SIMULATION AND EVALUATION OF BUTADIENE PRODUCTION FROM ETHANOL VIA ONE-STEP REACTION

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บิวตะไดอีนคือสารประกอบสำคัญที่สามารถผลิตได้จากกระบวนการแครกกิ้งสตีมรีฟอร์มมิ่ง จากความต้องการแหล่งผลิตพลังงานชีวภาพทดแทนพลังงานจากฟอสซิล เอทานอลสามารถใช้ทดแทนในการผลิตบิวตะไดอีนได้ งานวิจัยนี้ศึกษาการจำลองการผลิตบิวตะไดอีนโดยใช้ปฏิกิริยาขั้นตอนเดียว ใช้ตัวเร่งปฏิกิริยา ได้แก่ 1.Al_2O_3/ZnO (60:40), 2.MgO-SiO_2 -Na_2O (1:1)(0.1%) และ 3.$Hf_{2.5}ZM_{1.6}/SiO_2$ การจำลองและออกแบบจะใช้โปรแกรม Aspen plus เวอร์ชั่น 8.0 และประเมินประสิทธิภาพด้านพลังงานโดยใช้โปรแกรม Aspen energy analyzer โดยลำดับของการกลั่นจะถูกศึกษา เพื่อหาค่าตัวแปรที่เหมาะสม ซึ่งได้แก่ จำนวนชั้นของหอกลั่น ตำแหน่งที่ป้อน อัตราส่วนของสารที่กลั่นได้ต่อสารที่ป้อนเข้าไปในระบบ อัตราส่วนป้อนกลับเข้าในหอกลั่น และความดันภายในเครื่องควบแน่นของหอกลั่น จากนั้นจึงทำการประเมินประสิทธิภาพทางด้านพลังงานนั้น โดยตัวแปรที่จะศึกษา ได้แก่ พลังงานที่ใช้ในการกลั่น ความต้องการพลังงานของสาธารณูปโภคในระบบ และการประหยัดพลังงานภายหลังการประเมินประสิทธิภาพทางพลังงาน จากผลการทดลองพบว่า ตัวเร่งปฏิกิริยา MgO-SiO_2 -Na_2O (1:1)(0.1%) ผลิตบิวตะไดอีนได้มากที่สุด คือผลิตได้ 62,676 กิโลกรัมต่อชั่วโมง สำหรับผลการประเมินประสิทธิภาพทางพลังงาน ตัวเร่งปฏิกิริยา $Hf_{2.5}ZM_{1.6}/SiO_2$ ที่ออกแบบ จะมีค่าพลังงานที่ใช้ในการกลั่นสูงที่สุดคือ 17.14 เมกะจูลต่อกิโลกรัม และตัวเร่งปฏิกิริยา Al_2O_3/ZnO (60:40) จะให้ค่าพลังงานที่ใช้ในการกลั่นต่ำสุดคือ 0.5 เมกะจูลต่อกิโลกรัม นอกจากนี้ตัวเร่งปฏิกิริยา MgO-SiO_2 -Na_2O (1:1)(0.1%) มีค่าความต้องการพลังงานของสาธารณูปโภคในระบบต่ำที่สุดคือ 5.72 เมกะจูลต่อกิโลกรัม สุดท้ายตัวเร่งปฏิกิริยา The $Hf_{2.5}ZM_{1.6}/SiO_2$ จะประหยัดพลังงานในระบบมากที่สุดภายหลังการประเมินประสิทธิภาพทางด้านพลังงาน

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1,3-butadiene is an important compound produced from the steam cracking process. Raising demand for alternatives to fossil fuels has led to an increase in bio-derived ethanol production, which can also be used as a feedstock for 1,3-butadiene synthesis. This research investigated the simulation of 1,3-butadiene production from ethanol using one-step process with 1.Al_2O_3/ZnO (60:40), 2.$MgO-SiO_2-Na_2O$ (1:1)(0.1%) and 3.$Hf_{2.5}ZM_{1.6}/SiO_2$ as heterogeneous catalysts. The process simulation was carried out using commercial Aspen plus 8.0 program and the heat utilization efficiency was evaluated by Aspen energy analyzer software. The process optimal condition sequences were identified by adjusting the separation distillation parameters which include the number of stages, feed location, distillate to feed ratio (D/F), reflux ratio and condenser pressure. To assess the process energy usage, the parameters examined are heat duty in separation column, total utility requirement, and energy saving. The results show that $MgO-SiO_2-Na_2O$ (1:1)(0.1%) catalyst provides the highest production rate of 62,676 kg/hr. From heat integration, $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst has the highest heat duty in separation column (17.14 MJ/kg.) and Al_2O_3/ZnO (60:40) catalyst has the lowest heat duty in separation column (0.5 MJ/kg.) Moreover. $MgO-SiO_2-Na_2O$ (1:1)(0.1%) has the lowest total utility requirement (5.72 MJ/kg.) Finally,$Hf_{2.5}ZM_{1.6}/SiO_2$ process has the most energy saving after all total energy requirements have been assessed.

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CHAPTER 1

INTRODUCTION

1.1 Rationale

1,3-Butadiene (C_4H_6 or BD) is a colorless organic compound that is polymerized by conjugating with itself or other monomers. 1,3-Butadiene is commonly used in industries as a monomer for the synthesis of rubbers, elastomers, and polymer resins. [1] These polymers are utilized in a wide variety of consumer and industrial applications and are essential in improving the functionality and performance, enhancing safety, and reducing the costs of these consumer products. Butadiene-based products are mostly applied in components of automobiles, construction materials, appliance parts, computers, telecommunications equipment, clothing, protective clothing, packaging, and household articles. [2]

In Asia and Pacific, 142,000 ton of 1,3-butadiene was produced annually in 1998 [3] and around 11.9 billion pounds were produced globally. The production trend continuously increased until the demand for butadiene reached an estimated 10 million metric tons in 2012. [1] Most 1,3-butadiene is produced from the extraction of mixed butene stream as a by-product of ethylene production. This process accounts for approximately 85% of all BD production in the world. [4]

Nowadays, BD is generally produced by a steam cracking process, which initially feeds ethane, propane, and butane into a pyrolysis process at 790-830 °C to break down complex hydrogen molecules into lighter hydrocarbons by pyrolysis under high pressure and temperature. [5] However, stream cracking process consumes 8% of total primary energy compared to heat pyrolysis process and vent more than 180 Million tons of CO_2 into the environment. [6] Furthermore, Naphtha represents the large consumption of fossil fuel which is a finite resource. Therefore, there is a pressing priority to start looking at alternative renewable feedstock to substitute fossil fuel-derived feedstock.

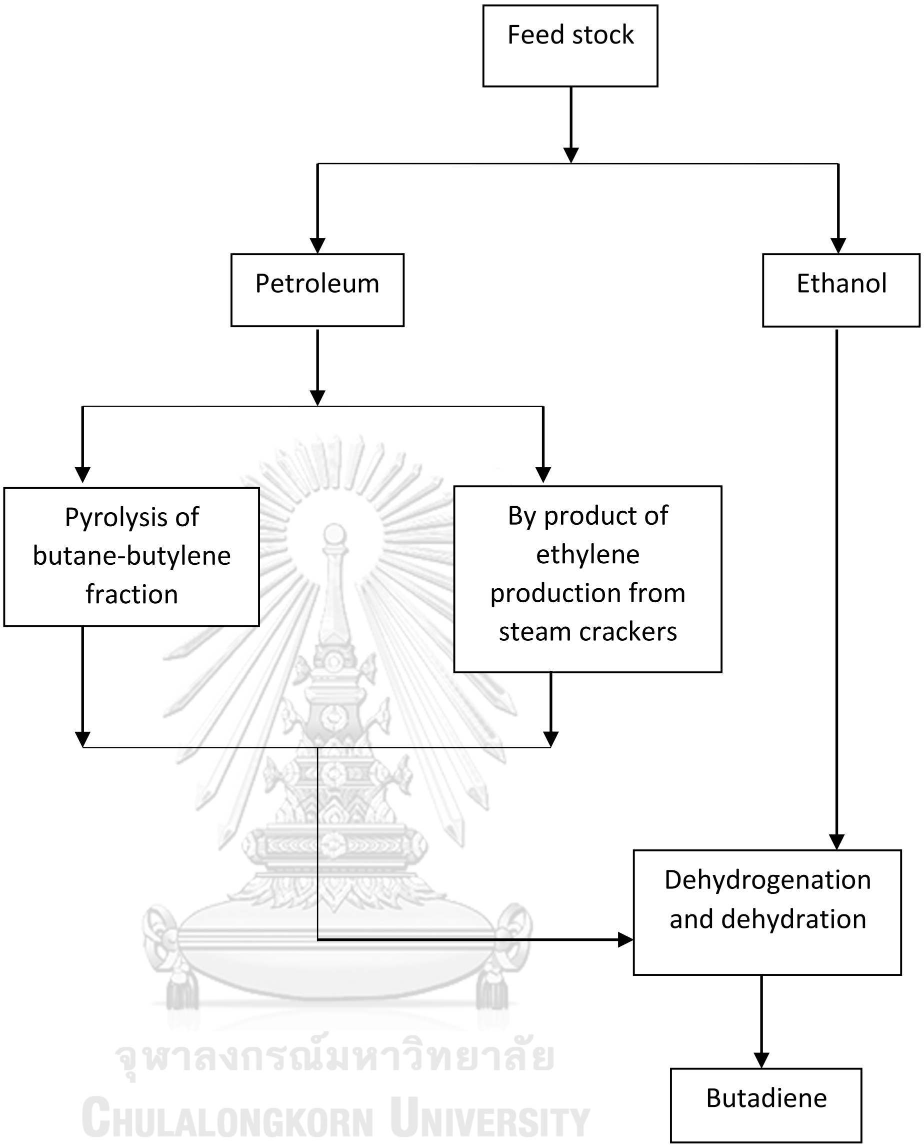

Figure 1 Overview butadiene production

Ethanol is an organic compound that not only has been used for chemical solvent and reactant in many industries but also use as renewable energy and a substitute for fossil fuel. Ethanol can be produced from the fermentation of biomass in a bioreactor, followed by a distillation process to obtain high purity ethanol. Due to diminishing fossil fuel supply, ethanol is a remarkable alternative which many researchers have recommended as a novel feedstock for butadiene production. In Union Carbide Company, they reported the capacity of butadiene production from alcohols in 1944 was 361,000 ton/year for synthetic rubber. [7] Ethanol-based butadiene production can be summarily produced by two-novel methods, including one-step and two-step method. One-step ethanol based butadiene production was first developed by Vladimir Nikolayevich Ipatiev [8], later Lebedev modified the method to obtain high butadiene yields by direct ethanol conversion. Two-step ethanol-based butadiene production was discovered by Ostromisslensky [8], a mixture of ethanol and acetaldehyde was used as a feedstock to obtain butadiene with 18 % yield under high temperature of 400 °C using zinc oxide and alumina catalysts. In order to study ethanol based butadiene production, a literature review was conducted to compare the one-step and two-step method in term of production yield, selectivity, and economic value. It can be concluded that there is no difference between of one-step and two-step method in term of butadiene yield. However, the one-step method is more suitable than the two-step method when an economic evaluation is compared.

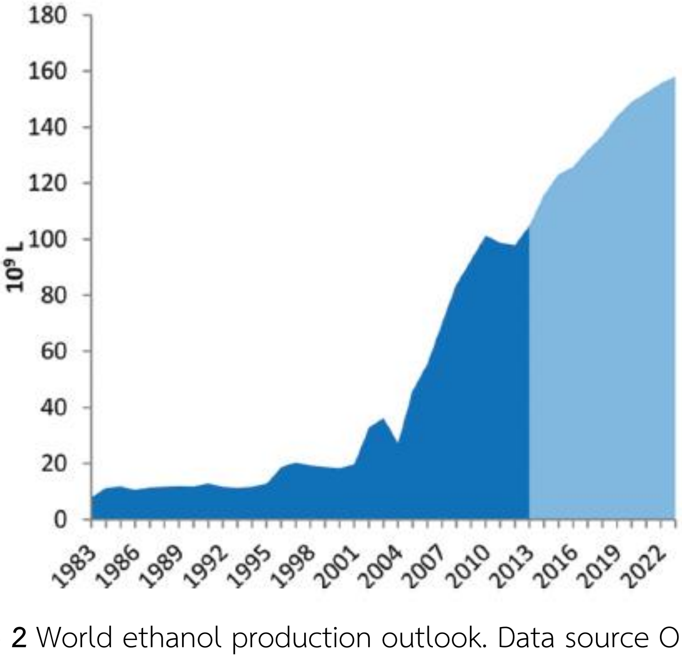

Figure 2 World ethanol production outlook. Data source OECD-FAO

In this work, the ethanol-based butadiene production process was designed using simulation software. The process energy requirement was evaluated by heat integration of the utility system and separation process. The conversion of redesigned one-step ethanol based butadiene production is obtained by a high yield of modified three new catalysts in the one-step process. The ethanol dehydrogenation, condensation of acetaldehyde, and Meerwein–Ponndorf–Verley reactions were simulated using yield reactors in Aspen plus software. Finally, the RADFRAC columns were designed in suitable sequence separation process to separate the butadiene product from other byproducts. The process of heat integration was required for efficient operation. The valuable product was butadiene and hydrogen which was obtained from the one-step synthesis process.

1.2 Research objectives

To design and evaluate process performance for butadiene production from ethanol via a one-step process.

1.3 Scope of work

1. Process simulation for butadiene production from ethanol carried out with Aspen plus software version 8.0 and Aspen energy analyzer version 8.8
2. The amount of feed rate of ethanol and water was set at 66,996 kg/hr and 3,526 kg /hr.
3. The percent purity of butadiene product was set to 99%.

CHAPTER 2

THEORY

2.1 General information from butadiene

2.1.1 Chemical properties

Butadiene is an organic compound gas that can easily condense to the liquid phase. Butadiene composed conjugated diene together resulting is from as two vinyl groups ($CH_2{=}CH_2$) joined together. **butadiene** always refer to 1,3-butadiene, which has the structure $H_2C{=}CH{-}CH{=}CH_2$ as shown in figure 3 [7]

Normally, butadiene has two isomers, including 1,2- butadiene and 1,3-butadiene. 1,2-butadiene is from accumulated diene with structure $H_2C{=}C{=}CH{-}CH_3$ that is difficult to prepare and no industrial significance. 1,2-butadiene properties do not behave as a 1,3-butadiene because of its formula structure. In this work, We are only focused on 1,3-butadiene. The chemical properties of butadiene are shown in table 1 [9]

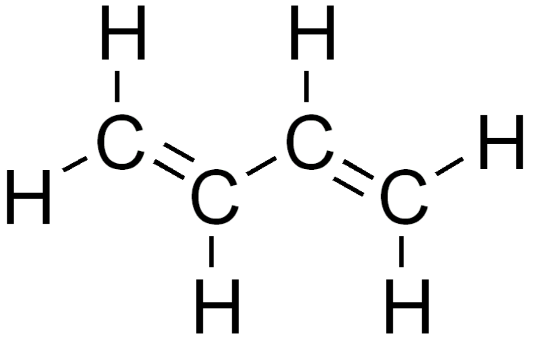

Figure 3 Structural of 1,3-butadiene

Table 1 Chemical properties of 1,3- butadiene

Properties	
Chemical formula	C_4H_6
Molar mass	54.0916 g/mol
Appearance	Colorless gas or refrigerated liquid
Odor	Mildly aromatic or gasoline-like
Density	0.6149 g/cm^3 at 25 °C, solid 0.64 g/cm^3 at -6 °C, liquid
Melting point	-108.9 °C (-164.0 °F , 164.2 K)
Boiling point	-4.4 °C (24.1 °F, 268.8 K)
Solubility in water	1.3 g/L at 5 °C, 735 mg/L at 20 °C
Solubility	Very soluble in acetone Soluble in ether, ethanol
Vapor pressure	2.4 atm (20°C)
Refractive index	1.4292
Viscosity	0.25 Cp at 0°C

2.1.2 Background of butadiene production

Butadiene is generally produced by three processes, including steam cracking of paraffinic hydrocarbon, Catalytic dehydrogenation of n-butane and n-butene and oxidative dehydrogenation of n-butene.

1. Steam cracking of paraffinic hydrocarbon

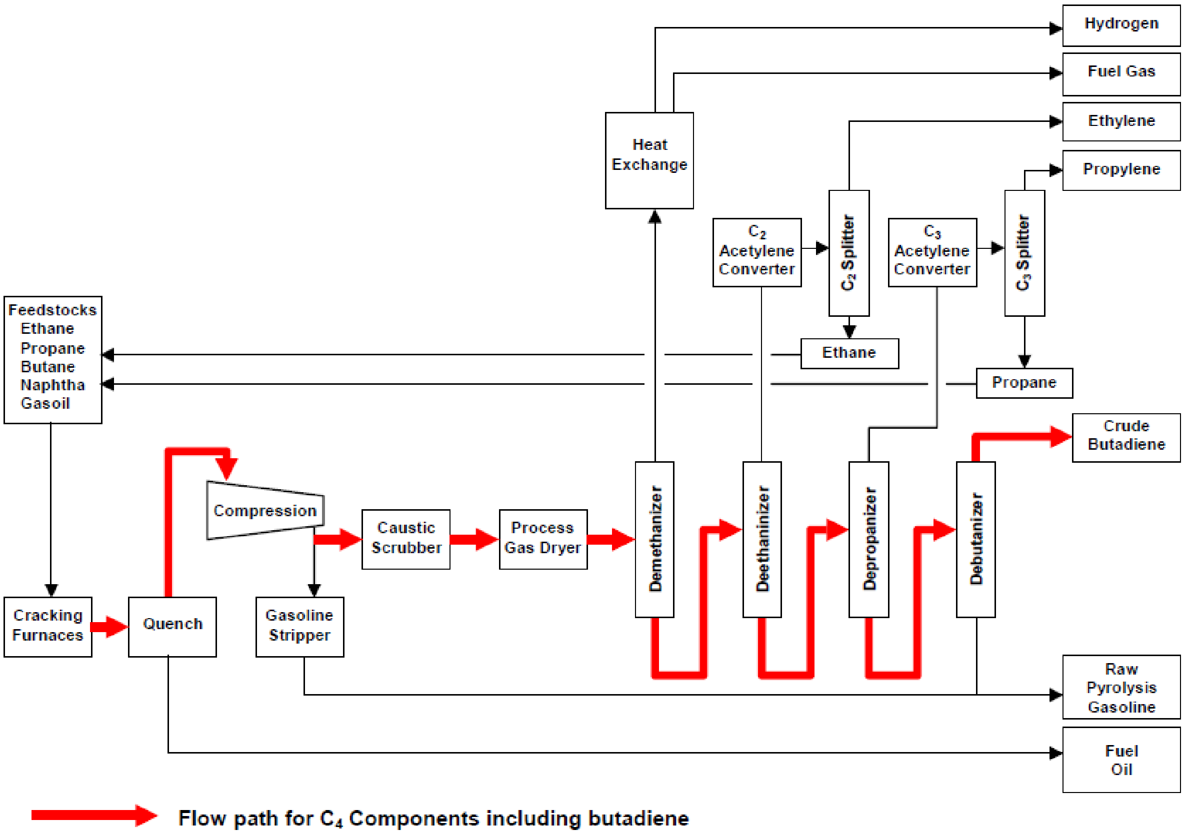

Figure 4 The steam cracking process.

The steam cracking process is a common method that produces butadiene of more than 91 % in the world. The steam cracking process can be explained following figure 4. Firstly, The mixture of petroleum feedstocks, including ethane, propane, butane naphtha and gas oil, was pass through to a pyrolysis process under temperature range between 790-830 °C.[2] The feedstock molecule was broken down to obtain hydrogen, ethylene, propylene, butadiene, benzene, toluene, etc. Then, the products are separated by many processes, including distillation, compression, process gas drying, hydrogenation, and heat transfer to achieve high purity products. Butadiene which produced by the steam cracking process has estimated concentrations of more than 75 %wt.[2] The quality of butadiene production depends on the feed precursor. Light feeds, such as ethane, is converted to primarily ethylene later thermal cracking process, on the other hand, heavier feeds precursor provides the formation of heavier olefins, butadiene, and aromatic hydrocarbons. Butadiene is typically separated from the product from steam cracking following extractive distillation with a polarity solvent such as acetonitrile, N-methylpyrrolidone, furfural, or dimethylformamide. The butadiene was finally obtained from the distillation process.

2. Catalytic dehydrogenation of n-butane

The catalytic dehydrogenation of n-butane was discovered by the Rubber Reserve Company, a part of the United States government, constructed several plants in Borger, TX, Toledo, OH, and El Segundo, CA to produce synthetic rubber for the war effort as part of the United States Synthetic Rubber Program.[10] The catalytic dehydrogenation of n-butane is a two-step process, which converts n-butane to n-butene to butadiene, respectively. The process is feed n-butane as a feedstock for dehydrogenation and chromium/alumina is utilized as a catalyst. The reaction temperature and pressure is control at 600-680 °C and 12-15 mmHg, respectively. Due to the hydrogenation reaction is an endothermic reaction, which a portion of coke is deposited on the catalyst after the reaction temperature decrease. Therefore, The reactor is required for catalyst regeneration. The catalyst is regenerated by burning coke with preheated air.

3. Oxidative dehydrogenation of n-butene

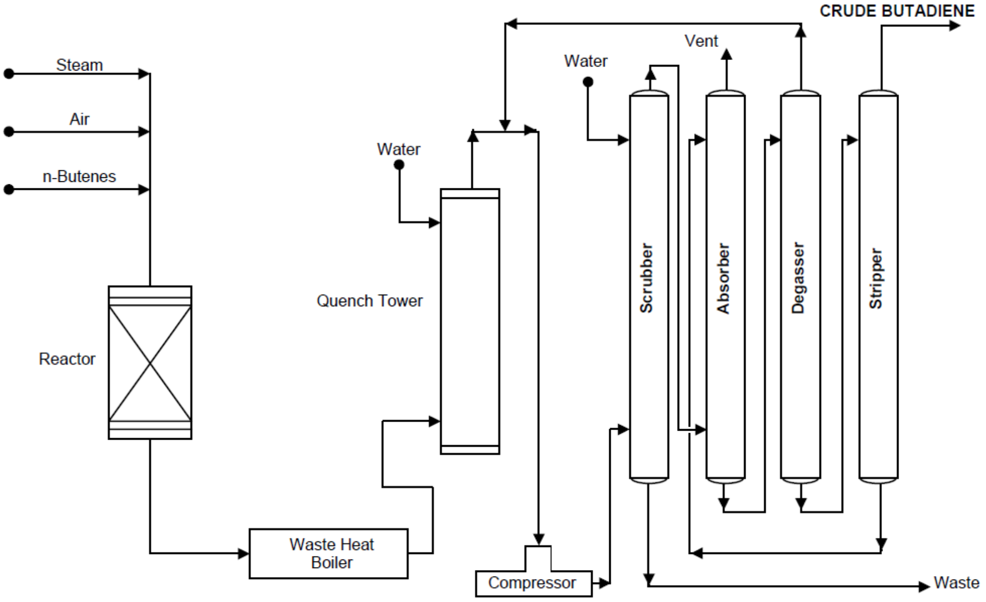

Figure 5 Oxidative dehydrogenation of n-butene

Oxidative dehydrogenation of n-butene is modified for replacing the catalytic dehydrogenation because butene is more reactive than butane. Therefore, The oxidative dehydrogenation requires less unit operation than the dehydrogenation of n-butane as shown in figure 5. The oxidative dehydrogenation of n-butene operated initially by a mixture of butenes, air and stream are fed into a catalytic bed reactor at a temperature of 500-600 °C. The air feed rate which is a mixture of oxygen and butene of 0.55 and a ratio of steam and butene of 10:1 have been set for preventing the overheat reaction resulting in the increase of temperature. The butadiene yield from oxidative dehydrogenation is about 70-90 %. The all product is separated by the absorber, degasser, and stripper column combination.[10]

2.1.3 Use of butadiene

1,3-Butadiene is a product that possesses low molecular weight and high chemical reactivity properties. Butadiene is used primarily as a monomer in the production of a wide range of polymers and copolymers. The butadiene can use as a precursor for styrene butadiene rubber polybutadiene styrene. It is also used as an intermediate in the production of several chemicals, including Adiponitrile ≫ HDMA

≫ Nylon, Acrylonitrile/Butadiene/Styrene Resin, etc. The butadiene can use as a precursor for styrene butadiene rubber polybutadiene styrene. Table 2 provides a listing of the use patterns for butadiene in the United States. The use of butadiene can be classified as above mention.[11]

Table 2 Use Patterns for 1,3-Butadiene in the US, 1996

End-Use	% of Total
Styrene Butadiene Rubber	30
Polybutadiene	24
Styrene Butadiene Latex	13
Adiponitrile ≫ HDMA ≫ Nylon	13
Acrylonitrile/Butadiene/Stryrene Resin	5
Chloroprene ≫ Neoprene	3
Nitrile Rubber	2
Other (includes Styrene-Butadiene Block Copolymers and Methyl Methacrylate - Butadiene - Styrene)	10

1) Styrene-Butadiene Rubber (SBR): the largest single use of butadiene (approximately 30%, as shown in table 2) is in the production of Styrene Butadiene Rubber. Produced by the polymerization of styrene and butadiene, the primary use of SBR is in tires and tire products. The SBR prefer to families of synthesis wheel rubber derived from styrene and butadiene. SBR is produced by emulsion polymerization at 50 °C, starting by a reaction of potassium peroxidisulphate with n-dodecyl mercaptan, generating chain free radical of mercaptyl attracting between butadiene or styrene.

2) Polybutadiene (PB): PB is a polymer that is formed by polymerization of the butadiene. There is four types of polybutadiene, including high cis-polybutadiene low cis polybutadiene, high vinyl polybutadiene, and high trans polybutadiene, which depend on the kinds of catalyst. High cis polybutadiene is composing of cis (92%) and vinyl (4%). High cis polybutadiene is composing of 70 % in tires. Low cis polybutadiene contains 36 % cis, 59 % trans and 10%vinyl. This polybutadiene is applied in tire manufacturing and blend with others polymer. High vinyl component of polybutadiene includes 70 % of vinyl, resulting in the polymer look like a high liquid-glass transition. High trans polybutadiene composes of high trans (90 %) Polybutadiene is usually applied as base-material in tires production, which consume about 70 % of the world production of polybutadiene. 25 % of polybutadiene is used as an improvement of mechanical of plastic, such as high impact polystyrene and acrylonitrile butadiene styrene. On the other hand, polybutadiene is produced for making of an elastic core of golf ball.

3) Styrene-Butadiene Latex (SBL): the 13 % of butadiene is used for styrene-butadiene latex in U.S.A. styrene-butadiene is a particle-dispersion slurry, which composes of 0.0- micrometer of discrete polymer particle. Styrene-butadiene latex is applied in the synthesis of foam rubber, adhesives, sealants, and paper planting.

4) Acrylonitrile-Butadiene-Styrene (ABS) Resins: Acrylonitrile-butadiene-styrene resin is produced by emulsion polymerization or suspension grafting polymerization. Acrylonitrile- butadiene styrene resin is utilized in a composed of automotive part, telephone, and composed of computer, which consumes 5 % of butadiene in the U.S.A.

5) Nitrile Rubber (NBR): The nitrile rubber is synthesized using the polymerization of butadiene and acrylonitrile. The nitrile rubber is applied in various products, including fuel line oil resistant clothing, etc that is estimated of 2% consumption of butadiene in the U.S.A.

6) Styrene-Butadiene Block Copolymers (SBS and SEBS): The styrene-butadiene is synthesized by polymerization of styrene and butadiene, following with casting to form of block polymer. The styrene-butadiene block copolymer is applied as a thermoplastic material, including asphalt extender, adhesives automotive, etc.

7. Use as chemical intermediate usage of butadiene: butadiene is utilized as an intermediated of various chemical, For example, The adiponitrile production is a one of largest use of butadiene that consumes 13 % of the consumption of butadiene. The adiponitrile production involves with a hydrocyanation reaction of butadiene following hydrocyanation reaction of pentenenitrile. Chloroprene is synthesized by chlorinating butadiene, following polymerization reaction to archive neoprene. Furthermore, butadiene is used as an intermediate reagent for many productions, including 1,4-hexadiene, sulfolane and 1,5,9 cyclododecatriene. Figure 6 is a summary of the usage of butadiene as intermediate.

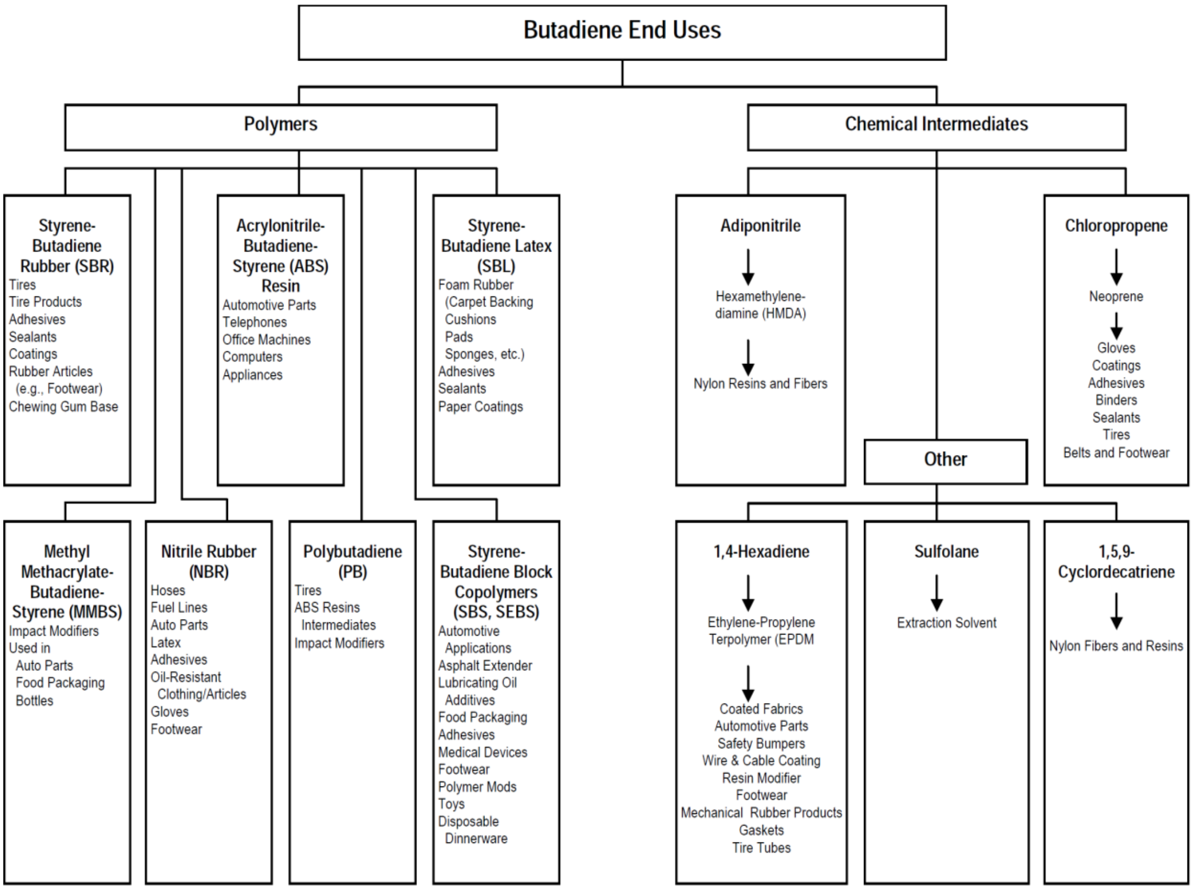

Figure 6 Some Uses of 1,3-Butadiene

2.2 Ethanol-based butadiene production

Ethanol is an organic compound that not only has been used for chemical solvent and reactant in many industries but also use as renewable energy within a concern of fossil fuel. Due to ethanol can be produced from the fermentation process of biomass in a bioreactor, following distillation process to obtain high purity ethanol. The concern of using fossil, ethanol is a remarkable choice which is many researchers have investigated a novel butadiene production base on ethanol.

