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แบบเกิดปฏิกิริยาร่วมกับเพอแวปพอเรชัน



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PROCESS SIMULATION OF SODIUM METHOXIDE PRODUCTION FROM METHANOL AND  
SODIUM HYDROXIDE USING REACTIVE DISTILLATION COUPLED WITH PERVAPORATION

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A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

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งานวิจัยนี้เป็นการศึกษาการผลิตโซเดียมเมทอกไซด์ซึ่งเป็นตัวเร่งปฏิกิริยาที่สำคัญในกระบวนการผลิตไบโอดีเซลจากปฏิกิริยาของเมทานอลและโซเดียมไฮดรอกไซด์ งานวิจัยนี้ประเมินผลของกระบวนการต่างๆในการผลิตสารละลายโซเดียมเมทอกไซด์ในเมทานอล กระบวนการนี้จำลองโดยใช้โปรแกรม Aspen Plus ทั่วไป กระบวนการผลิตโซเดียมเมทอกไซด์มีสามกระบวนการประกอบด้วย 1) เครื่องปฏิกรณ์-หอกลิ้น 2) หอกลิ้นแบบเกิดปฏิกิริยา-หอกลิ้น และ (3) หอกลิ้นแบบเกิดปฏิกิริยาร่วมกับเพอแวนพอเรชัน โดยตัวแปรอิสระที่ศึกษาสำหรับแต่ละกระบวนการ ณ ความดันบรรยากาศ ได้แก่ อัตราส่วนโดยมวลของเมทานอลต่อโซเดียมไฮดรอกไซด์ที่ป้อนเข้ามา อัตราของผลิตภัณฑ์ที่ล่องสู่อ่างของหอกลิ้นแบบเกิดปฏิกิริยา จำนวนขั้นตอนทั้งหมด และตำแหน่งขั้นตอนที่ป้อนเมทานอลเข้าไป ซึ่งมีการใช้ข้อมูลจำเพาะของผลิตภัณฑ์ ได้แก่ โซเดียมเมทอกไซด์ 675 กิโลกรัมต่อชั่วโมง ความเข้มข้นต่ำกว่า 45% โดยมวลในเมทานอลที่มีน้ำน้อยกว่า 0.1% โดยมวล ถัดจากนั้นประสิทธิภาพของกระบวนการทั้งหมดจะถูกเปรียบเทียบ โดยพบว่าอัตราส่วนโดยมวลของเมทานอลต่อโซเดียมไฮดรอกไซด์ที่ป้อนเข้าจะเหมาะสมที่อัตราส่วนเท่ากับ 1.4 สำหรับกระบวนการหอกลิ้นแบบเกิดปฏิกิริยา-หอกลิ้นและกระบวนการหอกลิ้นแบบเกิดปฏิกิริยาร่วมกับเพอแวนพอเรชัน ในขณะที่กระบวนการเครื่องปฏิกรณ์-หอกลิ้นค่าที่เหมาะสมจะอยู่ที่อัตราส่วนเท่ากับ 4 ถัดจากนั้น เมื่อพิจารณาถึงการใช้พลังงานของกระบวนการหอกลิ้นแบบเกิดปฏิกิริยาร่วมกับเพอแวนพอเรชัน จะดีกว่าระบบอื่นอีก 2 ระบบ โดยที่ค่าพลังงานที่ระบบต้องการคือ 2229.37, 35.13 และ 34.25 จิกะจูลต่อชั่วโมง สำหรับกระบวนการเครื่องปฏิกรณ์-หอกลิ้น กระบวนการหอกลิ้นแบบเกิดปฏิกิริยา-หอกลิ้น และกระบวนการหอกลิ้นแบบเกิดปฏิกิริยาร่วมกับเพอแวนพอเรชัน ตามลำดับ โดยจะเห็นได้ชัดว่ากระบวนการหอกลิ้นแบบเกิดปฏิกิริยาร่วมกับเพอแวนพอเรชัน เป็นทางเลือกที่ดีที่สุดในการผลิตโซเดียมเมทอกไซด์จากเมทานอลและโซเดียมไฮดรอกไซด์

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SIRIPORN AEAMSUKSAI: PROCESS SIMULATION OF SODIUM METHOXIDE PRODUCTION FROM METHANOL AND SODIUM HYDROXIDE USING REACTIVE DISTILLATION COUPLED WITH PERVAPORATION. ADVISOR: PROF. SUTTICHA ASSABUMRUNGRAT, Ph.D., 76 pp.

This research investigates production of sodium methoxide, which has been used as a significant catalyst in biodiesel production process, from the reaction of methanol and sodium hydroxide. This work evaluates in various processes for production of sodium methoxide solution in methanol. The processes are simulated using commercial Aspen Plus program. Three processes of manufacturing sodium methoxide include 1) reactor-distillation, 2) reactive distillation-distillation and 3) reactive distillation coupled with pervaporation. The independent variables are studied at atmosphere pressure for each process such as methanol to sodium hydroxide feed mass flow ratios, Bottom rate of reactive distillation, total number of stages and feed stage location of methanol. Using the product specifications, namely, the sodium methoxide of 675 kg/h under 45 wt.% in methanol solution, containing less than 0.1 wt.% water. Then, the performance of all processes are compared. It was found that the suitable methanol to sodium hydroxide feed mass flow ratio for the reactive distillation-distillation and reactive distillation coupled with pervaporation processes is 1.4 while it is 4 for the reactor-distillation. Next, considering the energy consumption, the reactive distillation coupled with pervaporation outperforms the other two systems. The values of the required energy are 2229.37, 35.13 and 34.25 GJ/h for the reactive distillation coupled with pervaporation, reactive distillation-distillation and reactor-distillation processes, respectively. It is clear that the reactive distillation coupled with pervaporation process is the best alternative for production of sodium methoxide from methanol and sodium hydroxide.

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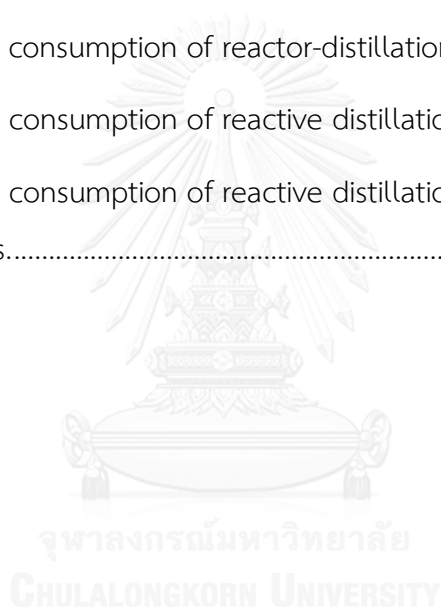


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# CHAPTER 1

## INTRODUCTION

### 1.1 Rationale

Sodium methoxide is a high performance alkoxide catalyst used by a wide variety of companies in markets of biodiesel production, food processing, pharmaceutical, plastic and petrochemicals. In biodiesel production, the base catalysts have been commonly used for catalyzing transesterification reactions that are chemical reactions between vegetable oil and alcohol or animal fat and alcohol to produce biodiesel [1]. It is a good choice because of faster and less corrosive. The strong base such as sodium hydroxide (NaOH) and sodium methoxide ( $\text{NaOCH}_3$ ) are usually used in the transesterification process. The sodium hydroxide is an attractive catalyst because it is cheap, offering higher conversion of triglycerides to biodiesel in moderate conditions. But it also causes a side reaction of saponification and emulsion happened [2]. The presence of water from raw materials and a reaction byproduct between methanol and sodium hydroxide are being negatively affected. The water accelerates hydrolysis of triglycerides and increases FFAs content in vegetable oils. The FFAs reacts with alkaline catalyst to produce soap, causing reduction of its catalytic effectiveness, conversion and yield of biodiesel. For sodium methoxide, there is no water present in the reaction system to cause soap formation. Thus, it is an alternative to be used instead of sodium hydroxide to overcome side reaction in biodiesel production [3].

There are a number of processes using different precursors for sodium methoxide synthesis. The top four precursors consist of sodium amalgam [4], sodium metal, sodium hydroxide and sodium acetate, as feedstock to be mixed with methanol. However, sodium amalgam and sodium acetate precursors have been abandoned because the processes are toxic and difficult to operate. Thus, sodium metal and sodium hydroxide are used industrially at present. Many designs have been proposed since then including reaction vessel, electrolytic cell and reactive distillation, etc.

In general, distillation columns are high-energy-consuming units. However, distillation is used by a wide variety of industries for separation. Therefore, the matured technology allows reliable design and easy operation as well as flexibility. In the chemical process industries, the desired product is separated from other products and reactants and purified by distillation after the reaction by differences in the relative volatilities of the components in the mixture. In various cases, integration of reaction and distillation in a single multifunctional process unit enhances the performance of the process. This particular combination is called reactive distillation, which is developed from conventional distillation columns. The prominent points of reactive distillation are shifting chemical reaction equilibrium, no additional auxiliary solvent, bypassing azeotrope, decreased investment and a fewer number of process steps compared to those of conventional processes. Thus, there are some reactive distillations which are designed for sodium methoxide production instead of conventional processes [5]. However, it is still interesting to find a novel process which outperforms the existing reactive distillation which still often uses more excessive methanol and requires high energy consumption for operation [6].

The work focuses on the comparison of sodium methoxide production using sodium hydroxide and methanol as feedstock by using 3 different processes including 1) reactor-distillation process, 2) reactive distillation-distillation process and 3) reactive distillation coupled with pervaporation process. It is believed that the reactive distillation coupled with pervaporation can improve performance and reduce energy consumption of the process. The design of reactor-distillation process includes a continuous reactor followed by a distillation train while the reactive distillation consists of one column having sodium hydroxide (limiting reactant) fed at the top of column and methanol fed at the bottom of column and a separate distillation column for methanol-water separation. In the part of reactive distillation coupled with pervaporation, a pervaporation membrane is used to separate methanol from water while the reaction occurs. Three processes are designed to produce a solution of sodium methoxide in methanol and the effects of several key parameters on the performance of three processes are studied.

## 1.2 Research Objectives

1.2.1 To simulate sodium methoxide production process using sodium hydroxide (limiting reactant) and methanol as feedstocks.

1.2.2. To compare the performance of the three processes which are reactor-distillation process, reactive distillation-distillation process and reactive distillation coupled with pervaporation process through Aspen Plus.

## 1.3 Scope of work

1. Validation of simulation of sodium methoxide production from sodium hydroxide and methanol by using reactive distillation as the base case study and simulations for determining optimal process.

2. Design of sodium methoxide production by reactor-distillation process including of a continuous reactor followed by a distillation trains and purpose reactive distillation coupled with pervaporation to improve reactive distillation process by using Aspen Plus program. The effect of key parameters such as methanol to sodium hydroxide feed mass flow ratios, Bottom rate of reactive distillation, total number of stages and feed stage location of methanol on composition of products and energy consumption are main considered.

3. Comparison of the performances of reactor-distillation process, reactive distillation process and reactive distillation coupled with pervaporation to produce a solution of sodium methoxide in methanol solution.

## 1.4 Expected Outputs

An efficient process for sodium methoxide production from sodium hydroxide and methanol by using reactive distillation coupled with pervaporation process is expected.

## CHAPTER 2

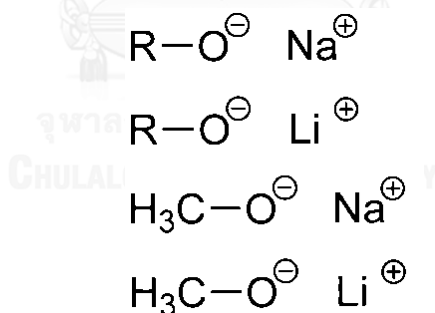
### THEORY

This chapter presents essential information of derivation for the sodium methoxide production including alkaline metal alkoxide, sodium methoxide, reaction of sodium methoxide synthesis and equipment in sodium methoxide synthesis.

#### 2.1 Alkaline metal alkoxide

##### 2.1.1 What is alkaline metal alkoxide ?

Alkoxide (also called alcoholate) is the conjugate bases of corresponding alcohol. They as chemical compounds consist of negatively charged oxygens atom that are found as intermediaries in various reactions. Alkaline metal alkoxide is a strong reducing agent. The alkoxide is a compound constructed from alcohol that replaces the hydrogen of the hydroxy group by monovalent metal. The structure of alkaline metal alkoxide shown in the Figure 2.1. It divides in three parts consisting of alkyl group (-CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -C<sub>3</sub>H<sub>7</sub>), oxygen atom and alkaline metal (Na<sup>+</sup>, Li<sup>+</sup>).



**Figure 2.1** The structures of typical alkoxide groups (from top to bottom): sodium alkoxide, lithium alkoxide, sodium methoxide, and lithium methoxide (R = organic substituent) [7].

##### 2.1.2 Sodium methoxide

Sodium methoxide is a chemical compound with the formula CH<sub>3</sub>ONa. Sodium methoxide as IUPAC name and other names are sodium methylate, methanol sodium salt, sodium methanolate, natriummethanolat (German), metanolato de sodio (Spanish), méthanolate de sodium (French), metilato di sodio, metanolato di sodio

(Italian) etc. It is either white or colorless in appearance. It is prominently used in industries as a reagent. Sodium methoxide is formed by removing a hydrogen ( $H^+$ ) proton from methanol and replace by sodium metal.

#### 2.1.2.1 Physical and chemical properties of sodium methoxide

The physical and chemical properties of sodium methoxide in solution and powder forms are summarized in Table 2.1.

**Table 2.1** Physical and chemical properties of sodium methoxide [8, 9]

Properties	Sodium methoxide (30 wt.%) in methanol solution	Sodium methoxide powder
Molecular Formula	$NaOCH_3$	$NaOCH_3$
Molecular Weight	53.02	53.02
Physical state and appearance	Liquid or light yellow	White solid
Odor	Alcohol-like	Not available
pH	No information available @ 20°C 20 g/L aq.sol.	Not available (1% solution/water)
Melting Point/Range	1 - 5 °C / 33.8 - 41 °F	Decomposition temperature: >126°C (258.8°F)
Boiling Point/Range	93 °C / 199.4 °F @ 760 mmHg	Not available
Flash Point	33 °C / 91.4 °F	Not available
Vapor Pressure	150 hPa @ 50 °C	Not applicable
Vapor Density	Not available	1.1 (Air = 1)
Relative Density	0.97	Not available
Solubility	Water reactive	Not available

#### 2.1.2.2 Reaction of sodium methoxide synthesis

The sodium methoxide can be synthesized by several methods from different precursors as summarized in Table 2.2. The reaction is carried out in vessel, electrochemical cell, and reactive distillation, etc.

**Table 2.2** Summary of synthesis of various sodium alkoxides.

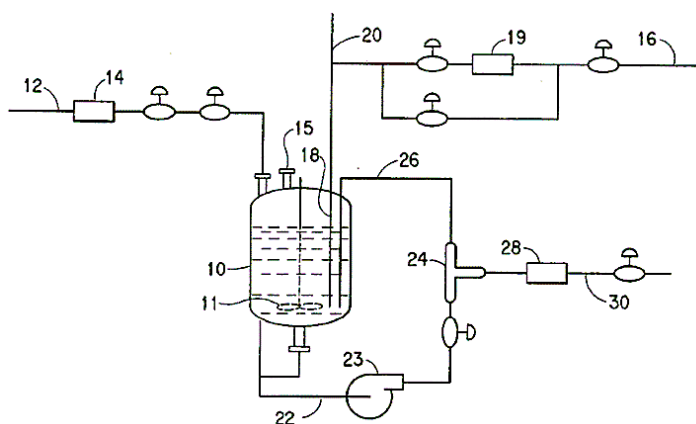
Authors	Reaction of alkoxide production
Greuter and Westrum (1957)	$\text{Na} + \text{CH}_3\text{OH} \rightarrow \text{NaOCH}_3 + 1/2 \text{H}_2$
Charles et al (1959) [10]	$\text{CH}_3\text{OH} + \text{MOH} \rightarrow \text{CH}_3\text{OM} + \text{H}_2\text{O}$ [M = alkali metal]
William et al (1962) [11]	$\text{MRCO}_3 + \text{M}^1\text{O} \rightarrow \text{MOR} + \text{M}^1\text{CO}_3$ [M =alkali metal, M <sup>1</sup> = alkaline earth metal,R = alkyl group ]
Weiss (1964)	$\text{Na} + \text{CH}_3\text{OH} \rightarrow \text{Na O CH}_3 + 1/2 \text{H}_2$
Blanchard et al (1976)	$\text{M} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OM} + 1/2\text{H}_2$ [M = Li, Na, K]
Vacek et al (1984)	$\text{C}_n\text{H}_{2n+1}\text{ONa} + \text{ROH} \rightarrow \text{RONa} + \text{C}_n\text{H}_{2n+1}\text{OH}$ [n = 3 to 5; R = -CH <sub>3</sub> , -C <sub>2</sub> H <sub>5</sub> ] $\text{NaOH} + \text{ROH} \rightarrow \text{RONa} + \text{H}_2\text{O}$ [R = -C <sub>3</sub> H <sub>7</sub> , -C <sub>4</sub> H <sub>9</sub> , -C <sub>5</sub> H <sub>11</sub> ]
Robert et al (1993)	$2\text{NaHg} + \text{CH}_3\text{OH} \rightarrow 2\text{NaOCH}_3 + \text{H}_2 + \text{Hg}$
Sridhar (1996)	$\text{CH}_3\text{COONa} + \text{CH}_3\text{OH} \rightarrow \text{NaOCH}_3 + \text{CH}_3\text{COOH}$ [electrolysis]
Ely et al (2002)	$\text{M} + \text{ROH} \rightarrow \text{ROM} + \text{H}_2$ [M = mixture of alkali + alkaline earth metals]
Evdokimov et al (2002)	$\text{M}_2\text{CO}_3 + 2\text{ROH} \rightarrow 2\text{ROM} + \text{CO}_2 + 1/2\text{H}_2\text{O}$ [M = Li, Na, K; R = -CH <sub>3</sub> , -C <sub>2</sub> H <sub>5</sub> ]
Guth et al. (2004)	$\text{NaOH} + \text{ROH} \rightarrow \text{NaOCH}_3 + \text{H}_2\text{O}$
Chandran et al (2006)	$\text{Na} + \text{ROH} \rightarrow \text{RONa} + 1/2 \text{H}_2$ [R = -CH <sub>3</sub> , -C <sub>2</sub> H <sub>5</sub> , -nC <sub>3</sub> H <sub>7</sub> ]
Balagopal et al (2010)	$2\text{CH}_3\text{OH} + 2\text{NaOH} \rightarrow 2\text{NaOCH}_3 + \text{H}_2 + 1/2\text{O}_2 + \text{H}_2\text{O}$
Granjo et al (2016)	$\text{CH}_3\text{OH} + \text{NaOH} \rightarrow \text{NaOCH}_3 + \text{H}_2\text{O}$

## 2.2 Equipment in sodium methoxide synthesis

### 2.2.1 Vessel

In the part, sodium methoxide is produced in a reaction vessel. Figure 2.2 shows the reaction vessel used to synthesize sodium methoxide. The description of this figure including the agitated reaction vessel 10 containing agitator 11 for suitable mixing inlets of sodium, methanol and nitrogen and transfer outlets of product and vapors. Vapor outlet 15 is near the top of the vessel 10. Molten sodium is transferred through line

12 to the reactor 10. The flow rate is controlled by a mass flow meter 14. Methanol is transferred through line 16 pass controller 19 to a dip-leg 18 in the reaction vessel. The reflux/cooling system obtained the return flow of methanol from line 20 and contact with line 16. On line 22, the product and unreacted sodium particles is drained to screen filter 24 by pump 23. The unreacted is recycled back to the reaction vessel on line 26, and the desired product leaves from reaction vessel through line 28 and line 30, respectively.



**Figure 2.2** Diagram of reaction vessel for sodium methoxide production [12].

### 2.2.2 Electrochemical cell

Electrochemical cell is a chemical equipment that occurs from either changing of chemical energy to electric energy or electric energy to chemical energy. There are two types of electrochemical cells including galvanic cells and electrolytic cells. Galvanic cells use the energy released during a spontaneous redox reaction ( $\Delta G < 0$ ) to generate electricity. In contrast, an electrolytic cell uses electrical energy from an external source that cause of nonspontaneous redox reaction to occur ( $\Delta G > 0$ ). Both types consist of two sections including electrodes and electrolyte. Electrodes are divided as anode (oxidation) and cathode (reduction). Also, electrolyte is substances that are liquid phase and conductive, due to mobile ions in solution. Electrolyte, ionic substance or solution as connecting of electrodes. They allow ions to transport between the electrode compartments, like that maintaining the system is electrical neutrality [13]. The diagram of galvanic cell and electrolytic cell was shown in Figure 2.3.

