การสังเคราะห์ 1,1-ไดอีท็อกซิอีเทนและ 1,1-ไดบิวท็อกซิอีเทนจากอะซิตัลดีไฮด์และไบโอแอลกอฮอล์โดยใช้หอกลั่นแบบเกิดปฏิกิริยา

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SYNTHESIS OF 1,1-DIETHOXYETHANE AND 1,1-DIBUTHOXYETHANE FROM ACETALDEHYDE AND BIOALCOHOL USING REACTIVE DISTILLATION

Miss Katewadee Chantowas

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By	Miss Katewadee Chantowas
Field of Study	Chemical Engineering
Thesis Advisor	Professor Suttichai Assabumrungrat, Ph.D.
Thesis Co-Advisor	Assistant Professor Worapon Kiatkittipong, D.Eng.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering

(Professor Bundit Chulasai, Ph.D.)

THESIS COMMITTEE

....Chairman

(Associate Professor Muenduen Phisalaphong, Ph.D.)

....Thesis Advisor

(Professor Suttichai Assabumrungrat, Ph.D.)

....Thesis Co-Advisor

(Assistant Professor Worapon Kiatkittipong, D.Eng.)

....Examiner

(Associate Professor Bunjerd Jongsomjit, Ph.D.)

....External Examiner

(Kanokwan Ngaosuwan, D.Eng.)

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This work focused on process development for synthesis of 1,1-diethoxyethane (DEE) and 1,1-dibutoxyethane (DBE) in reactive distillation. The RADFRAC module with equilibrium stage in Aspens Plus program was used to simulate the reactive distillation. The studies were divided into 2 main systems - one is combined synthesis of DEE and DBE in a single reactive distillation column and the other involves two reactive distillation columns for synthesis of each product in a separate column. The effects of design and operating parameters on acetaldehyde conversion, yield and purity of DEE and DBE were investigated. It was found that the synthesis in one reactive distillation column is not beneficial. For DEE synthesis, the suitable design and operating parameters are as follows: 3 stripping stages, 7 reaction stages, 2 rectifying stages, reboiler heat duty of 6000 kW and reflux ratio of 2, offering 70% conversion of acetaldehyde and DBE yield of 70% with 99.8% purity

Department:	Chemical Engineering	Student's Signature ....
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CHAPTER I

INTRODUCTION

In recent years, demand of refined oil are increased especially diesel. Diesel fuel is the essential for the agriculture, heavy-duty engines and transportation. Energy share of diesel in refined oil demand in Thailand is high as 42% [1]. The concern about exhaust emissions from diesel combustion has been increasing, since when compared to gasoline, diesels tend to emit higher NOx and particulate matter[2]. Therefore, emissions from diesel engine seriously threaten the environment and are considered as one of the major sources of air pollution. Increasing worldwide concern on combustion-related pollutants, such as particulate matter (PM), oxides of nitrogen (NOx), carbon monoxide (CO), total hydrocarbons (THC), acid rain, and photochemical smog, drives several countries to regulate emissions and to give directions for implementation and compliance. It is commonly accepted that clean combustion of diesel engines can be fulfilled only if engine development is coupled with diesel fuel reformulation or additive introduction [3-5]. Using additives of diesel fuel is a possible solution to reduce harmful emission problem and improve engine efficiency.

The groups of metal-based additives are important diesel additives. They are for examples, manganese (Mn), magnesium (Mg), copper (Cu), cerium (Ce) and calcium (Ca) which could help decrease freezing point of diesel fuel [6]. 0.2-0.5% of Mn content peroxides can reduce smoke 22-25% [7] and 50% reduction of aromatic hydrocarbons in fuel [8, 9]. Fe, Mn, and Ce additive can reduce PM [10]. Nevertheless, non-metallic, diesel enhancer additives such as 2-ethylhexyl nitrate (EHN) is the commercial diesel for cetane improver. Moreover, the diesel additives based on renewable resource are considered to be a better choice as they, avoid the metallic compounds emission.

Various diesel additives are widely studied such as dimethyl ether (DME), dimethyl carbonate (DMC) and dimethoxy methane (DMM) to reduce PM and NOx emissions [11, 12]. 2-methoxyethyl acetate (MEA) could decrease exhaust smoke [9].

Acetals are good candidates for diesel additives and they are recognized as green fuel additives which also increase cetane number in diesel fuel. The acetals are such as 1,1-diethoxyethane (DEE) [13-18], 1,1-dibutoxyethane (DBE) [19-22]. DEE and DBE are added to diesel to enhances the diesel cetane number, reduce PM and NOx emission from fuel combustion [22, 23], Moreover, DEE and DBE can be obtained from the reaction of bioalcohol and acetaldehyde, so they are completely from renewable origin. Bioalcohol such as ethanol and butanol are obtained from biomass fermentation. The conventional fermentation process converts lignocellulosic biomass to chemicals such as acetone-butanol-ethanol (ABE) fermentation process.

This process generates acetone, butanol and ethanol in a ratio of 3:6:1. Otherwise, acetaldehyde is obtained from ethanol dehydration process.

Kaulfhold et al., (1996) proposed in patent an industrial process for DEE production from ethanol and acetaldehyde in the presence of homogeneous strong acid catalyst. However, the process entails corrosion problem and is not environmental friendly. Using heterogeneous catalysts could overcome this problem. Silva V.M.T.M. and Rodrigues A.E. (2001, 2005(a) and 2005(b)) reported the thermodynamic and kinetic studies of DEE synthesis in a batch reactor by reacting ethanol and acetaldehyde in liquid phase, using acid resin Amberlyst 18 as a catalyst. Graça N.S. et al. (2010, 2011(a) and 2011(b)) performed the thermodynamic and kinetic studies of DBE synthesis in a batch reactor by reacting butanol with acetaldehyde in liquid phase using acid resin Amberlyst 15 as a catalyst. The kinetic rate models of both reactions were formulated in terms of activities.

The study of acetalization reactions indicate high thermodynamic limitation and low conversion achieved in batch reactor [11, 13, 15, 17-22, 24-26]. Reactive distillation is a promising technology to improve these limitations. [11, 24, 27, 28]. It combines chemical reaction and separation within one unit. When the products are removed from reaction mixture simultaneously, thermodynamic limitation can be shifted to higher conversion. Sharma and Chopade (1997(a) and 1997(b)) reported the acetalization reaction in reactive distillation for reactions between ethanol and formaldehyde, and ethylene glycol and formaldehyde. They found that the achieved conversion increase from 45% to 94% for the reaction of ethanol and formaldehyde and 42% to 72% for the reaction of ethylene glycol and formaldehyde, when compare with conventional batch reactor.

In this work, acetaldehyde is used to synthesize 1,1-diethoxyethane (DEE) and 1,1-dibutoxyethane (DBE) by reactingwith ethanol and butanol, respectively. The reactions of DEE and DBE synthesis can be enhanced by operating in reactive distillation systems. A suitable reactive distillation configuration will be investigated by using Aspens plus simulation program. The kinetic rate expression of reaction of DEE and DBE employed in this study are obtained from the literature.

1.1 Objective of this work

The objective of this research is to propose suitable reactive distillation configurations for synthesis of 1,1-diethoxyethane (DEE) and 1,1-dibutoxyethane (DBE) as diesel additives from bioalcohol.

1.2 Scope of Research

1. Study the synthesis of DEE and DBE from the reactions as below:

Reaction 1: 2Ethanol + Acetaldehyde ------> 1,1-Diethoxyethane (DEE) + Water (1.1)

Reaction2: 2Butanol + Acetaldehyde ------> 1,1-Dibutoxyethane (DBE) + Water (1.2)

The reactions are taken place in reactive distillation

2. Determine a suitable system for the synthesis of DEE and DBE in reactive distillation by using Aspen plus simulation program. The study is based on reaction kinetics obtained from literature Silva and Rodríguez, 2001 and Graça et al., 2010.

CHAPTER II

THEORY

This chapter presents basic knowledge of biomass as renewable energy sources. The conversion processes of biomass to chemicals, acetals formation, thermodynamic property estimation by group contribution techniques and reactive distillation are discussed.

2.1 Biomass to chemicals

Biomass has a great potential as renewable energy sources and can be derived from growing plant and animal materials such as woods from forest, wastes from agricultural and forestry processes and industrial, human and animal waste. Biomass has been used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities. The conversion technologies for utilizing biomass can be separated into four basic categories: direct combustion processes, thermochemical processes, biochemical processes and agrochemical processes.

2.1.1 Chemical from fermentation processes

Biological processes are principally microbial digestion and fermentation. The high moisture herbaceous plant such as sugar cane, corn, vegetable and cotton, marine crop and manure are suitable for biological digestion [29]. Some chemicals can be produced from renewable resources via fermentation. The advantage of fermentation processes is that the reactions are highly selective. The obtained products and by-products (e.g. hydrogen, ethanol, butanol, organic acids, etc.) can be directed toward the production of valuable chemicals as illustrated in Figure 1.

2.1.2 Acetone-Butanol-Ethanol fermentation process

The acetone-butanol-ethanol or called ABE fermentation process is the most widely potential process for production of acetone, butanol and ethanol. Moreover, yield of butanol and acetone produce from ABE fermentation are good yield and productivity. During the World War II, butanol can be synthesized from petroleum feedstock and became cheaper than the fermentation. Therefore, butanol from fermentation process was becoming to uneconomic process. However, in recently, The ABE fermentation process is of interest again because of the depletion and high cost of petroleum feedstock.

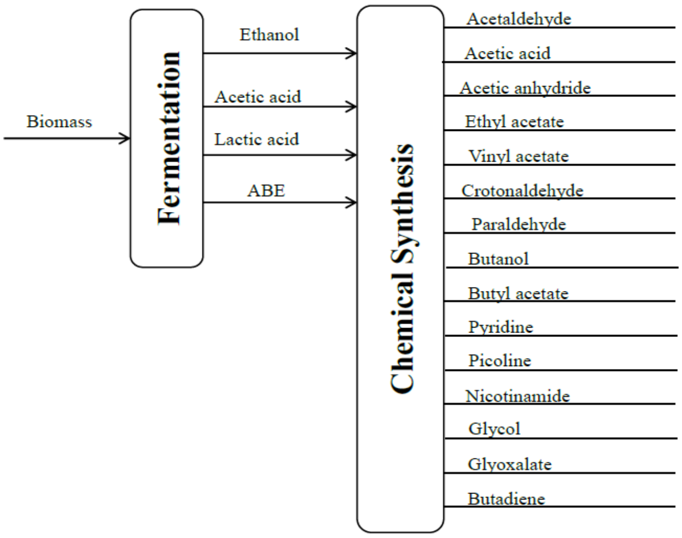

Figure 1 Chemicals produced by fermentation from carbohydrates [30].

A ratio of acetone:butanol:ethanol obtained fom ABE fermentation process is typically 3:6:1. Normally, this process is carried out at 308-310K in either batch or continuous fermentation using *Clostridium acetobutylicum,* a strictly anaerobic bacteria [31, 32].

2.2 Acetals formation

Acetals are oxygenated compounds that can be obtained from bioalcohol such as ethanol and butanol, react with carbonyl group such as acetaldehyde and acetone, in presence of acid catalyst. Water is obtained as a by-product [13-22, 27, 28].

The reaction mechanism of acetalization reaction includes two reversible steps. Firstly, one alcohol reacts with one molecule of carbonyl group, forming hemiacetal. This reaction is occurred relatively quickly at room temperature without a need of catalyst. In the second step, another molecule of alcohol reacts with the hydroxyl group of the hemiacetal arranged to form acetal and water. This second step is an exothermic reaction and can be occurred in presence of acid catalyst [11, 27].

The mechanisms of the acetalization of alcohol with aldehyde in the presence of cation-exchange resins catalyst are shown below:

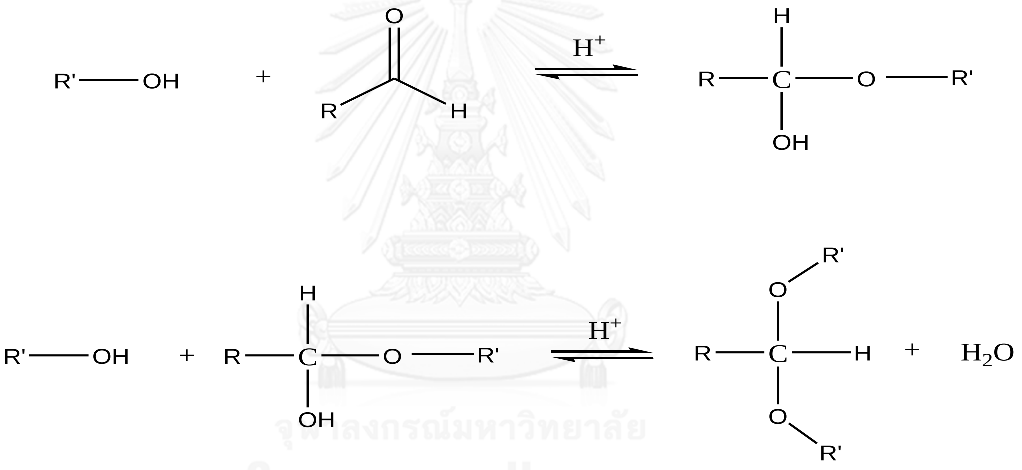

Figure 2 Mechanism for the formation of straight chain acetals [11]

2.3 Thermodynamic properties estimation technique

The missing properties of components could be estimated by using group contribution method. In this work, three estimation techniques including methods of Joback, Constantinou and Gani, and Benson are investigated [33].

2.3.1 Method of Joback

Joback method was developed from Lydersen's group contribution. The several new functional groups and contribution values were added for this method. The expressions for the estimation properties are as follows

$$T_c(K) = T_b[0.584 + 0.965\{\sum_k N_k(tck)\} - \{\sum_k N_k(tck)\}^2]^{-1} \tag{2.1}$$

$$P_c(bar) = [0.113 + 0.0032 N_{atoms} - \sum_k N_k(pck)]^{-2} \tag{2.2}$$

$$T_b = 198 + \sum_k N_k(tbk) \tag{2.3}$$

$$\Delta G_f^0 = 53.88 + \sum_k N_k(gfk) \tag{2.4}$$

where, tck and pck are the contributions. The estimation of critical properties of Joback's method for T_c involves experimental boiling point. When the estimation of boiling point is used, the error is increased. The errors are reduced for compounds with 3 or more carbon. The error of P_c parameter is increased for the large molecules such as ring compounds. For Gibb's free energy formation estimation, Joback's method is marginally accurate for all substances and slightly accurate for halogenated compounds. Joback's method is the simplest method for estimation of missing properties; however, large errors for some components might be occurred by this method.

2.3.2 Method of Constantinou and Gani

Method of Constantinou and Gani contains a more complicate function based on UNIFAC group for contribution at a “Second order” level. The special configuration compounds such isomer and resonance structure estimation, hence provide more flexibility. The Constantinou and Gani relations are as follows

$$T_c(K) = 181.128\ln[\sum_k N_k(tc1k) + W\sum_j M_j(tc2j)] \quad (2.5)$$

$$P_c(bar) = [\sum_k N_k(pc1k) + W\sum_j M_j(pc2j) + 0.10022]^{-2} + 1.3705 \quad (2.6)$$

$$T_b(K) = 204.359\ln[\sum_k N_k(tb1k) + W\sum_j M_j(tb2j)] \quad (2.7)$$

$$\Delta G_f^o(kJmol^{-1}) = -14.83 + [\sum_k N_k(gf1k) + W\sum_j M_j(gf2j)] \quad (2.8)$$

Method of Constantinou and Gani is quite reliable for the estimation of all critical properties. The large error was affected from the very smallest molecule and very largest molecules. Moreover, method of Constantinou and Gani is more accurate than method of Joback for normal boiling point estimation. For Gibb’s free energy formation estimation, method of Constantinou and Gani is quite reliable for components with three or more carbon atoms. However, for small molecules and perfluo-groups compounds the error is increase. Poling et al. (2001) claimed that with employing method of Constantinou and Gani for about 350 substances, the average absolute errors of $\Delta G^{o}{}_{f}$ at 298 K is 4.8 kJ/mol [33].

2.3.3 Method of Benson

The extensive method was developed by Benson. The thermodynamic properties such as standard enthalpy of formation and standard Gibb’s free energy of formation were estimated. This method is based on the next-nearest neighbor interactions and contributions of the bonding arrangements whose chosen groups can interact with other atom or group except for hydrogen. The Benson relations are

$$\Delta H_f^o(298.15K) = \sum_k N_k(\Delta H_{fk}^o) \tag{2.9}$$

$$S^o(298.15K) = \sum_k N_k(S_k^o + S_s^o) + S_s^o \tag{2.10}$$

$$S_{el}^o(298.15K) = \sum_e v_e(S_e^o) \tag{2.11}$$

$$\Delta G_f^o(298.15K) = \Delta H_f^o(298.15K) - 298.15[S^o(298.15K) - S_{el}^o(298.15K)] \tag{2.12}$$

The symmetry entropy ($S^{o}{}_{s}$) is independent of *T* and given below

$$S_s^o = R\ln(N_{oi}) - R\ln(N_{ts}) \tag{2.13}$$

where, N_{oi} is the number of structural isomers of the molecule that especially equal to 1 and N_{ts} is the total symmetry number. N_{ts} can be obtained from two distinct types of indistinguishability including internal (N_{is}) and external (N_{es}). The rotating terminal groups to interior groups can provide the value of N_{is}. N_{es} can be obtained from indistinguishability if the rigid molecule is rotated. Moreover, N_{ts} can be obtained from

$$N_{ts} = N_{es} \bullet \prod_{k=term} (N_{is})_k \tag{2.14}$$

Normally, Benson's method is the most accurate and reliable estimation method. For the comparison of three group contribution methods, the Poling et al. 2001 claim that Benson's method provided the smallest errors when the absolute property is less than 10 kJ/mol [33]; Moreover, this method is more complicated than Joback's and Gani's methods.

2.4 Reactive distillation

Reactive distillation (RD) is accepted as a high potential technology for process intensification. It combines reaction and separation processes in a single unit. In many cases, chemical reactions are restricted by equilibrium limitation. Reactive distillation technology could alleviate these problems. Moreover, it can solve complicate separation of mixture, high desired product purity, reduce the energy consumption and reduce of plant cost. However, reactive distillation has some difficulty such as the requirement of the some operation windows for both reaction and separation [34].

In a reactive distillation column, reaction and separation occur simultaneously within the part of column containing catalyst. By continuously separating products from reactants while the reaction is operated, the reaction can proceed to much high level of conversion. Reactive distillation process can successfully be used to several chemical reactions including esterification, etherification, acetalization, alkylation, hydrogenation and hydration.

2.4.1 Reactive distillation configuration

The reactive distillation configurations are composed of rectifying section taking place non-azeotropic chemical system and separation, reactive section in middle section of column and the purification of product take place in the stripping section. The flow diagram of application of reactive distillation is shown in Figure 3

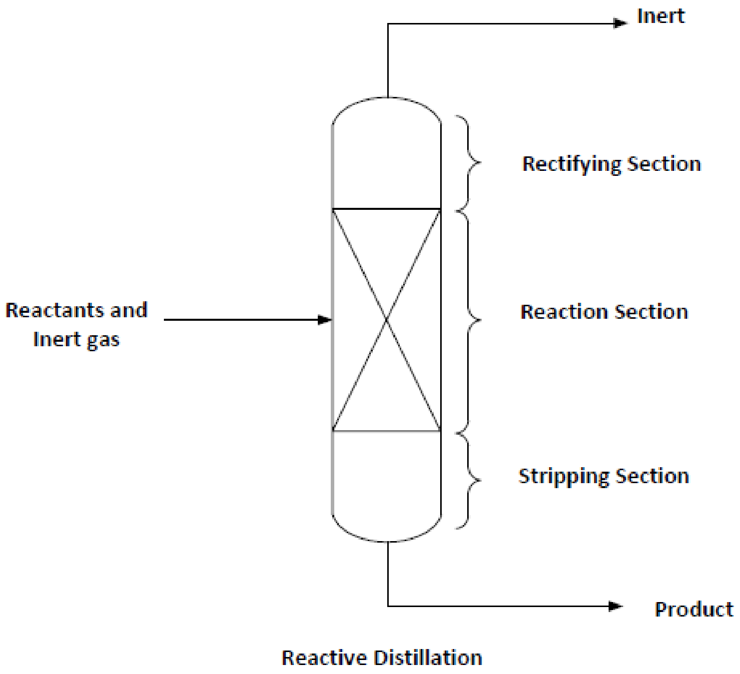

Figure 3. Application of reactive distillation for low volatility product process

The reactive distillation section of the column contains both the catalyst contact device and distillation device. A reaction occur the catalyst contact device and then the reacting phase passes to the distillation device for vapor/liquid contact and separation. These two steps occur alternatively. By making the steps of infinitely small size, this configuration becomes equivalent to the first one. For both configurations, a rectification section may be locate below it, depending upon purity specifications [35, 36].