Ethanol based butadiene production was firstly performed by Ipatiev et.al[12], ethanol was passed over aluminum powder at 550-600°C, providing a butadiene yield of 5 %. The development of ethanol-based butadiene production has been enhanced to obtain 70 % butadiene yield, was performed by Lebedev and et.al. which is known as "one-step ethanol-based butadiene production " The studies initially were fed ethanol over a mixture of zinc oxide and alumina at a temperature of 400 °C to obtain Butadiene following equation 1 [1]

$$2C_2H_5OH \rightarrow C_4H_6 + H_2 + 2H_2O \qquad (1)$$

Ostromyslensky et.al was fed a mixture of ethanol and acetaldehyde as precursors for catalytic synthesis of butadiene over alumina or clay under 440-460°C. The usage of a mixture of ethanol and acetaldehyde as feedstock is noted that "two-step ethanol-based butadiene production". The two-step reaction involves the partial dehydrogenation of ethanol to acetaldehyde following the conversion of ethanol and acetaldehyde into butadiene as shown in equations 2 and.3

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \qquad (2)$$

$$C_2H_5OH + C_2H_4O \rightarrow C_4H_6 + 2H_2O \qquad (3)$$

The Lebedev and Ostromyslensky investigated The Ethanol based butadiene reaction mechanism. They found that Ethanol-based butadiene reaction has many reaction formations, normally all proceeded through the intermediate formation of crotonaldehyde. The mechanism can divide into the formation of acetaldol via the aldol condensation of two acetaldehyde molecules, and dehydration of the aldol to crotonaldehyde. [1] Many researchers studied the synthesis mechanism of ethanol-based butadiene production, which are complicated and need more debate. However, there is a one synthesis mechanism are accepted and can explain as bellow.

The ethanol-based butadiene reaction is studied by different scientific teams studying the kinetics of the reaction. Firstly, the ethanol-based butadiene reaction was purposed by Kagan et al., and modified by Niiyama et al., Natta et al. and Bhattacharyya et al. The Ethanol based butadiene reaction can be described in 5 steps. Starting by ethanol is converted to acetaldehyde by dehydrogenation. Second, the condensation of acetaldehyde is transformed into aldol, which is promoted by dehydrating sites of the catalyst. Aldol was changed into crotonaldehyde, following react with the remnant of ethanol to crotyl alcohol on the dehydrating sites. Finally, crotyl alcohol was converted to butadiene and water, respectively.

Step 1 Production of acetaldehyde from ethanol on the dehydrogenating centers of the catalyst.[13]

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad (4)$$

Step 2. Condensation of acetaldehyde to form acetaldol on the dehydrating sites of the catalyst.

$$CH_3CHO + CH_3CHO \rightarrow C_4H_8O_2 \qquad (5)$$

Step 3. Dehydration of acetaldol to form crotonaldehyde.

$$C_4H_8O_2 \rightarrow C_4H_6O + H_2O \qquad (6)$$

Step 4. Meerwein-Ponndorf-Verley reaction between crotonaldehyde and ethanol to obtain crotyl alcohol and acetaldehyde.

$$C_4H_6O + C_2H_5OH \rightarrow C_4H_8O + CH_3CHO \qquad (7)$$

Step 5. Formation of butadiene from crotyl alcohol on the dehydrating sites of the catalyst.

$$C_4H_8O \rightarrow C_4H_6 + H_2O \qquad (8)$$

Then, consider by-product of ethanol-based butadiene production, It is seen that ethanol can be converted to a wide variety of chemicals that depend on several factors such as the reaction conditions and kinds of catalyst. Furthermore, the contact time between the reagents and catalyst also affect to the pathway of reaction, resulting in adjust carefully an optimization is required. The nature of the catalysts can also influence the kinds and quantity of the byproduct. For example, Silica-supported zirconium oxides were used for a procedure larger amounts of C6+ hydrocarbon species synthesis as side products, due to it may be their trend to condensation reactions. This issue is complicated by an incomplete understanding of the mechanism like the formation of ethylene. It is still a topic of debates that depends on the kinds of catalyst. In order to maximize the butadiene yield, the side reaction is also eliminated of the formation of such byproducts. Furthermore, the intermediate which undergoes an undesired pathway, are vanished by the adsorption process of carbon atoms.

Another issue explains a reaction network of the main byproducts and summarized in Figure 7

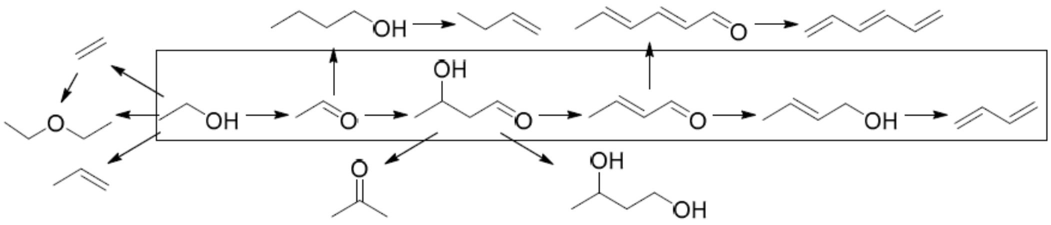

Figure 7 Reaction network of the main byproducts. The Kagan mechanism intermediates and product are in boxed.

The main byproduct of the ethanol-based butadiene reaction can explain staying by ethylene, which is converted by ethanol dehydration or ether cracking over acid sites. However, dehydration cannot be entirely restrained because of the formation of butadiene after the condensation reaction. Other byproducts composed: 1-butanol which is obtained by result the Guerbet reaction, butenes which are the result by dehydration of 1-butanol and propylene, possibly generated by acetone reaction or its own ethanol-to-propylene pathway, as well as C5+ hydrocarbons resulting from the aldol condensation of crotonaldehyde.[14]

2.3 The heuristic for determining the favorable sequences

Recently, the purity in chemical industrial products is used to put on the separation process. The distillation separation techniques are used to separate more than two of volatility compound in the chemical industry. However, the number of the distillation column is depending on the number of the components in the separation process. In the conventional columns, feed stream can separate in head product and bottom product. The complex column such as side product and side stripper. It can be composed in a sequence of conventional columns.[15]

This is the method for a finding of the optimal separation sequence, for instance

1. The algorithmic method which is related to the established optimization principle.

2. The rule of thumb of the heuristic method.

3. The Improvement of the created separation sequence in evolutionary strategies.

4. Principle of heat cascade application in thermodynamic methods.

Furthermore, for three or four products. The economical sequence is the main point to find designing and costing of all sequences. Nevertheless, the costing and the selection of sequence are not very much. If the feed mixture has a wide distribution component concentration and wide changing of relative volatiles in the separation process. The heuristic theory is starting in 1947 which it has used to decrease the number of the sequence.[15, 16] The example of the heuristic theory is

1. Take away the component which it is thermally, unstable, corrosive and chemically reactive components in the initial sequence.
2. Distillate the final product in direct sequence.
3. Remove the greatest molar percentage of feed in the first sequence.
4. Decreasing the relative compound and the hard split components.
5. Distillate the high purity products in the last sequence separation.
6. Separate the component which it can separate the amount of equimolar in bottom and distillate.
7. Separate the cheapest separation and easiest separation first but the heaviest separation last.
8. Remove the plenty of Perform sequence without non-key components.

The example of sequence with four component was sawed in Figure 8

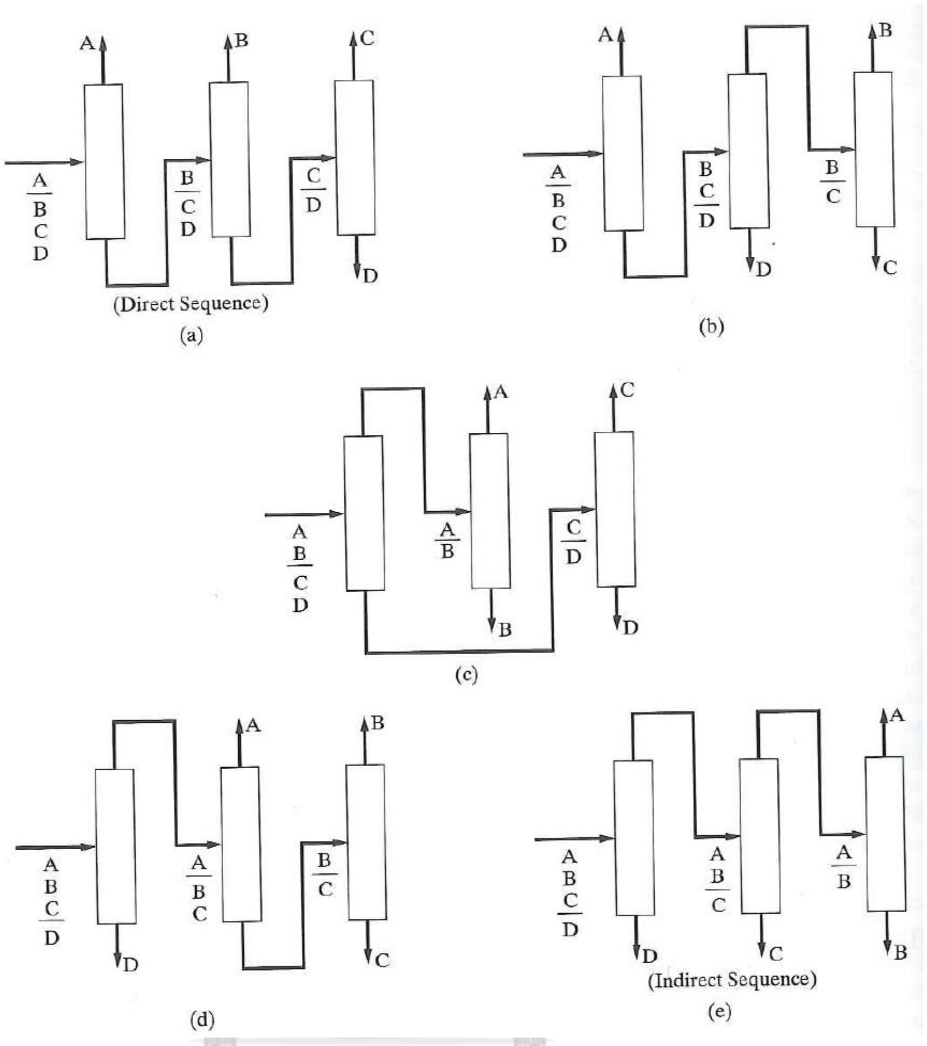

Figure 8 The five sequence for a four-component feed

2.4 Pressure swing adsorption

Pressure swing adsorption (PSA) system which used in industrial plant. It can be classified into three types such as PSA, VSA, and PVSA. For the PSA system conditions, Compressor is used to compress feed gas. The adsorption has occurred in high pressure, but The Desorption has occurred in atmospheric pressure. The product gas is separated in the many systems which can commonly in water, nitrogen, oxygen and hydrogen system. For the VSA system, turbo blower is used for adsorber. The pressure is increased in adsorber, but it is decreased by a vacuum pump for regenerating of an adsorbent. VSA system is generally operated in atmospheric pressure, so it is smaller than the PSA system. The separated product gas from VSA is commonly oxygen, and carbon dioxide or argon. PVSA system is a system which use roots blower to raise the pressure in raw material gas in the adsorber. Furthermore. The PVSA system has operated in pressure level in between the PSA system and VSA system. The number of adsorbents is filled in PSA < PVSA < VSA, so It is related to the size of equipment in the system. Table 3 shown the types and application of PSA in industries.[17]

The adsorption isotherm in the PSA system is related to the partial pressure of components and the equilibrium loading of adsorbent materials in operating temperature. Adsorption occurs in high pressure until the reacting of equilibrium loading which is generally in the range of 10 to 40 bar. When the adsorption capacity is usable. The adsorbent material must be generated. It is done in lower pressure or above atmospheric pressure, As a result. The impurity of adsorbent is desorbed and regenerated in adsorbent materials which the impurities are removed from the stream in one cycle, and they have related to the difference of adsorption to desorption loading. For the last step of regeneration. The pressure is increased to the adsorption step and restarted the process from the beginning step[18]. The step of adsorption and desorption in PSA are shown in Figure 9 and 10

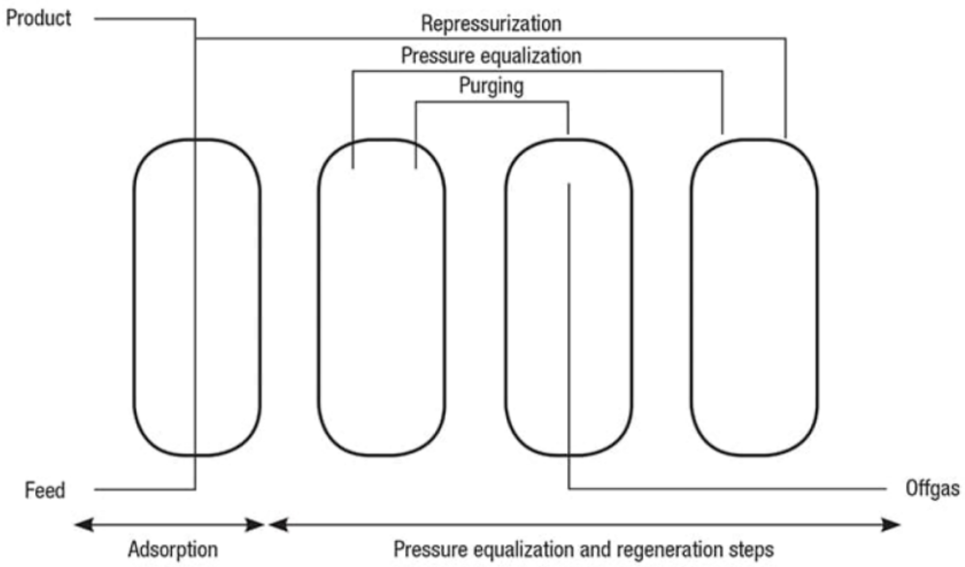

Figure 9 Diagram of The PSA system.

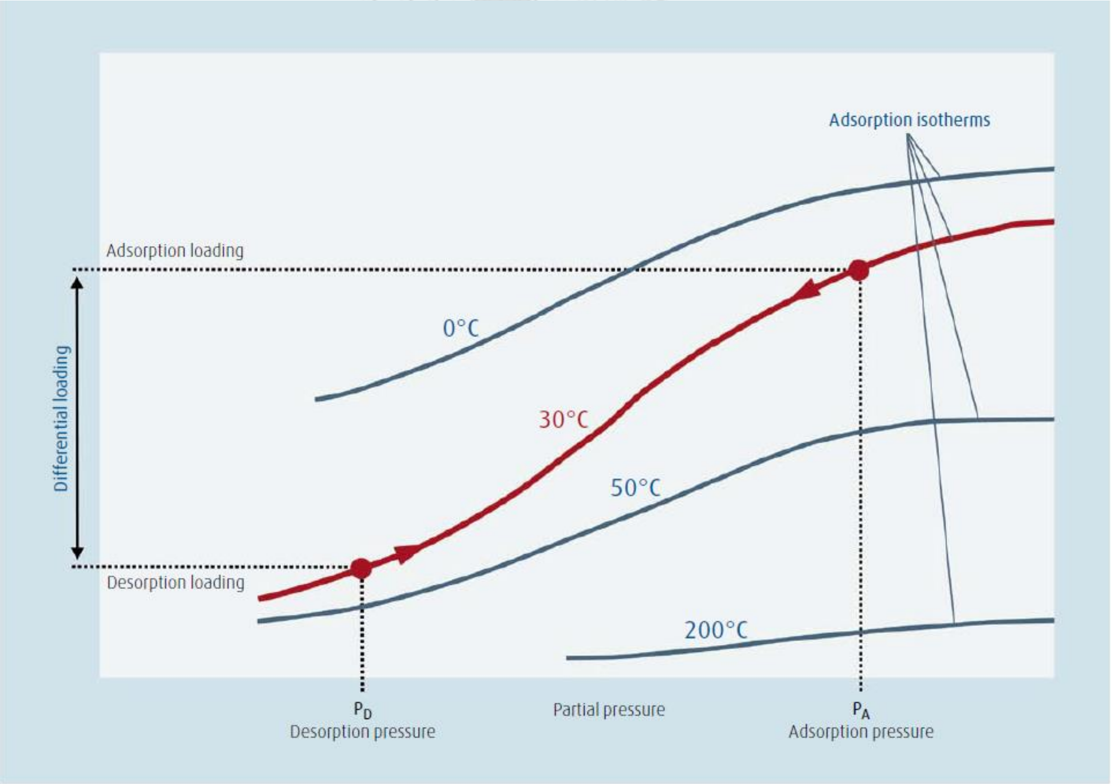

Figure 10 Isotherm of adsorption and desorption of adsorbent between partial pressure and equilibrium loading of gas.

Table 3 Applications of PSA in industries.

Operating pressure					Product gas		
Product gas	Adsorption pressure	Desorption pressure	System	Adsorbent	Purity	Product	Application
Water(Drying)	0.5-1 MpaG	1 atm	PSA	Alumina, ZMS	H_2O < 180 ppm	Non-Adsorption gas	Dryer, Instrument Air
N_2	0.5-1 MpaG	1 atm	PSA	MSC	Max.99.999%	Non-Adsorption gas	Heat treatment sealing
O_2	0.2-0.4 MpaG 1 atm 0.01-0.05 MpaG	1 atm Vacuum Vacuum	PSA VSA PVSA	ZMS ZMS ZM	Max.95%	Non-Adsorption gas	Mini-Mill,Incinerator Ozoneizer Glass Making Medical Use
H_2	over 0.5 MpaG	1 atm	PSA	Activated carbon,MSC,ZMS	Max.99.999%	Non-Adsorption gas	Semiconductor Manufacturing, Fuel Cell, Glass Making, Heat treatment
CO_2	1 atm	Vacuum	VSA	MSC, ZMS	Max.99%	Adsorption gas	Food additives, Dry Ice, Welding
CO	1 atm	Vacuum	VSA	Complex	Max.99%	Adsorption gas	Chemicals
Ar	1 atm	Vacuum	VSA	ZMS	Max.99.9%	Non-Adsorption gas	Steel Making. Silicon Wafer Manufacturing
CH_4	0.2-1 MpaG 0.01-0.05 MpaG	Vacuum Vacuum	PSA PVSA	MSC MSC	Max.99%	Non-Adsorption gas	Fuel

2.5 Extractive distillation column

The extractive distillation column is the unit separation which used to separate azeotrope and relative volatility component mixtures. Volatility components must be below 1.1 over an appreciable range of concentration. The minimum boiling point azeotrope and lower volatility components are fed in above the feed stage of the column which the solvent liquid phase is added to the bottom column. The solvent is vaporized and stripped to the overhead vapor. If the feed component mixtures are maximum boiling point azeotrope, feed mixture and solvent are fed in together. Generally, the feed mixture must have different affinities from solvent because to avoid the increasing of a relative of the volatility of key components. If they have high relative volatility, the process has become high feasible economic and extend the separation. So, the solvent should not from azeotrope. Furthermore, the molar ratio of solvent to feed is very important to achieve successfully separation. For the last step, the solvent must have to recover and recycle to completely extractive distillation.[19]

It is important to choose a proper solvent for extractive distillation. The relative volatility, quantity, and availability of solvent are significant for suitable separation. Moreover, the cost and wide enough margin of solvent are considered. The usable solvent must have easily to separate from other products and it must not react with other components or corrosive the equipment in the system. The example of solvents in the extractive distillation column is shown in Table 4 and the example of a process flow diagram for is shown in Figure 11 which A and B components are separated mixtures and E is solvent.[20]

Table 4 Reviews of extractive distillation column for some industrial

Key components in the feed mixture	Solvents
Acetone-methanol	Aniline, ethylene glycol, water
Benzene-cyclohexane	Aniline
Butanes-butenes	Acetone
Butenes-isoprene	Dimethylformamide
Cumene-phenol	Phosphates
Cyclohexane-heptanes	Aniline, phenol
Cyclohexanone-phenol	Adipic acid diester
Ethanol-water	Glycerine, ethylene glycol
Hydrochloric acid- water	Sulfuric acid
Isobutane-butene-1	Furfural
Isoprene-pentanes	Acetonitrile, furfural
Isoprene-pentenes	Acetone
Methanol-methylene bromide	Ethylene bromide
Nitric acid-water	Sulfuric acid
n-Nutane-butene-2s	Furfural
Propane-propylene	Acrylonitrile
Pyridine-water	Biphenol
Tetrahydrofuran-water	Dimethylformamide, propylene glycol
Toluene-heptanes	Aniline-phenol

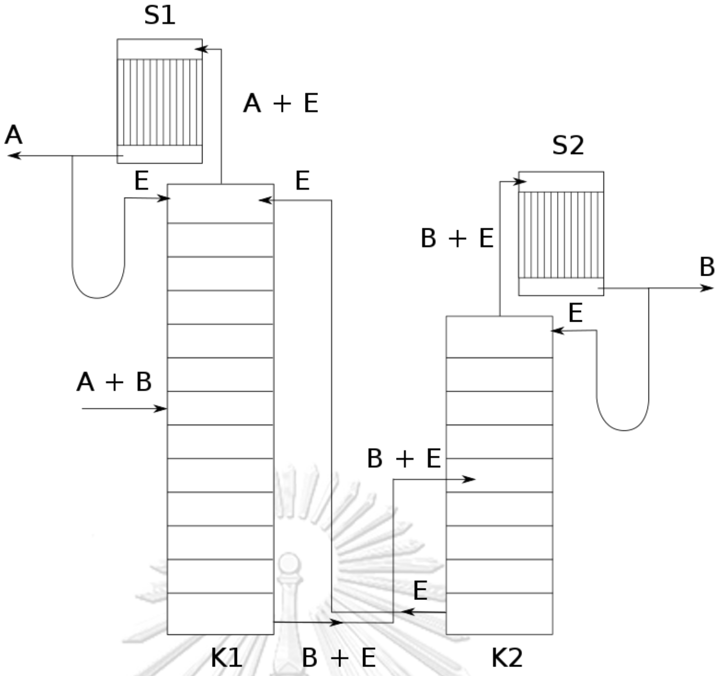

Figure 11 Example of PFD in the extractive distillation column for distillation

CHAPTER 3

LITERATURE REVIEWS

3.1 Catalyst development and reaction conditions for butadiene reaction

It is well known that Ethanol-based butadiene production is divided into 2 processes, including one-step ethanol-based butadiene production and two-step ethanol based butadiene production. In order to simulate and redesign a new model-ethanol based butadiene plant, investigating the nature of catalyst is necessary. The catalyst development and reaction condition of ethanol-based butadiene is normally studied in the kind of catalyst and reaction temperature. The sequence of reactions converting ethanol to butadiene is active under high temperature which involves the nature of hydrogenation and dehydration reaction. Therefore, the catalyst properties should be active for dehydrogenation, aldol condensation, and MPV reactions, meanwhile it has to avoid byproduct-reactions such as ethylene and butene formation. Accordingly, there is many literature reviews about the ethanol-to-butadiene conversion were investigated. The one-step and two-step processes will be summarized in the below section. Furthermore, classification of catalyst for ethanol-based butadiene process is based on the support type.

3.1.1 Catalysts in the one-step ethanol based butadiene process

In the past. The one-step process was improved in the Russian country. It was developed for the pilot plant but it was not put into commercial operation. 500 catalyst combination was The 500 combinations catalysts in the one-step process were analyzed in the preparatory screening program. They have defined the areas in a periodic system for production butadiene from ethyl alcohol.

Lebedev et al. were firstly investigated the composition requirement of the catalyst. They have been concluded that the good catalyst properties can remove water and hydrogen concurrently, which dehydration and dehydrogenation were the first priority to consider for the composition of catalyst. Lebedev et al. are utilized a mixture of zinc oxide and alumina to achieve butadiene yield of 18 wt%.[1] [21] In 1941, the Lebedev industrial catalyst was synthesized in the rubber production factory. The catalyst became available at the Yefremov city in the Russian army. There were had two types of compositions such as $ZnO\text{-}Al_2O_3$ and $MgO\text{-}SiO_2$ which defined in Lebedev's catalyst.

Other compositions such as uranium oxide, mixtures of aluminum hydrosilicate, and floridin with zinc or manganese oxide were purposed.[1] In order to obtain high butadiene's yield. It is supposed that the dehydrogenation and dehydration site of catalyst should be controlled for an optimal ratio of 1:3 for dehydrogenation and dehydration site for ethanol-based butadiene reaction. However, the ratio of the mixture of catalyst is optimized that depend on the catalyst nature. The ratio of catalyst component is induced to high yield butadiene, for example, the elemental composition of the favored catalyst achieve from 42 wt% butadiene selectivity with the catalyst which composes of 44.6 wt% of magnesia and 10 wt% of silica.[1] [22]

Although. The data of the one-step process from the literature were insufficient because they were protected by patents. Furthermore. The reactions of the one-step process were had complexity. So. Many researchers preferred higher yield and high purity from the two-step process. The alumina-based as catalysts with loading other metal oxide was observed by Bhattacharyya et al. It can be seen that the addition of ternary metal oxide-based alumina catalysts provides higher butadiene yield than the binary metal oxides. the binary metal oxides included mixtures of alumina with magnesia, zirconia, chromium oxide, calcium oxide, manganese oxide, silica, iron oxide, zinc oxide and nickel oxide as shown in Figure 12. The studies of binary catalyst exhibit the optimum component with a weight ratio of 40 : 60 of for $MgO–Al_2O_3$ and $SiO_2–Al_2O_3$ catalyst. It is seen that the catalysts containing 80% of alumina showed an increase of catalytic performance and the highest yield for butadiene is obtained by catalytic results with ZnO-alumina catalyst under 425 °C , which is approximately 56% with the butadiene selectivity of 59%. In addition, The result conforms to volume productivity of 421 g BD L h^{-1} and the catalyst exhibit a high activity by 500 g BD kg cat h^{-1}. Iron oxide on alumina was chosen as the second best catalyst. The materials which nickel oxide and manganese oxide have loaded that use for the active site in the dehydrogenation reaction, without considering of the synthesis of catalyst method.

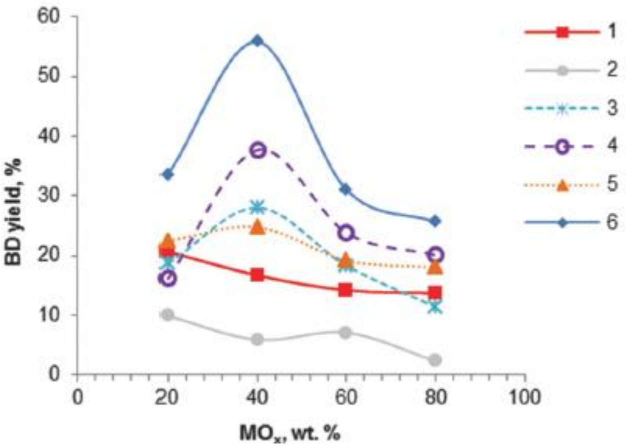

Figure 12 Effect of MOx–Al_2O_3 catalyst composition on butadiene yield: (1) MgO–Al_2O_3 (400 °C); (2) SiO_2–Al_2O_3 (425 °C); (3) ZrO_2–Al_2O_3 (425 °C); (4) Fe_2O_3–Al_2O_3 (425 °C); (5) Cr_2O_3–Al_2O_3 (425 °C); (6) ZnO–Al_2O_3 (425 °C), WHSV B 1.5 h^{-1}.

Binary oxide catalyst was generally synthesized by co-precipitation of the metal oxide salts in ammonia solution. Using of co-precipitation exhibit higher activity related to individual oxides properties because of synergetic effects between the two active sites of the catalyst. However, there are no physic-chemical properties of the different catalytic. Furthermore, it is clear that metal oxide precursors are preferred over chlorides and sulfates that the anion could be absolutely vanished by rinsing and calcination. Furthermore, Using of sodium or potassium hydroxides substitute aqueous ammonia as a precipitating agent resulted in catalyst contamination. Optimal contact times are investigated, result maximum BD yields were reported. The highest butadiene yield is a result of A WHSV of 1.5 h^{-1} of all catalyst except for the SiO_2–Al_2O_3 catalyst that exhibits the highest BD yields by a WHSV of 1 h^{-1}.