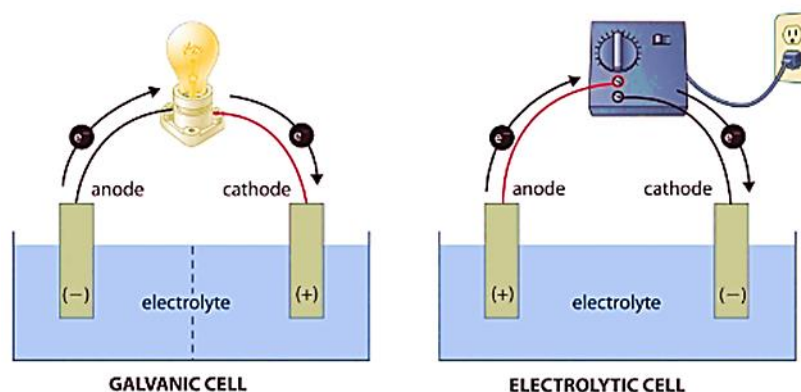
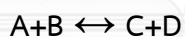


Figure 2.3 Diagram of galvanic cell (left) and electrolytic cell (right) [13].

### 2.2.3 Reactive Distillation

The process intensification of reactive distillation is an excellent process. It is an attractive alternative to improve conventional multiunit in some systems. Moreover, it can enhance an economically and environmentally. One interesting advantage of reactive distillation is the feature of simultaneous production and removal of products in a single step. The reactive distillation can separate both liquid and vapor phases [14]. Considering the system of reversible reaction scheme:

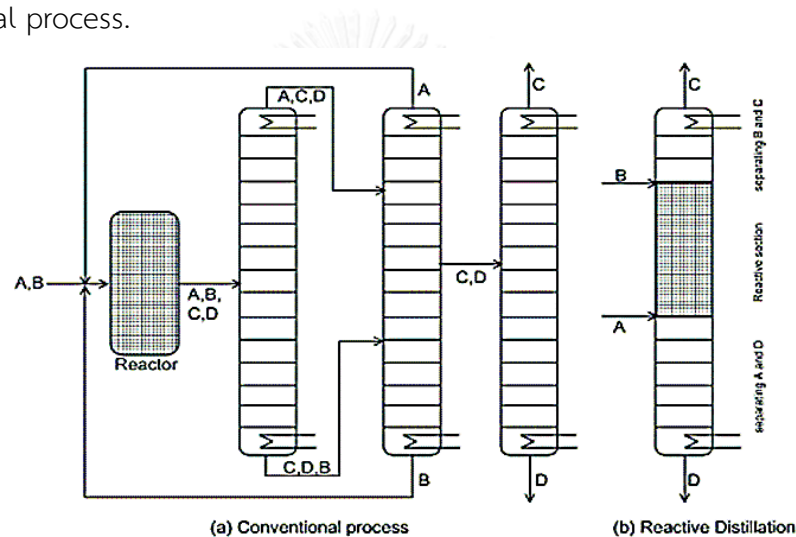


Where the reaction takes place in liquid phase and the desired product are C and D. The boiling points ranking of each component follow the sequence A, C, D and B. The conventional process consists of a reactor connected to the distillation columns that see in Figure 2.4 (a). The mixture of A and B is fed to the reactor consisting of a catalyst. When the reaction reaches to equilibrium, pure products C and D are separated by distillation. The unreacted components, A and B are recycled back to the reactor. Figure 2.4 (b) shows an alternative reactive distillation configuration. This column consists of three zones including rectifying, stripping and reactive sections. In the part of the rectifying zone, it recovers reactant B from the product stream C. In the part of stripping zone, the reactant A is stripped from the product stream D. Finally, the reactive zone, the products are separated from other components [15].

The column pressure is a more important parameter of reactive distillation than conventional distillation. Another, the temperatures in the column affect both the



phase equilibrium and chemical kinetics. At low temperature, it presents high relative volatilities but small specific reaction rates and thus requires very large liquid holdups to achieve the required conversion. In contrast, at high temperature may give a very small chemical equilibrium constant (for exothermic reversible reactions), which is more difficult to drive the reaction to produce products. High temperatures may also promote undesirable side reactions. Thus, selecting the optimum pressure in a reactive distillation column is very important. The reactive distillation is an easy step to operate and the number of process step is less than conventional process. As the result, in many industries reactive distillation has been implemented as alternative to replace conventional process.



**Figure 2.4** Processing schemes for a reaction sequence  $A+B \leftrightarrow C+D$  (a) The configuration of a conventional process (b) The reactive distillation configuration [15].

#### 2.2.4 Pervaporation

Pervaporation is a process for the separation of liquid mixtures using a nonporous membrane. This process has been investigated based on reverse osmosis membrane and gas permeation in twenty years ago, in literature pervaporation has been used in several applications including dehydration of organics, azeotropic separations and flavor recovery. Membrane for this process is divided following its properties of selective membrane as hydrophilic membrane (water passed membrane more than organic compound) and hydrophobic membrane (organic compound passed membrane more than water). The solution passed through membrane is called

“permeate” and the one which does not pass through the membrane is called the “retentate”. The performance of a membrane in the separation of a given feed-mixture is characterized by permeation rate and selectivity. The effect of properties of polymer in membrane consisting of chain arrangement of polymer in membrane, porous of membrane, interaction between molecule of component and membrane and diffusion of each component [16]. A key parameter that specifies the performance of membrane for separation is permeate flux through membrane. It is can be calculated by Eq. (2.1)

$$J_i = Q_i \Delta p_i \quad (2.1)$$

Where  $J_i$  is permeate flux of component  $i$ ,  $Q_i$  is the permeance or pressure normalized flux,  $\Delta p_i$  is the driving force expressed by partial pressure. The other separation performance of membrane in pervaporation is reported in the form of separation factor ( $\alpha$ ) by Eq. (2.2). The high value of separation factor indicates that the high performance of membrane for separation.

$$\alpha_{a/b} = \frac{y_a/y_b}{x_a/x_b} \quad (2.2)$$

Where  $y$  and  $x$  are permeate and feed compositions, respectively. Lastly, the pervaporation separation index (PSI) as another parameter to evaluate the performance of pervaporation expressed by Eq. (2.3):

$$PSI = J \cdot (\alpha - 1) \quad (2.3)$$

Where  $J$  is total permeate flux [ $\text{kg m}^{-2} \text{h}^{-1}$ ] and  $\alpha$  is separation factor. The mechanism of pervaporation is described in Figure 2.5.

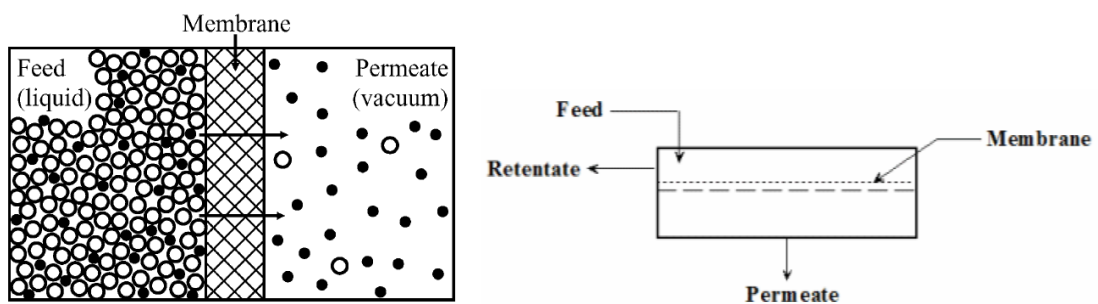


Figure 2.5 Diagram of pervaporation across a membrane [17].

## CHAPTER 3

### LITERATURE REVIEWS

Sodium methoxide production technologies have been studied for more than six decades. In this chapter, the literature reviews are mainly divided in three parts. The first part is conventional process and development for sodium methoxide production described about the method for preparation of metal methoxide from various raw materials and the effect of operating parameters and their optimal condition. Further, study on design parameters to adjust with reactive distillation to produce the highest yield of desired and safer operating cost. The second part is application of sodium methoxide as catalyst in biodiesel production. This particularly considers the effect of methoxide as a catalyst on transesterification reaction in biodiesel production. Also, it shows comparison of methoxide and hydroxide catalysts as homogeneous catalyst and heterogeneous catalyst, respectively, on the performance and activity of the catalysts. Moreover, this part describes the cause of decreasing in sodium hydroxide conversion and yield of biodiesel from side reaction of saponification as well as purposed strategies to overcome this problem. Lastly, it summarizes the studies on separation performance of several membranes in methanol/water systems for using in reactive distillation coupled with pervaporation process.

#### 3.1 Conventional process and development for sodium methoxide production

Many researchers have purposed the sodium methoxide production from different precursors and various methods. In the past, sodium methoxide is prepared by using a continuous reactor in combination of distillation column. The aqueous sodium hydroxide of 50 percentages by weight about 999.5 kg/h is fed on the top of column and gaseous methanol is fed on the bottom. The reactants are passed in countercurrent distillation column operating at atmospheric pressure. After reaction, sodium methoxide in methanol is drawn off from the bottom of the column and passes through a water-cooled product cooler and collected in a hold tank. The

temperatures in the top of the column in the range of about 70-80 °C and in the bottom of the column in the range of about 80-100 °C [10]. Also, Guth et al. [18, 19] prepared sodium methoxide in the same way by using a single reactive distillation column. The bed height about 20 theoretical plates and the column is operated without reflux. The methanol is fed in a liquid methanol stream that is different from previous work. The product stream from the bottom of the column comprises 30% by weight of sodium methoxide in methanol and contains about 60 ppm of water. The top of column contains methanol and water that are transferred to separate in a second column for recovering methanol to the process again. The second column has 40 bubble cap trays, 29 theoretical plates, the reflux ratio is 1.3 and is operated at atmospheric pressure. This process shows superior performance to produce sodium methoxide than in the single step. However, this process required high energy consumption to recovery methanol. The other method using electrochemical cell for the preparation of metal alkoxides by passing a direct current between an anode of a metal that depends on the reactivity of the metal consist of copper, silver, gold, bismuth and antimony on the electromotive series between about minus 0.20 volts and about minus 1.68 volts. They was characterized though separation of the anolyte from the catholyte by using an anion-exchange membrane having a permselectivity for anions of at least 70 percent whereby the metal alkoxide is formed in the anolyte [20]. In addition, electrolytic process of Balagopal et al. [21, 22] is used to produce sodium methoxide in methanol solution from sodium hydroxide placed in the anolyte compartment and methanol placed in the catholyte compartment as shown in Figure 3.1. After reaction, the product from two compartments is separated by a ceramic membrane that selectively transports sodium under the influence of current. The cell is operated at temperatures from about 20 °C to about 80 °C at ambient pressure. The sodium methoxide shows high purity more than 32 % by weight of sodium methoxide in methanol. However, the purity is limited by the purity of methanol that is used as raw material. Chandran et al. [23] studied the synthesis and characterization of various sodium alkoxides since 1957 until 2006. It indicated that the reaction was occurred in the solution of organic compound and alkaline metal or alkaline metal hydroxide. Then, in this work, the sodium methoxide was prepared from reaction of methanol

and solid sodium pieces. After that the sodium methoxide was purified by vacuum distillation method. In the part of characterization, the IR spectra of sodium alkoxide recorded by using mull and KBr methods. Also, a powder X-ray diffractometer was used to check the purity of sodium alkoxides. For anhydrous sodium methoxide, all peaks match well with those reported (JCPDS 19-1876). Presently, the fourth distinctive methods are described in terms of different raw materials that are mixing with methanol in the sodium methoxide synthesis. The first process, using sodium amalgam as precursor that was produced from the chlor-alkali electrolysis in a mercury cell [24]. It is the oldest process used in industry, but it is not popular because of the contamination of the product and the environmental issues from toxicity of mercury, a well known carcinogen. The second process, using sodium metal as precursor. This process is simple and provides high purity of sodium methoxide. However, sodium metal is dangerous goods and needs special awareness of safety requirements due to the process is highly exothermic reaction, potentially explosive. Therefore, it needs to be in well control for safety to avoid the risk of explosion <sup>[12]</sup>. Then, the third process uses sodium hydroxide as precursor, which is cheap, available, high yield of sodium methoxide and safer to operate, but it requires a lot of energy consumption to separate the methanol from the water for recovery. The final process uses sodium acetate as precursor, this process shows the advantages of obtaining the high purity of sodium methoxide and safer operation. However, there are more disadvantage such as it requires a lot of energy consumption, it has several steps in the separation and difficult to scale up [6].

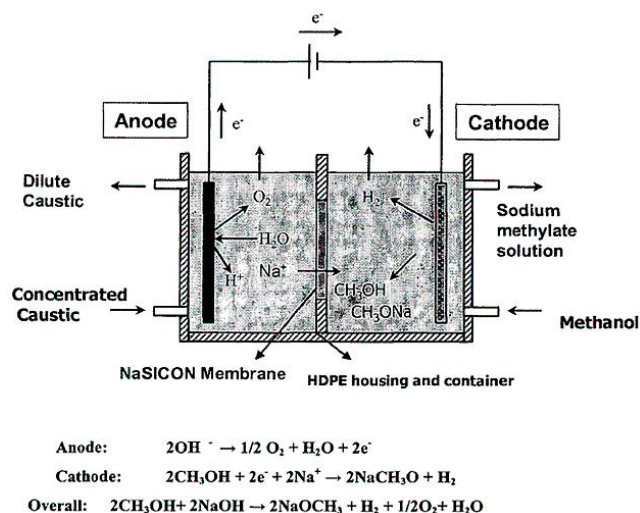


Figure 3.1 Electrolytic reactions on electrochemical cell via ceramic membrane [22].

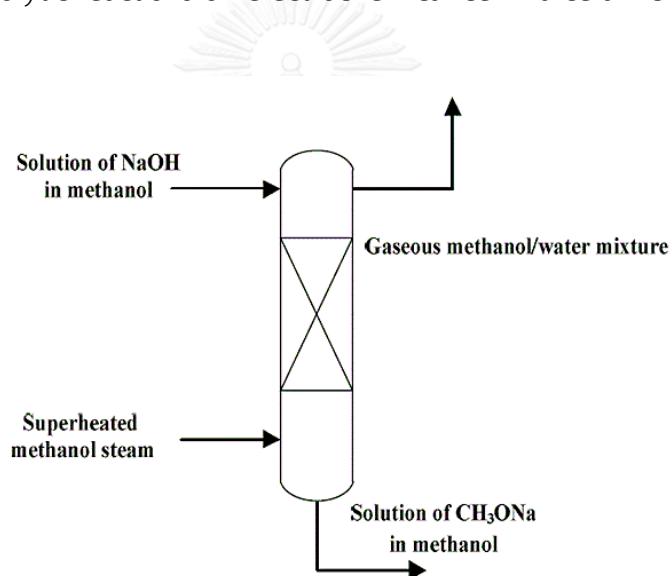


Figure 3.2 Simulation diagram of the reactive distillation column [19].

### 3.2 Application of sodium methoxide: Catalyst in biodiesel production.

Sodium methoxide is used as catalyst in various industries. Especially, in biodiesel production, sodium methoxide is an alternative catalyst in this process via transesterification reaction. The role of sodium methoxide as same as other catalysts both homogeneous and heterogeneous catalysts in biodiesel production. In homogeneous catalysts, a comparison of sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide are made of different basic catalysts for

methanolysis of sunflower oil operating at the same condition in a batch stirred reactor. It indicated that potassium hydroxide has highest of biodiesel purity about 99.80% by weight. In the term of biodiesel yield, sodium methoxide and potassium methoxide has higher than other catalysts. Because the yield loses due to triglyceride saponification, so that the methoxide catalyst has more activity than hydroxide catalyst. However, the transesterification reaction using sodium hydroxide still has benefit. It was the fastest, achieving nearly 100 % by weight methyl ester concentration in the biodiesel phase at 30 min and low cost of material. Thus, hydroxide catalyst has used as alternative catalyst for today [25]. Biodiesel made from waste cooking oil is an economical source that can effectively reduce raw material cost. To improve this process, after investigating effect of amount of catalyst in reaction, it was found that the catalyst concentration is 0.75% by weight of sodium methoxide methanol-to-oil molar ratio of 6, a reaction time of 3 min, and a microwave power of 750 W. as optimal condition for obtaining the highest yield of biodiesel of more than 97% by weight [26]. The advantages of sodium methoxide catalyst over sodium hydroxide catalyst consist of overcoming soap formation from saponification reaction caused by water from raw material and from byproduct of reaction between sodium hydroxide and alcohol [27], the mechanism of soap formation is shown in Figure 3.3. Furthermore, the water decreases heat of combustion, corrosion of fuel system components, and acceleration of hydrolytic reaction [28]. In some cases, heterogeneous catalyst is used in transesterification reaction because it is easy to separate, however, it presents low performance and less active than homogeneous catalyst. In example, when comparison between magnesium methoxide catalyst in term of solid and solution, it was found that magnesium methoxide solution shows higher performance and activity than magnesium methoxide solid because of deactivation effect [29]. Nevertheless, the problem from using homogeneous catalyst is difficult and costly to separate catalyst from other products.

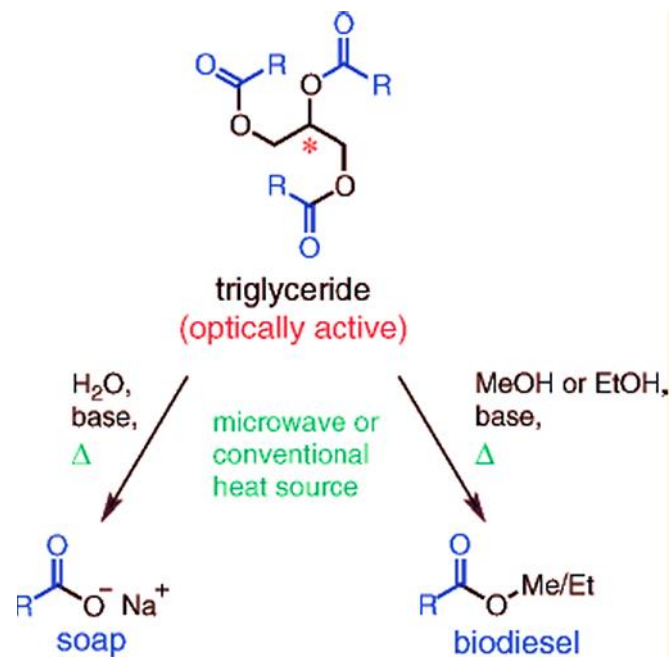


Figure 3.3 Mechanism of saponification reaction. [6]

### 3.3 Membrane for separation of methanol and water.

This section considers the separation performance of several membranes in methanol/water systems for using in reactive distillation coupled with pervaporation process. The best membrane has high selectivity of water and high water permeate. For investigation all of membrane, it found that A type zeolite of S. Sommer et al. presented highest performance for separation of water from methanol, it was shown 10000 of selectivity of water and 99.91 of water permeate. Thus, this membrane is an alternative to use in this system to produce sodium methoxide production.



**Table 3.1** The separation performance of several membranes in methanol/water systems.

Author	Membrane	Methanol feed (wt.%)	Temp. (°C)	Separation factor or selectivity of water	Water permeate (wt.%)	Permeate flux (kg/m <sup>2</sup> h)
S. Sommer, T. Melin (2005a)	T type zeolite (Mitsui)	90	90	2240	99.6	41.6
S. Sommer, T. Melin (2005b)	A type zeolite (Mitsui)	89.9	60	10000	99.91	12.8
	T type zeolite (Mitsui)	90.2	60	100	91.59	7.5
X. Liu et al.(2008)	PVA	85	40	35	86	0.18
X. Liu et al.(2008)	PAA-co-AN nano SiO <sub>2</sub>	98	60	1458	96.75	8.9
S.-T. Kao et al.(2010)	Aromatic polyamide Composite membr.	90	25	6.1	40	0.586
Pang et al. (2010)	PVA/P(AA-co-AN/SiO <sub>2</sub> )	98	60	1534	97	0.583
A. El-Gendi and H. Abdallah (2013)	Polyamide-6	90	30	891	99	17
Fu et al. (2014)	PPO composite membranes	90	70	27	75	36.1

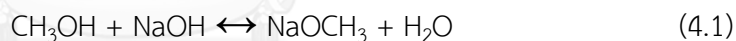
## CHAPTER 4

### SIMULATION AND DESIGN

In this chapter, simulation of sodium methoxide production from sodium hydroxide and methanol by using reactor-distillation process, reactive distillation-distillation process and reactive distillation coupled with pervaporation process were considered. Three processes were investigated through computer modeling by Aspen Plus program. The optimal condition and performances of processes consisting of composition of products and energy consumption were examined and compared. Moreover, the effect of key parameters including operating parameters (methanol to sodium hydroxide feed mass ratio, number of stages and feed stage location) were investigated. Lastly, the basic designs of three processes were performed.

#### 4.1 Reaction model

The production of sodium methoxide is based on Eq. (4.1), the reaction was assumed to be a reversible exothermic reaction.



