CHARACTERIZATION OF ZEOLITE NaX LOADED WITH Na AND K AS CATALYSTS FOR TRANSESTERIFICATION OF JATROPHA SEED OIL

Saowanee Manadee

A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of Master of Science in Chemistry

Suranaree University of Technology

Academic year 2013

การพิสูจน์เอกลักษณ์ของซีโอไลต์โซเดียมเอ็กซ์ที่บรรจุด้วยโซเดียมและ
โพแทสเซียมสำหรับใช้เป็นตัวเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมัน
จากเมล็ดสบู่ดำ

นางสาวเสาวนีย์ มานะดี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี
มหาวิทยาลัยเทคโนโลยีสุรนารี
ปีการศึกษา 2556

CHARACTERIZATION OF ZEOLITE NaX LOADED WITH Na AND K AS CATALYSTS FOR TRANSESTERIFICATION OF JATROPHA SEED OIL

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master Degree.

Thesis Examining Committee

_____

(Asst. Prof. Dr. Sanchai Prayoonpokarach)

Chairperson

_____

(Assoc. Prof. Dr. Jatuporn Wittayakun)

Member (Thesis Advisor)

_____

(Asst. Prof. Dr. Kunwadee Rangsriwatananon)

Member

_____

(Asst. Prof. Dr. Thanaporn Manyum)

Member

_____   _____

(Prof. Dr. Sukit Limpijumnong)   (Assoc. Prof. Dr. Prapun Manyum)

Vice Rector for Academic Affairs   Dean of Institute of Science

and Innovation

เสาวนีย์ มานะดี : การพิสูจน์เอกลักษณ์ของซีโอไลต์โซเดียมเอ็กซ์ที่โหลดด้วยโซเดียมและ
โพแทสเซียมสำหรับใช้เป็นตัวเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันจากเมล็ดสบู่
ดำ (CHARACTERIZATION OF ZEOLITE NaX LOADED WITH Na AND K AS
CATALYSTS FOR TRANSESTERIFICATION OF JATROPHA SEED OIL)
อาจารย์ที่ปรึกษา : รองศาสตราจารย์ ดร.จตุพร วิทยาคุณ, 116 หน้า.

จุดประสงค์ของงานวิจัยนี้เพื่อศึกษาการผลิตไบโอดีเซลจากปฏิกิริยาทรานส์เอสเทอริฟิเค
ชันของน้ำมันเมล็ดสบู่ดำโดยใช้ตัวเร่งปฏิกิริยาวิวิธพันธ์ประกอบด้วย โซเดียม และโพแทสเซียม
บนซีโอไลต์เอ็กซ์ ที่เตรียมด้วยวิธีการเอิบชุ่ม โดยใช้สารละลายบัฟเฟอร์แอซีเตต หรือ สารละลาย
เกลือแอซีเตตของโซเดียม และโพแทสเซียม โดยแปรปริมาณของโซเดียมและโพแทสเซียมเพื่อเพิ่ม
ความเป็นเบสของตัวเร่งปฏิกิริยา จากนั้นวิเคราะห์สมบัติของซีโอไลต์เอ็กซ์และตัวเร่งปฏิกิริยา
ทั้งหมดด้วยเทคนิค การเลี้ยวเบนของรังสีเอ็กซ์เพื่อยืนยันโครงสร้างซีโอไลต์ เทคนิค FTIR เพื่อ
ยืนยันหมู่ฟังก์ชันของแอซีเตตในตัวเร่งปฏิกิริยาเทคนิค CO_2-TPD เพื่อวิเคราะห์ปริมาณและความ
แรงของเบสในตัวเร่งปฏิกิริยา เทคนิคการดูดซับ-การคายแก๊สไนโตรเจน เพื่อหาพื้นที่ผิวของตัวเร่ง
ปฏิกิริยา ผลจากการวิเคราะห์พบว่า การแคลไซน์ตัวเร่งปฏิกิริยาโซเดียมที่ 400 °C ไม่เพียงพอในการ
เปลี่ยนแอซีเตตไปเป็นสปีชีส์ที่ว่องไว ต้องแคลไซน์ที่ 500 °C และแอซีเตตจะเปลี่ยนเป็นคาร์บอเนต
ความเป็นเบสของตัวเร่งปฏิกิริยาเพิ่มตามปริมาณโซเดียมและโพแทสเซียม โดยการเติมไม่ได้ทำลาย
โครงสร้างของซีโอไลต์ แต่ทำให้ความเป็นผลึก พื้นที่ผิว และ ปริมาตรไมโครพอร์ลดลง และพบว่า
โพแทสเซียมและโซเดียมส่วนใหญ่อยู่ในโพรงของซีโอไลต์ โดยตัวเร่งปฏิกิริยาที่เตรียมจาก
สารละลายบัฟเฟอร์มีความเป็นเบสและพื้นที่ผิวมากกว่า

ในการทดสอบการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชัน ได้วิเคราะห์ประสิทธิภาพการเร่ง
ปฏิกิริยาในเบื้องต้นโดยนำผลิตภัณฑ์จากปฏิกิริยาไปวิเคราะห์ด้วยเทคนิคโครมาโทกราฟีผิวบาง ผล
การศึกษาพบว่าประสิทธิภาพการเร่งปฏิกิริยาเพิ่มตามปริมาณโซเดียมและโพแทสเซียม โดยตัวเร่ง
ปฏิกิริยาที่เตรียมจากสารละลายบัฟเฟอร์มีประสิทธิภาพมากกว่า และตัวเร่งปฏิกิริยาที่ดีที่สุด คือ
16K/NaX-B จากนั้น นำผลิตภัณฑ์ที่ได้จากตัวเร่งดังกล่าวไปวิเคราะห์หาองค์ประกอบ และปริมาณ
ผลได้ของไบโอดีเซลด้วยแก๊สโครมาโทกราฟ พบว่าให้ผลที่สอดคล้องกับผลจากการศึกษาใน
เบื้องต้น ผลได้ไบโอดีเซลจาก 16K/NaX-B เท่ากับ 95%

สาขาวิชาเคมี   ลายมือชื่อนักศึกษา_____

ปีการศึกษา 2556   ลายมือชื่ออาจารย์ที่ปรึกษา_____

SAOWANEE MANADEE : CHARACTERIZATION OF ZEOLITE NaX LOADED

WITH Na AND K AS CATALYSTS FOR TRANSESTERIFICATION OF

JATROPHA SEED OIL.

THESIS ADVISOR : ASSOC. PROF. JATUPORN WITTAYAKUN, Ph.D.

116 PP.

ZEOLITE NaX/ SODIUM/ POTASSIUM/ IMPREGNATION/ HETEROGENEOUS

BASIC CATALYST/ TRANSESTERIFICATION/ JATROPHA SEED OIL/

BIODIESEL

The aim of this thesis was to study biodiesel production by transesterification of Jatropha seed oil catalyzed by hetergenous catalysts containing sodium and potassium on zeolite NaX. The catalysts were prepared by impregnation with a solution of acetate buffer or acetate salt of sodium and potassium. The metal loading was varied to increase the catalyst basicity. The catalysts were characterized by X-ray diffraction to confirm the zeolite structure; FTIR to confirm functional groups; CO_2-TPD to determine the amount and strength of basic sites; and nitrogen adsorption-desorption to determine the catalyst surface area. Results from characterization indicated that calcination of sodium catalysts at 400 °C was not enough to completely convert the acetate to active species. To do so, they must be calcined at 500 °C and the acetate was mainly transformed to carbonate species. The basicity of the catalysts increased with amount of sodium and potassium. The loading did not destroy the zeolite structure, but resulted in a decrease in crystallinity, surface area and micropore volume. Potassium and sodium species mainly resided in the zeolite cavities. The

catalysts prepared from buffer solution had higher basicity and surface area than those from acetate solution.

   The catalyst efficiency in transesterification was determined preliminarily by analysis of the reaction product by thin layer chromatography. The catalytic activity increased with amount of sodium and potassium. Those prepared from buffer solution were superior and the best catalyst was 16K/NaX-B. After that, the reaction products were analyzed by gas chromatography for compositions and biodiesel yield. The results were consistent with the preliminary analysis results. The biodiesel yield from 16K/NaX-B was 95%.

School of Chemistry   Student's Signature_____

Academic Year 2013   Advisor's Signature_____

ACKNOWLEDGEMENTS

I would like to express my gratitude to everyone who gave me the possibility to complete this thesis:

My thesis advisor, Assoc. Prof. Dr. Jatuporn Wittayakun, for giving me the chance to study at Suranaree University of Technology, his kind support, stimulating suggestions and encouragement throughout my research and thesis writing;

Asst. Prof. Dr. Sanchai Prayoonpokarach, Asst. Prof. Dr. Kunwadee Rangsriwatananon and Asst. Prof. Dr. Thanaporn Manyum for their valuable comments and suggestions during my defense and on the thesis itself;

All of the lecturers in the School of Chemistry, Suranaree University of Technology for their good attitude and useful advice; the staff at the Center for Scientific and Technological Equipment for their assistance in use of instruments. Special thanks go to Dr. Nuttinee Supamathanon, Nattawut Osakoo, Onsulang Sophiphun, Wina Rongjapo, Narongrit Sosa, Chaiwat Kongmanklang and all of my friends at Suranaree University of Technology.

Saowanee Manadee

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

CONTENTS (Continued)

CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

CHAPTER I

INTRODUCTION

1.1 Background of biodiesel and its feedstock

The world energy consumption increases with the population growth and petroleum resources are being used up quickly. Therefore, alternative energy sources are needed. One of the most interesting sources is biodiesel which is alkyl ester that is biodegradable, renewable and non-toxic (Ragauskas et al., 2006; Demirbas, 2007; Moser, 2009). Combustion of biodiesel generates fewer emission gases, hydrocarbon particles and carcinogens than that of the conventional diesel derived from petroleum (Demirbas, 2007). Properties of biodiesel such as cetane number are similar to those of the petroleum diesel (Deng, Fang and Liu, 2011). Consequently, biodiesel can be used directly in diesel engines or blended at various proportions with the petroleum diesel (Deng, Fang, Liu and Yu, 2010).

Biodiesel can be synthesized by a reaction called transesterification from vegetable oils or animal fats and alcohols such as methanol and ethanol (Dalai, Issariyakul and Baroi, 2012). However, animal fats are viscous and can partially turn to solid wax at room temperature and require more pretreatment in biodiesel production (Feddern et al., 2011). Several researchers produced biodiesel from renewable resources, including oil from edible plants such as soybean, palm, rapeseed, and oil from non-edible plants such as Jatropha (Gui, Lee and Bhatia,

2008). However, using edible oils as feedstocks in biodiesel production may affect the balance of food supply.

For example, in 2008 there was a shortage in cooking oil from palm in Thailand. Therefore, biodiesel production from non-edible resources becomes more interesting to researchers worldwide (Bankovic-Ilic, Stamenkovic and Velikovic, 2012; Singh S. P. and Singh D., 2010; Borugadda and Goud, 2012).

Among non-edible resources, Jatropha seed oil has been widely used in biodiesel production (Gui et al., 2008; Deng et al., 2011) because of several reasons. Jatropha is a fast growing non-food plant which has toxic compound such as curcin in its seed kernel (Deng et al., 2011). It grows well in Thailand (Supamathanon, Wittayakun and Prayoonpokarach, 2011) and can be established as an oil source for biodiesel because a large amount of oil (more than 30 wt %) can be obtained from the seeds (Deng et al., 2011). In this work, Jatropha seed oil was employed in the synthesis of biodiesel.

Jatropha seed oil can be obtained by chemical extraction which is simple and can be done at room temperature. This method provides high oil yield and the solvent can be reused (Adriaana, 2006; Supamathanon et al., 2011). Organic solvents such as *n*-hexane, acetone, and petroleum ether were used for the extraction (Roberie et al., 2001; Achten et al, 2008; Supamathanon et al., 2011) and n-hexane was found to be the best solvent in terms of price and the obtained oil yields (Warra, 2012). Furthermore, the extracted oil has low moisture content which can be removed simply by addition of sodium sulfate (Na_2SO_4) (Supamathanon et al., 2011).

Jatropha seed oil composes of 90–98% of triglycerides and a small amount of mono- and diglycerides (Borugadda and Goud, 2012). Fatty acid compositions of

triglycerides are unsaturated fatty acids with at least one double bond within the fatty acid chain, for example, oleic acid (C18:1) and linoleic acid (C18:2). The general structure of a triglyceride is shown in Figure 1.1. Triglyceride is tri-ester which is a derivative of fatty acid from a reaction of three fatty acid molecules and a glycerol molecule (Singh and Singh, 2010). Because glycerides are derivatives of saturated and unsaturated fatty acids, the components of oils are reported in term of fatty acids. The saturated fatty acids include palmitic acid (C16:0), heptadecanoic acid (C17:0), stearic acid (C18:0), arachic acid (C20:0); and unsaturated fatty acids include palmitoleic acid (C16:1 Δ7), oleic acid (C18:1 Δ9), linoleic acid (C18:2 Δ9, 12), and linolenic acid (C18:3 Δ9, 12, 15) (Supamathanon et al., 2011). The components of Jatropha seed oil vary with geological locations (Table 1.1). The major fatty acid components of Jatropha seed oil from Thailand are C16:0, C18:0, and C18:2 Δ9, 12.

Example for R group:

Figure 1.1 Structure of triglyceride (Berg et al., 2002).

Table 1.1 Components of Jatropha seed oil from various locations in term of fatty acids.