Bhattacharyya et al. are demonstrated an optimal of WHSV by one-step ethanol-based butadiene reaction via ZnO-Al_2O_3 as a catalyst. ZnO–Al_2O_3 exhibit the decrease of butadiene yield from 56 to 34% when decreasing a WHSV from 1.5 to 1 h^{-1}, and increase to 12% while WHSV was increased from 1.5 h^{-1} to 2 h^{-1}. It is concluded that high butadiene selectivity and yields of high feed rate provide essential resulting in high space-time yield was obtained the highest BD yield was obtained at temperature 425 °C. Temperature decreasing from 425 to 375 °C showed a decrease of BD yield from 56 to 14%, showing a sign of reaction temperature, Moreover, it is seen that fluidized bed reactor plays a significant role to increase BD yield to 73% while a fixed bed reactor is provided 56 % BD yield.[23] [24, 25]

$MgO-Al_2O_3$ catalysts were developed by Natta and Rigamonti. There gave 10% of yield and 11% of selectivity. From this experiment. Magnesia has high condensation activity when compared with zinc oxide. The paper referred to the ratio (3:2) of magnesium oxide-silica was the best ratio catalyst for one-step process reaction. They concluded that no information of conversion in the one-step process for butadiene production in publication. Several of chemicals from ethanol. Butadiene was important which synthesized from heterogeneous catalysts such as $MgO-SiO_2-Cr_2O_3$, $MgO-SiO_2-Ta_2O_5$, $Al_2O_3-ZnO_2$, $MgO-SiO_2$, and Sepiolite-MnO_2 (79mol %). Natta and Rigamonti studied the selectivity of the catalyst. They found that the selectivity of butadiene was not sufficient. So.$MgO-SiO_2$(1:1)-Na_2O(0.1%) was improved catalyst with low reaction temperature. The results referred that high-performance catalyst was related to the particular preparation method and adding composition of MgO-SiO2. Because. It was a small basic oxide which increased the activity of catalyst and selectivity in reaction.

Ohnishi et al. investigated the highest BD yields using magnesia-silica as a catalyst under temperature at 350 °C. the resulting exhibit the butadiene yield and selectivity is about 42 and 84%, respectively. The catalysts were synthesized using wet-kneading of precipitated magnesium salt and silica gel. It can be obverted that the use of the reagents is one of the most important parameters. The use of magnesium nitrate and nitric acid substitute magnesium chloride and hydrochloric acid result in the change of butadiene reaction pathway. This was involved with the removal of chloride ions washing of the catalyst that is confirmed with Bhattacharyya et al's results. The highest activity and BD selectivity were achieved by a using Mg to Si molar ratio of 1 as a catalyst.

Ohnishi et al. used an impregnation method to obtain $MgO–SiO_2$ catalysts by impregnation method and calcine catalysts at 500 °C. At reaction temperature of 350 °C and with a WHSV of 0.2 h^{-1}, $Na_2O/MgO–SiO_2$ and $K_2O/MgO–$ obtained SiO_2 yielded 87 and 70% BD, respectively.[26]

Then, Trimetallic Cu(II)-Zn(II)-Zr(IV) system was taken to study. This catalyst was high selectivity of butadiene which gave 61% of yield and nearly complete conversion. The system was produced ethene(>10%) and acid product after the reaction. Instead of trimetallic, there was used Hf(II) to replace Zr catalyst.it reduced ethane production and increased the selectivity of butadiene.

De Vos et al. used a novel mixture of silica-supported hafnium oxide and zinc silicate catalyst that observed 68% butadiene with a productivity of 0.26 $g_{BD}g^{-1}cat \cdot h^{-1}$ at 633 K with a WHSV of 0.64 h^{-1} for a TOS of 10 h. the interaction between Hf (IV) and Zn(II) can be described by, the zinc silicate hemimorphite (HM) was both used for support materials. Hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) is a zinc silicate that catalyzes the conversion of methanol to propyne, and the conversion of ethanol to Butadiene. hemimorphite can enhance the dehydrogenation to acetaldehyde and the butadiene selectivity. Hf(IV)-containing silica support material decreased the accumulation of acetaldehyde in the product stream and resulted in an increased butadiene selectivity. However, it also increased the ethene formation and the ethanol dehydration could not be restrained. HM, Hf(IV) deposited on SiO_2, in suspension exhibit largely suppresses the ethene formation (≈ 5% selectivity, resulting in a butadiene selectivity of 70%.[27]

3.1.2 Catalyst in the two-step process

The two-step ethanol based Butadiene involves the use of a mixture of ethanol and acetaldehyde for the dehydrogenation. The production composes of a many step reaction of a mixture of ethanol and acetaldehyde. However. The studies about two-step ethanol based butadiene process are not widespread. Most of the available the two-step ethanol based butadiene production are mention that development of Ostromyslensky et.al 's study which mixture ethanol and acetaldehyde were performed with a various catalysts and obverse reaction mechanism and evaluate the effect of the catalyst ratio composition.

Carbide and Carbon Chemicals Corporation have developed the Ostromislensky process organized by Koppers Company. This process grants 63% of ultimate yield from ethyl alcohol in commercial operation. There are three commercial plants for synthetic butadiene for synthetic rubber which located at Institute, W. Va., Kobuta, Pa., and Louisville, Ky.

Corson et al. are note that two-step ethanol-based Butadiene production is impressive. This product depends on the improvement of flexibility for operating conditions for each reaction and on the decreased complication catalyst choice Corson et al. reduced reaction temperature from 400–425 °C to 350 °C. and obtained about 98% butadiene yield for the two-step process while One-step process provides only 80 % butadiene yield.[21]

The two-step ethanol based butadiene reaction was studied using tantalum, zirconium or niobium oxide based on silica as the catalyst and use a mixture of 69%w/w ethanol, 24%w/w acetaldehyde and 7%w/w water as a feedstock. The high-performance catalyst was achieved by a 2 wt% tantalum oxide loading on silica. The studies were investigated reaction temperature at 325–350 °C and a space velocity of 0.4–0.6 h^{-1}The results exhibited 35% butadiene yield and a selectivity of 67%. Higher Ta_2O_5 loading in the catalyst results in a further increase of the BD yield but at the expensive of BD selectivity. However, the addition of less than 1 wt% is not favored for Ta_2O_5-SiO_2 catalyst. The catalytic activity of zirconium and niobium oxides based silica catalyst was lower than the Ta_2O_5–SiO_2 material. 1.6 wt% ZrO_2 on SiO_2 catalyst showed a butadiene selectivity of 59% at the same reaction conditions.

Corson et al. have exhibited that hafnia-support silica gel is selective material in the two-step ethanol-based butadiene process. The butadiene yield of 30–40% and a butadiene selectivity of 50–60% are obtained by a mixture of ethanol–acetaldehyde mixture as a feedstock.[1, 21, 22]

Toussaint et al.[22] studied the effect of the reaction temperature, the feed ratio of ethanol to Acetaldehyde and the space velocity of the catalyst activity. The study uses 2 %wt. Ta_2O_5 support silica as a catalyst. High BD selectivity was obtained under the reaction temperature of 325 °C with a mixture with ethanol to Acetaldehyde ratio of 3 as a feedstock. However, The outstanding results were obverted at the reaction temperature of 350°C with a mixture ratio of ethanol to Acetaldehyde of 2–2.5 as a feedstock an increase of butadiene yield was achieved under temperature 350°C with ethanol to acetaldehyde feed molar ratio of 2. Consider at loss in activity was existed after 160 hours on stream, when compared to a reaction at 325°C. Corson et al.[21] is reported that for a 2%Ta_2O_5–SiO_2 have been used as the catalyst to optimize conditions for butadiene production were obtained ay temperature 350°C with an LHSV of 0.6 h^{-1} and a mixture of ethanol to Acetaldehyde molar ratio of 2.75 as a feedstock. The high deposited coke from the reaction was found when the ethanol to Acetaldehyde molar ratio was decreased below 2.75.

2 wt% Ta_2O_5 on silica was applied as the preferred catalyst and a mixture of ethanol and acetaldehyde as a feedstock. High ethanol to acetaldehyde molar ratios is required to obtain high BD selectivity and avoiding coke deposition. The water in the feed mixture plays a significant role but it is not involved with the catalysis. Catalyst stability and high BD yield were investigated and an outstanding result is achieved at reaction temperatures 325-350°C and the contact times conform to an LHSV 0.3-1 h^{-1}. [1, 21, 22].

Furthermore. There were important parameters to increase the activity of the catalyst in the two-step processes such as ethanol to acetaldehyde ratio, catalyst composition, reaction temperature, contact time and feed molar ratio. The reaction temperature in the old commercial was between 325-350 °C. the feed was blended of 7 wt.% water and 93 wt.% ethanol to acetaldehyde which included 2.7 ethanol to acetaldehyde ratio.[1]

In conclusion, the 2 wt.% Ta_2O_5 on silica catalyst was performance catalyst which could convert ethanol and acetaldehyde to butadiene. It was shown high selectivity of butadiene and avoidance coke formation. The water in feed was beneficial in the reaction but it was not further determined the role in the catalytic reaction. Then. High stability of the catalyst and high yield butadiene were obtained in 325-350 °C which preferred LSHV from 0.3 to 1 hr. Finally. Mesoporous silica was beneficial for increasing yield and selectivity of butadiene because it was supported diffusion. From the literature. The 25% of yield and 80% of selectivity butadiene were reported.

3.1.3 Summary table of catalysts in one step and two-step process of butadiene production

Furthermore, Ta, Ag, Ni, Mn, Cu, Mo, Fe, Co, and Zr oxides were also used as support materials for MgO–SiO_2 catalysts in the ethanol-based BD production. Table 5 summarized the catalyst material for ethanol-based butadiene production.[1, 13, 23-25]. It is clear that all of the catalytic systems for ethanol base butadiene conversion, the outstanding two system catalyst are Al_2O_3/ZnO and MgO/SiO_2. This two-system material has exhibit high effective than bare forms or doped with other metals. The magnesia and zinc oxide was preferred as basic sites for catalytic dehydrogenation, whereas silica and alumina play a role of acidic sites for the dehydration reaction. It could also be seen that the yield of the main product depends on the ratio of acid-base sites catalyst mass and the nature of dopants

The catalytic system materials, reaction temperatures and yields of butadiene are assigned for selected key contributions. The optimal reaction temperature is observed in the reported papers that the range is about 350–425 °C. It should be noted that the reaction temperatures were controlled for the two-step of the Ostromislenskiy process which is generally lower ranging from 300 to 400 °C. Most studies of the one- and two-step processes are operated under atmospheric pressure. Corson and co-workers worked under atmospheric pressure for most of their catalytic tests.

Table 5 Summary of Catalysts for one-step and two-step process

Authors	Catalyst system	Process type	Process parameter		
			T (°C)	Conversion (%)	Yield BD (%)
Lebedev et al.(1930)	Al_2O_3/ZnO	One-step	400-450	-	18
Natta et al.(1947)	MgO/SiO_2/Cr_2O_5 (3:2:0.11)	One-step	415	-	41.9

Corson et al.(1950)	$MgO/SiO_2/Cr_2O_5$ (59:39:2)	One-step	425	-	39
Bhattacharyya et.al.(1962)	Al_2O_3/ZnO (60:40)	One-step	425	100	72.8
Bhattacharyya et.al.(1962)	$40\%ZnO_2$-$60\%Al_2O_3$	One-step	425	94	56
Bhattacharyya et.al.(1962)	$20\%MgO_2$-$80\%Al_2O_3$	One-step	425	-	48
Bhattacharyya et.al.(1962)	$40\%CrO_2$-$60\%Al_2O_3$	One-step	425	-	47
Bhattacharyya et.al.(1962)	$40\%ZrO_2$-$60\%Fe_2O_3$	One-step	425	-	40
Kitayama et.al.(1981)	Mn/sepiolites	One-step	300	-	33.4
Ohnishi et al.(1985)	MgO-SiO_2 (1:1)	One-step	350	50	42
Ohnishi et al.(1985)	MgO-SiO_2 -K_2O (1:1)(0.1%wt)	One-step	350	80	70
Ohnishi et al.(1985)	MgO-SiO_2 -Na_2O (1:1)(0.1%wt)	One-step	350	100	87
Kvisle et al.(1988)	MgO/SiO_2 (0.83:1)	One-step	350	53	16
Kitayama et.al.(1996)	$NiO/MgO/SiO_2$ (10:31:39)	One-step	280	-	53
Jones et al.(2011)	Zr(1.5%),Zn(0.5%)/SiO_2	One-step	375	46	11.5
Jones et al.(2011)	Cu(1%).Zr(1%),Zn(1%)/ SiO_2	One-step	375	44.6	30.1
Makshina et al.(2012)	CuO-MgO/SiO_2	One-step	350	100	58.2

Makshina et al.(2012)	ZnO-MgO/SiO_2	One-step	350	100	52.4
Makshina et al.(2012)	Ag-MgO/SiO_2	One-step	350	100	56.3
Ezinkwo et al.(2014)	Al_2O_3/ZnO+initiator	One-step	430-450	42	22.4
Ekaterina et al.(2014)	Wet-kneaded MgO-SiO_2	One-step	350	50	42
Ekaterina et al.(2014)	Commercial MgO-SiO_2	One-step	440	70	48
Ekaterina et al.(2014)	2% Cr_2O_3-59% MgO-39%SiO_2	One-step	400	68	38
Ekaterina et al.(2014)	3% Cr_2O_3-56% MgO-42%SiO_2	One-step	400	86	44
Ekaterina et al.(2014)	9.5%ZrO2-90.5 SiO_2	One-step	425	-	23
Sushkevish V.I. et al.(2014)	Ag / ZrO2 / SiO_2	One-step	325	34	24
Angelici C. et al.(2014)	1%CuO/MgO-SiO_2	One-step	425	74	74
Baylon R.A.L. et al.(2014)	2000 ppm Na/$Zn_1Zr_{10}O_{\pi}$	One-step	350	54.4	15.2
Janssens W. et al. (2015)	1%Ag/Mg-SiO_2	One-step	480	84	42
Larina O.V. et al. (2015)	2%ZnO/MgO-SiO_2	One-step	375	84.6	45
Han Z. et al.(2015)	2%ZrO_2/SiO_2	Two-step	320	45.4	31.6

De baerdemeaker T. et al.(2015)	$Hf_{2.5}ZM_{1.6}/SiO_2$	One-step	360	99.2	70.2
La-salvia N. et al.(2015)	1.4%Cr-16%Ba/Al-MCM-41	One-step	450	80	22.4
Chung S.H. et al.(2016)	$MgO-SiO_2$ (WK)	One-step	425	67	35
Larina O.V. et al. (2016)	$MgO-SiO_2$ (MC)	One-step	400	41.2	23.6
Larina O.V. et al. (2016)	$2\%ZrO-7\%La_2O_3/SiO_2-2\%ZrO_2$	One-step	375	80	60
Shylesh S. et al.(2016)	$3\%Au/Mg-SiO_2$	One-step	300	45	27
Da Ros S. et al.(2016)	$1.5\%Zr-1\%Zn/MgO-SiO_2$	One-step	375	40	30.4
Da Ros S. et al.(2016)	$1.2\%K/ZrZn/MgO-SiO_2$	One-step	375	26	13.1
Kyriienko P.I. et al.(2016)	1.2%Zn-Talc	One-step	400	41.6	21.5
Sushkevish V.L. et al.(2016)	3.5%Ag/Zr/BEA	One-step	320	-	-
Cheong J.L. et al.(2016)	4.7%Cu/MCF+2.7%Zr/MCF	Two-step	400	92	64.4
Kyriienko P.I. et al.(2016)	3%Ta/BEA	Two-step	350	58.9	43.1
Kyriienko P.I. et al.(2016)	0.7%Nb/BEA	Two-step	350	42.8	23.6

3.2 Process plant and simulation for butadiene production

The process simulation of butadiene production form ethanol was referred in two sections. Section one was converted ethanol and acetaldehyde to butadiene in vapor phase reaction and section two was separated butadiene from other byproducts from acetaldehyde. The heat was required to both sections that it could convert ethanol and acetaldehyde to butadiene in an economy in ease section.[28] In this production, the reactant converted to gaseous product and butadiene was separated from unreacted ethanol, acetaldehyde, and by-products. Distillation column was used to the separation for removing by-product. So. The reflux in distillation column was important to recover unreacted ethanol and acetaldehyde to reaction section.

Jonathan B. et al.[29] designed a plant two-step ethanol based butadiene process, which achieves 95% ethanol yield stream (by mass) and a 98%w/w butadiene stream. The production goal for this plant was 200,000 tons of butadiene. The process was described in figure 14, firstly feed ethanol to a catalytic dehydrogenation reactor for conversion of ethanol to acetaldehyde and hydrogen. A kinetic model was applied to estimate the reaction rates and optimized temperature and pressure in the reactor. The acetaldehyde is utilized as the intermediate which reacted with ethanol in a catalytic reactor. A hydrogen stream is also generated which is purified for sale.

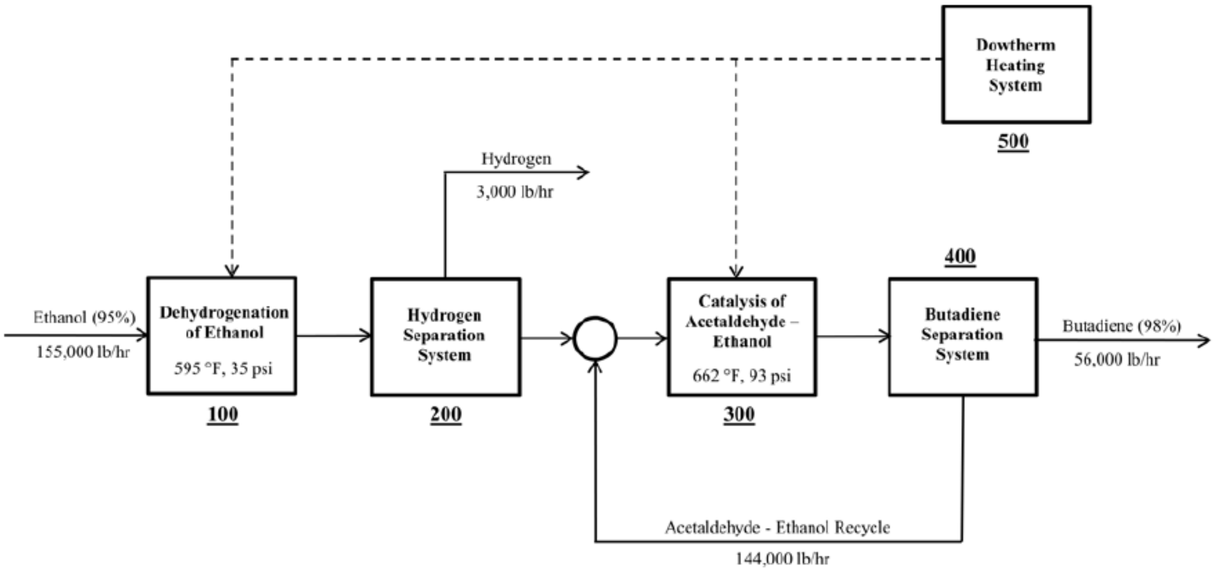

Figure 13 Block diagram of the two-step process in Jonathan B. et al.

The main point of this report of the Ostromislensky process exhibit large-scale butadiene production industrial plant, which results in a higher the potential for butadiene, and increases butadiene price. This research was completely successful by the Mellon Institute for the Carbide and Carbon Chemicals Corporation.[21]

The first section contains ethanol of 95 %v/v feed stream under ambient pressure and a room temperature of 80 °F. The amount of feed required 155,000 lb/hr, depending on the butadiene conversion and selectivity of the hydrogenation and dehydration reactions. Furthermore, the Carbide and Carbon Chemicals Corporation decide the feed molar ratio of ethanol to acetaldehyde of 2.75:1 for the optimal feed ratio for the second reactor.

The liquid feed stream is firstly pressurized to 50 psi (P-101) and the pressure will decrease in many process equipment resulting from the decrease of pressure at the optimum pressure of 35 psi before reaching the inlet of the first reactor. The liquid stream is maintained heat by a heat exchanger (E-101) where heat the mixture to 226 °F for the effluent of the first reactor. Then, the vapor/liquid stream is fed into a pressurized vessel (F-101) in order to split the liquid and vapor phase stream (F-101). The two streams were fed into a single heat exchanger (E-102) to heat inlet temperature to 595 °F, resulting in changing the mixture to a form of the vapor phase.

The single heat exchanger (E-102) is divided into two phases of stream, which is the inlet vapor stream and the inlet liquid stream. The reason which separates the inlet streams is guaranteed that two phases obtain equal contact. A heterogeneous copper-chromite binary system catalyst is used as a catalyst for the hydrogenation and dehydration reactions for acetaldehyde and hydrogen production.

The mixture acetaldehyde and ethanol which is fed to the second reactor. Firstly, the mixture is combined with the recycle stream from the distillation tray. The recycle stream play a feeding unreacted ethanol and acetaldehyde and ethyl acetate, which readily forms ethanol by hydrolysis reaction via a tantalasilica catalyst.

The mixture is controlled feed molar ratio of 2.75:1, and the condition is optimized at 150 °F and 108 psi. The recycle stream is assumed the pressure of 108 psi and decreases to inlet pressure of 93 psi after undergoing in subsequent process equipment. Then, the liquid stream is sent to a heat exchanger (E-301) to transform into the vapor phase. Likely the first reaction section, the heat exchanger (E-301) is used as a heating process for the second reactor fluid. The vapor stream is fed to a second heat exchanger (E-302), which uses the Downterm system to heat the stream to 662 °F for the optimal inlet temperature.

This butadiene reaction has a selectivity of 55%. The main byproducts include butanol, butene, ethylene, acetic acid, ethyl acetate, diethyl ether, water, and hexadiene. In order to simulate the reactor in ASPEN, the side reactions data will be assumed by specific selectivities. On the other hand, kinetic reaction data for the second reaction is not utilized for simulation, which conversion and operating conditions were select from the success studies by the Carbide and Carbon Chemicals Corporation, who optimized an operating temperature of 662 °F and conversion of 44.5%.[21]

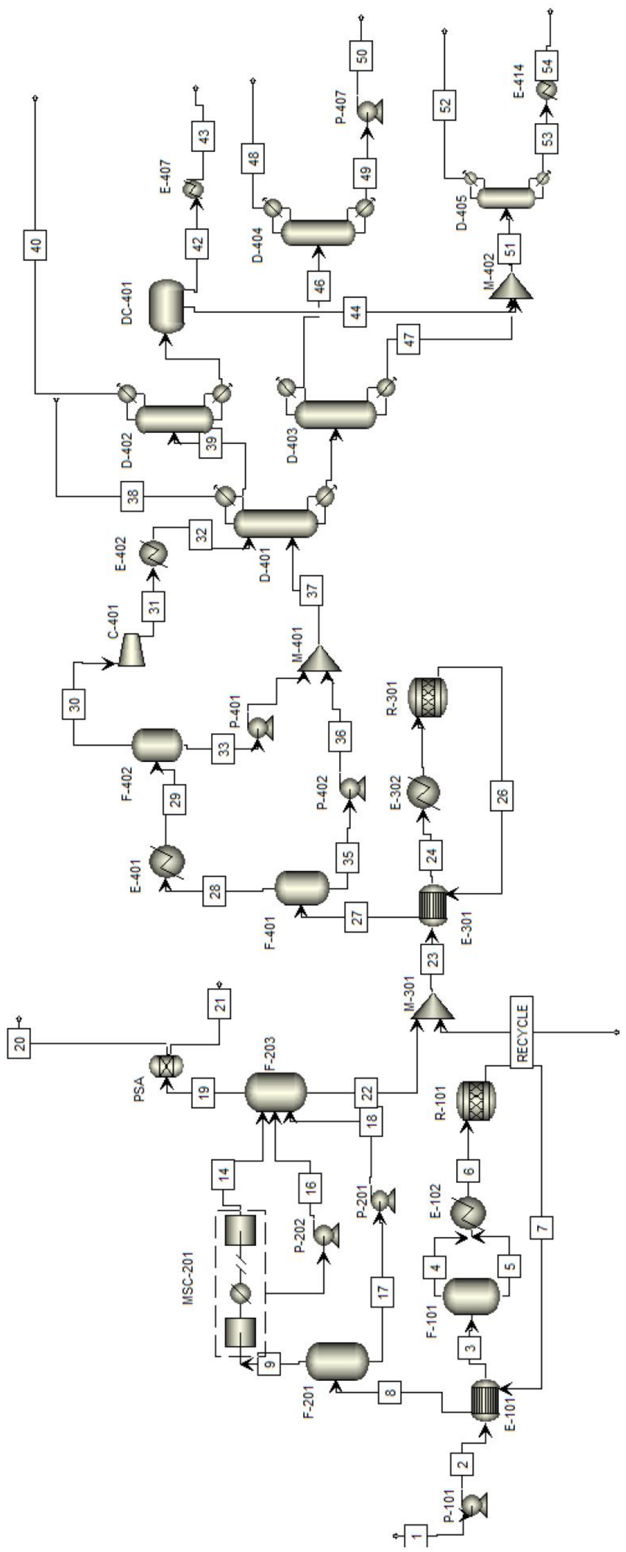

Figure 14 Simulation diagram in the two-step process in Jonathan B. et al.

3.3 Extractive distillation column for butadiene separation process

The simple separation technique of butadiene was extractive distillation. Because. It was easy and value efficient. There were 3 kinds of solvent in extractive distillation, for example, acetonitrile (ACN) method, dimethylformamide (DMF) method, and N-methyl-pyrrolidone (NMP) method.

The drawbacks of acetonitrile solvent were complexity to recycle the solvent and it was poisonous to the environment. So. Acetonitrile solvent was not thought out. Dimethylformamide was more advantage than acetonitrile. Because. There was low toxic and miscible in C4 at any proportion and there was not became azeotrope with other components of C4. Although. The dimethylformamide was not a good inhibitor to added to preventing polymerization. In addition. Some component of DMF might be hydrolyzed into formic acid and dimethylamine. For N-methyl-pyrrolidone solvent. There was provided good selectivity and solubility. Also. It was a good boiling point and low vapor pressure.

Xiaojian Y. et.al. studied butadiene production process from the extractive distillation column. It used Aspen plus software and used Dimethylformamide (DMF) because DMF is very low toxic and The thermodynamic method is NRTL-RK. The process divide into 4 sections which is shown in Figure 16. Section 1 is T1 and T3 were the extractive distillation column and T2 and T5 were stripping column.T6 and T7 columns are purifying column that it use purify product butadiene. Feed stream comprises butylene, butanes, butadiene, and impurity of C3 and C5. The solvent stream is consist of dimethylformamide (96%mass). The higher relative volatility, which it is compared to butadiene and dimethylformamide, is separated in the first extractive distillation section. After butadiene and dimethylformamide are separated in secondary extractive distillation column section and the components which have high boiling point differ from butadiene are removed in the third separation section. For the last section, it is a purification unit section for reuse solvent.

From the simulation, the best solvent ratios of T1 and T3 is 7.5 kg/kg and 2.0 kg/kg. The T2 and T5 columns are striping which the least reflux ratio are 0.14 kg/kg and 0.42 kg/kg. After separation. Butadiene product must go to purification section which it is T6 and T7 columns, the best ratios of T6 are 0.98 kg/kg and the bottom production ratio of T7 has the best ratio of 0.026 kg/kg. T8 is used to recycle DMF solvent. So, the range of product ratio is 0.94-0.962 kg/kg.[30]

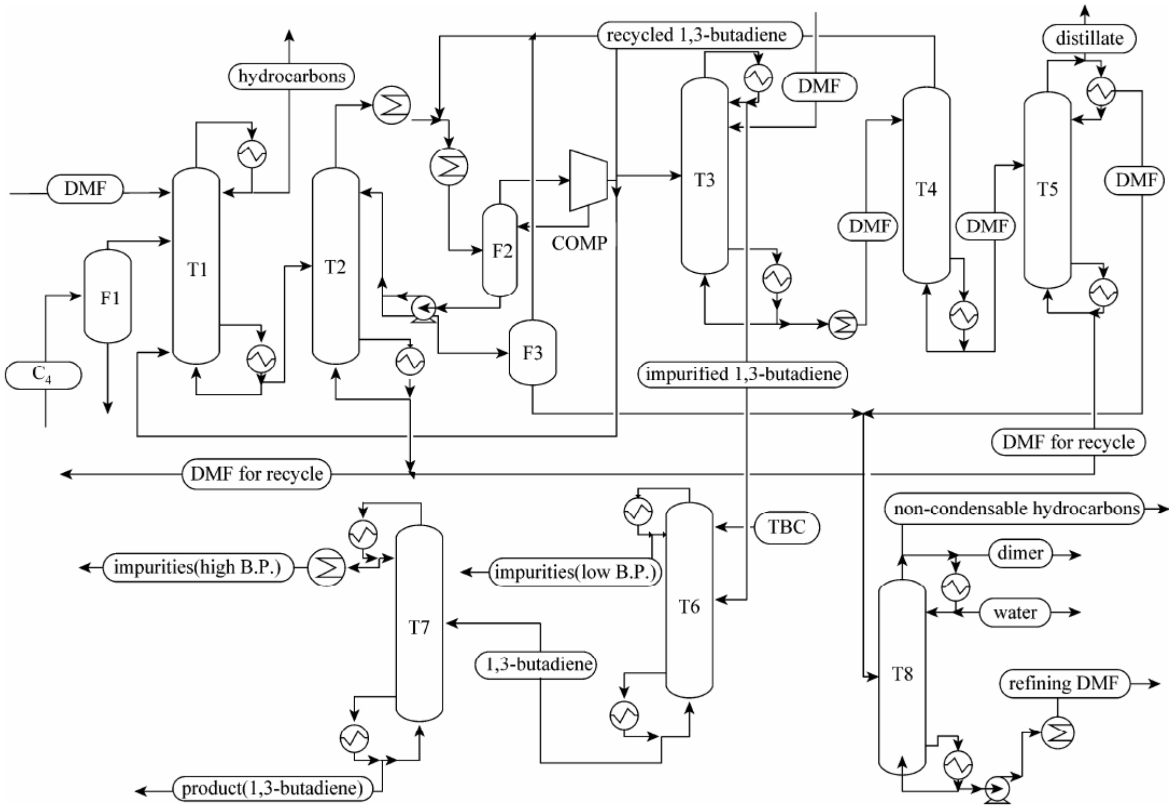

Figure 15 Butadiene production process which uses DMF solvent.

CHAPTER 4

METHODOLOGY

This chapter is divided into three parts: 1) consideration of catalysts for the one-step process to be studied, 2) process description and 3) determining the optimal separation sequence. Aspen plus software version 8.0 was selected for the simulation of the process. Energy and heat duty were the parameters used to determine the performance of each sequence.

4.1 Consideration of catalysts for the one-step process.

From the literature reviews, three different catalysts were chosen for the reaction. The scope of the project is to determine the best performance of catalyst which has high conversion and high yield of butadiene in the one-step process. So, in this project. Use the 3 best catalysts from table 5. In the third chapter that has been reviewed. The best performance catalysts can be written in Table 6. The parameters from this process such as temperature and pressure can be simulated by using the Ryield reactor in Aspen Plus program. This process has the reaction zone and the separation system which is designed for a suitable product using different catalysts.

