due to the temperature increase that occurs during compression. This layout was chosen for cost reasons. A single large compressor would require a very high pressure ratio—from 0.18 to 25 bar—which would be too expensive. Therefore, the pressure must be increased gradually. The total pressure increase achieved by the compressors is from 0.18 to 25 bar, which is necessary for the flash drum (D-101), operating at 19.5 bar and requiring a pressure drop.

Table 49. The characteristics of compressors

Compressor type	Isentropic compressor
Net work required	9435.5354 kW
Efficiency	0.72
Outlet pressure	23 bar

	C-101	C-102	C-103	C-104
Net work required (kW)	1757.5	1169	2817	2716
Inlet pressure (bar)	0.18	0.5	1	5
Outlet pressure (bar)	0.5	1	5	25

4.5. F-101 Design

The feed exits the heat exchanger at 150 °C and is then directed to the reactor, which requires an inlet temperature of 700 °C. To achieve this, a furnace is used to heat the stream to the required temperature. The calculated heat duty for this step is 29,616.7 kW. Stainless Steel 321 (SS 321) was selected as the furnace material due to its excellent high-temperature stability, good oxidation resistance, and cost-effectiveness compared to higher-grade alloys.

Table 50. The characteristics of furnace

	Furnace inlet	Furnace outlet
Phase	Vapor	Vapor
Temperature, ℃	150	700
Pressure, bar	0.8	0.8
Enthalpy flow, kW	3765	33381
Mass Flows, kg/hr		
N-Butane	19365.5	19365.5
1-Butene	25518.7	25518.7
1,3-Butadiene	21969.8	21969.8
Hydrogen	28.3	28.3
NMP	0	0
Water	297.2	297.2
Overall flow	67179.6	67179.6

4.6. Storage Tanks

Storage tanks are required to store feed and product in the liquid form. Here, you can see Table 51, where the storage tank volumes are written according to the chemicals that they contain. Here we chose that the storage time for the feed is 30 days, as it is always needed, and the storage time for waste and product streams are 15 days, as it is needed to get rid of them by selling/recycling. All the values for flow rates are taken from the material balance of the process, and the liquid densities for gaseous products are taken from the Aspen simulations. After getting the flow rates, and storage times, the required tank volume can be calculated by multiplying the storage time by the flow rate. Tank volumes are considered to be 800 m^3, and the number of tanks are estimated accordingly.

Table 51. Storage tanks description

Storage Tank	**ST-101**	**ST-102**	**ST-103**
Stored Material	n-Butane	Hydrogen	1,3-Butadiene
State	Liquid	Liquid	Liquid

Flow Rate, m^3/day	19	22	308
Storage time, days	30	15	15
Tank volume required, m^3	570	326	4620
Tank quantity	1	1	6
Tank material	Stainless Steel 304	Stainless Steel 304	Stainless Steel 304

4.7. Design of heaters and coolers

Heaters and coolers are required to heat or cool the different process streams to achieve the temperatures needed for subsequent processes. The H-102 heater is located between two tubular fixed-bed reactors. This heat exchanger is necessary to heat the stream after the first reactor, compensating for the temperature drop caused by the endothermic dehydrogenation reaction. It raises the temperature from 583.5°C to 700°C, which is required for the reaction. The next heat exchangers are in series, operating with the compressors, and are required to cool the product stream, which increases in temperature due to compression. The inlet and outlet temperatures of H-103, H-104, H-106, and H-107 are provided in Table 52. Next, the H-108 heat exchanger is used to heat the stream coming from the flash drum. This temperature increase is necessary for the next separation step in D-102. It raises the temperature from 11°C to 100°C. The final heat exchanger, H-109, is a cooler required for the conversion of the butadiene product from a gaseous to a liquid state. It cools the stream from 36°C to 25°C, at which temperature the butadiene condenses into a liquid. A summary of the heat exchangers, including their inlet and outlet temperatures and heat duties, can be found in Table 52.

Table 52. The characteristics of heaters and coolers

Parameters	**H-102**	**H-103**	**H-104**	**H-105**	**H-106**	**H-107**	**H-108**	**H-109**
Duty (kW)	7374	28837	1769	1188	2630	11507	9732	-935
Inlet temperature (°C)	583.5	622	100	84	130	146	11	36
Outlet temperature (°C)	700	50	50	50	60	8	100	25

5. Plant Location and Layout

5.1. Plant location

The plant location has been chosen in the Atyrau city region. The location of the plant can be seen on Figure 8. This decision was made for several reasons, including proximity to raw materials, developed transport infrastructure, availability of fuel and power, land availability, presence of related industries, and waste disposal options. Moreover, Atyrau is located within the Special Economic Zone (SEZ) of the National Industrial Petrochemical Technopark (NIPT) in Kazakhstan. Building the plant there will significantly reduce operational costs, as tariffs for electricity, water, heat energy, and waste drainage are considerably lower due to government regulations [48]. Another reason for selecting this location is the absence of existing butadiene production plants in the area, which means there will be less competition in the market.

The first advantage of choosing Atyrau is the availability of land for building the plant. Atyrau has an industrial zone specifically designated for various industries and plants. The SEZ NIPT has a total industrial area of 3,475 hectares, which is sufficient to accommodate one plant [49].

The availability of raw materials is crucial for the overall process, as it can reduce transportation costs and ensure a timely supply for planned production. Atyrau is located in the western region of Kazakhstan, where major oil fields such as Kashagan, Tengiz, and Karachaganak are situated. Due to this, sourcing raw materials in the region will not be a problem. Moreover, since the oil and gas extraction and transportation infrastructures are well developed in western Kazakhstan, there should be a steady and reliable supply of n-butane to the plant in Atyrau. For example, Tengizchevroil, one of the largest oil and gas companies in Kazakhstan, operates in the Atyrau region and can easily distribute LPG and n-butane gas. Choosing Atyrau as the plant location helps secure n-butane supply, ensuring the planned production of butadiene.

Another positive aspect of being in a developed zone is the availability of fuel and power. Considering that Atyrau is located in an industrial center, there are many fuel distributors and a variety of natural gases available. Having access to fuel at any time is very important for industrial processes. The Atyrau Oil Refinery (ANPZ), located in Atyrau, offers a range of fuels—liquid fuels such as petrol and diesel—and can also supply natural gas to industries [50-51].

The last advantage of the SEZ NIPT is that it collects and recycles all industrial waste, which is important for process costs. Having an already established waste management system significantly reduces the cost and time required to handle industrial waste.

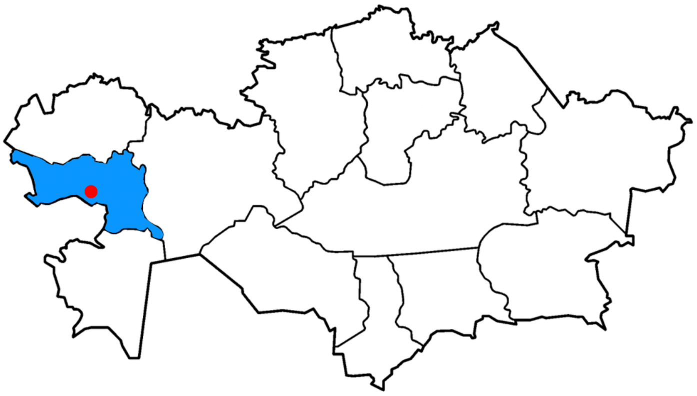


Figure 8. Plant location

5.2. Plant layout

The butadiene production plant is shown in Figure 9. The main entrance is through the security gatehouse. Two main zones are designated in the layout: the administrative area and the operational area. The administrative area includes facilities such as the office, canteen, locker room, and medical center, all located near the security gatehouse, just beyond the entry point. A buffer zone is maintained between the administrative and operational areas for safety reasons.

The operational area contains the plant, plant utilities, tank farm, maintenance workshop, laboratory, warehouse, and the shipping and receiving facility. The plant and tank farm are designed to allow for possible future expansions. A total of five fire stations are strategically placed near key facilities. Emergency water storage is located near the plant utilities and the plant itself, considering the high potential for disasters in those areas.

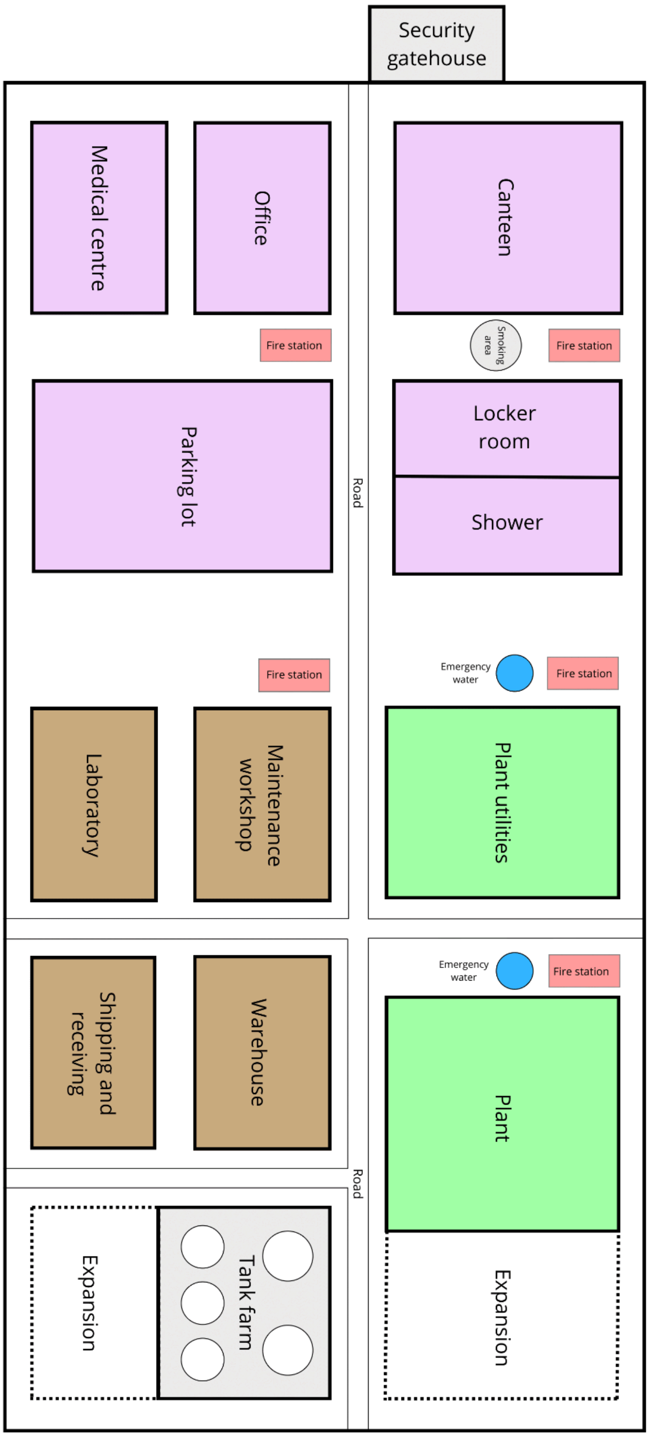


Figure 9. Plant layout

6. Environment and Waste Streams

Our proposed butadiene production process utilizes butane in a catalytic dehydrogenation reaction followed by a series of separation units. During the operation, gaseous waste streams are generated. According to the environmental regulations, those wastes need to be utilized properly. The units that generated waste streams are: reactors, furnace, flash drum and extractive distillation columns. Waste stream gases include light hydrocarbons byproducts generated from reaction, CO and CO_2 generated from burning the coke and also from reaction, and hydrogen with some hydrocarbons separating from the flash drum. Overall waste streams and unwanted chemicals in streams can be seen on Table 53.

Table 53. Overview of the waste types according to operation units

Unit operation	**Waste Stream**	**Type (Gas/Liquid/Solid)**	**Composition**	**Treatment needed**
Reactor	Coke burn-off	Gas	CO_2, CO, particulates	Flue gas treatment (scrubber/filter)
	Reaction byproducts	Gas	H_2, CH_4, C_2H_6, C_3H_8 etc.	Separation
Furnace	Flue gas	Gas	CO_2, H_2O, CO, NO_2, SO_2, O_2	Stack scrubber
Flash drum	Vapor off-gas	Gas	H_2, CO, light hydrocarbons (CH_4, C_2H_4)	Burn or recover light gases
Distillation columns	Used solvent	Liquid	NMP, H_2O, dissolved hydrocarbons	Separation

6.1. Reactor

According to the Table, the reactor produces byproducts during the reaction. This is due to the nature of the dehydrogenation reaction and the high temperature it requires. The operating temperature of the reactor is 700°C, and at that temperature, different light hydrocarbons, such as CH_4, C_2H_6, C_3H_8 etc., can be formed along with the main products. Hydrogen gas is another byproduct that is produced. Additional waste formed in the reactor includes CO_2 and CO gases. During the reaction at high temperatures, coke is deposited on the surface of the catalyst, which inhibits further reaction. Due to the formation of coke, it must be removed by burning it with air, which produces flue gas.

In the case of byproducts, they should be separated from the main product stream using a flash drum. After separation, they should be captured, as they have the potential to become an additional source of revenue. This is because hydrogen and light hydrocarbons are used in various processes such as hydrogenation, chemical conversion, and can also serve as fuel. CO_2 and CO gases, on the other hand, are considered waste gases. CO_2 is a non-toxic gas but contributes to global warming due to the greenhouse effect, and thus requires proper management. It should be captured and stored underground, as is commonly done. CO gas is highly toxic and must be properly treated. While it has potential uses in other processes such as reduction reactions and syngas production, the CO produced from the reactor is not pure. Therefore, the only viable option is to burn it into CO_2 and store it underground by compressing and injecting it.

6.2. Furnace

The furnace uses fuel to generate the heat required to raise the gas stream to the necessary temperature. The gas composition depends heavily on the type of fuel used in the combustion process. If conventional fuel in the form of natural gas is used, CO_2, CO, and H_2O are formed. This is very similar to the flue gas produced from coke burning, so the treatment process is also quite similar. There is a need to capture, compress, and inject it underground.

In the case of fuel oil, there can be traces of SO_2, which is toxic and can cause acid rain in the area. Another gas is the NO_2, which is also considered to be toxic and cause acid rains. To mitigate this problem, a scrubber must be used to adsorb the generated SO_2 and NO_2 gases from the waste stream. However, the fuel type used in the furnace should be natural gas, due to the fact that the plant is located in the western part of Kazakhstan, where many oil and gas-related industries are present. From nearby industries, there is likely an abundance of natural gas available at a comparatively lower price. Based on this information, carbon capture and storage units are required in the case of using natural gas as fuel.

6.3. Flash drum

During the separation of hydrogen and light hydrocarbons from the product stream, a waste gas stream is produced. Its composition can be estimated as a mixture of unreacted butane, butene, butadiene, light hydrocarbons, such as methane, ethane, propane, and hydrogen. There are different ways to utilize the generated waste stream, as it contains valuable gases that can be used in industry. As mentioned before, hydrogen can be used in hydrogenation, and light hydrocarbons can be used as fuels or in other chemical processes. Other hydrocarbons can be recycled back into the system to get all the value.