The dependence of the equilibrium constant of this reaction on the reaction temperature is expressed by Eq. (4.2), this equation was obtained from linear regression of the experimental data [6, 30]; K represents the equilibrium constant which is a function of temperature (T). With increasing temperature, the equilibrium constant decreases because the reaction is exothermic. Calculated values of K at some temperatures are shown in Table 4.1.

$$\ln K = -4.374 + 1751/T \quad (4.2)$$

**Table 4.1** The equilibrium constant ( $K$ ) at some temperatures ( $T$ ).

Temperature (°C)	Equilibrium constant
0	7.66
15	5.49
30	4.06
45	3.09
60	2.42
75	1.93
90	1.56

## 4.2 Process modeling

The units used in Aspen Plus for the simulation of the three processes described earlier are summarized in Table 4.2. The base-case simulation was performed with ENRTL-RK thermodynamic model for electrolyte system under asymmetric reference state for ionic species. Because the components contained in the mixtures are of comparable molecular sizes, the nonideal entropy of mixing tends to be negligible when compared with the heat of mixing, which is consistent with the underlying assumption of the eNRTL models and The Redlich–Kwong equation of state was selected to model the nonideality of the vapor phase. The electrolyte solution of this system consists of sodium hydroxide and sodium methoxide in methanol/water mixed solvents. The operating parameters of reactor-distillation process, reactive distillation and reactive distillation coupled with pervaporation process were designed to find the optimal condition for sodium methoxide production. Three processes are operated at a pressure of 1 atm and with 50 percent by weight of sodium hydroxide aqueous solutions are fed at a mass flow rate of 999.5 kg/hr. Therefore, this flow rate was produced 675 kg/hr or 5.4 kt/year of sodium methoxide capacity. The value was estimated based on an amount of catalyst of 300 kt/year needed by large-scale biodiesel production plant currently operating in Europe [add reference]. Other parameters of each process are set differently to obtain the highest purity of sodium methoxide in methanol solution. A reactor-distillation process purposed the basic process step to produce sodium methoxide production consisting of a continuous

reactor followed by distillation trains for separation of sodium methoxide and methanol recovery, respectively. This process is compared with the reactive distillation process that introduces a reactive distillation column combining reaction and separation in a single unit and a distillation column for methanol recovery. For the last process, reactive distillation coupled with pervaporation process was purposed to improve the reactive distillation-distillation process by addition of membrane that has performance to separate water from methanol.

**Table 4.2** Summary of method and units supplied on simulation of sodium methoxide production by ASPEN Plus program for different unit operations.

	reactor-distillation process	RD process	RD-PV process
Prediction of property model	ENRTL-RK	ENRTL-RK	ENRTL-RK
Unit operation number	3 units	2 units	2 units
reaction reactor	REquil	RadFrac <sup>a</sup>	RadFrac <sup>a</sup>
sodium methoxide separator	RadFrac	RadFrac <sup>a</sup>	RadFrac <sup>a</sup>
methanol separator	RadFrac	RadFrac	Sep (Membrane)

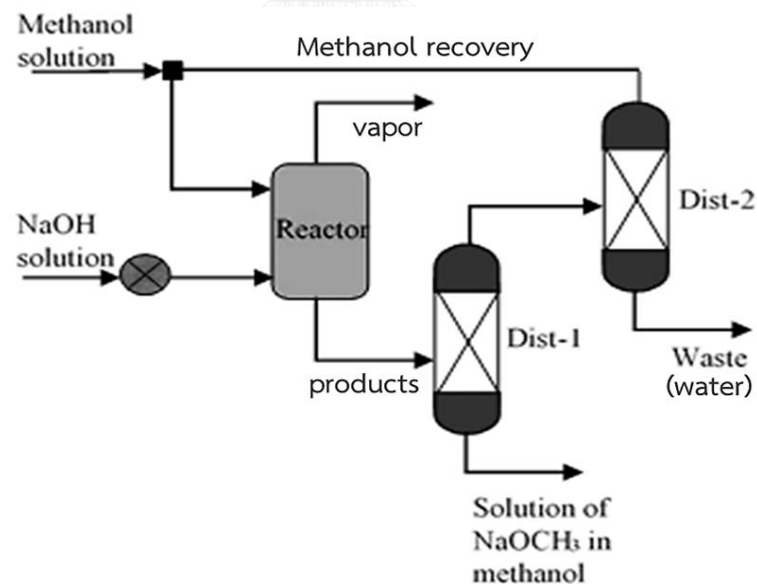
<sup>a</sup>The same unit.

#### 4.3 Process description

This part focuses on description of process simulation of sodium methoxide production from sodium hydroxide and methanol as feedstock by three different processes. They are reactor-distillation process, reactive distillation-distillation process and reactive distillation coupled with pervaporation process. Three processes are described in term of design process by varying operating parameters including of methanol to sodium hydroxide mass flow ratio, bottom rate, number of stage and feed stage location. These parameters were defined and investigated to obtain optimal condition for sodium methoxide production.

4.3.1 Sodium methoxide production from sodium hydroxide and methanol by using configuration of reactor-distillation process including of a continuous reactor followed by a distillation trains.

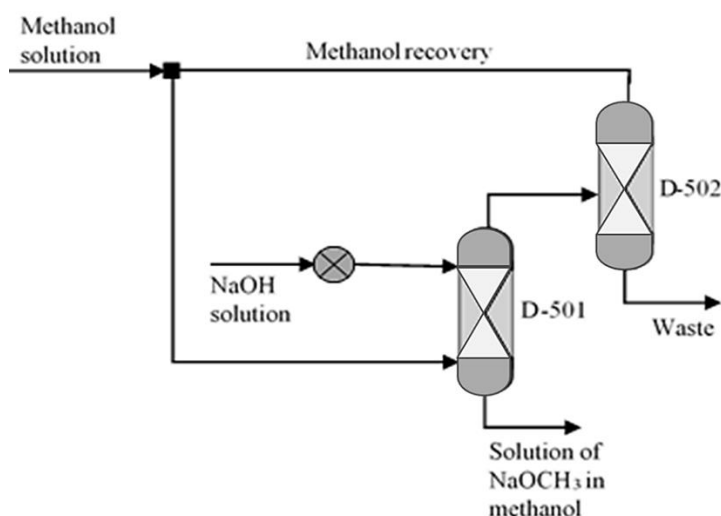
In this part, description of how to simulate the process of synthesis of sodium methoxide production in reactor-distillation process including of a continuous reactor followed by two distillation trains. First of all, A 50 wt.% sodium hydroxide aqueous solutions are fed from storage to the reactor to mix with methanol that was transported to the reactor at simultaneously. The reaction was occurred at 65 °C and pressure of 1 atm. After the reaction approaches to equilibrium, the product mixture was transferred to the first distillation column, a solution of sodium methoxide in methanol was separated at the bottom of column at 1 atm. The methanol/water gas mixture was transported through the top of the first column to the second distillation column for separation of methanol from water for recovery to the reactor at the same pressure. This process is not complex, but there is high number process steps and high of energy consumption for operating. The diagram of process is shown in Figure 4.1.



**Figure 4.1** The schematic diagrams of reactor-distillation process consisting of a continuous reactor followed by distillation trains.

#### 4.3.2 Sodium methoxide production from sodium hydroxide and methanol by using reactive distillation-distillation column.

The process of the sodium methoxide production by using the reactive distillation column can reduce the steps for the operation. Firstly, a 50wt.% of sodium hydroxide aqueous solution was preheated at the pressure of 1 atm, 75 °C, and it was fed on the top of the column. The aqueous solution of sodium hydroxide was transferred countercurrent with the methanol solution which was obtained from the mixture of the methanol make up and the methanol recycles. The solution of the methanol was fed on the bottom of the column at 1 atm and the temperature of 65 °C. The reactive distillation column was operated without a condenser and no catalyst. The operating parameter in this column was designed to find the optimal condition for the operation. The reaction was limited by the equilibrium constant model, when increasing the temperature, the equilibrium constant value was decreased, as the result from the exothermic reaction. After the reaction, the desired product of sodium methoxide in the methanol solution was introduced in the bottom. Almost methanol and water was vaporized on the top of the column and was transferred to the second column for separation of the methanol from the water. The operating condition of the second column was set at the pressure of 1 atm, the methanol was separated from the water on the top of the second column and recovered to mix with methanol feed make up. Then, after the methanol was mixed already, it was fed to the column again. The diagram of the schematic process was shown in Figure 4.2.



**Figure 4.2** The schematic diagrams of reactive distillation-distillation process.

#### 4.3.3 Sodium methoxide production from sodium hydroxide and methanol by using reactive distillation coupled with pervaporation.

Figure 4.3 presents the diagram of the reactive distillation coupled with the pervaporation process. This process was purposed to enhance the reactive distillation process by addition of the membrane for separation of the methanol from the water. The operating condition of the reactive distillation column was designed to find the optimal condition for obtaining a solution of sodium methoxide in methanol. Firstly, the sodium hydroxide aqueous solution of 50 percentages by weight was fed on the top of the column at 1 atm, 75 °C and the methanol was fed on the bottom of the column at 1 atm. Both reactants were flowed in countercurrent to mix in this column and the reaction occurs spontaneously. This process operated at 1 atm with none condenser and no catalyst addition. Among the reaction, the water from the reaction was permeated pass membrane out of the process and the methanol was not passed membrane, it called retentate, recovery to the reactive distillation column. At the same time, the sodium methoxide was separated on the bottom of column and almost methanol in the distillate section was transferred to combine with the methanol make up and recovered to the column again. This process believes that can decrease the energy consumption.

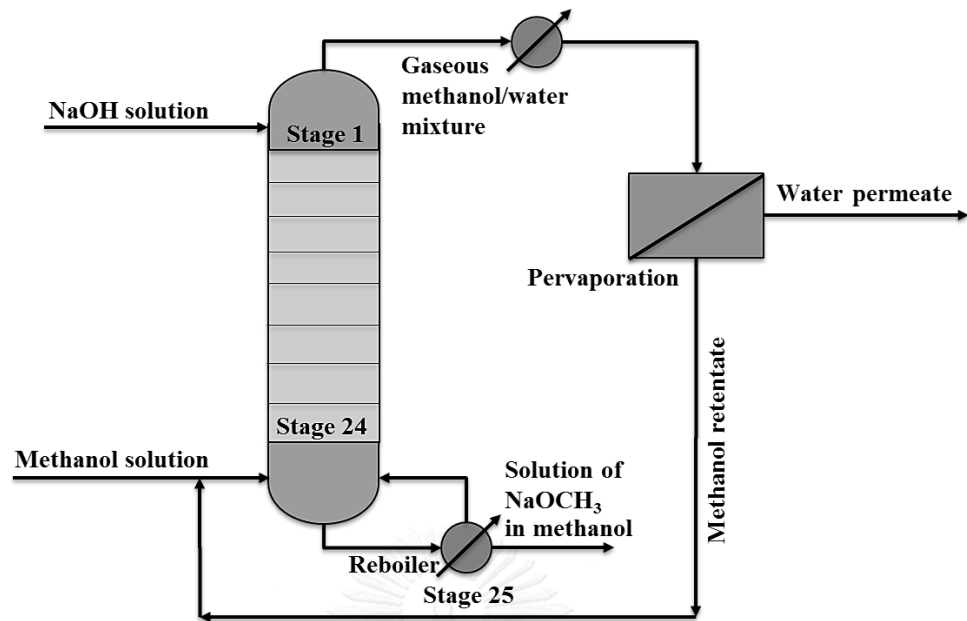


Figure 4.3 The schematic diagrams of reactive distillation coupled with pervaporation process.



## CHAPTER 5

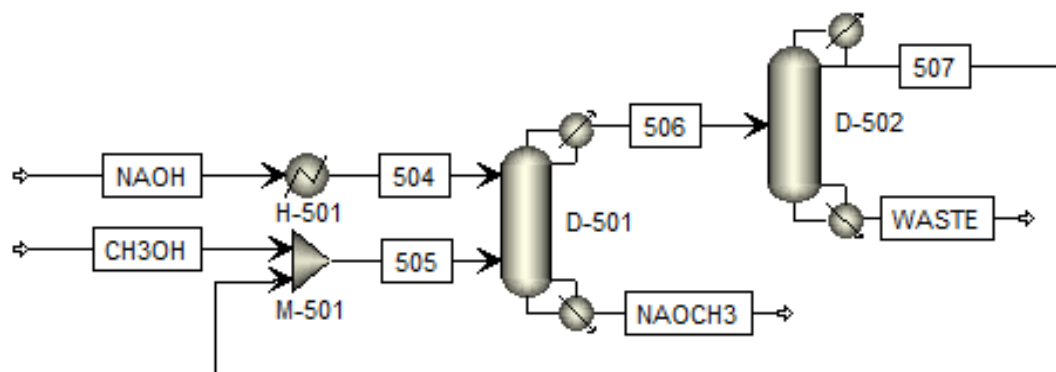
### RESULTS AND DISCUSSION

This chapter reports simulation results of the sodium methoxide production from various processes consisting of the reactor-distillation process, the reactive distillation-distillation process and the reactive distillation coupled with pervaporation process. It can be discussed and divided into five sections. The validation of the simulation results from the sodium methoxide production by the conventional process is investigated firstly in Section 5.1. Next, performance of the conventional process and the effects of parameters; e.g. methanol to sodium hydroxide feed mass flow ratio, number of stage and feed stage location on composition of sodium methoxide, methanol and water in the product and energy consumption of the process are provided in Section 5.2. For Section 5.3, performance of reactor-distillation process and the effects of parameters are studied to compare with the conventional process. In addition, for Section 5.4, performance of the reactive distillation coupled with pervaporation process was proposed to improve the reactive distillation-distillation process. This process differs from the conventional processes by addition of the membrane for separation water from products. Lastly, the performances of three processes are compared in Section 5.5.

#### 5.1 Validation of sodium methoxide production by conventional process

In this section, the simulation of sodium methoxide production from methanol and sodium hydroxide was validated with the data from the previous work [18]. This validation is purposed for verification of the simulations for predicting performances of sodium methoxide production process. The data for the validation is referred from the pilot plant. The system for model validation consists of two columns including a reactive distillation column and distillation column. The reactive distillation column is the main equipment for this process to produce the sodium methoxide. Also, a distillation column is used for separation of methanol/water mixture. The schematic diagram of process is shown in Figure 5.1. A 50 wt.% sodium hydroxide aqueous

solution of 27 g/h (504) is fed at 1 atm and 75°C on the top of the reactive distillation column (D-501). The methanol make up of 54 g/h at 1 atm and 30°C is mixed with methanol recycle of 478 g/h (507), the mixture of those methanol solutions (505) is fed at 1 atm and 61°C on the bottom of the reactive distillation column to react with the sodium hydroxide solution. The reactive distillation is operated at 1 atm without a condenser and using total number of stage of 20 stages. The sodium methoxide product is obtained at the bottom of this column and the mixture of methanol/water is transferred to the distillation column (D-502) for separation of methanol from water. Then, the methanol is recovered to the reactive distillation again. The distillation is operated at 1 atm with a reflux ratio of 1.3, total number of stages of 29 and the feed stage location at 25. The simulation results are exhibited in Table 5.1 to compare data from the pilot plant.



**Figure 5.1** The schematic diagram of sodium methoxide production process from methanol and sodium hydroxide by using reactive distillation and distillation for the model validation.

**Table 5.1** Simulation results of the sodium methoxide production using reactive distillation and distillation in comparison with data from literature [18].

Results	Pilot plant data[18]	Simulation results
D-501		
Distillate temperature (°C)	75	75.4
Distillate mass flow (g/h)	498	498
Product mass flow (g/h)	61	61
Methanol feed temperature (°C)	61	61
Methanol feed mass flow rate (g/h)	532	532.4
Water content in product (ppm)	60	24
Methanol in product (wt.%)	70	70
NaOCH <sub>3</sub> in product (wt.%)	30	30
D-502		
Distillate mass flow (g/h)	478	478
Bottom mass flow (g/h)	20	20
Water content in distillate (ppm)	30	4.1
Methanol content in bottom (wt.%)	1	0.2

According to the results from Table 5.1, it indicates that the simulation results are consistent with the data reported [18] at the same condition. It should be noted that although the simulation results show the values of water content in distillate and methanol content in bottom of the distillation deviated from those reported in the reference, their values are insignificantly small.

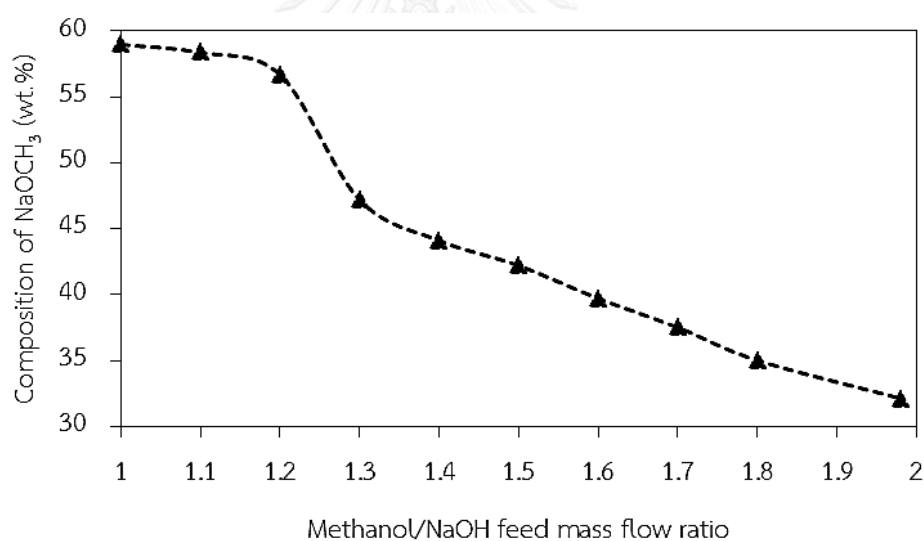
## 5.2 Improvement of conventional process and the effect of operating conditions

In the previous work, the validation condition was adopted as the reference condition to scale up the process from pilot plant to industrial application. The base-case conditions are chosen for the production capacity of sodium methoxide established at 675 kg/h for industrial process. Thus, the effects of key parameters need to be investigated to find the optimal condition for process operation. The parameters include methanol to sodium hydroxide feed mass flow ratio, number of stages and feed stage location. The system performances include the composition of sodium methoxide, methanol and water content in products and the energy consumption of process. Those parameters are varied in the simulation model. The simulation results of the reactive distillation-distillation process are described and discussed in this section.

The sodium methoxide production is produced by the reaction of methanol and sodium hydroxide aqueous solution. The sodium hydroxide is a limiting reactant, the fixed operating parameters of the reactive distillation and distillation are shown in Tables 5.2. For this process, the sodium hydroxide aqueous solution is constant at 999.5 kg/h for various of the methanol feed flow rate for studying the effect of methanol to sodium hydroxide feed mass flow ratio. The operating condition for reactive distillation and distillation columns are improved by setting the optimal condition. In the part of distillation column, the operating parameters are obtained by simulation through DSTWU model in Aspen Plus program that is a short cut method to find the estimation values of operating condition. After that, the suitable condition obtained from the DSTWU model was employed to RadFrac model. Lastly, it was the design specification of distillation to obtain the best performance for separation of methanol from water. The optimal operating conditions of distillation are operated at 1 atm, reflux ratio of 0.6456, distillate to feed ratio of 0.8471, total number of stages of 30 and the feed stage location at 20. However, for reactive distillation column, the effect of operating parameters are investigated as it is the main equipment that performs both reaction and separation for production of sodium methoxide.

**Table 5.2** Fixed operating conditions for sodium methoxide production by reactive distillation-distillation process.

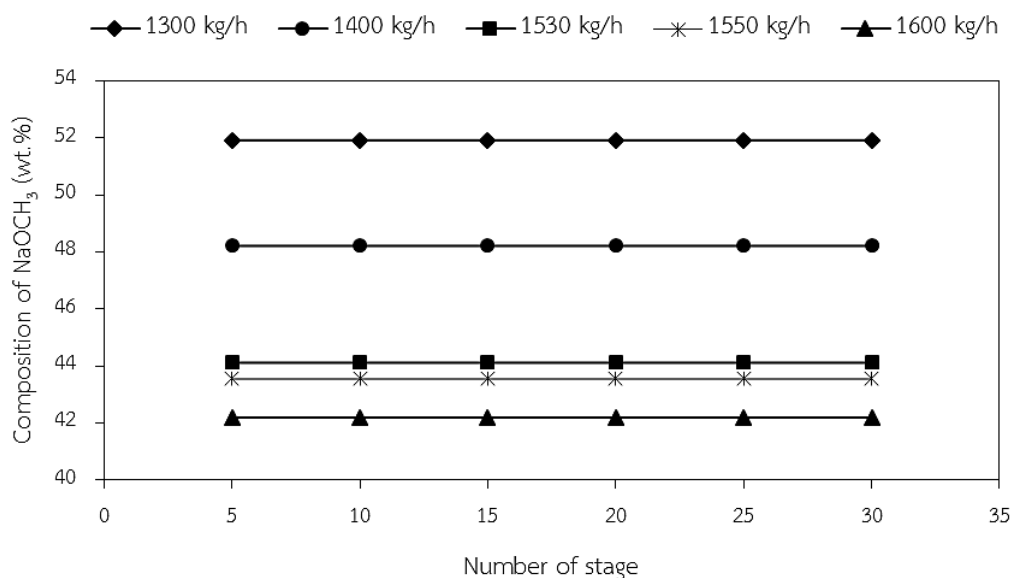
Parameters	Values
Pressure of process (atm)	1
Sodium hydroxide solution feed flow rate (kg/h)	999.5
Sodium hydroxide solution feed temperature (°C)	75
Methanol make-up feed temperature (°C)	30
<b>D-502</b>	
theoretical stages	30
Condenser	Partial-vapor
Distillate to feed ratio	0.8471
Reflux ratio	0.6456
Feed stage location	20



**Figure 5.2** Effect of methanol to sodium hydroxide feed mass flow ratio on composition of sodium methoxide in product (Reactive distillation (D-501) operated at 1 atm, 20 stages, and sodium hydroxide and methanol feed location at 1 and 19, respectively).