Location	Fatty acid (wt%)								Reference
	C16:0	C16:1	C17:0	C18:0	C18:1	C18:2	C18:3	C20:0	
Thailand	15.2	0.7	0.1	6.8	44.6	32.2	0.2	0.2	Supamatha non et al., 2011
India	16.0	1.0	NR	6.0	43.5	33.0	0.8	NR	Verma and Gaur, 2009
Indonesia	14.1-15.3	0-1.3	NR	3.7-9.8	34.3-45.8	29.0-44.2	0-0.3	0-0.3	Berchmans and Hirata, 2008
Malaysia	14.2	0.7	0.1	7.0	44.7	32.8	0.2	0.2	Akbar, Yaakob, Kamarudin, Ismail and Salimon, 2009
China	12.5	2.1	NR	6.4	32.0	42.3	NR	NR	Xue et al., 2009
Congo-Brazzaville	15.6	1.0	-	5.8	40.1	37.6	-	-	Nzikou et al., 2009
Paraguay	13.2	N/R	NR	3.0	40.2	42.6	NR	NR	Montes, Aliciardi, Chavez, Guzman and Calandri, 2011

NR= Not reported

1.2   Synthesis of biodiesel by transesterification

A reaction which is widely used to produce biodiesel is transesterification or alcoholysis (see Figure 1.2). It is a reaction between triglyceride and alcohol in the presence of a catalyst to produce alkyl esters (biodiesel) and glycerol (Meher, Sagar and Naik, 2006).
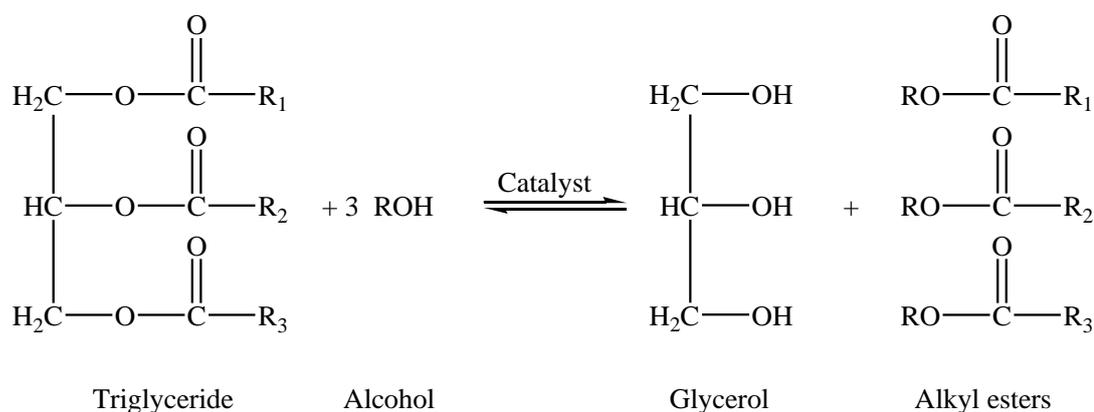
Figure 1.2 Transesterification for biodiesel production.

Methanol is the most widely used alcohol in transesterification because it is a small and polar molecule which can react rapidly with triglyceride to give high biodiesel yield (Deng et al., 2011, Lee D. –W., Park and Lee K. –Y., 2009). Because transesterification is a reversible reaction, excess methanol is generally used to shift the equilibrium to methyl esters (Vyas, Verma and Subrahmanyam, 2011). In addition, the transesterification consists of three reversible steps and methyl ester is produced in each step (see Figure 1.3). First, the triglyceride reacts with methanol to produce diglyceride. Then, the diglyceride reacts with methanol to produce monoglyceride which finally reacts with methanol to produce glycerol (Tapanes, Aranda, Carneiro and Antunes, 2008). The conversion of more than 90% is usually obtained within 2 h, depending on the catalysts (Lee et al., 2009, Demirbas, 2009). Catalysts for the reaction can be either homogeneous (solution of acid or/base) or heterogeneous (solid base) (Guerrero F. C. A., Guerrero R. A. and Sierra, 2011).

Triglyceride   +   MeOH $\underset{\longleftarrow}{\overset{\text{Catalyst}}{\longrightarrow}}$ Methyl ester   +   Diglyceride

Diglyceride   +   MeOH $\underset{\longleftarrow}{\overset{\text{Catalyst}}{\longrightarrow}}$ Methyl ester   +   Monoglyceride

Monoglyceride   +   MeOH $\underset{\longleftarrow}{\overset{\text{Catalyst}}{\longrightarrow}}$ Methyl ester   +   Glycerol
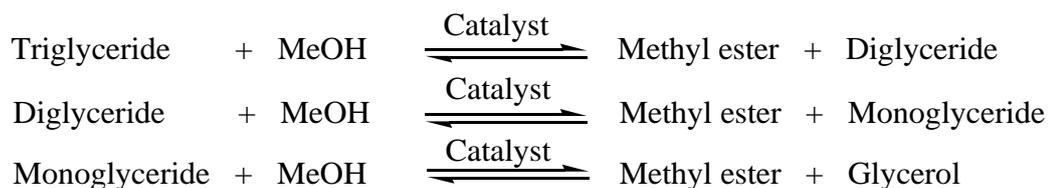
Figure 1.3 Steps in transesterification (Tapanes et al., 2008).

1.3   Catalysts for transesterification

There are two types of catalysts for transesterification based on the reaction phase, namely, homogeneous and heterogeneous when the catalyst phase is similar or different from that of the reactants, respectively. In general, heterogeneous catalysts are solid materials which can be used in the reaction of liquid or gas (Hagen, 1998). Examples of each type for transesterification are given below.

1.3.1   Homogeneous catalysts

Homogeneous catalysts that have been employed in transesterification are acid and base. The acid catalysts include sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) (Hanh, Dong, Okitsu, Maeda and Nishimura, 2007). If the oil source has high free fatty acid (FFA) content, acid-catalyzed transesterification is generally favored because the FFA is also converted to biodiesel. However, the most common catalysts are base, including sodium hydroxide (NaOH) and potassium hydroxide (KOH). They give a fast reaction rate and high biodiesel yield at low temperature (60 – 75 °C).

Although homogeneous catalysts show a great performance in transesterification, they produce soap as a by-product from the reaction of the FFA. Furthermore, separation of catalysts from the reaction mixture is difficult and a large

amount of wastewater is generated to wash out the catalysts from the products (Guo, Peng, Dai and Xiu, 2010). In addition, it is difficult to recover the homogeneous catalyst (Andrade, Perez, Sebastian and Eapen, 2011).

1.3.2 Heterogeneous catalysts

Heterogeneous catalysts for the transesterification of Jatropha seed oil that have been developed include basic zeolites, alkaline earth metal oxides and hydrotalcites (Borugadda and Goud, 2012). An advantage of heterogeneous catalysts is that they can be separated easily from the products and can be used with a low quality feedstock, i.e. oil containing FFA and water (Guo et al., 2010). The use of heterogeneous base catalysts does not generate soap through FFA neutralization and triglyceride saponification (Romero, Martinez and Natividad, 2011). In addition, heterogeneous catalysts could be used efficiently in a continuous process due to reusability of the catalyst. The solid base catalysts are easily regenerated and have a less corrosive nature leading to safer, cheaper and more environmentally friendly operations (Borugadda and Goud, 2012).

Agarwal, Chauhan, Chaurasia and Singh (2012) compared homogeneous KOH and heterogeneous KOH/alumina as catalysts for biodiesel production from waste cooking oil. The homogeneous catalyst gave biodiesel yield of 98.2% in the optimum condition (temperature 70 °C, reaction time of 1 h, and methanol to oil molar ratio 6:1). In this process warm water was used to wash the catalyst out from the product. The heterogeneous catalyst gave biodiesel yield of 96.8% in different condition (temperature 70 °C, reaction time of 2 h, and methanol to oil molar ratio 9:1). The catalyst was separated easily and reused for 3 cycles. Due to high biodiesel yield obtained, simple catalyst separation and reusability,

heterogeneous base catalysts have been employed for catalyzing the reaction (Demirbas, 2009).

Several researchers studied transesterification using supported base catalysts. Zeolites are widely used as supports because they have a porous structure and high surface area that can improve dispersion of active metals. In terms of basicity, zeolite X has a higher concentration of super-basic sites than other zeolites (Ramos, Casas, Rodriguez, Romero and Perez, 2008). Zeolite NaX could be synthesized from rice husk silica (RHS) as a silica source and used as a catalyst support. The basicity of zeolite NaX can be further increased by impregnation with cations of high electropositive metals like K and Na (Jothiramalingam and Wang, 2009). With different metal loading, the catalyst basic strength and the number of basic sites were increased from that of the NaX and the catalytic activity for biodiesel production was increased.

Recently, zeolite NaY was used as a support for potassium catalysts for biodiesel production from Jatropha seed oil. The solution of potassium precursors including acetate salt (CH_3COOK) and actetate buffer (CH_3COOK/CH_3COOH) are used to prevent collapses of the zeolite structure (Supamathanon et al., 2011). The 12 wt% of K loading gave a biodiesel yield of 73.4%. The result showed a high oil conversion with high biodiesel yield with a short reaction time (3 h). The catalyst performance could be improved by changing the type of zeolite to a more basic one and by changing the type of metal. In this work, zeolite NaX, which is more basic than NaY, was used as a support for potassium. In addition, sodium precursors including acetate salt (CH_3COONa) and acetate buffer (CH_3COONa/CH_3COOH) were used as catalyst precursors.

1.4   Research objective

The objectives of this thesis is to understand properties of sodium and potassium catalysts supported on zeolite NaX and the correlation to their catalytic performance in transesterification of Jatropha seed oil.

1.5   Scope and limitations of the study

RHS was used as a silica source in the synthesis of zeolite NaX. The procedure was taken from the literature (Khemthong, Wittayakun and Prayoonpokarach, 2007). The NaX-supported potassium and sodium (K/NaX and Na/NaX) were prepared by the impregnation method using a solution of acetate salt and acetate buffer of sodium and potassium with a method from the literature (Li and Rudolph, 2008; Ramos et al., 2008; Supamathanon et al., 2011). The zeolite NaX and the catalysts were characterized by x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), N_2 adsorption-desorption and temperature programmed desorption of carbon dioxide (CO_2-TPD). Jatropha seed oil was extracted by hexane from the seeds with a method similar to the literature (Supamathanon et al., 2011). The conversion of Jatropha seed oil in transesterification on each catalyst was estimated by thin layer chromatography (TLC) and the compositions and yield of biodiesel were determined by gas chromatography with a flame ionization detector (GC-FID) (Supamathanon et al., 2011).

1.6 References

Achten, W. M. J., Verchot, L., Franken, Y., Mathijs, E., Singhc, V. P., Aerts, R. and Muys, B. (2008). Jatropha bio-diesel production and use. **Biomass and Bioenergy**. 32: 1063-1084.

Adriaana, T. (2006). **Suitability of solvent extraction for jatropha curcas**. [online]. Available: http://www.fact-foundation.com/en/FACT/Publications.

Agarwal, M., Chauhan, G., Chaurasia, S. P. and Singh, K. (2012). Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production. **Journal of the Taiwan Institute of Chemical Engineers**. 43: 89-94.

Akbar, E., Yaakob, Z., Kamarudin, S. K. Ismail, M. and Salimon, J. (2009). Characteristic and composition of *Jatropha curcas* oil seed from Malaysia and its potential as biodiesel feedstock feedstock. **European Journal of Scientific Research**. 29: 396-403.

Andrade, J. E., Perez, A., Sebastian, P. J. and Eapen, D. (2011). A review of biodiesel production processes. **Biomass and Bioenergy**. 35: 1008-1020.

Bankovic-Ilic, I. B., Stamenkovic, O. S. and Veljkovic, V. B. (2012). Biodiesel production from non-edible plant oils. **Renewable and Sustainable Energy Reviews**. 16: 3621-3647.

Berchmans, H. J. and Hirata, S. (2008). Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. **Bioresource Technology**. 99: 1716-1721.

Berg, J. M., Tymoczko, J. L. and Stryer, L. (2002). **Biochemistry** (5th ed., pp. 345-370). New York: W. H. Freeman and Company.

Borugadda, V. B. and Goud, V. V. (2012). Biodiesel production from renewable feedstocks: Status and opportunities. **Renewable and Sustainable Energy Reviews**. 16: 4763-4784.

Dalai, A. K., Issariyakul, T. and Baroi, C. (2012). Biodiesel production using homogeneous and heterogeneous catalysts: A Review. Guczi, L. and Erdohelyi, A. (eds.). **Catalysis for alternative energy generation** (pp 237-262). New York: Springer Science Business Media.

Demirbas, A. (2007). Importance of biodiesel as transportation fuel. **Energy Policy**. 35: 4661-4670.

Demirbas, A. (2009). Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification. **Energy Conversion and Management**. 50: 923-927.

Deng, X., Fang, Z. and Liu, Y. (2010). Ultrasonic transesterification of *Jatropha curcas* L. oil to biodiesel by a two-step process. **Energy Conversion and Management**. 51: 2802-2807.

Deng, X., Fang, Z., Liu, Y. and Yu, C. (2011). Production of biodiesel from Jatropha oil catalyzed by nanosized solid basic catalyst. **Energy**. 36: 777-784.

Feddern, V., Junior, A. C., de Pra, M. C., de Abreu, P. G., dos Santos Filho, J. I., Higarashi, M. M., Sulenta, M. and Coldebella, A. (2011). Animal fat wastes for biodiesel production. Stoytcheva, M., and Montero, G. (eds.). **Biodiesel – feedstocks and processing technologies** (pp 23-44). Croatia: InTech.

Guerrero F., C. A., Guerrero R., A. and Sierra, F. E. (2011). Biodiesel Production from Waste Cooking Oil. Stoytcheva, M., and Montero, G. (eds.). **Biodiesel – feedstocks and processing technologies** (pp 45-70). Croatia: InTech.

Gui, M. M., Lee, K. T. and Bhatia, S. (2008). Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. **Energy**. 33: 1646-1653.

Guo, F., Peng, Z. G., Dai, J. Y. and Xiu, Z. L. (2010). Calcined sodium silicate as solid base catalyst for biodiesel production. **Fuel Processing Technology**. 91: 322-328.

Hagen, J. (1998). **Industrial Catalysis**. 2nd ed (pp. 15-30). Wijngaarden, R. I., Westerterp, K. R. and Kronberg, A. (eds.). Weinheim, Germany: betz-druck GmbH, Darmstadt.

Hanh, H. D., Dong, N. T., Okitsu, K., Maeda, Y. and Nishimura, R. (2007). Effects of molar ratio, catalyst concentration and temperature on transesterification of triolein with methanol under ultrasonic irradiation. **Journal of the Japan Petroleum Institute**. 50: 195-199.

Jothiramalingam, R. and Wang, M. K. (2009). Review of recent developments in solid acid, base, and enzyme catalysts (heterogeneous) for biodiesel production via transesterification. **Industrial and Engineering Chemistry Research**. 48: 6162-6172.

Khemthong, P., Wittayakun, J. and Prayoonpokarach, S. (2007). Synthesis and characterization of zeolite LSX from rice husk silica. **Suranaree Journal of Science and Technology**. 14: 367-379.

Lee, D. -W., Park, Y. -M. and Lee, K. -Y. (2009). Heterogeneous base catalysts for transesterification in biodiesel synthesis. **Catalysis Surveys from Asia**. 13: 63-77.

Li, E. and Rudolph, V. (2008). Transesterification of vegetable oil to biodiesel over MgO- functionalized mesoporous catalysts. **Energy and Fuels**. 22: 145-149.

Meher, L. C., Sagar, D. V. and Naik, S. N. (2006). Technical aspects of biodiesel production by transesterification-a review. **Renewable and Sustainable Energy Reviews**. 10: 248-268.

Montes, J. M., Aliciardi, R. M., Chavez, V. J., Guzman, C. and Calandri, E. (2011). Characterization of *Jatropha curcus* L. seed and its oil, from Argentina and Paraguay. **The Journal of the Argentine Chemical Society**. 98: 1-9.