Detailed description

The only stream that is not recycled in this process is the hydrogen gas-rich stream coming from the flash drum, where butadiene and most of the hydrogen are separated from the product stream coming from the reactor. The schematics can be seen in Figure 10. In the flash drum, Stream 9 is the waste stream, Stream S2 is the cooled product stream, and Stream 10 is the butadiene-rich stream. The chemical composition of Stream 9 can be seen in Table 54:

Table 54. Composition of the waste stream 9

	Mass flow rate (kg/hr)	Mass fractions
Butane	252.4	0.092
Butenes	846.9	0.31
Butadiene	934.4	0.34
Hydrogen	704.7	0.26
Water	4.6	0.0017
Total	2742.9	1

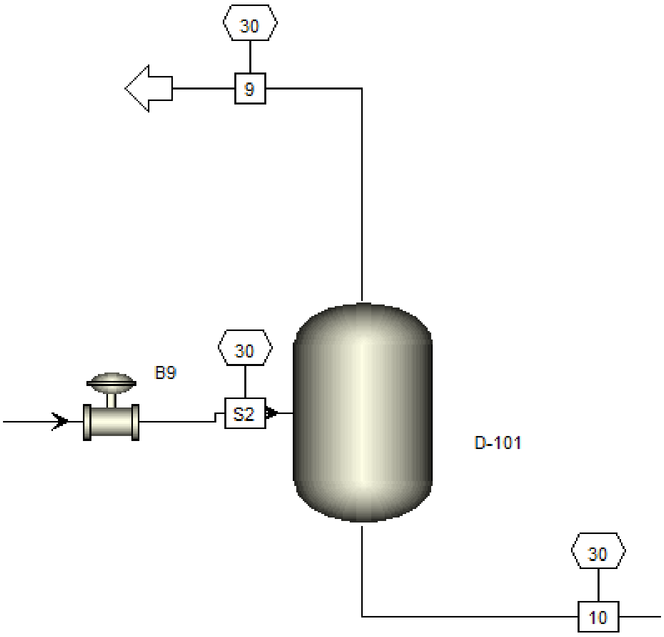


Figure 10. Flash drum with the waste stream

As mentioned before, hydrogen is a byproduct of the reaction, and water comes from the extractive distillation process, where the top stream is used as a recycle. In Table 54, it can be seen that along with the hydrogen, a portion of the butadiene product is also lost. This is undesirable; however, under these conditions, it is the optimal way to remove hydrogen from the product stream.

Environmental information (butadiene)

Butadiene is a colorless gas that is regularly monitored in the air as a volatile organic compound (VOC). It is considered a human carcinogen with long-term exposure [52]. Butadiene contaminates the air without affecting soil and water, as it quickly evaporates when spilled into aquatic environments or onto the ground. Half of the butadiene in the air breaks down within 6 hours [53]. The EPA has stated that the allowable concentration of butadiene in breathing air must not exceed 0.9 ppb.

Environmental information (butane)

Butane is a colorless gas with an odor similar to natural gas. It can cause cancer and reproductive system problems upon exposure. According to NIOSH, the allowable concentration of butane in the air must not exceed 800 ppm [54].

Flammability

The main hazard from the waste stream is its high reactivity, making it prone to burning and explosion. All the gases - including butane, butenes, butadiene, and hydrogen—are flammable, with flash points of -60°C [55], -79°C [56], and -85°C [57] for butane, butene, and butadiene, respectively. Precise transportation measures must be taken to avoid incidents.

6.4. Extractive distillation columns

During the separation of butadiene from other products, an NMP and water mixture is used. According to the mass balance of this process, some portions of butadiene and other products dissolve in the solvent, and after many cycles, the solvent will accumulate these chemicals. This is undesirable, as the efficiency of separation will decrease, and using fresh solvent is not feasible due to its high cost. The only option is to reuse the solvent by first separating the unwanted chemicals from it. This can be done using a stripping column, which can be added as a separate unit. The separated C4 mixture contains the desired butadiene, which can be recycled back into the separation unit.

7. Total Investments and Profitability

7.1. Bare Modulus Cost

Table 55 represents the major units' equipment cost, calculated using Aspen Process Economic Analyzer (APEA) and these indexes were used for further economic analysis estimation. In total, all of the equipment costs approximately $15 mln. More detailed costs and installed capital costs are available in the Economics Excel sheet.

Table 55. Equipment Cost of major units by APEA [Economics.xlsx].

Unit	Equipment Cost [$US]

R-101	1,188,000
R-102	1,033,100
H-101	284,200
D-101	81,400
D-103	1,033,900
D-104	22,000
Minors	11,133,073
Total	14,775,673

7.2. Initial Total Investment

Using Total Equipment Cost of the plant and typical factors for estimation, it is possible to calculate the Total Installation Cost of the equipment. For this extent, we used the next equation [58.]:

$$C = \sum_{i=1}^{i=M} C_{e,i,A}[(1 + f_p) + (f_{er} + f_{el} + f_i + f_c + f_s + f_l)/f_m] \tag{7.1}$$

In addition, it is important to consider location and time factors of the equipment, as they also affect the final cost of investments. As the plant is planned to be constructed in Atyrau region, the nearest major industrial center for plant location is Xinjiang province, China. As shown in Equation 7.1, using a simple rule of thumb, which states the 10% addition of total cost for each 1000 miles of transportation, it is possible to calculate the location factor of the equipment [58]. The indigenous location factor for China is 0.61; considering that the distance between Xinjiang and Atyrau is approximately 1730 miles and by dividing cost of CNY in USD in 2003 and cost of CNY in USD in 2025, the location factor was calculated as 0.74 [59]. Further, time factor can be found by using Chemical Engineering Plant Cost Index (CEPCI). Considering the reference period as 2013 (publishing year of the reference textbook) and taking its ratio with the index of 2024, we obtained a time factor of 1.5 [60]. All calculations were provided in the Economics Excel Sheet.

$$LF = 0.61 \times \frac{0.1426}{0.137} \times (1 + 0.1 \times \frac{1730}{1000}) = 0.745 \tag{7.2}$$

Table 56. Total Initial Investments [Economics.xlsx].

Total Equipment Cost [$US]		14,775,673
1.	Equipment Erection	0.3
2.	Piping	0.8
3.	Instrumentation and Control	0.3
4.	Electrical	0.2
5.	Civil	0.3
6.	Structures and building	0.2
7.	Lagging and Painting	0.1
Total Installation Cost [$US]		42,508,475
8.	Location factor	0.745
9.	Time factor	1.5
10.	Material Cost factor (SS 316)	1.3
ISBL [$US]		35,572,420
OSBL [$US]		14,228,968
Engineering Costs [$US]		4,980,139
Contingency [$US]		14,940,416
Fixed Capital Investment [$US]		69,721,944
Working Capital [$US]		10,458,292
Total Capital Cost [$US]		80,180,235

7.3. Fixed Cost of Production

The following Table 57 given below, reveals the details of fixed cost which is spent every year of production. Operating labor cost was simply determined by assumptions made based on the literature. So the number of shifts for work was taken as 4, and the number of operators was estimated as 26 per shift. Alos, the average salary of a plant operator was taken as 12500 US dollars [61]. Other values such as supervision, maintenance, and general plant overhead were estimated based on the operating labor cost, or ISBL and OSBL costs.

Table 57. Estimated values of fixed cost of production per year

Operating Labor [$US]	1,300,000
Supervision [$US]	325,000
Direct salary overhead [$US]	812,500
Maintenance [$US]	1,422,897
Property taxes and insurance [$US]	355,724
Rent of land [$US]	498,014
General plant overhead [$US]	2,509,258
Allocated environmental charges [$US]	498,014
Total [$US]	7,721,407

7.4 Variable Cost of Production

The variable cost of production consists of the cost of raw materials used in producing butadiene, which is butane-rich LPG, consumables (including catalyst, NMP, ethylene glycol, and catalyst), and utility costs, which cover electricity, heat, etc. The variable costs are shown in Table 58, where the year is given in plant operating years starting from 2028, with the inflation rate accounted for accordingly.

To calculate the cost of raw materials, the cost of LPG was calculated as follows: The required fresh butane flow rate was taken from the material balance, which is 86.8 kt/year. The cost of this amount of LPG was then calculated using local LPG vendor prices, which were found to be 168.61 US$/ton [price], and the percentage of butane in the LPG, which is 60%. The costs for the second operating year are slightly higher due to inflation considerations.

Consumables are chemicals purchased for plant operations. The cost of NMP is based on prices from Alibaba [ali], where it is 0.04 US$/kg. In the first operational year, the batch of NMP is larger because it is the initial amount needed for plant operations. After the first year, the cost changes, as NMP is purchased only to replace the NMP lost during regeneration.

Utility costs refer to the money spent on the operation of the plant. These include cooling water and electricity. The utility costs were determined using Aspen Economics tools.

Table 58. Variable cost of production.

Type of expenses	Cost (1st year, $)	Cost (2nd year, $)

Cost of raw materials	32,201,173	35,324,686
Consumables	892,368	279,829
Utilities	8,401,118	9,216,027
Total	41,494,659	44,820,542

7.5 Revenue and profitability of the production

In order to estimate the annual revenue obtained from 1,3-butadiene production, details such as 1,3-butadiene price, annual production rate, inflation rate should be clarified. By monitoring the global market, it was determined that a suitable price for 1,3-butadiene can be taken as 1040 USD/ton [62]. Also, the targeted production rate is 69500 tonnes, and inflation rate was taken as 9.7% [63]. Based on these data, revenue is equal to:

$$Revenue \ = \ rate\ of\ production\ *\ price\ per\ ton\ *\ 1000\ *\ (1\ +\ inflation\ rate)^{year}$$

The Table 59 below gives some information of estimated revenue corresponding to a particular year.

Table 59. Example of revenue for a particular years

Year	3	4	10	20
Revenue [$US]	95,419,696	104,675,406	182,425,027	460,416,305

The next task was to decide whether it is worthy to invest in this project, therefore, economic metrics such as Net Present Value (NPV), Internal Rate of Return (IRR), Payback Period, and Return of Investments (ROI) were calculated. NPV helps to identify whether there is a reason to invest in the project, so this value should be positive. IRR in this case, shows how fast the invested capital is returned, and the payback period clearly shows the year when this happens. ROI reveals the value at what extent it is expected to return the initial capital expenditures. All of the results are clearly summarised in the Table 60 below.

Table 60. Econometric metrics of profitability

NPV, [$US]	596,110,235
IRR, %	42.4
Payback period, year	5
ROI, %	109.0

According to Table 60, project can be considered as profitable because of given results. For example, IRR 42% means that capital expenditures are expected to be returned quickly, which is supported as a payback period of 5 years. Als, ROI value more than 100% means that there is a more profit than expenditures for this project.

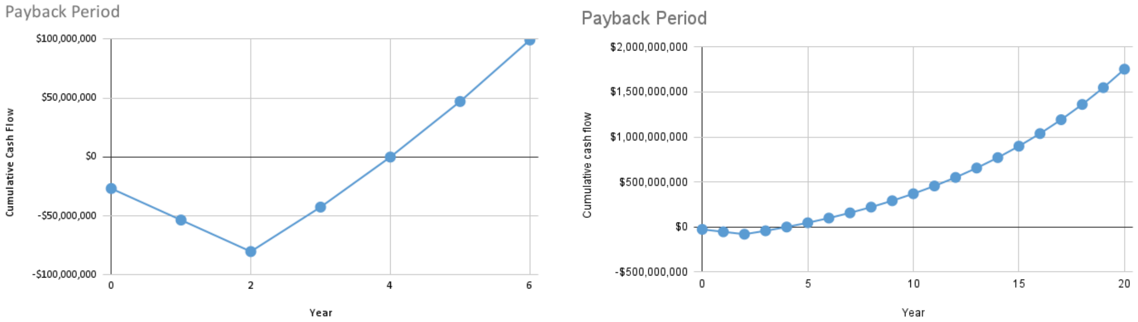


Figure 11. Graphical illustration of payback period

Based on the chart given in the Figure 11 above, it is clearly seen that the payback period is 5 years which is considered to be quite a good result for industrial plants.

8. Conclusions and Future work

To conclude, this project established a viable butadiene production route from butane using a dehydrogenation reaction. The production of butadiene can enhance industrial facilities in Kazakhstan, fostering the production of synthetic rubber and offering an opportunity to become an exporter of butadiene in the CIS region. This was achieved by analyzing the butadiene market, exploring various industrial butadiene synthesis processes, studying the reaction kinetics, and optimizing the conditions and unit parameters. This report describes the butadiene production process, including the PFD and equipment list, from the feed stage to the final 99.5% pure product. Additionally, the design of both major and minor units is discussed, along with the most probable plant location and an efficient plant layout. Environmental considerations are also addressed throughout the report, with potential management strategies outlined.

Among the various processes considered, butane dehydrogenation over a chromia-alumina catalyst was selected. The reaction kinetics were chosen based on literature and validated using Aspen Plus. To obtain the desired product, a system of two reactors in series was selected, followed by extractive distillation using NMP solvent. The overall conversion of butane and butadiene selectivity in the reactor are 55% and 93%, respectively. The butadiene production rate is 69.5 kt/year with a purity of 99.5%.

A material balance was conducted throughout the process, followed by the design of major equipment, including heat exchangers, reactors, flash drums, and distillation columns. The major equipment parameters were designed using various shortcut methods and equations, and were validated in Aspen Plus. The minor units, such as compressors, storage tanks, heaters, coolers, a furnace, and a distillation column, were designed with their respective heat duties and capacities.

The plant location was then evaluated based on factors such as proximity to raw materials, availability of facilities, transportation costs, and fuel availability. Considering all these factors, the best choice is the Atyrau region, specifically the NIPT special economic zone in Kazakhstan, due to the advantages it offers. After selecting the plant location, an efficient plant layout was designed, meeting all safety requirements.

Next, the total investments and revenues from the plant were considered. ISBL and OSBL costs were calculated. Fixed costs, variable costs, revenue, and profit were determined using market prices. The NPV of the plant was found to be $596,110,235, with a payback period of 5 years.

One limitation of this project is the simplicity of the kinetic model used. In real applications, the dehydrogenation reaction produces many byproducts, such as methane, ethane, and other light hydrocarbons. In the future, it is possible to include these byproducts in the reaction kinetics, which would improve the accuracy of the project. Another area for future research is the NMP extractive distillation. Due to a lack of data, it is difficult to design the extractive distillation columns with NMP. By gathering the necessary data, such as ternary diagrams for NMP, butane, and butadiene, improvements can be made to the column design.

9. References

[1] White, W. C. (2007). Butadiene production process overview. *Chemico-biological interactions*, *166*(1-3), (pp. 10-14). https://doi.org/10.1016/j.cbi.2007.01.009

[2] Coran, A. Y. (1994). Vulcanization. In *Science and technology of rubber* (pp. 339-385). Academic Press. https://doi.org/10.1016/B978-0-08-051667-7.50012-3

[3] Chembk.com. https://www.chembk.com/en (accessed Apri. 12, 2025).