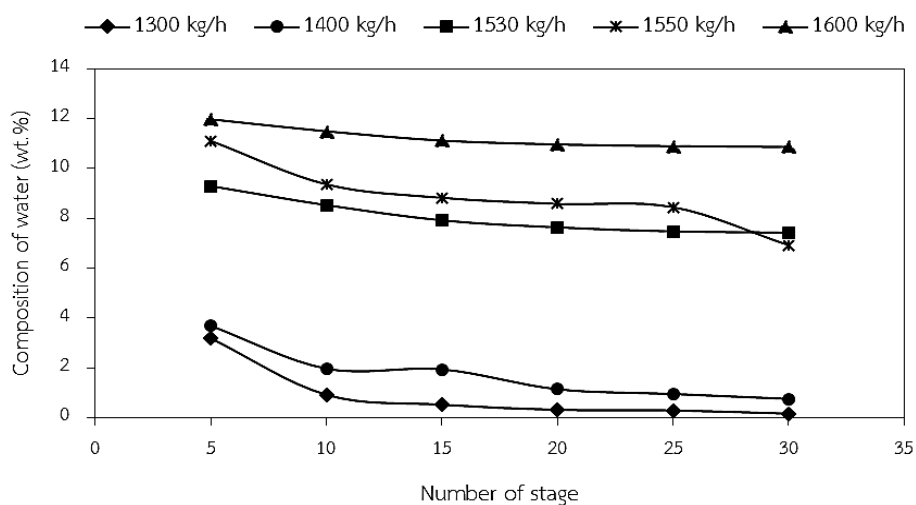
Figure 5.2 shows the effect of methanol to sodium hydroxide feed mass flow ratios on composition of sodium methoxide product. It indicates that when increasing the methanol feed, the composition of sodium methoxide is decreased slightly at the methanol to sodium hydroxide mass flow ratio of 1-1.2 and after that, it decreases

shapely. Therefore, when the methanol feed increases at the constant of sodium hydroxide feed flow rate, the concentration of sodium methoxide is more diluted. Next, the other operating parameters such as the number of stages, the feed stage location and the bottom rate of reactive distillation column are investigated to obtain the optimal condition. The effects of the number of stages and bottom rate on the composition of the product are investigated at different values of the methanol to sodium hydroxide feed mass ratios. The followings are the operating condition: operating pressure of 1 atm, sodium hydroxide and methanol feed location at top and bottom of column, respectively; distillation (D-502) pressure at 1 atm, reflux ratio of 0.6456, distillate to feed ratio of 0.8471, total number of stages of 30 and the feed stage location at 20. The methanol to sodium hydroxide feed mass flow ratios including of 1.2, 1.4 and 1.6 are studied at constant amount of the sodium hydroxide feed flow rate of 999.5 kg/h. The effect of bottom rate at 1300, 1400, 1530, 1550 and 1600 kg/h are also studied in this section. Next, the simulation results are shown in Figure 5.3, this graph presents the effect of number of stages and bottom rate of reactive distillation column on composition of sodium methoxide at overall ratios of methanol to sodium hydroxide feed mass flow, it is found that all of methanol to sodium hydroxide feed mass flow ratios are shown exactly the same results. To consider at the specified values of bottom rate of reactive distillation column, the composition of the sodium methoxide remains the same regardless of changing the number of stages. But it decreases when the bottom rate of reactive distillation column is varied from 1300 to 1600 kg/h because at high bottom rate leads to enhance the methanol in products. As the result, the concentration of sodium methoxide is reduced. However, the composition of the sodium methoxide is limited at concentration to be lower than 45 wt.% since the viscous liquid is formed when the concentration is beyond 45 wt.%. In addition, the water content in products must be less than 0.1 wt.% to prevent reversible reaction [18].

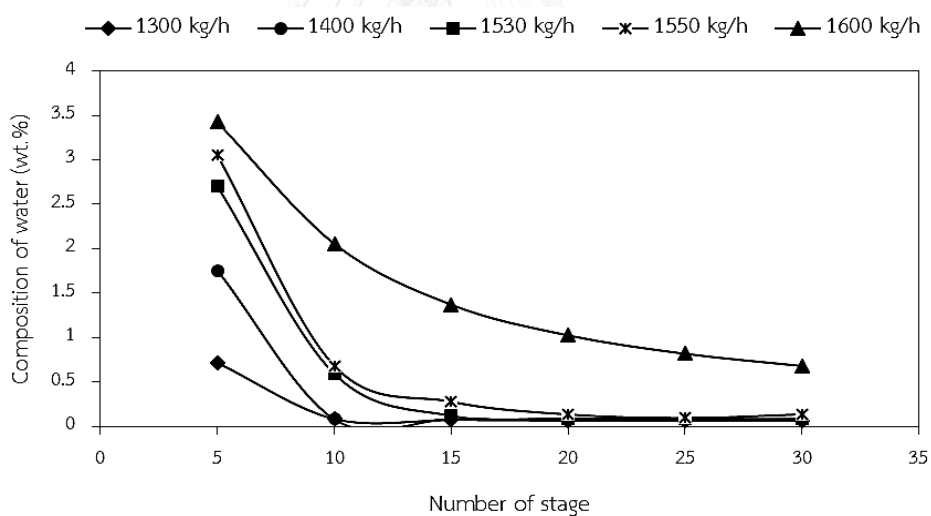


**Figure 5.3** The effect of number of stages on composition of sodium methoxide at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio are 1.2, 1.4 and 1.6).

To consider the water content in products for all ratios of methanol to sodium hydroxide feed mass flow, it indicates that the water content is increased at high bottom rate of reactive distillation column. Figure 5.4 shows the water content at methanol to sodium hydroxide feed mass flow rate of 1.2. It was found that for all of bottom rate, the resulting water content is more than 0.1 wt.%. Thus, using the methanol to sodium hydroxide feed mass flow ratio of 1.2 is not a favorable choice. Next, the water content at methanol to sodium hydroxide feed mass flow ratio of 1.4 is shown in Figure 5.5. The suitable condition is considered from concentration of sodium methoxide coupled with water content in products. The best condition of this ratio is presented at bottom rate in the range of 1530 to 1550 kg/h with the number of stages from 25 and above, concentration of sodium methoxide between of 43 and 45 wt.% and water content of 0.1 wt.%.

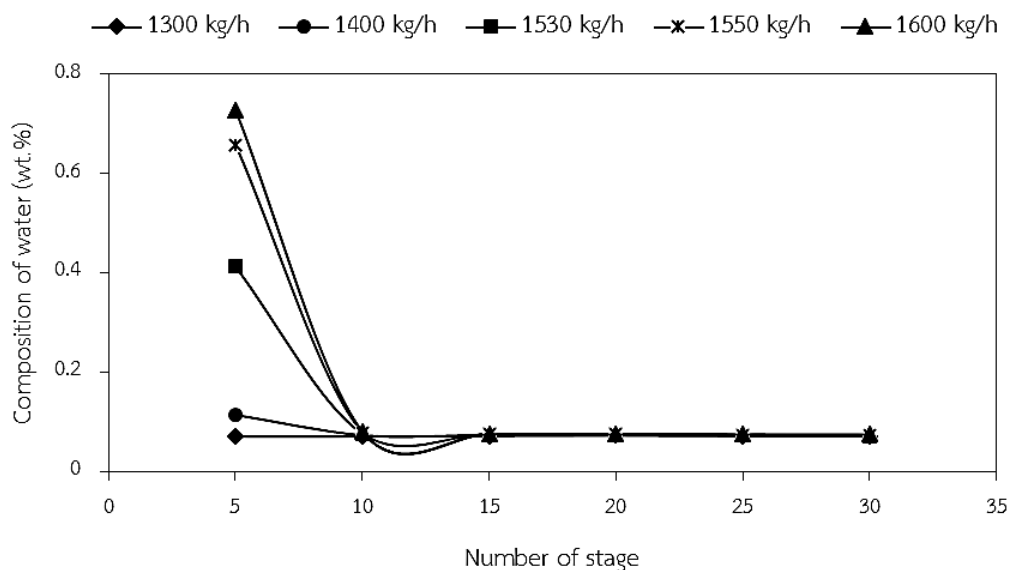


**Figure 5.4** The effect of number of stages on composition of water in product at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.2).



**Figure 5.5** The effect of number of stages on composition of water in product at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.4).

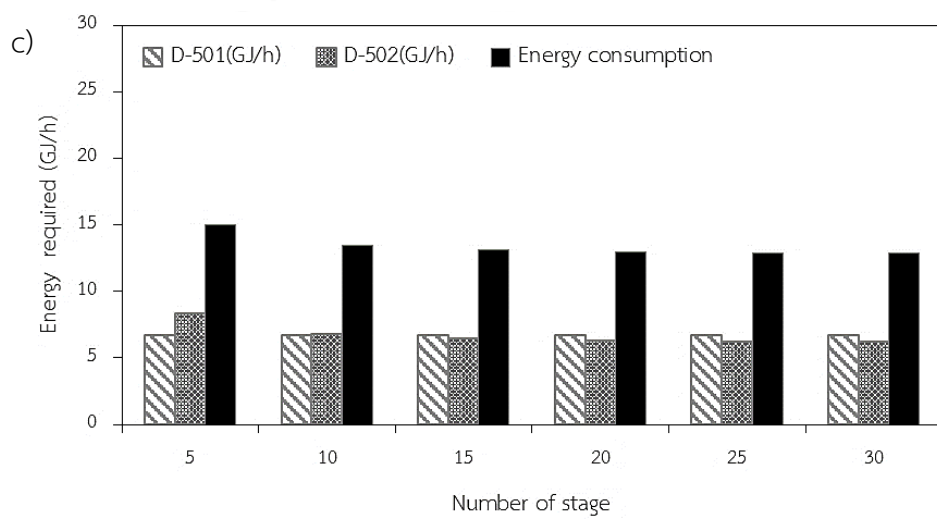
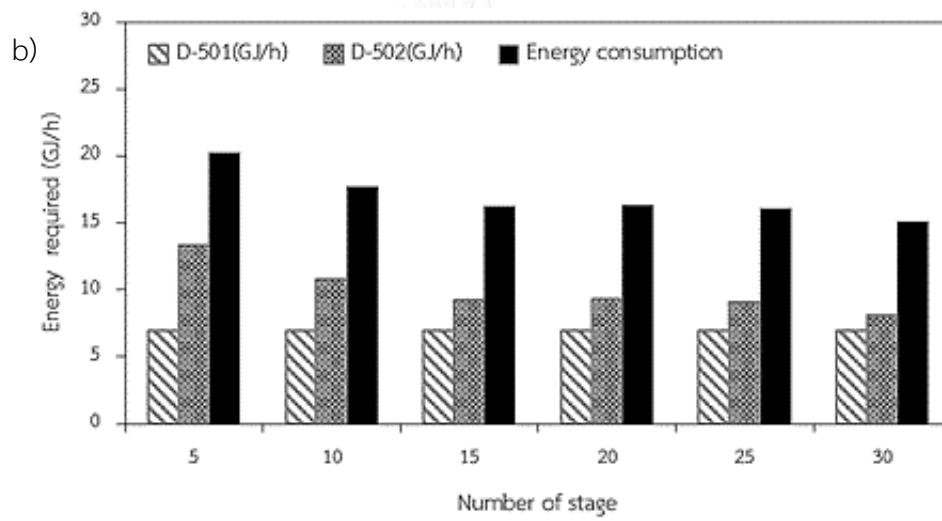
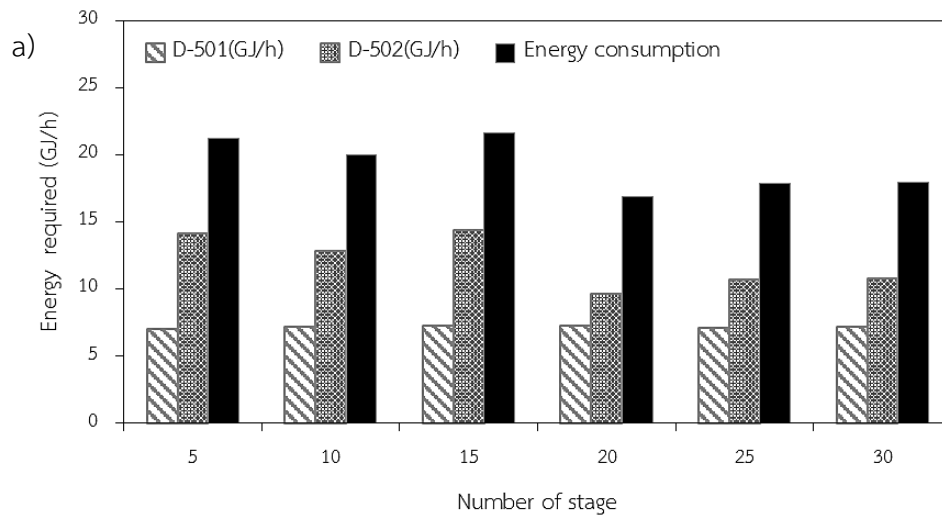


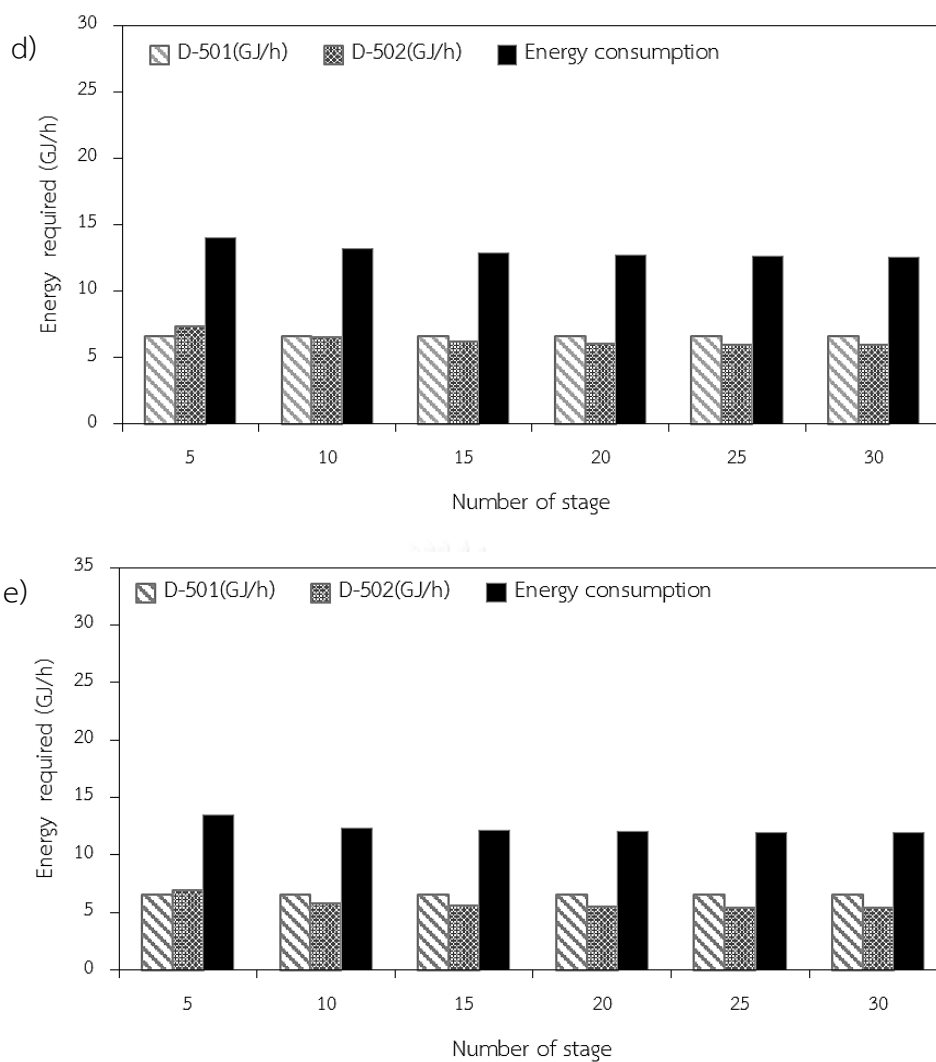


**Figure 5.6** The effect of number of stages composition of water in product at different bottom rate of reactive distillation (methanol to sodium hydroxide feed mass flow ratio = 1.6).

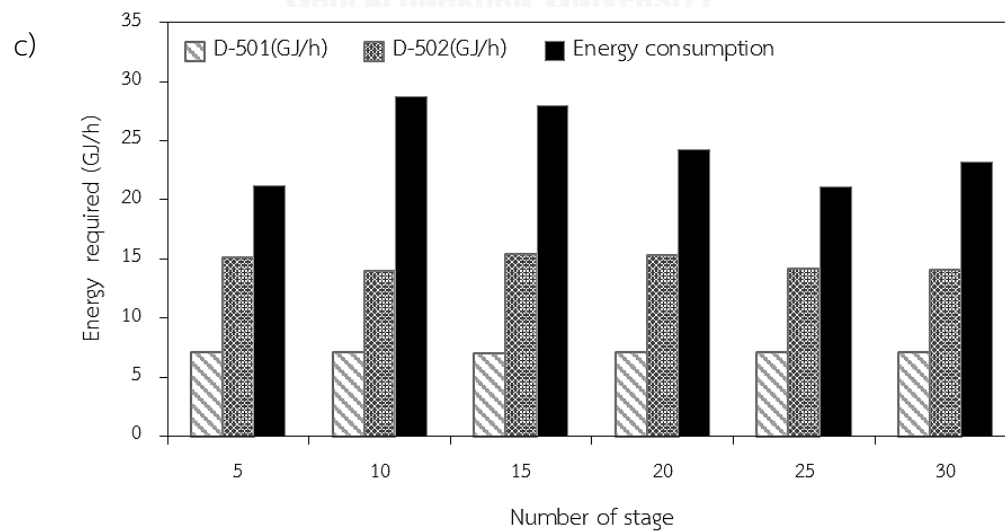
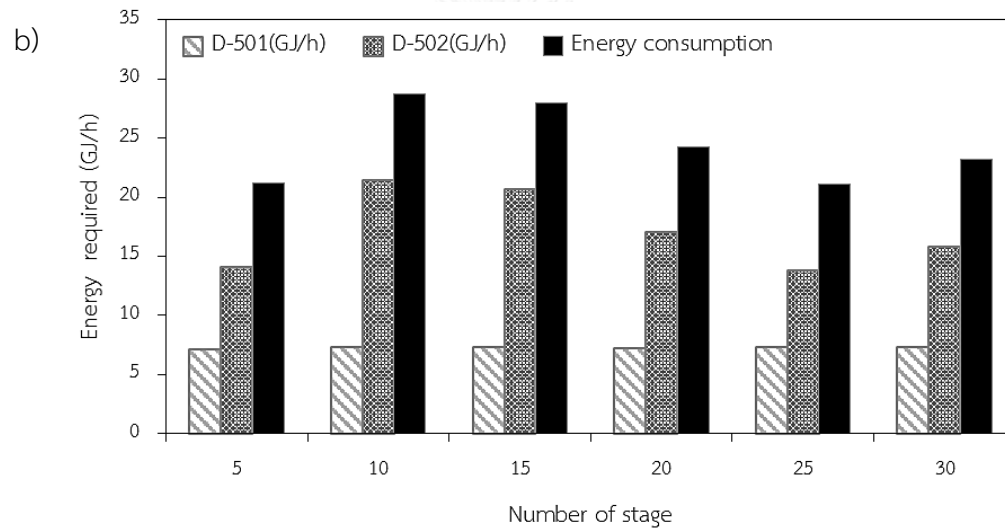
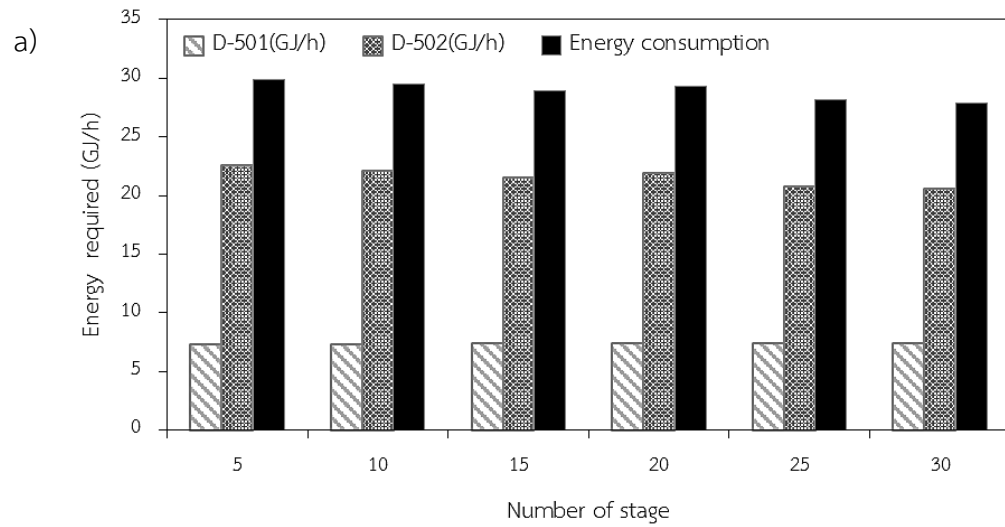
Lastly, Figure 5.6 shows that water content at methanol to sodium hydroxide feed mass ratio of 1.6. It is studied at the same values of the bottom rate of reactive distillation, the composition of the sodium methoxide in the products is similar to previous ratios. Since methanol to sodium hydroxide feed mass flow ratio of 1.4 and 1.6 contain water content lower than 0.1 wt.%. Thus, at methanol to sodium hydroxide feed mass flow ratio of 1.4 is adequate to apply in this process due to the need of lower methanol feed. In addition, this system will be further considered for the energy consumption of the process associated with the previous parameters to find the best feed flow rate and the number of stages for the operation. Figures 5.7 to 5.9 present the effect of number of stages on overall energy required for reactive distillation-distillation process at different values of bottom rate of reactive distillation column: a) 1300 kg/h, b) 1400 kg/h, c) 1530 kg/h, d) 1550 kg/h and e) 1600 kg/h (methanol to sodium hydroxide feed mass flow ratio are 1.2, 1.4 and 1.6, respectively). Firstly, at the specified values of methanol to sodium hydroxide feed mass flow ratio, it indicates that the bottom rate of the reactive distillation column increases. As a result, the heat duty of the methanol/water separation column (D-502) is decreased. Therefore, the