Moser, B. R. (2009). Biodiesel production, properties, and feedstocks. **In Vitro Cellular and Developmental Biology**. 45: 229-266.

Nzikou, J. M., Matos, L., Mbemba, F., Ndangui, C. B., Pambou-Tobi, N. P. G., Kimbonguila, A., Silou, Th., Linder, M. and Desobry, S. (2009). Characteristics and composition of *Jatropha curcas* oils, variety Congo-Brazzaville. **Journal of Applied Sciences, Engineering and Technology**. 1: 154-159.

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick Jr., W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., Mielenz, J. R., Murphy, R., Templer, R. and Tschaplinski, T. (2006) The path forward for biofuels and biomaterials. **Science**. 311: 484-489.

Ramos, M. J., Casas, A., Rodriguez, L., Romero, R. and Perez, A. (2008). Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. **Applied Catalysis A: General**. 346: 79-85.

Roberie, T. G., Hildebrandt, D., Creighton, J. and Gilson, J. -P. (2001). Preparation of zeolite catalysts. Guisnet, M. and Golson, J. -P. (eds.). **Zeolites for Clean Technology** (pp. 57-63). Clearance center, USA: Imperial college press.

Romero, R., Martinez, S. L. and Natividad, R. (2011). Biodiesel production by using heterogeneous catalysts. Manzanera, M. (ed). **Alternative Fuel** (pp. 1-19). Toluca Estado, Mexico.

Singh, S. P. and Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. **Renewable and Sustainable Energy Reviews**. 14: 200-216.

Supamathanon, N., Wittayakun, J. and Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. **Journal of Industrial and Engineering Chemistry**. 17: 182-185.

Tapanes, N. C. O., Aranda, D. A. G., Carneiro, J. W. M. and Antunes, O. A. C. (2008). Transesterification of Jatropha curcas oil glycerides: Theoretical and experimental studies of biodiesel reaction. **Fuel**. 87: 2286-2295.

Verma, K. C. and Gaur, A. K. (2009). *Jatropha curcas* L.: Substitute for conventional energy. **World Journal of Agricultural Sciences**. 5: 552-556.

Vyas, A. P., Verma, J. L. and Subrahmanyam, N. (2011). Effects of molar ratio, alkali catalyst concentration and temperature on transesterification of Jatropha oil with methanol under ultrasonic irradiation. **Advances in Chemical Engineering and Science**. 1: 45-50.

Warra, A. A. (2012). Cosmetic potentials of physic nut (*Jatropha curcas* Linn.) seed oil: A review. **American Journal of Scientific and Industrial Research**. 3: 358-366.

Xue, W., Zhou, Y. -C., Song, B. -A., Shi, X., Wang, J., Yin, S. -T., Hu, D. -Y., Jin, L. -H. and Yang, S. (2009). Synthesis of biodiesel from *Jatropha curcas* L. seed oil using artificial zeolites loaded with CH_3COOK as a heterogeneous catalyst. **Natural Science**. 1: 55-62.
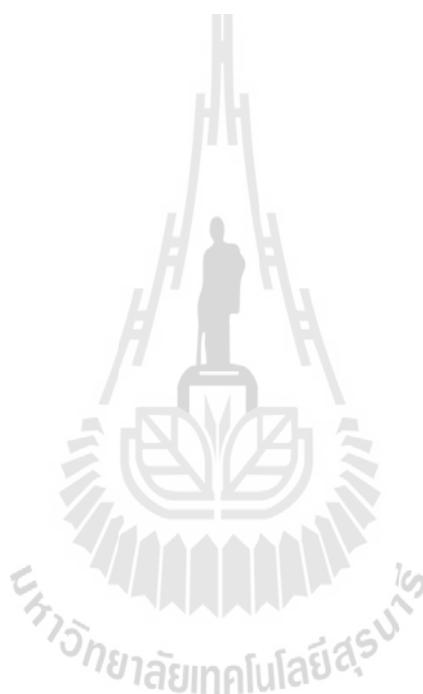
CHAPTER II

LITERATURE REVIEW

2.1   Supported catalysts for transesterification reaction

Desired properties of catalyst support materials in transesterification include large surface area, proper porosity and stable structure (Refaat, 2011). One popular type of materials are zeolites, which are microporous aluminosilicate minerals containing SiO_4- and AlO_4- units that share oxygen atoms (Jacobs, 1977). Zeolites can be classified as natural and synthetic. Zeolites have been used as catalyst supports because they have porous structure and high surface area that allow good dispersion of active metal more than other materials (Wang, Dang, Chen and Lee, 2012). An example is a comparison between supported KOH on zeolite NaY and alumina. From N_2 adsorption-desorption technique, the surface area of zeolite NaY was 738 m^2/g, whereas that of alumina was 208 m^2/g (Noiroj, Intarapong, Luengnaruemitchai and Jai-In, 2009). When the 25 wt% KOH/Al_2O_3 and 10 wt% KOH/NaY were employed as catalysts for transesterification of palm oil with methanol, they gave the highest biodiesel yield. Based on the K weight, KOH/NaY was more catalyticly active. Moreover, potassium oxide bound to NaY more strongly than to alumina. As a result, potassium on NaY was not leached out as much as that on alumina. The leached active species could act as a homogeneous catalyst which is difficult to separate from the product mixture.

A general chemical formula of zeolites is $M_{x/n}[(AlO_2)x(SiO_2)y] \bullet zH_2O$ and the Si/Al ratio can be varied. When Al atoms are present in the zeolite framework,

negative charges are generated. Then, cations are required to neutralize the negative charges. The cations reside in the zeolite cavities and can be exchanged with other cation (Auerbach, Carrado and Dutta, 2003). The cations can be moved from one site to the other upon heat treatment or adsorption of certain molecules such as water and organic compounds. When these cations are calcined, they form metal oxides in cavities of zeolite and can serve as strong basic sites for catalysis. (Barthomeuf, 1996).

Generally, basic properties of zeolites can be change when they are loaded with alkali cations. The precence of the cations can enhance an electron density of bridging oxygen atoms in zeolite framework which are basic sites. Moreover, an increase in of Al contents or ionic radius of the cation can increase an average oxygen charge or basicity on catalysts (Barthomeuf, 1991). Xue et al. (2009) studied transesterification of Jatropha seed oil and methanol using artificial zeolites (Kalsilite) loaded with CH_3COOK as a precursor. Catalyst characterization revealed that K_2O, surface hydroxyl groups and Al-O-K (or Si-O-K) groups were the main basic sites. The basicity depended on metal loading and the catalytic activity increased with the basicity. The methyl ester content in the biodiesel product exceeded 91% after 4 h of reaction time at reflux temperature in the presence of 2% solid catalyst and no water washing process was needed during workup. They found that the highest biodiesel yield but the use of K loading (19 wt%) leading to homogeneous phase and short reaction time.

To use zeolite either as a catalyst or support for transesterification, its basicity zeolite can be further improved by loading cations with various methods such as ion exchange and impregnation. Ramos et al. (2008) compared the methods of Na loading

on NaX by ion exchange and impregnation. They found that the activity of the catalyst prepared by impregnation was better than that by ion exchange because high loading could be produced. The occlusion of alkali metal oxide clusters in zeolite cages through the decomposition of impregnated alkali metal salts resulted in an increase in the basicity of these catalysts (Chopade, Kulkarni K. S., Kulkarni A. D. and Topare, 2012). Table 2.1 shows more examples of metal supported on zeolites prepared by impregnation for transesterification.

Table 2.1 Examples of metals loaded on supported catalysts for transesterification.

Catalysts	Precursor	Oil types	Conditions/ time	Biodiesel yield (%)	References
28 wt% K/natural zeolite (MOR)	KOH	Palm oil	60 °C, 2h	95.1	Kusuma, Hadinoto, Ayucitra, Soetaredjo and Ismadji, 2012
15 wt% K/NaY	KOH	Palm oil	60 °C, 7 h	92.2	Intarapong et al., 2011
12 wt% K/NaY	CH_3COOK/ CH_3COOH	Jatropha seed oil	65 °C, 3 h	73.4	Supamathanon et al., 2011
Na/MOR (mordenite)				12.7	
Na/BEA (beta)	CH_3COONa	Sunflower oil	60 °C, 7 h	65.4	Ramos et al., 2008
4.2 wt% Na/NaX				95.1	

Kusuma et al. (2012) loaded KOH on natural zeolite (major component: MOR) with various concentrations of 7, 14, 21, and 28 wt% and used as catalysts for transesterification. In this study, the 21 wt% of K gave the highest biodiesel yield and a short reaction time. The catalyst could be used three cycles and only 3.40% loss of active site upon leaching from zeolite. The KOH/natural zeolite was the best catalyst

but high K loading could change the zeolite structure. The biodiesel yield decreased because the K species in zeolite were leached out and deactivated in the reaction.

Intarapong et al. (2011) investigated KOH loaded on NaY catalyst in transesterification reaction of palm oil with methanol. They found that basicity and agglomeration increased with K loading. The 15 wt% K/NaY which had the highest basicity gave the best catalytic activity and the highest biodiesel yield. However, the increasing of K contents can destroy the zeolite NaY structures and the K species could be leached out. After the transesterification the catalyst cannot be reused. To solve this problem, a catalyst preparation was proposed in this work by use of buffer solution to prevent collapses of the zeolite support.

Supamathanon et al. (2011) studied transesterification of Jatropha seed oil and methanol using K/NaY as a catalyst prepared from a CH_3COOK/CH_3COOH mixture. Such precursor did not cause collapse of the zeolite structure and make it possible for the catalysts to be reused. The result showed a high oil conversion with high biodiesel yield with a short reaction time.

Ramos et al. (2008) used Na loaded on MOR, BEA, and NaX for transesterification of sunflower oil with methanol. The Na/NaX shows the highest biodiesel yield. The greater activity of Na supported on zeolite NaX compared to other zeolites could be explained by the presence of a higher concentration of super-basic sites on zeolite NaX (Na_2O in supercage of zeolite X) which were not present in the other. Occlusion of metals clusters in the zeolite cavities enhances the basicity by increasing the negative charge of the framework oxygen atoms (Martinez et al., 2011). Thus, in this work zeolite NaX was used as a support.

2.2   Metals supported on zeolite NaX for transesterification

Zeolites X and Y have the same faujasite (FAU) structural framework but they are markedly different in composition and properties. The typical Si/Al ratio of zeolite X is in the range of 1-2 (Xie, Huang and Li, 2007) while Si/Al ratio of zeolite Y is in the range of 2-4 (Marchetti, Miguel and Errazu, 2007). Because zeolite X is more basic than zeolite Y, it is expected to be more active and provide a higher biodiesel yield. An example of zeolite X has a chemical formula $Na_{73}K_{22}Al_{95}Si_{97}O_{384}$ • $212H_2O$ (Kuhl, 2001). Framework of zeolite NaX containing double 6 rings linked through sodalite cages that generate pore diameter about 7.4 Å in supercage. It has high negative framework charge, high exchangeable cation, and high basicity (Ramos et al., 2008).

From the literature review above, the basicity and basic strength of zeolite NaX can be improved with loading alkali metal into the zeolite cavities. Table 2.2 shows examples of catalysts prepared by loading potassium and sodium on zeolite NaX.

Suppes et al. (2004) prepared potassium-exchanged NaX by using potassium acetate as a precursor. The result showed a low biodiesel yield with a long reaction time. Xie et al. (2007) studied transesterification of soybean oil and methanol with zeolite NaX loaded by KOH as a catalyst and the best catalyst was from the 10% loaded KOH. After KOH loading was increased, the basic strength of zeolite NaX increased from < 9.3 to 15.0-18.4. They reported that the KOH modification in the preparation of KOH/NaX did not destroy the zeolite pore structure. However, the zeolite framework collapsed by loading a high concentration of KOH leading to

agglomeration of active KOH species. This can decrease active basic sites on the zeolite and impair the conversion.

Pena et al. (2012) studied transesterification of sunflower oil with methanol by using KNO_3/NaX. The results demonstrated that biodiesel yield was highly influenced by basicity and the catalyst with the highest catalytic activity was prepared from 35 wt% KNO_3. Although the catalyst gave the high biodiesel yield, it used a long reaction time (6 h), high amount of catalyst (10 g) and high K loading (14 wt%) on zeolite.

From the literatures above, potassium-based catalysts give better biodiesel yields than sodium-based ones but there are examples of active Na catalysts (Borugadda and Goud, 2012). Zeolite NaX can be loaded by Na ion to increase basicity and high biodiesel yield. Suppes et al. (2004) used NaO_x/NaX as a catalyst obtained from sodium acetate or sodium azide precursor. The NaO_x/NaX from both precursors gave biodiesel yield more than 80% because the occluded sodium oxide species increased the base strength and number of basic sites compared to the parent NaX.

Table 2.2 Example of metals loaded on zeolite NaX and used as a catalyst for transesterification.

Catalysts	Precursor	Oil type	Condition/ time	Biodiesel yield (%)	References
K/NaX	CH_3COOK	Soybean oil	60 °C, 24 h	10.3	Suppes et al., 2004
7 wt% K/NaX	KOH	Soybean oil	120 °C, 8 h	85.6	Xie et al., 2007
14wt% K/NaX	KNO_3	Sunflower oil	60 °C, 6 h	98.2	Pena et al., 2012
NaO_x/NaX	NaN_3, CH_3COONa	Soybean oil	60 °C, 24 h	>80.0	Suppes et al., 2004
4.2 wt% Na/NaX	CH_3COONa	Sunflower oil	60 °C, 7 h	95.1	Ramos et al., 2008

Ramos et al. (2008) used Na loaded on NaX for transesterification of sunflower oil with methanol. The Na/NaX showed the highest biodiesel yield due to its strong basicity (Na_2O in supercage of zeolite X). These catalysts gave high biodiesel yield but used long reaction time.

From literatures above K and Na are interesting for transesterification because they have high basicity to give high biodiesel yield and conversion. In this work, zeolite NaX was used as a support for K and Na shortens the reaction time. The precursor of K and Na are buffer and acetate solution of K and Na used to protect zeolite structure.

2.3   References

Auerbach, S. M., Carrado, K. A. and Dutta, P. K. (eds.). (2003). **The Physical Chemistry of Materials** (pp. 1-20). Marcel Dekker, New York: CRC press.

Barthomeuf, D. (1991). Acidity and basicity in zeolites. **Studies in Surface Science and Catalysis**. 65: 157-169.

Barthomeuf, D. (1996). Basic zeolites: Characterization and uses in adsorption and catalysis. **Catalysis Reviews: Science and Engineering**. 38: 521-612.

Borugadda, V. B. and Goud, V. V. (2012). Biodiesel production from renewable feedstocks: Status and opportunities. **Renewable and Sustainable Energy Reviews**. 16: 4763-4784.