Table 6 Summary of the best performance catalysts in one-step and two-step process

Authors	Catalyst system	Process type	Process parameter		
			T (°C)	Conversion (%)	Yield BD (%)
Bhattacharyya et.al.(1962)	Al_2O_3/ZnO (60:40)	One-step	425	100	72.8
Ohnishi et al.(1985)	$MgO\text{-}SiO_2\text{-}Na_2O$ (1:1)(0.1%)	One-step	350	100	87
De baerdemeaker T. et al.(2015)	$Hf_{2.5}ZM_{1.6}/SiO_2$	One-step	300	99.2	70.2

4.2 Design process description

This research, process modeling was used PSRK (Predictive Soave-Redlich-Kwong) thermodynamic model system because the reaction occurs in the gas phase So. There must use the equation of state to calculate the thermodynamics in the process. The thermodynamic data from NIST experiment and PSRK method were compared in APPENDIX A. For ethanol to butadiene reaction, the first dehydrogenation reaction has occurred from ethanol to acetaldehyde. The second reaction was dehydration reaction, acetaldehyde was transformed to get butadiene and the byproducts including light gas, such as ethylene, butane, propylene, and butanol, etc. which the reaction was shown in the chapter 2.Although. Extractive distillation columns were used NRTL-RK method. It appropriated method for separating butadiene and butene in the last step separation.

The process consists of two main parts: the reaction zone and separation zone, In the reaction zone, it was used Ryield reactor for simulating reaction. The feed mixture is ethanol and water which have a flow rate of 66,996 kg/hr and 3,526 kg /hr.

Before the reaction. Feed stream was taken to the heater for heating the mixture into the gas phase. The reaction condition in reactors has occurred at a pressure of 1 atm. According to Table 6, then the product and byproduct were cooled and increased the pressure by the compressor into 28 bars before entering to the separation process. The separation zone was designed in different each product and byproduct which there will choose the appropriate separation system. The design of the distillation section will be discussed in the next section.

After the raw material was finished the reaction in the reactor. There was cool down the stream to room temperature and take the pressure to stream. If the reaction occurred the hydrogen in the product stream. The hydrogen was separated in separation unit by using the pressure swing adsorption (PSA) as a hydrogen separator. Also, it was sold to add a profit in the process. Finally. Feed steam was prepared to the distillation for design and optimizing the best sequence.

For design distillation, DSTWU distillation tower was used in the Aspen plus program to calculate the feed stage, minimum reflux ratio and a number of stages based on the number of stages which had a minimum reflux ratio. Then, the RADFRAC distillation towers were calculated and separated the product stream. The sequence of the process stream and equipment description are shown in Figure 18–25 and Table 11-22.

4.3 Find the optimal sequence in distillation separation.

Products can be divided into 3 major groups, which are butadiene, light gas hydrocarbon (C2-C4), water and others. These products are sequent shown as a boiling point temperature in Table 4.2. The theory of Heuristic was considered in this process. Because it separates the product easily. Separation sequences are designed into two strategies which the example are shown in figure 16 and 17 respectively.

For $MgO\text{-}SiO_2\text{-}Na_2O$(1:1)(0.1%) and $Hf_{2.5}ZM_{1.6}/SiO_2$ catalysts, Sequence number 1 of the first column distillate the components with the lower boiling point temperature than butadiene by DSTWU column. Products can be light gas such as ethylene, ethane, propane, butane, etc. The second column of sequence number 1 was separated the components with a higher boiling point than butadiene such as acetaldehyde, water, diethyl ether, etc. For sequence number 2, higher boiling point components were distillate in column number 1 and the lower components were distillate in column number 2.

For Al_2O_3/ZnO (60:40) catalyst in sequence 1, the equipment will separate alternatively. As the first column separates the higher boiling point such as water by Decanter, and the second column distillate the lower boiling point than butadiene by DSTWU column which it is light gas such as ethylene, etc. For sequence number 2. The way of separation is changed. The light gas was separated by DSTWU in the first step, and water was separated by Decanter in the second step

Table 7 List of products and number of sequences in a distillation column

Catalysts	No. of sequence	Products
Bhattacharyya et.al.(1962)	2	1,3-butadiene, Water, Ethylene, Carbon dioxide, Methane, Hydrogen
Ohnishi et al. (1985)	2	1,3-butadiene, Ethane, Ethylene, Propane, Propylene, Acetaldehyde, Diethyl ether
De baerdemeaker T. et al. (2015)	2	1,3-butadiene, Propylene, Acetaldehyde, Ethylene, Butene, Diethyl ether, Butanol, Water, Butanal

As the above issue mentioned using catalysts to get a higher yield of distilled products. Different products from the Butadiene distillation process can be classified by the boiling point into three groups of A, B and C. Group A is the lighter boiling components than Butadiene. Group B is butadiene. Group C is the heavy components and adding the catalysts such as Al_2O_3/ZnO (60:40), $MgO\text{-}SiO_2\text{-}Na_2O$ (1:1)(0.1%) and $Hf_{2.5}ZM_{1.6}/SiO_2$as shown in table 8, 9 and 10. There are demonstrate some the example of sequences separation in Figure 16 and Figure 17

Table 8 List of products in Al_2O_3/ZnO (60:40) catalyst

Name	Boiling point (°C)	Group
Hydrogen	-252.9	A
Methane	-161	
Ethylene	-103	
Carbon dioxide	-78.3	
Butadiene	-4.4	B
Water	100	C

Table 9 List of products group in $MgO\text{-}SiO_2\text{-}Na_2O$ (1:1)(0.1%) catalyst

Name	Boiling point (°C)	Group
Ethylene	-103	A
Ethane	-89	
Propylene	-47.6	
Propane	-42	
Butadiene	-4.4	B
Acetaldehyde	20.2	C
Diethyl ether	34.6	

Table 10 List of products group in $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst

Name	Boiling point (°C)	Group
Ethylene	-103	A
Propene	-47.6	
Butene	-6.4	
Butadiene	-4.4	B
Acetaldehyde	20.2	C
Diethyl ether	34.6	
Butanal	74.8	
Water	100	
Butanol	117.7	

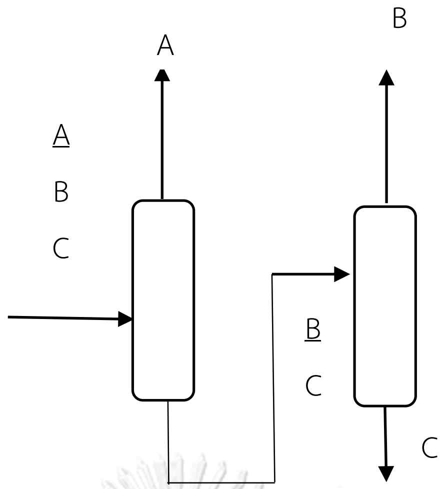

Figure 16 Example of sequence number 1

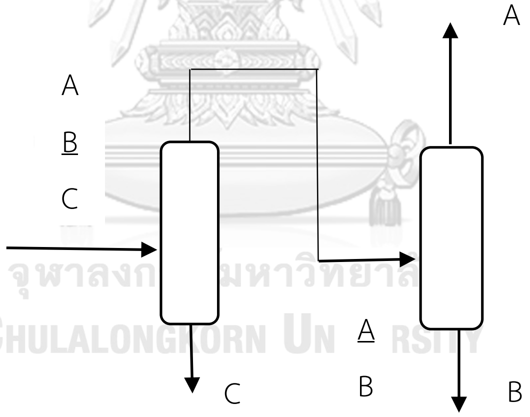

Figure 17 Example of sequence number 2

For three catalyst. There have six sequences of designing process flow diagram which the process stream and equipment description are showed in Figure 18–25 and Table 11-22

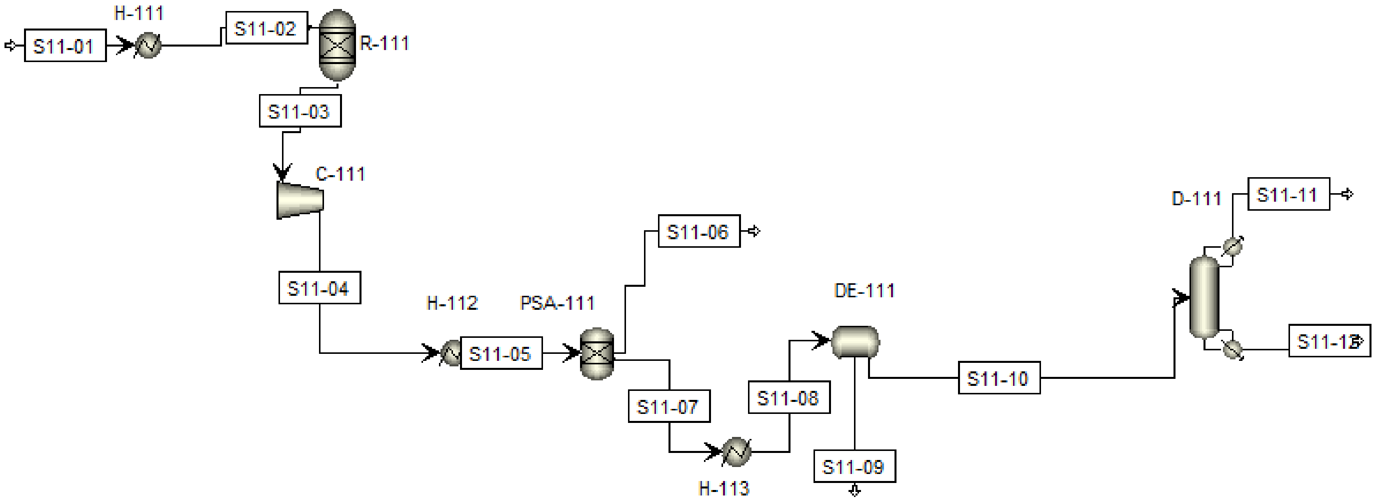

Figure 18 Process flow diagram of Al_2O_3/ZnO (60:40) catalyst in sequence 1

Table 11 Steam description process of Al_2O_3/ZnO (60:40) catalyst in sequence 1

Steam name	From	To	Stream descriptions
S11-01		H-111	Ethanol is fed into the heat exchanger
S11-02	H-111	R-111	Ethanol liquid is vaporized by the heat exchanger
S11-03	R-111	C-111	Converted ethanol vapor to archive butadiene and byproduct
S11-04	C-111	H-112	The product is pressurized before the feeding into the pressure swing adsorption process
S11-05	H-112	PSA-111	The product is cooled and fed to pressure swing adsorption.
S11-06	PSA-111	-	Hydrogen gas is separated by pressure swing absorption
S11-07	PSA-111	H-113	The products are fed into heat exchanger for cooling them
S11-08	H-113	DE-111	The products are fed into a decanter to liquid separation.
S11-09	DE-111		H_2O is separated from the product
S11-10	DE-111	D-111	The butadiene and light gases are fed into distillation.
S11-11	D-111	-	The light gas is separated by distillation
S11-12	S11-11	-	The butadiene is achieved by distillation

Table 12 Equipment descriptions process of Al_2O_3/ZnO (60:40) catalyst in sequence 1

Unit name	Model	Unit description
H-111	HEATER	Heat ethanol feedstock in the form of the vapor phase.
R-111	R-YIELD REACTOR	Convert ethanol gas to products including butadiene, light gases water and hydrogen.
C-111	COMPRESSOR	All products are pressurized for pressure swing adsorption process
H-112	COOLER	The temperature of products is decreased before to separate hydrogen gas by pressure swing adsorption
PSA-111	PRESSURE SWING ADSORPTION	The hydrogen gas is separated from the products
H-113	COOLER	The temperature of products is reduced for liquid separation process
DE-111	DECANTER	Separate water from the mixture of butadiene and light gases
D-111	DISTILLATION	The light gases and butadiene are separated.

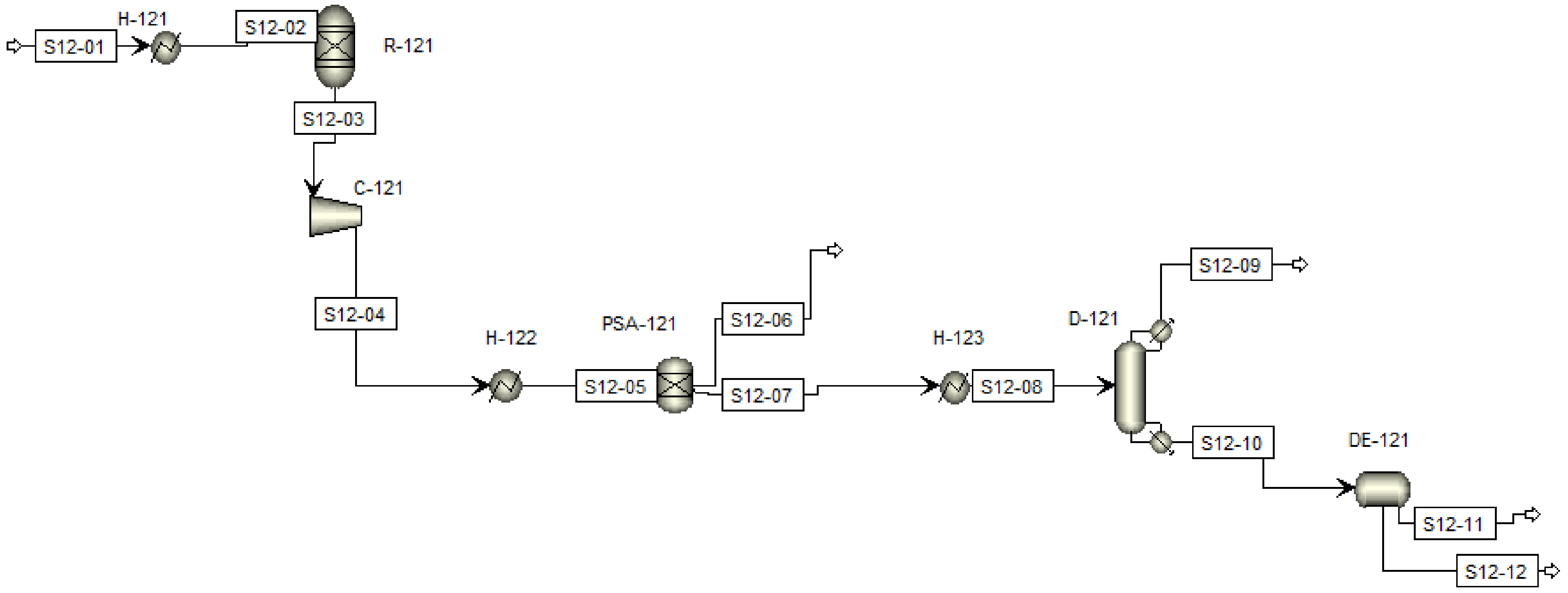

Figure 19 Process flow diagram of Al_2O_3/ZnO (60:40) catalyst in sequence 2

Table 13 Steam description process of Al_2O_3/ZnO (60:40) catalyst in sequence 2

Steam name	from	To	Stream description
S12-01		H-121	Ethanol is fed into the heat exchanger.
S12-02	H-121	R-121	Ethanol liquid is vaporized by the heat exchanger.
S12-03	R-121	C-121	Ethanol vapor is converted to archive butadiene and byproduct.
S12-04	C-121	H-122	The all products pressurized before the feeding into swing absorption process.
S12-05	H-112	PSA-121	The products are cooled and fed to pressure swing absorption.
S12-06	PSA-121	-	The hydrogen is separated from the products.
S12-07	PSA-121	H-123	The products are feed into the heat exchanger to cooling them before feeding into the distillation process.
S12-08	H-123	D-121	The products are cooled and fed into the distillation process
S12-09	D-121	-	The light gases are separated from butadiene and water by distillation
S12-10	D-121	DE-121	The light gas and water are fed into a decanter for the liquid separation
S12-11	DE-121	-	Butadiene is separated by decanter
S12-12	DE-121	-	Water is separated from butadiene

Table 14 Equipment descriptions process of Al_2O_3/ZnO (60:40) catalyst in sequence 2

Unit name	Model	Unit description
H-121	HEATER	The ethanol feedstock is heated at the optimum temperature for the reaction.
R-121	R-YIELD REACTOR	Ethanol is converted to butadiene, light gases water and hydrogen.
C-121	COMPRESSOR	All products are pressurized for pressure swing adsorption operation.
H-112	COOLER	The product temperature is reduced for pressure adsorption operation
PSA-121	PRESSURE SWING ADSORPTION	Pressure swing adsorption play as a hydrogen separation from products
H-123	COOLER	The temperature of the product is reduced for the distillation process operation.
D-121	DISTILLATION	The distillation column is a light gases separation form butadiene
DE-121	DECANTER	The decanter play as a water separation from butadiene

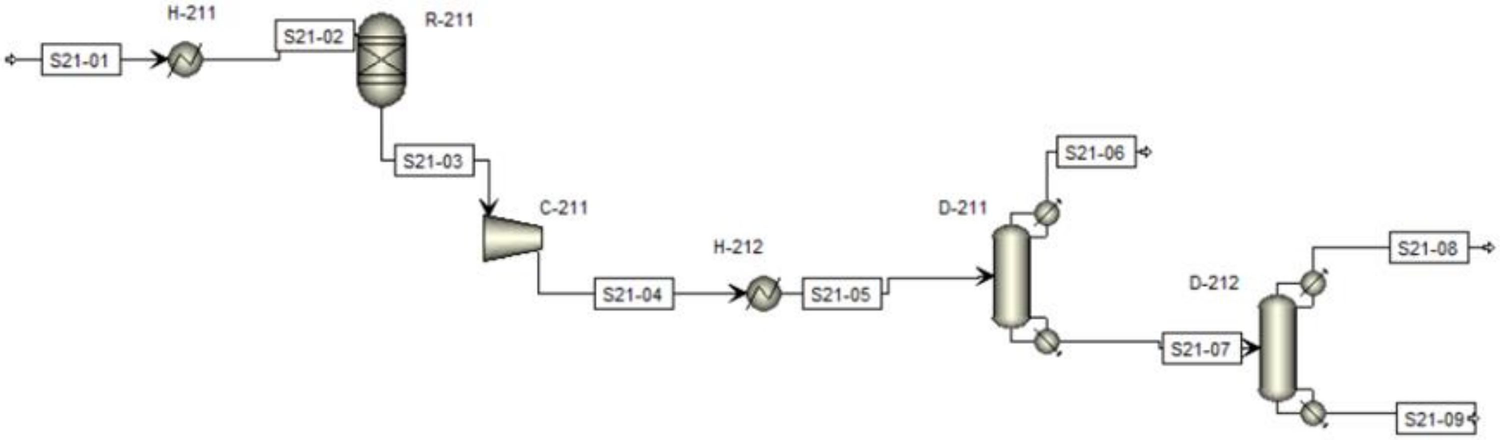

Figure 20 Process flow diagram of MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 1

Table 15 Steam description process of MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 1

Steam name	from	To	Stream description
S21-01	-	H-211	The ethanol feedstock is heated by the heat exchanger to form of vapor phase
S21-02	H-211	R-211	The ethanol vapor is fed into the R-yield to maintain reaction operation
S21-03	R-211	C-211	All products are fed into the compressor to increase pressure for distillation operation
S21-04	C-211	H-212	All products are fed into the cooler to reduce temperature for distillation operation
S21-05	H-212	D-211	All products are fed into the distillation column to separate light gases
S21-06	D-211	-	The light gases are separated from the product
S21-07	D-211	D-212	The products are fed into the second distillation column
S21-08	D-212	-	Butadiene is separated from the unseparated product
S21-09	D-212	-	The diethyl ether and acetaldehyde are separated from the product

Table 16 Equipment descriptions process of MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 1

Unit name	Model	Unit description
H-211	HEATER	The heat exchanger is heated the ethanol in the form of vapor phase maintain the butadiene reaction at the appropriate temperature
R-211	R-YIELD REACTOR	The ethanol is converted to butadiene and byproducts
C-211	COMPRESSOR	The compressor has pressurized the products in the process to maintain the distillation process
H-212	COOLER	The heat exchanger is positioned as a cooler for the distillation column
D-211	DISTILLATION	The distillation column is light gases separation from products
D-212	DISTILLATION	The distillation column is diethyl ether and acetaldehyde from butadiene

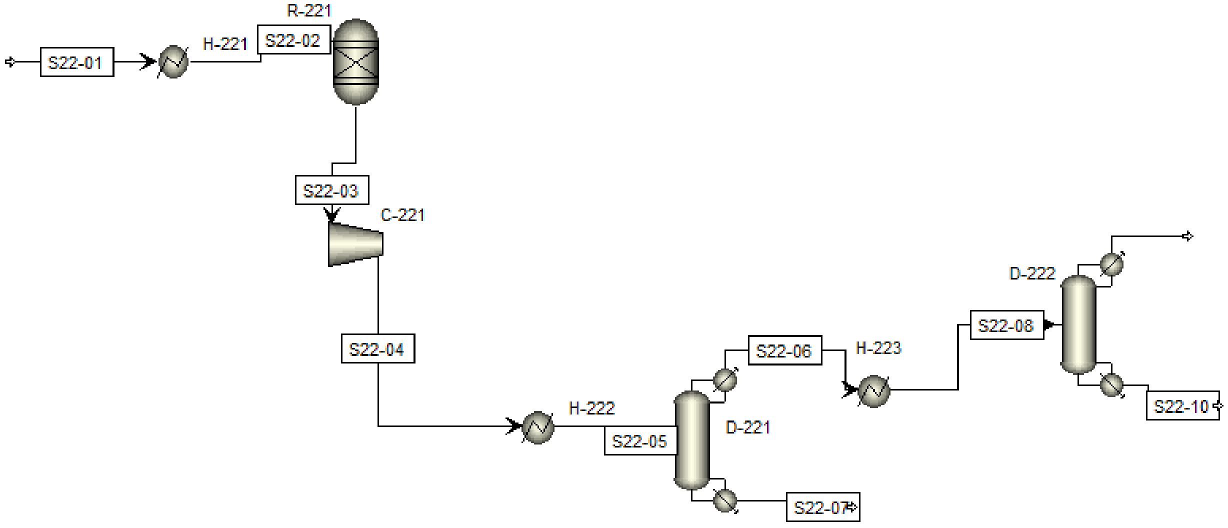

Figure 21 Process flow diagram of MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 2

Table 17 Steam description process of MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 2

Steam name	from	To	Stream description
S22-01		H-221	The ethanol feedstock is heated by the heat exchanger to form vapor phase
S22-02	H-221	R-221	The ethanol vapor is fed into the R-yield to maintain reaction operation
S22-03	R-221	C-221	All products are fed into the compressor to increase pressure for distillation operation
S22-04	C-221	H-222	All products are fed into the cooler to reduce temperature for distillation operation
S22-05	H-222	D-221	All products are fed into the distillation column to separate diethyl ether and acetaldehyde
S22-06	D-221	H223	The butadiene and light gases temperature are fed into the second distillation column
S22-07	D-221	-	The diethyl ether and acetaldehyde are separated from the product
S22-08	H-302	D-222	The butadiene and light gases are fed into the second distillation column
S22-09	D-222	-	The light gases are separated from the product
S22-10	D-222	-	Butadiene is separated from light gas

Table 18 Equipment descriptions process of MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 2

Unit name	Model	Unit description
H-221	HEATER	The heat exchanger heats the ethanol in the form of vapor phase maintain the butadiene reaction at an appropriate temperature
R-221	R-YIELD REACTOR	The ethanol is converted to butadiene and byproducts
C-221	COMPRESSOR	The compressor pressurizes in the process to maintain the distillation process
H-222	COOLER	The heat exchanger is positioned as a cooler for the distillation column
D-221	DISTILLATION	The distillation column separates diethyl ether and acetaldehyde from unseparated products
H-302	COOLER	The heat exchanger is positioned as a cooler for the distillation column
D-222	DISTILLATION	The distillation column plays as light gases separation from butadiene

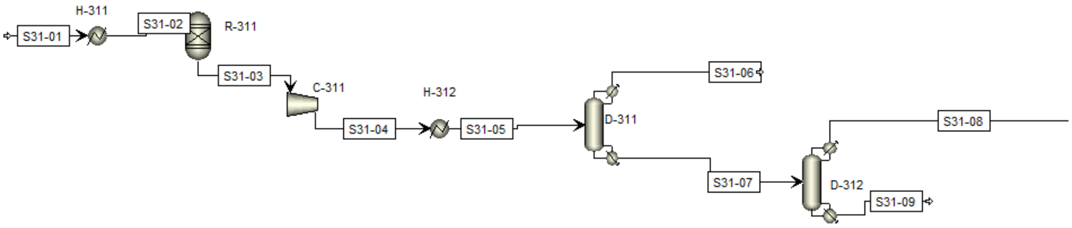

Figure 22 Process flow diagram of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1

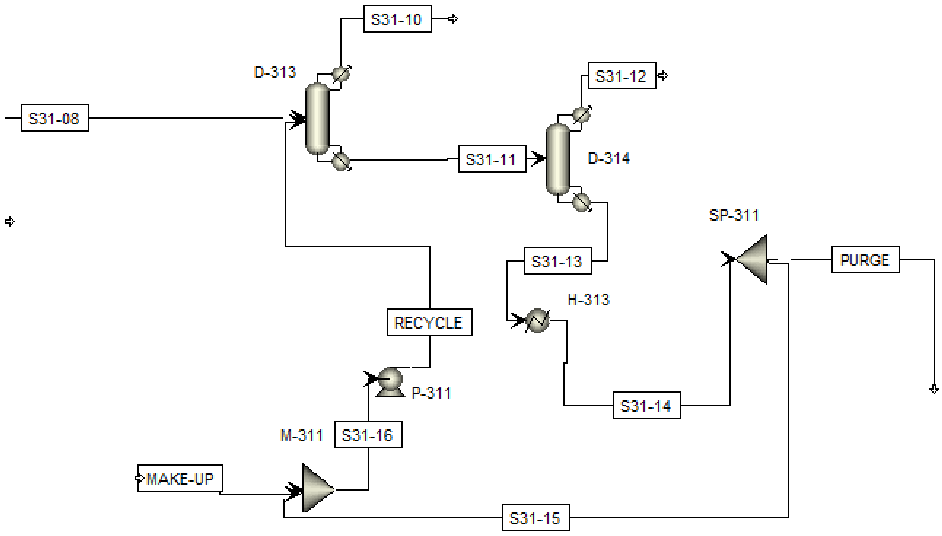

Figure 23 Process extractive distillation column of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1

Table 19 Steam description process of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1

Steam name	from	To	Stream description
S31-01	-	H-311	The ethanol feedstock is heat by the heat exchanger to form of vapor phase
S31-02	H-311	R-311	The ethanol vapor is fed into the R-yield to maintain reaction operation
S31-03	R-311	C-311	The compressor pressurizes in the process to maintain the distillation process
S31-04	C-311	H-312	All products are fed into the cooler to reduce temperature for distillation operation
S31-05	H-312	D-311	All products are fed into the distillation column to separate ethylene and propylene
S31-06	D-311	-	The ethylene and propylene are separated from products
S31-07	D-311	D-312	The products are fed into distillation separation
S31-08	P-312	D-313	The products are fed into extractive distillation to separate butadiene and butene from by-products
S31-09	D-312	-	The undesired products are separated from butadiene and butene
S31-10	D-312	-	The butene is separated from butadiene and dimethylformamide
S31-11	H-313	D-314	The butadiene and dimethylformamide are fed into the extractive distillation column
S31-12	D-314	-	The butadiene is separated from dimethylformamide
S31-13	D-313	H-313	The butadiene and dimethylformamide are cooled into for recycling feed in the extractive distillation column

S31-14	H-313	SP-311	The solvent of dimethylformamide is cooled for purging and recycling
S31-15	SP-311	M-311	The unseparated butadiene mixture is feed into a mixer which adds dimethylformamide for extractive distillation column
S31-16	M-311	P-313	The mixture of butadiene and dimethylformamide is fed into a pump for recycling steam
PURGE	SP-311	-	Release the partial mixture of product
MAKE UP		M-311	Adding dimethylformamide in process for extractive distillation

Table 20 Equipment descriptions process of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1

Unit name	Model	Unit description
H-311	HEATER	The heat exchanger is positioned as a heater for the reaction operation
R-311	R-YIELD REACTOR	The ethanol vapor is fed into the R-yield to maintain reaction operation
C-311	COMPRESSOR	The compressor pressurizes in process to maintain the distillation process
H-312	COOLER	All products are feed into the cooler to reduce temperature for distillation operation
D-311	DISTILLATION	The distillation column separates ethylene and propylene from products
D-312	DISTILLATION	The distillation column separates butene and butadiene from the byproduct
P-311	PUMP	To Pressurize the recycle stream into the extractive distillation column

D-313	DISTILLATION	The distillation column separates butene from the mixture of butadiene and dimethylformamide
D-314	DISTILLATION	The distillation column separates butadiene from dimethylformamide
H-313	COOLER	To reduce temperature for recycling steam
SP-311	SPITTER	To split some dimethylformamide out of the system
M-311	MIXER	To mix dimethylformamide into the system.