CHAPTER III

LITERATURE REVIEWS

This chapter presents a literature review of oxygenate biofuel additives from biomass. Detail on biomass production especially ABE fermentation process, diesel additives concerning types and benefits, acetals as oxygenate biofuel additive and applications of reactive distillation are discussed.

3.1 Biomass production

Biomass has great potential as renewable energy sources and can be derived from growing plant and animal materials such as woods from forest, wastes from the agricultural and forestry process and industrial, human and animal wastes. Biomass is used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities. The conversion technologies for utilizing biomass can be separated into four basic categories: direct combustion processes, thermochemical processes, biochemical processes and agrochemical processes [29].. Four major agro industries that have been commonly utilized biomass as fuel for cogeneration in Thailand are sugar, rice, palm oil and wood industries [37]. Currently, in Thailand, biomass materials can be used to generate electricity or liquid fuel such as ethanol. Ethanol can be blended with gasoline to produce gasohol. This is the one choice for reducing the amount of fuels obtained from fossil fuel [38]. Moreover, it can produce acetals group as biofuel for diesel pool [39]. There are various fermentation routes for biomass conversion to chemicals such as the commercial method like acetone-butanol-ethanol (ABE) fermentation process and ethanolic fermentation process.

3.1.1 Acetone-butanol-ethanol (ABE) fermentation process

The acetone-butanol-ethanol or called ABE fermentation process was discovered over 100 years ago. In 1861, Pasteur discovered the production of acetone and butanol by microorganism and in 1912 Weizmann reported isolation of the bacterium *Clostridium acetobutylicum,* which had the capability of producing acetone and butanol from starchy substances and showed result greater solvent yields than original discovery [31, 32, 40]. Normally, the acetone-butanol-ethanol fermentation is carried out at 308-310 K and the ratio of acetone: butanol: ethanol from this fermentation process is 3:6:1. In 1950, ABE fermentation has been the standard industrial for produce butanol but not competitive with product from petrochemical process because of the low cost of fossil carbon feedstock. In recently, ABE fermentation is starting become in industrial scale [40]. The major challenges for ABE production in large scale are

- Expensive Feedstock
- Strong product inhibition by acetone and butanol

- Low productivity

Since ABE producing microorganisms are able to catabolize a wind variety of carbohydrates, effort to being made to use agricultural residues to reduce cost of feed stock [41]. The solutions of product inhibition improvement are proposed by various authors, such as adsorption [42, 43], gas stripping [44], pervaporation [45]. Include distillation and liquid-liquid extraction [46].

3.1.2 ABE product recovery techniques

The major problem of ABE fermentation process is the product inhibition at the total solvent concentration. The development of product removal techniques is the one solution. Possible of these techniques are report as bellow:

Adsorption

For this technique is focus on the desired characteristic of adsorpbent for use in ABE product removal. The adsorpbents must be have the high capacity for solvent (acetone, butanol and ethanol) but not acids, sugar and any nutrients in the ABE broth, favourable adsorption kinetics and efficient adsorption over varies solvent concentration [42]. The adsorpbents have been investigated for ABE fermentation are Zeolite and silicalite [43, 47], XAD series [44, 47], Bonopore [48] and Charcoal and activated carbon [44, 49].

Gas Stripping

This technique is use gas stripping to remove the inhibition solvent during ABE fermentation. Ennis et al., report gas stripping in batch fermentation and use nitrogen as gas stripping. In the comparison with solid adsorpbents and liquid extraction, gas stripping only removes the volatile solvent from the culture and recommend to superior to use XAD series or silicalite [47].

Liquid-Liquid Extraction

In the extractive, a solvent is contract with broth during the fermentation. The inhibition is reduced due to the inhibitory product (butanol and acetone) dissolve in solvent. The performance of extraction process are depends on extractive agent selection. There are various author propose the extractive agent screening and the wide range of possible to be consider as following criteria: [40].

- Immiscibility with fermentation broth
- Non-toxicity to the producing organism
- High selectivity for the fermentation product
- High capacity (i.e. high distribution coefficient for butanol
- Easily to separate product from solvent and solvent recovery
- The solvent can be sterilized, is non-flammable, and low viscosity

- The solvent does not form stable emulsions with the fermentation broth
- The solvent is cheap and available in large quantities

Alcohols and alkanes are the main groups of solvent have been identified. Alcohols are exhibit high capacities but low selectivities for butanol, while alkanes group are high selectivities but low capacity for butanol [50].

Oleyl alcohol has become the solvent of choice for extractive ABE product removal. There are many authors are chosen oleyl alcohol because of its non-toxicity to ABE product organism.

Pervaporation

Pervaporation is membrane process for separate ABE product from the broth. The liquid diffuse through solid membrane are evaporated and remove by gas stream or vacuum application. For the batch fermentation the results of pervaporation show high productivity values. Then, the pervaporation is applied to continuous fermentation using aliginate immobilized cells [45]. The productivity is increased to 70% couple with increased sugar utilization. The recent development of pervaporation techniques is “perstraction”. The liquid passes through a membrane, but instead of being evaporated by gas stream. It is withdrawn by liquid extractant. The advantage over the conventional extraction is the aqueous and organic phase are separated from each other, not form to the emulsions. And advantage over pervaporation is the higher selectivity of the system [40].

Hybrid downstream processing

Groot et al., propose the comparison of hybrid process. The hybrid processing with pervaporation or extraction are show high selectivity and operations advantages. So these processes are the most attractive for product removal. By the way, Qureshi et al., suggest that the hybrid processing of adsorption and extraction combined with distillation are the one of most energy efficient. In addition, Liu et al., prefer the combination of extraction and distillation are the conventional unit operations for ABE product separation. Ali M. Dadgar and Gary L. Foutch proposed the ABE product separation by liquid-liquid extraction and the requirement process downstream modification as distillation. 2-ethyl-1-hexanol is the good extractive solvent for separate ABE from water for this work. The economic design process was compared with Marlatt and Datta’s design. The improved process result is show that 15% reduction over distillation process when compare with the cost of butanol production as overall economic indicator. The cost reduction of this process is essential to competitive with the convectional petrochemical process. Kraemer et al., 2011 report the hybrid process downstream with extraction-distillation process for butanol separation from ABE fermentation. Mesitylene is identified as novel solvent with the excellent properties for ABE extraction from the fermentation broth by means of computer-aided molecular design (CAMD). Mesitylene is favorable when comparing with Oleyl alcohol solvent, which is the commonly used for ABE extraction. An optimization of flowsheet structure and operating point, consideration of heat integration, and evaluation of the minimum energy demands are coved. The total annualized cost of novel process hybrid downstream process are lower than the operation cost of the hybrid downstream process with common solvent Oleyl alcohol or pure distillation process.

3.2 Diesel additives

The additives of diesel fuel are possible solution to reduce harmful emission problem such as particle matter (PM), oxides of nitrogen (NOx), carbon monoxide (CO) and improve engine efficiency.

Ribeiro et al., 2007 proposed that the diesel additives can be classified according to the purpose for which they were designed. Preflame additives are designed to resolve the problems that occur before burning. Flame additives were used to improve the ignition efficiency, increase cetane number, reduces carbon deposits and contamination of fuel. Postflame are designed to reduce carbon deposits in fuel engine, smoke and emission [3].

Metal-Based Additives

Groups of metal-based fuel additives have been used as combustion catalysts for hydrocarbon fuels. These metals are manganese, iron, copper, barium, cerium, calcium and platinum which have catalytic activity in combustion process. The metal-based additives reduce diesel engine pollution emission and fuel combustion value. Reason of emission reduction is that the metal function either by reacting with water to produce hydroxyl radicals, which enhance soot oxidation, or by direct reaction with the carbon atom in the soot, thereby lowering the oxidation temperature [9].

Manganease (Mn) metal-based additives can act as catalysts enhancing the oxidation process and reducing regulate pollutants such as PM, CO, HC and Nox emission [9]. Moreover, Mn metal-based can reduce the feezing point [6]). Ferrocene additives can reduce carbonaceous matter in combustion. Smoke suppressant (Primary barium, Manganease and calcium compound), they were used to reduce emission of black smoke. Cerium (Ce) can be reducing the particulate matter. Platinum (Pt) combine with cerium was very active in the catalytic oxidation of diesel [3].

Oxygenated additives

Another group of additives is oxygenated compounds. Oxygenated additives have been considered for reducing the ignition temperature of particulates matter (PM), without causing serious penalties on NOx, unburned hydrocarbon (UHC) and carbon monoxide (CO) emission. However, the composition of diesel and the use of additives directly affect properties, such as density, viscosity, volatility, behavior at low temperature, and the cetane number [3]. Some oxygenate compounds used are ethanol [12], Dimethyl ether (DME), Dimethyl carbonate (DMC), Dimethoxy methane (DMM), 2-Methoxyethyl acetate (MEA) [9], biodiesel, ketal and acetals. Ketals and acetals are recognized as green fuel additives, for example 2,2-Diethoxypropane (DEP), 2,2-Dibutoxypropane (DBP) [39], 1,1-Diethoxyethane (DEE) [13, 16-18], 1,1-Dibutoxyethane (DBE) [19-22] and others. So the acetals can be produced from a completely renewable origin.

Depressants and wax dispersants

Wax dispersant additives are especially important in countries with long winter. It can be separated from the oil at lower temperature and the waxes crystallize as an interlocking network of fine sheets and cause of cold-flow problems such as clogging of fuel lines and filters in engine fuel system. The wax deposition and the continuous addition of polymeric inhibitor are considered to minimize the problems. The addition of copolymer such as polyacrylates, polymethacrylates, or poly (ethylene-co-vinyl acetate) (EVA) inhibits the deposition phenomenon. Those copolymers are known as cold-filter plugging point (CFPP) additive or pour point depressants (PPDs). EVA presents good efficiency as diesel fuel CFPP additives [3].

Ignition promoters

The ignition promoters are designed for improving cetane number of diesel fuel, increase ignition efficiency and reducing NOx emission such as 2-ethylhexyl nitrate (EHN) which currently dominates the cetane improvement market [3]. The commercial market considers several factors when selecting and using cetane improvers, these include (a) efficacy toward improving ignition properties, (b) hazards associated with storage and transport, (c) additional cost associated with diluting cetane improvers to allow safe transport, and (d) nitrogen content [51].

Diesel-vegetable oil blends

The direct use of vegetable oil to diesel engine is restricted by some unfavorable physical properties such as viscosity. The viscosity of vegetable oil is approximately 10 times higher than that of diesel fuel. For this reason, the use of vegetable oil direct to injection diesel engine create the poor fuel atomization, incomplete combustion and fuel buildup in the lubricant oil, resulting in serious engine fouling [3]. Biomass and vegetable oil are widely studied for using to alternative fuel or diesel blends such as palm oil, Jatropha oil and Hydroprocessed vegetable oil.

3.3 Acetals possible to oxygenate biofuel additives

Acetals are one kind of oxygenate fuel additives that can be produced from different types of reaction. Then, ketals and acetals can be obtained from renewable origin (bioalcohol) and good candidates for fuel additive such as the production of 1,1-Diethoxyethane [13, 14, 16-18], 1,1-Dibutoxyethane [19-22], can be obtained from bioalcohol and acetadehyde, so bioalcohol and acetaldehyde can be obtained from biomass.

1,1-Diethoxyethane or acetaldehyde diethylacetal can be synthesized from ethanol react with acetaldehyde. Kaufhold et al., (1996) proposed in patent an industrial process for 1,1-Diethoxyethane production from ethanol and acetaldehyde. In this process, a part from a homogeneous strong acid catalyst an entrainer (hexane, pentane) was used with a normal boiling point between 298 K and 348 K. This entrainer must be water insoluble (<3% soluble in water), thus the water was continuously removed from the reacting phase shifting the acetalization reversible reaction to desired direction. However, this process conduces to corrosion problem, uneconomical and not environment friendly. The heterogenous catalytic process were used and overcome to solve these problems. Capeletti et al.(2000) reported the performance of several solid catalysts, from commercial, natural and laboratory sources for produce 1,1-diethoxyethane from ethanol react with acetaldehyde. They concluded that exchange resins show enough surface acidity to allow reaching equilibrium values much faster than other less acid solid catalysts. Silva V.M.T.M. and Rodrigues A.E. (2001, 2005(a) and 2005(b)) reported the thermodynamic and kinetic studies of 1,1-diethoxyethane synthesis in a batch reactor by reacting ethanol and acetaldehyde in liquid phase, using the acid resin Amberlyst 18 as catalyst. The reaction equilibrium constant was determined experimentally in the temperature range 293-330 K at 1.0 MPa. Kinetic experiments show that the pressure does not affect the reaction rate for temperature 283-298 K. Because of the strong non-ideality of the liquid reaction mixture, the reaction rate model was formulated in terms of activities. Application in simulated moving-bed reactor (SMBR) technology was proposed. The methodology used combines modeling/simulation with laboratory and pilot-scale experiments. The SMBR technology was applied for 1,1-diethoxyethane production and separation with 87% purity and the acetaldehyde conversion was about 98%.

1,1-Dibutoxyethane or acetaldehyde dibuthylacetal can be synthesized from butanol and acetaldehyde. Graça N.S. et al. (2010, 2011(a), and 2011(b)) reported the thermodynamic and kinetic studies of dibutylacetal synthesis in a batch reactor by reacting n-butanol and acetaldehyde in liquid phase, using the acid resin Amberlyst 15 as catalyst. The reaction equilibrium constant was determined experimentally in the temperature range 293-310 K at 0.6 MPa. Kinetic experiments showed that the rate of reaction increases with the temperature. However, the equilibrium conversion decreases with the temperature because of the exothermic nature of the reaction.

Delfort et., al. (2010) proposed a method of converting biomass to acetal groups products and use in biofuel. The methods were comprising a first stage of fermentation of renewable raw materials of vegetable origin at the end of which a least one alcohol and at least one compound containing a carbonyl group are obtained, and a second stage corresponding to an acetalization reaction involving said alcohol and said compound containing a carbonyl group.

3.4 Reactive distillation

The combination of chemical reaction and separation process into one apparatus so called “Reactive distillation (RD)” has become an interesting alternative to overcome improve restrict chemical reaction, especially for thermodynamic limitations like the esterification, etherification and acetallization reactions. Sharma and Chopade (1997(a), and 1997(b)) reported the acetalization reaction between ethanol and ethylene glycol with formaldehyde respectively. The both reactions presence in Indion 130 and Amberlyst 15 cation exchange resin catalyst, they indicate both batch experiments and RD experiments. The reaction between ethanol react with formaldehyde in batch reactor show the achieve conversion around 45%, reaction carried out at 333, 343 and 353 K. They found that the temperature have no significant effect to equilibrium conversion. After, they showed the performance of reactive distillation system for this reaction, they found that the achieve conversion around 86-94%, for lower reflux ratio show high conversion than higher reflux ratio. (at R=0.5 conversion 94% and R=4 conversion 86%). In the part of catalyst, both Indion 130 and Amberlyst 15 were approximately identical. For the reaction between ethylene glycol and formaldehyde using initial feed mole ratio 1.5:1 of ethylene glycol to formaldehyde. They studied both batch reactor and RD experiments, the results show that the achieved conversion was increased from 42% to 72%, when using RD instead of batch reactor. Agirre et al., (2010 and 2011) reported the acetalization of ethanol and butanal and using Amberlyst 47 ion exchange resin as catalyst. They studied both batch and RD experiment as well as Shaema and Chopade. The part of batch experiment allowed gathering chemical kinetics data of the reaction and observing the achieve conversions between 40% at 333 K and 50% at 293 K. For RD experiments were not satisfactory, the maximum conversion achieve around 50% while in batch reactor the conversion around 39% as same condition. Furthermore, conversion achieve higher when reflux ration increased also.

CHAPTER IV

SIMULATIONS

This chapter describes the simulation method for synthesis of 1,1-diethoxyetahne (DEE) and 1,1-butoxyethane (DBE) from acetaldehyde and ethanol and butanol respectively, by using reactive distillation. For this work, the simulation studies are divided into two parts. Firstly, the kinetic rate constants in power law model based on mole fraction was estimated by MATLAB program and further investigated using RBATCH module in Aspen Plus simulation program. The reaction rate expressions obtained in this section is important for implementation in simulation of reactive distillation. In second part, the suitable process configurations for synthesis of DEE and DBE were simulated by RADFRAC module.

4.1 Estimation and investigation of kinetic rate constants

4.1.1 Estimation of kinetic rate constants by MATLAB program

The following equation shows the main reaction for synthesis of 1,1-diethoxyethane (DEE). Stoichiometric reaction requires 2 mol of ethanol and 1 mol of acetaldehyde per 1 mol of DEE and no side reaction.

Reaction 1:

$$2\text{Ethanol (A)} + \text{Acetaldehyde(B)} \leftrightarrow 1{,}1-\text{Diethoxyethane (C)} + \text{Water (D)} \tag{4.1}$$

The equilibrium constant of DEE was reported by Silva V.M.T.M. and Rodrígues AE. 2005(a)

$$Keq = 0.015033 \exp (1466.5/T(K)). \tag{4.2}$$

It was determined in the temperature range 293-333 K at 0.6 Mpa The previous literature [17], reported the synthesis of DEE using a temperature range of 289-333 K at 0.6 Mpa. The proposed kinetic model was based on Langmuir-Hinshelwood rate expression. The activation energy of reaction is 47.874 kJ/mol

$$R = k_c \frac{a_A a_B - \frac{a_C a_D}{K_{eq} a_A}}{\left(1+K_{s,D} a_D\right)^Z} \tag{4.3}$$

where Z is 0 for power law model and is 1 for Langmuir-Hinshelwood model.

The equilibrium constant of 1,1-Diethoxyethane (DEE) in power model based on mole fraction of component is shown as below:

$$K_{eq} = \frac{x_{water} x_{DEE}}{x_{ethanol}^2 x_{Acetaldehyde}} \tag{4.4}$$

Similarly, the following equation shows the main reaction for synthesis of 1,1-dibutoxyethane (DBE). Stoichiometric reaction requires 2 mol of butanol and 1 mol of acetaldehyde per 1 mol of DBE and no side reaction.

Reaction 2:

$$2\mathrm{Butanol}\ (\mathrm{A}) + \mathrm{Acetaldehyde}(\mathrm{B}) \leftrightarrow 1{,}1 - \mathrm{Dibutoxyethane}\ (\mathrm{C}) + \mathrm{Water}\ (\mathrm{D})$$ **Error! Digit expected.** (4.5)

The equilibrium constant of DBE was reported by [20].

Keq = 0.00959 exp (1755.3/T(K)). (4.6)

It was determined in the temperature range 293-333 K at 0.6 Mpa. The previous literature [20], reports the synthesis of 1,1-DBE using a temperature range of 283-323K at 0.6 Mpa. The proposed kinetic model was based on Langmuir-Hinshelwood rate expression. The activation energy of reaction is 51.6 kJ/mol

The equilibrium constant of 1,1-Dibutoxyethane (DBE) in power model based on mole fraction of component is shown below:

$$\mathrm{K_{eq}} = \frac{x_{\mathrm{water}} x_{\mathrm{DBE}}}{x_{\mathrm{butanol}}^{2} x_{\mathrm{Acetaldehyde}}} \tag{4.7}$$

Moreover, the expressions for the rate equations in mole fraction form are required in Aspen Plus program for the further studies. Therefore, the kinetic rate constants for the synthesis of DEE and DBE were converted to power law model based on mole fraction of all components by MATLAB calculation program.