Chopade, S. G., Kulkarni, K. S., Kulkarni, A. D. and Topare, N. S. (2012). Solid heterogeneous catalysts for production of biodiesel from trans-esterification of triglycerides with methanol: A review. **Acta Chimica and Pharmaceutica Indica**. 2: 8-12.

Intarapong, P., Luengnaruemitchai, A. and Jai-In, S. (2011). Transesterification of palm oil over KOH/NaY zeolite in a packed-bed reactor. **International Journal of Renewable Energy Research**. 1: 271-280.

Jacobs, P. A. (1977). **In: Carboniogenic activity of zeolites** (pp. 19-26). Elsevier, Amsterdam.

Kuhl, G. (2001). Low Silica Type X. Robson, H. (ed.). **In: Verified syntheses of zeolitic materials** (pp. 153-154). 2nd ed. Amterdam, Netherland: Elsevier Science B. V.

Kusuma, R. I., Hadinoto, J. P., Ayucitra, A., Soetaredjo, F. E. and Ismadji, S. (2012). Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil. **Applied Clay Science**. 74: 121-126.

Marchetti, J. M., Miguel, V. U. and Errazu, A. F. (2007). Possible methods for biodiesel production. **Renewable and Sustainable Energy Reviews**. 11: 1300-1311.

Martinez, S. L., Romero, R., Lopez, J. C., Romero, A., Mendieta, V. S. and Natividad, R. (2011). Preparation and characterization of CaO nanoparticles/NaX zeolite catalysts for the transesterification of sunflower oil. **Industrial and Engineering Chemistry Research**. 50: 2665-2670.

Noiroj, K., Intarapong, P., Luengnaruemitchai, A. and Jai-In, S. (2009). A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. **Renewable Energy**. 34: 1145-1150.

Pena, R., Romero, R., Martinez, S. L., Natividad, R. and Ramirez, A. (2012). Characterization of KNO_3/NaX catalyst for sunflower oil transesterification. **Fuel**. 110: 63-69.

Ramos, M. J., Casas, A., Rodriguez, L., Romero, R. and Perez, A. (2008). Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. **Applied Catalysis A: General**. 346: 79-85.

Refaat, A. A. (2011). Biodiesel production using solid metal oxide catalysts. **International Journal of Environmental Science and Technology**. 8: 203-221.

Supamathanon, N., Wittayakun, J. and Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. **Journal of Industrial and Engineering Chemistry**. 17: 182-185.

Suppes, G. J., Dasari, M. A., Doskocil, E. J., Mankidy, P. J. and Goff, M. J. (2004). Transesterification of soybean oil with zeolite and metal catalysts. **Applied Catalysis A: General**. 257: 213-223.

Wang, Y. -Y., Dang, T.H., Chen, B. -H. and Lee, D. -J. (2012). Transesterification of triolein to biodiesel using sodium-loaded catalysts prepared from zeolites. **Industrial and Engineering Chemistry Research**. 51: 9959-9965.

Xie, W., Huang, X. and Li, H. (2007). Soybean oil methyl ester preparation using NaX zeolite loaded with KOH as a heterogeneous catalyst. **Bioresource Technology**. 98: 936-939.

Xue, W., Zhou, Y. -C., Song, B. -A., Shi, X., Wang, J., Yin, S. -T., Hu, D. -Y., Jin, L. -H. and Yang, S. (2009). Synthesis of biodiesel from *Jatropha curcas* L. seed oil using artificial zeolites loaded with CH$_3$COOK as a heterogeneous catalyst. **Natural Science**. 1: 55-62.

CHAPTER III

CHARACTERIZATION AND CATALYTIC TESTING OF

CATALYSTS CALCINED AT 400 °C

Abstract

The goal of this chapter was to prepare and characterize catalysts consisting of sodium supported on zeolite NaX (xNa/NaX-A and xNa/NaX-B with x = 4, 8, 12, and 16 wt%) and test their, use in transesterification of Jatropha seed oil to produce biodiesel. The catalysts were prepared by impregnation with sodium acetate (A) and sodium acetate buffer (B) solution, respectively and calcined at 400 °C for 3 h. From analysis by XRD, the structure of NaX was not destroyed but a peak corresponding to sodium acetate was observed on the samples with 12 and 16 wt% sodium loading. Although, further analysis by FTIR could not confirmed the functional groups of acetate, it was concluded that the calcination temperature was not high enough to decompose the acetate completely. In the catalytic testing, the biodiesel yield increased with sodium loading, namely, with the increase of basicity. The highest catalytic activity was achieved from 16Na/NaX-A. The reaction was complete in 2 h and the biodiesel yield was 86.6 wt%. Because some acetate still remained after calcination, it could be leached out and behaved as a homogenous catalyst along with the heterogeneous sodium oxide on the zeolite.

3.1   Introduction

Zeolites are widely used as supports because they have a porous structure and high surface area that can improve dispersion of active catalyst phase. In term of basicity, zeolite X has more concentration of super-basic sites than other zeolites (Ramos et al., 2008). Zeolite NaX could be synthesized by using rice husk silica (RHS) as a silica source and used as a catalyst support. The basicity of zeolite NaX can be further increased by impregnation with cation of high electropositive metals like K and Na (Jothiramalingam and Wang, 2009). With different metal loading, the catalyst basic strength and the number of basic sites were increased from that of the NaX and the catalytic activity for biodiesel production was increased.

Recently, zeolite NaY was used as a support for potassium catalysts for biodiesel production from Jatropha seed oil. The solution of potassium precursors including acetate (CH_3COOK) and actetate buffer (CH_3COOK/CH_3COOH) were used to prevent collapses of the zeolite structure (Supamathanon et al., 2011). The 12 wt% of K loading gave high oil conversion with high biodiesel yield with a short reaction time (3 h). The catalytic performance could be improved when a more basic zeolite, NaX is used.

The aim of this work was to investigate the properties of catalysts consisting of sodium (Na) loaded on zeolite NaX and performance as heterogeneous basic catalysts for transesterification of Jatropha seed oil to produce biodiesel. The Na-loaded catalysts were prepared by impregnation method with acetate (A) and acetate buffer (B) solution.

3.2   Experimental

3.2.1   Chemicals and materials

Hydrochloric acid (37% HCl, Merck) was used in the extraction of rice husk silica (RHS). The chemicals for zeolite NaX synthesis were RHS (SiO_2), sodium aluminate ($NaAlO_2$ containing Al_2O_3 ~ 55-56%, Riedel-de Haën), sodium hydroxide (97% NaOH, Carlo Erba), potassium hydroxide (85% KOH, Ajax Fine Chem) and deionized (DI) water.

The chemicals for catalysts preparation were zeolite NaX, sodium acetate (99% CH_3COONa, BDH laboratory supplies), and glacial acetic acid (100% CH_3COOH, BDH). The chemicals for Jatropha seed oil extraction were hexane (99% C_6H_{10}, Lab-scan) and anhydrous sodium sulfate (Na_2SO_4, AR grade, Carlo Erba)

The chemicals for biodiesel production were methanol (99.8% CH_3OH, Merck) and Jatropha seed oil. The chemicals for preliminary determination of Jatropha seed oil conversion by thin layer chromatography (TLC) were petroleum ether (AR grade, JT Baker), diethyl ether ($C_4H_{10}O$, AR grade, JT Baker), glacial acetic acid (100% CH_3COOH, BDH), TLC plate (Silica Gel 60 F254, Merck), fatty acid methyl ester standard (F.A.M.E. Mix, C8-24, Supelco, 18918-1AMP) and iodine (UNICHROM).

The chemicals for the determination of biodiesel composition by gas chromatography (GC) were hexane (99% C_6H_{10}, Lab-scan), chloroform (99.9% $CHCl_3$, Mallinckrodt), and standards including methyl palmitoleate (99% $C_{17}H_{32}O_2$), methyl lynoleate (99% $C_{19}H_{32}O_2$), methyl linoleate (99% $C_{19}H_{34}O_2$), methyl nonadecanoate (98% $C_{20}H_{40}O_2$), methyl oleate (99% $C_{19}H_{36}O_2$), methyl arachidate

(99% $C_{21}H_{42}O_2$), methyl palmitate (99% $C_{17}H_{34}O_2$), methyl stearate (99% $C_{19}H_{36}O_2$), and methyl pentadecanoate (99% $C_{16}H_{36}O_2$), all supplied by Sigma.

3.2.2 Preparation of silica from rice husk

The preparation of silica from rice husk was similar to a method in literature (Wittayakun, Khemthong and Prayoonpokharach, 2008). Rice husk from a local rice mill was washed with water, dried at 100 °C overnight, refluxed in 3 M HCl for 6 h, filtered and washed repeatedly with water until the filtrate was neutral and dried at 100 °C overnight. The refluxed rice husk was then calcined in a muffle furnace at 550 °C for 6 h resulting in white powder of rice husk silica (RHS). The RHS was dissolved in 4.5 M NaOH solution (4.52 g of RHS in 10 ml of NaOH solution) to produce Na_2SiO_3 solution for NaX synthesis.

3.2.3 Synthesis of zeolite NaX

Zeolite NaX was synthesized by the procedure described by Khemthong et al. (2007). The gel with molar ratio 5.5 Na_2O: 1.65 K_2O: 1 Al_2O_3: 2.2 SiO_2: 122 H_2O was prepared from Na_2SiO_3 and $NaAlO_2$. First, solution 1 was prepared by adding 1.76 g of $NaAlO_2$ in 2.52 g of DI water and stirring until dissolved. Next, solution 2 was prepared by dissolving 2.45 g of NaOH and 1.76 g of KOH in DI water and stirring until a clear solution was obtained. Then, solution 1 was slowly added into solution 2 and stirred until a clear solution was obtained and this solution was referred to as solution 3. The dilute Na_2SiO_3 solution was prepared by dissolving 7.24 g of Na_2SiO_3 (from 3.2.2) in 11 ml of DI water and stirring for 48 h. The mixture was transferred into a polypropylene bottle, closed and sealed with paraffin film. Then, the crystallization was carried out at 70 °C for 3 h and 95 °C for 2 h. The solid sample was filtered, washed with DI water and dried at 110-125 °C

overnight. The obtained zeolite NaX was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF) and N_2 adsorption-desorption.

3.2.4 Preparation of Na/NaX catalysts

The Na/NaX was prepared by impregnation adapted from Supamathanon et al. (2011) and Ramos et al. (2008). First, the zeolite NaX was dried in an oven at 110 °C for 2 h to remove adsorbed water. Then, 1.6 g of zeolite NaX was impregnated with 2 mL of acetate buffer (B) solution of sodium (producing Na/NaX-B) and just acetate (A) solutions (producing Na/NaX-A). The catalysts with various Na loadings of 4, 8, 12 and 16 wt% were prepared. The samples were dried at room temperature for 8 h and in an oven at 80 °C overnight, calcined at 400 °C for 3 h. The obtained catalysts were denoted as xNa/NaX-B and xNa/NaX-A, where x = 4, 8, 12 and 16 wt%. All catalysts were characterized by XRD and FTIR.

3.2.5 Characterization of catalysts

Powder XRD patterns were obtained on a Bruker axs D5005 diffractometer. The Cu Kα X-ray (λ = 1.54 Å) is generated with a current of 40 mA and a potential of 40 kV. The powder of catalysts was recorded in the same day with the same amount (1.5 g) to compare the peak intensity of catalysts. The catalyst was ground to fine powder, with agate mortar packed in a sample holder and pressed with a thick glass to get smooth surface. The catalysts were scanned from 5 to 50 degrees (2θ) in steps of 0.05 degrees per minute with slit 0.2.

FTIR was used to investigate the characteristic functional groups of the synthesized samples. In the determination of the functional groups, KBr pellet technique was employed by the following approach. The samples and KBr were dried at the temperature of 110 °C for 3 h to remove water, and then each sample was

mixed with KBr at the sample to KBr ratio of 1:50. The mixture was put in sample holder and then pressed with hydraulic apparatus. All samples were measured at room temperature, and all spectra were recorded from the wavenumber range from 400 cm^{-1} to 4000 cm^{-1} with Perkin Elmer Spectrum GX spectrometer.

3.2.6 Jatropha seed oil extraction

Jatropha oil was extracted from seeds of Jatropha Curcas cultivated in Nakhon Ratchasima, Thailand (Supamathanon et al., 2011). The Jatropha seeds were dried in an oven at 105 °C for 4 h, cooled down at room temperature, ground with a grinder (Warring Commercial, Model 32BL79, USA). The 100 g of ground seed was put in a 1000 mL erlenmeyer flask and added with 400 mL of n-hexane. Then, the mixture was shaken in every 20 min at room temperature for 3 h. After extraction the mixture was filtered by using a filter paper (Whatman no. 1) place in Buchner funnel. The moisture in the liquid was removed by adding Na$_2$SO$_4$ and the liquid was poured into 250 mL a round bottom flask to remove hexane by using rotary evaporator (BÜCHI, Rotavapor R-114, and UK) and obtain the Jatropha seed oil. The oil yield was calculated by equation 3.1.

$$\text{Oil yield (\%w/w)} = \frac{\text{weight of the seed oil (g)}}{\text{weight of the ground seed (g)}} \times 100$$

(3.1)

3.2.7 Catalytic performance for transesterification reaction

The prepared catalysts were tested for biodiesel production. Firstly, a mixture solution containing 5.0 g of Jatropha seed oil, preheated to 65 °C by using water bath (Heto Lab Equipment, AT110, Denmark), 0.2 g of catalyst and 2.9 g of methanol (the methanol to oil molar ratio of 16:1) were stirred at 400 rpm with a

magnetic stirrer in a 50 mL round-bottom flask equipped with a water-cooled condenser as shown in Figure 3.1. After a desired reaction time, the mixture was centrifuged (Heraeus SEPATECH, Labofuge 200, Germany) at 3000 rpm to separate catalyst, the upper layer of the reaction mixture was separated in a separatory funnel (Figure 3.2) and the excess methanol was removed by a rotary evaporator.
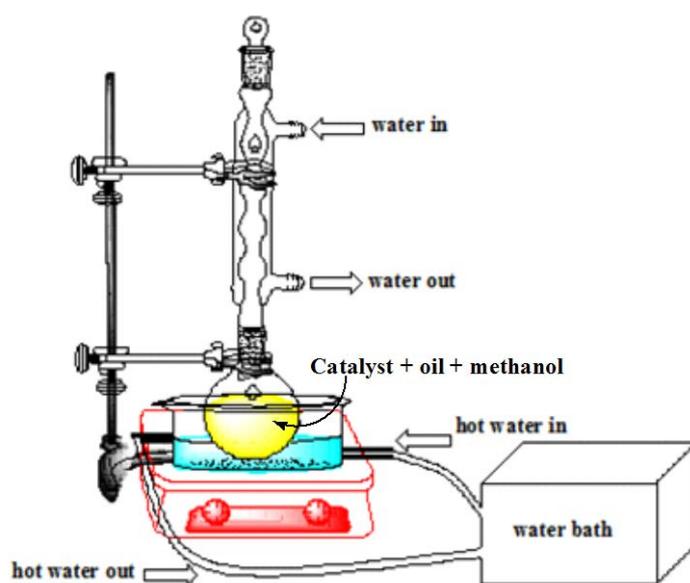
Figure 3.1 Apparatus set up for transesterification.
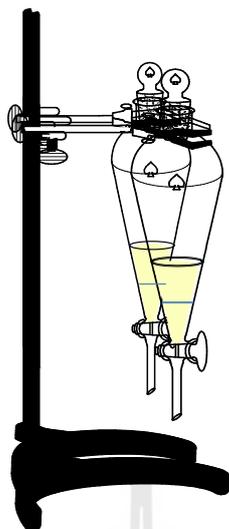
Figure 3.2 Apparatus set up for separation of biodiesel.