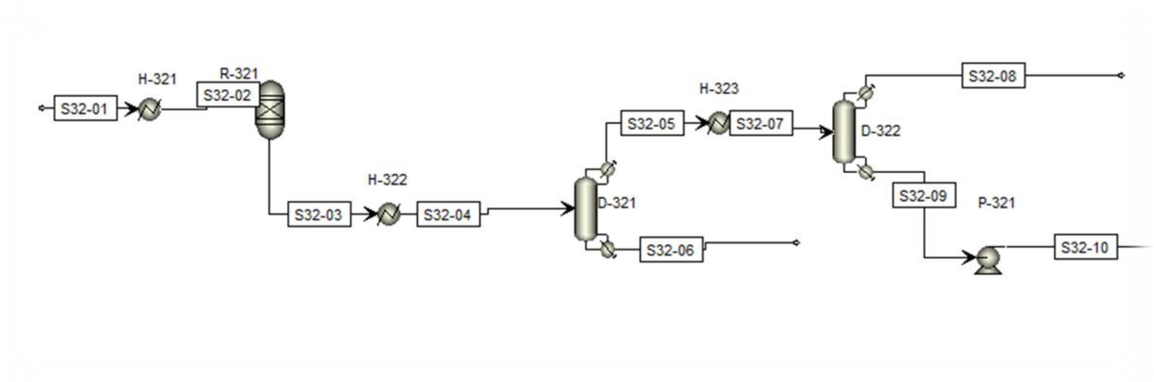

Figure 24 Process flow diagram of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 2

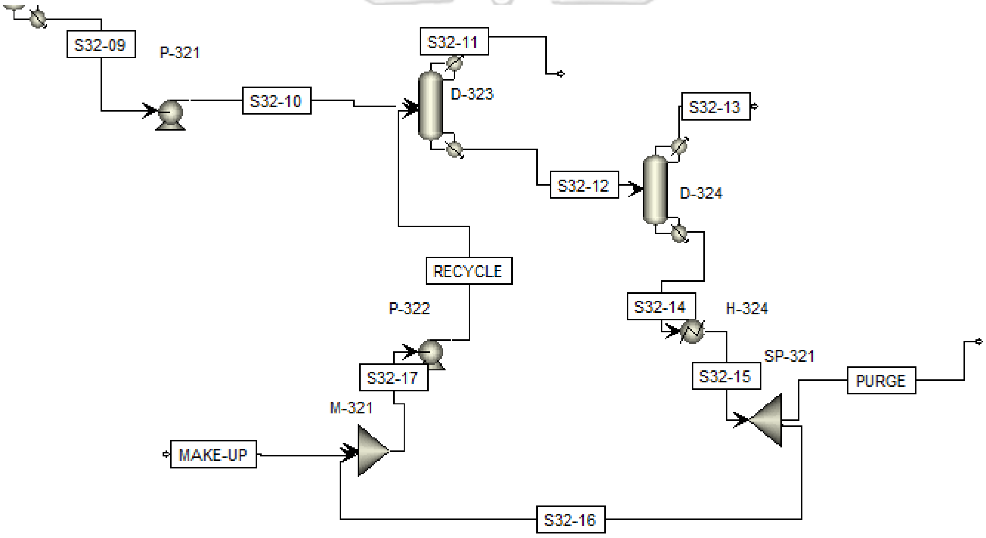

Figure 25 Process extractive distillation column of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 2

Table 21 Steam description process of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 2

Steam name	from	To	Stream description
S32-01	-	H-321	The ethanol feedstock is heated by the heat exchanger to form of vapor phase
S32-02	H-321	R-321	The ethanol vapor is fed into the R-yield to maintain reaction operation
S32-03	R-321	H-322	All products are fed into the cooler to reduce temperature for distillation operation
S32-04	H-322	D-321	Cooling products are fed into the distillation column
S32-05	D-321	H-323	All products are cooled before separation
S32-06	D-321	-	The byproducts are separated from the product
S32-07	H-323	D-322	All products are fed into the distillation column to separate ethylene and propylene
S32-08	D-322	-	ethylene and propylene are separated from the product
S32-09	D-322	P-321	The products are fed into the pump to increase pressure in the process
S32-10	P-321	D-323	The products are fed into the pump to increase pressure in the process
S32-11	D-323	-	The butene is separated from butadiene and dimethylformamide
S32-12	D-323	D-324	The butadiene is separated from the remained butene
S32-13	D-324	-	All butadiene is separated from dimethylformamide
S32-14	D-324	H-324	The unseparated product of dimethylformamide is cooled for purging and recycling

S32-15	H-324	SP-321	The unseparated butadiene and dimethylformamide are split for recycling feed in the extractive distillation column
S32-16	SP-321	M-321	The unseparated butadiene mixture is fed into a mixer which adds dimethylformamide for extractive distillation column
S32-17	M-321	P-322	The mixture of butadiene and dimethylformamide is fed into a pump for recycling steam
RECYCLE	P-322	D-323	Dimethylformamide is returned to the extractive distillation column
PURGE	SP-321	-	Release the partial mixture

Table 22 Equipment descriptions process of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1

Unit name	Model	Unit description
H-321	HEATER	The heat exchanger is positioned as a heater for the reaction operation
R-321	R-YIELD REACTOR	The ethanol vapor is fed into the R-yield to maintain reaction operation
H-322	COOLER	The compressor pressurizes in the process to maintain the distillation process
D-321	DISTILLATION	The distillation column separate butadiene and butene from the byproduct
H-323	COOLER	All products are fed into the cooler to reduce temperature for distillation operation
D-322	DISTILLATION	The distillation column separates ethylene and propylene from products
P-321	PUMP	The products are fed into the pump to increase pressure in the process

D-323	DISTILLATION	The extractive distillation column separates butene from the mixture of butadiene and dimethylformamide
D-324	DISTILLATION	The extractive distillation column separates butadiene from dimethylformamide
SP-321	SPITTER	To split some butadiene out of the system
H-324	COOLER	To cool some dimethylformamide for recycle system
M-321	MIXER	To mix dimethylformamide into the system.
P-322	PUMP	The butadiene and butene are pressurized and fed into the extractive distillation column

4.4 Heat integration and utility system

The last step is heat integration and utility system. Aspen energy analysis software was used to evaluate the value of total energy requirement, total utility requirement, minimum heating utility requirement and minimum cooling utility requirement of all sequences and saving energy after heat integration. The cold and hot composite curve is determined to form the pinch analysis method. The benefit of the curve is used to minimize the energy and utility which find the very performance sequences in the butadiene separation process.

CHAPTER 5

RESULT AND DISCUSSIONS

The result and discussions in this chapter consist of 2 major parts. Part one is the results from the simulation of butadiene production from ethanol by the one-step process using three different catalysts in ASPEN PLUS 8.0 software. Part two is the heat integration after simulation. The performance parameters were then compared to find the optimal process.

5.1 Performance simulation of three catalysts in 1,3-butadiene production in the one-step process

5.1.1 Product distribution of three catalysts

The product distribution for using Al_2O_3/ZnO (60:40), $MgO\text{-}SiO_2\text{-}Na_2O$ (1:1)(0.1%) and $Hf_{2.5}ZM_{1.6}/SiO_2$ catalysts are shown in Figure 26 – 28 when compared with experimental results from literature reviews.

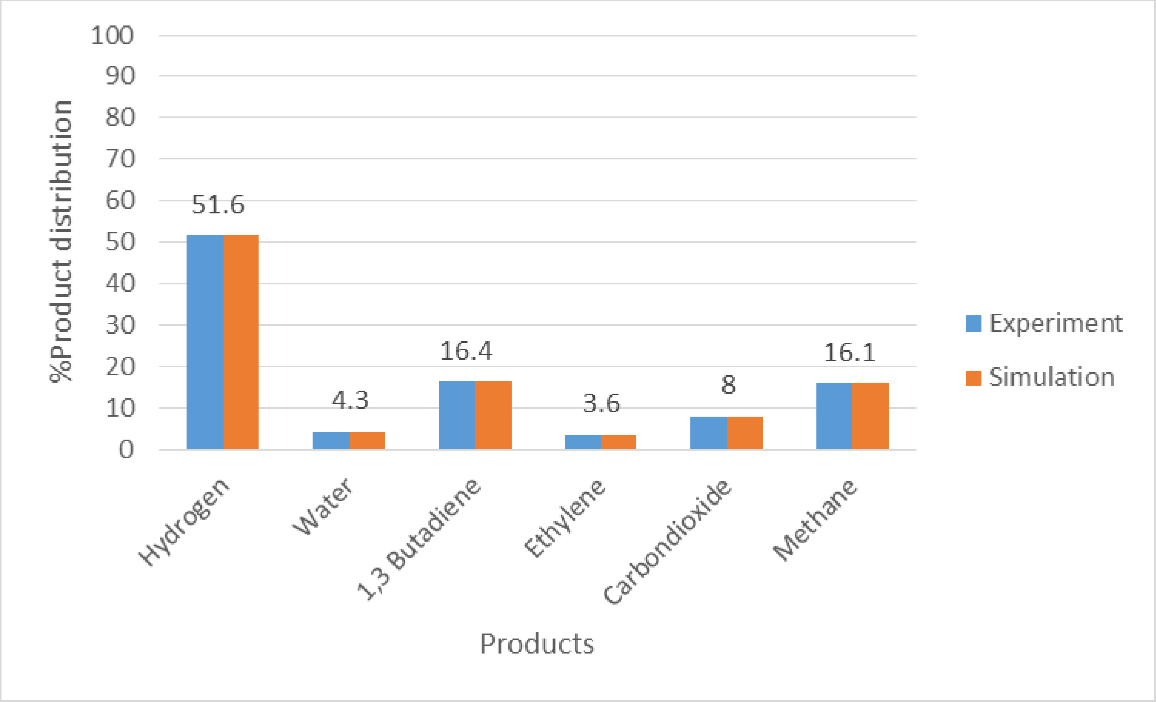

Figure 26 Products distribution from Al_2O_3/ZnO (60:40) catalyst in sequence 1 and 2

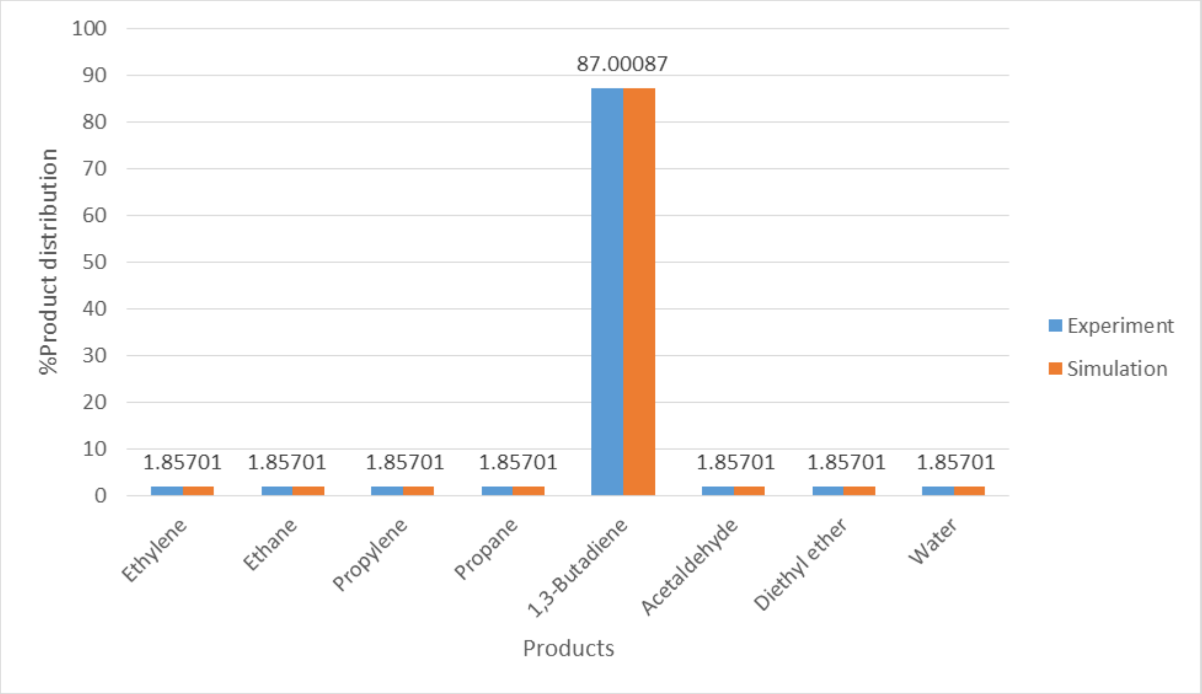

Figure 27 Products distribution from MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 1 and 2

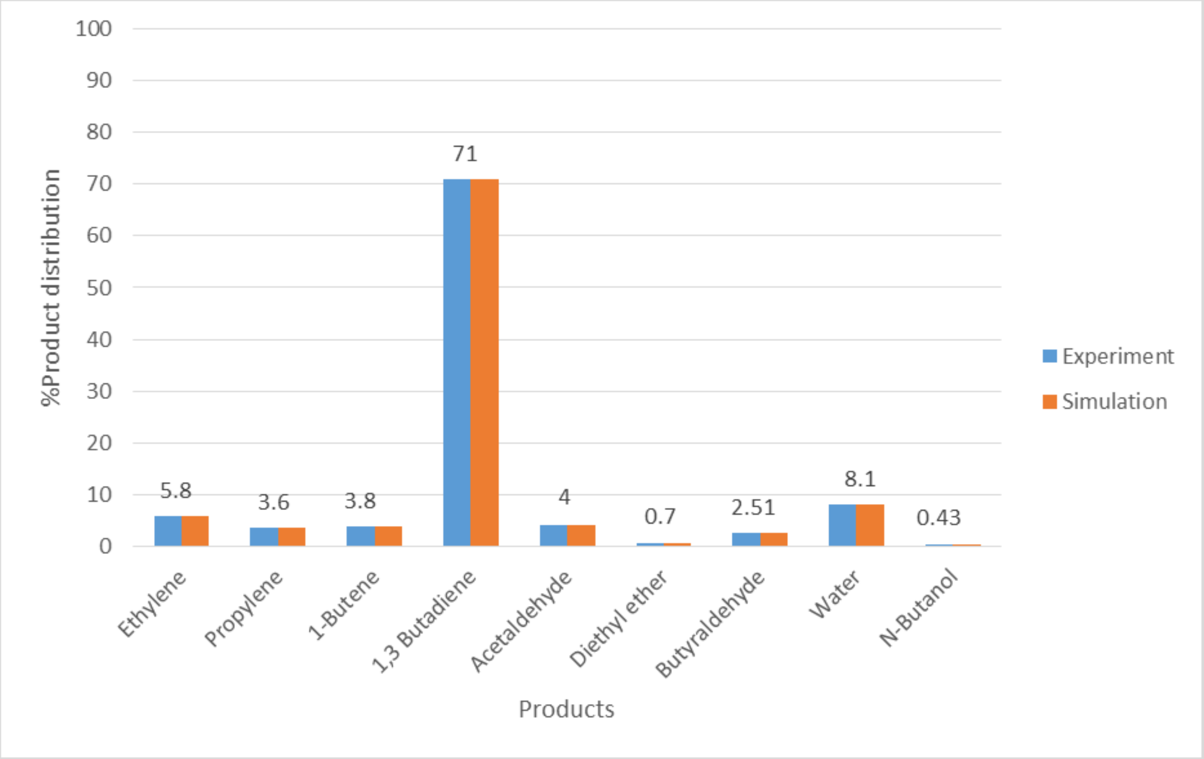

Figure 28 Products distribution from $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1 and 2

The reaction processes were observed by yield, temperature and pressure of Al_2O_3/ZnO, MgO-SiO_2 -Na_2O and $Hf_{2.5}ZM_{1.6}/SiO_2$ from the literature are utilized and calculated in Ryield reactor in ASPEN software, and the product distribution of the three aforementioned catalysts are shown in figure 26, 27 and 28, respectively. The products from Ryield reactor when Al_2O_3/ZnO was used as a catalyst include hydrogen, water butadiene ethylene carbon dioxide, and methane. As shown in figure 26, the butadiene production distribution was determined at 16.4 %, which is lower than the hydrogen production rate at 51 %. Furthermore, the methane production distribution is 16.1 % which is equivalent to that of butadiene. The production distributions of Ryield reactor from MgO-SiO_2 -Na_2O, as shown in figure 27, include ethylene, ethane, propane, acetaldehyde, diethyl ether, water. It is clear that this catalyst gives the highest production distribution of butadiene at 87 % while other byproducts each only accounts for about 1.87 % of the total distribution due to low yield, which was estimated from the average remaining yield of byproduct distributions. The production distributions from $Hf_{2.5}ZM_{1.6}/SiO_2$ include ethylene, propylene, butene, butadiene, acetaldehyde, diethyl ether, butyraldehyde, water, and butanol. From figure 28, the butadiene production distribution is higher than the other products at approximately 71 %. It can be concluded that butadiene production from MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst is higher than those of $Hf_{2.5}ZM_{1.6}/SiO_2$ and Al_2O_3/ZnO catalyst, respectively. However, the distribution of byproducts generated by the three catalysts resulting from the design and simulation of the separation process in each sequence are different, which are discussed in the next section.

5.1.2 The results of the process simulation for separation in 1,3 butadiene production

This section shows the optimal parameters of equipment in the separation process which was calculated from ASPEN PLUS 8.0 software. The six sequences were designed for separating 1,3 butadiene from other byproducts as shown in Table 5.1-5.6.

Table 23 Result of the optimal separation condition from sequence 1 using Al_2O_3/ZnO (60:40) catalyst in the butadiene production process

Parameters	Values
PSA-111	
Temperature(°C)	35
Pressure (Psia)	415
% H_2 Split	99.99
DE-111	
Temperature(°C)	20
Pressure(Psia)	415
%Efficiency	99.95
D-111	
Number of stages	23
Feed-stage location	7
Condenser	Partial condenser
Pressure condenser(Psia)	415
Reflux ratio	0.165
D/F ratio	0.6279
Condenser duty (MJ/hr)	4,201.6
Reboiler duty (MJ/hr)	13,122

Table 24 Result of optimal separation condition from sequence 2 using Al_2O_3/ZnO (60:40) catalyst in butadiene production process

Parameters	Values
PSA-121	
Temperature(°C)	35
Pressure (Psia)	415
% H_2 Split	99.99

DE-121	
Temperature(°C)	20
Pressure(Psia)	415
%Efficiency	99.95
D-121	
Number of stages	15
Feed stage location	5
Condenser	Partial condenser
Pressure condenser(Psia)	415
Reflux ratio	0.2901
D/F ratio	0.568
Condenser duty (MJ/hr)	4,311
Reboiler duty (MJ/hr)	38,320

The reaction processes were observed in terms of yield, temperature, and pressure using Al_2O_3/ZnO. The separation processes were designed and simulation results of all the corresponding process parameters are shown in table 23 and 24. The separation processes are designed into 2 sequences based on the different arrangement of pressure swing adsorption, decanter and distillation processes. Sequence 1 was ordered by pressure swing adsorption, decanter, and distillation processes, respectively, while sequence 2 was ordered by pressure swing absorption, distillation processes, and decanter, respectively. The design parameters of pressure swing adsorption and decanter processes are similar in both sequences which referred to the same efficiency from the literature. [17, 31] It realized that pressure in the system is 415 psia which is quite high for the separation process. However, the pressure condenser in every column can be adjusted following the handbook. [32] It is considered that the different sequence of decanter and pressure swing adsorption does not affect the design parameters for hydrogen and water separation process. The design parameters of distillation process are calculated by DSTWU shortcut distillation model to obtain the number of stages, reflux ratio, feed stage location, D/F ratio and all parameters are used to determine the condenser and reboiler duties of the distillation process. The number of distillation stages in sequence 1 and sequence 2 is 23 and 15 stages, respectively. It is speculated that the presence of water in the distillation process resulted in the lower number of stages in sequence 2 compared to sequence 1, which involved the liquid/vapor equilibrium in two or more mixture components. [33]

Table 25 Result of optimal separation condition from sequence 1 using MgO-SiO_2-Na_2O (1:1)(0.1%) catalyst in the butadiene production process

Parameters	Values
D-211	
Number of stages	45
Feed-stage location	23
Condenser	Partial condenser
Pressure condenser(Psia)	215
Reflux ratio	0.3551
D/F ratio	0.17
Condenser duty (MJ/hr)	1,442.39
Reboiler duty (MJ/hr)	14,652.2
D-212	
Number of stages	70
Feed-stage location	30
Condenser	Partial condenser
Pressure condenser(Psia)	215
Reflux ratio	8
D/F ratio	0.9365
Condenser duty (MJ/hr)	100,776
Reboiler duty (MJ/hr)	117,519

Table 26 Result of optimal separation condition from sequence 2 using MgO-SiO_2-Na_2O (1:1)(0.1%) catalyst in the butadiene production process

Parameters	Values
D-221	
Number of stages	50
Feed-stage location	25
Condenser	Partial condenser
Pressure condenser(Psia)	215
Reflux ratio	3
D/F ratio	0.9442
Condenser duty (MJ/hr)	50,770
Reboiler duty (MJ/hr)	80,662
D-222	
Number of stages	43
Feed-stage location	22
Condenser	Partial condenser
Pressure condenser(Psia)	215
Reflux ratio	7
D/F ratio	0.0794
Condenser duty (MJ/hr)	11,644
Reboiler duty (MJ/hr)	14,734

The reaction processes were observed in terms of yield, temperature, and pressure of MgO-SiO_2-Na_2O. The separation processes were designed and simulation results of all the corresponding process parameters are shown in table 25 and 26. The separation processes in sequence 1 were ordered by light gases distillation, diethyl ether, and acetaldehyde distillation process while the separation processes in sequence 2 were ordered by the acetaldehyde distillation process followed by light gases distillation. The number of distillation stages in sequence 1 is 45 and 70 stages while the number of stages in sequence 2 is 50 and 43 stages. It was observed that the presence of light gases, diethyl ether, and acetaldehyde resulted in a high number of distillation stages and high reflux ratio because the mixture components all have similar boiling points. Therefore, the design parameters of the separation process in sequence 2 are more efficient than those of sequence 1 in terms of the number of stages and reflux ratio.

Table 27 Result of optimal separation condition from sequence 1 using $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in the butadiene production process

Parameters	**Values**
D-311	
Number of stages	144
Feed-stage location	64
Condenser	Partial condenser
Pressure condenser(Psia)	215
Reflux ratio	9
D/F ratio	0.0942
Condenser duty (MJ/hr)	17304.5
Reboiler duty (MJ/hr)	22,332.9
D-312	
Number of stages	80
Feed-stage location	50
Condenser	Partial condenser
Pressure condenser(Psia)	215
Reflux ratio	8
D/F ratio	0.8259
Condenser duty (MJ/hr)	135,958
Reboiler duty (MJ/hr)	152,698

D-313	
Number of stages	50
Feed-stage location	25
Condenser	Partial condenser
Pressure condenser(Psia)	29.39
Reflux ratio	20
D/F ratio	0.0255
Condenser duty (MJ/hr)	69,965
Reboiler duty (MJ/hr)	63,836
D-314	
Number of stages	40
Feed-stage location	20
Condenser	Partial condenser
Pressure condenser(Psia)	29.39
Reflux ratio	1.064
D/F ratio	0.14
Condenser duty (MJ/hr)	19,934
Reboiler duty (MJ/hr)	84,853
SP-311	
Split fraction	0.9

Table 28 Result of optimal separation condition from sequence 2 using $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in the butadiene production process

Parameters	**Values**
D-321	
Number of stages	50
Feed-stage location	25
Condenser	Partial condenser
Pressure condenser(Psia)	14.7
Reflux ratio	10

D/F ratio	0.8
Condenser duty (MJ/hr)	260,087
Reboiler duty (MJ/hr)	290,008
D-322	
Number of stages	50
Feed-stage location	25
Condenser	Partial condenser
Pressure condenser(Psia)	14.7
Reflux ratio	2.5
D/F ratio	0.1177
Condenser duty (MJ/hr)	6,427.03
Reboiler duty (MJ/hr)	12,815.7
D-323	
Number of stages	47
Feed-stage location	25
Condenser	Partial condenser
Pressure condenser(Psia)	29.39
Reflux ratio	10
D/F ratio	0.02
Condenser duty (MJ/hr)	26,068
Reboiler duty (MJ/hr)	57,227
D-314	
Number of stages	50
Feed-stage location	20
Condenser	Partial condenser
Pressure condenser(Psia)	29.39
Reflux ratio	1.061
D/F ratio	0.148
Condenser duty (MJ/hr)	20,095

Reboiler duty (MJ/hr)	137,937
SP-321 Split fraction	 0.9

The reaction processes were observed in terms of yield, temperature and pressure of $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst and the separation processes were designed and simulation results of all the corresponding process parameters are shown in table 27 and 28. The separation processes in sequence 1 were ordered by distillation column for ethylene and propylene, and distillation for acetaldehyde, diethyl ether butyraldehyde, ethanol, water, and butanol, respectively. Butene and butadiene were separated by double extractive distillation column which uses dimethylformamide as an extractive solvent. The separation processes in sequence 2 were ordered by distillation of acetaldehyde, diethyl ether butyraldehyde, ethanol, water, and butanol; and distillation column for ethylene and propylene, and double extractive distillation column, respectively. The extractive distillation column served as a butene and butadiene separation unit, which could be not separated by general distillation process because the boiling points of both components are similar. Instead, two extractive distillation columns were used alongside dimethylformamide solvent extraction. [30] The extractive distillation columns had 7.5 of solvent to feed ratio and the total feed rate of the solvent was 103.065 kg/s.

In sequence 1, the number stages of first distillation and second distillation processes are 144 and 80 stages, which are hardly practical in the real application. Moreover, the very high reflux ratios require a high-efficiency pump for feed circulation. On the other hand, the number of stages for both extractive distillation columns are approximately 40 stages. [34] It was observed that the sequence of chemical separation does not affect the design parameters of the extractive distillation column in both sequences. It could be stated that by using the acetaldehyde, diethyl ether butyraldehyde, ethanol, water, and butanol separations following ethylene and propylene distillation column is feasible in term of design parameters and equipment design knowledge. Furthermore, the extractive distillation column requires a large operating cost for an extractive medium in the distillation process. However, Table 29 shows the solvent capacity and solvent purity of the recycling stream from the extractive distillation process, which revealed that the amount of solvent recovered in the system is as high as expected.

5.1.3 Comparison of production rates of three catalysts after process simulation

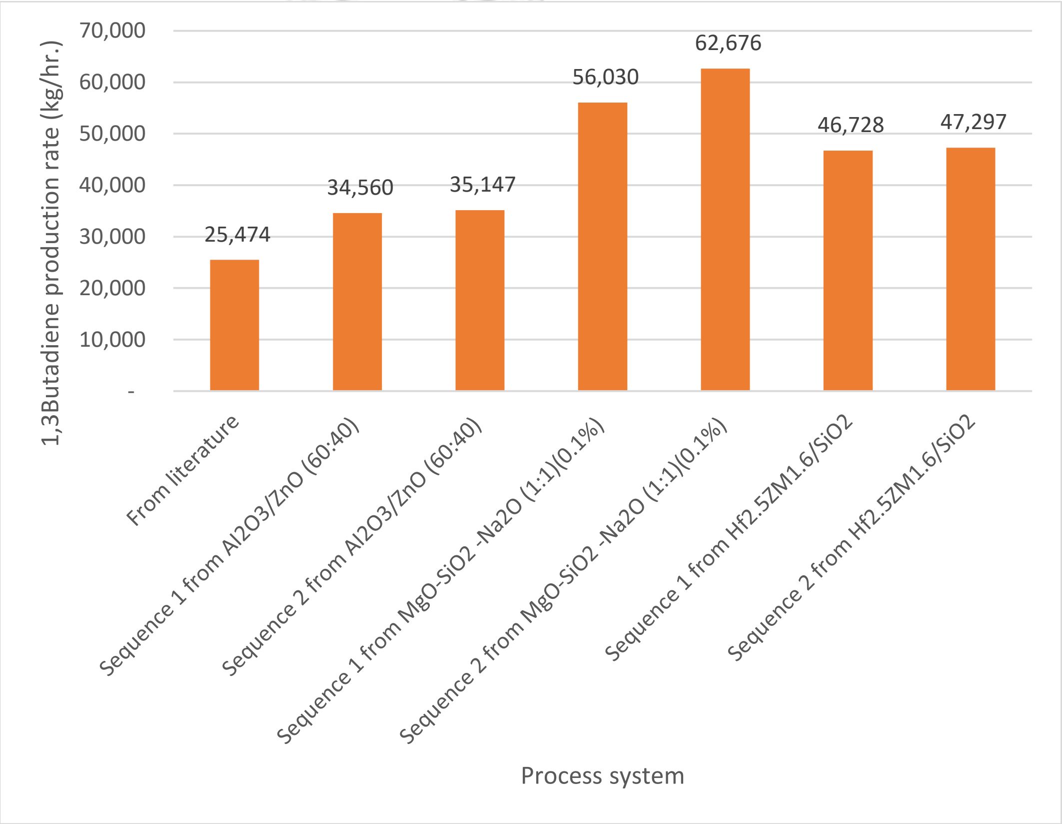

Figure 29 Comparison of butadiene production rate from literature and three catalysts with two different sequences

Table 29 Results of solvent capacity and purity in recycle stream using $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in the butadiene production process

Recycle systems	The solvent capacity of recycle stream (kg/hr.)	Solvent purity of recycle stream (%)
sequence 1 from $Hf_{2.5}ZM_{1.6}/SiO_2$	384,804	96.41
sequence 2 from $Hf_{2.5}ZM_{1.6}/SiO_2$	371,030.40	99.97

After the butadiene production process using the three catalysts were designed and simulated, the butadiene production rate is one of the most important parameters that should be considered in each sequence compared with the other works in literature as shown in figure 29 from the two-step production of 1,3-butadiene from ethanol. It was explicitly observed that the production rate from MgO-SiO_2-Na_2O $Hf_{2.5}ZM_{1.6}/SiO_2$ and Al_2O_3/ZnO catalysts are higher than the two-step ethanol production from previous research. The use of MgO-SiO_2-Na_2O as a catalyst in the reactor exhibits the highest butadiene production rate compared with $Hf_{2.5}ZM_{1.6}/SiO_2$ and Al_2O_3/ZnO. It is evident that use of MgO-SiO_2-Na_2O as a catalyst is best suited for butadiene production when considering design parameters in reaction and separation processes in term of equipment design. The drawbacks of butadiene production from $Hf_{2.5}ZM_{1.6}/SiO_2$ are the requirement for the massively high number of stages and high reflux ratio in the distillation process. The drawback of butadiene production from Al_2O_3/ZnO, on the other hand, is a low butadiene production rate. However, the butadiene production rate which used the same catalyst is equivalent in different sequence design except that of MgO-SiO_2-Na_2O. It is observed that the butadiene production rate using MgO-SiO_2-Na_2O catalyst in sequence 1 and 2 is not equivalent. The butadiene production rate of sequence 2 is higher than that of sequence 1 because some butadiene is lost in light gases steam in light gas distillation in sequence 1. The butadiene purity from all catalysts is shown to be more than 99 % as shown in

Table 30. Moreover, the reflux ratio and D/F ratio of each sequence do not significantly affect the production rate and the purity of butadiene. The effect of reflux ratio and D/F ratio may obtain by varying them then observed the effect on production rate and butadiene purity. Another important factor to consider is the heat transfer requirement in the heat exchanger network that will be discussed in the next section.

Table 30 Purity of 1,3-Butadiene production from simulation compared with literature

Systems	The purity of 1,3 Butadiene production (%)
From literature	98
Sequence 1 from Al_2O_3/ZnO (60:40)	99.06
Sequence 2 from Al_2O_3/ZnO (60:40)	99.01
Sequence 1 from MgO-SiO2 -Na2O (1:1)(0.1%)	99.02
Sequence 2 from MgO-SiO2 -Na2O (1:1)(0.1%)	99.05
Sequence 1 from $Hf_{2.5}ZM_{1.6}/SiO_2$	99
Sequence 2 from $Hf_{2.5}ZM_{1.6}/SiO_2$	99.08

5.2 Heat integration and utility system

After process design using the three catalysts, the heat integration system was evaluated by ASPEN energy analyzer software version 8.8, which was used to estimate the performance of heat exchanger network and calculated the key performance parameters to be considered in butadiene process simulation. The key performance parameters of interest are the total energy requirement and total utility requirement for the process.