4.1.2 Investigation of batch reaction by Aspen Plus program

In this part, the kinetic rate constants estimated from MATLAB were investigated by RBATCH module in Aspen Plus simulation program. The condition of reaction 1 was set as: the volume of reactant = 0.53 l/s, mole fractions of ethanol and acetaldehyde = 0.7 and 0.3 respectively, catalyst loading = 0.5 g, pressure = 0.6 MPa and T = 289 and 299 K. Similarly, The condition of reaction 2 was set as: the volume of reactant = 0.53 l/s, mole fractions of butanol and acetaldehyde = 0.7 and 0.3 respectively, catalyst loading = 1.8 g, pressure = 0.6 MPa and T = 293 and 313 K. The physical and chemical properties of all components were available in Aspen Plus data base except DEE and DBE. The group contribution method was used to estimate boiling point and standard Gibb's free energy of formation and so forth.

4.2 Reactive distillation simulation

The reactive distillation column was simulated using Aspen Plus simulation program. The steady state RADFRAC module was used to simulate DEE and DBE productions. In this work, the conditions were set as: no pressure drop in the column (0.6 MPa), pressure of feed stream = 0.6 MPa and temperature of feed stream = 283 K, the stream of alcohol feed at above the first stage of reaction section and acetaldehyde stream feed at the bottom stage of reaction section, total condenser and Kettle reboiler. The order of column stage was assigned from the top to the bottom of column, stage 1 as the condenser and the stage N as the reboiler. Effects of design and operating variable including number of rectifying stage, reaction stage, stripping stage, reflux ratio and reboiler heat duty in reactive distillation performance were studied.

4.2.1 Configuration of reactive distillation systems

According to the previous work, Ali M. Dadgar and Gary L. Foutch proposed the ABE product separation by liquid-liquid extraction and the downstream modification by distillation. 2-ethyl-1-hexanol is extractive solvent for separating ABE from water. The ABE separation process flow diagram is shown in Figure 4, broth from the fermenter is sent to extraction column prior to distillation for water removal. The raffinate phase contains 99.6% water and the extract phase is sent to solvent stripper unit for solvent recovery. The stripper overhead is sent to the first distillation column for acetone recovery and the bottom sent to the second distillation column for butanol and ethanol separation. For this work, the synthesis of DEE and DBE were simultaneously produced from ABE product separation process and use feed condition from Ali M. Dadgar and Gary L. Foutch’s work.

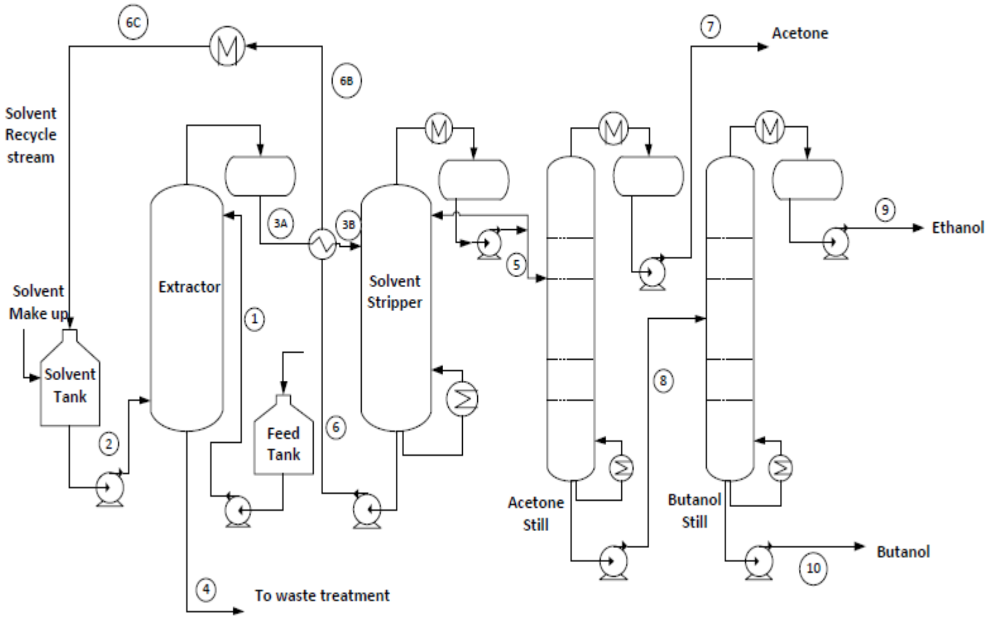

Figure 4 ABE separation process using Extraction with 2-ethyl-1-hexanol

Table 1 Stream weight composition of ABE process separation

Stream ID	1	2	4	5	7	8	9	10
Acetone	6.0E-3	-	2.20E-3	2.02E-1	9.89E-1	0.93E-6	1.57E-5	Neglig.
Ethanol	2.0E-3	-	1.03E-3	1.03E-2	1.00E-2	6.27E-2	9.99E-1	4.00E-3
Butanol	1.5E-2	-	4.5E-4	7.45E-1	Negli	9.37E-1	6.9E-	9.95E

					g.		5	-1
2-Ethyl-1-hexanol	-	1.00	4.0E-5	2.00E-4	Neglig.	2.51E-4	Neglig.	2.67E-4
Water	9.77E-1	-	9.96E-1	-	-	-	-	-
Total (lbs/hr)	1814900	1951500	1779800	34390	7020	27370	1610	25750
Temperature (F)	77	77	77	77	137	258	173	271
Pressure (psia)	14.7	14.7	24.7	14.7	14.7	24.7	14.7	24.7

Stream ID	3A	3B	6B	6C
Acetone	3.5E-3	3.5E-3	Neglig.	Neglig.
Ethanol	0.9E-3	0.9E-3	Neglig.	Neglig.
Butanol	1.33E-2	1.33E-2	3.97E-4	3.99E-4
2-Ethyl-1-hexanol	9.83E-1	9.83E-1	99.9E-1	9.99E-1
Total (lbs/hr)	1986548	1986548	1952158	1952158
Temperature (F)	77	363	120	105
Pressure (psia)	40.0	35	24.7	14.7

4.2.2 System of two reactive distillation columns

For this case, the synthesis of DEE and DBE were separately produced in reactive distillation as shown in Figure 5. Ethanol and butanol feeds are calculated based on data of the ABE product separation process as summarized in Table 1. [52].

Therefore, the reaction of DEE was investigated in the reactive distillation 1, ethanol feed is 16 kmol/hr and acetaldehyde feed 8 kmol/hr.

Similarly, the reaction of DBE was investigated in the reactive distillation 2, butanol feed is 158 kmol/hr and acetaldehyde feed is 79 kmol/hr. The reactive distillation for each reaction was investigated the effect of design variables such as numbers of rectifying, reaction and stripping stage.

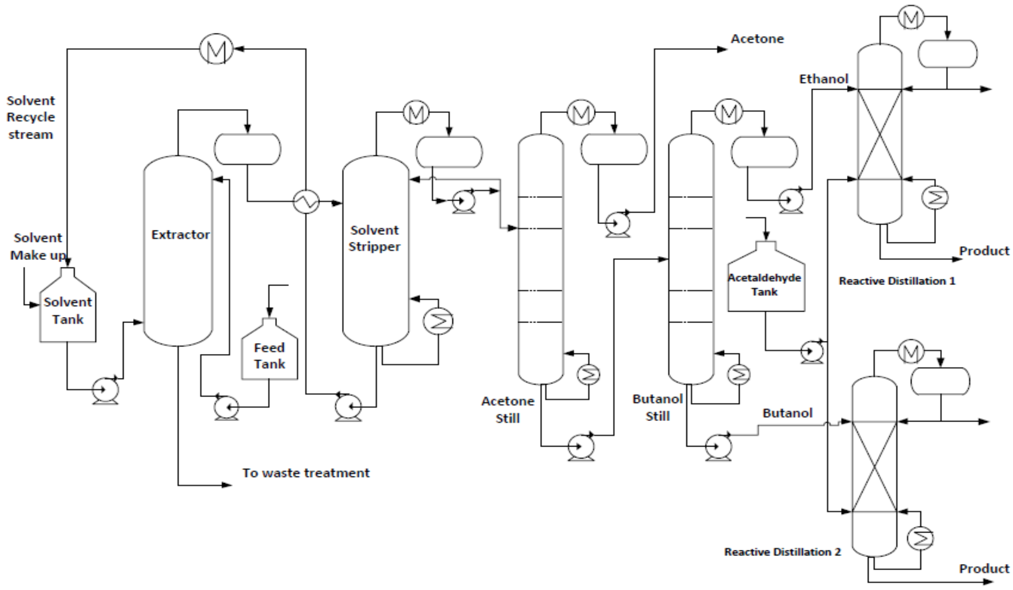

Figure 5 : System with two reactive distillation columns for separate synthesis of DEE and DBE

4.2.3 Combined synthesis in single reactive distillation system

For this case, the combined synthesis of DEE and DBE was carried out in one reactive distillation column as shown in Figure 6. Ethanol and butanol feeds were based on the ABE product separation process data [52]. Therefore, the alcohol feed is 174 kmol/hr and acetaldehyde feed is 8 kmol/hr. Similarly, the reaction of DBE production, butanol feed is 158 kmol/hr (ethanol:butanol ratio as 0.098:0.902) and acetaldehyde feed is 79 kmol/hr. The reactive distillation for the combined reactions was investigated the effect of design variables such as numbers of rectifying, reaction and stripping stage.

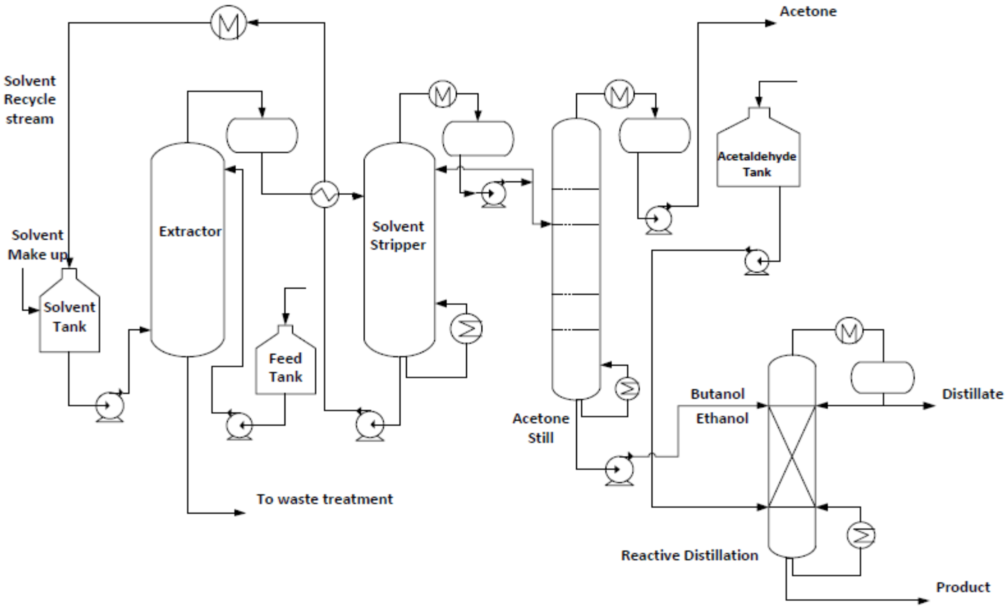

Figure 6 Combined synthesis of DEE and DBE in single reactive distillation system

4.3 Process performance

The performances of the systems were considered in terms of conversion of acetaldehyde, yield of acetaldehyde, and purity of DEE and DBE as defined below:

$$X_{\textbf{acetaldehyde}} = \frac{\text{Diffrence in molar flow rate of inlet and outlet of acetaldehyde}}{\text{Feed molar flow rate of acetaldehyde}} \text{ x } 100 \qquad (4.8)$$

$$\mathrm{Y_{acetaldehyde}} = \frac{\text{Molar flow rate of 1,1−Dibutoxyethane in bottomstream}}{\text{Feed molar flow rate of acetaldehyde}} \times 100 \qquad (4.9)$$

$$\mathrm{P_{DEE}} = \frac{\text{Molar flow rate of 1,1−Diethoxyethane (DEE) in bottomstream}}{\text{Total molar flow rate of all componant at bottomstream}} \times 100 \qquad (4.10)$$

$$\mathrm{P_{DBE}} = \frac{\text{Molar flow rate of 1,1−Dibutoxyethane (DBE) in bottomstream}}{\text{Total molar flow rate of all componant at bottomstream}} \times 100 \qquad (4.11)$$

CHAPTER V

RESULTS AND DISCUSSION

5.1 Estimation and investigation of kinetic rate constants

5.1.1 Estimation of kinetic rate constants by MATLAB program

The work in this part is to develop reaction rate expressions for further implementation in Aspen Plus program for simulating reactive distillation system. The reaction rate constants were estimated from molar fraction profiles of all components using MATLAB program. The best-fit kinetic constants were determined by minimizing the relative root mean square deviation (RSMD) values as expressed by:

$$RMSD_i = \frac{1}{M}\sqrt{\sum_{t=1}^{M}\left(\frac{\left(x_{i,t} - x_{i,exp,t}\right)}{\left(x_{i,exp,t}\right)}\right)^2} \tag{5.1}$$

For the synthesis of DEE, Table 2. summarizes the reaction rate expression and the constants estimated by MATLAB program. Figures 7 and 8 illustrate the mole change with time at temperatures of 289 and 299 K, respectively. The simulated mole change profiles from the power law model based on mole fraction agree well with those from literature [17].

Table 2 Reaction rate expression and parameters based on mole fraction of component estimated by MATLAB program.

Reaction rate expression	$R = k_c(\mathrm{x_A x_B} - \frac{\mathrm{x_C x_D}}{\mathrm{K_{eq} x_A}})$
Equilibrium Constant (Dimensionless)	0.015033 exp (12192.42/RT)
Kinetic constants (Mol/g.sec)	$1.92\mathrm{x}10^{9}$ exp (-47874/RT)
Activation Energy (kJ/mol)	47.874

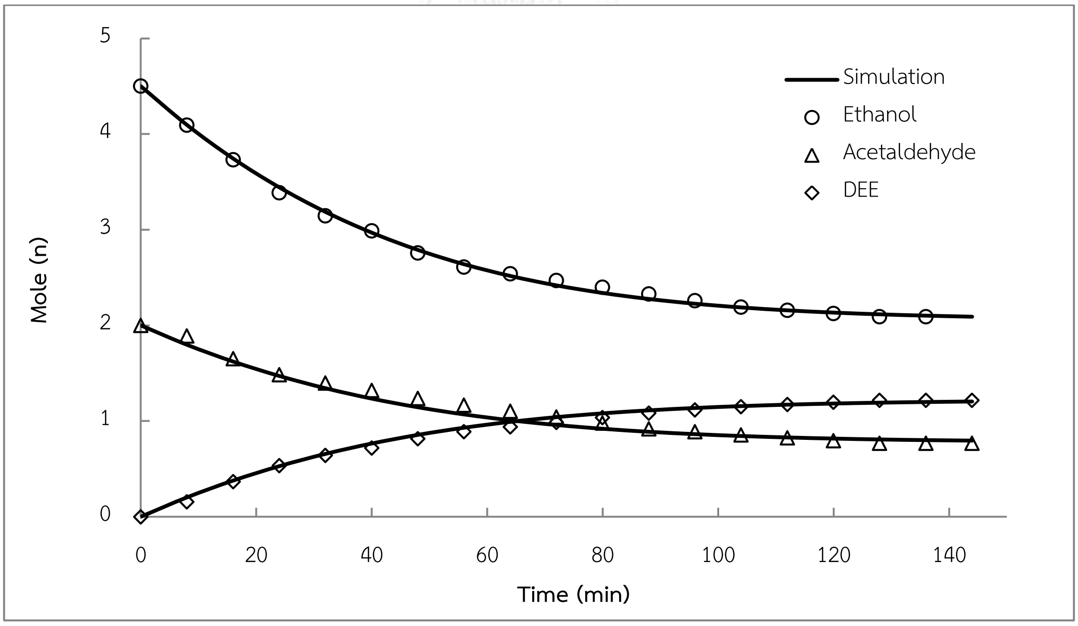

Figure 7 Mole profiles of reactants and products $n_{iEthanol}$ = 0.45, $n_{iAcetaldehyde}$ = 0.2 P = 0.6 MPa, , ω_{cat} = 0.5 g, and T = 289 K

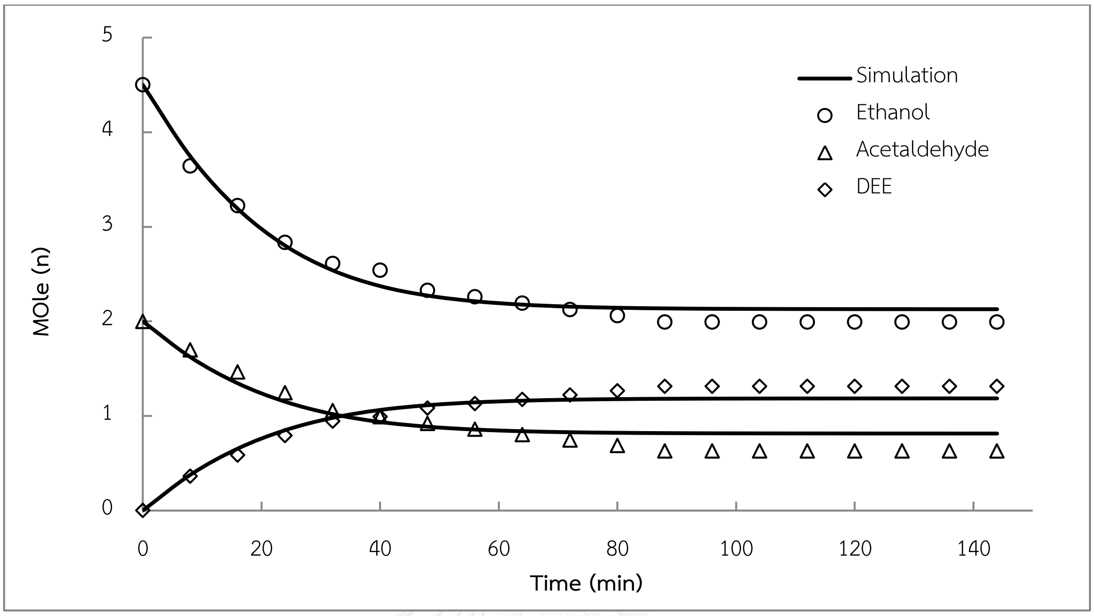

Figure 8 Mole profiles of reactants and products $n_{iEthanol}$ = 0.45, $n_{iAcetaldehyde}$ = 0.2 P = 0.6 MPa, ω_{cat} = 0.5 g, and T = 299 K

For the synthesis of DBE, Table 3 summarizes the reaction rate expression and constants estimated by MATLAB program. Figures 9 and 10 illustrate the mole changes with time at temperatures of 293 and 313 K, respectively. The simulation results of mole change data agree well with those from literature [20].

Table 3 Reaction rate expression and parameters based on mole fraction of component estimated by MATLAB program.