3.2.8 Analysis and determination of biodiesel yield

3.2.8.1 Primarily estimation of conversion of biodiesel by TLC

The biodiesel obtained was monitored by TLC (Supamathanon et al., 2011). The upper layer of liquid from the reaction mixture was spotted on a TLC plate of size 5 cm × 2 cm and 5 cm × 3 cm. A start line was drawn 1 cm from the bottom and 0.5 cm on the top using a pencil. F.A.M.E. mix and Jatropha crude oil were supported on the TLC plate as reference. Then the plate was dried at room temperature. The dried plate was immersed in a solvent mixture of petroleum ether/diethyl ether/glacial acetic acid with a ratio 85:15:1, v/v/v after the solvent reached the final line; the plate was taken out from the solvent and exposed to iodine vapor to estimate the conversion. A picture of the spots of Jatropha seed oil, standard methyl ester and biodiesel shown on the plate was taken using a digital camera (Panasonic Lumix DMC-FX80).

3.2.8.2 Biodiesel yield determination by GC

The compositions of biodiesel from the reaction were determined by a gas chromatograph (Hewlette Packard, GC-HP6890-Series) equipped with a flame ionization detector (FID) and a 30-meter HP-INNOWAX polyethylene glycol capillary column with a 0.32 mm inner diameter and 0.15 µm film thickness (Supamathanon et al., 2011). The biodiesel yield was obtained from a separate calibration curve using the internal standard method. The details of the preparation of stocks solutions and standard calibration curves can be found in the Appendix A. The initial column temperature was held at 140 °C for 3 min before ramping to 240 °C with a rate of 10 °C/min and held for 8 min at the final temperature. The volume of a sample injected was 1 µL. Biodiesel yield was calculated by equation 3.2 (Supamathanon et al., 2011; Liu et al., 2008).

$$\text{yield} = \frac{(C_{ester} \times n)}{\rho \text{oil}} \times 100\% \tag{3.2}$$

where Cester (g/mL) is the mass concentration of methyl ester which was acquired by GC, n is the diluted multiple of methyl esters, which can be calculated using the total volume of hexane and internal standard solution divided by the volume of methyl ester sample and ρoil (g/mL) is the density of Jatropha seed oil which is 0.91 g/mL (Supamathanon et al., 2011; Liu et al., 2008).

3.3   Results and discussion

3.3.1   Catalysts characterization by XRD

Figures 3.3 and 3.4 show XRD patterns of zeolite NaX and xNa/NaX-A (NaX impregnated with sodium acetate solution) and xNa/NaX-B (NaX impregnated with sodium acetate buffer solution) after calcined at 400 °C where x = 4, 8, 12 and 16 wt% Na loading. All patterns from both precursors consisted of characteristic peaks of NaX indicating that the structure of zeolite NaX was retained after impregnation and calcination. However, the intensity of zeolite peaks decreased with Na loading. The coverage of the zeolite surface by sodium oxides could partially block the reflecting planes of zeolites. Other possibility is the decrease in the zeolite crystallinity by hydrolysis in the solution. The peak corresponding to sodium oxide was not observed possibly because of a good dispersion on the support. In addition, the peak intensities of xNa/NaX-A were lower than that of xNa/NaX-B with similar loading. This indicated that the use of acetate solution as a precursor gave a poorer dispersion or caused more changes in the zeolite structure.
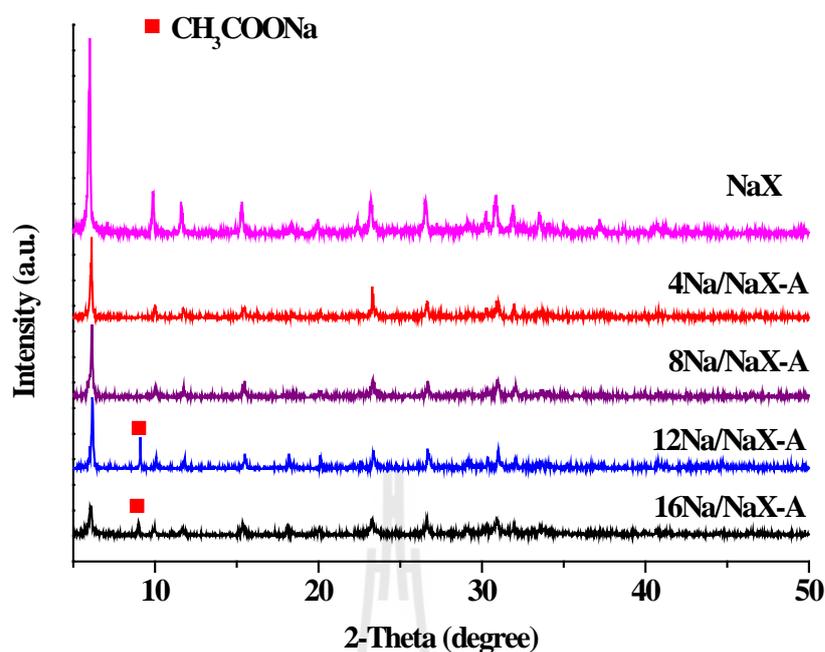
Figure 3.3 XRD patterns of the zeolite NaX and xNa/NaX-A catalysts (x = 4, 8, 12 and 16 wt% Na loading).

Montalbo et al. (2013) explained that the decrease of diffraction peaks in zeolite after impregnation of NaY by potassium acetate solution was caused by hydrolysis of Si–O–Al bonds during the thermal treatment of the zeolite. Hydrolysis may occur at greater extent when potassium acetate was used because it is more basic than the acetate buffer solution. Moreover, a peak at 9° corresponding to CH_3COONa (JCPDS 29-1160) was observed in the catalysts with Na loading of 12 and 16 wt%. The presence of the peak indicated that the calcinations at 400 °C was not enough to completely convert Na acetate to oxide which was supposed to be an active phase of the heterogenous catalyst. If acetate is still present on the zeolite, it could be re-dissolved back into a solution and behave as a homogenous catalyst. To ensure

sodium acetate was still present in the calcined catalysts, these samples were characterized by FTIR.
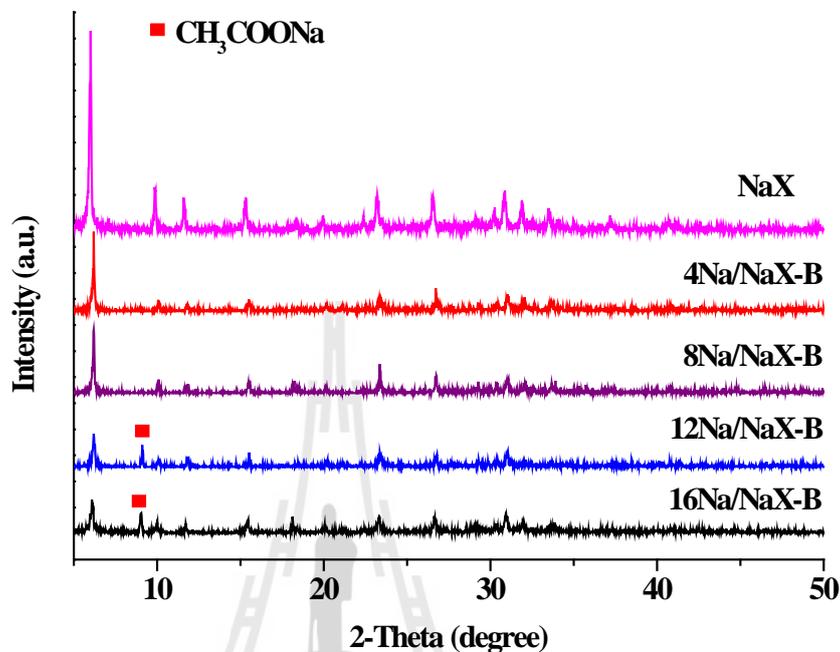
Figure 3.4 XRD patterns of the zeolite NaX and xNa/NaX-B catalysts (x = 4, 8, 12 and 16 wt% Na loading).

3.3.2 Catalysts characterization by FTIR

The FTIR spectrum of sodium acetate is shown in Figure 3.5. The main bands at 3172 cm^{-1} correspond to the symmetric stretching of methyl group. The reported value in literature for this group was at 2978 cm^{-1} (Ibrahim, Nada and Kalmal, 2005). The band at 2334 cm^{-1} assigns to C–H stretching and band at 2241 cm^{-1} assigns to C=C stretching (Settle, 1997). The bands at 1564 cm^{-1} and 1413 cm^{-1} corresponds to the C=O stretching vibration of the acetate group and the sodium associated with acetate, respectively (Ibrahim et al., 2005; Mellouk, Belhakem, Marouf, Schott and Khelifa, 2011). The sharp bands at 1251 cm^{-1} and 1709 cm^{-1}

corresponds to C-C vibration and C=O symmetric stretching, respectively. The band at 1641 cm^{-1} corresponds to asymmetric stretching of COO group (Ibrahim et al., 2005). The bands at 1056 cm^{-1} and 1023 cm^{-1} assigns to C-O stretching. The bands at 930 cm^{-1}, 811 cm^{-1}, 651 cm^{-1}, and 532 cm^{-1} correspond to C-H bending (Settle, 1997).
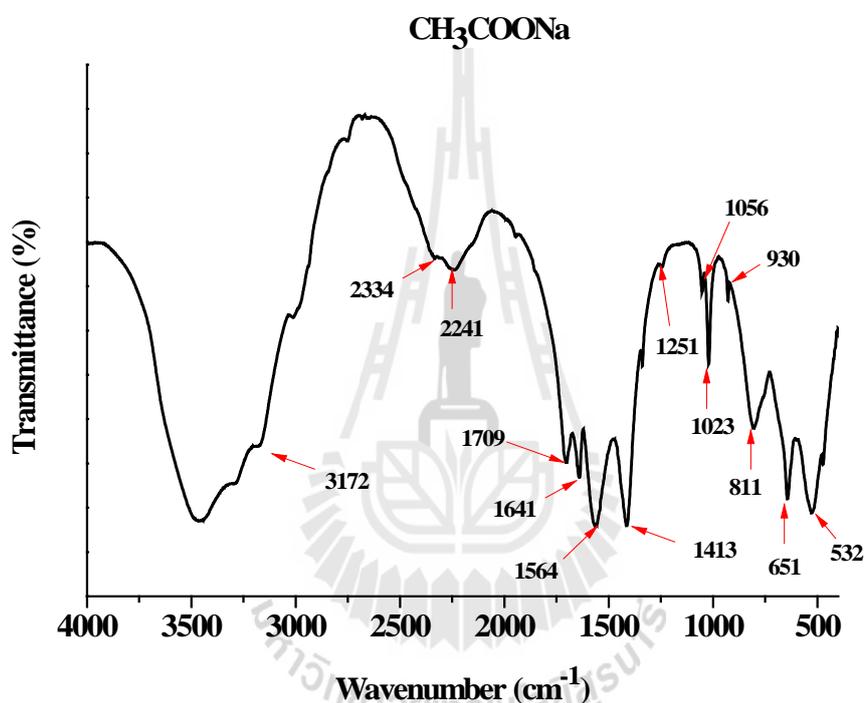
Figure 3.5 FTIR spectrum of CH_3COONa.

The results of FTIR spectra of as prepared NaX (not calcined) and NaX calcined at 400 °C for 3 h and 500 °C for 4 h are presented in Figure 3.6. The characteristic bands of calcined NaX were similar to that of the as prepared samples in the following details. The band at 979 cm^{-1} was assigned to T–O (T= Al, Si) asymmetric stretching. The bands at 663 cm^{-1} and 671 cm^{-1} corresponded to symmetric stretching mode of TO_4 tetrahedral groups in double 4- and double 6-