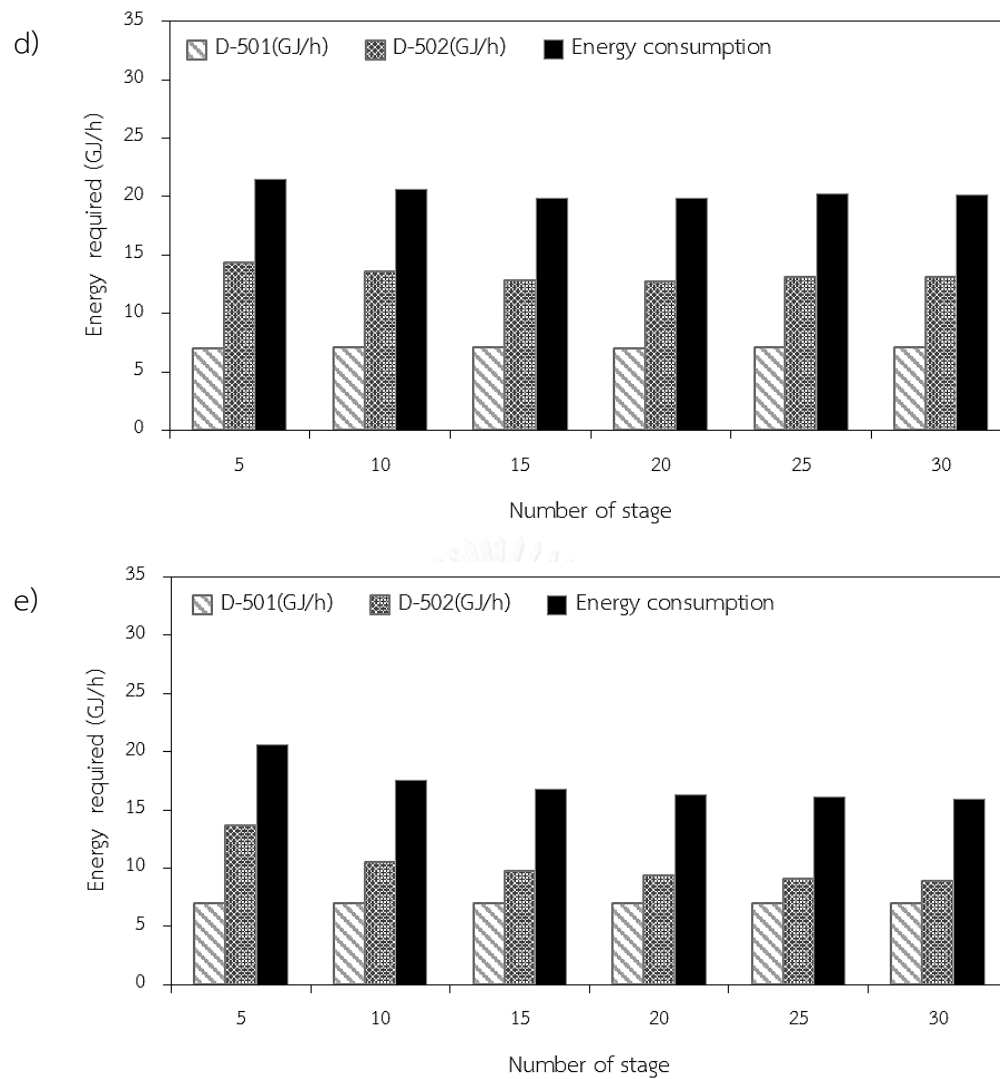
increasing of bottom rate of the reactive distillation column can reduce vaporization rate of the products approached to the methanol/water separation column (D-502). Thus, the D-502 column requires less energy to separate the methanol/water mixture. Then, considering the energy required at several of methanol to sodium hydroxide feed mass flow ratios. It is found that the energy required proportionally increases with the value of methanol to sodium hydroxide feed mass flow ratio from 1.2 to 1.6 due to excess of methanol feed flow rate. The optimal operating condition of this process is selected by examining the previous parameters associated with energy required in this part. Since, the bottom rates of reactive distillation column at 1530 and 1550 kg/h show an acceptable value of concentration of sodium methoxide and water content. But energy consumption at bottom rate of reactive distillation column of 1550 kg/h is lower than at 1530 kg/h. Thus, the optimal condition of this process is operated at 1550 kg/h for the bottom rate of reactive distillation column, the methanol to sodium hydroxide feed mass flow ratio of 1.4, total number of stages of 25, energy consumption of process is 35.13 GJ/h and the feed stage location of methanol at 24. This feed stage location is obtained from the effect of the feed stage location of the methanol on water content in products as presented in Figure 5.10. It is noted that this is only one stage presenting the water content lower than 0.1% by weight when comparing to the other stages.



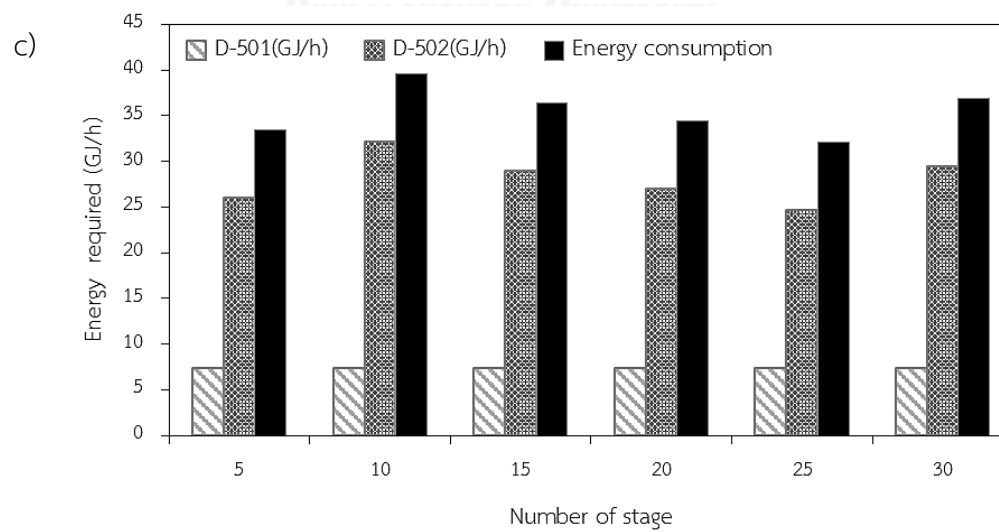
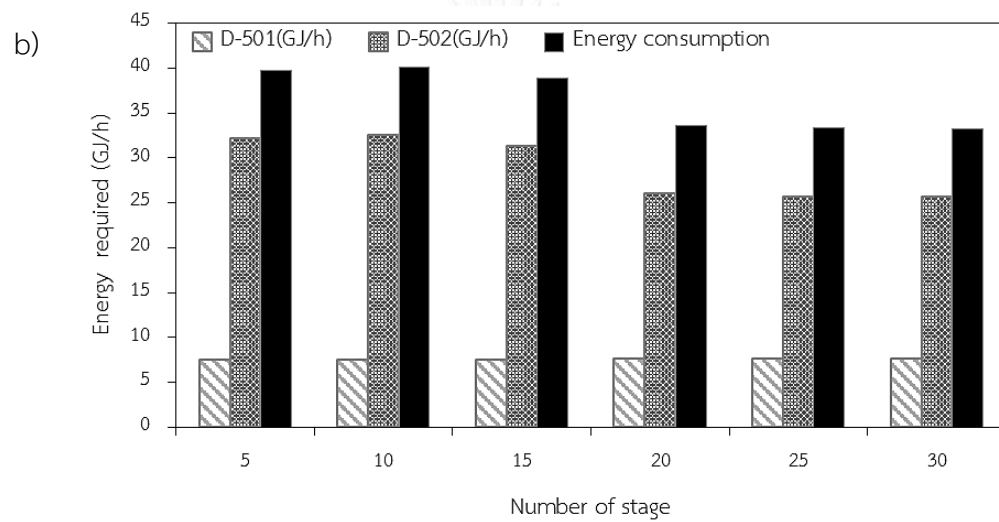
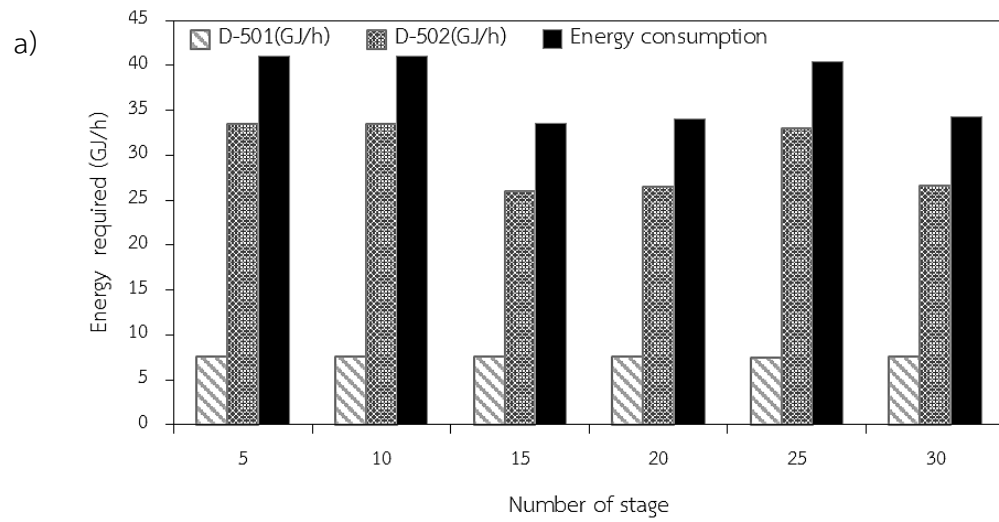


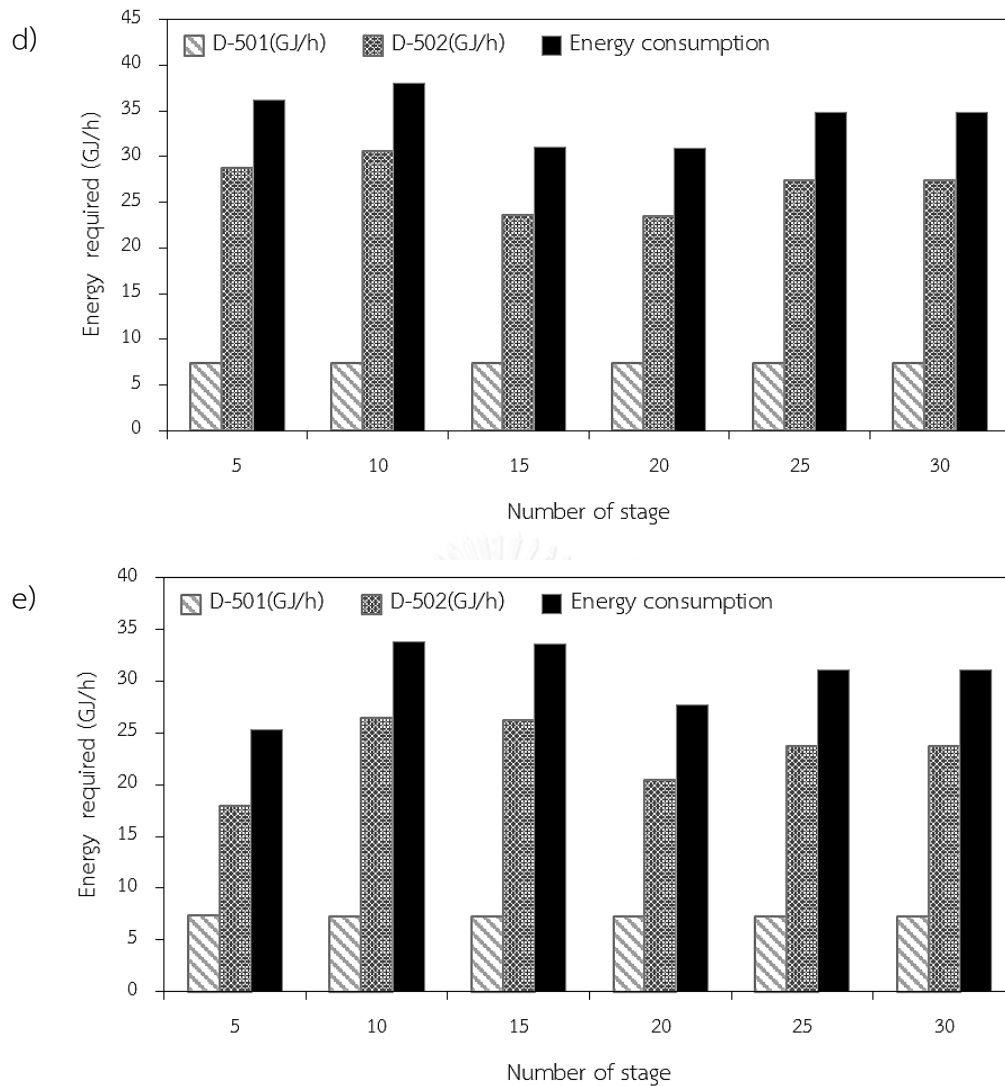
**Figure 5.7** The effect of number of stages on overall energy required of reactive distillation-distillation process at different values of bottom rate of reactive distillation column: a) 1300 kg/h, b) 1400 kg/h, c) 1530 kg/h, d) 1550 kg/h and e) 1600 kg/h (methanol to sodium hydroxide feed mass flow ratio = 1.2).





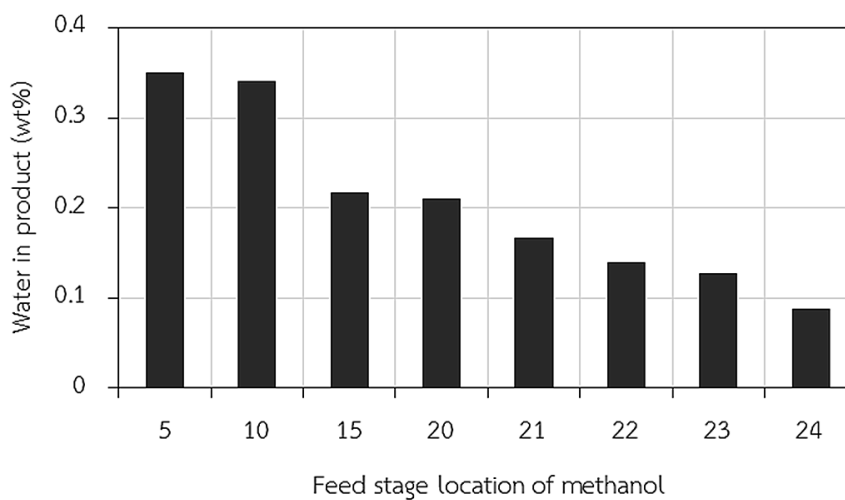
**Figure 5.8** The effect of number of stages on overall energy required of reactive distillation-distillation process at different values of bottom rate of reactive distillation column: a) 1300 kg/h, b) 1400 kg/h, c) 1530 kg/h, d) 1550 kg/h and e) 1600 kg/h (methanol to sodium hydroxide feed mass flow ratio = 1.4).





**Figure 5.9** The effect of number of stages on overall energy required of reactive distillation-distillation process at different values of bottom rate of reactive distillation column: a) 1300 kg/h, b) 1400 kg/h, c) 1530 kg/h, d) 1550 kg/h and e) 1600 kg/h (methanol to sodium hydroxide feed mass flow ratio = 1.6).





**Figure 5.10** The effect of feed stage location of methanol on water content in product (the bottom rate of reactive distillation of 1550 kg/h and number of stages of 25).

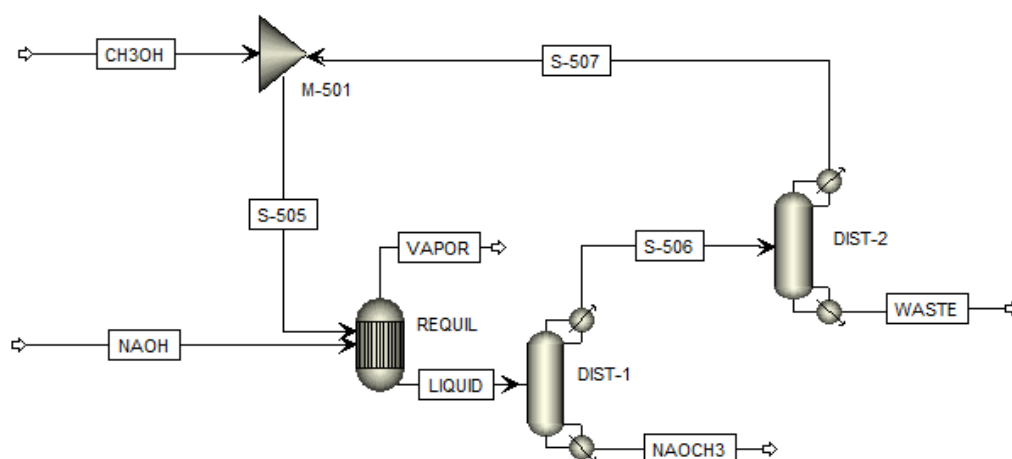
The effect of several parameters is studied to obtain the optimal operating parameters to operate the system of sodium methoxide production by using reactive distillation and distillation columns, the optimal condition is presented in Table 5.3. The main parameters for decision are the concentration of the sodium methoxide in methanol solution and the water content in the products. Also, the energy consumption, the number of stages and the feed stage location of the methanol associated with the main parameters are also considered. The optimal operating condition in the previous paragraph shows amount of the water content is smaller than 0.1 wt.% and the concentration of the sodium methoxide is lower than 45 wt.% at less energy consumption.

**Table 5.3** The optimal conditions for sodium methoxide production by reactive distillation-distillation process.

Parameters	Values
Sodium hydroxide solution feed flow rate (kg/hr)	999.5
Sodium hydroxide solution feed temperature (°C)	75
Methanol make-up feed rate (kg/hr)	1400
Methanol make-up feed temperature (°C)	30
NaOCH <sub>3</sub> production (kg/hr)	675
<b>D-501 (RD)</b>	
pressure (atm)	1
theoretical stages	25
Condenser	No condenser
Bottom rate (kg/h)	1550
Feed stage location	1 (NaOH), 24 (Methanol)
<b>D-502 (distillation)</b>	
pressure (atm)	1
theoretical stages	30
Condenser	Partial-vapor
Distillate to feed ratio	0.8471
Reflux ratio	0.6456
Feed stage location	20

### 5.3 The design of reactor-distillation process and the effect of various parameters

In this section, the design of reactor-distillation process is purposed to compare with the reactive distillation-distillation process. The performance and effect of several parameters of process are investigated. The schematic diagram of the reactor-distillation process is shown in Figure 5.11. The reactor is operated at 1 atm and 55 °C. It is connected with the first distillation (DIST-1) where the sodium methoxide is separated and left the column at the bottom. Next, the mixture of methanol and water at the top of column is transported to the second distillation (DIST-2) that separates methanol from water. Then, the methanol is recovered to the reactor again. The fixed operating conditions of feed, reactor and second distillation for sodium methoxide production are presented in Tables 5.4. In the part of first distillation, the operating parameters are investigated to find the optimal condition for sodium methoxide production.