Reaction rate expression	$R = k_c(\mathrm{x_A x_B} - \frac{\mathrm{x_C x_D}}{\mathrm{K_{eq} x_A}})$
Equilibrium Constant (Dimensionless)	0.007701 exp (131523.3/RT)
Kinetics constants (Mol/g.sec)	$1.88\mathrm{x}10^{9}$exp (-51600/RT)
Activation Energy (kJ/mol)	51.6

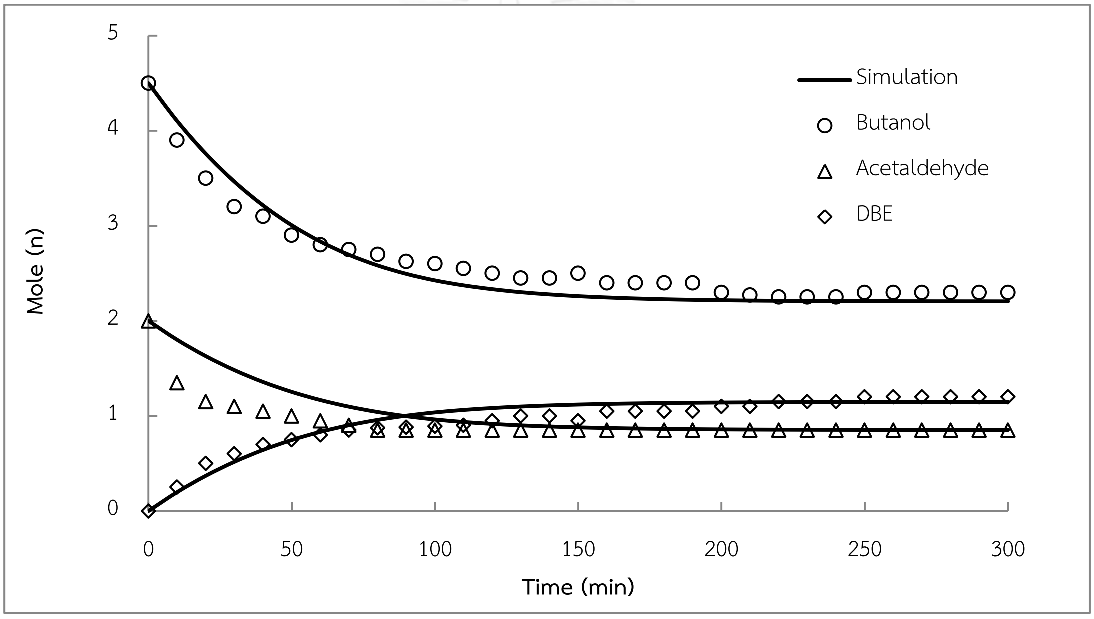

Figure 9 Mole profiles of reactants and products n_{iButanol} = 0.45, $n_{\mathrm{iAcetaldehyde}}$ = 0.2 P = 0.6 MPa, ω_{cat} = 1.8 g, and T = 293 K

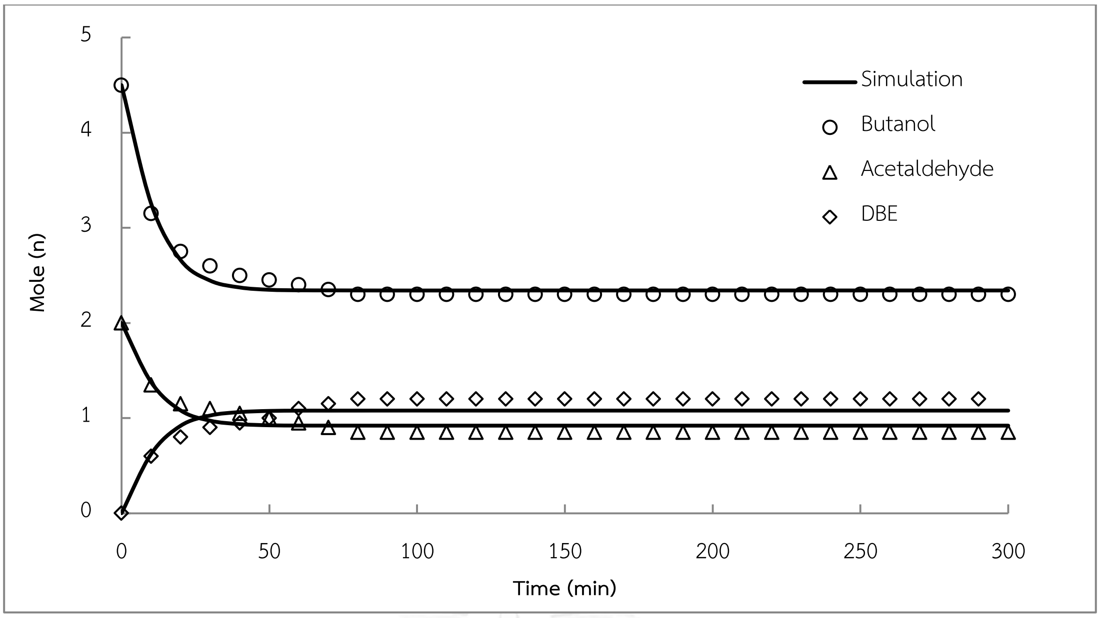

Figure 10 Mole profiles of reactants and products $n_{iButanol}$ = 0.45, $n_{iAcetaldehyde}$ = 0.2 P = 0.6 MPa, ω_{cat} = 1.8 g, and T = 313 K

5.1.2 Simulation of batch reactor using Aspen Plus program

In this part, the kinetic rate constants estimated by using MATLAB were employed in RBATCH module in Aspen Plus program. The values of standard Gibb free energy of formation of DBE are not available. Table 4 shows the standard Gibb free energy of formation estimated by Joback's method, Gani method and Benson's method. It was found that Benson's method shows the lowest percent deviation compared to the other methods.

Table 4 Summary of standard Gibbs free energy values estimated by group contribution methods compared with data base

Substance	G°KJ/mol				
	Data base[a][53]	Literature[b]	Joback	Gani	Benson
Acetaldehyde	-133.3		-133.56	-130.72	-133.76
Butanol	-150.7		-154.02	-156.75	-153.36
Ethanol	-167.85		-170.86	-173.22	-170.38
DEE	-245	-239.42	-212.8	-222.20	-258.30
DBE	-	-	-179.12	-189.27	-224.25
Substance	%Deviation				
	Joback	Gani	Benson		
Acetaldehyde	0.20	-1.94	0.35		
Butanol	2.20	4.02	1.76		
Ethanol	1.79	3.20	1.51		
DEE	-13.14	-9.31	5.43		
DBE	-	-	-		

For DEE synthesis, Figures 11 and 12 illustrate the mole changes with time at temperatures of 289 and 299 K respectively. The simulation results show good agreement with those from the power law model based on mole fraction. In addition, the kinetic rate constants were carried out with different temperatures, the rate of reaction increases with increasing temperature as shown in Figure 13. However, the equilibrium conversion of acetaldehyde was decreased due to exothermic nature of reaction as depicted in Figure 14 [17].

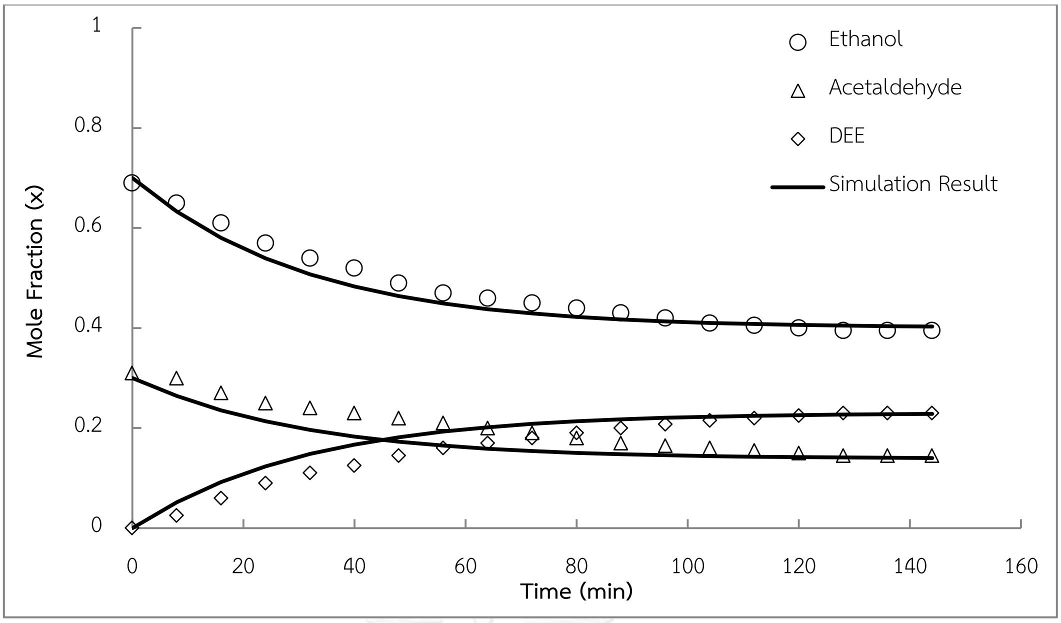

Figure 11 Simulation results of DEE synthesis by Aspen Plus program at *T* = 289 K.

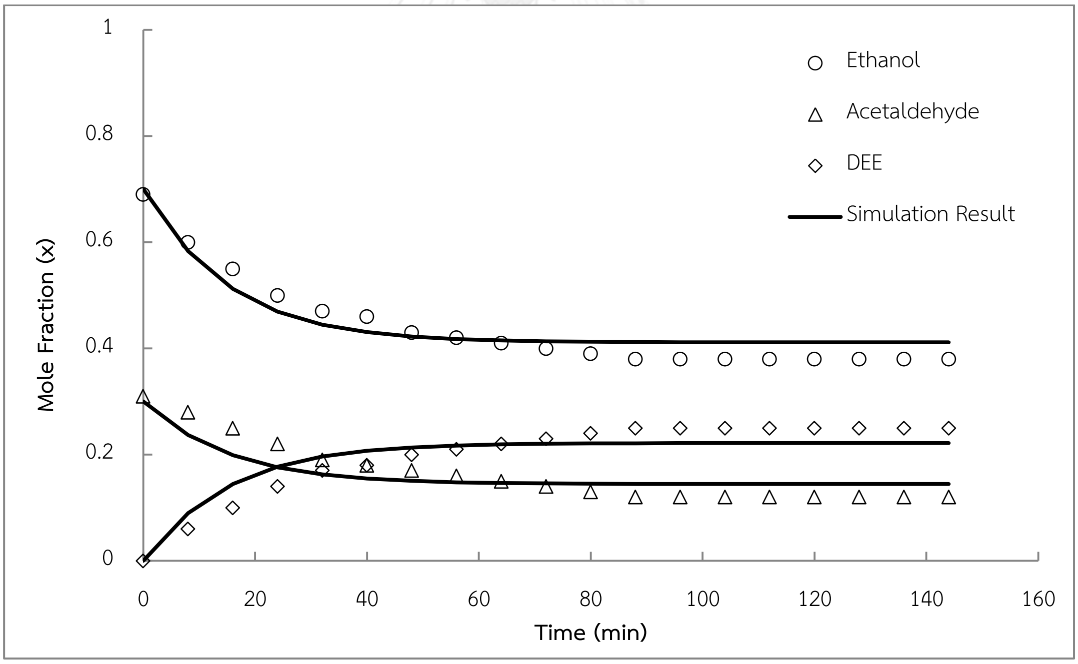

Figure 12 Simulation results of DEE synthesis by Aspen Plus program at *T* = 299 K.

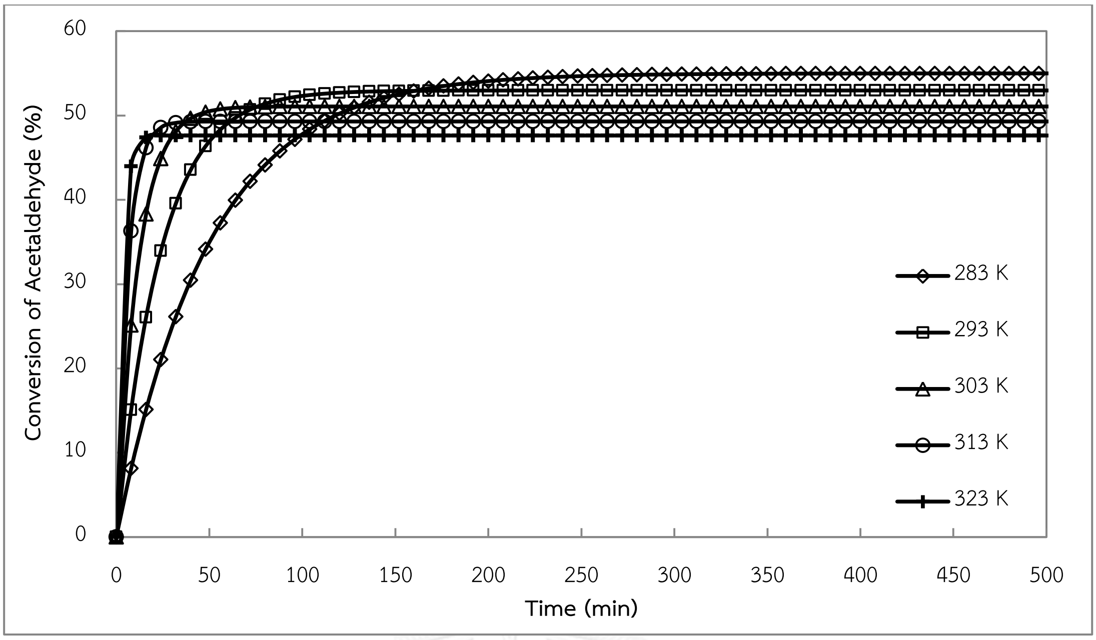

Figure 13 Simulation results of effect of temperature on conversion of acetaldehyde for DEE synthesis

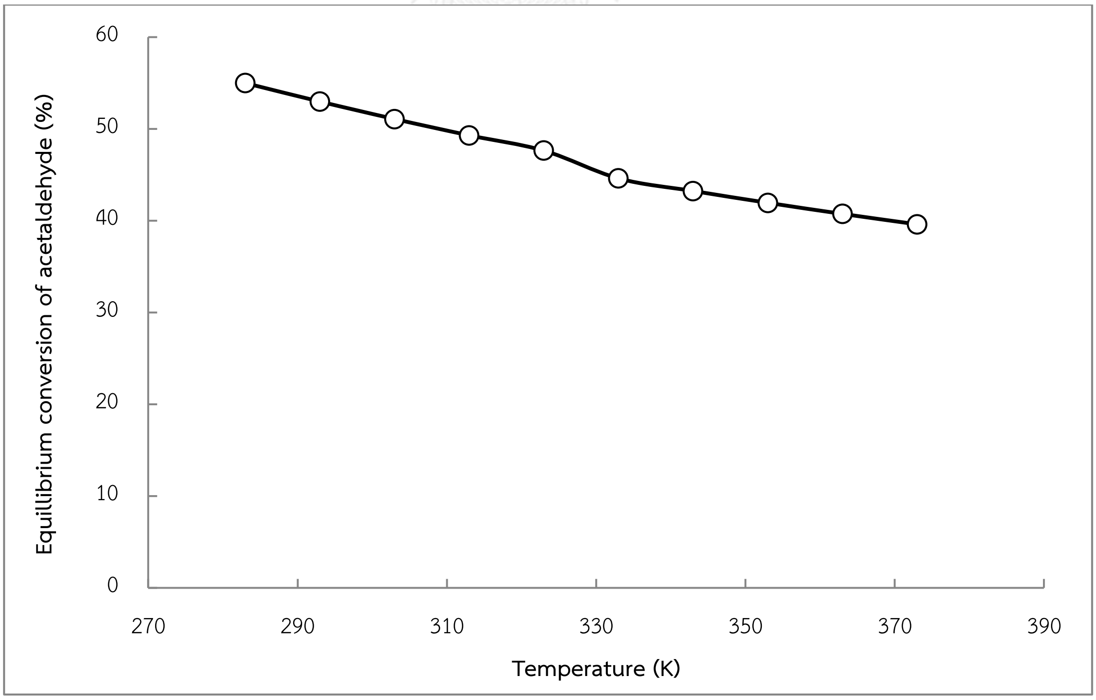

Figure 14 Simulation results of the effect of temperature on equilibrium conversion of acetaldehyde for DEE synthesis

For DBE synthesis, Figures 15 and 16 illustrate the mole changes with time at temperatures 293 and 313 K, respectively. The simulation results show good agreement with those simulated using power law model based on mole fraction. In addition, the kinetic rate constants were carried out at different temperatures. The rate of reaction increases with temperature as shown in Figure 17. However, the equilibrium conversion of acetaldehyde was decreased due to exothermic nature of reaction as shown in Figure 18 [20].

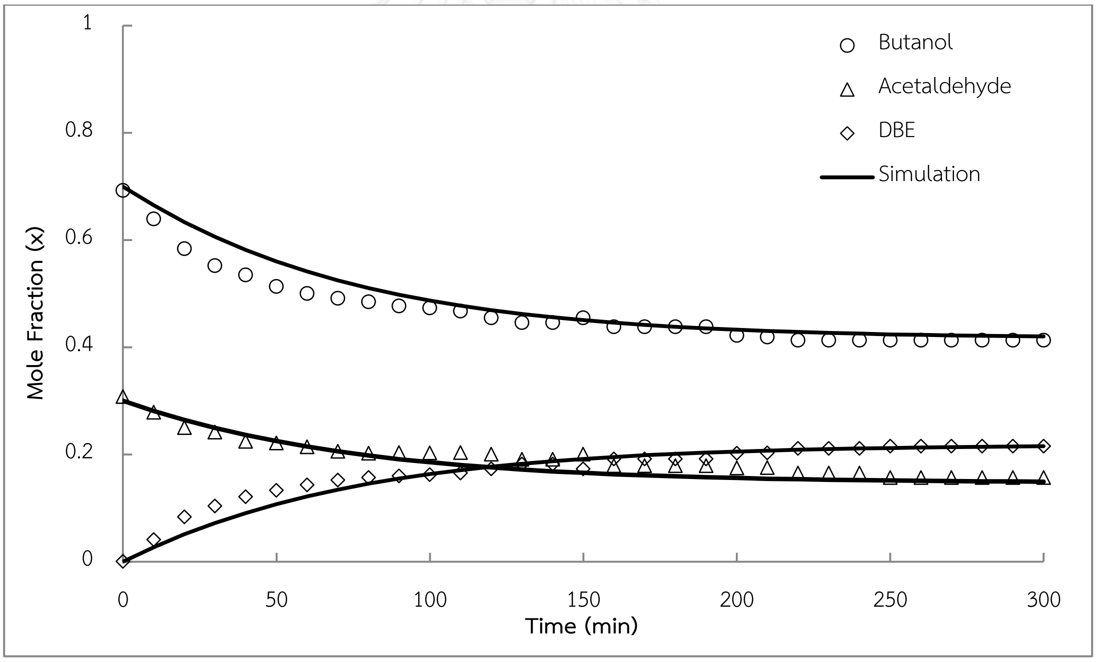

Figure 15 Simulation results of DBE synthesis by Aspen Plus program at T = 293K.

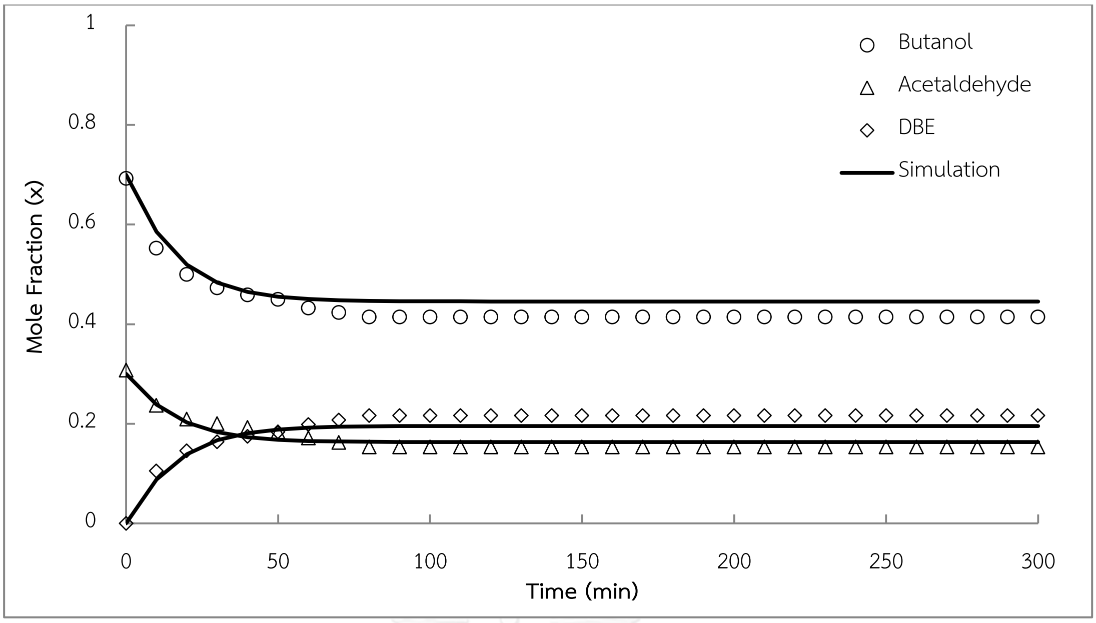

Figure 16 Simulation results of DBE synthesis by Aspen Plus program at T = 313 K.