member rings in the zeolite structure, respectively. Babajide, Musyoka, Petrik and Ameer (2012) assigned the vibration band at 950 cm^{-1} to a T–O stretch and the bands at around of 740 cm^{-1} and 620 cm^{-1} to stretching modes of the tetrahedral atoms in the region. Generally, stretching modes are sensitive to the Si–Al composition of the framework which may shift to a lower frequency with increasing number of tetrahedral aluminum atoms, resulting in the occurrence of the second group of frequencies that are sensitive to the linkages (Babajide et al., 2012). The bands in the range of 500–600 cm^{-1}, referring to double ring stretching in the zeolite framework, was observed in all the samples that contained the double 4 and double 6-rings (AlO$_6$). Moreover, the bands at 1644 cm^{-1} and 1652 cm^{-1} were ascribed to the stretching vibrations of –OH groups adsorbed onto the surface of the samples, the band range at 752 cm^{-1} and 760 cm^{-1} were attributed to O–Al–O stretching of aluminate group, and the band at 460 cm^{-1} was attributed to T-O bending. According to the work by Chen et al. (2012) the band range at 748–837 cm^{-1} was attributed to O–Al–O stretching of aluminate group, the band at 462 cm^{-1} was assigned to T-O bend (T= Al or Si) and the band at about 1648 cm^{-1}was related to the presence of H$_2$O deformation mode due to incomplete dehydration in the zeolite samples. In addition, the strong bands at 3467-3476 cm^{-1} were related to the stretching mode of silanol group (Si–OH) of the samples. However, Xie and Li (2006) reported that the band at 3432 cm^{-1} could be attributed to the stretching mode of Al–O–K group which was considered to be the active basic sites. For the parent zeolite NaX not calcined could be observed the band at 1401 cm^{-1} attributed to the carbonate species. Liu et al. (2011) reported that there were two strong bands in curve C at 1457 cm^{-1} to 1385 cm^{-1} attributed to carbonate species.
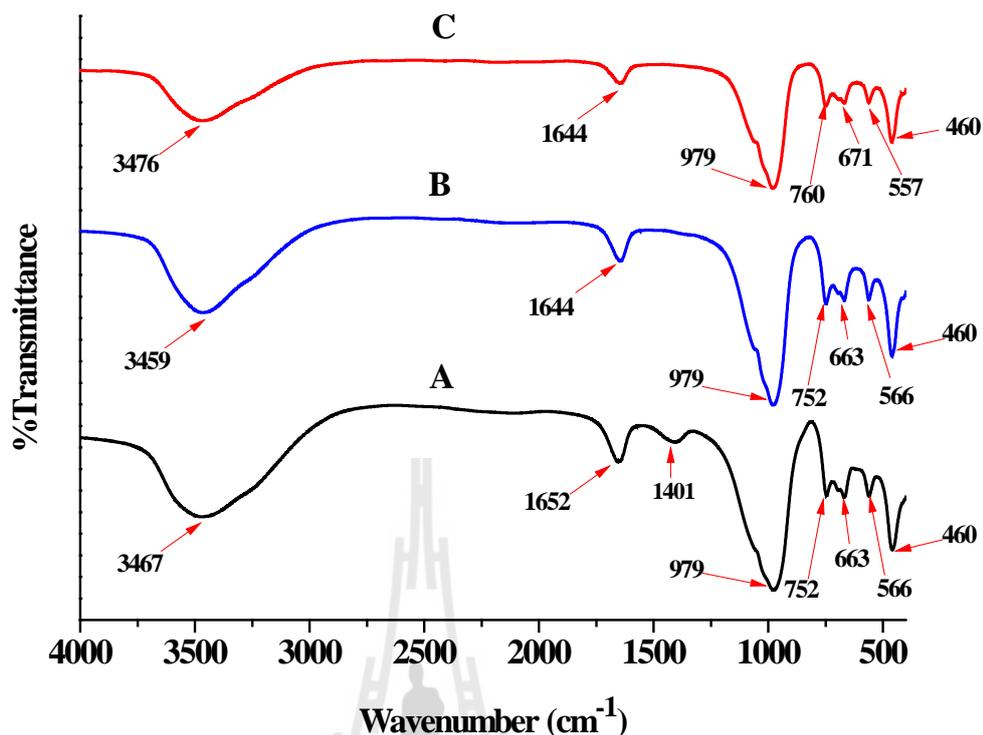
Figure 3.6 FTIR spectra of parent zeolite NaX (A), zeolite NaX calcined 400 °C (B), and zeolite NaX calcined 500 °C (C).

The FTIR spectra of xNa/NaX-A catalysts calcined at 400 °C are shown in Figure 3.7A. The band in the range of 1200–400 cm^{-1} was attributed to the vibration of (Al, Si) TO_4 tetrahedral, which was the building unit of zeolite framework (Xie, Huang and Li, 2007). However, the bands at 1564 cm^{-1} and 1413 cm^{-1} which correspond to the C=O stretching vibration of the acetate group and the sodium associated with acetate (Ibrahim et al., 2005; Mellouk et al., 2011) were not observed. From Figure 3.7B, the bands in the range of 1414-1430 cm^{-1} and 871-879 cm^{-1} in the spectrum of 12Na/NaX-A and 16Na/NaX–A catalysts were assigned to the sodium carbonate species. Huang and Kerr (1960) reported that the bands of sodium carbonate were observed at around 1450 cm^{-1} and 881 cm^{-1}. When the intensities of

the C=O stretching of the catalyst and sodium acetate were compared, the band from catalyst had higher frequency than that of sodium acetate because the force constant of the carbonyl bond was increased by the electron-attracting nature of the adjacent oxygen atom due to inductive effect (Ibrahim et al., 2005). Because the spectra of all catalysts were similar to the zeolite NaX but different from the spectra of sodium acetate, it could be concluded that calcinations at 400 °C for 3 h was sufficient for the catalysts with high sodium loading.

The FTIR spectra of sodium acetate and xNa/NaX-B calcined at 400 °C are presented in Figure 3.8A. The spectra of all catalysts showed band in the range of 1200–400 cm^{-1} attributes to the vibration of (Al, Si) TO_4 tetrahedral of zeolite framework (Xie et al., 2007). However, the catalysts with loading of 16 wt% (Figure 3.8B) showed the band at 1576 cm^{-1} assigns to the sodium associated with acetate (Ibrahim et al., 2005) and the band at 1430 cm^{-1} which correspond to the C=O stretching vibration of the acetate group (Mellouk et al., 2011). In addition, for the 12Na/NaX-B the band of C=O stretching vibration of the acetate group was observed. The results suggested that acetate was not removed completely after calcination at 400 °C. It was expected that sodium acetate could be leached from the zeolite during the catalytic testing and acted as homogeneous catalyst.

A

(B)
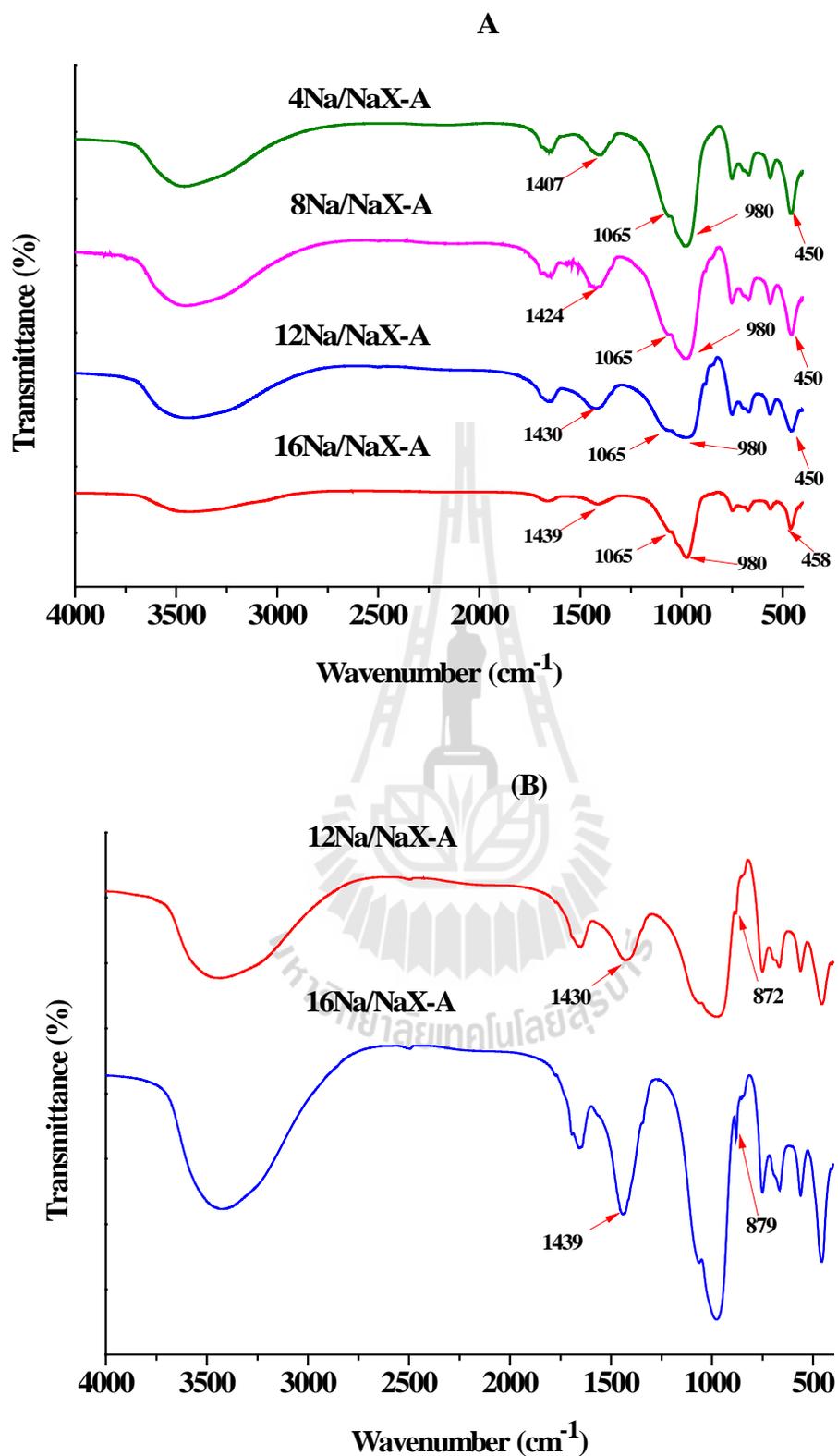
Figure 3.7 FTIR spectra of xNa/NaX-A (A), and 12Na/NaX-A, 16Na/NaX-A (B).
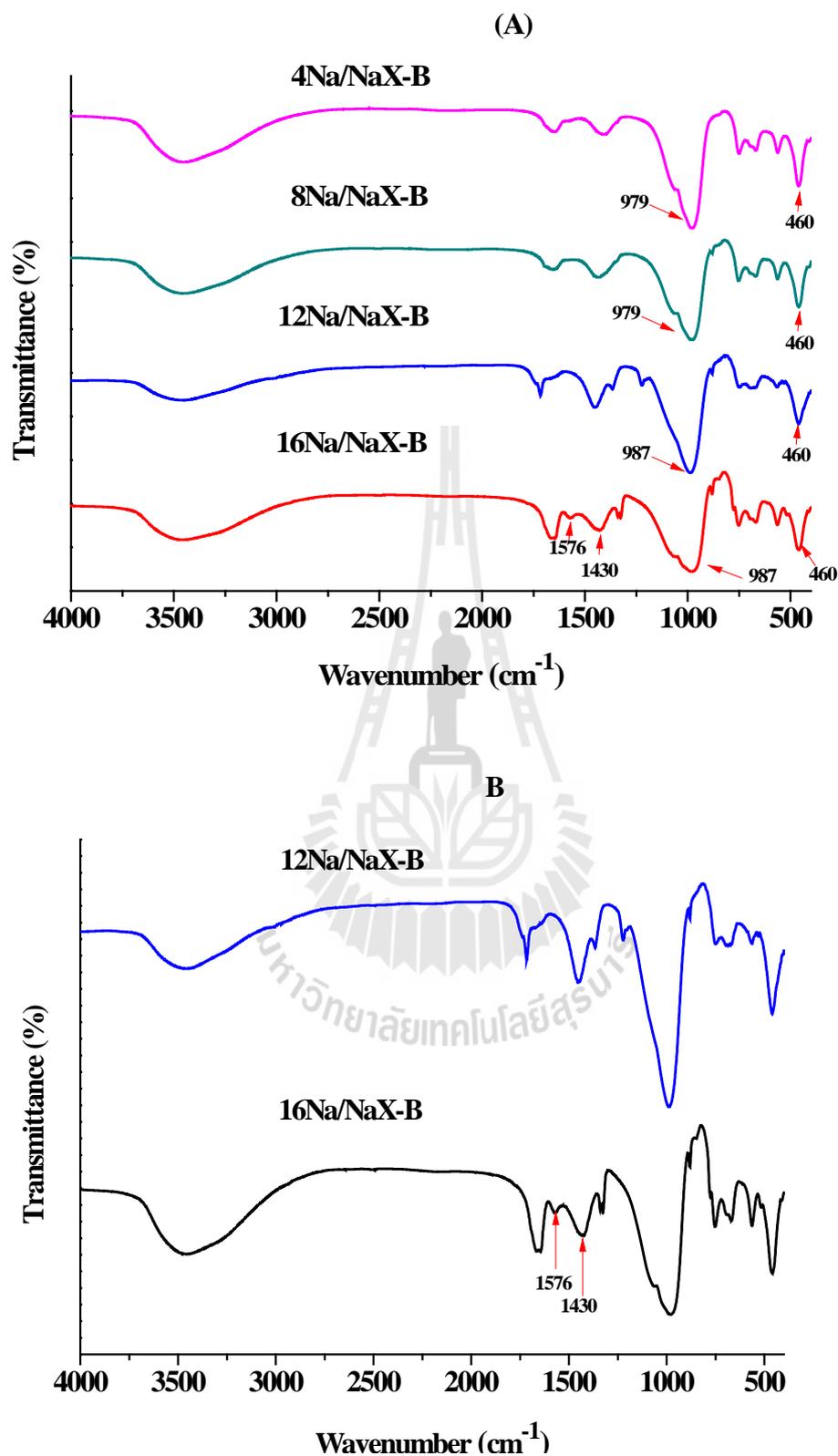
Figure 3.8 FTIR spectra of xNa/NaX-B (A), and 12Na/NaX-A, 16Na/NaX-A (B).

3.4 Catalytic performance for transesterification of Jatropha seed oil to biodiesel

3.4.1 Effect of Na loading in Na/NaX-A

Analysis of products from transesterification by TLC could preliminary determine the conversion of the crude Jatropha seed oil to biodiesel. This could simply done by comparing the position and size of the product with that of methyl ester standard (biodiesel), crude Jatropha seed oil, fatty acids, diglycerides and monoglycerides. The size of the spot of biodiesel relative to that of the oil indicates the extent of the reaction completeness. Figure 3.9 shows the TLC plates containing spots from products of transesterification of Jatropha seed oil using xNa/NaX-A (x = 4, 8, 12 and 16 wt% of sodium loading) with 3 h of testing period. The spot size corresponding to biodiesel increased with sodium loading and a complete conversion was observed from the catalyst 16Na/NaX-A. The increase in conversion with sodium loading was consistent with the increase in basicity of the catalysts. The catalysts presented low concentration of free fatty acids (FFA) was indicated by the very light spots in the FFA position (Santos, Rodrigues and Fernandes, 2009).
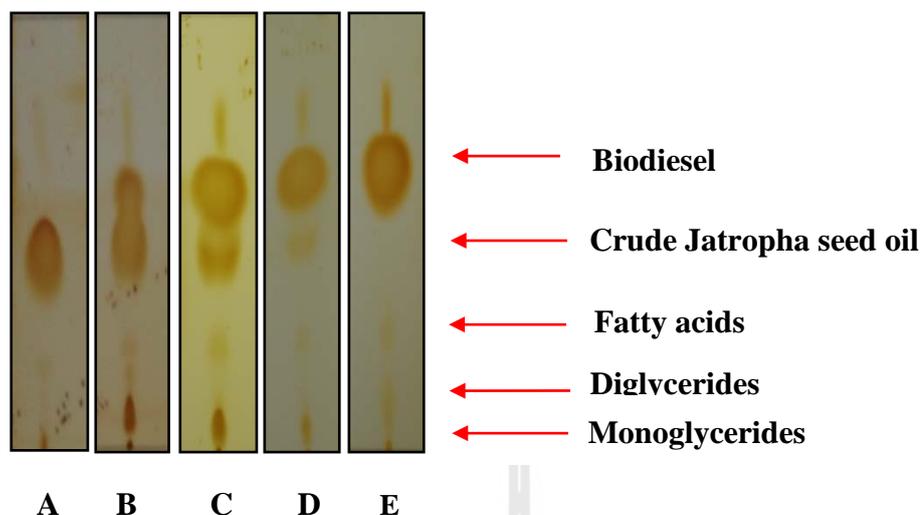
Figure 3.9 TLC plate showing mixture from transesterification with xNa/NaX-A comparing with the crude Jatropha seed oil (A), (B) x = 4, (C) x = 8, (D) x = 12, (E) x = 16 wt% Na loading. Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time = 3 h.