[4] American Chemistry Council. (2024, June 10). Butadiene Product Stewardship Guidance Manual - American Chemistry Council. *American Chemistry Council*. https://www.americanchemistry.com/industry-groups/olefins/resources/butadiene-product-stewardship-guidance-manual

[5] Chandrasekaran, C. (2017). Raw materials for rubber lining compounds. In *Elsevier eBooks* (pp. 77–86). https://doi.org/10.1016/b978-0-323-44371-5.00011-6

[6] Chern, C. S. (2008). *Principles and applications of emulsion polymerization*. John Wiley & Sons. (pp. 5-11). https://books.google.com/books?hl=ru&lr=&id=kyFg9AOW2FYC&oi=fnd&pg=PR5&dq=Principles+and+Applications+of+Emulsion+Polymerization&ots=TeWCRrZJAh&sig=UIqshZcvolI_mUelgLcpYVIglBQ

[7] Ramakrishnan, S. (2017). Condensation polymerization. *Resonance*, *22*, (pp. 355-368). https://doi.org/10.1007/s12045-017-0475-0

[8] Rajanibabu, T. V. (2012). Hydrocyanation of alkenes and alkynes. *ChemInform*, *43*(6), (pp. 17-20). https://doi.org/10.1002/0471264180.or075.01

[9] BASF. Butadiene Safety Data Sheet. https://download.basf.com/p1/000000000030475728_SDS_GEN_00/en_UN/1%252C3_Butadiene_30475728_SDS_GEN_00_en_6-0.pdf (accessed Sep. 9, 2024).

[10] TPC Group. 1,3-Butadiene Safety Data Sheet. https://cdn2.hubspot.net/hubfs/5146414/Datasheets/Butadiene.pdf (accessed Sep. 7, 2024).

[11]Lummus Technology. (2020). Butadiene Extraction Technology. https://www.lummustechnology.com/getmedia/b9694881-4803-41ff-8e0a-06f5afc17992/2020-09-15-butadiene-extraction-technology-tech-sheet.pdf (accessed Sep. 6, 2024).

[12] International Agency for Research on Cancer. (1999). *1,3-Butadiene*. Re-evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide - NCBI Bookshelf. https://www.ncbi.nlm.nih.gov/books/NBK499340/

[13] J. Yang, P. Wang, H. Neumann, R. Jackstell, and M. Beller. (2023, May). "Industrially applied and relevant transformations of 1,3-butadiene using homogeneous catalysts," Industrial Chemistry & Materials, vol. 1, no. 2, (pp. 155-174). https://doi.org/10.1039/D3IM00009E.

[14] H. Duan, Y. Yamada, S. Sato. (2016, Jul.). "Future Prospect of the Production of 1,3-Butadiene from Butanediols," Chemistry Letters, vol. 45, no. 9, (pp. 1036-1047). https://doi.org/10.1246/cl.160595.

[15] "Top 10 Companies in Butadiene Market in 2024," emergenresearch.com. https://www.emergenresearch.com/blog/top-10-companies-in-butadiene-market (accessed Sep. 6, 2024).

[16] "Butadiene Market Size, Share, and Trends 2024 to 2034," precedenceresearch.com. https://www.precedenceresearch.com/butadiene-market (accessed Sep. 6, 2024).

[17] Lyondellbasell Industries, "2021 Data Book," Feb. 2022. https://www.lyondellbasell.com/4a521e/globalassets/investors/data-book-2021.pdf

[18] "Shell completes its largest petrochemicals project," shell.com. https://www.shell.com/business-customers/chemicals/media-releases/2010-media-releases/shell-completes-its-largest-petrochemicals-project.html (accessed Sep. 8, 2024).

[19] "Butadiene," ineos.com. https://www.ineos.com/businesses/ineos-olefins-polymers-europe/products/ (accessed Sep. 8, 2024).

[20] Tengrinews.kz. (2022, November 15). Началась практическая реализация проекта по производству бутадиена. *Главные Новости Казахстана - Tengrinews.kz*. https://tengrinews.kz/kazakhstan_news/nachalas-prakticheskaya-realizatsiya-proekta-proizvodstvu-483197/ (accessed Sep. 11, 2024).

[21] "Татнефть" создала с компанией из Казахстана СП по производству бутадиеновых каучуков. (2021, November 30). https://www.interfax.ru/business/805673 (accessed Sep. 11, 2024).

[22] *Шины Bars: особенности производства в Узбекистане и перспективы в России*. (n.d.). Журнал Движок. https://dvizhok.su/parts/shinyi-bars-osobennosti-proizvodstva-v-uzbekistane-i-perspektivyi-v-rossii (accessed Sep. 12, 2024).

[23] *Tyres - Embassy of the Republic of Belarus to the United Kingdom of Great Britain and Northern Ireland*. (n.d.). https://uk.mfa.gov.by/en/exportby/invest/Tyres/ (accessed Sep. 13, 2024).

[24] *В 2021 году «Белшина» выпустила более 4,24 миллиона шин*. (n.d.). Новости Мира Шин - Интернет-магазин 4точки. https://www.4tochki.ru/news/novosti-rynka-shin-i-avtokomponentov/2022/mart/11/v-2021-godu-belshina-vypustila-bolee-424-milliona-shin/ (accessed Sep. 10, 2024).

[25] Weissermel, K., & Arpe, H. J. (2004). Industrial organic chemistry. Synthesis-Journal of Synthetic Organic Chemistry, (7), (pp. 1127-1127). Available: https://www.academia.edu/download/51536690/Industrial_Organic_Chemistry.pdf

[26] "Mitsubishi Chemicals On-Purpose Butadiene Production Process ," Mitsubishi Chemical Group. https://www.m-chemical.co.jp/en/petrochem-license/technologies/pdf/Introduction_MCC_BTcB_Process.pdf

[27] Makshina, E. V., Dusselier, M., Janssens, W., Degreve, J., Jacobs, P. A., & Sels, B. F. (2014). Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene. Chemical Society Reviews, 43(22), (pp. 7917-7953). https://doi.org/10.1039/C4CS00105B

[28] Grub, J., & Löser, E. (2005). Butadiene. Ullmann's Encyclopedia of Industrial Chemistry, 1-17. http://dx.doi.org/10.1002/14356007.a04_431.pub2

[29] Lummus Technology. (2011). LUMMUS CATADIENE® N-Butane Dehydrogenation Unit for butadiene production.

[30] Happel, J., Blanck, H., & Hamill, T. D. (1966). Dehydrogenation of Butane and Butenes over Chrome-Alumina Catalyst. *Industrial & Engineering Chemistry Fundamentals*, *5*(3), 289–294. https://doi.org/10.1021/i160019a001

[31] BBC Bitesize. (2023, March 7). *Effect of catalysts - Rates of reaction - (CCEA) - GCSE Chemistry (Single Science) Revision - CCEA - BBC Bitesize*. https://www.bbc.co.uk/bitesize/guides/zdkr6v4/revision/8

[32] Zhang, Y., Qi, L., Leonhardt, B., & Bell, A. T. (2022). Mechanism and Kinetics of n-Butane Dehydrogenation to 1,3-Butadiene Catalyzed by Isolated Pt Sites Grafted onto ≡SiOZn–OH Nests in Dealuminated Zeolite Beta. *ACS Catalysis*, *12*(6), 3333–3345. https://doi.org/10.1021/acscatal.2c00059

[33] Nawaz, Z. (2015). Light alkane dehydrogenation to light olefin technologies: a comprehensive review. *Reviews in Chemical Engineering*, *31*(5). https://doi.org/10.1515/revce-2015-0012

[34] Wang, C., Lu, Y., Ma, J., & Wang, H. (2024). Study on the synergistic effect of several sulfur compounds to the corrosion attack of copper in liquefied petroleum gas. *Coatings*, *14*(10), 1329. https://doi.org/10.3390/coatings14101329

[35] Rezel Catalysts (shanghai) Co., Ltd. (n.d.). *Pdh Fixed Bed Dehydrogenation Catalyst Dehydrogenation Of Propane,Dehydrogenation Catalysts,Pdh Catalyst - Buy Fixed Bed Dehydrogenation Catalyst Dehydrogenation Of Propane pdh Catalyst Fixed Bed dehydrogenation Catalysts Product on Alibaba.com*. www.alibaba.com. https://www.alibaba.com/product-detail/PDH-Fixed-Bed-Dehydrogenation-Catalyst-Dehydrogenation_1600890057277.html?spm=a2700.details.popular_products.3.78de296aTUnzob

[36] Uchida, S., Osuda, S., & Shindo, M. (1975). On the dehydrogenation reaction of n‐butane with the deactivation of alumina‐chromia catalyst. *The Canadian Journal of Chemical Engineering*, *53*(6), 666–672. https://doi.org/10.1002/cjce.5450530613

[37] Ledakowicz, S., Nowicki, L., Petera, J., Nizioł, J., Kowalik, P., & Gołębiowski, A. (2013). KINETIC CHARACTERISATION OF CATALYSTS FOR METHANOL SYNTHESIS. *Chemical and Process Engineering New Frontiers*, *34*(4), 497–506. https://doi.org/10.2478/cpe-2013-0040

[38] Iggland, M., & Mazzotti, M. (2018). Introduction to chemical engineering for lecture 7: Flash distillation. *ETH Zurich, Institute of Process Engineering: Zurich, Switzerland*. https://ethz.ch/content/dam/ethz/special-interest/mavt/process-engineering/separation-processes-laboratory-dam/documents/education/bce%20notes/Lec7-Flash.pdf

[39]Gunt Distillation Rectification. https://www.gunt.de/images/download/distillation_rectification_english.pdf

[40] C. Branan, Rules of thumb for chemical engineers : a manual of quick, accurate solutions to everyday process engineering problems. Amsterdam ; Boston: Elsevier, 2005.

[41] Towler, G., & Sinnott, R. (2021). Chemical engineering design: principles, practice and economics of plant and process design. Butterworth-Heinemann.

[42] Al-Fulaij, H., Cipollina, A., Micale, G., Bogle, D., & Ettouney, H. (2011). CFD modelling of the demister in the multi stage flash desalination plant. In Computer Aided Chemical Engineering (Vol. 29, pp. 1618-1622). https://doi.org/10.1016/B978-0-444-54298-4.50102-1

[43] W. L. Luyben, *Distillation Design and Control Using Aspen Simulation,* 2nd ed. New Jersey: John Wiley and Sons, 2013.

[44] Towler, G., & Sinnott, R. (2012). Capital cost estimating. In *Elsevier eBooks* (pp. 307–354). https://doi.org/10.1016/b978-0-08-096659-5.00007-9

[45] Y. H. Kim, S. Y. Kim, and B. Lee, “Simulation of 1,3-butadiene extractive distillation process using N-methyl-2-pyrrolidone solvent,” *Korean Journal of Chemical Engineering,* vol. 29, no. 11, pp. 1493-1499, 2012. DOI: 10.1007/s11814-012-0075-3.

[46] Manzolini, G., & Gallucci, F. Techno-Economic Analysis of the Butane Dehydrogenation Process with Membrane Reactors. https://pure.tue.nl/ws/portalfiles/portal/203528735/2021_10_Maruzzi.pdf

[47] Z. Lei, C. Li, and B. Chen, “Extractive Distillation: A Review,” *Separation & Purification Reviews,* vol. 32, no. 2, pp. 121-213, 2003. https://doi.org/10.1081/SPM-120026627

[48] *Инвестируйте в Казахстан | Специальные экономические зоны*. (n.d.). https://invest.gov.kz/ru/doing-business-here/fez-and/the-list-of-sez-and/

[49] *Общая информация о СЭЗ*. (n.d.). СЭЗ «НАЦИОНАЛЬНЫЙ ИНДУСТРИАЛЬНЫЙ НЕФТЕХИМИЧЕСКИЙ ТЕХНОПАРК». https://nipt.kz/o-kompanii/55-obschaja-informacija-o-sjez.html

[50] *Продукция | www.anpz.kz*. (n.d.). https://www.anpz.kz/product/

[51] *Природный газ – стратегия обеспечения сбалансированной работы производства | www.anpz.kz*. (n.d.). https://www.anpz.kz/press_center/news/?ELEMENT_ID=74154

[52] Chen, W., & Zhang, X. (2022). 1,3-Butadiene: a ubiquitous environmental mutagen and its associations with diseases. *Genes and Environment*, *44*(1). https://doi.org/10.1186/s41021-021-00233-y

[53] *1,3-Butadiene | Public Health Statement | ATSDR*. (n.d.). https://wwwn.cdc.gov/TSP/PHS/PHS.aspx?phsid=457&toxid=81

[54] New Jersey Department of Health. (2008, February). *Hazardous Substance Fact sheet*. https://nj.gov/health/eoh/rtkweb/documents/fs/0273.pdf

[55] Wikipedia contributors. (2025c, April 15). *Butane*. Wikipedia. https://en.wikipedia.org/wiki/Butane

[56] Wikipedia contributors. (2025b, April 8). *1-Butene*. Wikipedia. https://en.wikipedia.org/wiki/1-Butene

[57] Wikipedia contributors. (2025a, February 15). *Butadiene*. Wikipedia. https://en.wikipedia.org/wiki/Butadiene

[58] Sinnott, R. A. Y. (2014). Chemical engineering design (Vol. 6). Elsevier.

[59] Exchange Rates UK (2024). *Chinese Yuan to US Dollar History: 2024* https://www.exchangerates.org.uk/CNY-USD-spot-exchange-rates-history-2024.html (Accessed April 15, 2025).

[60] Maxwell, C. (2020). *Cost indices*. Towering Skills. https://toweringskills.com/financial-analysis/cost-indices/ (Accessed April 16, 2025).

[61] ERI Economic Research Institute. (2025). *Plant Operator Chemical Salary Kazakhstan*.SalaryExpert. https://www.salaryexpert.com/salary/job/plant-operator-chemical/kazakhstan (Accessed April 16, 2025).

[62] Echemi. (n.d.). *1,3-Butadiene Price Trend in China*. Retrieved April 20, 2025, from https://www.echemi.com/pip/13-butadiene-pid_Seven2409/china.htmlRes (Accessed April 16, 2025).

[63] Bureau of National Statistics of the Agency for Strategic Planning and Reforms of the Republic of Kazakhstan. (2025, April 1). *Inflation in the Republic of Kazakhstan (March 2025)*. https://stat.gov.kz/en/industries/economy/prices/publications/340808/ (Accessed April 16, 2025).

Appendix A: Tables

Table A1. Liquid heat capacity of 1,3-butadiene comparison.

T [F]	Reference Liquid Heat Capacity [BTU/lb*F]	Aspen Liquid Heat Capacity [BTU/lb*F]
-150	0.455899	0.4624294
-100	0.466841	0.4716889
-50	0.478735	0.4891666
0	0.499667	0.5120123
50	0.529638	0.5391289
100	0.565319	0.5723859
150	0.606946	0.6187742

Table A2. Ideal gas heat capacity of 1,3-butadiene comparison.