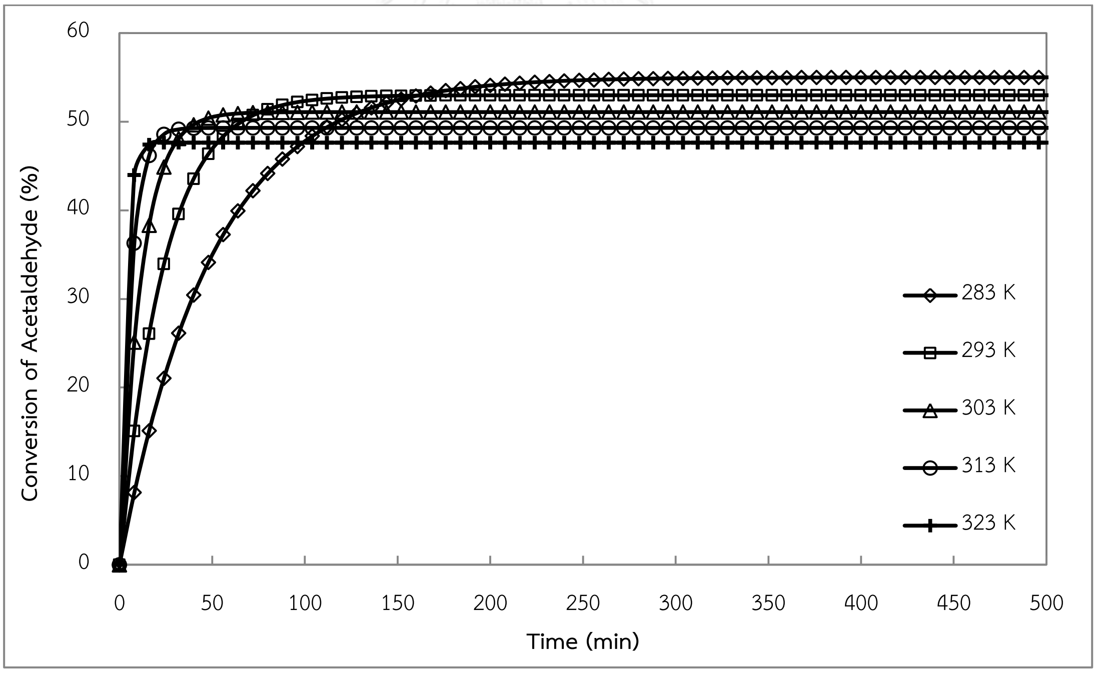

Figure 17 Simulation results of the effect of temperature on conversion of acetaldehyde for DBE synthesis

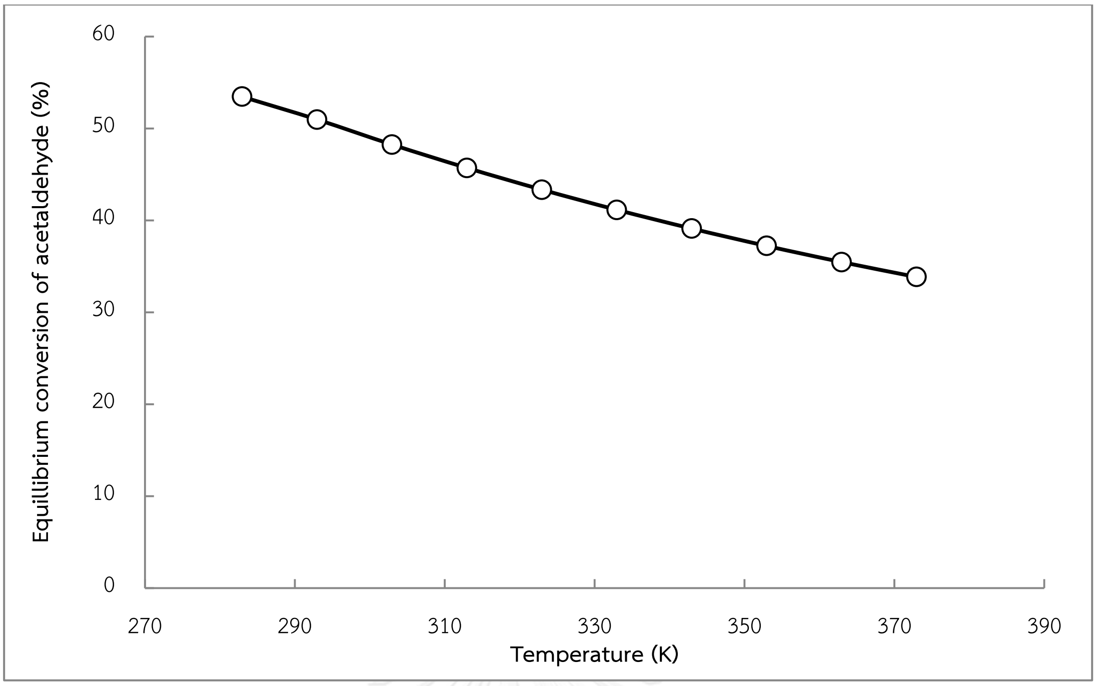

Figure 18 Simulation results of the effect of temperature on equilibrium conversion of acetaldehyde for DBE synthesis

5.2 Reactive distillation simulations

Reactive distillation was simulated by using Aspen plus program. The RADFRAC module with equilibrium stage model was used. The thermodynamic properties were estimated using NRTL. The study assumed negligible pressure drop along the column and vapor-liquid equilibrium on each stage. The scheme of reactive distillation is shown in Figure 19.

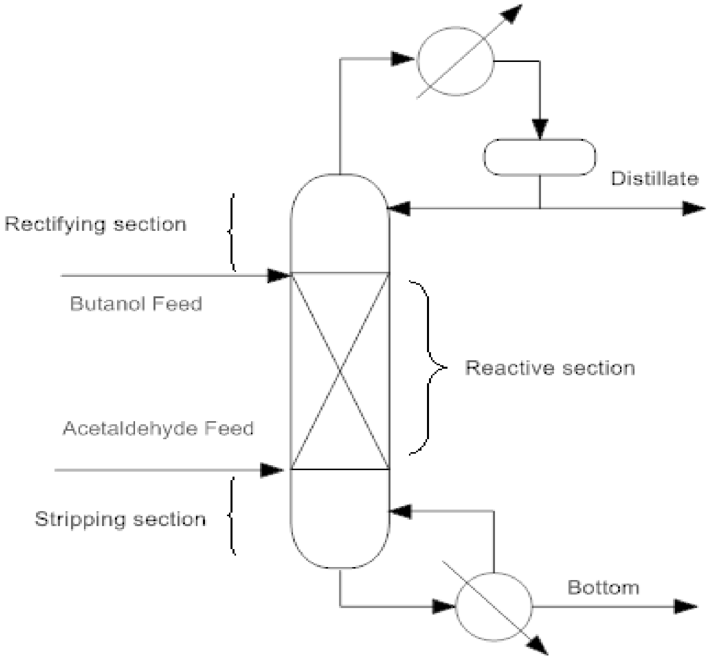

Figure 19 Reactive distillation process for product synthesis

5.2.1 Separate synthesis of DEE and DBE in two reactive distillation systems

5.2.1.1 DEE synthesis

Table 5 Standard conditions of reactive distillation column for DEE synthesis

Feed condition	Column specification

Ethanol flow rate (kmol/hr)	16	Rectifying stages	1
Acetaldehyde flow rate (kmol/hr)	8	Reaction stages	2
Temperature (K)	283	Stripping stages	11
Pressure (MPa)	0.6	Total stages	16
		Reflux ratio	2
		Reboiler heat duty (kW)	Vary
		Pressure (MPa)	0.6

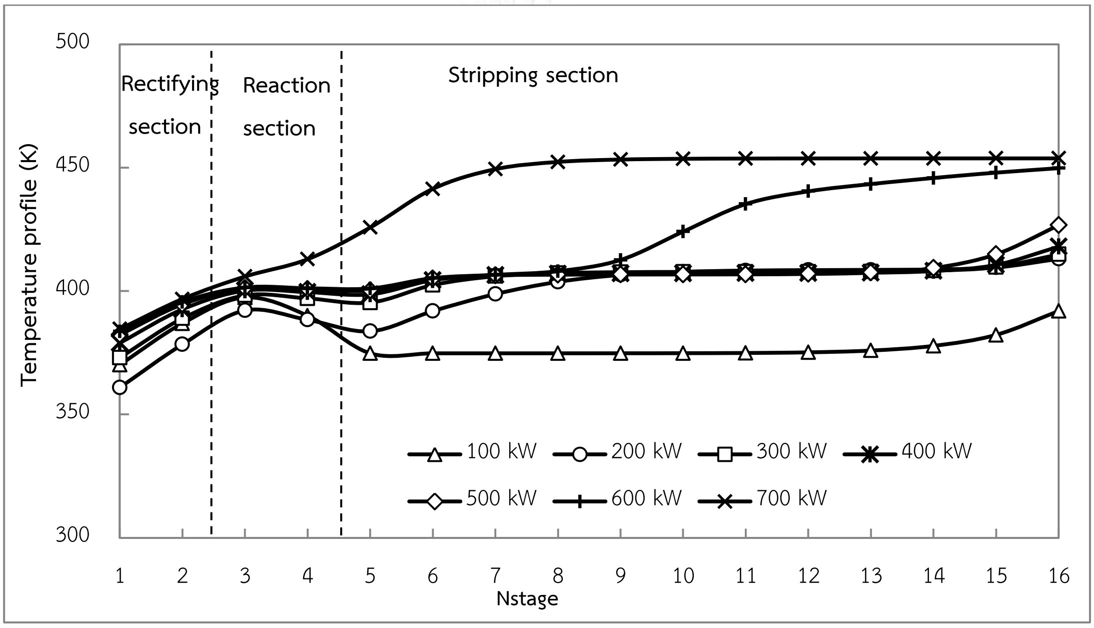

Figure 20 Temperature profiles at standard condition.

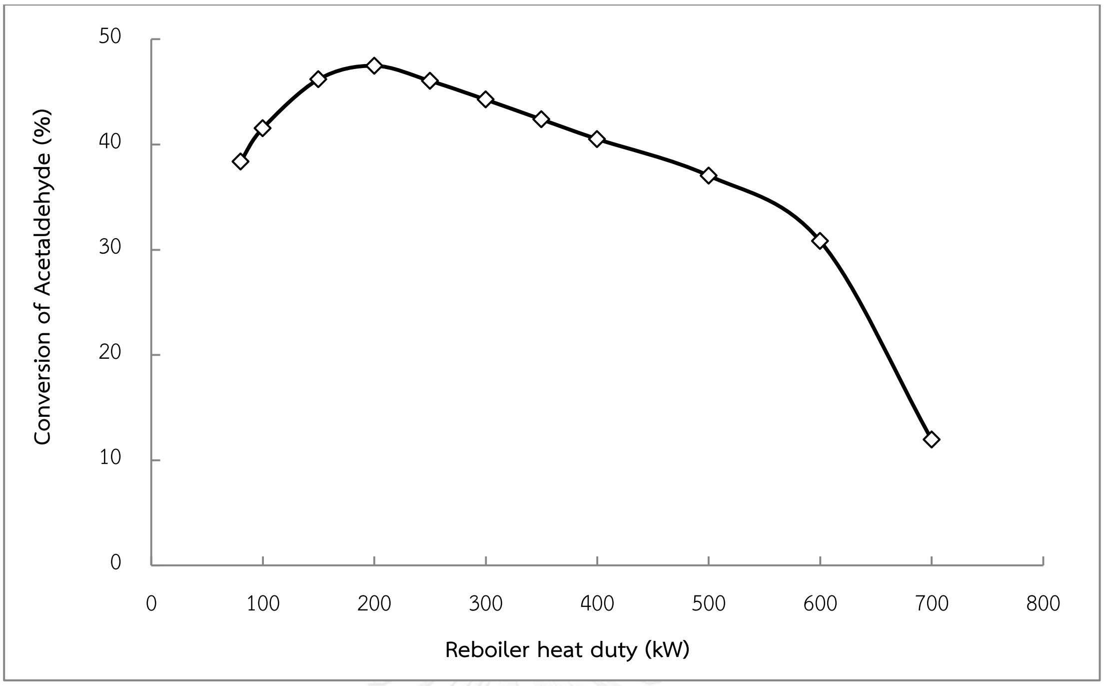

Figure 21 Simulation results of effect of reboiler heat duty on conversion of acetaldehyde

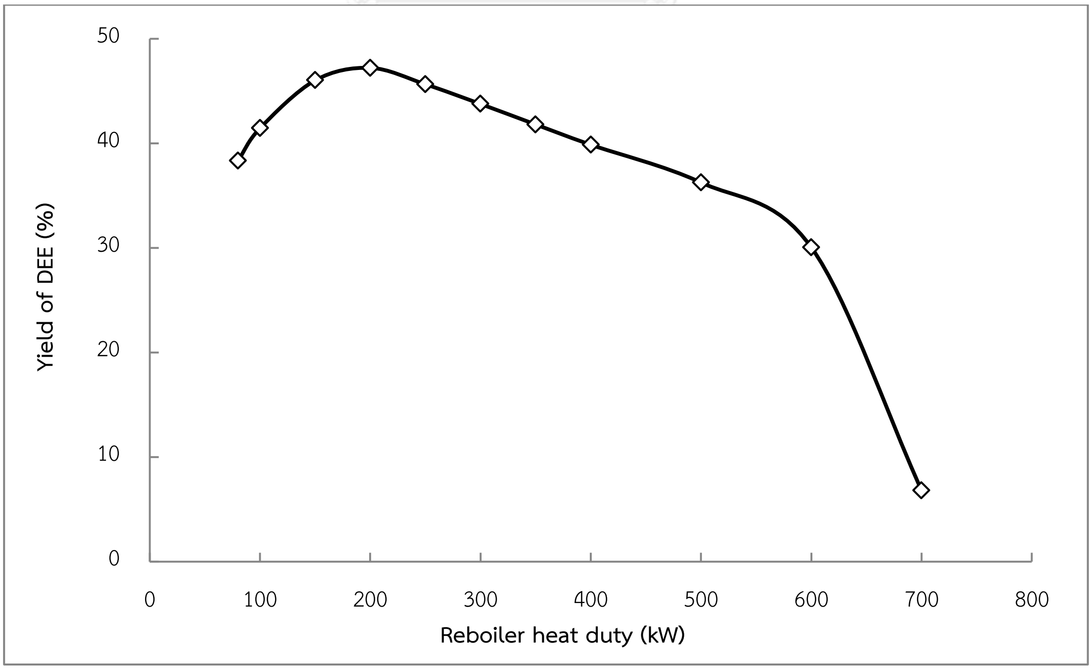

Figure 22 Simulation result of effect of reboiler heat duty on yield of DEE

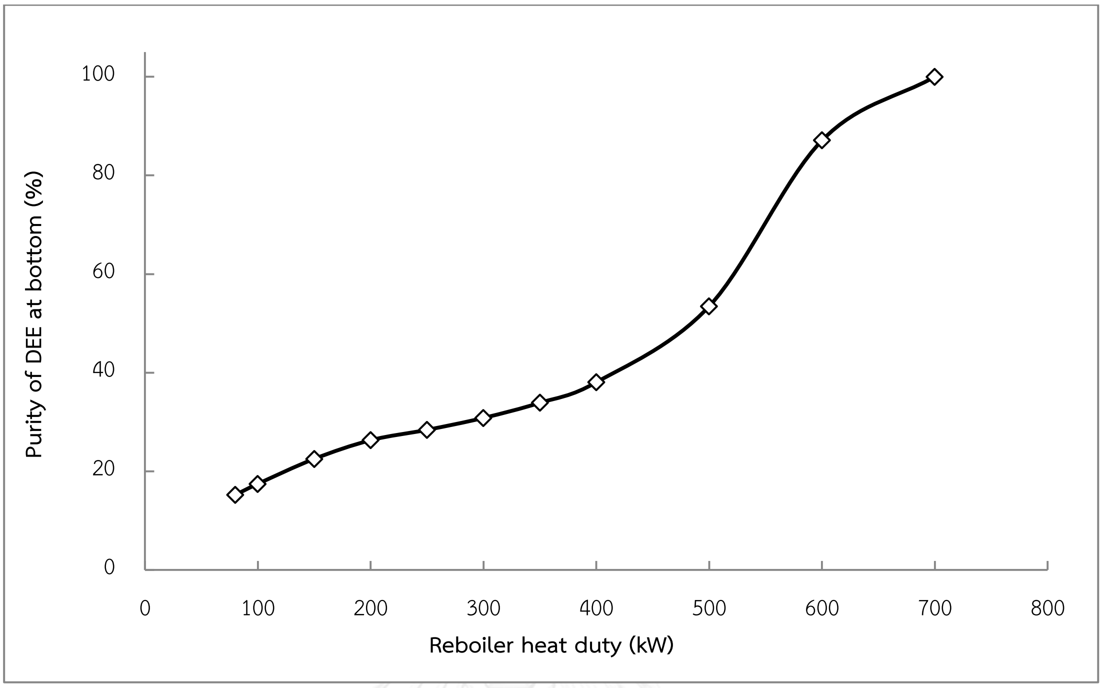

Figure 23 Simulation results of the effect of reboiler heat duty on purity of DEE

For DEE synthesis in reactive distillation column, the ethanol feed flow rate was obtained from data of the ABE product separation process [52]. The standard condition is summarized in Table 5 and reboiler heat duty was studied in a range of 100-700 kW. The temperature profile along with reactive distillation column was illustrated in Figure 20. It could be seen that the temperature was increased with reboiler heat duty. Figure 21 illustrates the effect of reboiler heat duty on conversion of acetaldehyde. Although the rate of reaction increases with reboiler heat duty whereas the equilibrium conversion was decreased because of exothermic nature of reaction. Similarly, yield of DEE decreases with reboiler heat duty as shown in Figure

22. Even though, the low reboiler duty show higher conversion but Figure 23 shows that the purity of DEE in the bottom of column is very low at low reboiler heat duty and increasing with increase of reboiler heat duty. Therefore, DEE synthesis in reactive distillation column was studied in 2 cases, firstly use low and the second is use high reboiler heat duty.

Case I: Low reboiler heat duty

Table 6 Standard conditions of reactive distillation column for DEE synthesis at low reboiler heat duty

Feed condition		Column specification	
Ethanol flow rate (kmol/hr)	16	Rectifying stages	1
Acetaldehyde flow rate (kmol/hr)	8	Reaction stages	3
Temperature (K)	283	Stripping stages	6
Pressure (MPa)	0.6	Total stages	12
		Reflux ratio	2
		Reboiler heat duty (kW)	200
		Pressure (MPa)	0.6

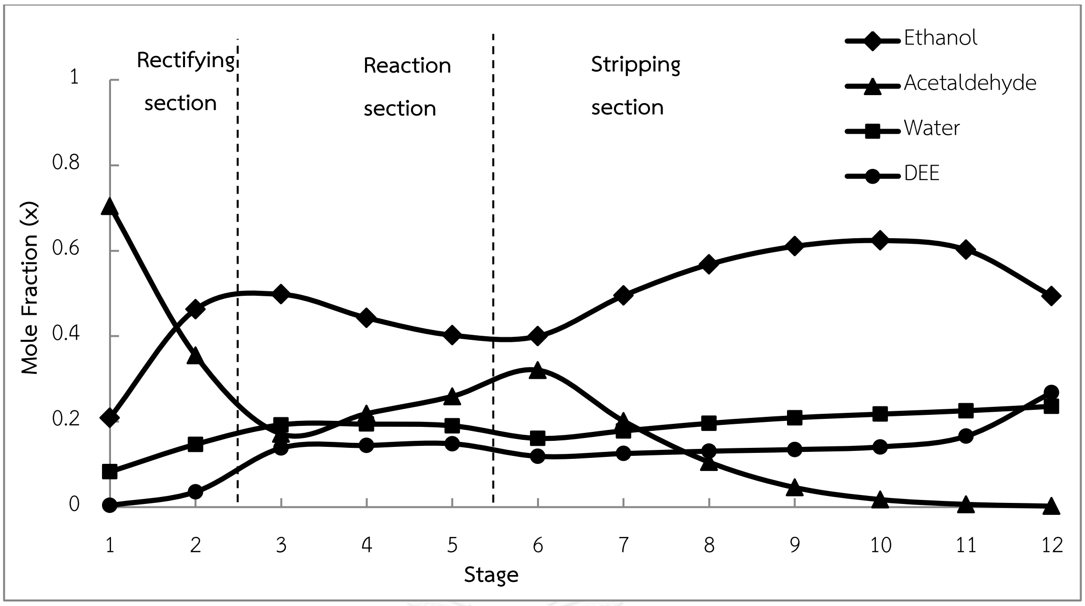

Figure 24 Mole fraction profiles in reactive distillation column with reboiler heat duty of 200 kW.