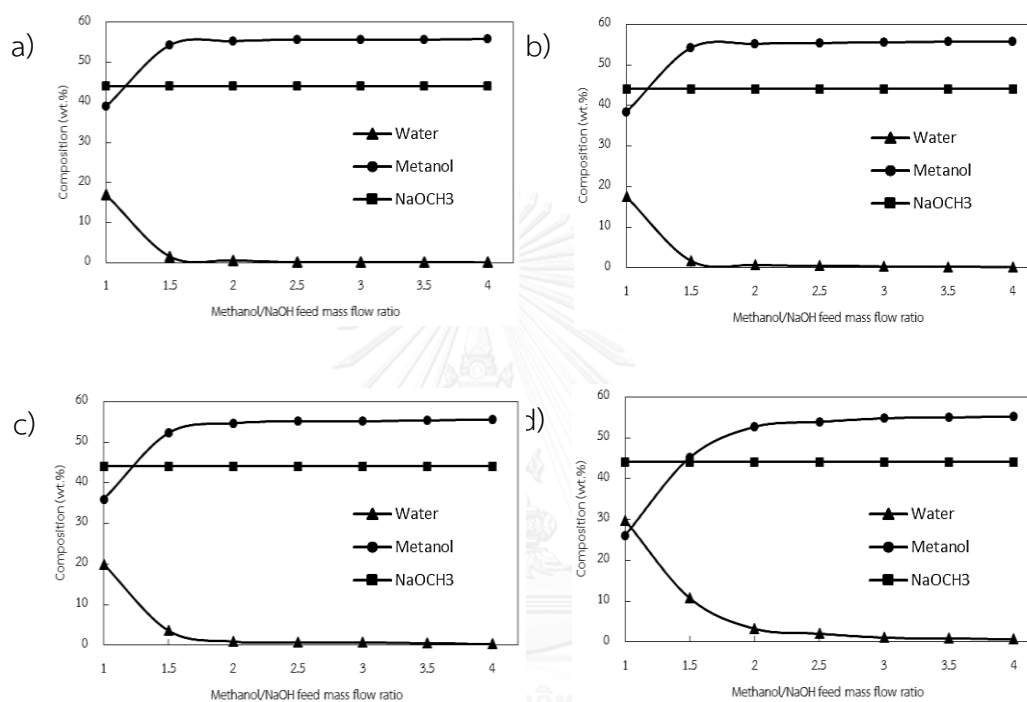
**Figure 5.11** The schematic diagram of sodium methoxide production from methanol and sodium hydroxide by reactor-distillation process.

**Table 5.4** Fixed operating conditions of feed and reactor for sodium methoxide production by reactor-distillation process.

Parameters	Values
Pressure (atm)	1
Temperature of reactor (°C)	55
Sodium hydroxide solution feed rate (kg/hr)	999.5
Sodium hydroxide solution feed temperature (°C)	30
Methanol make-up feed temperature (°C)	30
<b>DIST-2</b>	
pressure (atm)	1
theoretical stages	34
Condenser	Partial-vapor
Distillate to feed ratio	0.7841
Reflux ratio	0.8495
Feed stage location	24

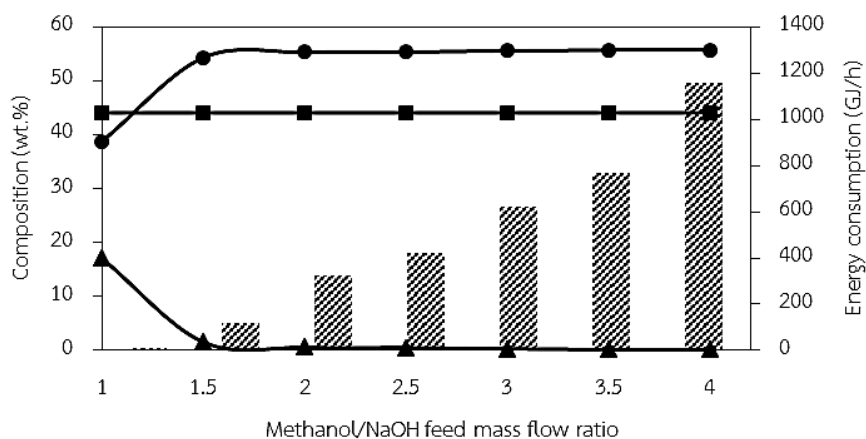
The results from simulation of the reactor-distillation process are shown in this paragraph. Figure 5.12 presents the effect of the reflux ratio of the first distillation at 0.001, 0.1 0.4 and 0.8 on the composition of the product at the different methanol to sodium hydroxide feed mass flow ratios. It was found that the composition of the sodium methoxide is constant at any ratios of methanol to sodium hydroxide and any reflux ratios due to constant of the sodium hydroxide feed mass flow rate. Next, the water content in the product is increased with increasing reflux ratio because the reflux ratio is defined as the ratio of the liquid returned to the column divided by the liquid removed as the product (distillate). Therefore, when the reflux ratio increases, the water content in product is returned to the column at higher extent. As a result, the water can react with the sodium methoxide product and then converted to reactant (sodium hydroxide). Consequently, using a high reflux ratio is not advantageous. So that this process can describe why reactive distillation-distillation process is operated without using a condenser. After that, we consider the ratios of methanol to sodium hydroxide feed mass flow. From Figures 5.13, it is found that when increasing the methanol to sodium hydroxide feed mass flow ratio, the energy consumption of the

process is increased. In contrast, the water content is decreased because of excess in methanol feed. The water content is an important parameter to evaluate this process. From the results in Figure 5.14, the water content is the lowest at the methanol to sodium hydroxide feed mass flow ratio of 4 and the reflux ratio of 0.001 as well as 2229.37 GJ/h of energy consumption. However, this reflux ratio is negligible because the value is very close to zero.

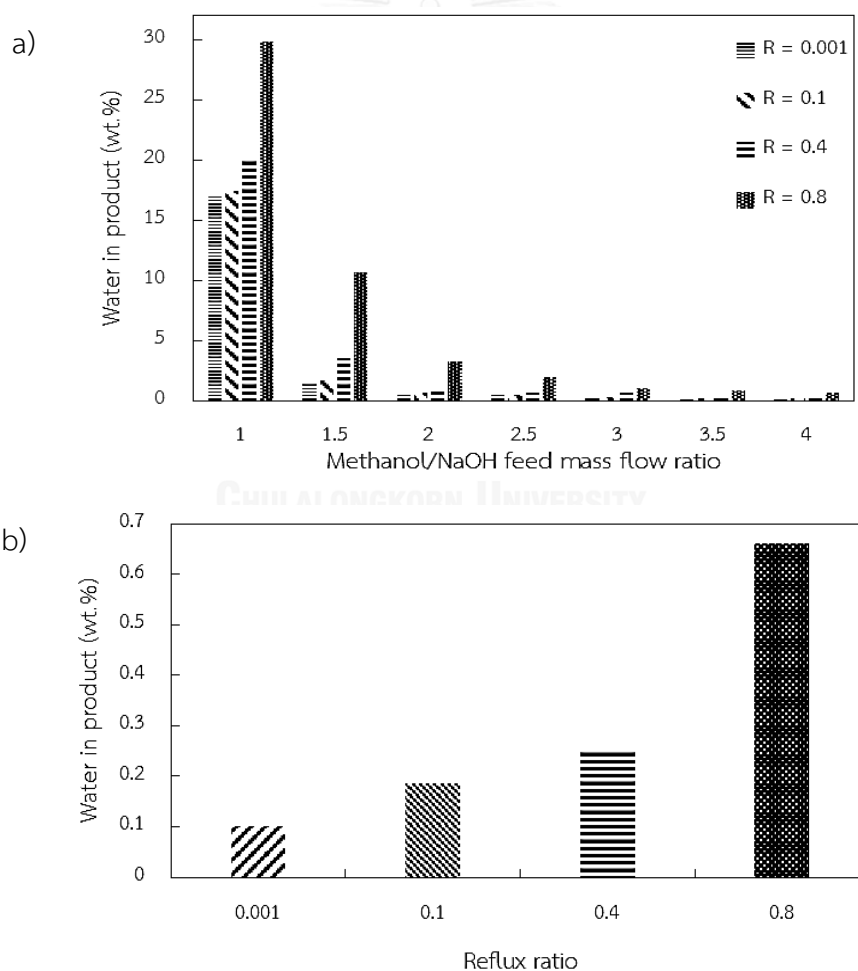


**Figure 5.12** Effect of reflux ratio of first distillation followed: a) 0.001; b) 0.1; c) 0.4; and d) 0.8 on composition of product at different methanol to sodium hydroxide feed mass flow ratio.

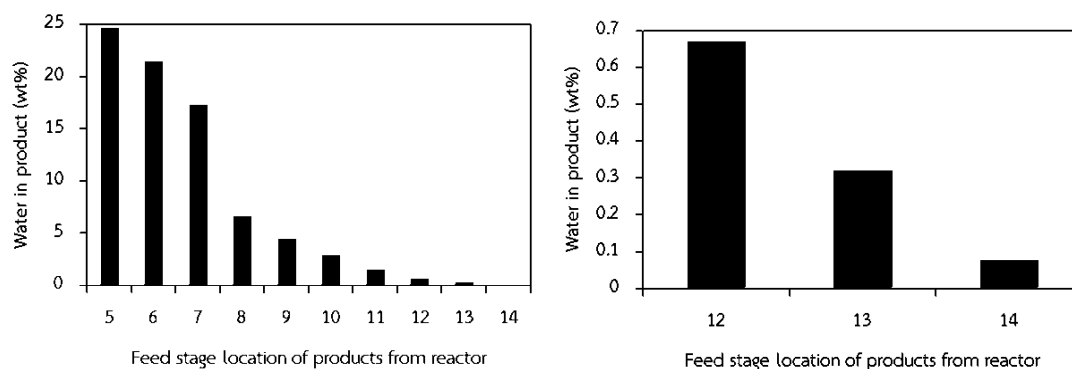
To investigate the effect of feed stage location of products from reactor on the water content in the first distillation column, the stage location is varied from 5 to 14 at the same condition. From the result shown in Figure 5.15, the best feed stage location of methanol is at stage 14 because the water content in the product is lower than 0.1% by weight which is the standard value. The summary of the optimal condition for reactor-distillation process is shown in Tables 5.5.



**Figure 5.13** Effect of methanol to sodium hydroxide feed mass ratio on composition of product and reboiler duty at reflux ratio of 0.001.



**Figure 5.14** a) Effect of methanol to sodium hydroxide feed mass ratio at different reflux ratios and b) Effect of reflux ratio at methanol to sodium hydroxide feed mass flow ratio of 4 on water content in products.



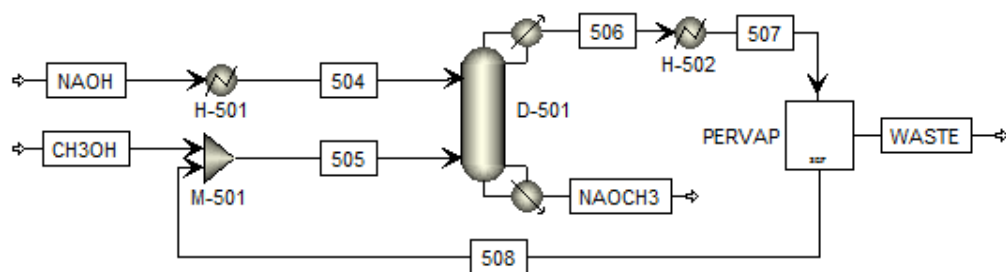
**Figure 5.15** Effect of feed stage location of products from reactor on water content in products (the bottom rate of reactive distillation of 1550 kg/h and number of stages of 25).

**Table 5.5** The optimal feed conditions for sodium methoxide production by reactor-distillation process.

Parameters	Values
Sodium hydroxide solution feed rate (kg/h)	999.5
Sodium hydroxide solution feed temperature (°C)	30
Methanol make-up feed rate (kg/h)	4000
Methanol make-up feed temperature (°C)	30
NaOCH <sub>3</sub> production (kg/h)	675
<b>DIST-1</b>	
pressure (atm)	1
theoretical stages	15
Condenser	Partial-vapor
Reflux ratio	0.001
Bottom rate (kg/h)	1550
Feed stage location	14
<b>DIST-2</b>	
pressure (atm)	1
theoretical stages	34
Condenser	Partial-vapor
Distillate to feed ratio	0.7841
Reflux ratio	0.8495
Feed stage location	24

#### 5.4 The design of reactive distillation coupled with pervaporation process

This section studies the design of the reactive distillation coupled with pervaporation process to improve the reactive-distillation process. This process added a A-type zeolite membrane for separation of the methanol from the methanol/water mixture, a top product of the reactive distillation column. Initially, the constant sodium hydroxide aqueous solution at 999.5 kg/h is fed on the top of column at 75 °C and 1 atm. It is reacted with various methanol to sodium hydroxide feed mass flow ratio. After that, sodium methoxide product is separated at the bottom and the mixture of methanol/water is transferred on the top of column to the pervaporation unit at 60 °C and 1 atm. The water permeates through the membrane while the methanol is recycled back to reactive distillation column. Then, the schematic diagram is shown in Figure 5.16. After that, the fixed operating conditions for sodium methoxide production are shown in Table 5.6.



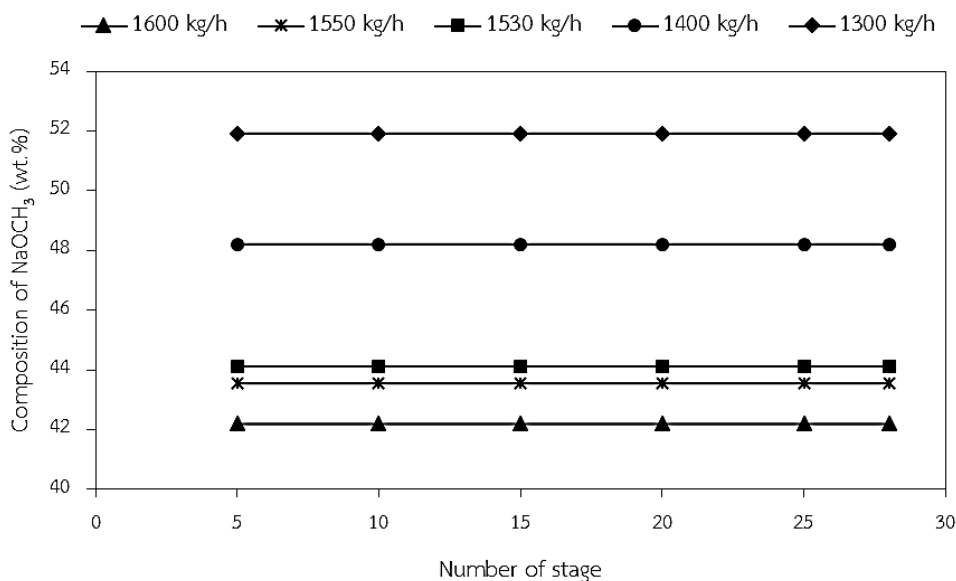
**Figure 5.16** The schematic diagram of sodium methoxide production from methanol and sodium hydroxide by reactive distillation coupled with pervaporation process.



**Table 5.6** Fixed operating conditions for sodium methoxide production by reactive distillation coupled with pervaporation process.

Parameters	Values
Pressure (atm)	1
Sodium hydroxide solution feed flow rate (kg/hr)	999.5
Sodium hydroxide solution feed temperature (°C)	75
Methanol make-up feed temperature (°C)	30
Type of membrane	A-type zeolite
Membrane area (m <sup>2</sup> )	3.76
Temperature of pervaporation (°C)	65

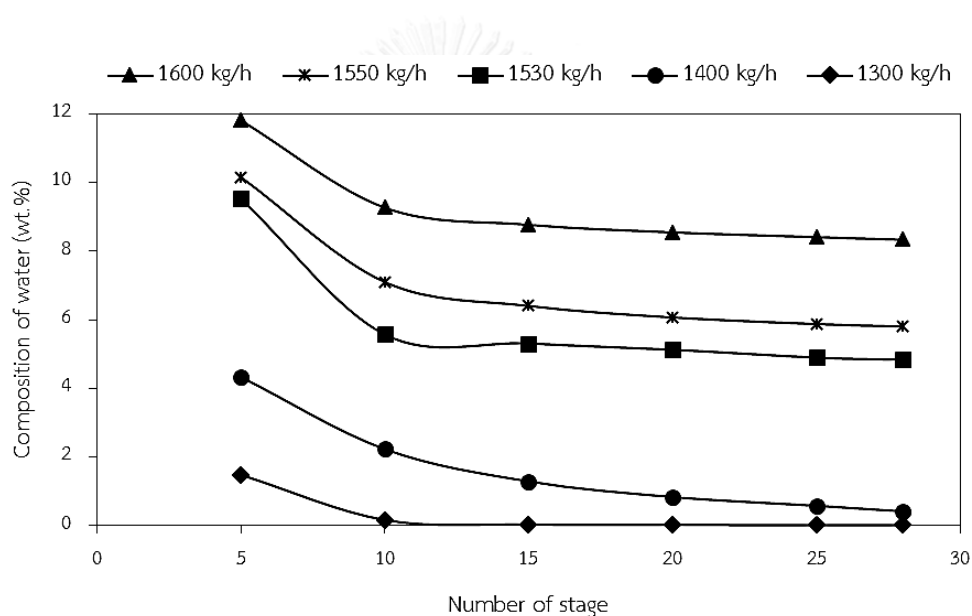
Firstly, the reactive distillation column is investigated. The simulation results were reported for the bottom rate of reactive distillation column at 1300, 1400, 1530, 1550 and 1600 kg/h. This parameter is considered with the number of stage at different values of methanol to sodium hydroxide feed mass flow ratios. Figure 5.17 shows effect of those parameters on composition of sodium methoxide. It is found that all of methanol to sodium hydroxide feed mass flow ratios are shown exactly the same results. The composition of sodium methoxide is constant at any number of stage while it is decreased when the bottom rate is increased. The cause of these result occurs from the increase of methanol/water mixtures in products. As a result, the concentration of sodium methoxide is diluted at constant flow rate of sodium hydroxide aqueous solution. The sodium methoxide production is limited by the composition of sodium methoxide is not more than 45 wt.% in methanol solution. Because this concentration causes to viscous liquid. Consequently, this process cannot operate at bottom rate of reactive distillation column of 1300 and 1400 kg/h because composition of sodium methoxide is higher than limitation value. Considering the bottom rates of 1530, 1550 and 1600 kg/h, the composition of sodium methoxide is lower than the limitation value but it needs to be considered the water content in the next step.



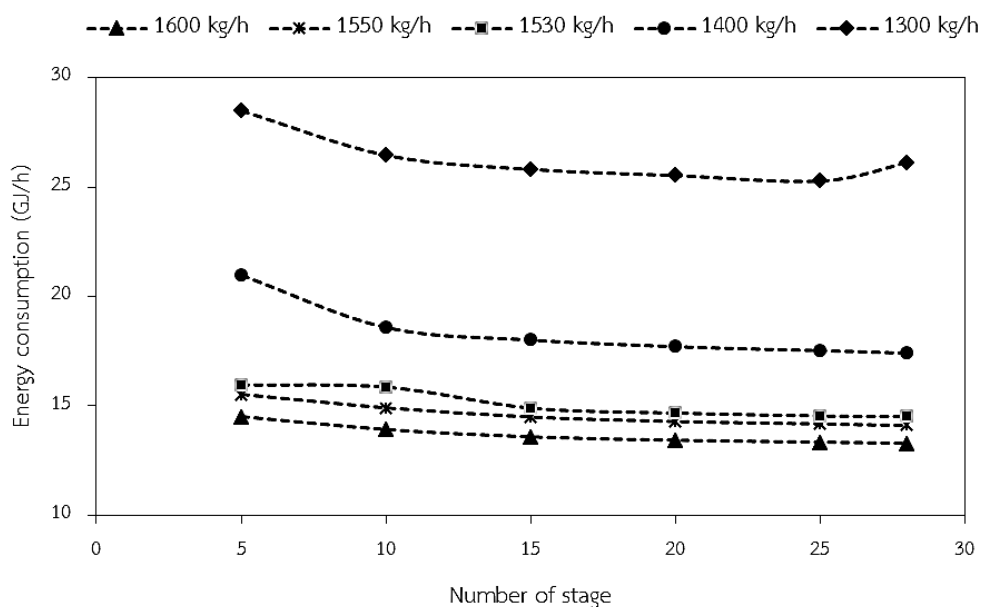
**Figure 5.17** The effect of number of stages on composition of sodium methoxide at different bottom rates of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio are 1.2, 1.4 and 1.6).