T [F]	Reference Ideal Gas Heat Capacity [BTU/lb*F]	Aspen Ideal Gas Heat Capacity [BTU/lb*F]
-100	0.256027	0.2540455
100	0.364031	0.3650308
300	0.472035	0.4770164
500	0.559113	0.5622539
700	0.630665	0.628087
900	0.683317	0.6811557
1100	0.731919	0.7247638
1300	0.76297	0.7607866
1500	0.791321	0.7905932
1700	0.818997	0.8153095
1900	0.847348	0.8358769
2100	0.860849	0.8530725

Table A3. Liquid viscosity of 1,3-butadiene comparison.

T [F]	Reference Liquid Viscosity [lb/ft*s]	Aspen Liquid Viscosity [lb/ft*s]
0	0.000157	0.0001596321944
25	0.000135	0.0001338746389

50	0.000113	0.0001129327778
75	9.41E-05	0.00009579894444
100	8.20E-05	0.00008169525
125	7.02E-05	0.00007001783333
150	6.12E-05	0.00006029516667
175	5.25E-05	0.00005215661111
200	4.35E-05	0.00004530930556
225	3.76E-05	0.00003952033333
250	3.37E-05	0.00003460341667

Table A4. Thermal conductivity of liquid 1,3-butadiene comparison.

T [F]	**Reference Liquid Thermal Conductivity [BTU/ft-s-F]**	**Aspen Liquid Thermal Conductivity [BTU/ft-s-F]**
-150	2.55E-05	0.00002556313889
-125	2.48E-05	0.00002474638889
-100	2.39E-05	0.00002392963889
-75	2.31E-05	0.00002311288889
-50	2.23E-05	0.00002229613889
-25	2.15E-05	0.00002147938889
0	2.06E-05	0.00002066263889

Table A5. Ideal gas heat capacity of butane comparison.

T [F]	Reference Ideal Gas Heat Capacity [BTU/lb*F]	Aspen Ideal Gas Heat Capacity [BTU/lb*F]
0	0.36	0.3693048
25	0.377	0.3798897
50	0.392	0.3915325
75	0.408	0.4040793
100	0.424	0.4173709
125	0.439	0.4312507
150	0.454	0.4455705
175	0.468	0.4601943

200	0.483	0.4750006
225	0.497	0.4898832
250	0.511	0.5047512
275	0.525	0.5195287
300	0.539	0.5341533
325	0.552	0.5485754
350	0.565	0.5627563
375	0.578	0.576667
400	0.591	0.5902871
425	0.603	0.6036032
450	0.615	0.6166076
475	0.628	0.6292979
500	0.639	0.6416752
525	0.651	0.6537438
550	0.663	0.6655106
575	0.674	0.6769839
600	0.685	0.6881737

Table A6. Liquid viscosity of n-butane comparison.

T [F]	Reference Liquid Viscosity [cp]	Aspen Liquid Viscosity [cp]
-110	0.535	0.54077
-105	0.511	0.5159284
-100	0.489	0.4928121
-95	0.468	0.4712674
-90	0.449	0.4511567
-85	0.431	0.432357
-80	0.414	0.4147579
-75	0.398	0.39826
-70	0.383	0.3827736
-65	0.369	0.3682179
-60	0.356	0.3545199
-55	0.344	0.341613

-50	0.332	0.3294373
-45	0.321	0.3179378
-40	0.311	0.3070647
-35	0.301	0.2967725
-30	0.292	0.2870196
-25	0.283	0.2777678
-20	0.275	0.2689823
-15	0.267	0.2606308
-10	0.26	0.252684
-5	0.253	0.2451146
0	0.246	0.2378975
5	0.239	0.2310096
10	0.233	0.2244293
15	0.227	0.2181368

Table A7. Thermal conductivity of liquid n-butane comparison.

T [F]	**Reference Liquid Thermal Conductivity [BTU/ft-h-F]**	**Aspen Liquid Thermal Conductivity [BTU/ft-h-F]**
-150	0.0936	0.0957231
-125	0.0901	0.0916723
-100	0.0864	0.08769
-75	0.0826	0.0837801
-50	0.0788	0.0799469
-25	0.075	0.076195
0	0.0713	0.0725297

Table A8. Liquid heat capacity of 1,3-butadiene comparison.

T [F]	Reference Liquid Heat Capacity [BTU/lb*F]	Aspen Liquid Heat Capacity [BTU/lb*F]
-30	0.535	0.5391157
-20	0.542	0.5432369
-10	0.55	0.5476379

0	0.557	0.5523218
10	0.564	0.5572944
20	0.571	0.5625649
30	0.578	0.5681459

Table A9. Typical butadiene specifications.

Chemical	Specifications
1,3-butadiene, wt%	$\geq 99.5\%$
1,2-butadiene, ppm	< 20
4-tert-butylcatechol, ppm	$< 50 - 150$
Propadiene, ppm	< 10
Dimers, ppm	< 500
Isoprene, ppm	< 10
C_5 compounds, ppm	< 500
Sulfur, ppm	< 5
Acetylenes, ppm	< 20
Water, ppm	< 300

Table A10. Comparative yields of butanes by different processes.

Raw material	i-Butane		n-Butane	
Product/yield in wt. %	Catalytic dehydrogenation	Steam cracking	Catalytic dehydrogenation	Steam cracking
Hydrogen	3.0	2.0	3	2
Ethylene	-	20.0	2	35
Propene	3.0	30.0	2	28
i-Butene	80.0	42.0	2	1
n-Butenes	9.0	1.0	79	19

Butadiene	0.3	1.0	2	4
i-Butane	-	-	2	-
n-Butane	1.7	1.0	-	-
Remainder	3.0	3.0	8	11

Table A11. Processes, implied by large companies

Company name	**Process**	**Feedstock**	**Operating conditions**	**Catalysts**	**Conversion**	**BD selectivity**	**Source**
Phillips	O-X-D (ODH)	n-butene	480-600°C (adiabatic)	unknown	~75-80%	88-92%	[28]
Lummus Technology	Catadiene (catalytic dehydrogenation)	butane	600-620°C at 0.2-0.4 bar	Cr-oxide and Al-oxide	30-40%	Up to 63%	[28]
Dow Chemical	Catalytic dehydrogenation	butane	600-675°C at 1 bar	Ca-Ni-phosphate stabilized with Cr_2O_3	~50%	~90%	[28]
Petro-Tex	Oxo-D (ODH)	butene	550-600°C (adiabatic)	probably ferrite-Zn-Mn-Mg	65%	Up to 93%	[28]
Mitsubishi Chemicals	BTcB (ODH)	butene	300~400°C at ambient pressure	unknown	unknown	Crude butadiene	[29]

Table A12. Advantages and disadvantages of 1,3-butadiene production methods

Method	Advantages	Disadvantages
Naphtha cracking	● Production of other products such as ethylene and propylene	● Low selectivity towards 1,3-butadiene ● High temperature conditions
Catalytic dehydrogenation	● Considerable selectivity towards butenes	● Low conversion of n-butane and low selectivity towards 1,3-butadiene

Catalytic oxydehydrogenation	● High yields of 1,3-butadiene from butenes	● A little formation of 1,3-butadiene from n-butane ● Too many side products at high temperature from n-butane

Table A13. Properties of n-Butane and 1,3-Butadiene.

	n - Butane	1,3 - Butadiene
Chemical formula	C_4H_{10}	C_4H_6
Molecular weight [g/mol]	58.1234	54.0916
Normal boiling point [℃]	-0.49	-4.41
Freezing point [℃]	-	-108.91
Liquid density [kg/m^3]	600	640
Water solubility [mg/litre]	73.24	735
Critical pressure [bar]	37.96	43.2
Critical temperature [℃]	151.97	151.85
Critical volume [cc/mol]	255	221
Critical compressibility factor	0.274	0.270

Table A14. Thermodynamic data of compounds.

	n-butane	1-butene	2-butene(cis)	2-butene(trans)	1,3-butadiene	Water
ΔH_f^o	-125.79 kJ/mol	-0.54 kJ/mol	-7.4 kJ/mol	-11 kJ/mol	109.24 kJ/mol	-241.814 kJ/mol
ΔG_f^o	-16.7 kJ/mol	70.27 kJ/mol	65.36 kJ/mol	63.16 kJ/mol	149.72 kJ/mol	-228.59 kJ/mol

Table A15. Thermodynamic data of reactions.

	ΔH_r^o (kJ/mol)	ΔG_r^o (kJ/mol)	K_{eq}
Butane → 1-Butene + H_2	125.25	86.97	$5.69*10^{-16}$
Butane → 2-Butene(z) + H_2	118.39	82.06	$4.13*10^{-15}$
Butane → 2-Butene(e) + H_2	114.79	79.86	$4.92*10^{-15}$
1-Butene + $^1/_2O_2$ → Butadiene + Water	-132,034	-149.14	$1.39*10^{26}$
2-Butene(z) + $^1/_2O_2$ → Butadiene + Water	-125,174	-144.23	$1.91*10^{25}$
2-Butene(e) + $^1/_2O_2$ → Butadiene + Water	-121,574	-142.03	$7.88*10^{24}$

Table A16. Reaction thermodynamics in Aspen.

	ΔH_r^o (kJ/mol) (SRK)	ΔH_r^o (kJ/mol) (PR)	K_{eq} (SRK)
Butane → 1-Butene + H_2	125.388	125.386	$5.48*10^{-16}$
Butane → 2-Butene(z) + H_2	118.483	118.481	$4.20*10^{-15}$
Butane → 2-Butene(e) + H_2	114.883	114.881	$1.00*10^{-14}$
1-Butene + $^1/_2O_2$ → Butadiene + Water	-132,199	-132.195	$1.41*10^{26}$
2-Butene(z) + $^1/_2O_2$ → Butadiene + Water	-125,291	-125.288	$1.84*10^{25}$
2-Butene(e) + $^1/_2O_2$ → Butadiene + Water	-121,691	-121.688	$7.70*10^{24}$

Table A17. Exposure limits of 1,3-Butadiene and LPG in selected countries.

Country	Exposure limit for 1,3-Butadiene	Exposure limit for Liquefied Petroleum Gas (LPG)
Belgium	TWA 10 ppm	-
Philippines	TWA 1000 ppm	TWA 1000 ppm
United Kingdom	TWA 10 ppm	TWA 1000 ppm
Turkey	TWA 1000 ppm	TWA 1000 ppm
Switzerland	MAK-W 5 ppm	MAK-W 1000 ppm

Table A18. Flammability of 1,3-Butadiene and LPG.

	1,3-Butadiene	Liquefied Petroleum Gas (LPG)
Autoignition temperature	420°C	Propane: 466°C Butane: 405 C
Flash point	-76°C (liquid)	Propane: -104°C Butane: -60°C
Lower explosive limit (LEL)	2%, 20 000 ppm	Propane: 2.1% Butane: 1.9%
Upper explosive limit (UEL)	11.5%	Propane: 9.5% Butane: 8.5%

Table A19. 1,3-Butadiene Carcinogenicity Classifications.

Organization	Classification
International Agency for Research on Cancer (IARC)	Group 1 - Carcinogenic to Humans
Environmental Protection Agency (EPA)	Carcinogenic to Humans by Inhalation
National Toxicology Program (NTP)	Known Human Carcinogen
National Institute for Occupational Safety and Health (NIOSH)	Carcinogen, with no Further Categorization
American Conference on Governmental	Group A2 - Suspected Human Carcinogen

Industrial Hygienists (ACGIH)	

Table A20. Ideal gas heat capacity of hydrogen comparison [engineeringtoolbox].

T [F]	Reference Ideal Gas Heat Capacity [BTU/lb*F]	Aspen Ideal Gas Heat Capacity [BTU/lb*F]
-144	3.13	3.300
-99.4	3.23	3.321
-54.4	3.3	3.344
-9.4	3.36	3.368
35.6	3.39	3.391
80.6	3.42	3.412
126	3.44	3.428
171	3.45	3.442
216	3.45	3.453
261	3.46	3.460
351	3.46	3.469
441	3.47	3.473
531	3.47	3.473

Table A21. Vapor thermal conductivity of hydrogen comparison.

T [F]	Reference Ideal Gas Heat Capacity [BTU/lb*F]	Aspen Ideal Gas Heat Capacity [BTU/lb*F]
-434.55	0.00599	0.00594
-434	0.00603	0.00609
-431	0.00733	0.00692
-427	0.00848	0.00802
-424	0.00966	0.00885
-420	0.011	0.00995
-416	0.0124	0.0110
-413	0.0141	0.0119
-409	0.0163	0.0130
-406	0.0193	0.0137

-402	0.025	0.0148

Table A22. Ideal gas heat capacity of 1-butene comparison [BTN.pdf].

T [F]	Reference Ideal Gas Heat Capacity [BTU/lb*F]	Aspen Ideal Gas Heat Capacity [BTU/lb*F]
0	0.334	0.327
25	0.349	0.338
50	0.364	0.351
75	0.379	0.364
100	0.394	0.377
125	0.408	0.391
150	0.422	0.405
175	0.436	0.418
200	0.449	0.432
225	0.462	0.445
250	0.475	0.459
275	0.488	0.472
300	0.501	0.484
325	0.513	0.497
350	0.525	0.509
375	0.537	0.521
400	0.548	0.533
425	0.559	0.544
450	0.57	0.555
475	0.581	0.566
500	0.592	0.577
525	0.602	0.587
550	0.612	0.597
575	0.622	0.607
600	0.632	0.617

Table A23. Liquid heat capacity of 1-butene comparison.

T [F]	Reference Liquid Heat Capacity [BTU/lb*F]	Aspen Liquid Heat Capacity [BTU/lb*F]
-30	0.527	0.529
-20	0.533	0.536
-10	0.539	0.544
0	0.545	0.553
10	0.551	0.561

Table A24. Liquid density of 1-butene comparison.

T [F]	Reference Liquid Density [lb/ft^3]	Aspen Liquid Density [lb/ft^3]
-110	44.06	43.89
-100	43.68	43.54
-90	43.29	43.19
-80	42.91	42.84
-70	42.53	42.49
-60	42.15	42.13
-50	41.77	41.76
-40	41.39	41.40
-30	41.01	41.02
-20	40.62	40.64
-10	40.24	40.26
0	39.86	39.87
10	39.48	39.48
20	39.10	39.08

Table A25. Liquid viscosity of 1-butene comparison.

T [F]	Reference Liquid Viscosity [cP]	Aspen Liquid Viscosity [cP]
-120	0.496	0.482
-110	0.451	0.441
-100	0.412	0.405
-90	0.378	0.374

-80	0.348	0.346
-70	0.323	0.322
-60	0.3	0.301
-50	0.28	0.282
-40	0.262	0.265
-30	0.246	0.250
-20	0.231	0.236
-10	0.218	0.224
0	0.206	0.213
10	0.196	0.202
20	0.186	0.193

Table A26. Liquid heat capacity of 1,3-butadiene comparison.

T [F]	Reference Liquid Heat Capacity [BTU/lb*F]	Aspen Liquid Heat Capacity [BTU/lb*F]
-150	0.456	0.462
-100	0.467	0.472
-50	0.479	0.489
0	0.500	0.512
50	0.530	0.539
100	0.565	0.572
150	0.607	0.619

Table A27. Ideal gas heat capacity of 1,3-butadiene comparison.