Heating duty and cooling duty of equipment of six processes using two different sequences and three catalysts were calculated by ASPEN PLUS 8.8. The highest heat duty of equipment in the process can be attributed to Ryield reactor because the reaction was endothermic. Heat duty was then used to calculate the total energy requirement of the process. The total energy requirement of the process using $Hf_{2.5}ZM_{1.6}/SiO_2$ in both sequence 1 and 2 was significantly higher compared with Al_2O_3/ZnO (60:40) and $MgO-SiO_2-Na_2O$ (1:1)(0.1%) catalysts as shown in figure 31-33. Summary of heating and cooling duty using the three catalysts are reported in APPENDIX B.The processes that used $Hf_{2.5}ZM_{1.6}/SiO_2$ and $MgO-SiO_2-Na_2O$ (1:1)(0.1%) catalysts in sequence 1 and 2 have high values of total energy requirement because the processes contain more equipment than the process that used Al_2O_3/ZnO (60:40) catalyst such as distillation columns, heaters, pumps, and etc.

In addition, the total energy requirement parameter also depends on the amount of by-product type selected. In the Al_2O_3/ZnO (60:40) catalyst. Byproducts contain hydrogen and ethylene, methane, carbon dioxide and water which hydrogen can separate by pressure swing adsorption in 99.99% efficiency. Other light gas from Al_2O_3 / ZnO (60:40) can be separated by the RADFRAC column. The heat duty in the distillation column is less than that of other catalysts. Their values are 0.5 MJ / kg. in sequences 1 and 1.21 MJ / hr. in sequence 2. Figure 30 shows the heat duty of distillation columns in each sequence.

For $MgO-SiO_2-Na_2O$ (1: 1)(0.1%) catalyst, there are 7 byproduct products, namely ethylene, ethane, propylene, propane, acetaldehyde, diethyl ether, and water. Two sequences are designed and used 2 columns of the RADFRAC distillation. The heat duty of distillation in sequence 1 is 4.18 MJ / kg. and the heat duty of the distillation column in sequence 2 is 2.52 MJ / kg. it is shown that the number of by-products is affecting the heat duty in the distillation column.

Using $Hf_{2.5}ZM_{1.6}/SiO_2$, it has high total energy requirement in sequence 2 and it also has the highest heat duty of the distillation tower (17.14 MJ / kg.) Because the catalyst will receive 8 byproducts: Ethylene, propylene, butene, acetaldehyde, diethyl ether, butyraldehyde, water and butanol which requires 2 RADFRAC distilleries column for separation. The byproducts are separated which have lower boiling points than butene and the higher boiling point than butadiene. Then extractive distillation columns are used to separate butene and butadiene. Therefore. The heat duty of the distillation towers are increased in the separation process and it has the same effects on the total energy requirement and the total utility requirement.

Furthermore, the number of trays in the distillation column also affected the heating and cooling duty required when using $Hf_{2.5}ZM_{1.6}/SiO_2$ and $MgO\text{-}SiO_2$ -Na_2O (1:1)(0.1%) catalysts. When the column contains a high number of trays, the heating and cooling duty are increased.

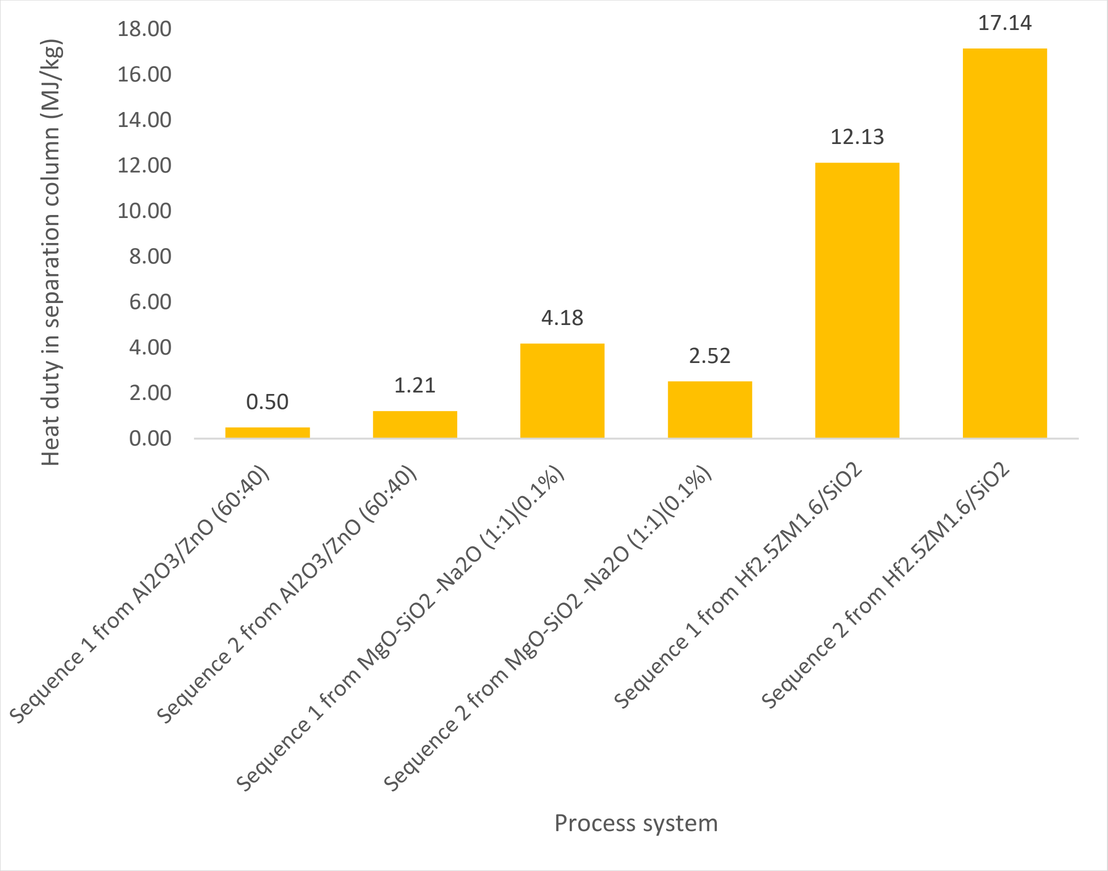

Figure 30 Comparison of the total heat duty of separation columns in six process systems in butadiene production from ethanol

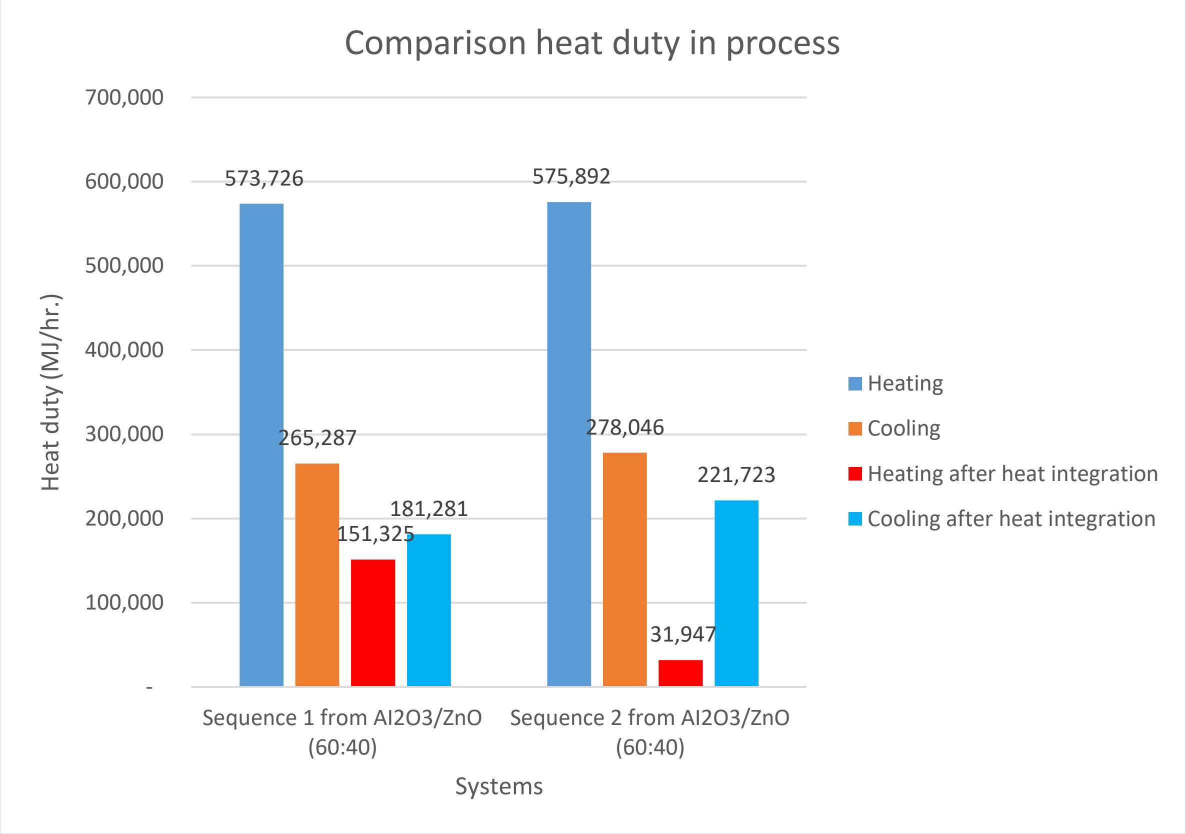

Figure 31 Comparison of the total energy requirement of Al_2O_3/ZnO(60:40) process systems in butadiene production from ethanol

Aspen energy analyzer was used to evaluate the heat integration of heat exchangers which enable the calculation of composite curves, total utility requirement of the process which are reported in APPENDIX C, APPENDIX D, and APPENDIX E. Figure 31-33 showed the total energy requirement of the six process systems from distillations before and after heat integration. The results are agreeable that the total energy requirement is decreased when heat integration is performed. The majority of heating utility was used to support heat exchangers before it was fed to reactor for an endothermic reaction at 300-425 °C. The cooling utility was used to cool the products after they exited from the reactor and before they are separated in the distillation column. It was also used to adjust the temperature of the solvent for the extractive distillation column. From figure 33, the highest total utility is from the process using $Hf_{2.5}ZM_{1.6}/SiO_2$ in sequence 2 due to the high heat duty demand of H-324 and reboiler in extractive distillation columns. Also found that the amount of heat duty that occurs in the reactor are Increases when used the MgO-SiO_2 -Na_2O (1:1)(0.1%) because of increasing the amount of a byproduct. It is affecting to total energy requirement in this process. The resulting in the total energy requirement of the entire system with increasing value as It is also speculated that the high total utility requirement increased from heat duty of condensers and reboilers in distillation columns.

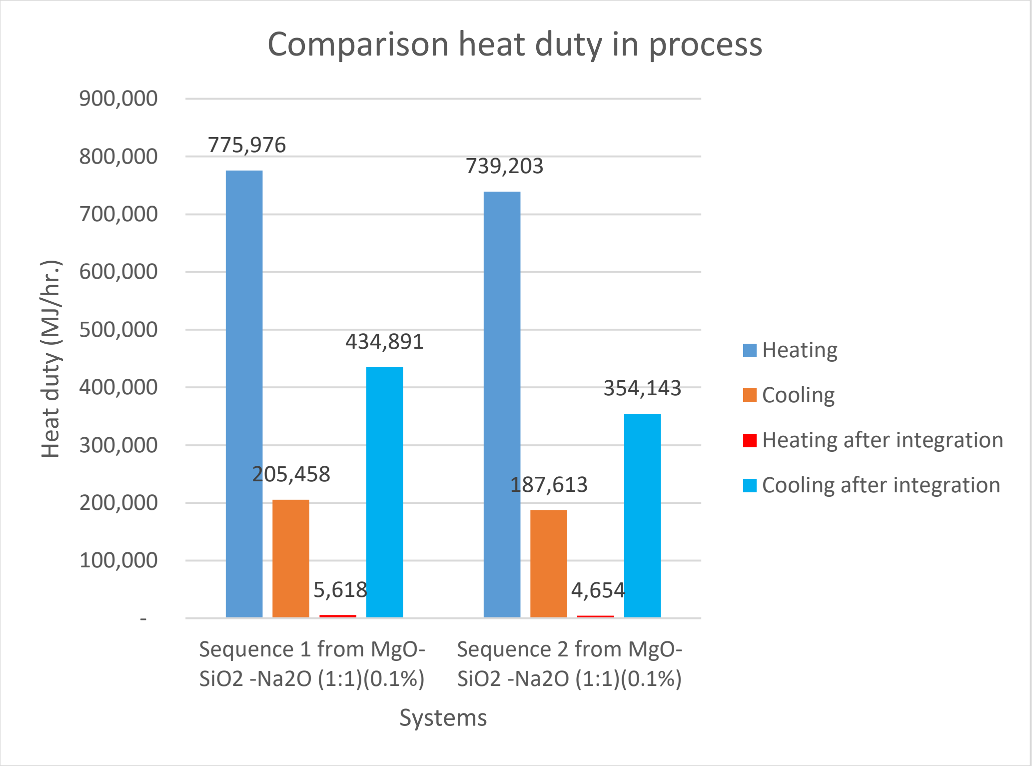

Figure 32 Comparison of the total energy requirement of MgO-SiO_2 -Na_2O (1:1)(0.1%) process systems in butadiene production from ethanol

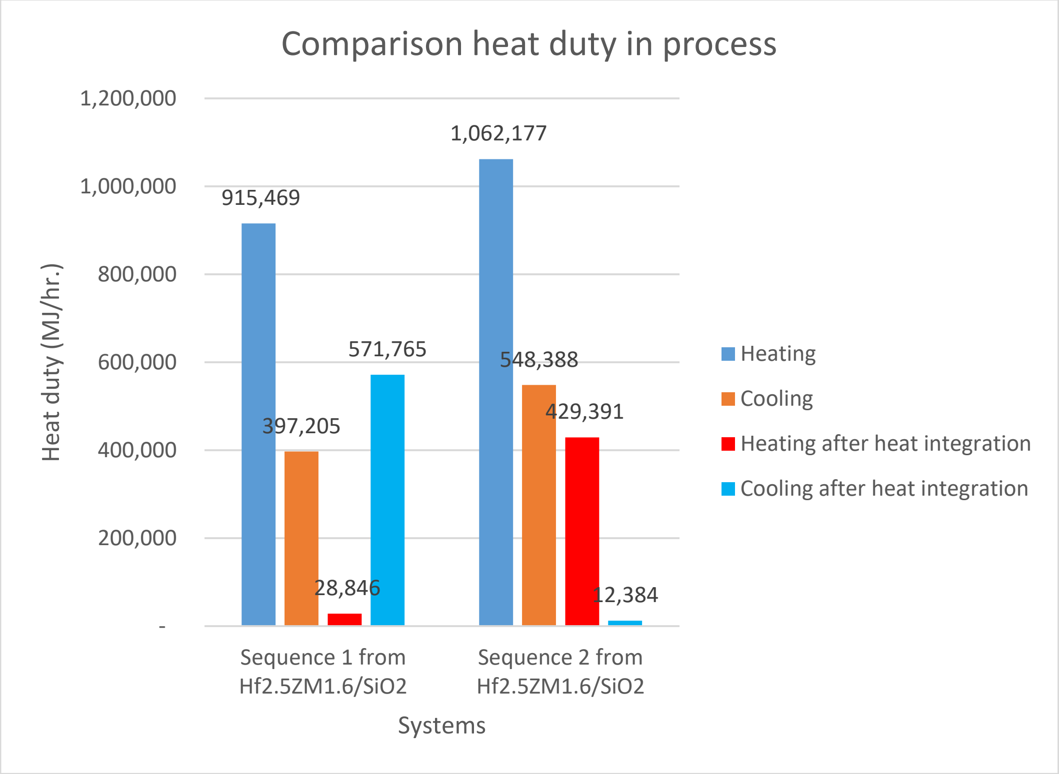

Figure 33 Comparison of the total utility requirement of $Hf_{2.5}ZM_{1.6}/SiO_2$ process systems in butadiene production from ethanol

For the total utility requirement, the total heating and cooling utility were calculated from the integrated heat exchanger system using ASPEN energy analyzer software, which matched the hot and cold streams in the composite curve. In this research, the hot and cold composite curves were determined using the ΔT_{min} of 10 °C obtained from the literature. [29]

The hot composite curve was presented in the left side of pinch analysis diagram while the cold composite curve was presented on the right side. When the temperature and enthalpy were changed, the cold and hot composite curves would overlap which yielded the maximum heat exchanging in the process. The top excess point of the cold composite curve represents the minimum cooling utility requirement for supporting hot stream while the bottom of the hot composite curve represents the minimum heating utility requirement for supporting cold stream. [35, 36]

The composite curves are presented in APPENDIX C which was used to calculate the total utility requirement. The lowest total utility requirement after heat integration can be attributed to MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 1 while the highest total utility requirement after heat integration can be attributed to $Hf_{2.5}ZM_{1.6}/SiO_2$ in sequence 1 that the values were shown in figure 34. Hot and cold streams were exchanged inside the system and the optimal pathway was selected by the ASPEN program. The total utility requirement is related to the heating duty of the equipment which needs cooling or heating from the utility in the system before heat integration. So Extractive distillation column for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst is desired the high total utility. For the same reason. MgO-SiO_2 -Na_2O (1:1)(0.1%) are desired the low total utility requirement because it is used 2 columns in process.So. the lowest total utility requirement is MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 1 (5.72 MJ/kg) and the highest total utility requirement is $Hf_{2.5}ZM_{1.6}/SiO_2$ in sequence 1(12.85 Mj/kg).

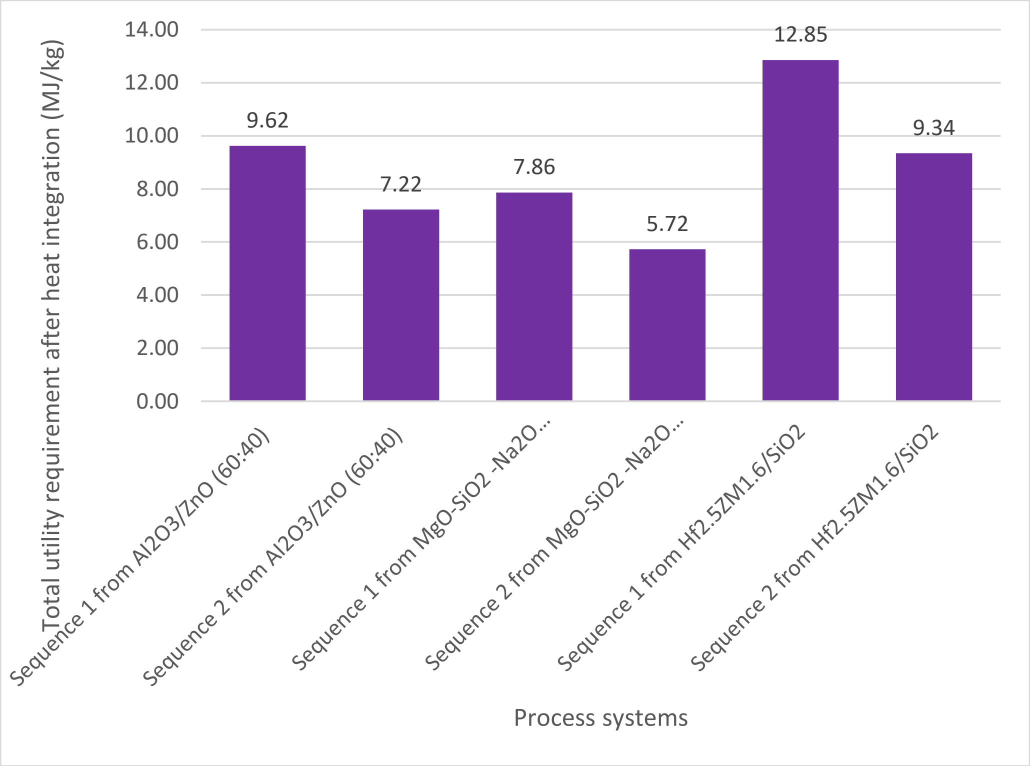

Figure 34 Comparison of the total utility requirement of six process systems after heat integration in butadiene production from ethanol

For the final step, the energy saving factor of six process systems was compared as shown in figure 35. The value of total energy requirement and total utility energy requirement of the process were compared and the energy saving of the process was calculated after heat integration. From figure 35, $Hf_{2.5}ZM_{1.6}/SiO_2$ in sequence 2 has the highest energy saving at 72.57% after comparing the total energy requirement with the total utility requirement of the process.

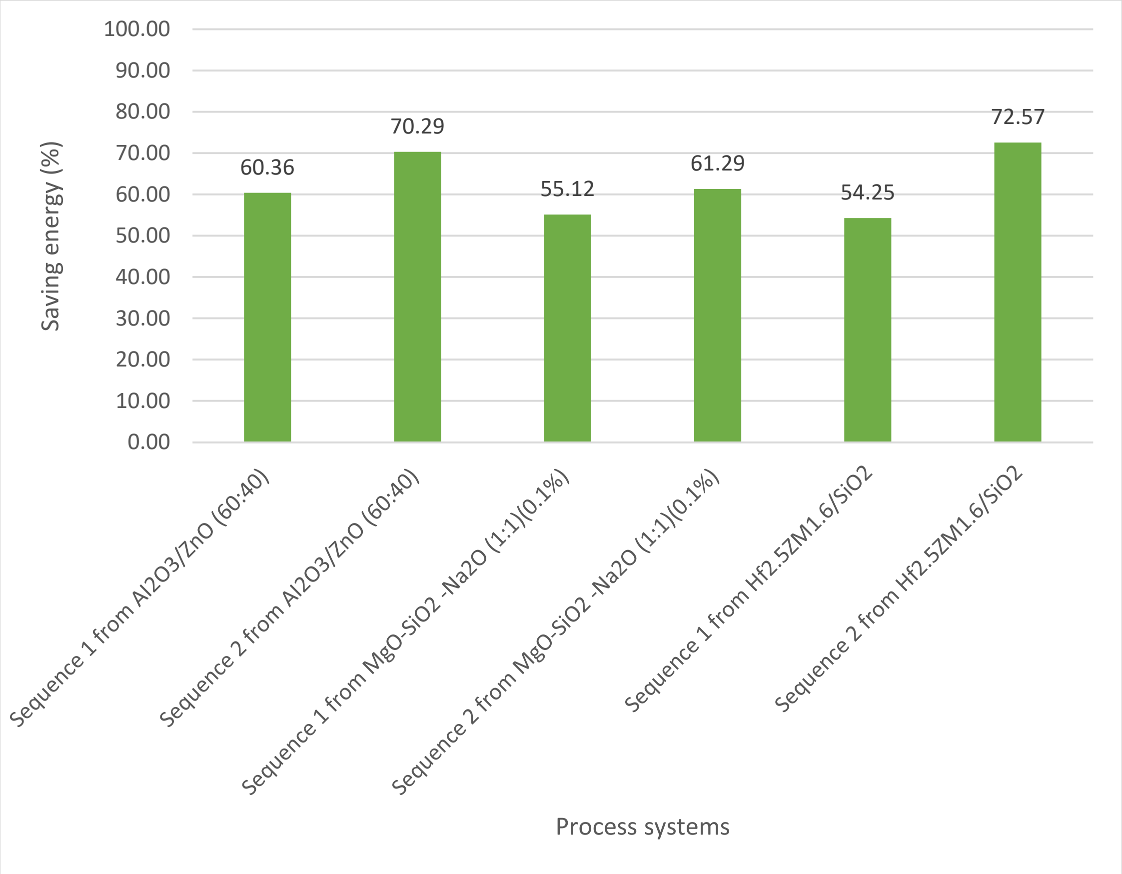

Figure 35 Comparison of the energy saving of six process systems in butadiene production from ethanol

CHAPTER 6

CONCLUSION

Performance simulation of 1,3-butadiene production from the one-step process was developed using data from various literature. This work studied sequences of distillation and the performance of heat integration after the separation process in 1,3-butadiene production. The parameters in sequence distillations are adjusted to find the optimal condition of separation which includes the number of stages, feed location, distillate to feed ratio (D/F), reflux ratio, and condenser pressure. Heat integration was employed to study the total energy requirement, total utility requirement, and process energy saving using Aspen energy 8.8 software. The following conclusions can be drawn.

6.1 Optimal condition in sequence separation

From the simulation, the MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 2 provides the highest production rate at 62,676 kg/hr. All catalyst has the highest purity of 1,3-butadiene at 99% of purity after the distillation process. For two recycle streams of dimethylformamide solvent in the extractive distillation column, the mass flow rate of recycling streams are 384,804 and 371,030.4 kg/hr. The purity of the two recycle streams is 96.41% and 99.97%.

6.2 Performance of heat integration and utility system

From heat integration, Total energy requirement in six processes is decreased after heat integration. The highest heat duty in the separation column can be attributed to $Hf_{2.5}ZM_{1.6}/SiO_2$ in sequence number 2 at 17.14 MJ/kg. Although. Al_2O_3/ZnO(60:40) is the lowest of heat duty in the separation column(0.5 MJ/kg). Then. $Hf_{2.5}ZM_{1.6}/SiO_2$ in sequence number 1 is the highest total utility requirement of 12.85 MJ/kg. But. The MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence number 2 is the process that has the lowest total utility requirement (5.72 MJ/hr.). Finally,

$Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence number 2 has the highest energy saving which is 72.57%.

6.3 Recommendations

1. The kinetic parameters and important feed process were interested parameters in screening catalysts method before simulation. The important parameters such as GHSV, WHSV, and rate constant, etc. Furthermore. The number of byproducts should have considered in process design because they were affecting the heat in the design separation process.

2. The cost of the process not included in this works such as operating cost, capital cost, and utility cost should be investigated. These parameters would greatly help in deciding which process would be best employed for butadiene production from ethanol in the one-step process.

3. Recently, several catalysts are developed for the two-step process in 1,3 butadiene production from ethanol, which should be examined and compared with the one-step process.

4. The process was a liquid hydrocarbon. So, water was necessary to treat byproduct in the wastewater treatment section. For greenhouse gas. The Adsorption would be concerned about CO_2 emission to the environment.

5. A high flow rate of hydrocarbon in streams was dangerous. Material safety data sheet (MSDS) would be studied to protect the accident in the process. Moreover. There were had to risk chemicals in the process. So. The toxic of chemicals were concerned.