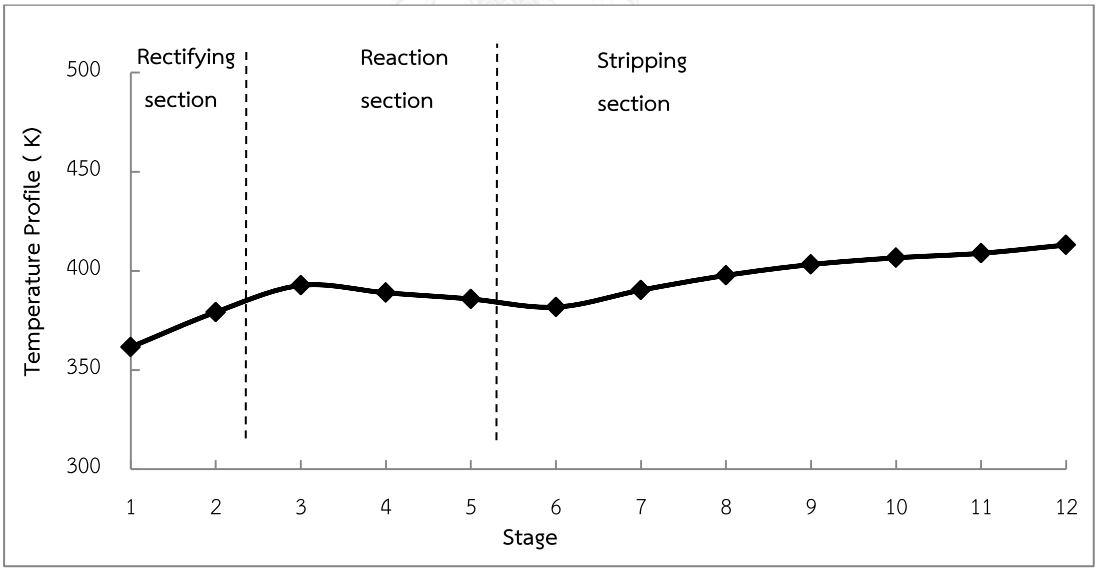

Figure 25 Temperature profile at standard condition.

Table 6 shows the standard condition of DEE synthesis using reactive distillation column operated with a low reboiler heat duty (200 kW). Figure 24 shows the mole fraction profiles along with reactive distillation column at the standard condition. The reaction between ethanol and acetaldehyde occurs in the reaction section to produce DEE. The results show that DEE, water, and ethanol are presence at stripping section and bottom, because the reboiler heat duty is not enough to obtain high purity of DEE in the bottom stream. Moreover, the light component is removed at the rectifying section (stage 2). In distillate stream there is more acetaldehyde in liquid phase due to lower boiling point than ethanol and DEE. Temperature profile was illustrated in Figure 25. As shown in the figure, temperature of reboiler and condenser are 413 K and 200 kW, respectively. Temperature slightly increased in the reaction section due to the exothermic reaction. At standard conditions, 47% conversion of acetaldehyde and 26.7% purity of DEE at bottom column were achieved.

Effect of design parameters

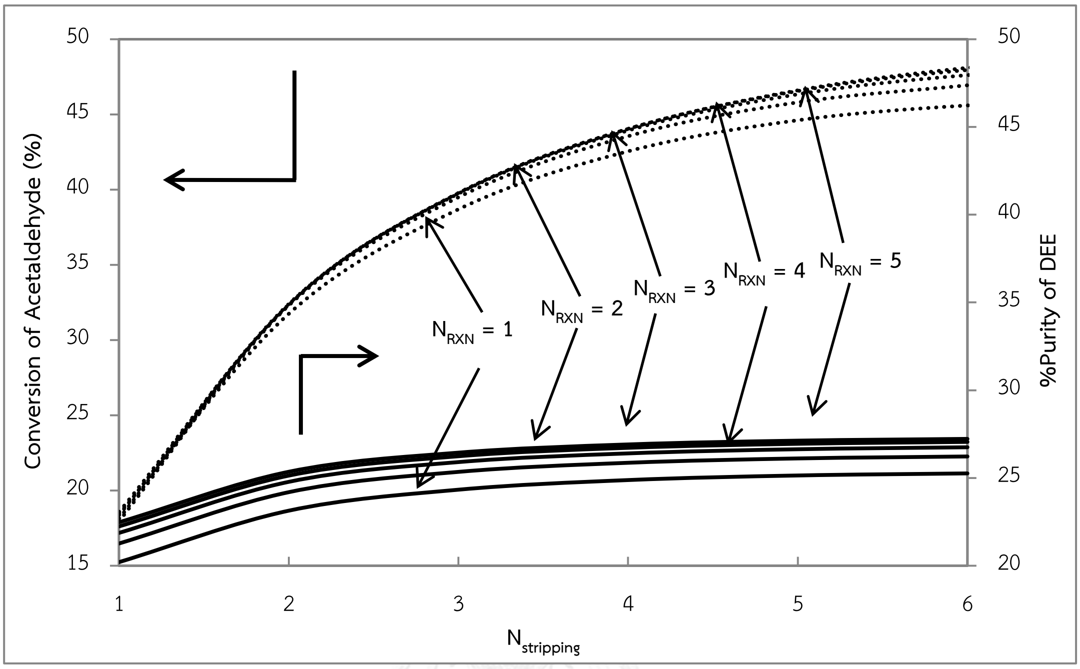

Figure 26 Effect of the number of stripping stage on conversion of acetaldehyde and purity of DEE in the bottom stream. (Rectifying section = 1 stages)

The effect of the number of stripping stages on the conversion of acetaldehyde and purity of DEE in the bottom stream is investigated and the results are shown in Figure 26. It is noted that the other design and operating variables including the number of rectifying stages, reflux ratio and reboiler heat duty were set at standard conditions. The relation between reaction stages and stripping stages were determined by varying the number of these stages from 1 to 5 stages. The results show that conversion of acetaldehyde increased by increasing the number of stripping stages for 1 to 6 reaction stages. Purity of DEE is improved with increasing the number of stripping stages from 1 to 2; however, insignificant improvement with further increase number of stripping stage. The increased of acetaldehyde conversion and DEE purity become negligible with increasing the number of reaction stages higher than 2.

Effect of operating variables

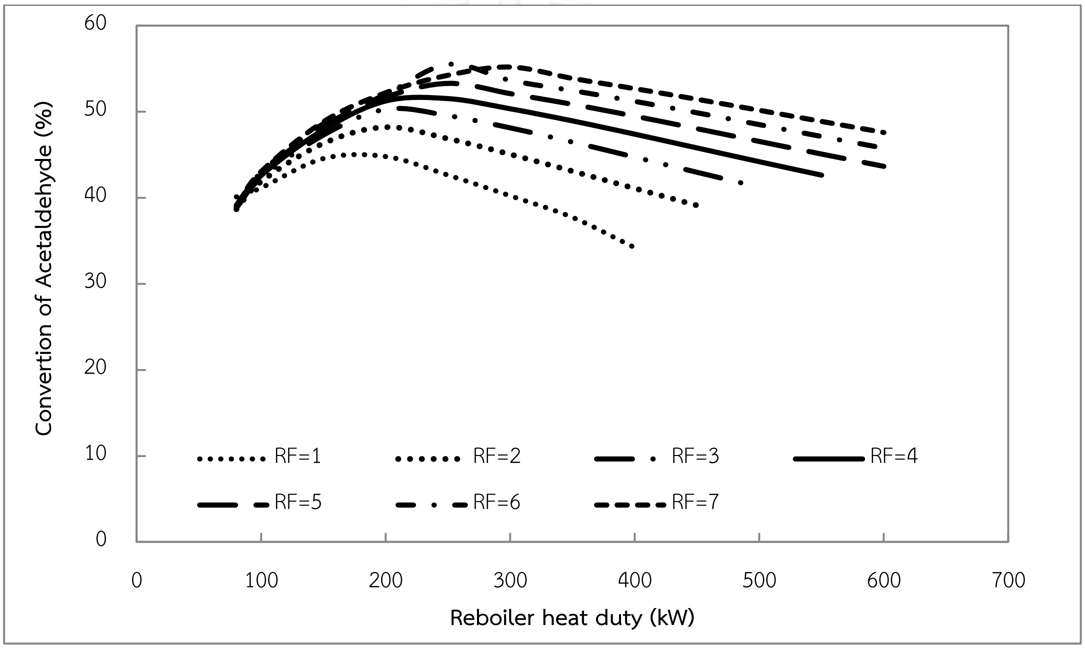

Figure 27 Effect of heat duty of reboiler on conversion of acetaldehyde at various reflux ratios. (Rectifying =1 stage, Reaction =3 stage, Stripping = 6 stage)

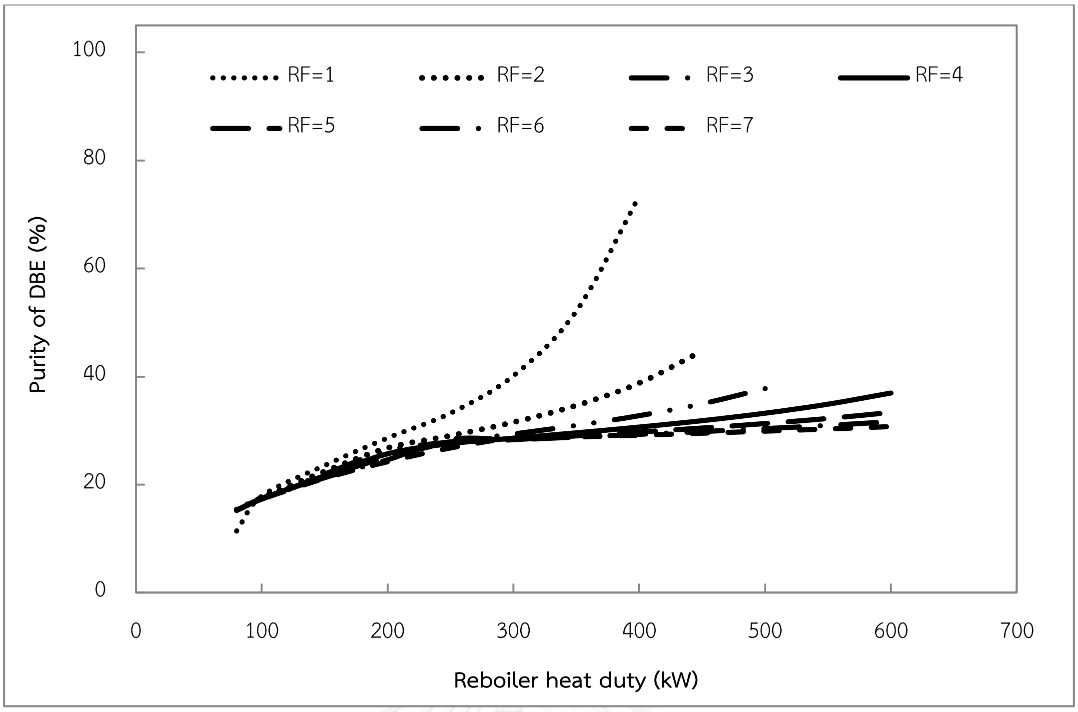

Figure 28 Effect of heat duty of reboiler on purity of DEE at various reflux ratio.

(Rectifying section =1 stages, Reaction section =3 stages, Stripping section = 6 stages).

The effect of reflux ratio on the conversion of acetaldehyde and purity of DEE in bottom stream are shown in Figures 27 and 28, respectively. The conversion of acetaldehyde increased by increasing reflux ratio because increasing reflux ratio could provide higher concentration of ethanol and acetaldehyde in the reactive section of the column that could react to produce DEE. Ethanol and acetaldehyde in distillate were recycled to the reactive section. Accordingly, this was favorable to the reaction of ethanol with acetaldehyde.

Case II: High reboiler heat duty

Table 7 Standard conditions of reactive distillation column for DEE synthesis by use high reboiler heat duty

Feed condition		Column specification	
Ethanol flow rate (kmol/hr)	16	Rectifying stages	1
Acetaldehyde flow rate (kmol/hr)	8	Reaction stages	2
Temperature (K)	283	Stripping stages	11
Pressure (MPa)	0.6	Total stages	16
		Reflux ratio	2
		Reboiler heat duty (kW)	630
		Pressure (MPa)	0.6

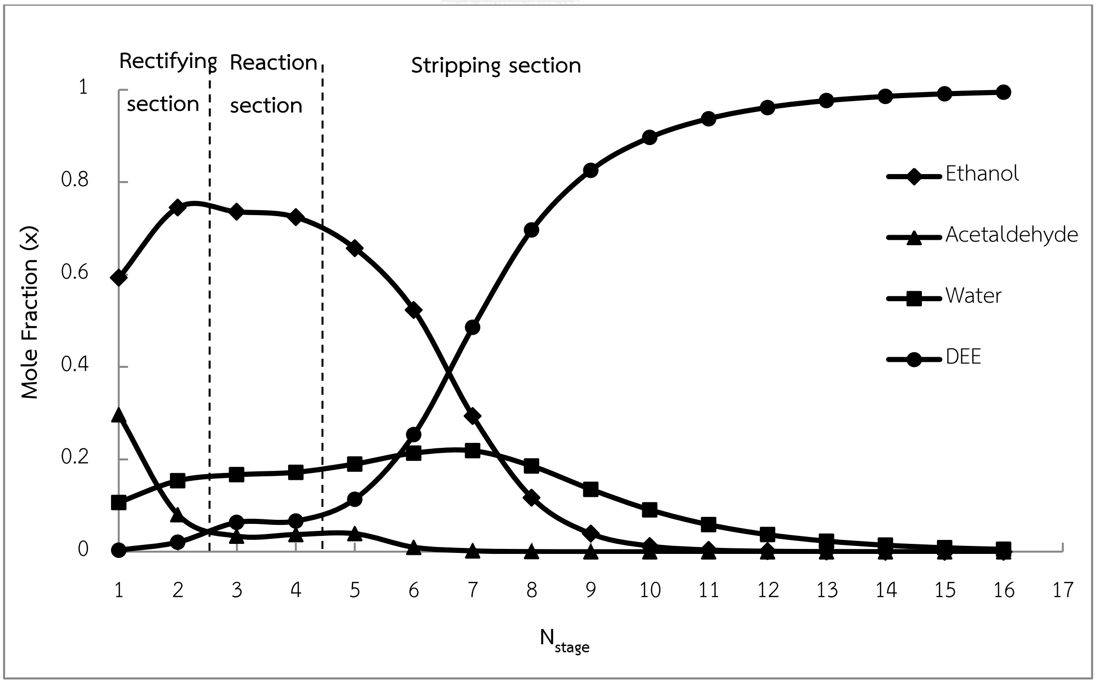

Figure 29 Mole fraction profiles in reactive distillation column.

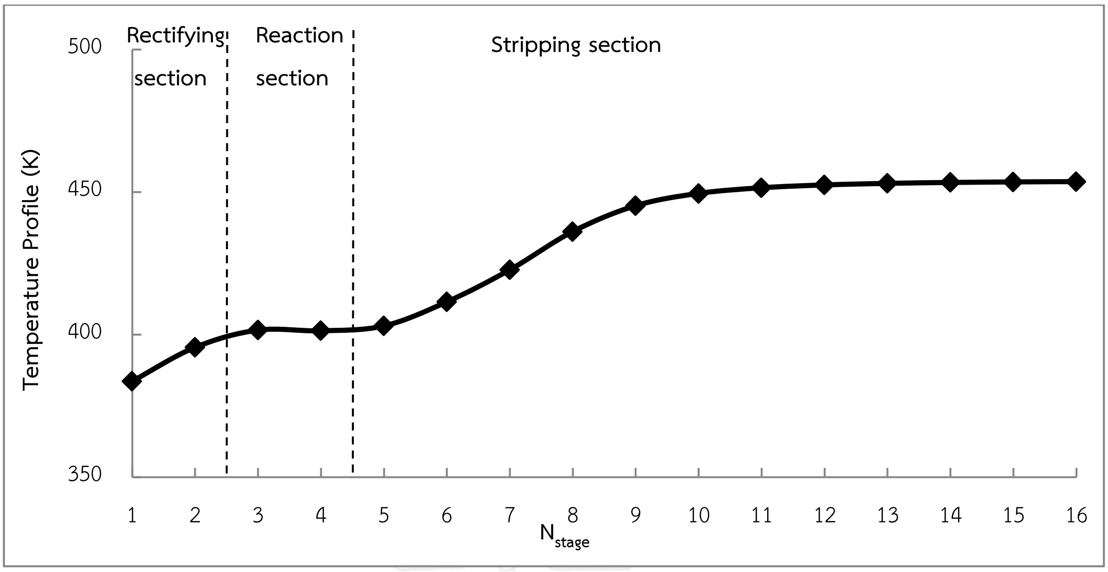

Figure 30 Temperature profile at standard condition.

Table 7 shows the standard condition of DEE synthesis using reactive distillation column operated at a high reboiler heat duty (630 kW). Figure 29 shows the mole fraction profiles along with reactive distillation column at standard condition. The results show that high purity DEE (99.2%) could be obtained at bottom with reboiler heat duty 630 kW and insignificantly loss in the distillate stream due to its high boiling point.

In the distillate stream, there are ethanol, acetaldehyde and water in liquid phase because of the lower boiling point when compared with DEE. Temperature profile was illustrated in Figure 30. It could be seen that the high temperature was observed in the bottom of column and decreased in the middle of column. At standard conditions, 26.6% conversion of acetaldehyde and 99.2% purity of DEE at bottom column were achieved.