Because the complete conversion was obtained from 16Na/NaX-A after 3 h, this catalyst was tested for 2 h and 1.5 h. The TLC results from those times are shown in Figure 3.10. A complete conversion was observed after 2 h but not 1.5 h. Thus, the optimum reaction time for complete conversion is 2 h. The biodiesel yield from this catalyst determined by GC was 86.6%. When these catalysts were tested for transesterification, the complete conversions were obtained because the initial reagent, Jatropha seed oil, in the measured reaction was disappearing on TLC plate. Although homogeneous catalysts show a great performance in transesterification, they produce soap as a by-product and difficult to separate of catalysts from the product. However, they were not further studied because the homogeneous contribution was not the scope of this work.
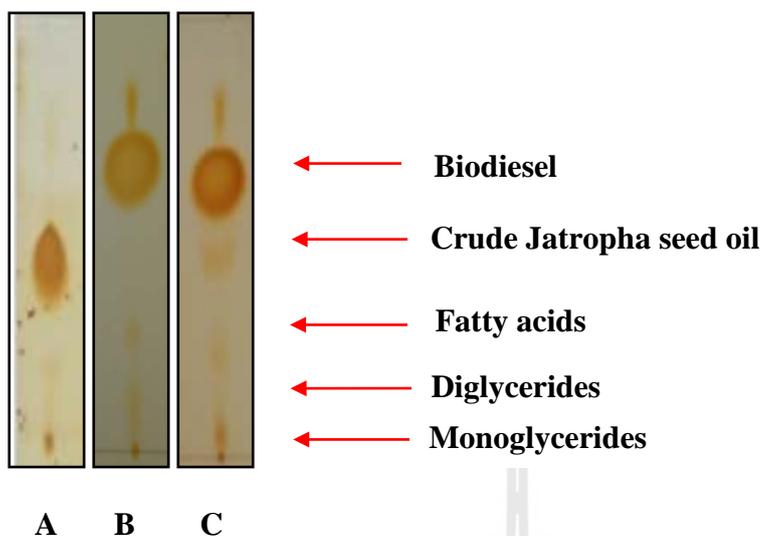
Figure 3.10 TLC plate showing mixture from transesterification with 16Na/NaX-A comparing with the crude Jatropha seed oil (A). Reaction condition: methanol to oil molar ratio = 16:1, and temperature = 65 °C. Testing time in (B) = 2 h and in (C) = 1.5 h.

3.4.2 Effect of Na loading in Na/NaX-B

The TLC plates containing spots of products from transesterification for 3 h using xNa/NaX-B where x = 4, 8, 12 and 16 wt% are shown in Figure 3.11. The results showed a similar trend to that from xNa/NaX-A that the conversion increased with sodium loading. The difference is that a spot of crude oil was observed indicating incomplete conversion prepared from sodium acetate buffer solution. Thus, the catalysts prepared from sodium acetate buffer solution were less active than those prepare from sodium acetate solution. It was believed that the catalysts prepared from acetate solution had more basic sites than those prepared from the acetate buffer solution.
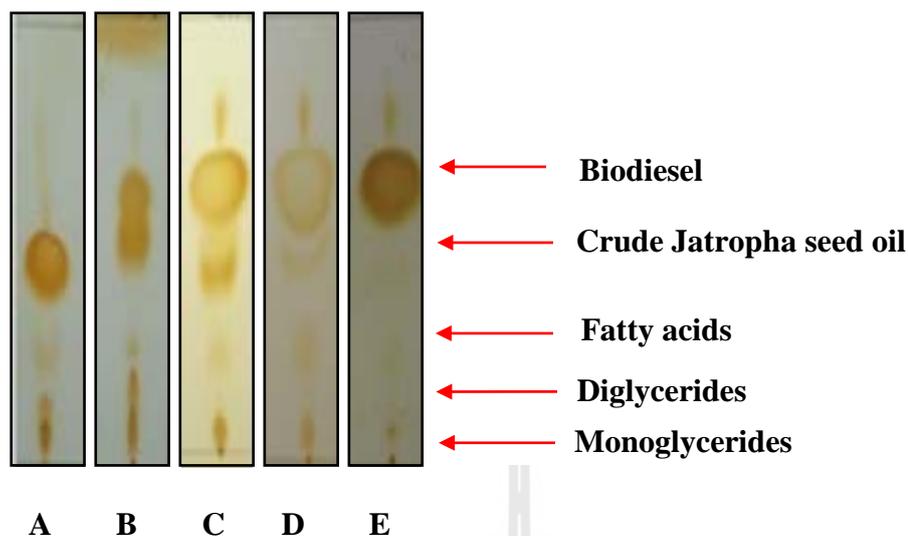
Figure 3.11 TLC plates showing mixture from transesterification with xNa/NaX-B; Crude Jatropha seed oil (A), (B) x = 4, (C) x = 8, (D) x = 12, (E) x = 16 wt% Na loading. Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time = 3 h.

3.5 Conclusions

Catalysts consisting of sodium supported on zeolite NaX (xNa/NaX-A and xNa/NaX-B with x = 4, 8, 12 and 16 wt%) were prepared by impregnation with sodium acetate and sodium acetate buffer solution, respectively and calcined at 400 °C for 3 h. From analysis by XRD, the structure of NaX was not destroyed after impregnated with both precursors. A peak at 9° corresponding to sodium acetate was observed on the samples with 12 and 16 wt% loading. Although the functional groups of acetate were not observed by FTIR, it could be concluded that the calcination temperature was not high enough to decompose the acetate completely. These catalysts were tested for transesterification of Jatropha seed oil at 65 °C for 3 h with methanol: oil molar ratio of 16:1. The oil conversion was first estimated by thin layer

chromatography (TLC) by comparing the separated spot size with that of crude oil and methylester standards. The results demonstrated that biodiesel yield increased with by sodium loading which were basic sites. The catalyst with the highest catalytic activity, 16Na/NaX-A, gave a biodiesel yield of 86.6 wt% when the reaction was carried out for 2 h. Because some acetate remained on the catalysts after calcination, it could be leached out and undesired action as homogenous catalyst along with the heterogeneous sodium oxide on the zeolite. Thus, higher calcination temperature was used in the catalyst activation in other chapters.

3.6   References

Babajide, O., Musyoka, N., Petrik, L., and Ameer, F. (2012). Novel zeolite Na-X synthesized from fly ash as a heterogeneous catalyst in biodiesel production. **Catalysis Today**. 190: 54-60.

Chen, D., Hu, X., Shi, L., Cui, Q., Wang, H., and Yao, H. (2012). Synthesis and characterization of zeolite X from lithium slag. **Applied Clay Science**. 59-60: 148-151.

Huang, C. K., and Kerr, P. F. (1960). Infrared study of the carbonate minerals. **The American Mineralogist**. 45: 311-324.

Ibrahim, M., Nada, A., and Kalmal, D. -E. (2005). Density functional theory and FTIR spectroscopic study of carboxyl group. **Indian Journal of Pure and Applied Physics**. 43: 911-917.

Jothiramalingam, R., and Wang, M. K. (2009). Review of recent developments in solid acid, base, and enzyme catalysts (heterogeneous) for biodiesel production via transesterification. **Industrial and Engineering Chemistry Research**. 48: 6162-6172.

Khemthong, P., Wittayakun, J., and Prayoonpokharach, S. (2007). Synthesis and characterization of zeolite LSX from rice husk silica. **Suranaree Journal of Science and Technology**. 14: 367-379.

Liu, H., Su, L., Liu, F., Li, C., and Solomon, U. -U. (2011). Cinder supported K_2CO_3 as catalyst for biodiesel production. **Applied Catalysis B: Environmental**. 106: 550-558.

Mellouk, S., Belhakem, A., Marouf, K. -K., Schott, J., and Khelifa, A. (2011). Cu(II) adsorption by halloysites intercalated with sodium acetate. **Journal of Colloid and Interface Science**. 360: 716-724.

Montalbo, K. D., De Leon, R. L., Sophiphun, O., Manadee, S., Prayoonpokarach, S., and Wittayakun, J. (2013). Characterization and catalytic performance of potassium loaded on rice husk silica and zeolite NaY for tranesterification of Jatropha seed oil. **Quimica Nova**. 36: 1116-1120.

Ramos, M. J., Casas, A., Rodriguez, L., Romero, R., and Perez, A. (2008). Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. **Applied Catalysis A: General**. 346: 79-85.

Santos, F. F. P., Rodrigues, S., and Fernandes, F. A. N. (2009). Optimization of the production of biodiesel from soybean oil by ultrasound assisted methanolysis. **Fuel Processing Technology**. 90: 312-316.

Settle, F. S. (ed.). (1997). **Handbook of instrumental techniques for analytical chemistry** (pp. 247-283). Upper Saddle River, NJ: Prentice Hall PTR.

Supamathanon, N., Wittayakun, J., and Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. **Journal of Industrial and Engineering Chemistry**. 17: 182-185.

Xie, W., Huang, X., and Li, H. (2007). Soybean oil methyl ester preparation using NaX zeolite loaded with KOH as a heterogeneous catalyst. **Bioresource Technology**. 98: 936-939.

Xie, W., and Li, H. (2006). Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. **Journal of Molecular Catalysis A**: **Chemical**. 255: 1-9.

Wittayakun, J., Khemthong, P., and Prayoonpokharach, S. (2008). Synthesis and characterization of zeolite NaY from rice husk silica. **Korean Journal Chemical Engineering**. 25: 861-864.

CHAPTER IV

CHARACTERIZATION AND CATALYTIC TESTING OF CATALYSTS CALCINED AT 500 °C

Abstract

Zeolite NaX was impregnated with the solution of sodium acetate (A) or sodium acetate buffer (B) with sodium loading of 4, 8, 12 and 16 wt%. The samples were calcined at 500 °C for 4 h to transfrom sodium acetate to sodium oxide. Characterization by XRD indicated that the NaX structures in all samples was retained after Na loading. Results from N_2 adsorption-desorption analysis showed decreases in surface area and micropore volumes of NaX, indicating that sodium oxide resided in the zeolite cavities. Temperature programmed desorption of CO_2 (CO_2-TPD) confirmed that the catalyst basicity increased with sodium loading. The catalysts were tested for transesterification of Jatropha seed oil to produce biodiesel. The oil conversion was estimated by thin layer chromatography (TLC) by comparing spot size with that of crude oil and methylester standards. On 4Na/NaX-A, conversion was merely observed, whereas nearly complete conversions were observed on 8, 12 and 16 Na/NaX-A. Similar results were obtained from xNa/NaX-B, except that 16Na/NaX-B gave a complete conversion. In general, the conversion increased with Na loading. The biodiesel yields were determined by GC-FID. In addition, 16Na/NaX-B was tested for 2 h, but the complete conversion was not obtained.

4.1   Introduction

One direction of research on biodiesel synthesis is development of heterogeneous catalysts because they can be easily separated from the reaction products. Heterogeneous base catalysts are preferred over acid ones because they showed faster reaction rates. One example of heterogeneous base catalyst is zeolites which contain a large number of basic sites. The number of basic sites can be increased conveniently by impregnation with a solution of alkali metal precursor. For example, Ramos et al. (2008) studied transesterification of sunflower oil with methanol using Na/NaX prepared by loading zeolite NaX with sodium acetate (CH_3COONa) and calcined at 500 °C for 4 h. The highest biodiesel yield of 95.1 wt% was obtained. The greater activity of zeolite NaX compared to other zeolites could be explained by the presence of a higher concentration of super-basic sites on zeolite NaX (Na_2O in supercage of zeolite X). In another example, zeolite NaY was loaded with a buffer solution of potassium acetate and used in transesterification of Jatropha seed oil (Supamethanon et al., 2011). In addition, the use of potassium acetate buffer provided a more active catalyst than the use of potassium acetate (Montalbo et al., 2013).

In the present work, the heterogeneous base catalyst consisting of sodium on zeolite NaX was prepared. It was shown in chapter 4 that calcinations at 400 °C could not completely convert sodium acetate to sodium oxide. Consequently, the calcinations temperature was increased to 500 °C in this chapter. The catalysts were characterized and their catalytic activity in transesterification of Jatropha seed oil was determined. The influence of the metal loading and the catalyst concentration on the biodiesel yield was studied.

4.2   Experimental

4.2.1   Catalysts preparation and characterization

The preparation procedures of xNa/NaX-A and xNa/NaX-B were similar to those in Chapter III except that the samples were calcined at 500 °C for 4 h. All catalysts were characterized by XRD and FTIR with the procedures mentioned in Chapter III.

The surface area of the catalysts was determined by N_2 adsorption-desorption analysis (Micromeritics ASAP, 2010). Prior to the adsorption measurement, the catalyst (0.1-0.2 g) was degassed at 300 °C for 8 h. The relative pressure (P/P_0) used for the BET surface area calculation was in the range of 0.01 to 0.2. The pore size and pore volumes were calculated from the adsorption-desorption branches of the isotherm using Barrett-Joyner-Halenda (BJH) method.

The CO_2 temperature programmed desorption (CO_2-TPD) analysis was done on a BELCAT-B instrument to obtain information on the basic sites of the catalytic samples. The temperature of desorption and the maximum desorbed CO_2 are illustrative of the strength and amount of basic sites, respectively. The 0.05 g of catalyst was packed into the sample cell and topped with quartz wool, heated at 10 °C/min under a flow of helium (He) from room temperature to 500 °C and held at this temperature for 60 min. After cooling to 50 °C, CO_2 diluted with inert gas (He, 99%) was fed at a rate of 30 ml/min for 30 min. Later, the sample was purged with He for 1 h to eliminate physisorbed species. The temperature was ramped at 10 °C/min from 100 to 810 °C. Then, the amount of CO_2 desorbed versus temperature was obtained. The basic site density was obtained by integration of area under the curve.

4.2.2   Catalytic performance for transesterification and determination of biodiesel yield

The prepared catalysts were tested for biodiesel production with procedure and condition similar to that in Chapter III. The product from the reaction was analyzed by TLC and the compositions of biodiesel from the reaction were determined by GC-FID.