T [F]	Reference Ideal Gas Heat Capacity [BTU/lb*F]	Aspen Ideal Gas Heat Capacity [BTU/lb*F]
-100	0.256	0.254
100	0.364	0.365
300	0.472	0.477
500	0.559	0.562
700	0.630	0.628
900	0.683	0.681
1100	0.732	0.725

1300	0.763	0.761
1500	0.791	0.791
1700	0.819	0.815
1900	0.847	0.836
2100	0.861	0.853

Table A28. Liquid viscosity of 1,3-butadiene comparison.

T [F]	Reference Liquid Viscosity [lb/ft*s]	Aspen Liquid Viscosity [lb/ft*s]
0	0.000157	0.000160
25	0.000135	0.000134
50	0.000113	0.000113
75	9.41E-05	9.58E-05
100	8.20E-05	8.17E-05
125	7.02E-05	7.00E-05
150	6.12E-05	6.03E-05
175	5.25E-05	5.22E-05
200	4.35E-05	4.53E-05
225	3.76E-05	3.95E-05
250	3.37E-05	3.46E-05

Table A29. Thermal conductivity of liquid 1,3-butadiene comparison.

T [F]	**Reference Liquid Thermal Conductivity [BTU/ft-s-F]**	**Aspen Liquid Thermal Conductivity [BTU/ft-s-F]**
-150	2.55E-05	2.56E-05
-125	2.48E-05	2.47E-05
-100	2.39E-05	2.39E-05
-75	2.31E-05	2.31E-05
-50	2.23E-05	2.23E-05
-25	2.15E-05	2.15E-05
0	2.06E-05	2.07E-05

Table A30. Ideal gas heat capacity of butane comparison.

T [F]	Reference Ideal Gas Heat Capacity [BTU/lb*F]	Aspen Ideal Gas Heat Capacity [BTU/lb*F]
0	0.360	0.369
25	0.377	0.380
50	0.392	0.392
75	0.408	0.404
100	0.424	0.417
125	0.439	0.431
150	0.454	0.446
175	0.468	0.460
200	0.483	0.475
225	0.497	0.490
250	0.511	0.505
275	0.525	0.520
300	0.539	0.534
325	0.552	0.549
350	0.565	0.563
375	0.578	0.577
400	0.591	0.590
425	0.603	0.604
450	0.615	0.617
475	0.628	0.629
500	0.639	0.642
525	0.651	0.654
550	0.663	0.666
575	0.674	0.677
600	0.685	0.688

Table A31. Liquid viscosity of n-butane comparison.

T [F]	Reference Liquid Viscosity [cP]	Aspen Liquid Viscosity [cP]
-110	0.535	0.541
-105	0.511	0.516
-100	0.489	0.493

-95	0.468	0.471
-90	0.449	0.451
-85	0.431	0.432
-80	0.414	0.415
-75	0.398	0.398
-70	0.383	0.383
-65	0.369	0.368
-60	0.356	0.355
-55	0.344	0.342
-50	0.332	0.329
-45	0.321	0.318
-40	0.311	0.307
-35	0.301	0.297
-30	0.292	0.287
-25	0.283	0.278
-20	0.275	0.269
-15	0.267	0.261
-10	0.260	0.253
-5	0.253	0.245
0	0.246	0.238
5	0.239	0.231
10	0.233	0.224
15	0.227	0.218

Table A32. Thermal conductivity of liquid n-butane comparison.

T [F]	Reference Liquid Thermal Conductivity [BTU/ft-h-F]	Aspen Liquid Thermal Conductivity [BTU/ft-h-F]
-150	0.0936	0.0957
-125	0.0901	0.0917
-100	0.0864	0.0877
-75	0.0826	0.0838
-50	0.0788	0.0799
-25	0.0750	0.0762

0	0.0713	0.0725

Table A33. Liquid heat capacity of n-butane comparison.

T [F]	Reference Liquid Heat Capacity [BTU/lb*F]	Aspen Liquid Heat Capacity [BTU/lb*F]
-30	0.535	0.539
-20	0.542	0.543
-10	0.550	0.548
0	0.557	0.552
10	0.564	0.557
20	0.571	0.563
30	0.578	0.568

Appendix B: Figures

Figures B2, B3, B4 and B5 in the report were made according to the data on the tables A1,A2,A3 and A4 of this appendix.

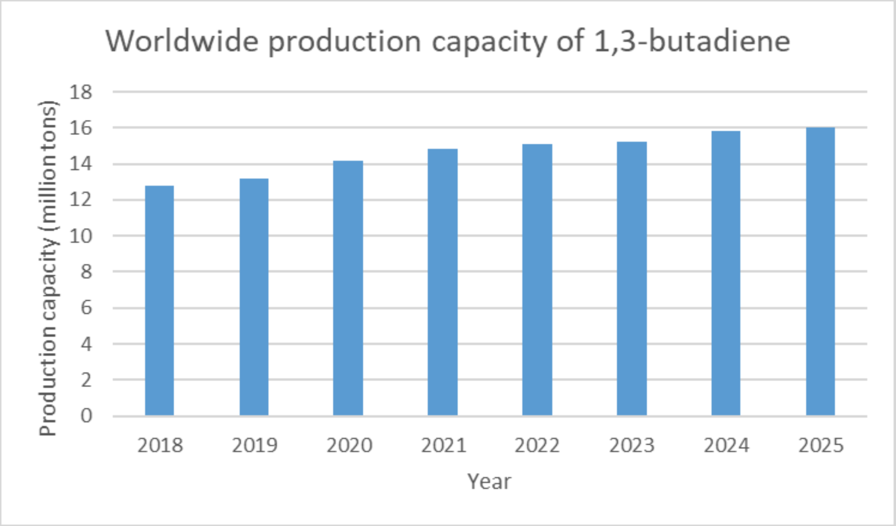


Figure B1. Trend present in production capacity of 1,3-butadiene.

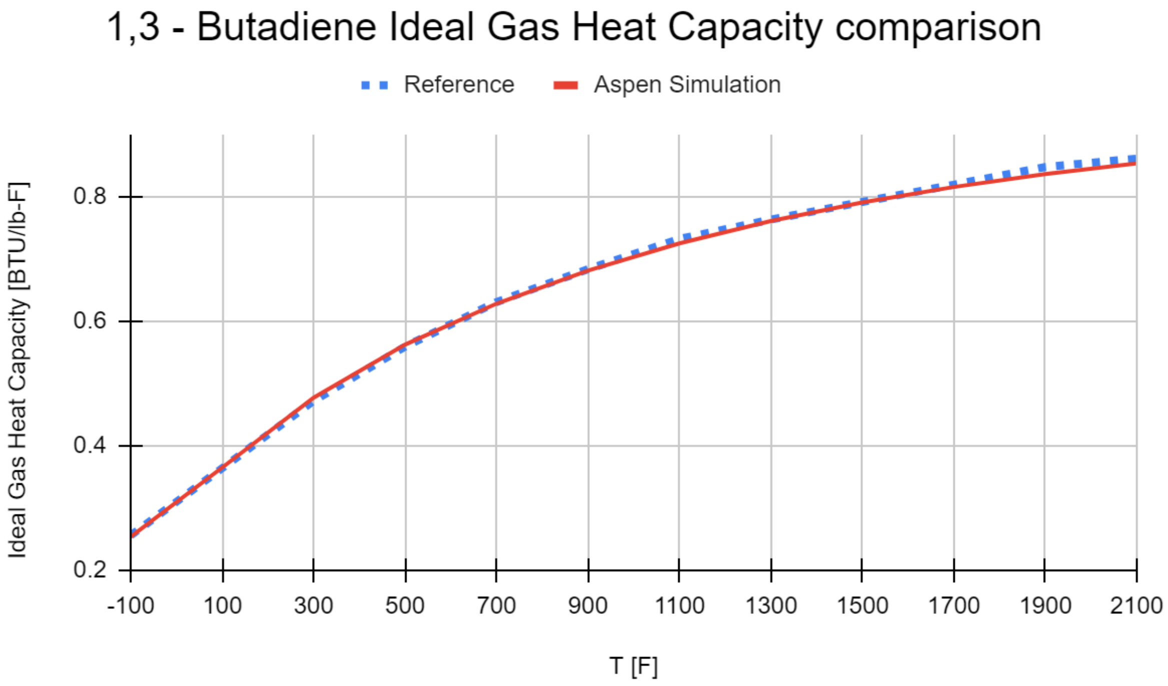


Figure B2. 1,3-butadiene ideal gas heat capacity comparison.

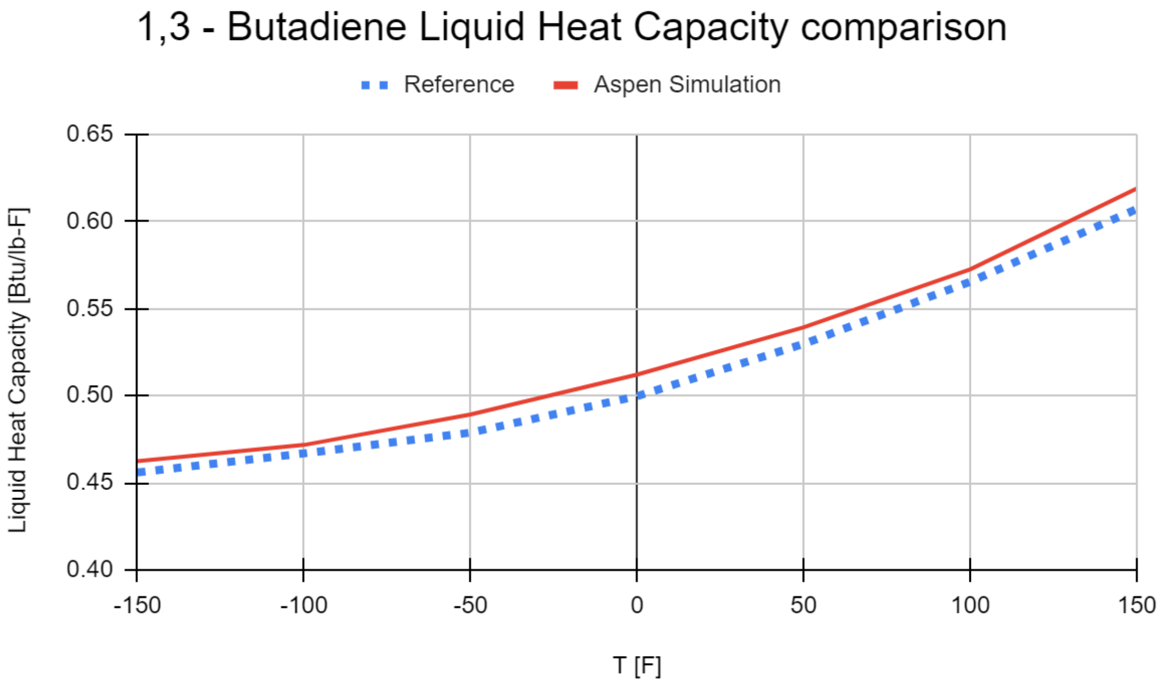


Figure B3. 1,3-butadiene liquid heat capacity comparison.

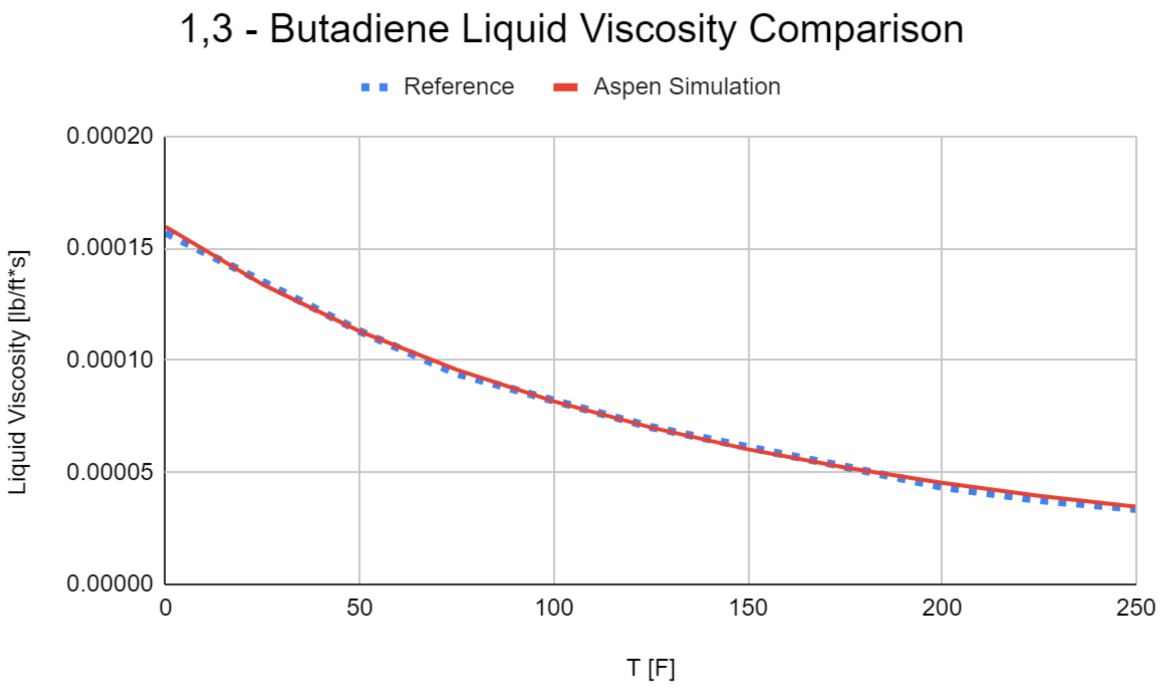


Figure B4. 1,3-butadiene liquid viscosity comparison.