From all of the methanol to sodium hydroxide feed mass flow ratios, it is found that the tendency of water content appears lower when number of stages are higher. In contrast, the bottom rate of reactive distillation column must be less. To consider the water content and energy consumption at methanol to sodium hydroxide feed mass flow ratio of 1.2 are shown in Figures 5.18 and 5.19, respectively. The increment of bottom rate results in increasing water content in products due to high accumulation of water in the bottom. On the other hand, the water content is slowly decreased at higher number of stages. Then, considering the effect of the number of stages on energy consumption, the tendency of energies are decreased slightly at higher number of stage. Thus, from the previous discussion although the sodium hydroxide at bottom rate of 1530, 1550 and 1600 kg/h are lower than 45 wt.% but the water content is higher than 0.1 wt.%. So that at the methanol to sodium hydroxide feed mass flow ratio of 1.2 is not found the optimal parameters. Next, for the methanol to sodium hydroxide feed mass flow ratio of 1.4 and 1.6, the tendency of the results is the same with the result from methanol to sodium hydroxide feed mass flow ratio of 1.2. Also, the different results are the composition of the water in products and the

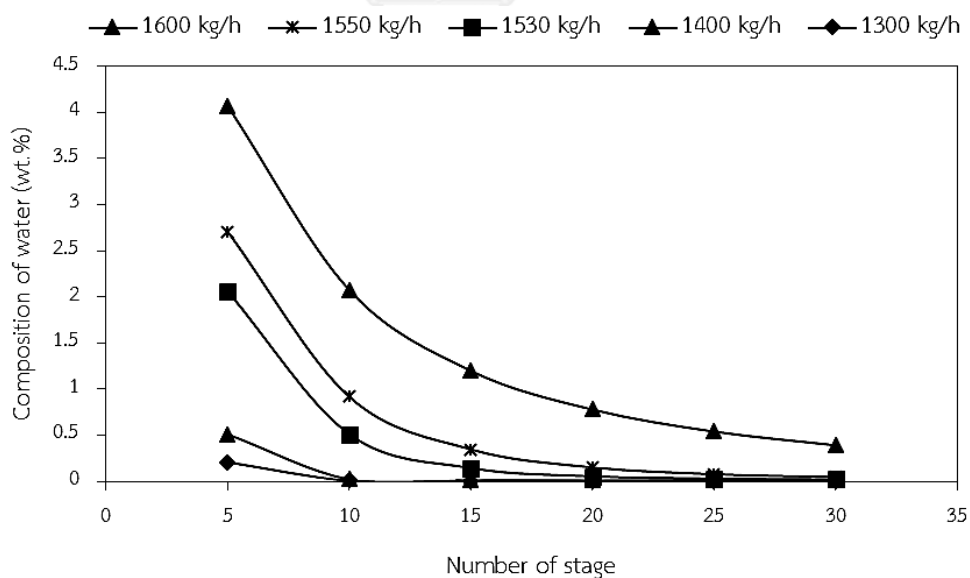
energy required. Therefore, the optimal parameters at the methanol to sodium hydroxide feed mass flow ratio of 1.4 are shown at bottom rate of 1550 kg/h, total number of stage of 25, the composition of sodium methoxide in methanol solution of 43.55 wt.%, water content is lower than 0.1 wt.% and energy consumption of 34.25 GJ/h. Those results are presented in Figures 5.20 and 5.21. Then, at methanol to sodium hydroxide feed mass flow ratio of 1.6, the optimal parameters is shown at higher of energy consumption than the methanol to sodium hydroxide feed mass flow ratio of 1.4. Thus, the methanol to sodium hydroxide feed mass flow ratio of 1.4 is an optimal parameter applying to this process.



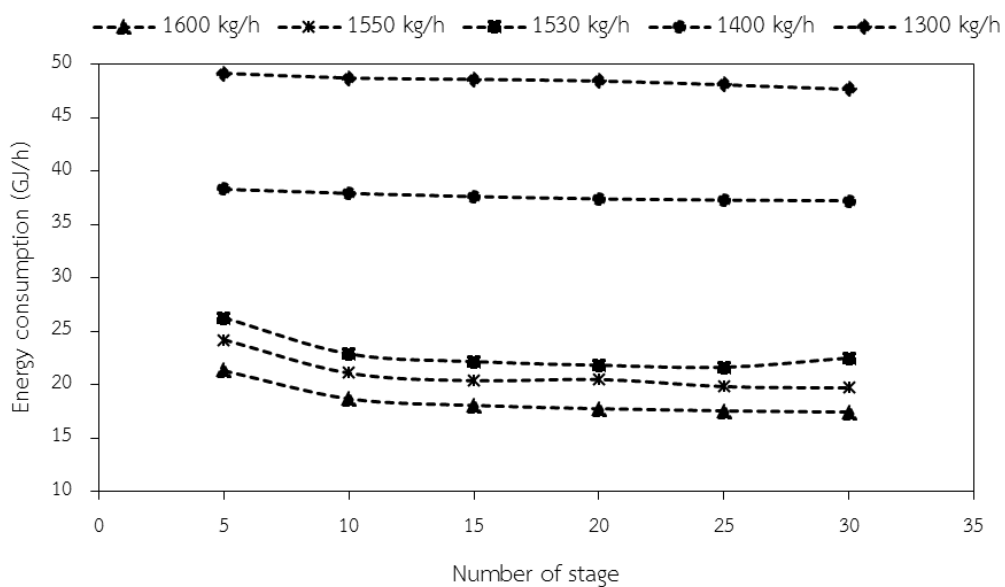
**Figure 5.18** The effect of number of stages on composition of water in product at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.2).



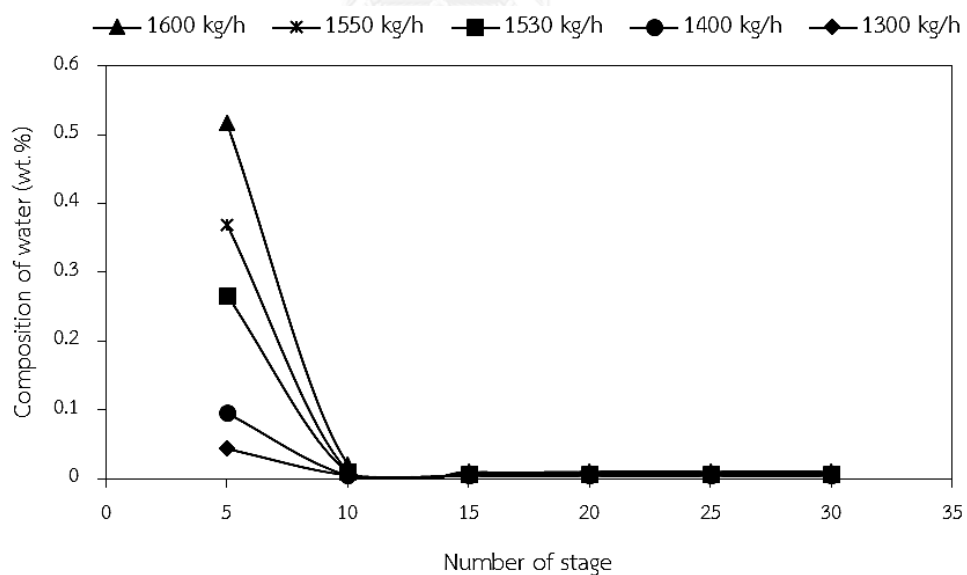
**Figure 5.19** The effect of number of stages on energy consumption of process at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.2).



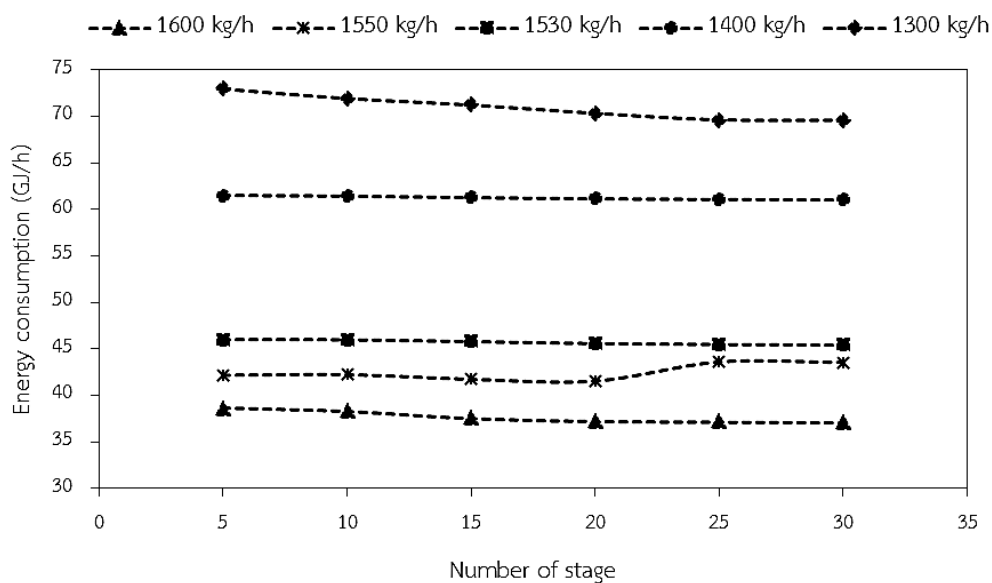
**Figure 5.20** The effect of number of stages on composition of water in product at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.4).



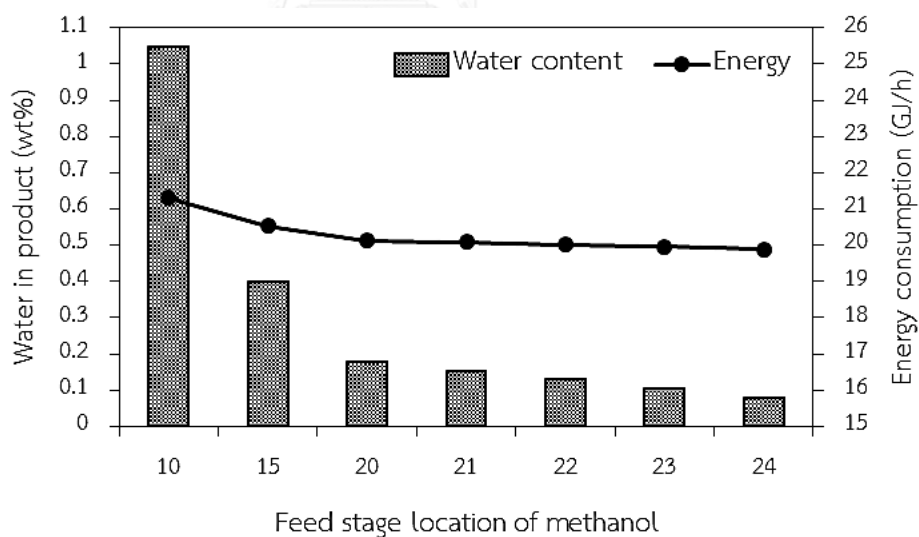
**Figure 5.21** The effect of number of stages on energy consumption of process at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.4).



**Figure 5.22** The effect of number of stages on composition of water in product at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.6).

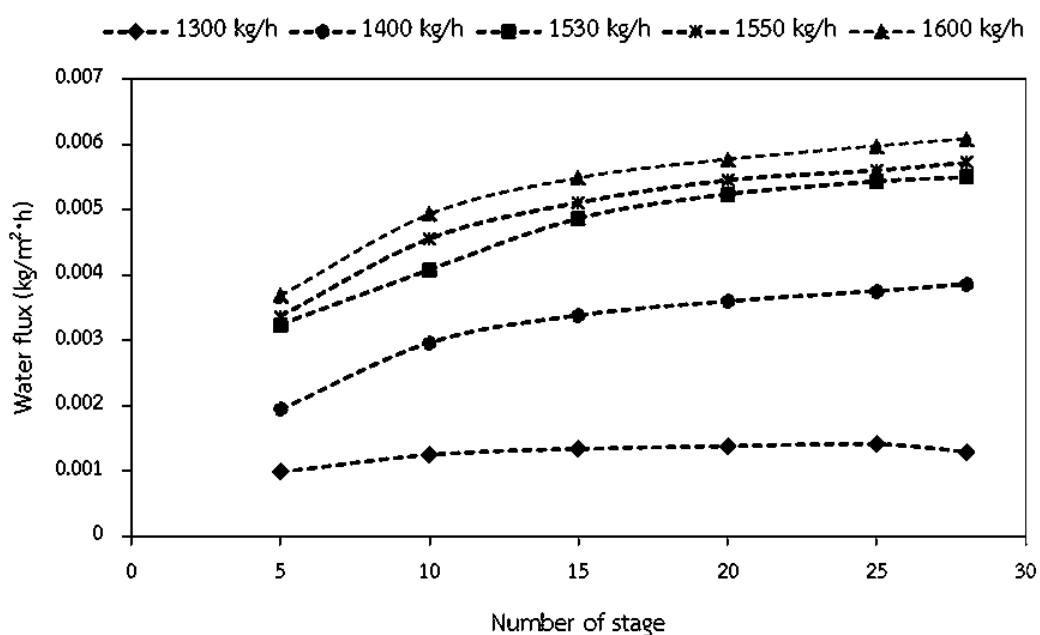


**Figure 5.23** The effect of number of stages on energy consumption of process at different bottom rate of reactive distillation column (methanol to sodium hydroxide feed mass flow ratio = 1.6).

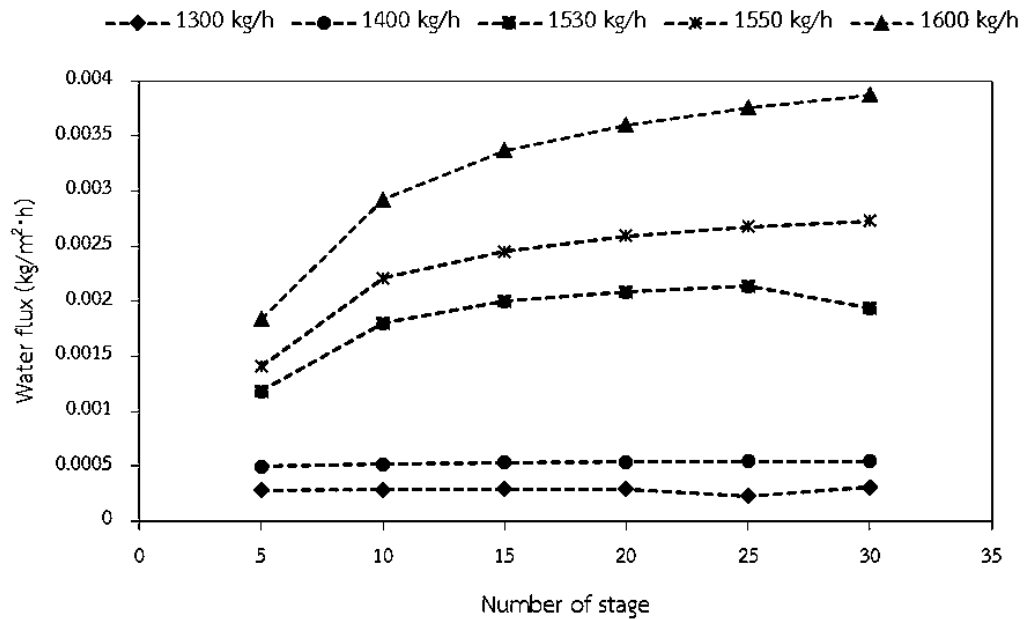


**Figure 5.24** Effect of feed stage location of methanol on water content in product and energy consumption (the bottom rate of reactive distillation of 1550 kg/h and number of stages of 25).

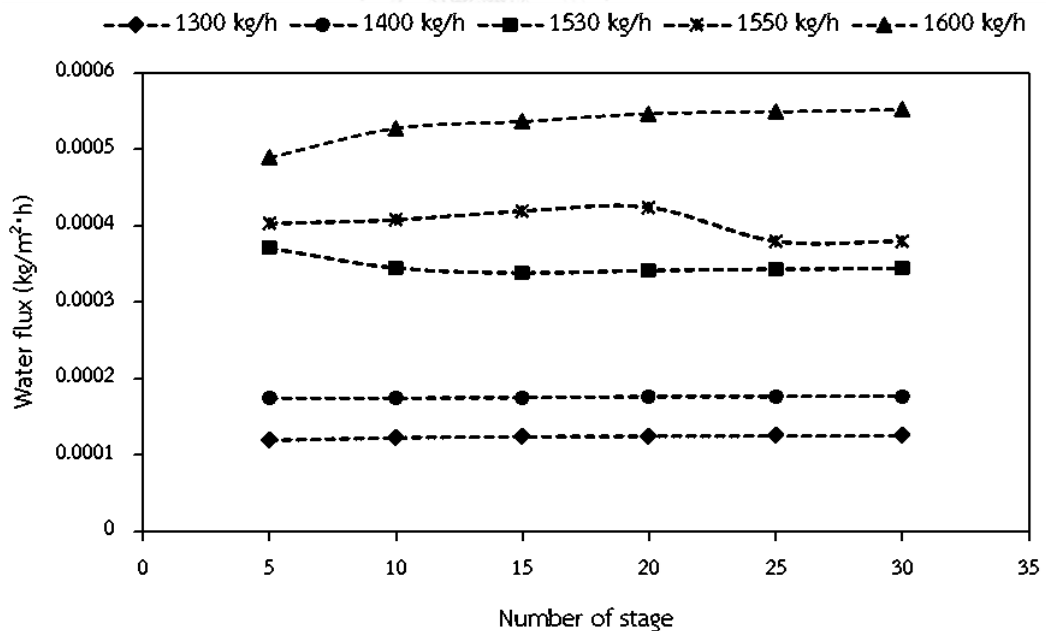
To investigate the effect of the feed stage location on the water content in the product and the energy consumption are shown in Figure 5.24, the water content is shown in form of the histogram and the energy consumption is shown in form of line graph. The optimal feed stage location of methanol is 24 at energy consumption of 34.25 GJ/h. This condition is chosen because of the lowest of the water content and the lowest of the energy consumption. It also confirms that the feed stage location of methanol is kept fixed at the bottom of column.



**Figure 5.25** Effect of number of stage and bottom rate of reactive distillation process are 1300, 1400, 1530, 1550 and 1600 kg/h on water flux of pervaporation at methanol to sodium hydroxide feed mass ratio of 1.2.

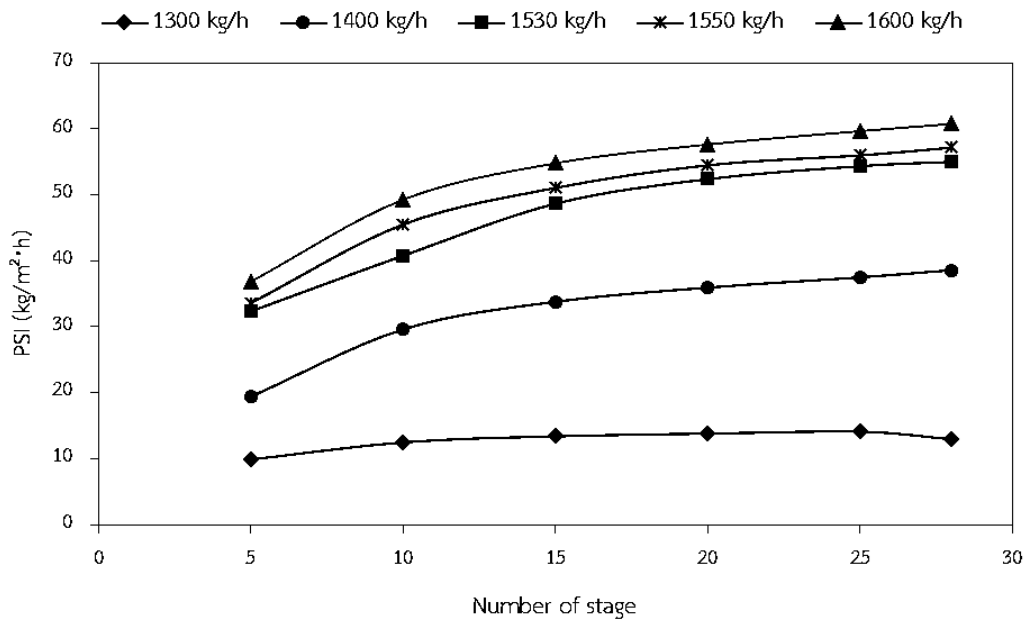


**Figure 5.26** Effect of number of stage and bottom rate of reactive distillation process are 1300, 1400, 1530, 1550 and 1600 kg/h on water flux of pervaporation at methanol to sodium hydroxide feed mass ratio of 1.4.