Effect of design parameters

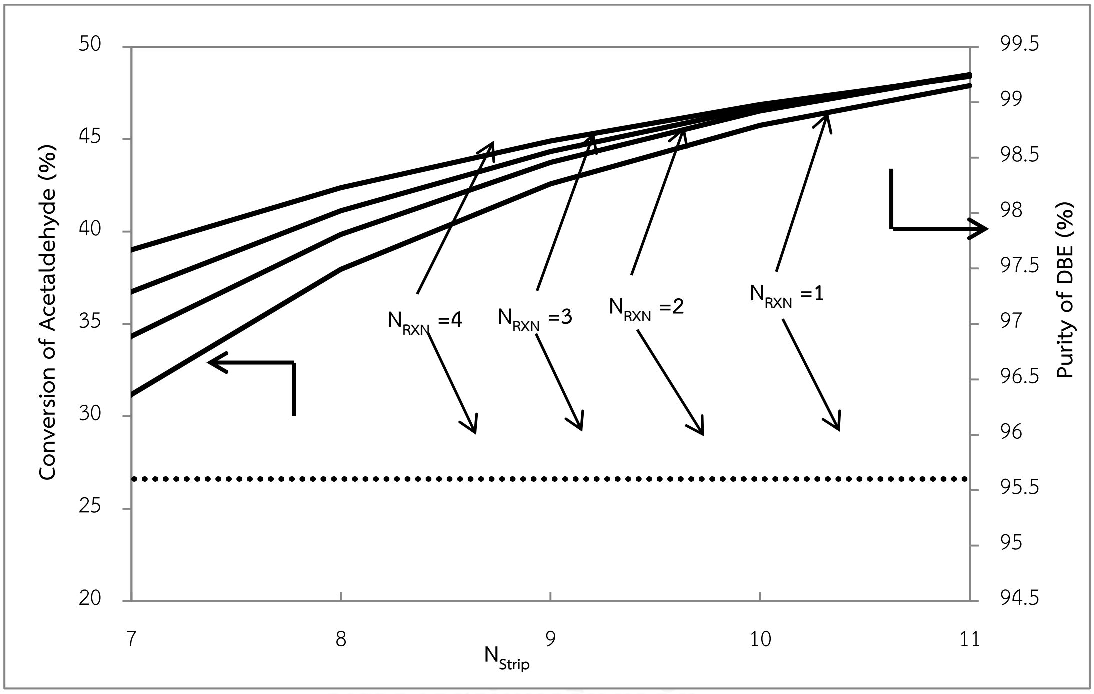

Figure 31 Effect of the number of stripping stage on conversion of acetaldehyde and purity of DEE in the bottom stream. (Rectifying section = 1 stages)

The effect of the number of stripping stages and reaction stages on the conversion of acetaldehyde and purity of DEE in the bottom stream is investigated and the results are shown in Figure 31. It is noted that the other design and operating variables including the number of rectifying stages, reflux ratio and reboiler heat duty were set at standard conditions. The results show that conversion of acetaldehyde are very low and not change with increasing reaction stages. Due to high heat duty, more reactants (ethanol and acetaldehyde) are removed at the rectifying section

Effect of operating variables

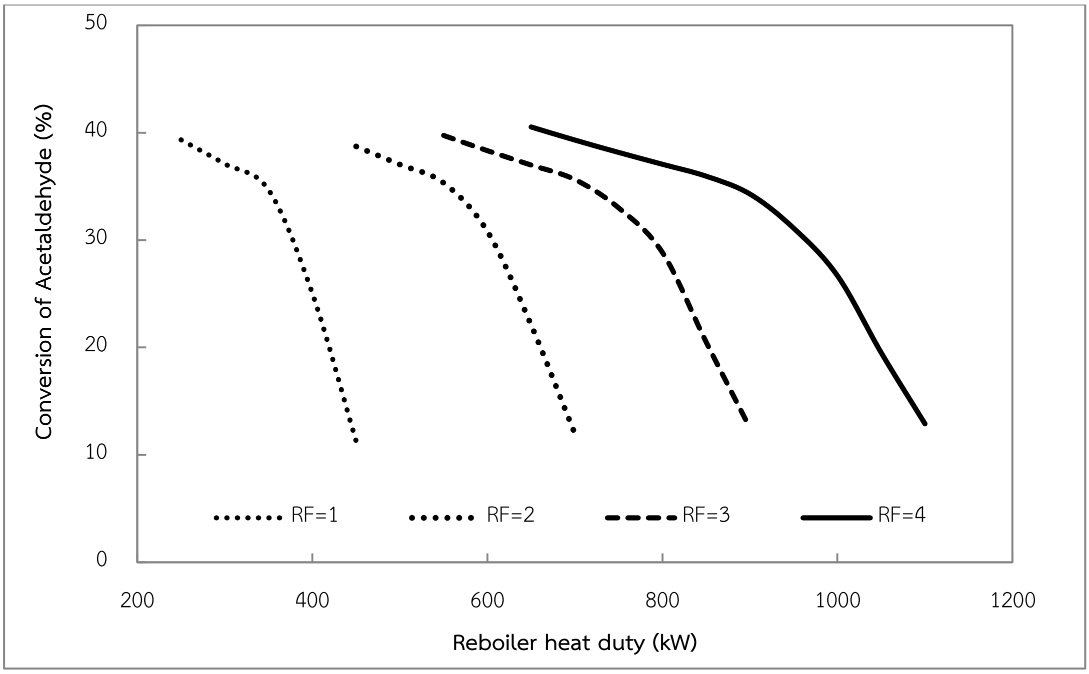

Figure 32 Effect of heat duty of reboiler on conversion of acetaldehyde at various reflux ratio. (Rectifying =1 stage, Reaction =2 stage, Stripping = 11 stage)

The effect of reflux ratio on the conversion of acetaldehyde and purity of DEE in bottom stream are shown in Figures 32 and 33, respectively. The conversion of acetaldehyde and purity of DEE are achieve 26% and 99% respectively, with reboiler heat duty was increasing.

For DEE synthesis in reactive distillation with constant reflux ratio, the conversion of acetaldehyde becomes lower with higher reboiler heat duty, whereas the purity was higher. Therefore, its need to use the additional unit for separate DEE from the mixed components in the bottom of column when use low reboiler heat duty conditions

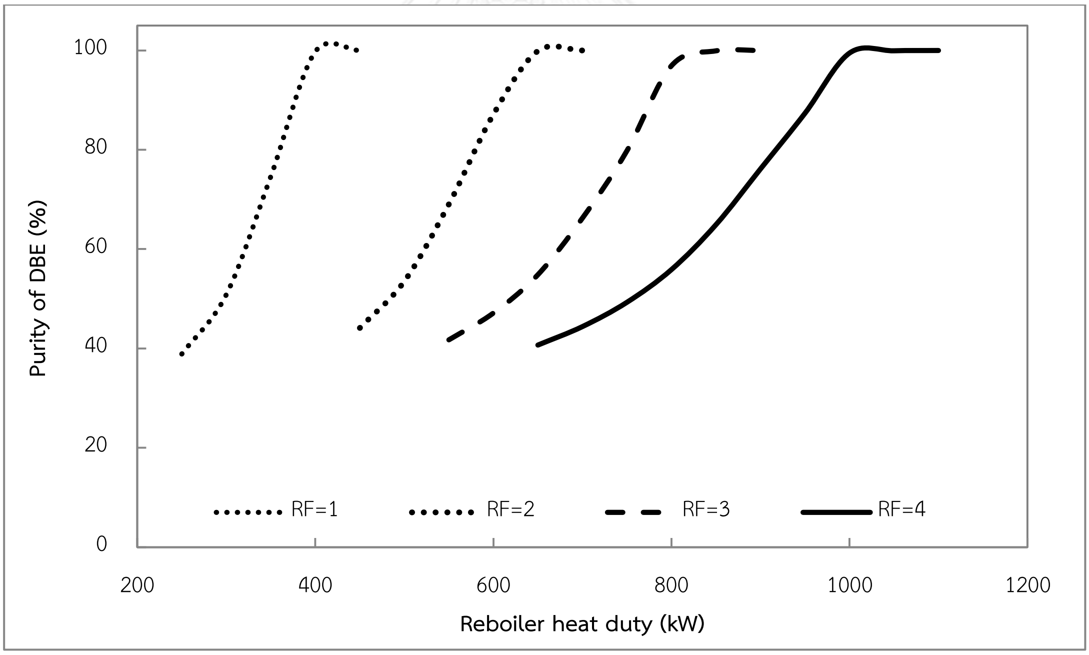

Figure 33 Effect of heat duty of reboiler on purity of DEE at various reflux ratio. (Rectifying section =1 stages, Reaction section =2 stages, Stripping section = 11 stages).

5.2.1.2 DBE synthesis

Table 8 Standard conditions of reactive distillation column for DBE synthesis

Feed condition		Column specification	
Butanol flow rate (kmol/hr)	158	Rectifying stages	2
Acetaldehyde flow rate (kmol/hr)	79	Reaction stages	7
Temperature (K)	283	Stripping stages	3
Pressure (MPa)	6	Total stages	14
		Reflux ratio	2
		Reboiler heat duty (kW)	6000
		Pressure (MPa)	0.6

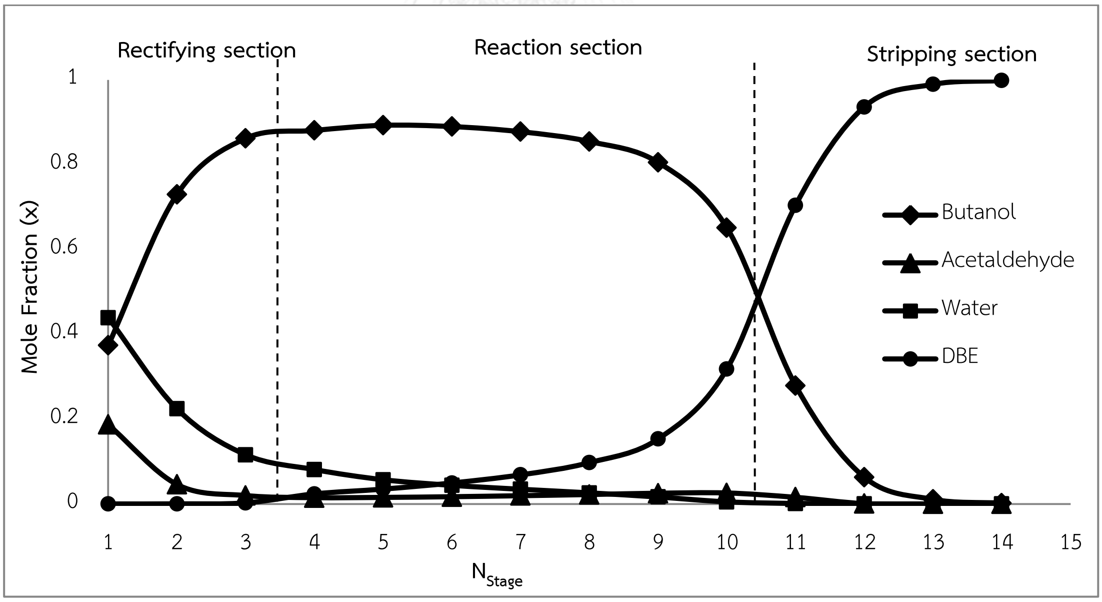

Figure 34 Mole fraction profiles in reactive distillation column.

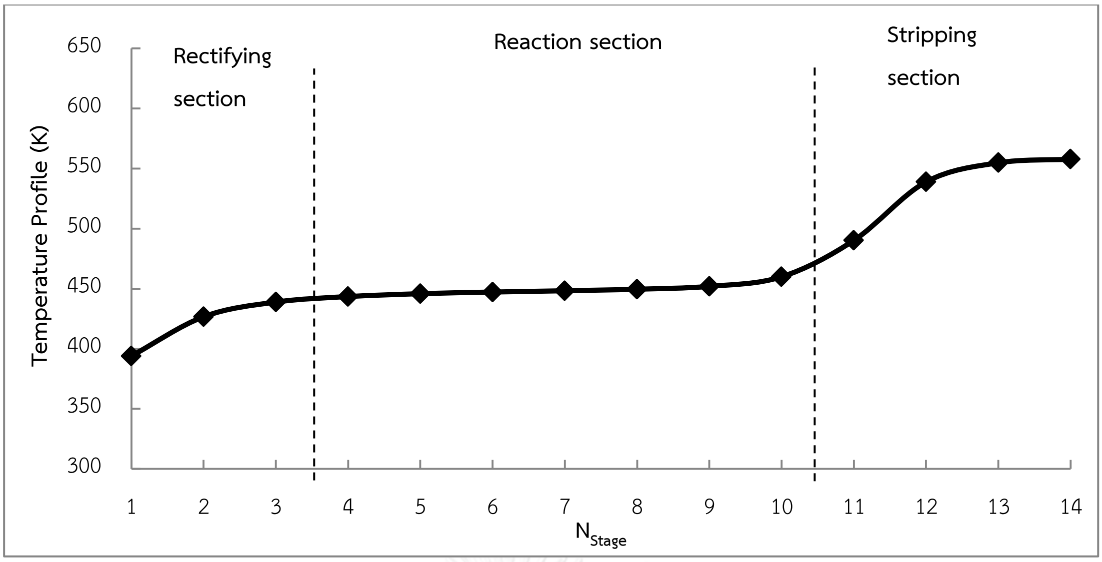

Figure 35 Temperature profile at standard condition.

Table 8 shows the standard condition of DBE synthesis in reactive distillation column. The flow rate of butanol feed is corresponding with the flow rate of ethanol for DEE production with the ratio of 6:1 which is referred from ABE fermentation process. The kinetic model of the reaction between butanol and acetaldehyde was used to predict reaction in the reactive section of column. Figure 34 shows the mole fraction profiles along with reactive distillation column at standard condition. The results show that DBE is obtained at bottom, because of its high boiling point. The light components are removed at the rectifying section as the distillate stream, containing butanol, acetaldehyde and water because of the lower boiling point values compared with DBE. Temperature profile was illustrated in Figure 35. At standard conditions, 70% conversion of acetaldehyde and 99.8% purity of DBE at the bottom stream were achieved.

Effect of design parameters

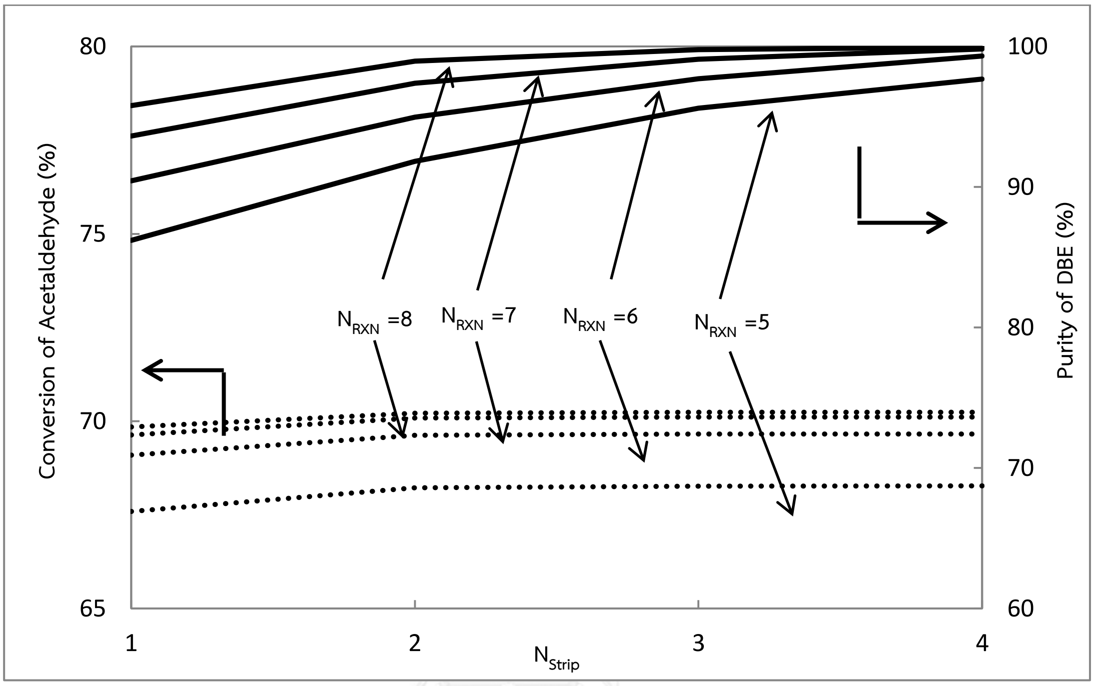

Figure 36 Effect of the number of stripping stage on conversion of acetaldehyde and purity of DBE in the bottom stream. (Rectifying section = 2 stages)

The effect of the number of stripping stages on the conversion of acetaldehyde and purity of DBE in the bottom stream is investigated and the results are shown in Figure 36. It is noted that the other design and operating variables including the number of rectifying stages, reflux ratio and reboiler heat duty were set at standard conditions. The relation between reaction stages and stripping stages were determined by varying the number of these stages from 5 to 8 stages. The results show that conversion of acetaldehyde and purity of DBE increased by increasing the number of stripping stages for 1 to 4 reaction stages. The temperature of the reaction zone was slightly decreased by increasing the number of stripping stages. However, most DBE appears at the bottom of the column when the number of stripping stages was increased.

Effect of operating variables

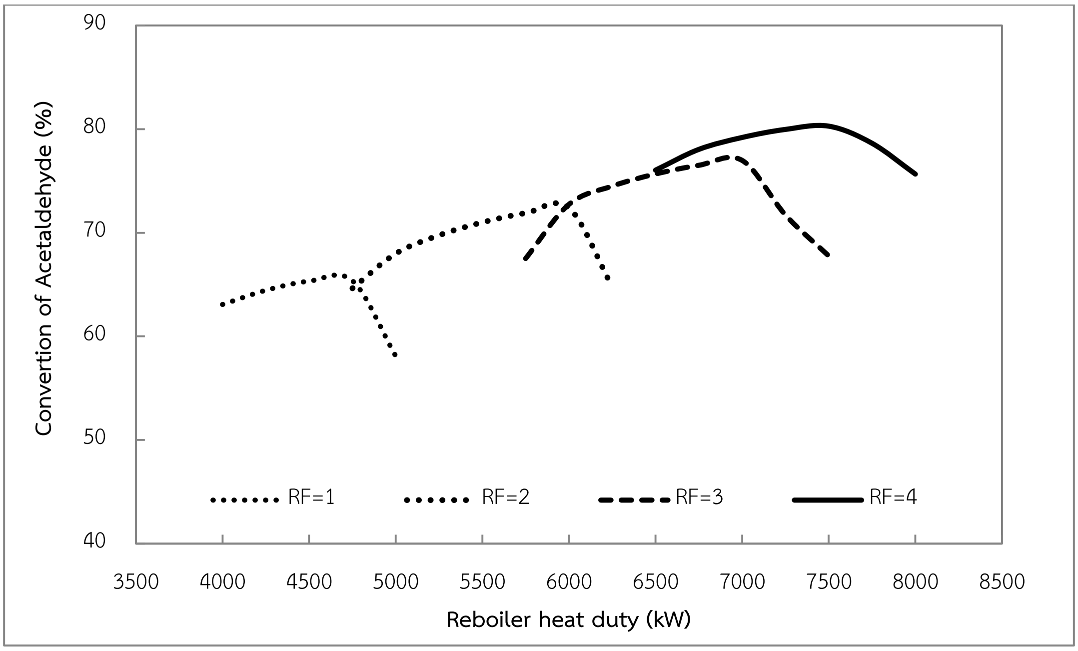

Figure 37 Effect of heat duty of reboiler on conversion of acetaldehyde at various reflux ratio. (Rectifying =2 stage, Reaction =7 stage, Stripping = 3 stage)

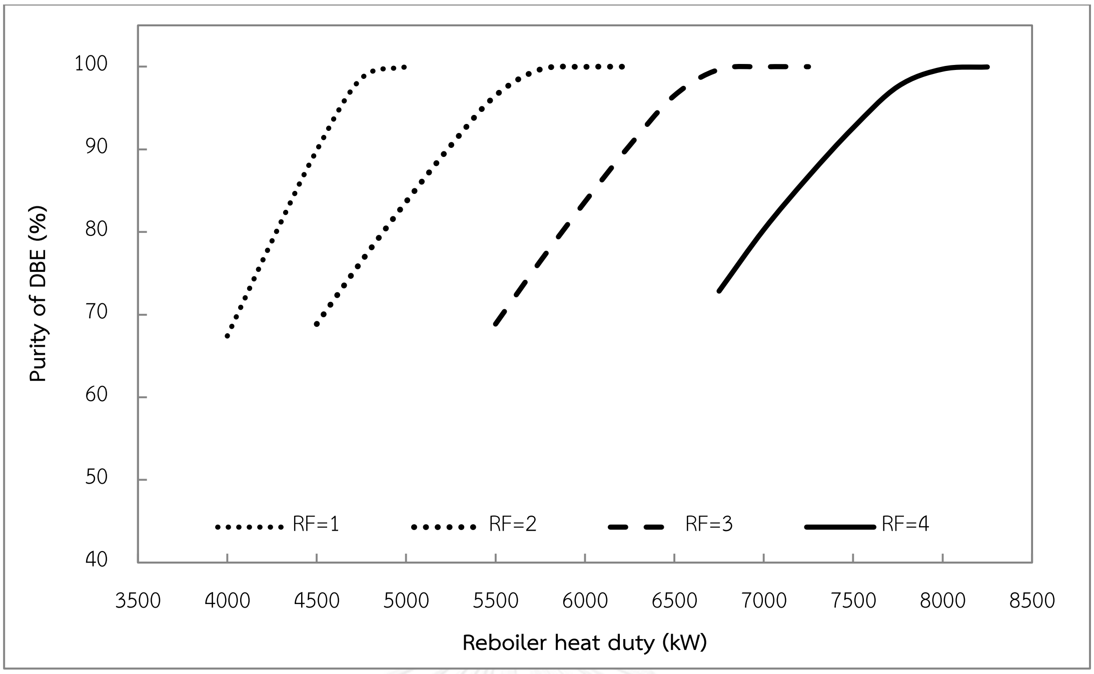

Figure 38 Effect of heat duty of reboiler on purity of DBE at various reflux ratio. (Rectifying section =2 stages, Reaction section =7 stages, Stripping section = 3 stages).