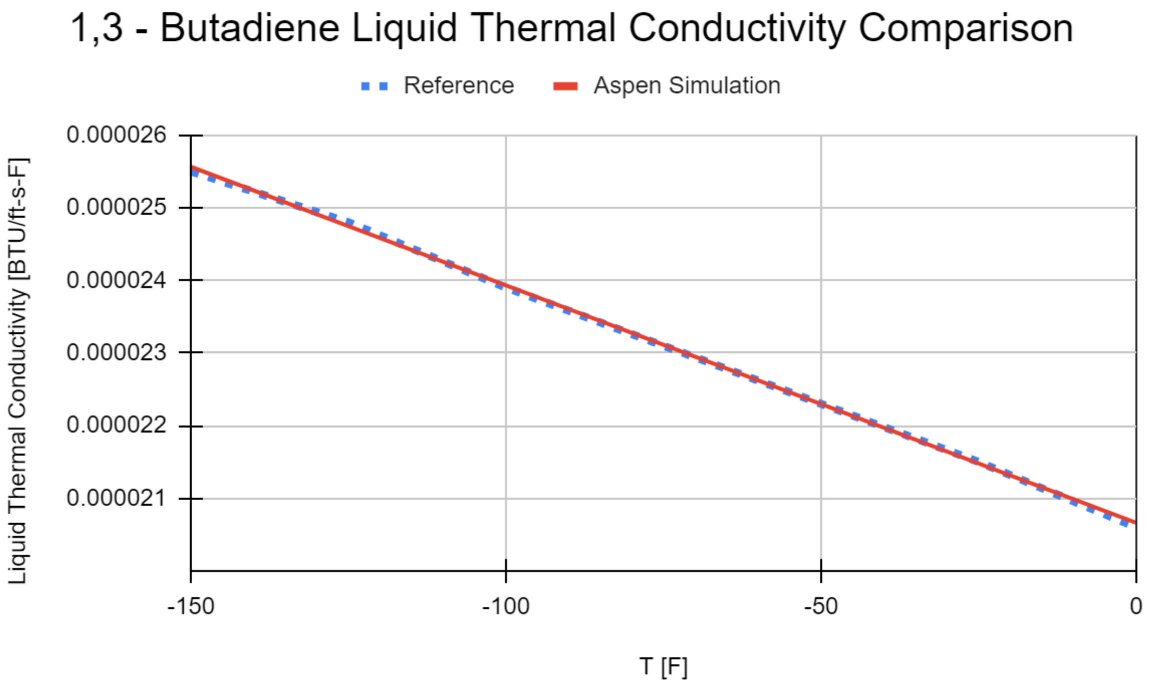
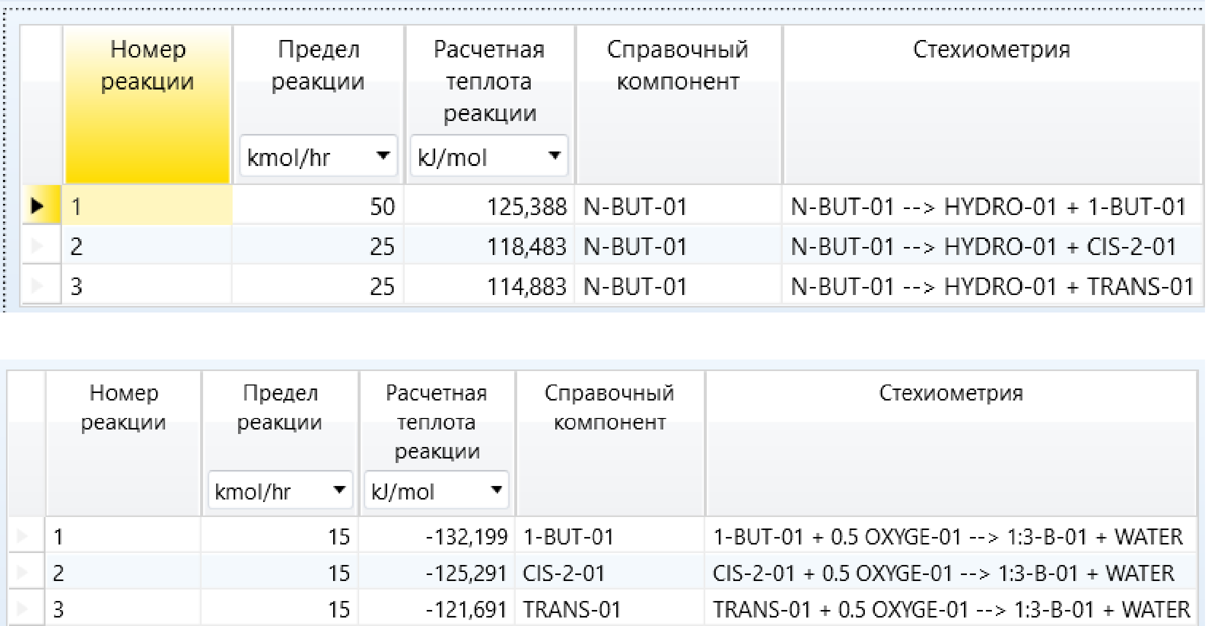


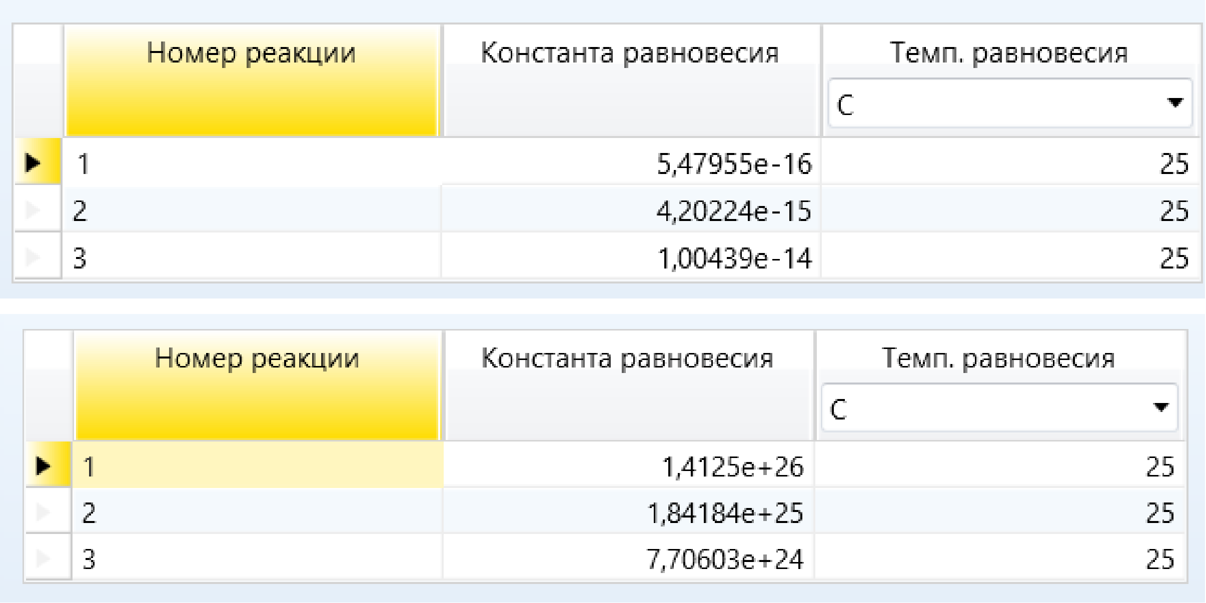
Figure B5. 1,3-butadiene liquid thermal conductivity comparison.



Номер реакции	Предел реакции kmol/hr	Расчетная теплота реакции kJ/mol	Справочный компонент	Стехиометрия
1	50	125,388	N-BUT-01	N-BUT-01 --> HYDRO-01 + 1-BUT-01
2	25	118,483	N-BUT-01	N-BUT-01 --> HYDRO-01 + CIS-2-01
3	25	114,883	N-BUT-01	N-BUT-01 --> HYDRO-01 + TRANS-01

Номер реакции	Предел реакции kmol/hr	Расчетная теплота реакции kJ/mol	Справочный компонент	Стехиометрия
1	15	-132,199	1-BUT-01	1-BUT-01 + 0.5 OXYGE-01 --> 1:3-B-01 + WATER
2	15	-125,291	CIS-2-01	CIS-2-01 + 0.5 OXYGE-01 --> 1:3-B-01 + WATER
3	15	-121,691	TRANS-01	TRANS-01 + 0.5 OXYGE-01 --> 1:3-B-01 + WATER

Figure B6. Enthalpies of reactions in Aspen.



Номер реакции	Константа равновесия	Темп. равновесия C
1	5,47955e-16	25
2	4,20224e-15	25
3	1,00439e-14	25

Номер реакции	Константа равновесия	Темп. равновесия C
1	1,4125e+26	25
2	1,84184e+25	25
3	7,70603e+24	25

Figure B7. K_{eq} of reactions calculated in Aspen (SRK).

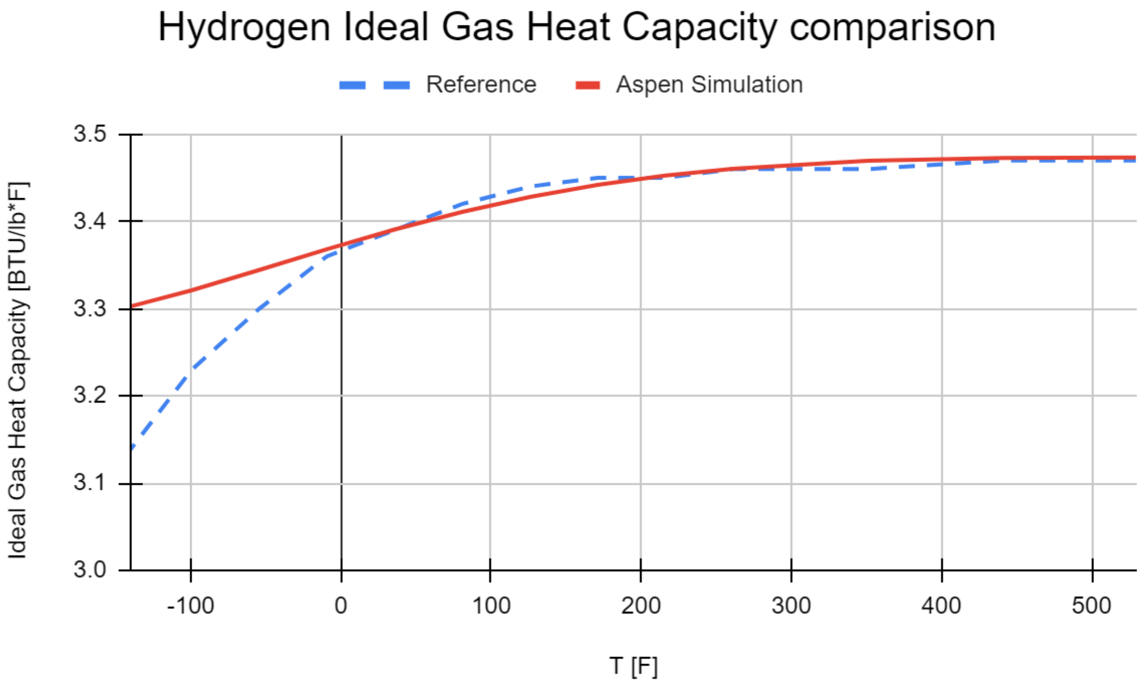


Figure B8. Hydrogen ideal gas heat capacity comparison.

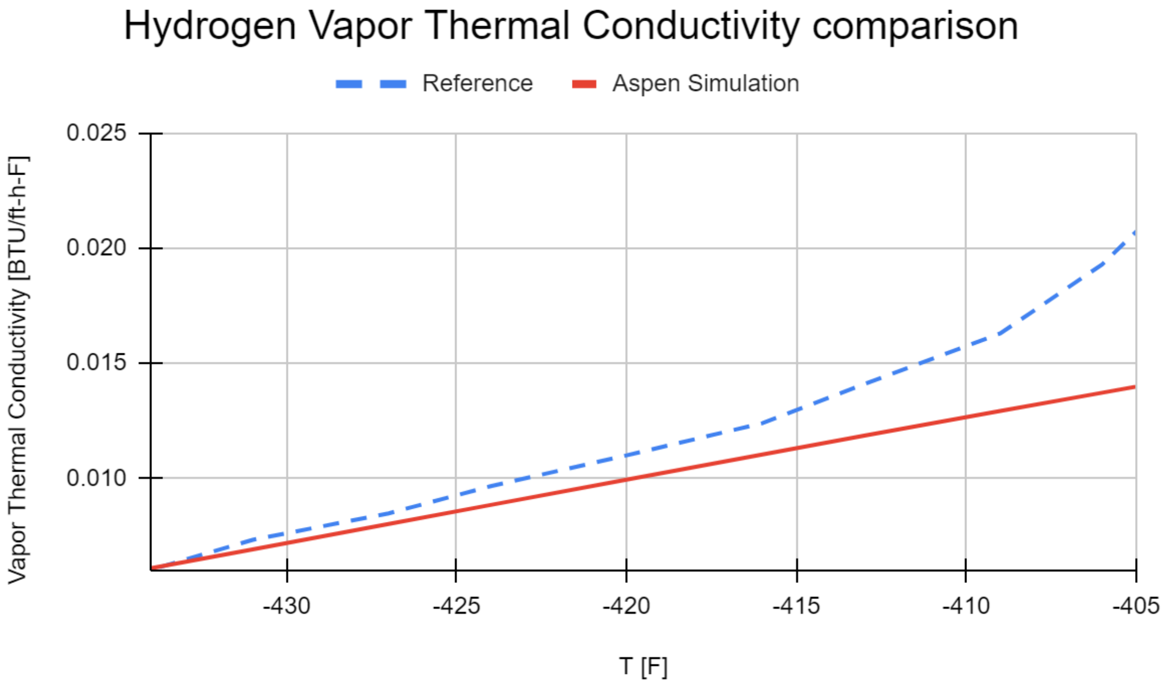


Figure B9. Hydrogen vapor thermal conductivity comparison.

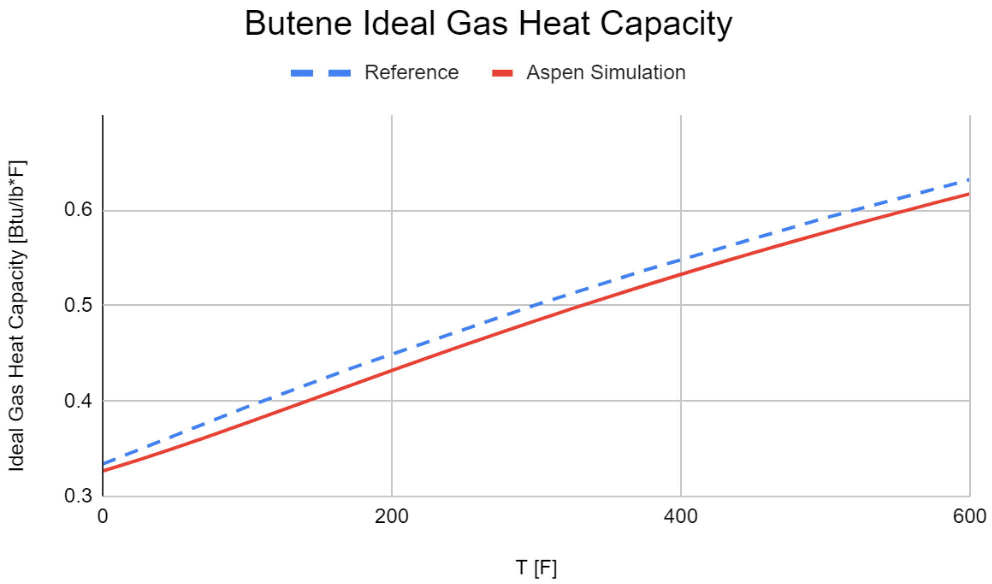


Figure B10. 1-butene ideal gas heat capacity comparison.