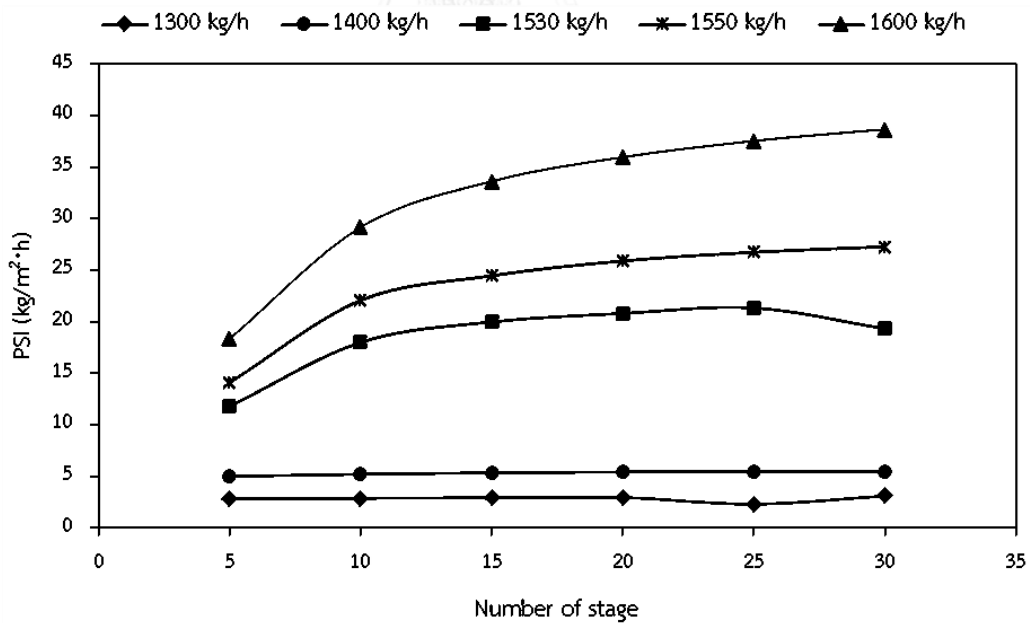


**Figure 5.27** Effect of number of stage and bottom rate of reactive distillation process are 1300, 1400, 1530, 1550 and 1600 kg/h on water flux of pervaporation at methanol to sodium hydroxide feed mass ratio of 1.6.

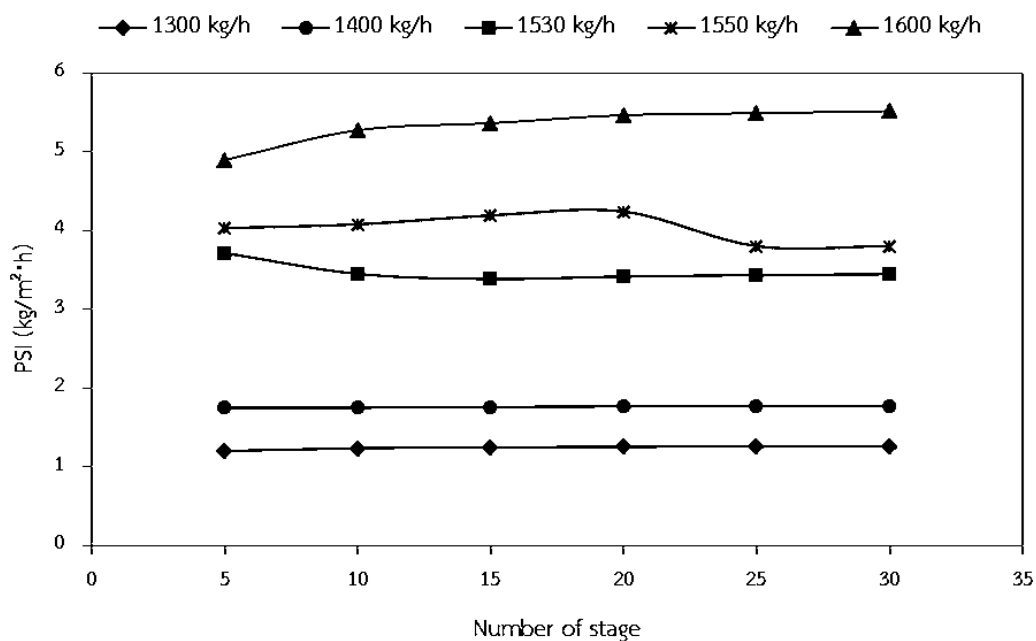




**Figure 5.28** Effect of number of stage and bottom rate of reactive distillation process are 1300, 1400, 1530, 1550 and 1600 kg/h on pervaporation separation index (PSI) at methanol to sodium hydroxide feed mass ratio of 1.2.



**Figure 5.29** Effect of number of stage and bottom rate of reactive distillation process are 1300, 1400, 1530, 1550 and 1600 kg/h on pervaporation separation index (PSI) at methanol to sodium hydroxide feed mass ratio of 1.4.



**Figure 5.30** Effect of number of stage and bottom rate of reactive distillation process are 1300, 1400, 1530, 1550 and 1600 kg/h on pervaporation separation index (PSI) at methanol to sodium hydroxide feed mass ratio of 1.6.

**Table 5.7** Simulation results of performance of pervaporation in comparison with data from literature [31].

Results	reference data [31]	Simulation results
Type of membrane	A-type zeolite	A-type zeolite
Temperature of feed (°C)	60	60
Permeate pressure (mbar)	7	7
Membrane area (cm <sup>2</sup> )	60	60
Water feed (wt.%)	10.1	10
Water permeate (wt.%)	99.91	99.91
Water flux (kg/m <sup>2</sup> h)	0.46	0.46
Separation factor	10000	9998.78
PSI (kg/m <sup>2</sup> h)	4599.54	4611.81

In the part of pervaporation, the pervaporation unit obtains excellent separation of methanol from water instead of distillation. It was validated with the data from the previous work [31]. This validation is purposed for verification of the simulations for predicting performances of pervaporation though the values of water flux, pervaporation separation index (PSI) and separation factor. The results is shown in Table 5.7, it indicates that the simulation results are consistent with the data reported [31] at the same condition. It should be noted that although the simulation results show the values of separation factor and PSI deviated from those reported in the reference, their values are insignificantly small. At different methanol to sodium hydroxide feed mass flow ratios, number of stage and bottom rate of reactive distillation column are studied. Those parameters are evaluated for the performance of pervaporation on water flux, pervaporation separation index (PSI) and separation factor. The separation factor is estimated by Eq. (2.2) that is constant at 9991 for all methanol to sodium hydroxide feed mass flow ratios, number of stage and bottom rate of reactive distillation column. Because this process is operated by using single type of both membrane and solvent, to consider the water flux of pervaporation that is calculated by Eq. (2.1), the trend of water flux at all of methanol to sodium hydroxide feed mass flow ratios are shown in Figures 5.25 to 5.27. When the bottom rate and number of stage of reactive distillation are increased, the water flux also increases. However, the water flux is become lower with increasing the methanol to sodium hydroxide feed mass flow ratios due to less water content in products. For pervaporation separation index (PSI), the value is raised slightly as a function of water flux that is evaluated from Eq. (2.3). The results are shown in Figure 5.28 to Figure 5.30. The summary of optimal condition for reactive distillation coupled with pervaporation is shown in Table 5.8.

**Table 5.8** The optimal operating conditions for sodium methoxide production by reactive distillation coupled with pervaporation process.

Parameters	Values
Sodium hydroxide solution feed rate (kg/h)	999.5
Sodium hydroxide solution feed temperature (°C)	75
Methanol make-up feed rate (kg/h)	1400
Methanol make-up feed temperature (°C)	30
NaOCH <sub>3</sub> production (kg/h)	675
<b>D-501 (RD)</b>	
pressure (atm)	1
theoretical stages	25
Condenser	None condenser
Bottom rate (kg/h)	1550
Feed stage location	24
<b>Pervaporation</b>	
Type of membrane	A-type zeolite
pressure (atm)	1
Temperature of feed (T <sub>f</sub> )	65
Membrane area (m <sup>2</sup> )	3.76
Water permeate (wt.%)	99.8
Water flux (kg/m <sup>2</sup> h)	2.68 × 10 <sup>-3</sup>
Separation factor	9991
PSI (kg/m <sup>2</sup> h)	26.75

### 5.5 Performance comparison of the three processes

This section is proposed to compare the performance of three processes including of reactor-distillation process, reactive distillation-distillation and reactive distillation coupled with pervaporation process. Table 5.9 presents the comparative results from the simulations. In term of methanol make-up, the reactive distillation-distillation and reactive distillation coupled with pervaporation processes are used at the same flow rate of 1400 kg/h, but reactor-distillation process was used at 4000 kg/h because this flow rate is needed to decrease the water content in products to a value lower than the standard one. Next, the sodium methoxide production was produced at 675 kg/h or 43.55 wt.% in methanol solution for three processes. Then, the water content in products of reactive distillation coupled with pervaporation is the lowest. In the term of energy consumption, it is found that the reactive distillation coupled with pervaporation can lower the energy consumption of the process compared to the reactive distillation-distillation process.

**Table 5.9** The comparison of optimal conditions for three processes.

Parameters	Re-D	RD-D	RD-PV
Sodium hydroxide solution feed rate (kg/h)	999.5	999.5	999.5
Methanol make-up feed rate (kg/h)	4000	1400	1400
NaOCH <sub>3</sub> production (kg/h)	675	675	675
Concentration of NaOCH <sub>3</sub> solution (wt.%)	43.55	43.55	43.55
Water content in product (ppm)	776	874	770
Energy consumption (GJ/h)	2229.37	35.13	34.25

## CHAPTER 6

### CONCLUSIONS

Process simulation of sodium methoxide production from methanol and sodium hydroxide by using Aspen Plus program was investigated in this work. The case studies of this work consisted of reactor-distillation, reactive distillation-distillation, and reactive distillation coupled with pervaporation processes. Then, the effects of various parameters including methanol to sodium hydroxide feed mass flow ratio, number of stages and feed stage location on composition of products and energy consumption of process were examined. The optimal conditions from the three processes were purposed and the results were concluded in this section.

#### 6.1 Effect of various parameters

##### 6.1.1 Reactor-distillation process

1. A change in reflux ratios exhibited significant effect on water content in products. On the other hand, the concentration of sodium methoxide was unchanged.
2. The increase of methanol to sodium hydroxide mass flow ratio causes the decrease of water content in products, but the energy consumption of process was increased.

##### 6.1.2 Reactive distillation-distillation process

1. The increase of methanol to sodium hydroxide feed mass flow ratios resulted in lowering concentration of sodium methoxide and water content in products. In contrast, the energy consumption of process was higher.
2. A change in number of stages showed significant effect on water content in products and energy consumption of process. But the concentration of sodium methoxide was not significantly affected.
3. The increase of bottom rate of reactive distillation decreased the concentration of sodium methoxide and energy consumption of process, but the water content in products was increased.

### 6.1.3 Reactive distillation coupled with pervaporation process

1. The increase of methanol to sodium hydroxide feed mass flow ratio resulted in lowering concentration of sodium methoxide, water content in products, water flux and pervaporation separation index (PSI) while separation factor was constant. In contrast, the energy consumption of process was higher.

2. A change in number of stages showed significant effect on water content in products, water flux, pervaporation separation index (PSI) and energy consumption of process. However, the concentration of sodium methoxide and separation factor were invariable.

3. The increase of bottom rate of reactive distillation decreased the concentration of sodium methoxide and energy consumption of process while the separation factor was unchanged. On the other hand, the water content in products, water flux and pervaporation separation index (PSI) were increased.

## 6.2 Process performance for sodium methoxide production processes at optimal conditions

### 6.2.1 Optimal Conditions

1. For reactor-distillation process, the optimal conditions were at the methanol to sodium hydroxide feed mass flow ratio of 4, the D-501 operated with partial-vapor condenser, reflux ratio of 0.001, the number of stages of 15, feed stage location at 14 and bottom rate of 1550 kg/h. In addition, the fixed operating conditions were shown in Table 5.5.

2. For reactive distillation-distillation process, the optimal conditions were at the methanol to sodium hydroxide feed mass flow ratio of 1.4, the DIST-1 operated without using condenser, the number of stages of 25, feed stage location at 24 and bottom rate of 1550 kg/h. Furthermore, the fixed operating conditions were shown in Table 5.2.

3. For Reactive distillation coupled with pervaporation process, the optimal conditions were at the methanol to sodium hydroxide feed mass flow ratio of 1.4, the D-501 operated without using condenser, the number of stages of 25, feed stage location at 24 and bottom rate of 1550 kg/h. In the part of pervaporation unit, the performance

of this unit was presented at water flux of  $2.68 \times 10^{-3}$  kg/m<sup>2</sup>h, separation factor of 9991 and the pervaporation separation index (PSI) of 26.75 of kg/m<sup>2</sup>h. Moreover, the fixed operating conditions were shown in Table 5.8.

#### 6.2.2 The comparison in process performances

1. The methanol to sodium hydroxide feed mass flow ratio of both reactive distillation-distillation and reactive distillation coupled with pervaporation processes were lower than the reactor-distillation process about 65%.

2. The energy consumption of reactor-distillation, reactive distillation-distillation and reactive distillation coupled with pervaporation processes were 2229.37, 35.13 and 34.25 GJ/h, respectively. The results showed that the reactive distillation coupled with pervaporation process required less energy consumption than reactive distillation-distillation and reactor-distillation processes.

### 6.3 Recommendation

6.3.1 Other alternative pathways to produce sodium methoxide production such as crystallization should be further studied and compared with this work.

6.3.2 The cost including capital and operating cost for 3 processes (Reactor-distillation, Reactive distillation-distillation and Reactive distillation coupled with pervaporation) should be further investigated.



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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย  
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## Appendix A. Nomenclature of three processes.

**Table A.1** Nomenclature of conventional process.

Nomenclature	Description
CH <sub>3</sub> OH	Methanol solution
NAOH	Sodium hydroxide solution
NAOCH <sub>3</sub>	Sodium methoxide product
WASTE	Water content from separation
504	Sodium hydroxide after preheat
505	Methanol mixture
506	Distillate product
507	Methanol recovery
H-501	Heater of sodium hydroxide
M-501	Methanol Mixer
D-501	Reactive distillation column
D-502	Distillation column for separation of water from methanol

**Table A.2** Nomenclature of reactor-distillation process.

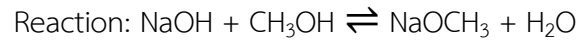
Nomenclature	Description
CH <sub>3</sub> OH	Methanol solution
NAOH	Sodium hydroxide solution
NAOCH <sub>3</sub>	Sodium methoxide product
VAPOR	Vapor product from reactor
LIQUID	Liquid product from reactor
WASTE	Water content from separation
S-505	Methanol mixture
S-506	Distillate product
S-507	Methanol recovery
M-501	Methanol Mixer
REQUIL	Reactor by REQUIL model in Aspen plus
DIST-1	Distillation for separation of NaOCH <sub>3</sub> production
DIST-2	Distillation for separation of water from methanol

**Table A.3** Nomenclature of reactive distillation couple with pervaporation process.

Nomenclature	Description
CH <sub>3</sub> OH	Methanol solution
NAOH	Sodium hydroxide solution
NAOCH <sub>3</sub>	Sodium methoxide product
WASTE	Water content from separation
504	Sodium hydroxide after preheat
505	Methanol mixture
506	Distillate product
507	Methanol after preheat
508	Methanol recovery
H-501	Heater of sodium hydroxide
H-502	Cooler of methanol-water mixture
M-501	Methanol Mixer
D-501	Reactive distillation column
PERVAP	Pervaporation of methanol-water mixture

## Appendix B. Calculation of performance of process.

### B.1 Calculation of equilibrium constant and equilibrium conversion.



Substitute:  $A+B \rightleftharpoons C+D$

$$C_{A0}=35.8858 \text{ mol/L}, C_{B0}=24.3154\text{mol/L}$$

$$C_{A0} = (F_{A0}/V) \cdot X_{Ae} \quad (1)$$

$$K_e = (C_c)/C_A C_B \quad (2)$$

$$K_e = (C_{A0} X_{Ae}) / (C_{A0}^2 (1 - X_{Ae}) (C_{B0} X_{Ae} C_{A0})) \quad (3)$$

$$K_e C_{A0} (1 - X_{Ae}) (\theta - X_{Ae}) = X_{Ae} \quad (4)$$

$$K_e C_{A0} [X_{Ae}^2 - X_{Ae} (1 + \theta) + \theta] - X_{Ae} = 0 \quad (5)$$

$$K_e C_{A0} X_{Ae}^2 - X_{Ae} [K_e C_{A0} (1 + \theta) - 1] + K_e C_{A0} \theta - X_{Ae} = 0 \quad (6)$$

**Table B.1** The equilibrium constant and equilibrium conversion at various temperature.

Temperature (°C)	$K_e$	$X_e$
0	7.6900	0.9885
25	4.4899	0.9799
30	4.0750	0.9777
40	3.3880	0.9729
50	2.8492	0.9674
60	2.4212	0.9610
70	2.0771	0.9537
75	1.9302	0.9496
100	1.3776	0.9242

## B.2 Calculation of water flux, separation factor and pervaporation separation index.

### B.2.1 Water flux (J)

$$J_i = Q_i \Delta p_i \text{ [kg} \cdot \text{m}^2 \text{h}^{-1}] \quad (7)$$

$$Q_i = Q_{i,\text{ref}} \exp \left[ \left( \frac{E_i}{R} \right) \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T_F} \right) \right] \quad (8)$$

$$\Delta p_i = x_i F_i \gamma_i p_{iF} - y_i p_p \quad (9)$$

$$J_i = Q_{i,\text{ref}} \exp \left[ \left( \frac{E_i}{R} \right) \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T_F} \right) \right] (x_i F_i \gamma_i p_{iF} - y_i p_p) \quad (10)$$

$$\ln a_w = \left( -\frac{\Delta H_f}{R} \right) \left( \frac{T_f - T}{T_f T} \right) + \left( \frac{\Delta C_f}{R} \right) \left[ \left( \frac{T_f - T}{T} \right) - \ln \left( \frac{T_f}{T} \right) \right] \quad (11)$$

$$\gamma_i = a_w x_i \quad (12)$$

### B.2.2 Separation factor ( $\alpha$ )

$$\alpha_{wm} = (y_w/y_m)/(x_w/x_m) \quad (13)$$

### B.2.3 Pervaporation separation index (PSI)

$$\text{PSI} = J \cdot (\alpha - 1) \text{ [kg} \cdot \text{m}^2 \text{h}^{-1}] \quad (14)$$



**Table B.2** The water flux, separation factor and pervaporation separation index at optimal condition.

Parameters	Values
Latent heat of water, $\Delta H_f$ (J mol/K)	6008
The change of specific heat of water, $\Delta C_f$ (J K/mol)	38.7
Gas constant, R (J/mol K)	8.314
Freezing point of water, T (K)	273.15
Freezing point of water-methanol mixture, $T_f$ (K)	170.15
Activity of water, $a_w$	0.372685451
Activity coefficient of water, $\gamma_i$	0.022361127
Partial pressure of water, $p_w$ (bar)	0.200070447
Water permeance ( $\text{kg/m}^2 \text{ h bar}$ )	10.39
Activation energy, E (kJ/kmol)	12.6
Reference temperature, $T_{ref}$ (K)	353.15
Pervaporation temperature, T (K)	338.15
Water flux ( $\text{kg/m}^2 \text{ h}$ )	0.002678099
The weight fraction of water in the permeate	0.998188380
The weight fraction of methanol in the permeate	0.001811609
The weight fraction of water in the feed	0.052266707
The weight fraction of methanol in the feed	0.947733293
Separation factor	9990.999889
PSI	26.75421017

### B.3 Calculation of energy consumption of three process.

**Table B.3** The energy consumption of reactor-distillation process.

Unit operation	Energy required (GJ/h)
Reactor	542.52
Dist-1	
- Condenser	0.54
- Reboiler	555.87
Dist-2	
- Condenser	566.07
- Reboiler	564.37
Energy consumption	2229.37

**Table B.4** The energy consumption of reactive distillation-distillation process.

Unit operation	Energy required (GJ/h)
H-501	0.063
D-501	
- Reboiler	7.07
D-502	
- Condenser	14.84
- Reboiler	13.16
Energy consumption	35.13

**Table B.5** The energy consumption of reactive distillation coupled with pervaporation process.

Unit operation	Energy required (GJ/h)
H-501	0.063
D-501	
- Reboiler	19.67
H-502	14.52
Pervaporation	
- P-501	0.002
- Vacuum pump	$1.6 \times 10^{-10}$
Energy consumption	34.25

The energy required of vacuum pump in pervaporation unit was calculated by equation from reference data [32].

$$W^* = (RT_1/\gamma - 1)[1 - (P_2/P_1)^{\gamma - 1/\gamma}] \quad (15)$$

Where R is gas constant (8.314 J/mol·K)

$T_1$  is feed temperature (65°C)

$\gamma$  is  $C_p/C_v$  of water (1.32)

$P_1$  is feed pressure (2 atm)

$P_2$  is permeate pressure (0.007 atm)

Thus,  $W^* = [(8.314 \times 338 / (1.32 - 1)) [1 - (0.007/2)^{(1.32 - 1)/1.32}]$

$W^* = 6552.20 \text{ J/mol}$

Therefore feed flow rate of water is 40.205 kmol/h.

So,  $W^* = 0.16 \text{ J/h.}$

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