6. Process of instrument and control values were important for consideration in this design process.

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APPENDIX

APPENDIX A

Thermodynamic property method of Predictive Soave-Redlich-Kwong (PSRK)

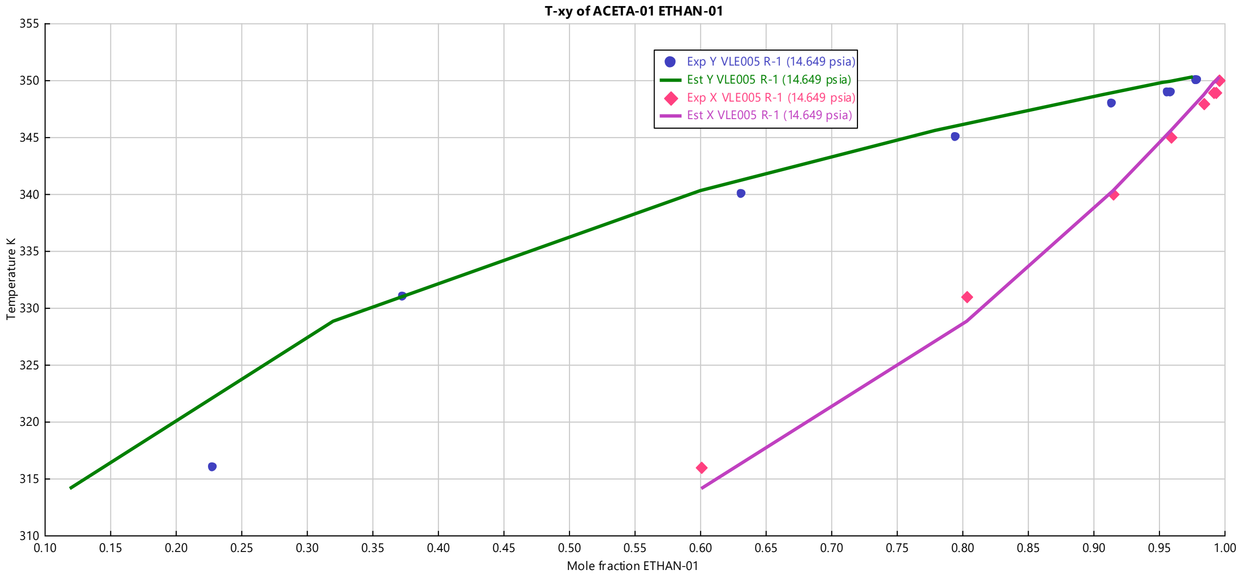

Figure A-36 T-xy diagram of ethanol and acetaldehyde compare the experiment with NIST data in ASPEN PLUS 8.0

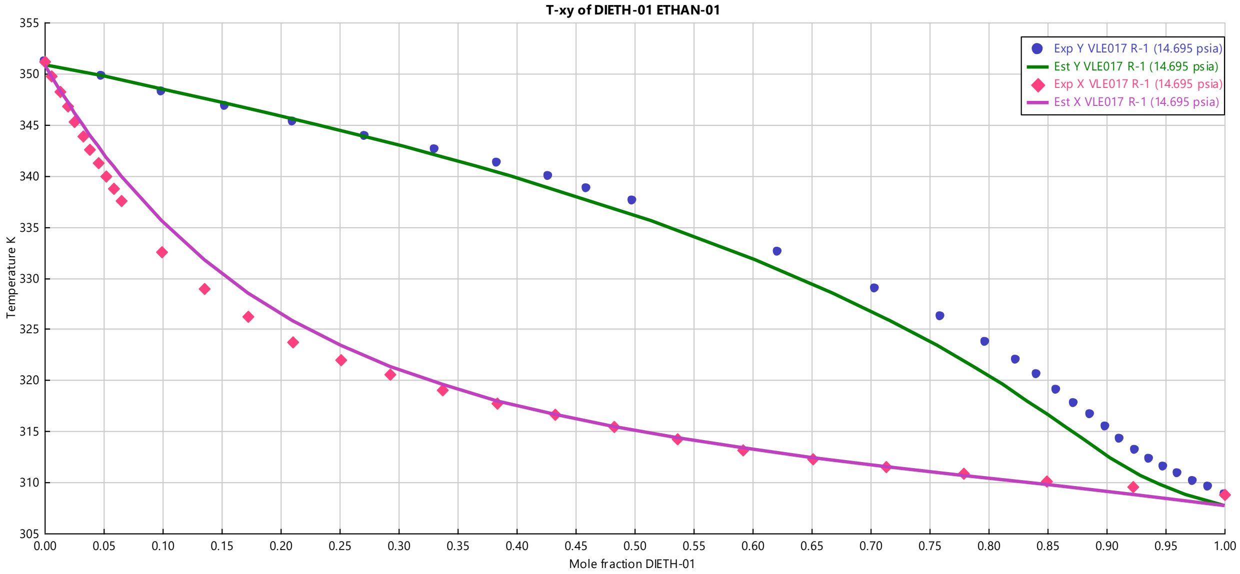

Figure A-37 T-xy diagram of ethanol and diethyl ether compare the experiment with NIST data in ASPEN PLUS 8.0

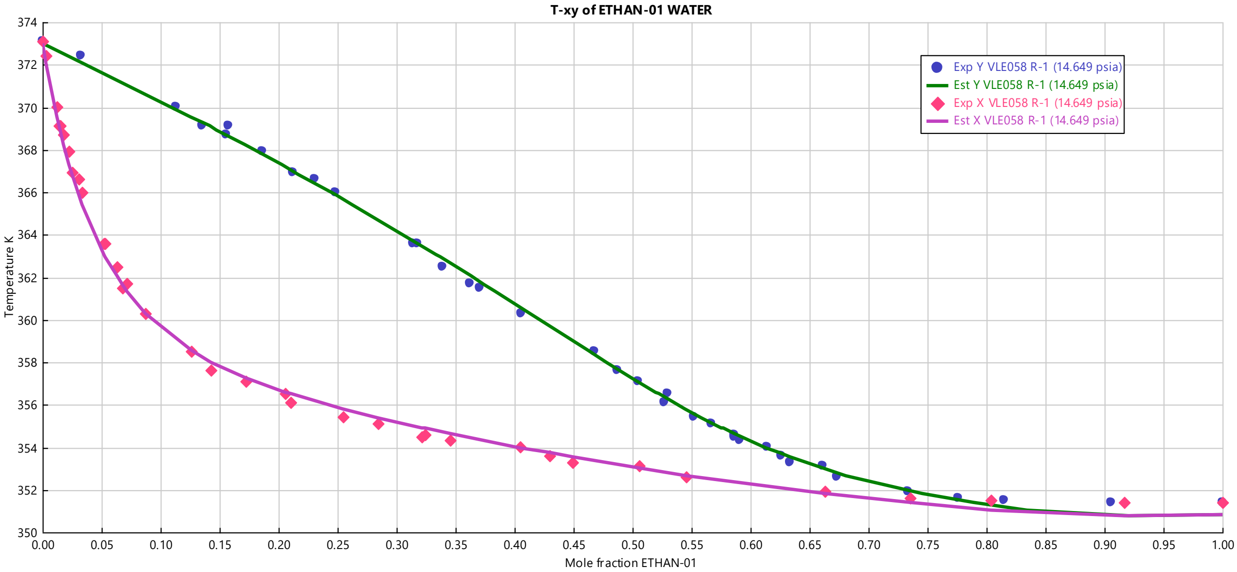

Figure A-38 T-xy diagram of ethanol and water compare experiment with the NIST data in ASPEN PLUS 8.0

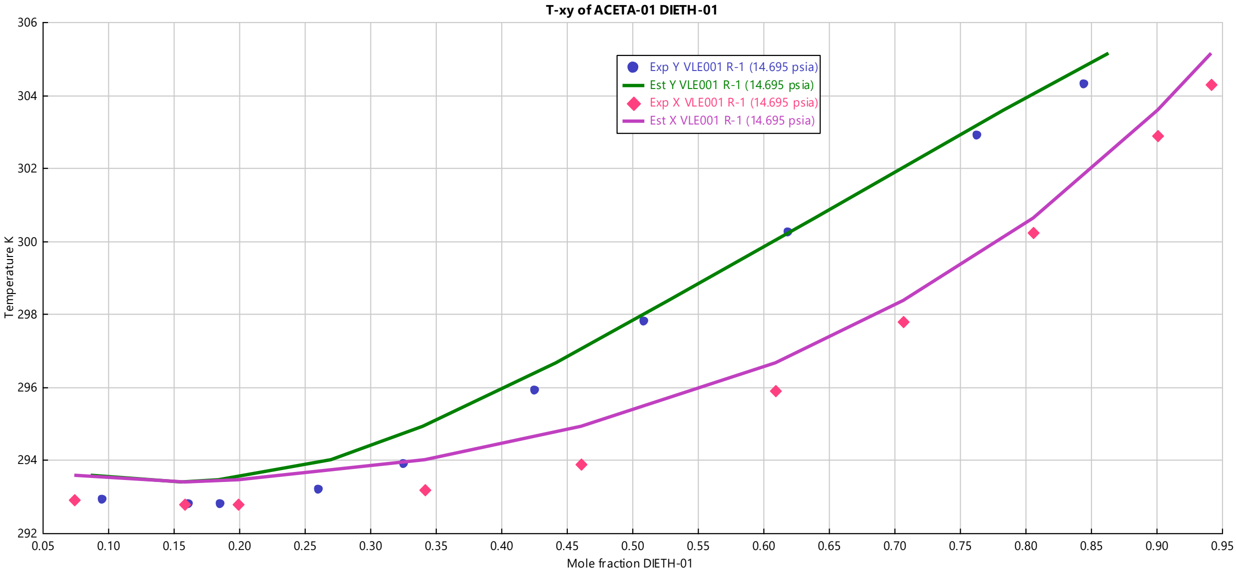

Figure A-39 T-xy diagram of acetaldehyde and diethyl ether compare experiment with the NIST data in ASPEN PLUS 8.0

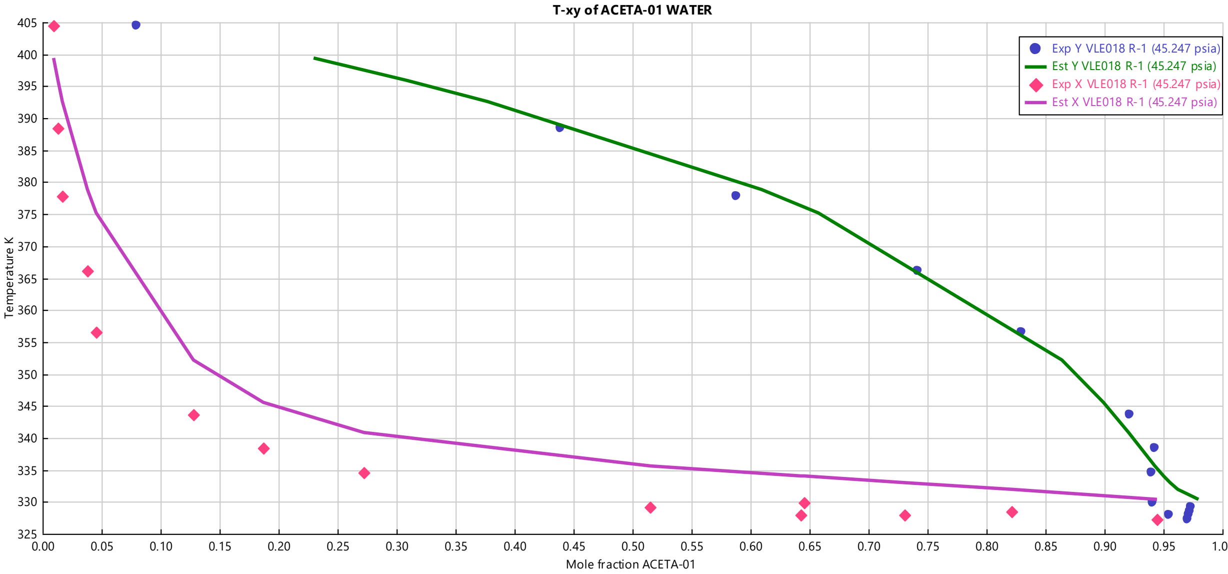

Figure A-40 T-xy diagram of acetaldehyde and water compare experiment with the NIST data in ASPEN PLUS 8.0

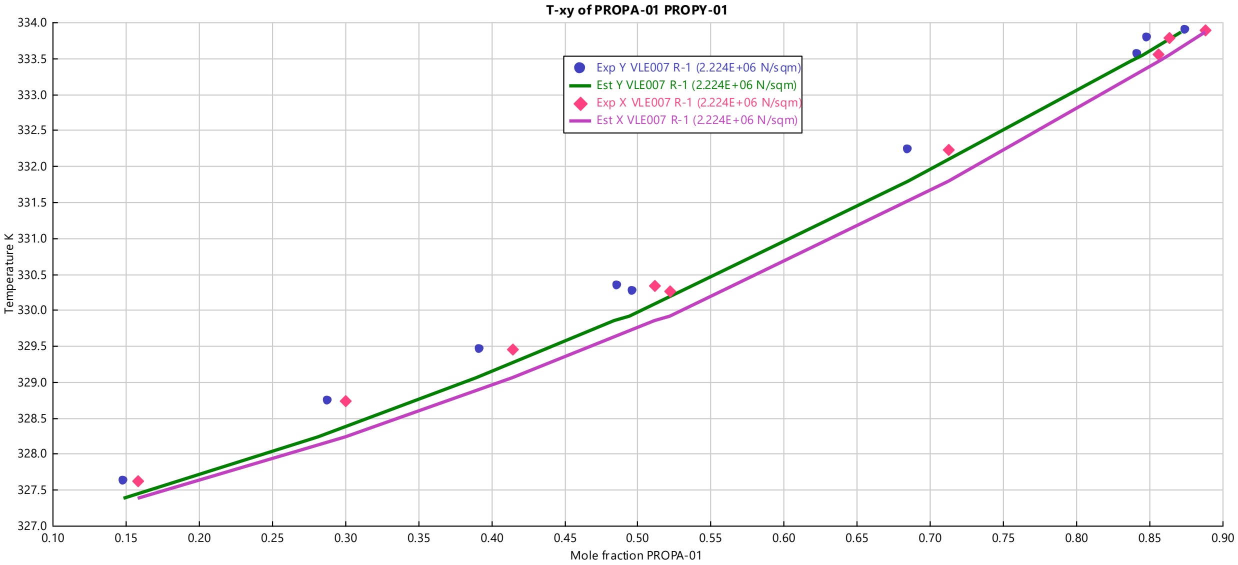

Figure A-41 T-xy diagram of propane and propylene compare experiment with the NIST data in ASPEN PLUS 8.0

APPENDIX B

Total energy requirement

Table B-31 Total energy requirement for Al_2O_3/ZnO (60:40) catalyst in sequence 1

Catalyst process	No. Sequence	Name of Equipment	Stream name	Type	Inlet temperature(°C)	Outlet temperature(°C)	mCp	Heat duty (MJ/hr)
Al_2O_3/ZnO (60:40)	1	H-111	S11-01	Cold	35.00	425.00	326.59	127,368.54
		R-111	S11-02	Hot	425.00	424.50	549,504.20	274,752.10
		C-111	S11-03	Cold	424.50	956.98	254.38	135,452.16
		H-112	H11-04	Hot	956.98	34.85	241.05	-222,282.06
		PSA-111	S11-05	Hot	34.85	25.66	1,283.17	11,792.32
		H-113	S11-07	Hot	25.66	-69.68	283.32	27,011.91
		DE-111	S11-08	Cold	-69.68	19.85	257.37	23,041.95
		DCON-111	s11-10	Cold	19.85	-30.58	83.32	4,201.60
		DREB-111	s11-10	Cold	19.85	122.65	127.55	13,112.00
Total cooling (MJ/hr)								265,287.89
Total heating (MJ/hr)								573,726.74
Total energy requirement(MJ/hr)								839,014.63

Table B-32 Total energy requirement for Al_2O_3/ZnO (60:40) catalyst in sequence 2

Catalyst process	No. Sequence	Name of Equipment	Stream name	Type	Inlet temperature(°C)	Outlet temperature(°C)	mCp	Heat duty (MJ/hr)
Al_2O_3/ZnO (60:40)	2	H-121	S12-01	Cold	35	425	326.59	127,368.54
		R-121	S12-02	Hot	425	424.5	549,504.20	274,752.10
		C-121	S12-03	Cold	424.5	956.98	254.38	135,452.16
		H-122	S12-04	Hot	956.98	35	239.10	-220,446.22
		PSA-121	S12-05	Hot	35	34.5	21,131.29	10,565.64
		H-123	S12-07	Hot	34.5	-69.69	283.34	29,521.07
		DCON-121	S12-08	Cold	-69.69	-43.43	164.17	4,311.00
		DREB-122	S12-08	Cold	-69.69	126.33	195.49	38,320.00
		DE-121	S12-10	Hot	130.06	19.85	119.80	13,202.78
Total cooling (MJ/hr)								278,046.72
Total heating (MJ/hr)								575,892.79
Total energy requirement(MJ/hr)								853,939.51

Table B-33 Total energy requirement for $MgO-SiO_2$ -Na_2O (1:1)(0.1%) catalyst in sequence 1

Catalyst process	No. Sequence	Name of Equipment	Stream name	Type	Inlet temperature(°C)	Outlet temperature(°C)	mCp	Heat duty (MJ/hr)
$MgO-SiO_2$-Na_2O(1:1)(0.1%)	1	H-211	S21-01	Cool	35	350	362.87	114,304.66
		R-211	S21-02	Hot	350	349.5	1,002,619.37	501,309.68
		C-211	S21-03	Cool	349.5	498.18	189.62	28,193.43
		H-212	S21-04	Hot	498.18	35	222.89	103,239.54
		DCON-211	S21-05	Cold	35	71.4	39.63	1442.39
		DREB-211	S21-05	Cold	35	92.03	256.92	14,652.20
		DCON-212	S21-07	Hot	92.03	91.09	106,927.38	100,776.91
		DREB-212	S21-07	Cold	92.03	131.01	3,014.56	117,519.52
Total cooling (MJ/hr)								205,458.85
Total heating (MJ/hr)								775,979.48
Total energy requirement(MJ/hr)								981,438.33

Table B-34 Total energy requirement for MgO-SiO$_2$ -Na$_2$O (1:1)(0.1%) catalyst in sequence 2

Catalyst process	No. Sequence	Name of Equipment	Stream name	Type	Inlet temperature(°C)	Outlet temperature(°C)	mCp	Heat duty (MJ/hr)
MgO-SiO$_2$-Na$_2$O(1:1)(0.1%)	2	H-221	S22-01	Cool	35	350	362.87	114,304.66
		R-221	S22-02	Hot	350	349.5	1,002,619.37	501,309.68
		C-221	S22-03	Cool	349.5	498.18	189.62	28,193.43
		H-222	S22-04	Hot	498.18	35	222.89	103,239.54
		DCON-221	S22-05	Cool	35	87.82	961.20	50,770.82
		DREB-221	S22-05	Cool	35	124.73	898.94	80,662.05
		H-223	S22-06	Hot	87.82	76.9	2,010.93	21,959.35
		DCON-222	S22-08	Hot	76.9	24.64	222.81	11,644.00
		DREB-222	S22-08	Cool	76.9	91.07	1039.80	14,734.00
Total cooling (MJ/hr)								187,613.72
Total heating (MJ/hr)								739,203.82
Total energy requirement(MJ/hr)								926,817.54

Table B-35 Total energy requirement for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1

Catalyst process	No. Sequence	Name of Equipment	Stream name	Type	Inlet temperature(°C)	Outlet temperature(°C)	mCp	Heat duty (MJ/hr)
Hf2.5Zm1.6/SiO2	1	H-311	S31-01	Cool	35	300	400.33	106,088
		R-311	S31-02	Hot	300	299.5	916,203.44	458,101.72
		C-311	S31-03	Cool	299.5	453.31	179.18	27,559.45
		H-312	S31-04	Hot	453.31	72.54	235.19	89,552.43
		DCON-311	S31-05	Hot	72.54	3.3749	250.19	17,304.49
		DREB-311	S31-06	Cool	72.54	96.1578	945.60	22,332.88
		DCON-312	S31-08	Hot	96.15	91.31	28,063.82	135,958
		DREB-312	S31-08	Cool	96.15	145.10	3,119.21	152,698
		DCON-313	S31-09	Hot	91.3	14.12	906.52	69,965
		DREB-313	S31-09	Cool	91.3	52.02	1,625.15	63,836
		DCON-314	S31-12	Hot	52.03	14.7	533.99	19,934
		DREB-314	S31-12	Cool	52.03	110.67	1,447.02	84,853
		H-313	S31-16	Hot	110.67	35	852.28	64,492
		SP-311	S31-17		35	35		
		M-311	S31-18		35	35		
		P-311	S31-19		35	35		
Total cooling (MJ/hr)								397,205.92
Total heating (MJ/hr)								915,469.05
Total energy requirement(MJ/hr)								1,312,674.97

Table B-36 Total energy requirement for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 2

Catalyst process	No. Sequence	Name of Equipment	Stream name	Type	Inlet temperature(°C)	Outlet temperature(°C)	mCp	Heat duty (MJ/hr)
$Hf_{2.5}Zm_{1.6}/SiO_2$	2	H-321	S32-01	Cool	35	300	400.33	106,088
		R-321	S32-02	Hot	300	299.5	916,204.00	458,102
		H-322	S32-03	Hot	299.5	-41.05	238.89	81,355.51
		DCON-321	S32-04	Hot	-41.05	-7.52	7,756.84	260,086.71
		DREB-321	S32-04	Cool	-41.05	12	5,466.69	290,008
		H-323	S32-05	Hot	-7.53	-45.17	776.70	29,234.8
		DCON-322	S32-07	Hot	-45.18	-65.47	316.76	6,427.03
		DREB-322	S32-07	Cool	-45.18	-4.628	316.03	12,815.74
		P-321	S32-09		-4.63	-4.63		
		DCON-323	S32-12	Cool	-4.56	14.04	1,400.97	26,058
		DREB-323	S32-12	Cool	-4.56	60.61	878.12	57,227
		DCON-324	S32-14	Hot	60.61	14.7	437.70	20,095
		DREB-324	S32-14	Cool	60.61	179.05	1,164.61	137,937
		SP-321	S32-16		179.05	179.05		
		H-324	S32-18	Hot	179.05	35	868.66	125,131
		M-321	S32-19		35	35		
		P-322	S32-21		35	35		
Total cooling (MJ/hr)								548,388.05
Total heating (MJ/hr)								1,062,177.74
Total energy requirement(MJ/hr)								1,610,565.79

APPENDIX C

Composite curves

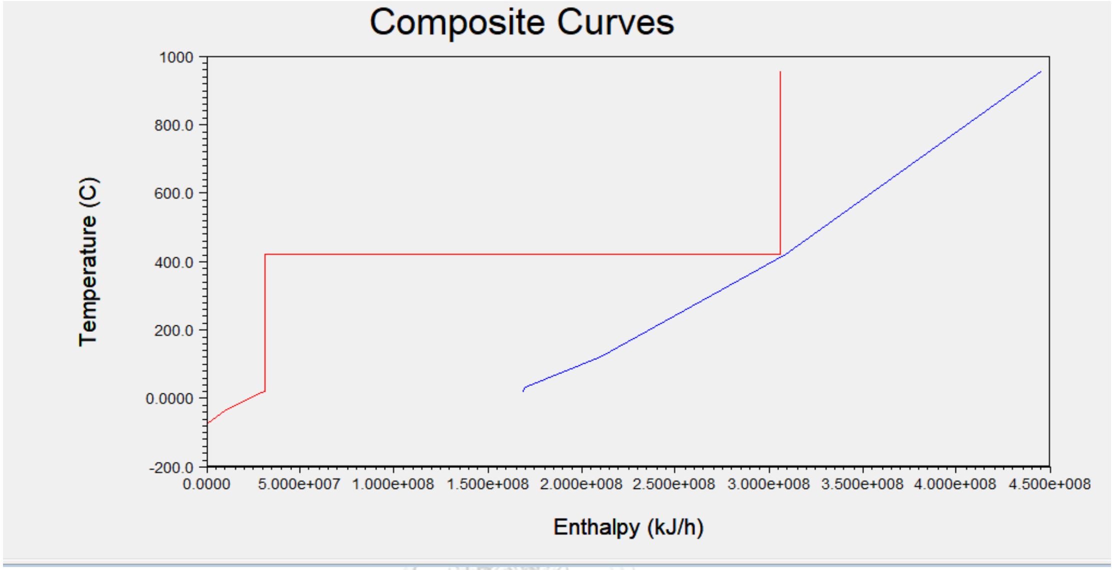

Figure C-42 Composite curve for Al_2O_3/ZnO (60:40) catalyst sequence 1

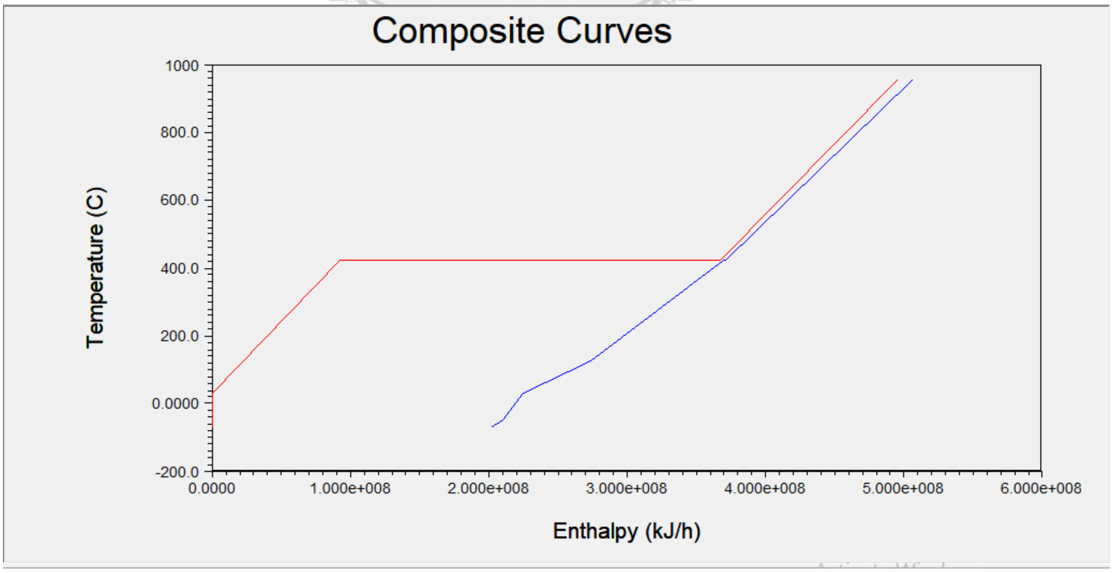

Figure C-43 Composite curve for Al_2O_3/ZnO (60:40) catalyst sequence 2

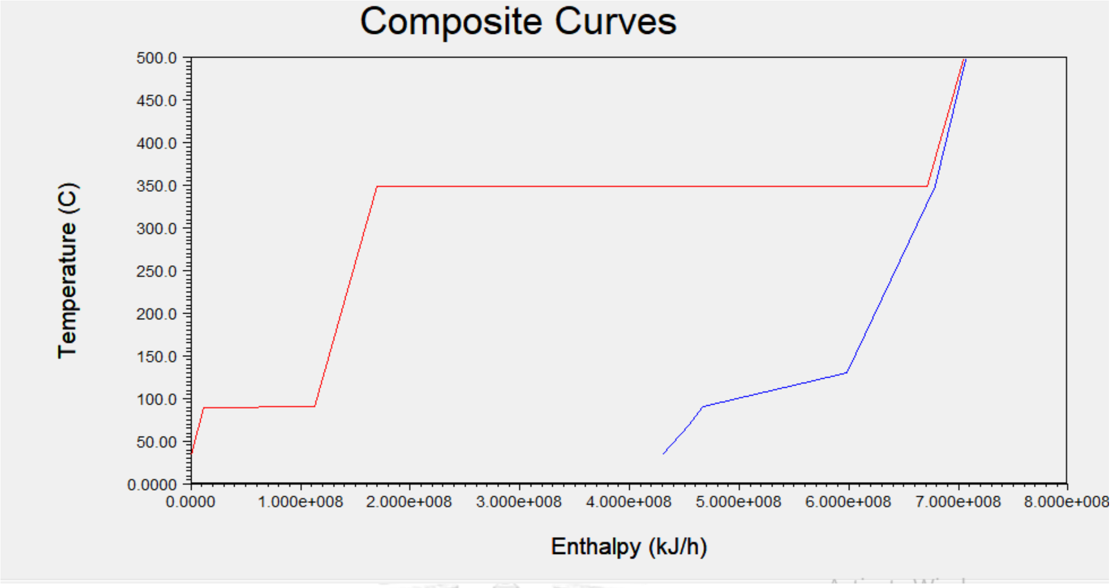

Figure C-44 Composite curve for MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst sequence 1

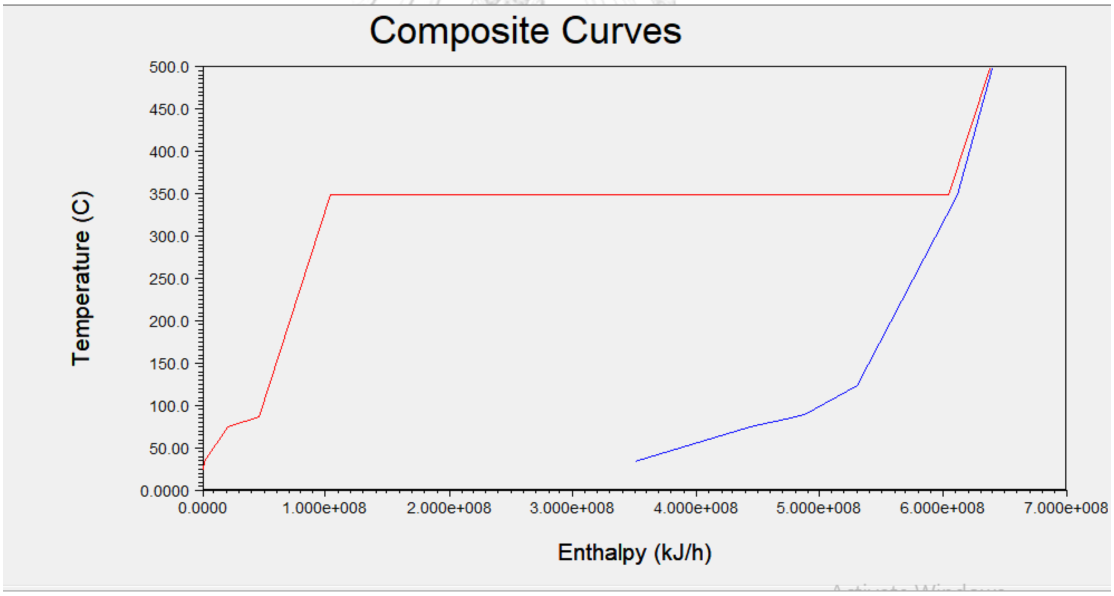

Figure C-45 Composite curve for MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst sequence 2

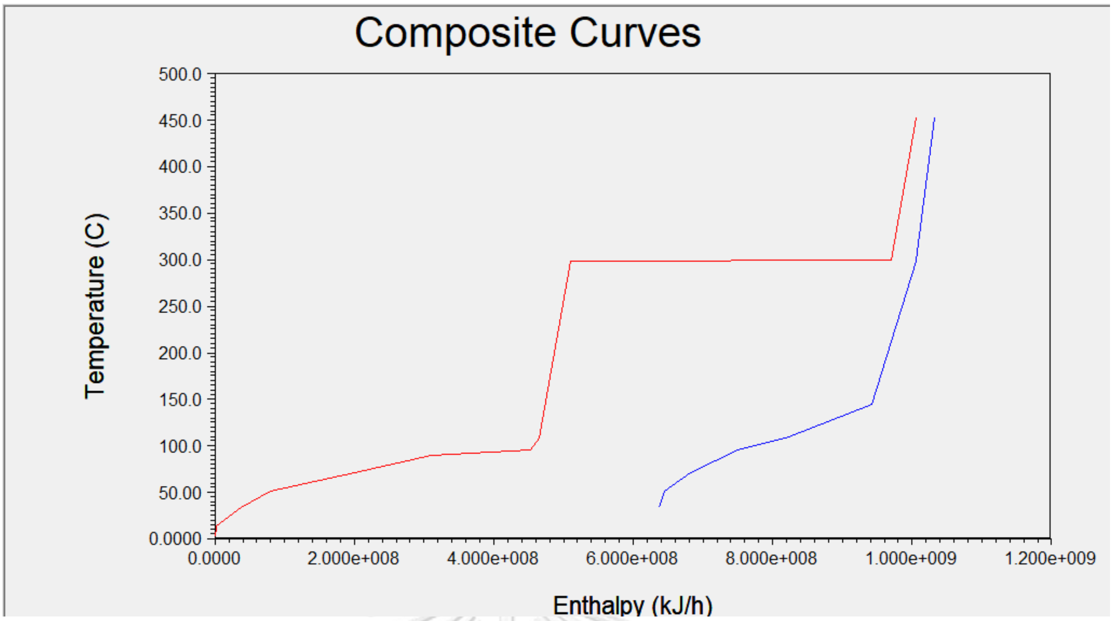

Figure C-46 Composite curve for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst sequence 1

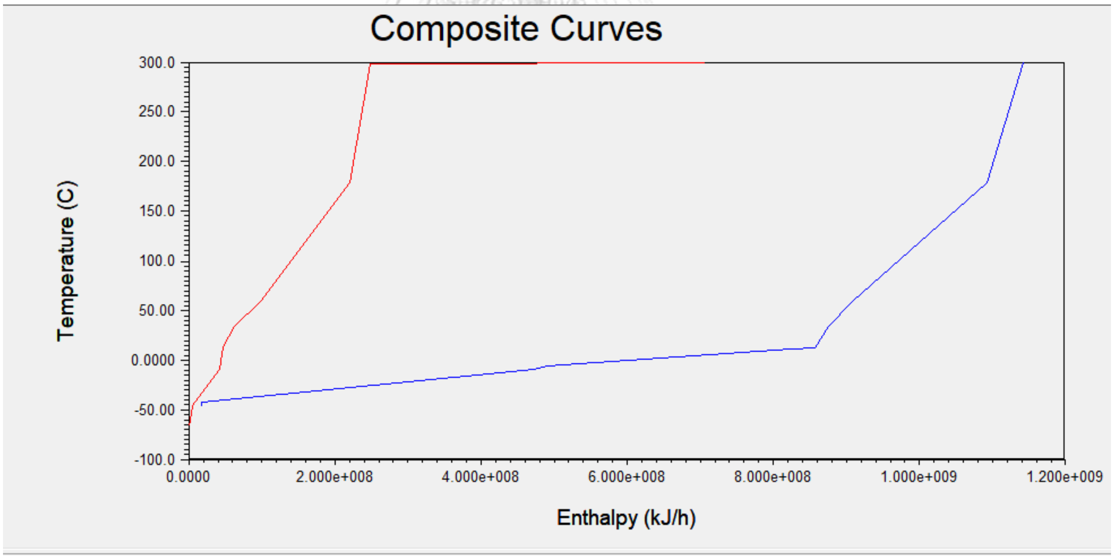

Figure C-47 Composite curve for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst sequence 2