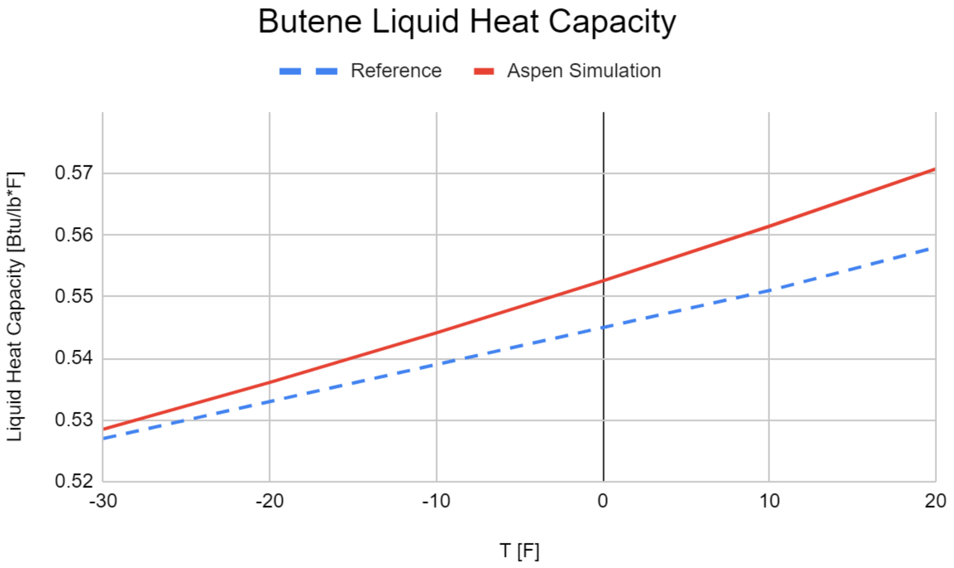


Figure B11. 1-butene liquid heat capacity comparison.

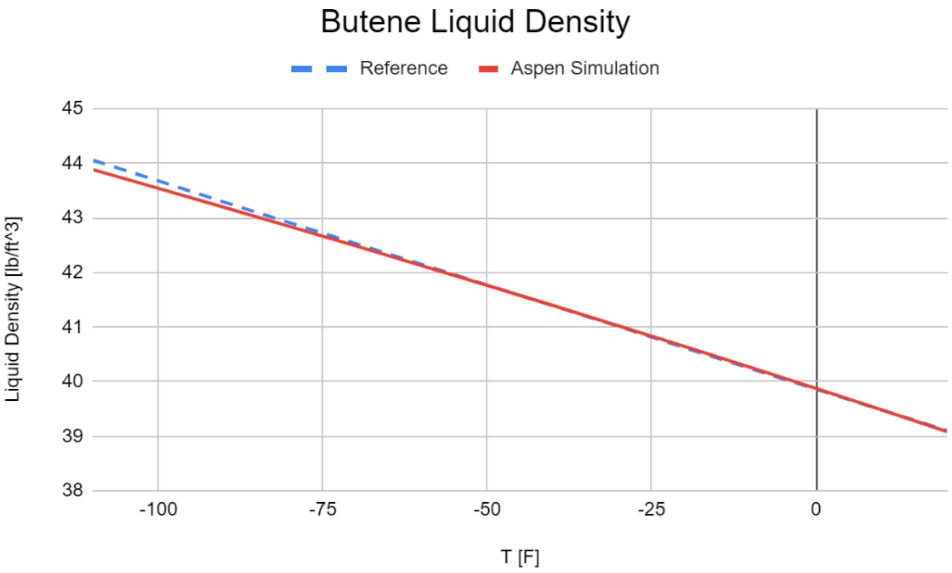


Figure B12. 1-butene liquid density comparison.

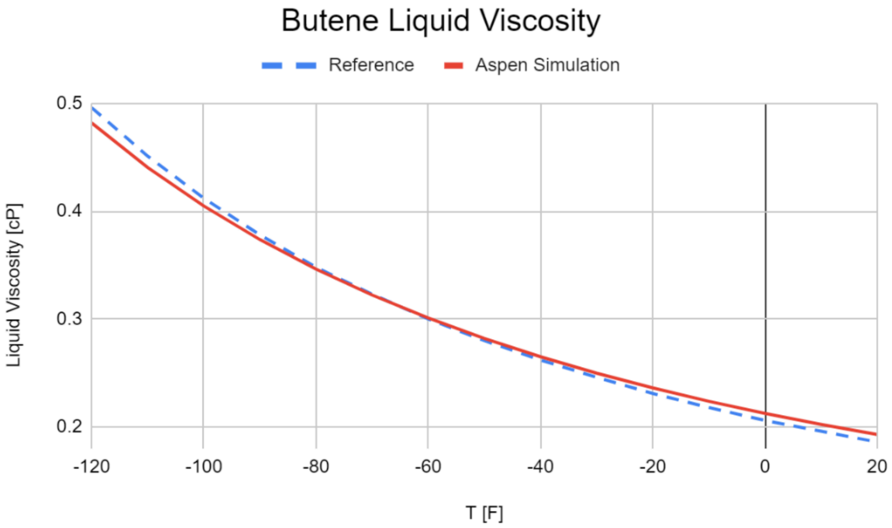


Figure B13. 1-butene liquid viscosity comparison.

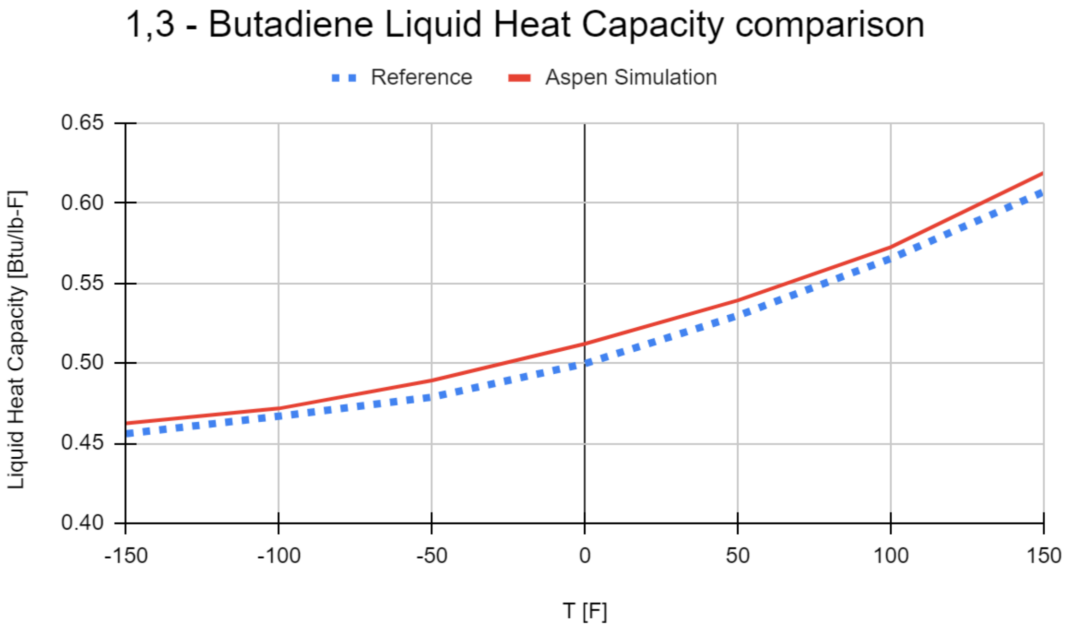


Figure B14. 1,3-butadiene liquid heat capacity comparison.

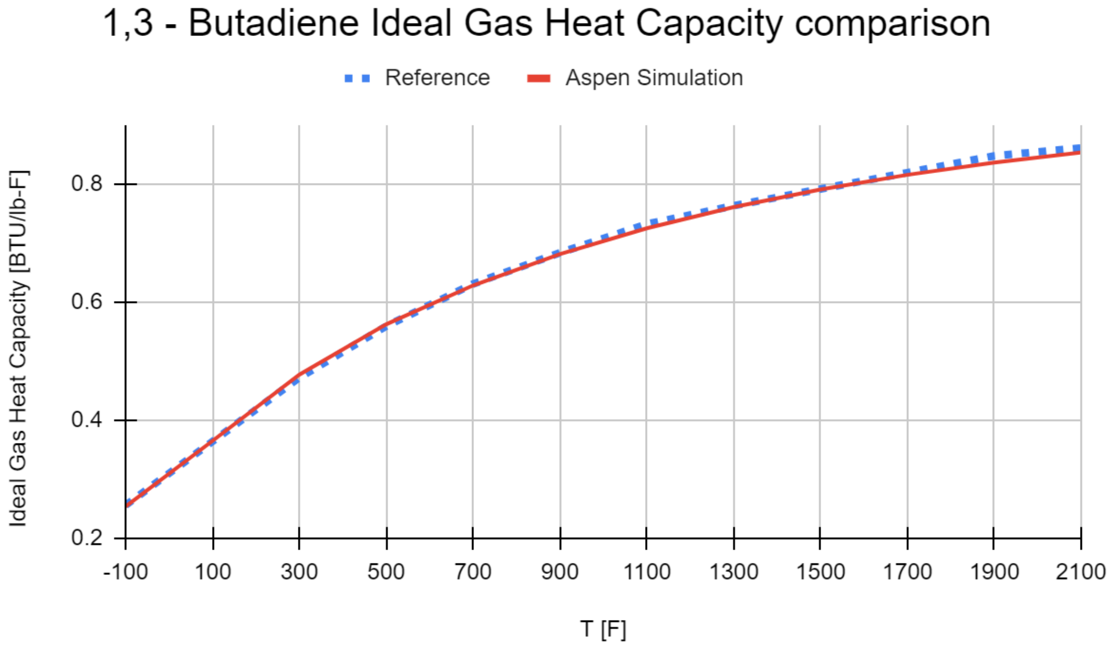


Figure B15. 1,3-butadiene ideal gas heat capacity comparison.

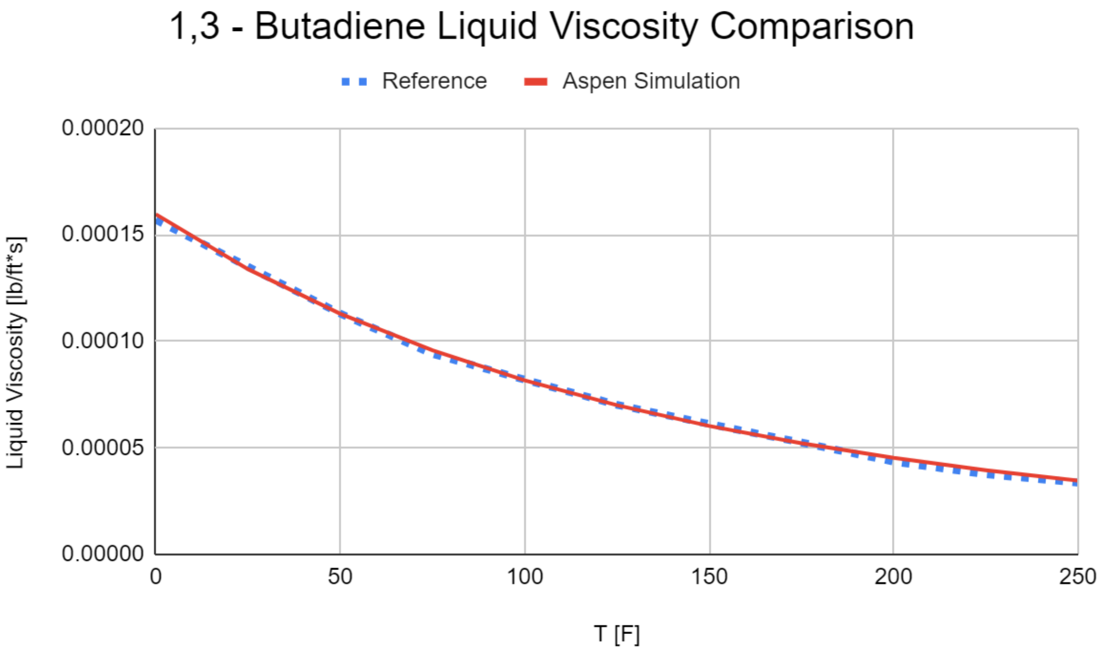


Figure B16. 1,3-butadiene liquid viscosity comparison.

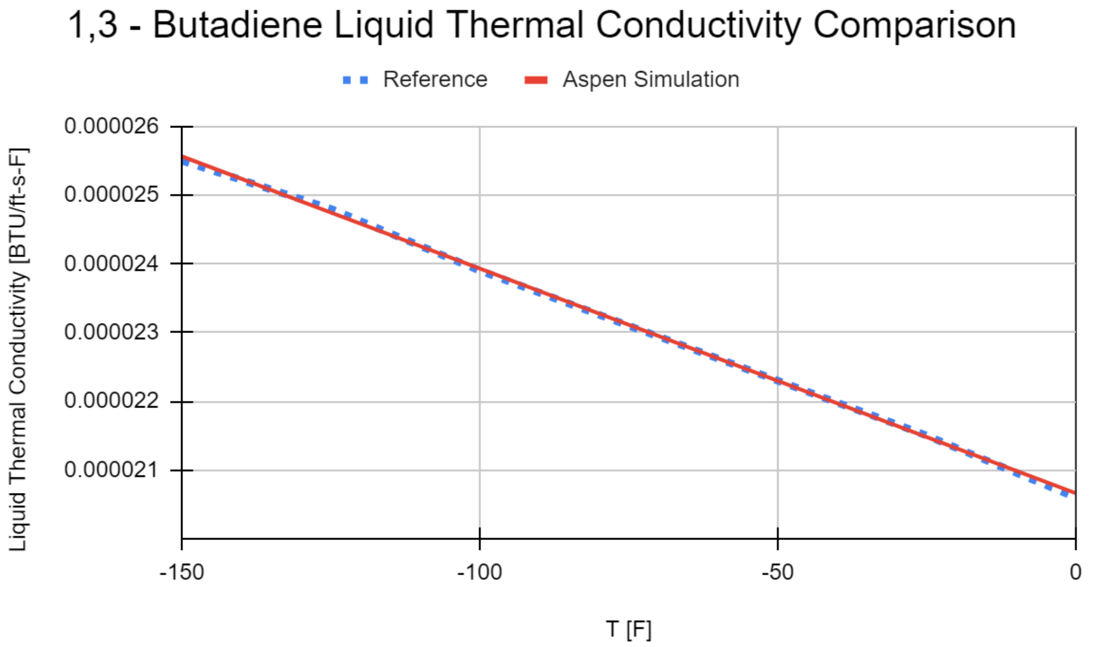


Figure B17. 1,3-butadiene liquid thermal conductivity comparison.