The effect of reflux ratio on the conversion of acetaldehyde and purity of DBE in bottom stream are shown in Figures 37 and 38, respectively. The conversion of acetaldehyde increased by increasing reflux ratio because increasing reflux ratio could provide higher concentration of butanol and acetaldehyde in the reactive section of the column that could react to produce DBE. Accordingly, this was favorable to the reaction of butanol with acetaldehyde. At specific reflux ratio, there is an optimal reboiler heat duty to obtain the highest yield. The almost 99.9% purity of DBE could be obtained with high enough of reboiler heat duty (Fig. 38). For example, approximately 4600 kW for the reflux ratio of 1. However operating at rebolier heat duty higher than optimal value, acetaldehyde conversion is decreased. This might be due to the concentration in reaction section is decreasing by butanol and acetaldehyde are removed to the top of column.

5.2.2 Combined synthesis of DEE and DBE in single reactive distillation system

For this part, the combined reactions for synthesis of DEE and DBE were carried out in the single reactive distillation column. Ethanol and butanol feed are calculated from the ABE product separation process [52]. Table 9 shows the standard condition for DEE and DBE synthesis in reactive distillation column. Figure 39 shows the mole fraction profiles along with reactive distillation column at standard condition. The reactions between butanol, ethanol and acetaldehyde occur in the reaction section to produce DEE and DBE. The light components such as reactants (ethanol and butanol) and by product (water) are removed at the rectifying section. The results show that DBE is obtained at bottom because of DBE is high boiling point than any components in the column. However, DEE is not found. This might be due to much lower reaction rate comparing to DBE formation. One of the reasons might be due to ethanol fed at much lower concentration compared to butanol. Temperature profile was illustrated in Figure 5.34. At standard conditions, 70% conversion of acetaldehyde and 99.8% purity of DBE at bottom column were achieved.

Table 9 Standard conditions of reactive distillation column for DEE and DBE synthesis

Feed condition		Column specification	
Butanol flow rate (kmol/hr)	157	Rectifying stages	2
Ethanol flow rate (kmol/hr)	17	Reaction stages	7
Acetaldehyde flow rate (kmol/hr)	87	Stripping stages	3
Temperature (K)	283	Total stages	14
Pressure (MPa)	0.6	Reflux ratio	2
		Reboiler heat duty (kW)	6400
		Pressure (MPa)	0.6

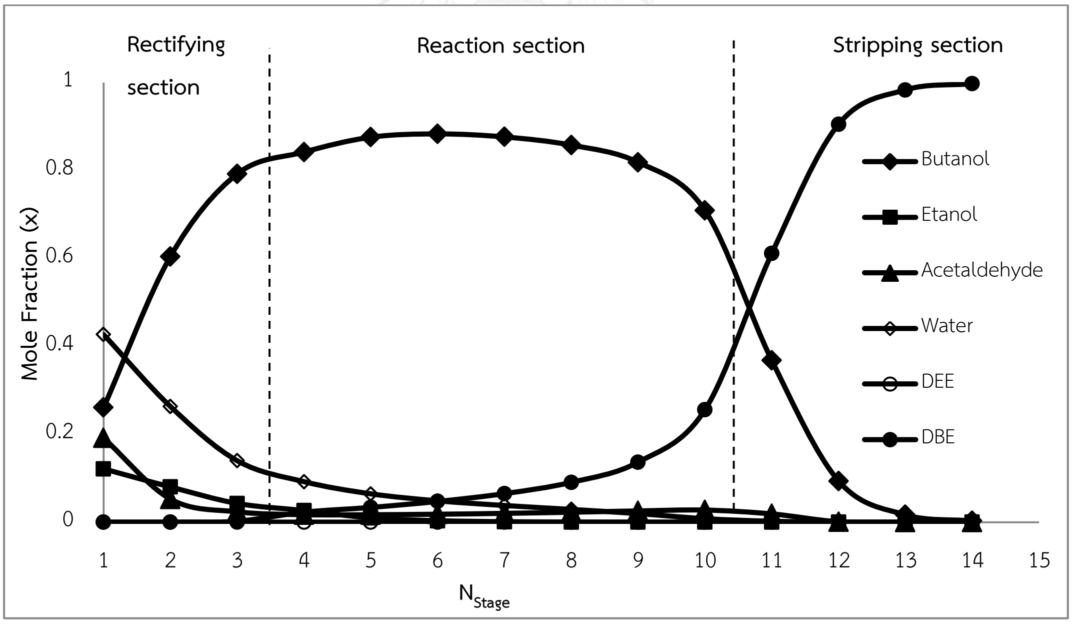

Figure 39 Mole fraction profiles in reactive distillation column.

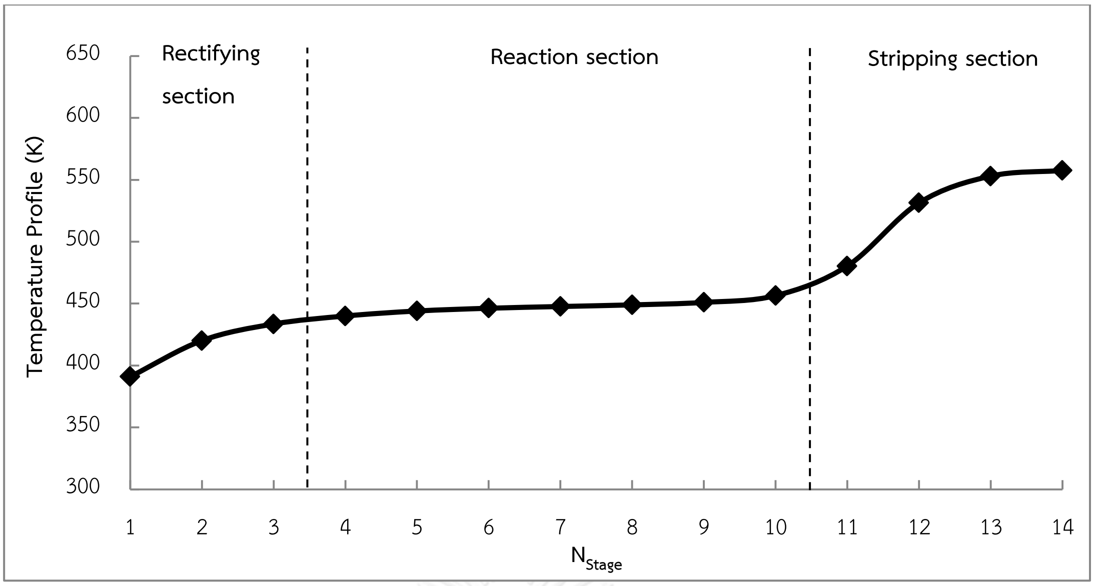

Figure 40 Temperature profile at standard condition.

Effect of design parameters

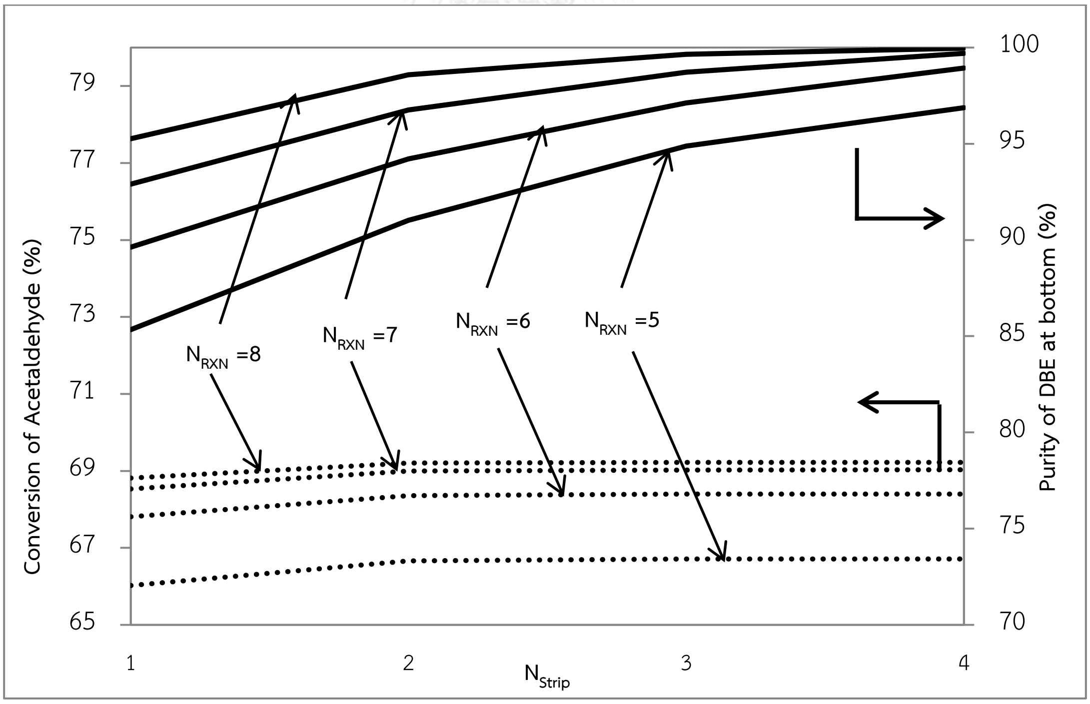

Figure 41 Effect of the number of stripping stage on conversion of acetaldehyde and purity of DBE in the bottom stream. (Rectifying section = 2 stages)

The effect of the number of stripping stages on the conversion of acetaldehyde and purity of DBE in the bottom stream is investigated and the results are shown in Figure 41. It is noted that the other design and operating variables including the number of rectifying stages, reflux ratio and reboiler heat duty were set at standard conditions. The relation between reaction stages and stripping stages were determined by varying the number of these stages from 5 to 8 stages. The results show that conversion of acetaldehyde and purity of DBE increased by increasing the number of stripping stages for 1 to 4 reaction stages. The temperature of the reaction zone was slightly decreased by increasing the number of stripping stages. However, most DBE appears at the bottom of the column when the number of stripping stages was increased.

Effect of operating variables

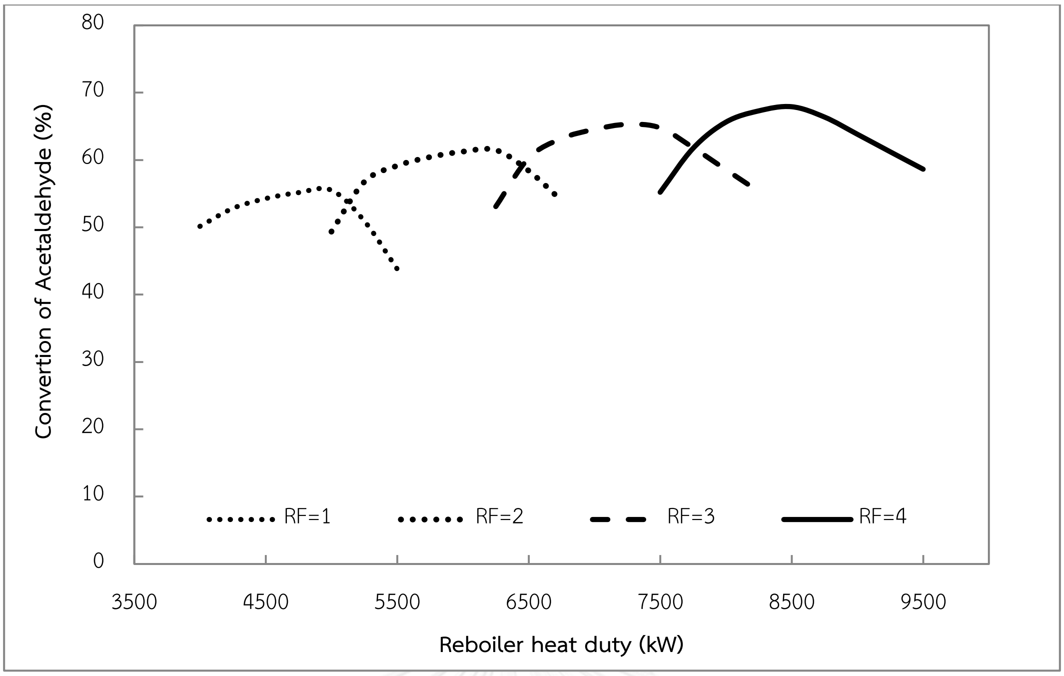

Figure 42 Effect of heat duty of reboiler on conversion of acetaldehyde at various reflux ratio. (Rectifying =2 stage, Reaction =7 stage, Stripping = 3 stage)

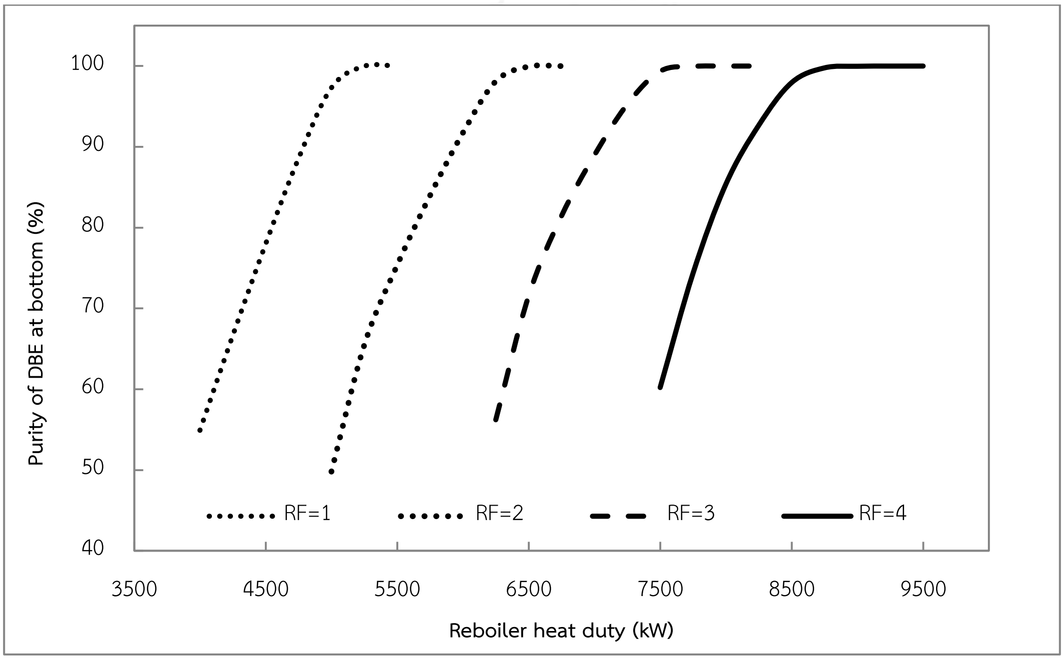

Figure 43 Effect of heat duty of reboiler on purity of DBE at various reflux ratio. (Rectifying section =2 stages, Reaction section =7 stages, Stripping section = 3 stages).

The effect of reflux ratio on the conversion of acetaldehyde and purity of DBE in bottom stream are shown in Figures 42 and 43, respectively. The conversion of acetaldehyde increased by increasing reflux ratio because increasing reflux ratio could provide higher concentration of butanol and acetaldehyde in the reactive section of the column that could react to produce DBE. Butanol and acetaldehyde in distillate were recycled to the reactive section. Accordingly, this was favorable to the reaction of butanol with acetaldehyde. As the reflux ratio increased over 2, the highest conversion of acetaldehyde changed insignificantly and did not affect to the purity of DBE.

5.3 Reactive distillations results and comparison with batch reactor

Table 10 Summary of simulation results for DEE and DBE synthesis in reactive distillation

Characteristics	DEE synthesis with low heat duty	DEE synthesis with high heat duty	DBE synthesis	Combined DEE and DBE in single system
Rectifying stage	1	1	2	2

Reaction stage	3	2	7	7
Stripping stage	6	11	3	3
Reflux ratio	2	2	2	2
Reboiler heat duty (kW)	200	630	6000	6400
Conversion of acetaldehyde (%)	48	26.6	70	70
Yield of product	47	25.6	70	70
Product purity (%)	26.7	99.2	99.8	99.8

Due to all cases simulation results for DEE and DBE synthesis from the acetalization of ethanol and butanol with acetaldehyde respectively in reactive distillation. The suitable design and operating variables was summarized as table 10. The results of DEE synthesis show the conversion of acetaldehyde and product purity are not achieved with reactive distillation. Because of the volatility constrain and the close boiling point of DEE and water.

For DBE synthesis with reactive distillation, the conversion of acteladehyde (70%) show higher than batch reactor (55%) and product purity are achieved (99.8%). Because of the reactive distillation shifted equilibrium reaction by remove water in vapor phase to the top of column and DEE are presence in the bottom of column by stripping section. Moreover, the residues of ethanol and acetaldehyde in the distillate are recycled to reactive section by control reflux ratio of column.

For combined synthesis in single column, the results show that the most of DBE are presence in the bottom of column by stripping section, while DEE not found because of the very low initial feed ratio compare with butanol, the volatility constrain and the close boiling point of DEE and water. Furthermore, the residues of butanol and acetaldehyde in the distillate are recycled to reactive section by control reflux ratio of column. Consequently, the synthesis of DBE from butanol and acetaldehyde by single reactive distillation system could provide higher conversion and product purity. Moreover DBE are shown high cetane number [22].

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The synthesis of l,1-diethoxyetahne (DEE) and 1,1-butoxyethane (DBE) from acetaldehyde and ethanol and butanol respectively, in reactive distillation systems was simulated by using aspen plus simulation program. The kinetic rate constants of the reactions were estimated from literature. This work focused on studying the effects of operating variables on performance of reactive distillation and searching the suitable configuration for synthesis of DEE and DBE. The followings are the conclusions drawn from this study.

For the estimation of missing parameters of DBE, the group contribution methods including Joback's, Gani's and Benson's methods were studied. Benson's method provided the lowest deviation by comparison with the data from literature.

The reaction rate constants in power law model based on mole fraction were estimated by MATLAB program and compared with experimental data as described below:

For DEE synthesis:

kc = 1.92x109exp (-47874/RT) mol/g.s

For DBE synthesis:

kc = 1.88x109exp (-51600/RT) mol/g.s

For the reactive distillation system of DEE and DBE synthesis were studied includes (i) DEE synthesis in reactive distillation column both using low and high reboiler heat duty, (ii) DBE synthesis in reactive distillation column, (iii) Combined synthesis of DEE and DBE in one reactive distillation column. Ethanol and butanol feed flow rate were obtained from data of the ABE product separation process [52].

(i) DEE synthesis in reactive distillation column using low and high reboiler heat duty

The suitable configuration design and operating variable for DEE synthesis by using reactive distillation at low reboiler heat duty are 1 rectifying stage, 3 reactive stages, 6 stripping stages, reflux ratio of 2 and reboiler heat duty of 200 kW. From this configuration, 48% conversion of acetaldehyde, 47.9% yield of DEE with 26.7% purity can be achieved. For the DEE synthesis at high reboiler heat duty, the suitable configuration design and operating variable for the reactive distillation at are 1 rectifying stage, 2 reactive stages, 11 stripping stages, reflux ratio of 2 and reboiler heat duty of 630 kW. From this configuration, 26.6% conversion of acetaldehyde, 25.6% yield of DEE with 99.2% purity can be achieved.

(ii) DBE synthesis in reactive distillation column

The suitable design and operating variables for synthesis of DBE by using reactive distillation are 2 rectifying stages, 7 reactive stages, 3 stripping stages, reflux ratio of 2 and reboiler heat duty of 6000 kW. From this configuration, 70% conversion of acetaldehyde, 70% yield of DBE with 99.8% purity can be achieved.

(iii) Combined synthesis of DEE and DBE in one reactive distillation column

The suitable design and operating variables for synthesis of DEE and DBE by using reactive distillation are 2 rectifying stages, 7 reactive stages, 3 stripping stages, reflux ratio of 2 and reboiler heat duty of 6400 kW. From this configuration, 70% conversion of acetaldehyde, 70% yield of DBE with 99.8% purity can be achieved with small production of DEE.

6.2 Recommendations

In this work, the recommendations are as following:

1. The synthesis of only DBE in reactive distillation is better than the combined reaction with DEE synthesis in single column.

2. The synthesis of DBE from the reaction between butanol and acetaldehyde by using reactive distillation should be experimentally performed and the obtained results to be compared with those from simulations.

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APPENDIX

VITA

Miss. Katewadee Chantowas was born on April 19, 1986 in Nakhonphanom, Thailand. She finished high school from Princess Chulabhorn's collage Mukdahan School, Mukdahan in 2006. She received a Bachelor's Degree of Chemical Engineering, in Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University in 2010. She has been further studying Master's Degree of Chemical Engineering, in Department of Engineering, Chulalongkorn University, Thailand, 2012,