APPENDIX D

Heat exchanger network and heat flow after heat integration

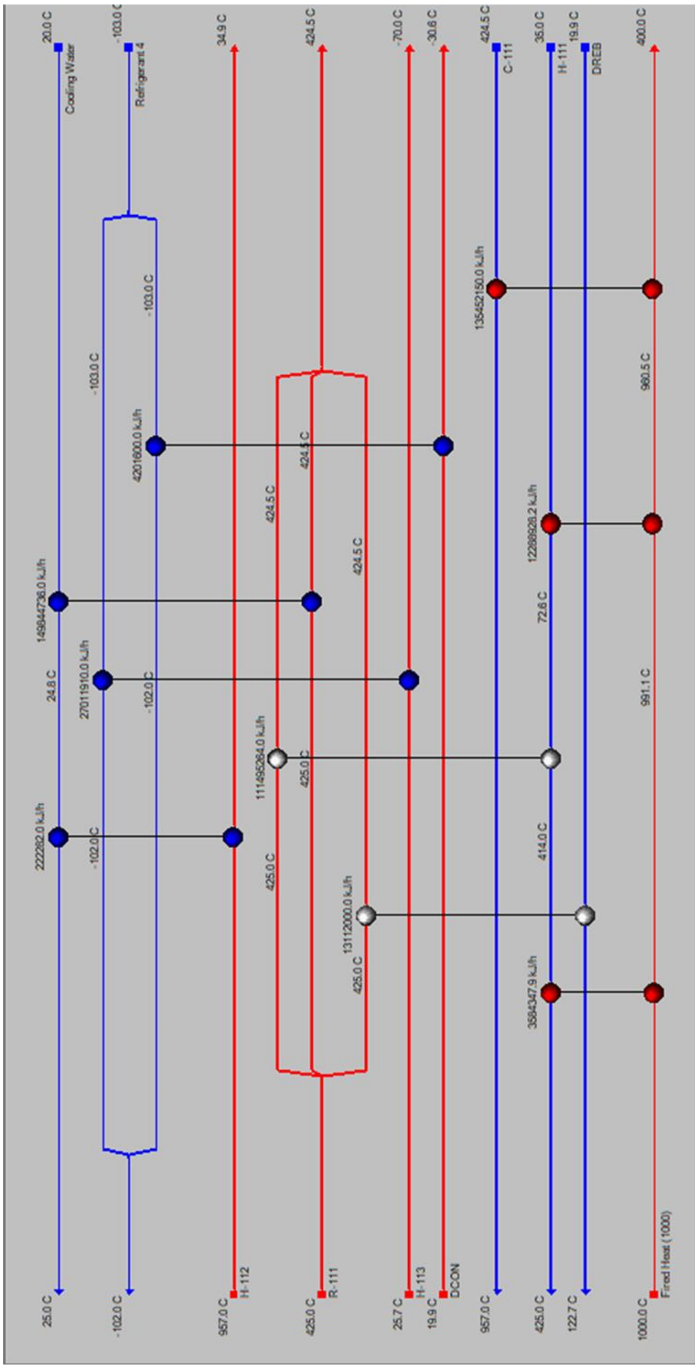

Figure D-48 Heat integration for Al_2O_3/ZnO (60:40) catalyst in sequence 1

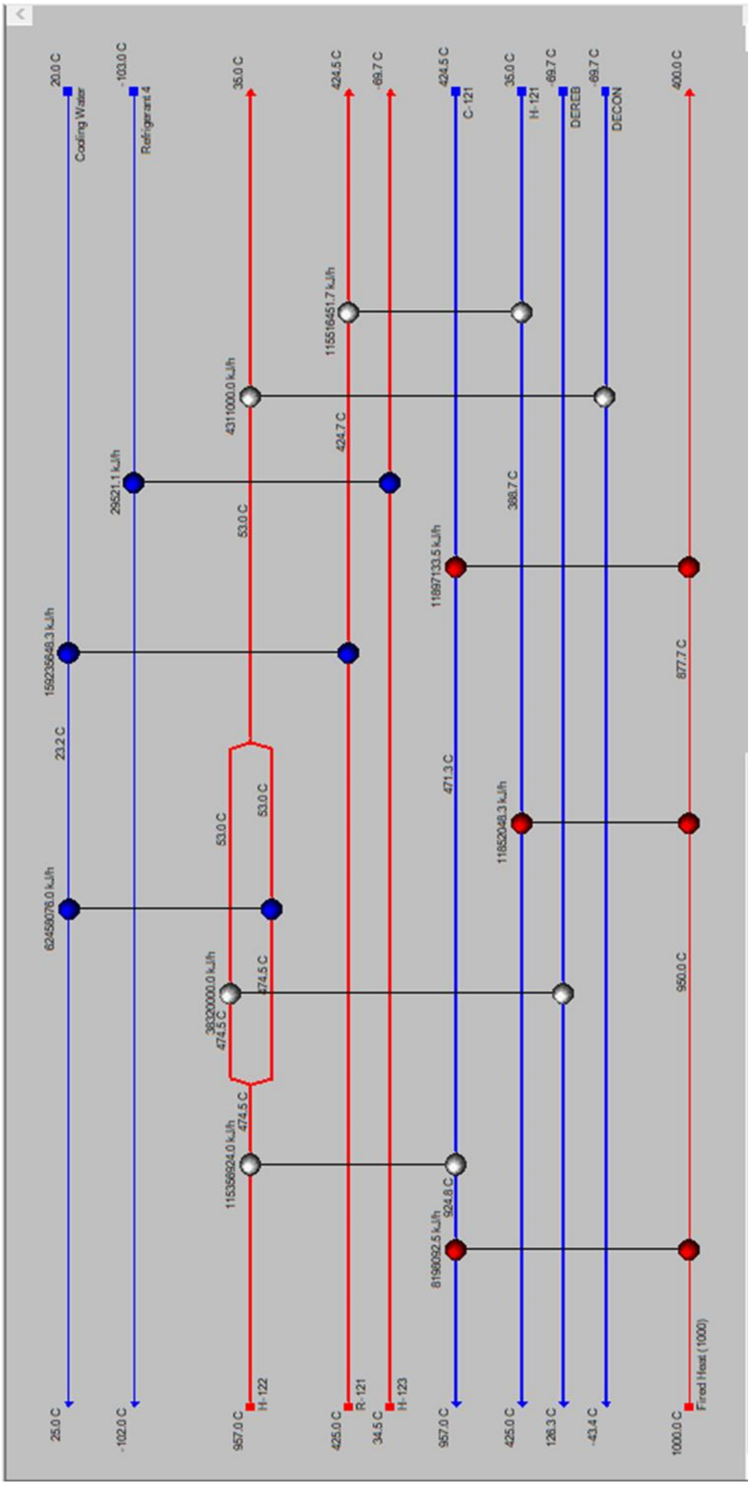

Figure D-49 Heat integration for Al_2O_3/ZnO (60:40) catalyst in sequence 2

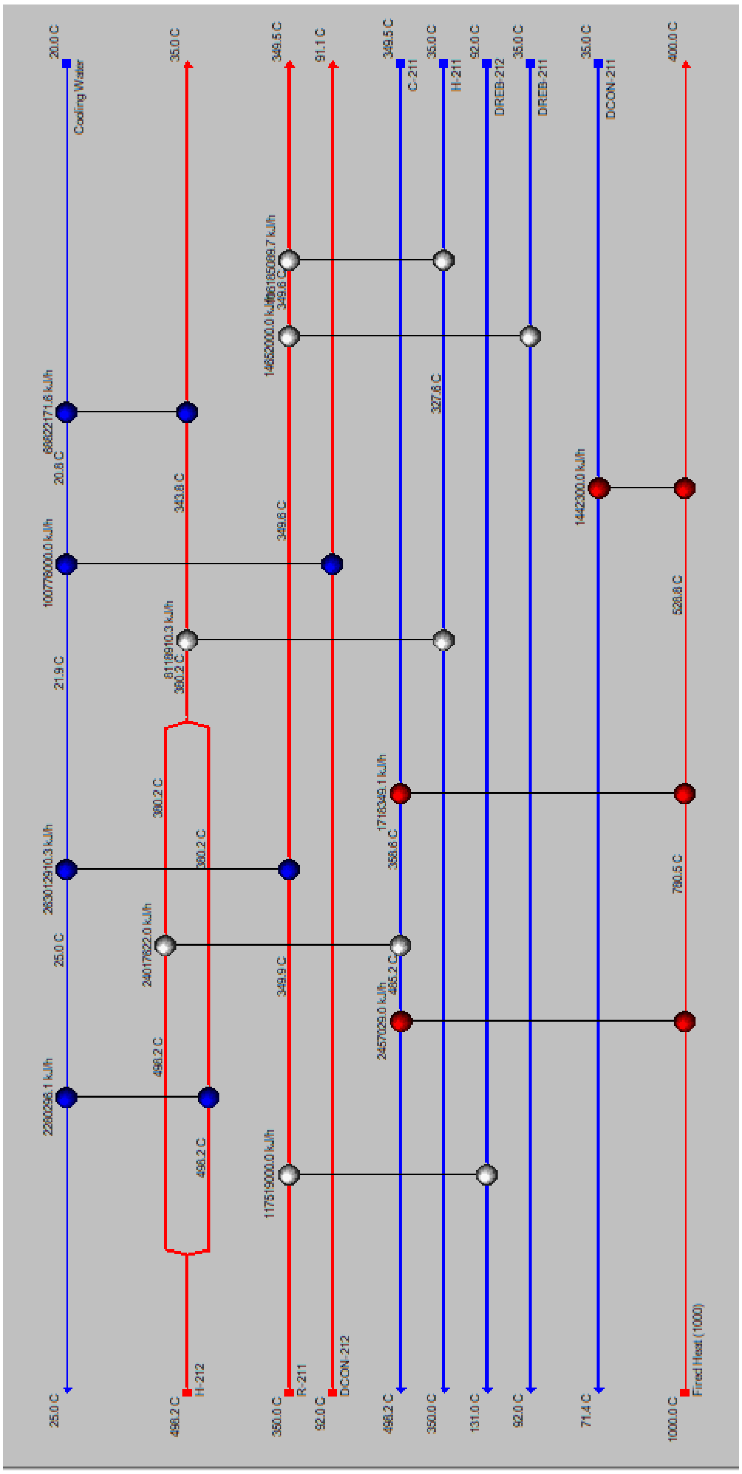

Figure D-50 Heat integration for MgO-SiO$_2$ -Na$_2$O (1:1)(0.1%) catalyst in sequence 1

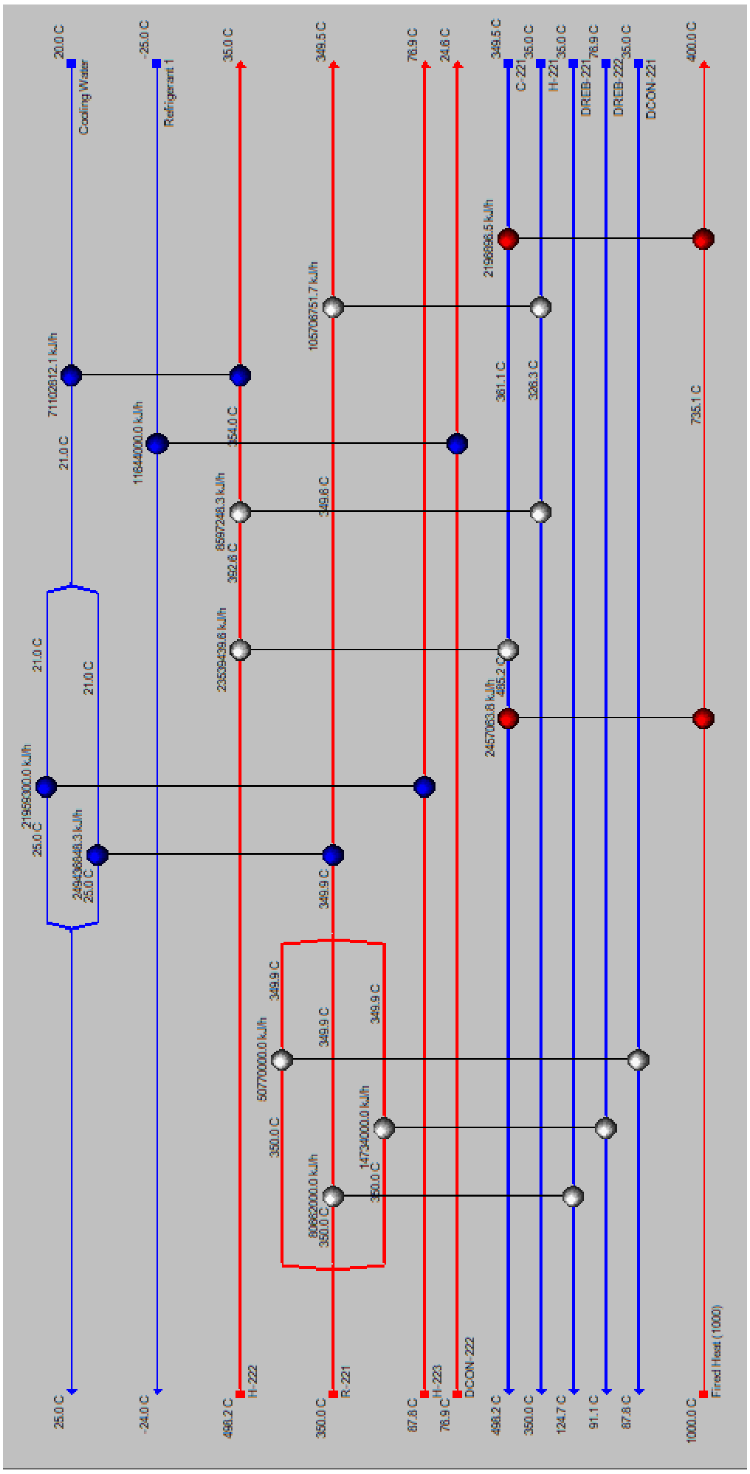

Figure D-51 Heat integration for MgO-SiO_2-Na_2O (1:1)(0.1%) catalyst in sequence 2

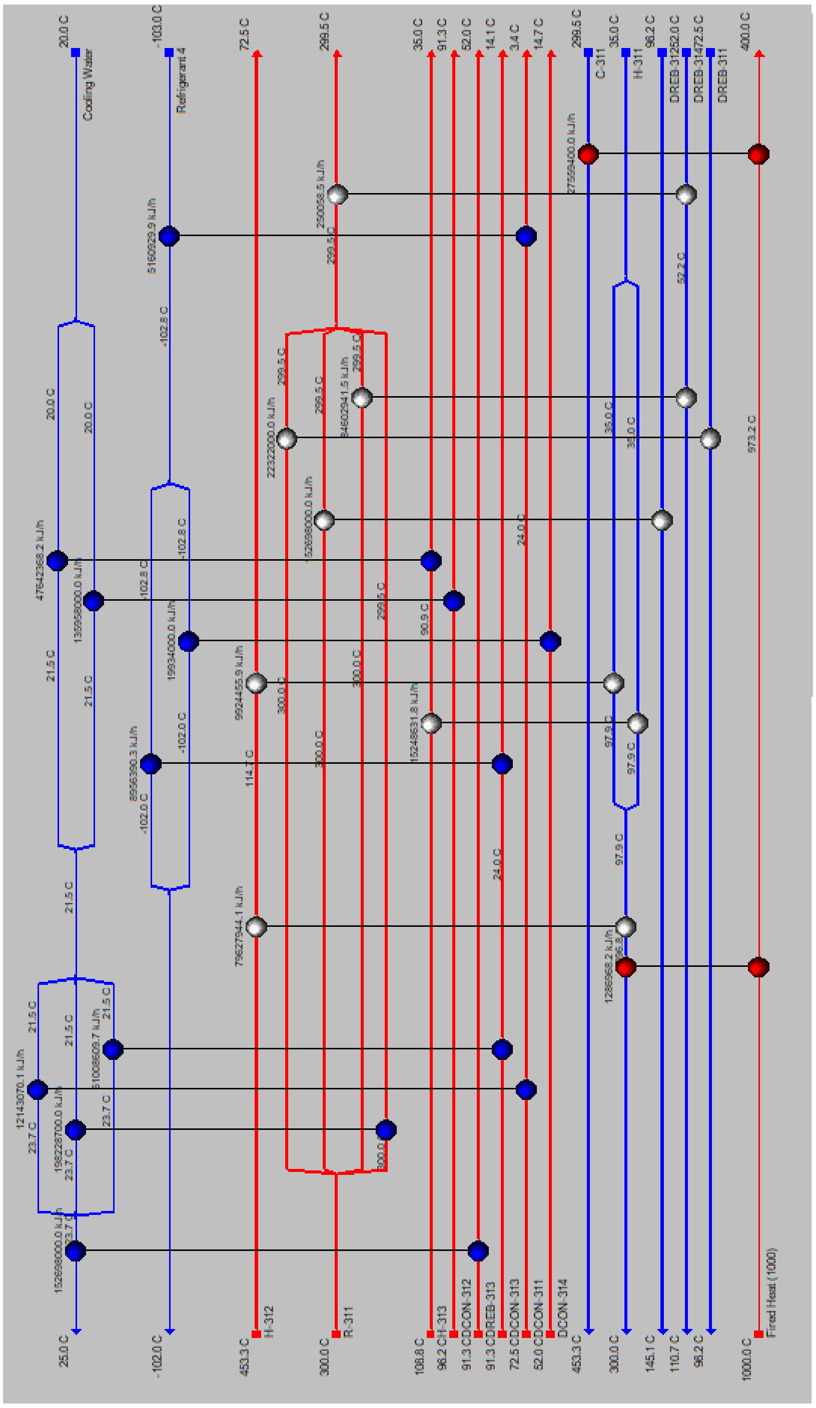

Figure D-52 Heat integration for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst sequence 1

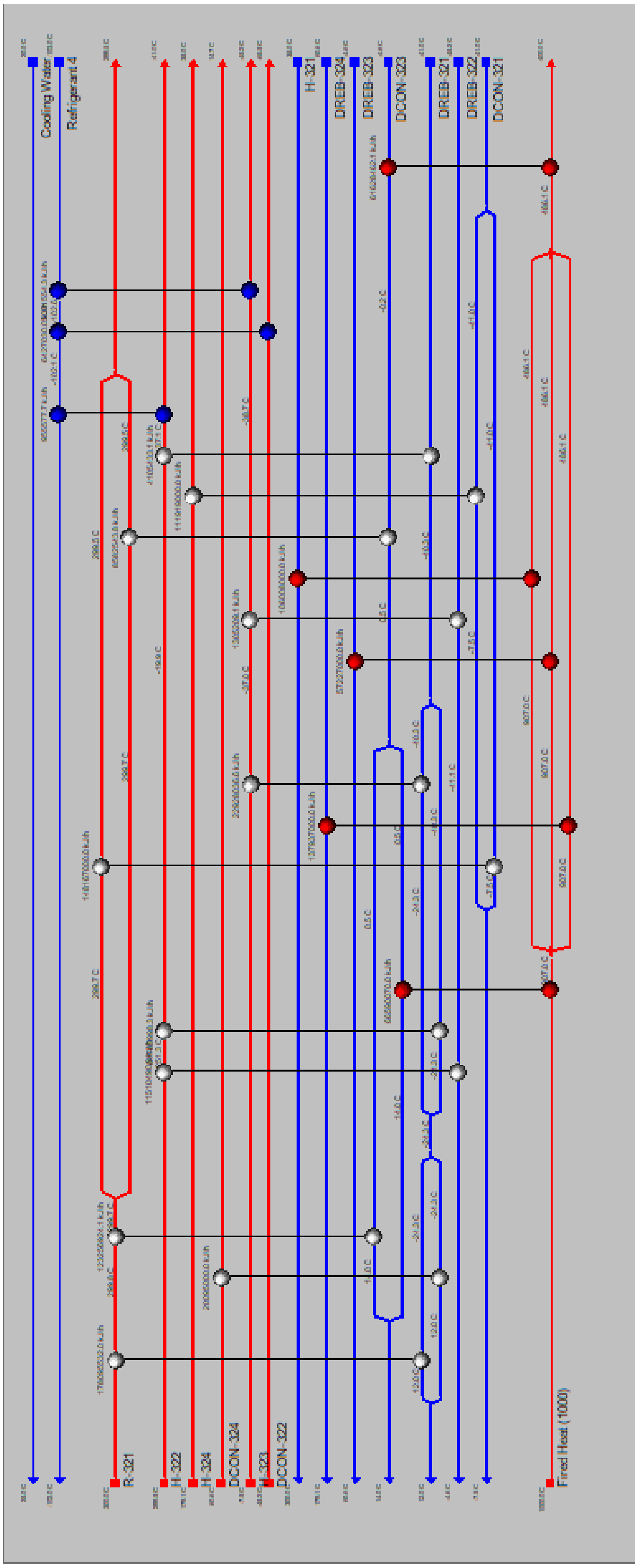

Figure D-53 Heat integration for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst sequence 2

APPENDIX E

Heat exchanger network and heat flow after heat integration

Table E-37 Summarization of temperature after heat integration for Al_2O_3/ZnO (60:40) catalyst in sequence 1

Heat exchanger	Hot	Cold	Hot inlet temperature	Hot outlet temperature	Cold inlet temperature	Cold outlet temperature	Load(MJ/hr)
	stream	stream	(°C)	(°C)	(°C)	(°C)	(MJ/hr.)
E-103	Fired Heat (1000)	H-111	1000	991	414.02	425	3,584.3
E-104	R-111	H-111	425	424.5	72.62	414.02	11,1495
E-105	R-111	Cooling Water	425	424.5	20	24.77	14,9844
E-106	R-111	DREB	425	424.5	19.85	12,2.65	13,112
E-107	Fired Heat (1000)	H-111	991	960	35	72.62	12,288.92
E-108	Fired Heat (1000)	C-111	960	623	424.5	956.98	135,452.15
E-109	H-113	Refrigerant 4	25.66	-69.98	-103	-102	27,011.91
E-110	H-112	Cooling Water	956.98	34.85	24.77	25	222.28
E-111	DCON	Refrigerant 4	19.85	-30.58	-103	-102	4,201.6
Total cooling utility							181,281
Total heating utility							151,325
Total utility from heat integration							332,606
Saving (%)							60.36

Table E-38 Summarization of temperature after heat integration for Al_2O_3/ZnO (60:40) catalyst in sequence 2

Heat exchanger	Hot	Cold	Hot inlet temperature	Hot outlet temperature	Cold inlet temperature	Cold outlet temperature	Load(MJ/hr)
	stream	stream	(°C)	(°C)	(°C)	(°C)	(MJ/hr.)
E-102	Fired Heat (1000)	C-121	1000	950	924	956.98	8,198.09
E-103	R-121	Cooling Water	425	424.5	20	23.16391865	159235.6483
E-104	H-122	C-121	956	474.51	471.26	924.75	115,356.92
E-105	Fired Heat (1000)	H-121	950.00	877.71	388.70	425	11,852.04
E-106	H-122	DEREB	474.51	53.03	-69.69	126.33	38,320
E-107	H-122	Cooling Water	474.51	53.03	23.16	25	62,458.07
E-108	R-121	H-121	424.71	424.5	35	388.70	115,516.45
E-109	Fired Heat (1000)	C-121	877.71	805.15	424.5	471.26	11,897.13
E-110	H-122	DECON	53.03	35	-69.69	-43.43	4311
E-111	H-123	Refrigerant 4	34.5	-69.69	-103	-102	29.52
Total cooling utility							221,723
Total heating utility							31,947
Total utility from heat integration							253,671
Saving (%)							70.29

Table E-39 Summarization of temperature after heat integration for MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 1

Heat exchanger	Hot	Cold	Hot inlet temperature	Hot outlet temperature	Cold inlet temperature	Cold outlet temperature	Load
	stream	stream	(°C)	(°C)	(°C)	(°C)	(MJ/hr.)
E-101	Fired Heat (1000)	C-211	1000	780.51	485.22	498.18	2,457
E-102	R-211	DREB-212	350	349.88	92.03	131.01	117,519
E-103	H-212	C-211	498.18	380.19	358.56	485.22	24,018
E-104	H-212	Cooling Water	498.18	380.19	24.97	25	2,280
E-105	H-212	H-211	380	343.76	327.62	350	8,119
E-106	R-211	Cooling Water	349.88	349.62	21.94	24.97	263,013
E-107	Fired Heat (1000)	C-211	780.51	528.83	349.5	358.56	1,718
E-108	Fired Heat (1000)	DCON-211	528.83	400	35	71.4	1,442
E-109	R-211	DREB-211	349.62	349.60	35	92.03	14,652
E-110	DCON-212	Cooling Water	92.03	91.09	20.79	21.94	100,776
E-111	R-211	H-211	349.60	349.5	35	327.62	106,185
E-112	H-212	Cooling Water	343.76	35	20	20.79	68,822
Total cooling utility							434,891
Total heating utility							5,618
Total utility from heat integration							440,509
Saving (%)							55.12

Table E-40 Summarization of temperature after heat integration for MgO-SiO_2 -Na_2O (1:1)(0.1%) catalyst in sequence 2

Heat exchanger	Hot	Cold	Hot inlet temperature	Hot outlet temperature	Cold inlet temperature	Cold outlet temperature	Load
	stream	stream	(°C)	(°C)	(°C)	(°C)	(MJ/hr.)
E-103	Fired Heat (1000)	C-221	1000	735.06	485.22	498.18	2,457
E-104	H-222	C-221	498.18	392.57	361.08	485.22	23,539
E-105	R-221	DCON-221	350	349.85	35	87.82	50,770
E-106	R-221	DREB-221	350	349.85	35	124.73	80,662
E-107	R-221	DREB-222	350	349.85	76.9	91.07	14,734
E-108	H-222	H-221	392.57	354	326.30	350	8,597
E-109	H-223	Cooling Water	87.82	76.9	21.03	24.99	21,959
E-110	R-221	Cooling Water	349.85	349.60	21.03	24.99	249,437
E-111	Fired Heat (1000)	C-221	735.06	400	349.5	361.08	2,197
E-112	DCON-222	Refrigerant 1	76.9	24.64	-25	-24	11,644
E-113	R-221	H-221	349.60	349.5	35	326.30	105,707
E-114	H-222	Cooling Water	354	35	20	21.03	71,103
Total cooling utility							354,143
Total heating utility							4,654
Total utility from heat integration							358,797
Saving (%)							61.29

Table E-41 Summarization of temperature after heat integration for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 1

Heat exchanger	Hot	Cold	Hot inlet temperature	Hot outlet temperature	Cold inlet temperature	Cold outlet temperature	Load
	stream	stream	(°C)	(°C)	(°C)	(°C)	(MJ/hr.)
E-111	H-312	H-311	453.31	95.08	86.33	300	84,249
E-112	Fired Heat (1000)	H-311	1000	973.23	86.33	300	1,286.96
E-113	H-313	Cooling Water	108.8	97.25	22.76	25	9,837.24
E-114	R-311	Cooling Water	300	299.78	22.76	25	198,228.7
E-115	H-312	H-311	95.08	72.54	35	86.33	5,303.17
E-116	H-313	H-311	97.25	79.36	35	86.33	15,248.63
E-117	DCON-313	Refrigerant 1	29	14.12	-24.26	-24	13,488.97
E-118	DCON-312	Cooling Water	96.15	91.31	20.31	22.76	135,958
E-119	DREB-313	Cooling Water	91.3	52.02	20.31	22.76	152,698
E-120	R-311	DREB-311	299.78	299.50	72.54	96.15	22,322
E-121	R-311	DREB-312	299.78	299.50	96.15	145.1	152,698
E-122	R-311	DREB-314	299.78	299.50	52.20	110.67	84,602.94
E-123	H-313	Cooling Water	79.36	35	20	20.31	37,805.11
E-124	Fired Heat (1000)	C-311	973.23	400	299.5	453.31	27,559.4
E-125	DCON-311	Refrigerant 1	72.54	3.37	-25	-24.26	17,304
E-126	DCON-314	Refrigerant 1	52.03	14.7	-25	-24.26	19,934
E-127	R-311	DREB-314	299.50	299.5	52.03	52.20	250.05
Total cooling utility							571,765
Total heating utility							28,846

Total utility from heat integration							600,611
Saving (%)							54.29

Table E-42 Summarization of temperature after heat integration for $Hf_{2.5}ZM_{1.6}/SiO_2$ catalyst in sequence 2

Heat exchanger	Hot	Cold	Hot inlet temperature	Hot outlet temperature	Cold inlet temperature	Cold outlet temperature	Load
	stream	stream	(°C)	(°C)	(°C)	(°C)	(MJ/hr.)
E-111	R-321	DREB-321	300	299.80	-24.25	12	178,095.53
E-112	H-322	DREB-322	299.5	251.31	-41.05	-4.628	11,510.49
E-113	DCON-324	DREB-321	60.61	14.7	-24.25	12	20,095
E-114	H-322	DREB-321	251.31	-19.86	-40.29	-24.25	64,783.99
E-115	H-322	DREB-321	-19.86	-37.05	-41.05	-40.29	4,105.43
E-116	H-322	Refrigerant 4	-37.05	-41.05	-102.07	-102	955.57
E-117	R-321	DCON-323	299.80	299.67	0.46	14.04	123,256.92
E-118	Fired Heat (1000)	DCON-323	1,000	906.95	0.46	14.04	66,590.06
E-119	Fired Heat (1000)	H-321	906.95	486.1152598	35	300	10,6008
E-120	H-324	DCON-321	179.05	35	-41.05	-7.52	111,919
E-121	R-321	DCON-321	299.67	299.5	-41.05	-7.52	148,167
E-122	DCON-322	Refrigerant 4	-45.18	-65.47	-102.59	-102.07	6,427.03
E-123	R-321	DCON-323	299.67	299.5	-0.15	0.46	8,582.54
E-124	Fired Heat (1000)	DREB-323	906.95	486.11	-4.56	60.61	57,227
E-125	Fired Heat (1000)	DREB-324	906.95	486.11	60.61	179.05	13,7937
E-126	H-323	Refrigerant 4	-38.73	-45.17	-103	-102.59	5,001.55
E-127	Fired Heat (1000)	DCON-323	486.11	400	-4.56	-0.15	61,628.46
Total cooling utility							12,384
Total heating utility							429,391

Total utility from heat integration							441,775
Saving (%)							72.57

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