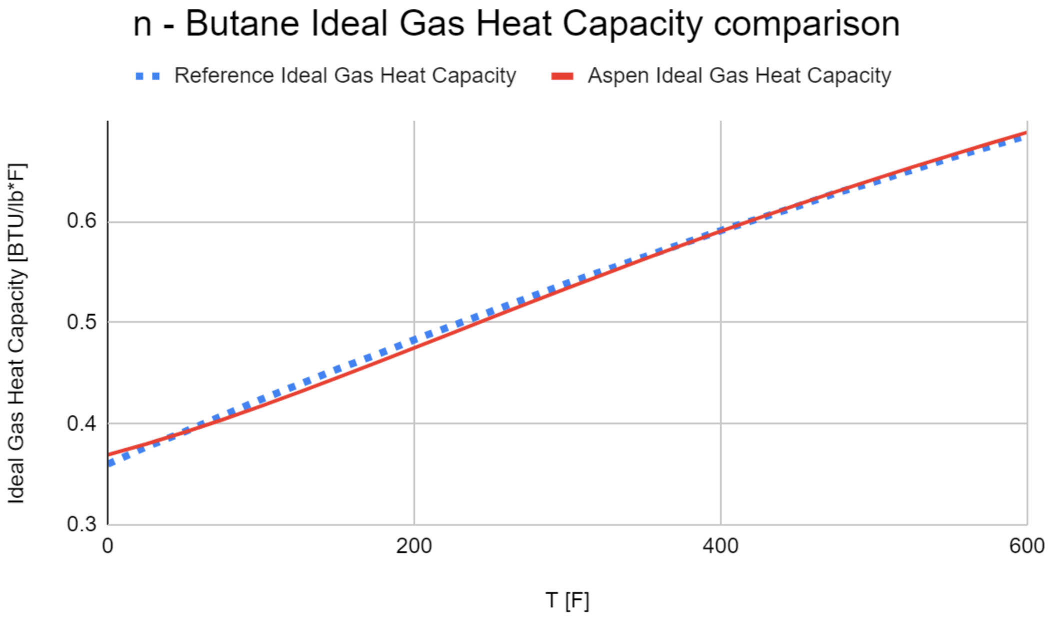


Figure B18. n-Butane ideal gas heat capacity comparison.

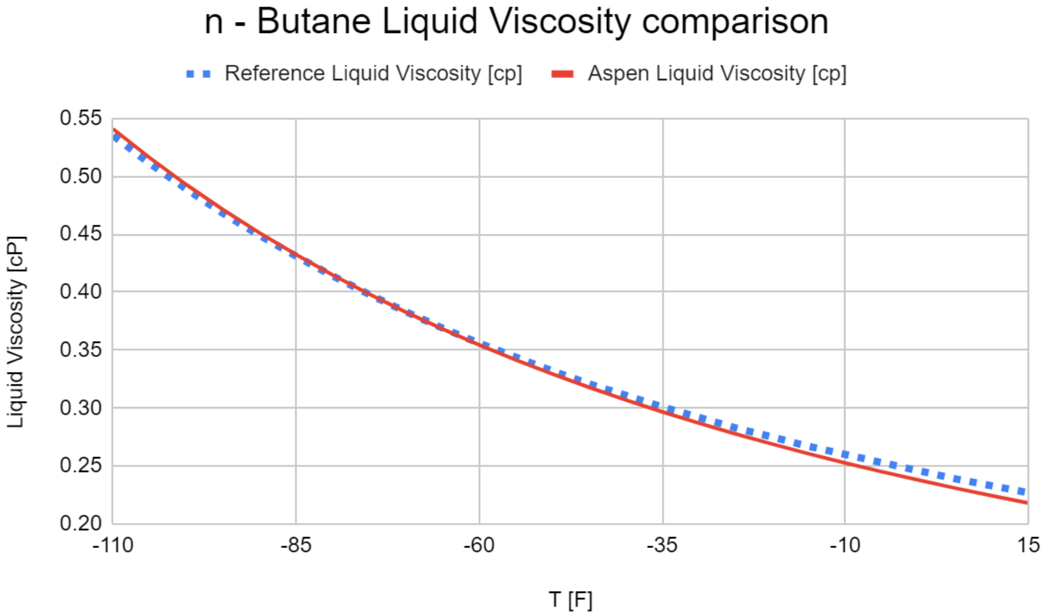


Figure B19. n-Butane liquid viscosity comparison.

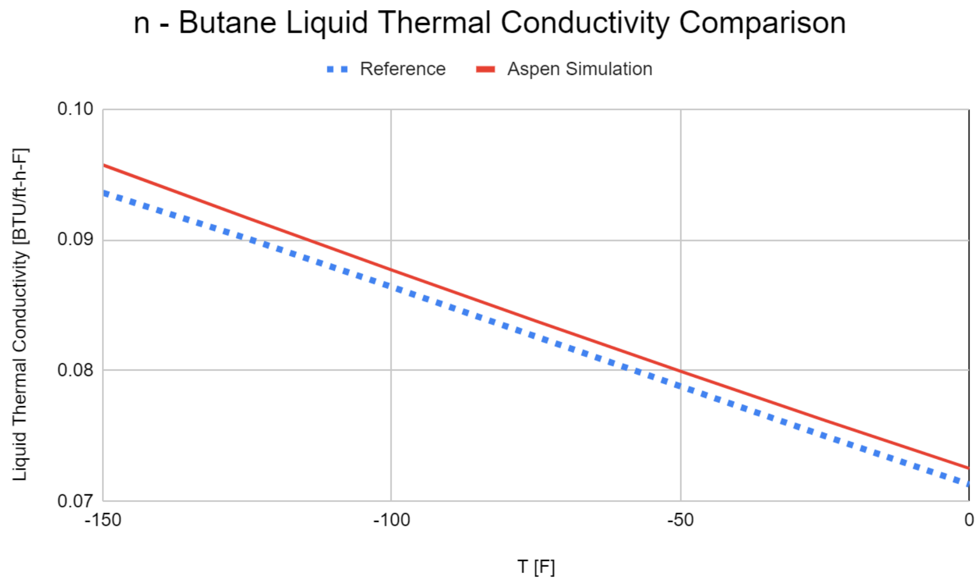


Figure B20. n-Butane liquid thermal conductivity comparison.

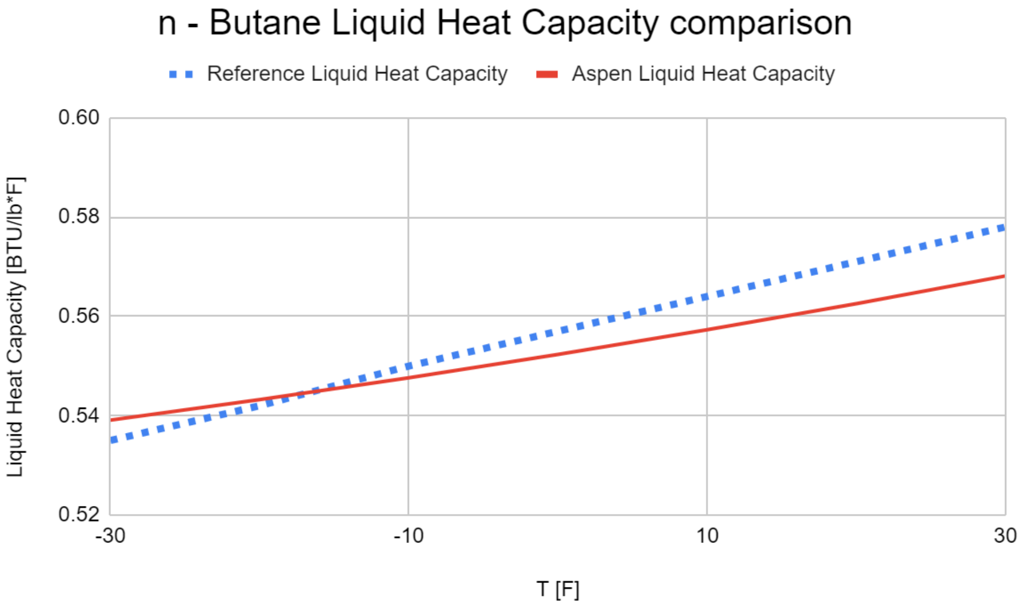


Figure B21. n-Butane liquid heat capacity comparison.

Binary Comps

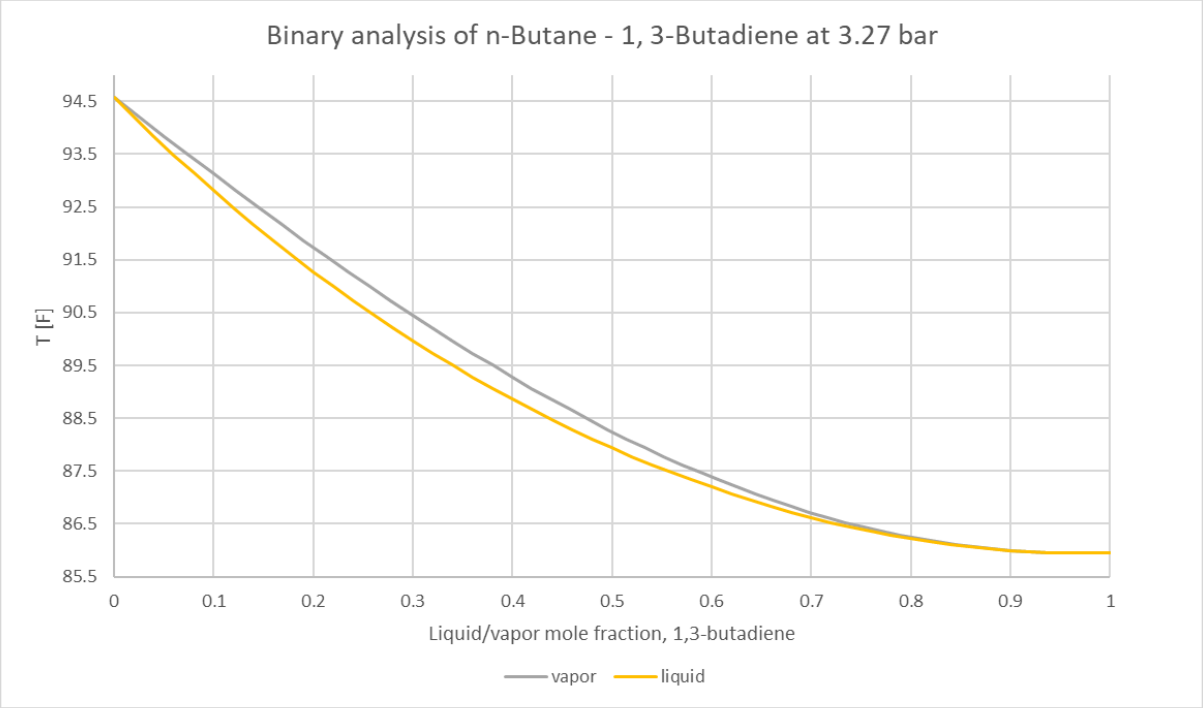


Figure B22. Binary analysis of n-C_4H_{10} and 1, 3-C_4H_6 at 3.27 bar pressure.

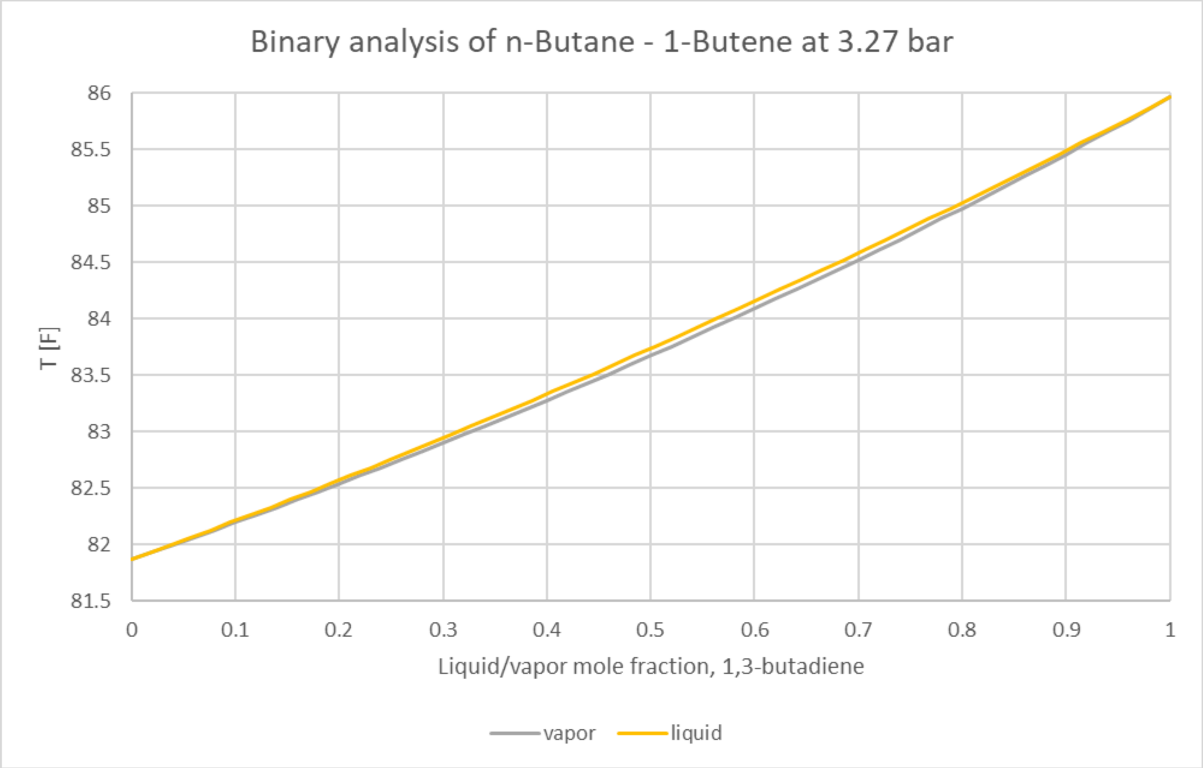
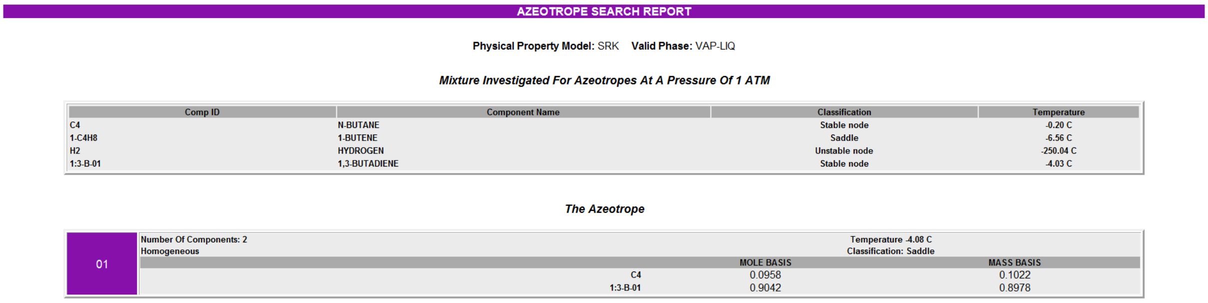


Figure B23. Binary analysis of n-C_4H_{10} and 1-C_4H_6 at 3.27 bar pressure.



AZEOTROPE SEARCH REPORT

Physical Property Model: SRK **Valid Phase:** VAP-LIQ

Mixture Investigated For Azeotropes At A Pressure Of 1 ATM

Comp ID	Component Name	Classification	Temperature
C4	N-BUTANE	Stable node	-0.20 C
1-C4H8	1-BUTENE	Saddle	-6.56 C
H2	HYDROGEN	Unstable node	-250.04 C
1:3-B-01	1,3-BUTADIENE	Stable node	-4.03 C

The Azeotrope

01

Number Of Components: 2
Homogeneous

Temperature -4.08 C
Classification: Saddle

	MOLE BASIS	MASS BASIS
C4	0.0958	0.1022
1:3-B-01	0.9042	0.8978

Figure B24. Azeotropic report of the mixture at 1 atm.