4.3   Results and discussion

4.3.1   Catalysts characterization by XRD

Figures 4.1 shows XRD patterns of zeolite NaX and xNa/NaX-A (NaX impregnated with sodium acetate solution, x = 4, 8, 12 and 16 wt% Na loading) after calcined at 500 °C for 4 h. The characteristic peaks of NaX were observed in the pattern of all catalysts (Khemthong et al., 2007) but the intensity decreased with sodium loading. After NaX was impregnated with sodium acetate solution, the structure of NaX was not destroyed. There are two possible reasons for the decrease in peak intensity. First, the NaX structure was partially collapsed by excess occlusion of sodium in the cavities. Second, the Na species on external surface of the zeolite could also scatter X-ray and resulted in lower reflection from the zeolite planes.

The peaks at 9° corresponding to sodium acetate (JCPDS 29-1160) were not observed in all catalysts indicating that calcination at 500 °C was sufficient to transform all sodium acetate to sodium oxide (Na_2O). However, the peaks of Na_2O were not observed indicating a good dispersion and the absence of large clusters of Na_2O.
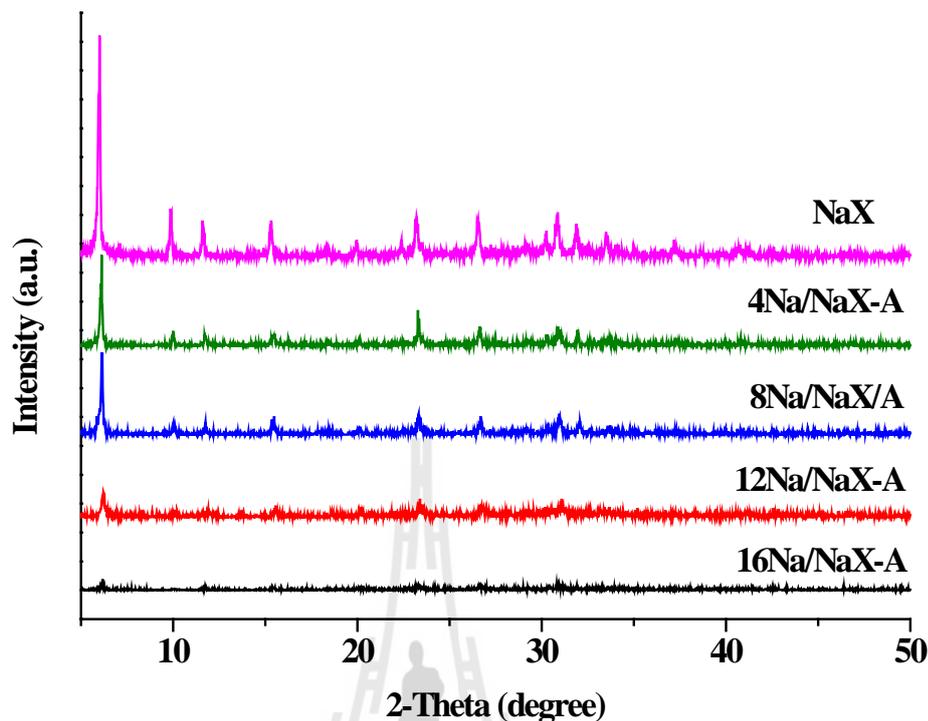
Figure 4.1 XRD patterns of the zeolite NaX and xNa/NaX-A (x = 4, 8, 12 and 16 wt% of Na loading).

Figures 4.2 shows XRD patterns of zeolite NaX and xNa/NaX-B (NaX impregnated with sodium acetate buffer solution, x = 4, 8, 12 and 16 wt% Na loading) after calcined at 500 °C for 4 h. Characteristic peaks of NaX similar to those in the literature were still observed in all catalysts (Khemthong et al., 2007). The crystalinity of NaX decrease with an increased of the Na loading. There were no peaks that indicated the presence of new phases such as alkali metal acetate or new metal phase. This implied a good dispersion of the Na species on the zeolite framework. However, the peak intensities in the patterns of 12Na/NaX-B and 16Na/NaX-B were weak suggesting that the zeolite framework might collapse and convert to an amorphous phase. Supamathanon et al. (2011) prepared K/NaY catalyst by impregnation zeolite

NaY with potassium acetate buffer solution with potassium loading of 4, 8 and 12 wt%. The XRD peak intensities of NaY also decreased with potassium loading but the NaY characteristic peaks were still clearly observed. Therefore, the impregnation with buffer solution did not destroy the zeolite structure.
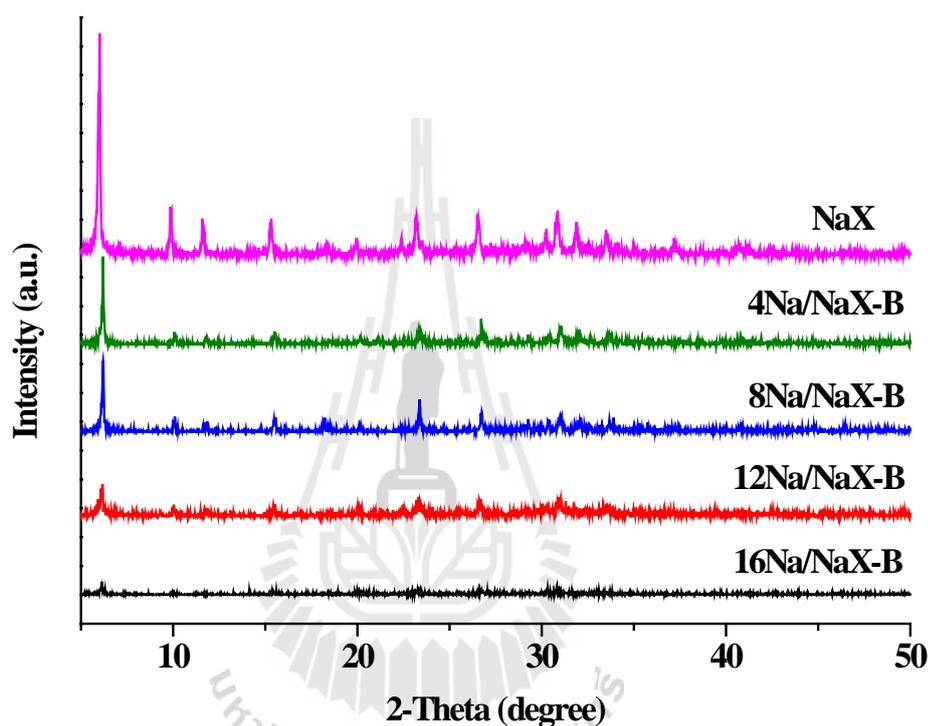
Figure 4.2 XRD patterns of the zeolite NaX and xNa/NaX-B catalysts (x = 4, 8, 12 and 16 wt% of Na loading).

The comparison between XRD patterns of Na/NaX-A and Na/NaX-B with 12 and 16 wt% loading are shown in Figure 4.3. Although the only observed diffraction peaks were assigned to the parent zeolite structure in all catalysts, there were differences between the catalysts from sodium acetate solution and the sodium acetate buffer solution. The intensities of the samples from sodium acetate were lower

even at high amount of Na loading because the hydrolysis of Si–O–Al bonds could occur by the alkali metal during the thermal treatment of the zeolite. Moreover, hydrolysis could occur in a more extent when sodium acetate solution was employed because it is more basic than the sodium acetate buffer solution (Man, Ramli and Nur, 2005). The intensities of the peaks of Na/NaX-B were higher than those of Na/NaX-A indicating that the use of the acetate buffer could preserve the structure of zeolite NaX better than that of the acetate. From other precursor, Zhu, Chun, Wang and Xu, (1999) reported that the XRD peaks of NaY disappeared after a 16% KF/NaY was evacuated at 700 °C, indicating the collapse of the framework because the interaction between the KF and the AlO_4 and the SiO_4 tetrahedral of the zeolite, was accelerated at high temperatures. Therefore, the collapse of the zeolite framework is strongly affected not only by the loading amount of K but also by the temperature.

58
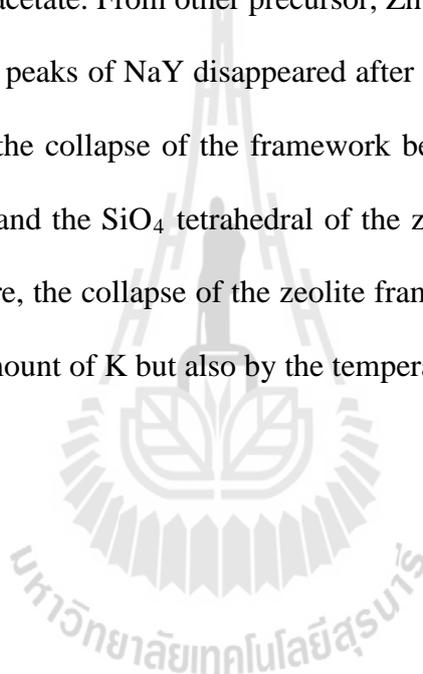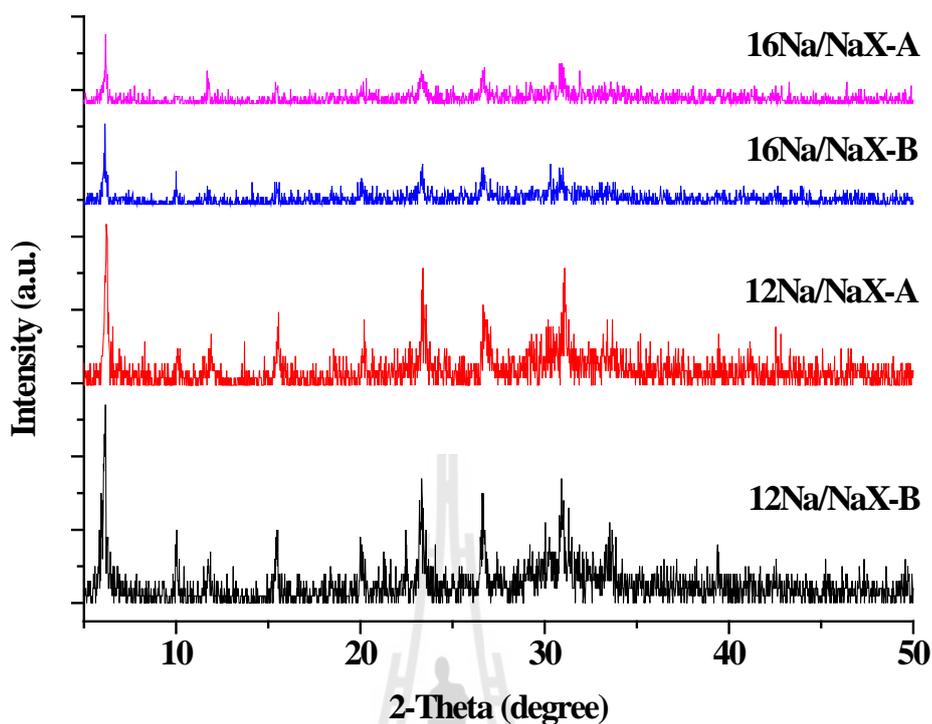
Figure 4.3 XRD patterns of the xNa/NaX-A and xNa/NaX-B catalysts with loading 12 and 16 wt%.

4.3.2 Catalysts characterixation by FTIR spectroscopy

The FTIR spectra of zeolite NaX and xNa/NaX-A calcined at 500 °C are presented in Figure 4.4A. The spectra of all catalysts consisted of peaks similar to that of the parent NaX but different from the spectra of sodium acetate. The band at 1407 cm^{-1} corresponding to asymmetry vibration COO$^-$ of CH$_3$COONa was not observed, even on the catalysts with high loading (Figure 4.4B). The results confirmed that calcinations at 500 °C for 4 h were enough to decompose acetate completely. However, a band in the range of 1403-1452 cm^{-1} corresponding to carbonate species was observed. In addition, a new band at 878 cm^{-1} attributing to sodium carbonate (Na$_2$CO$_3$) was observed in the spectra of 12Na/NaX-A and

16Na/NaX-A. Yan, Kim, Steven, Salley and Simon, (2009) suggested that the band around 1445 cm^{-1} is assigned to the stretching vibration of surface carbonate (CO_3^{2-}) group from adsorption of a small amount of CO_2 on the catalyst surface.
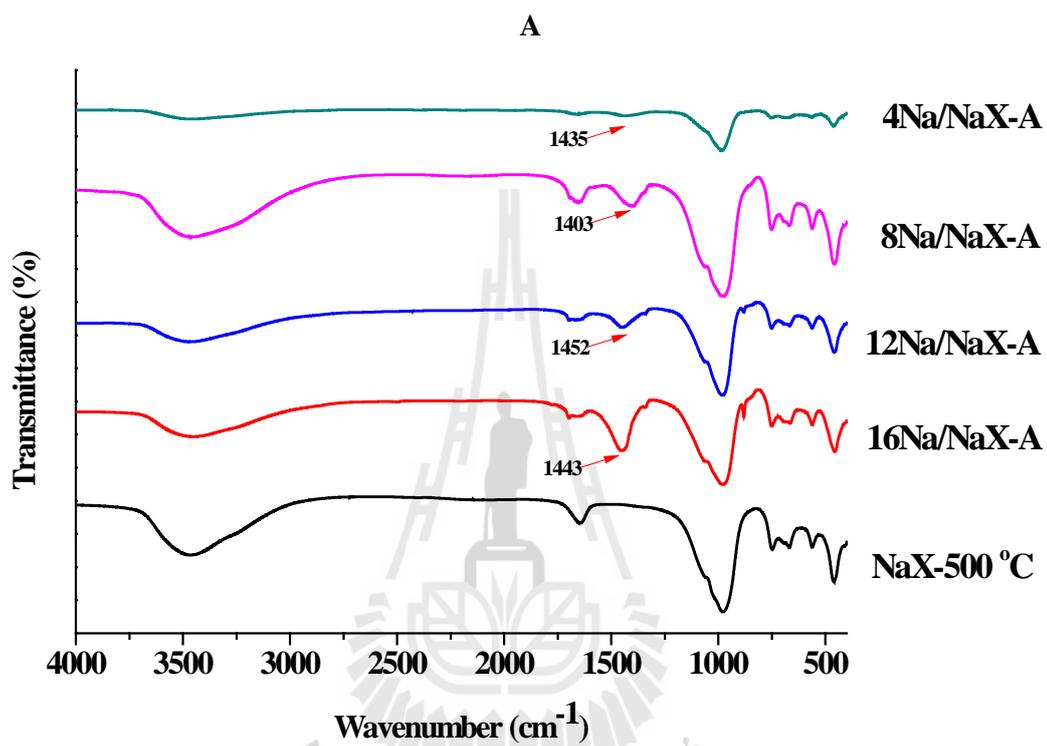
Figure 4.4 FTIR spectra of zeolite NaX and xNa/NaX-A (A).
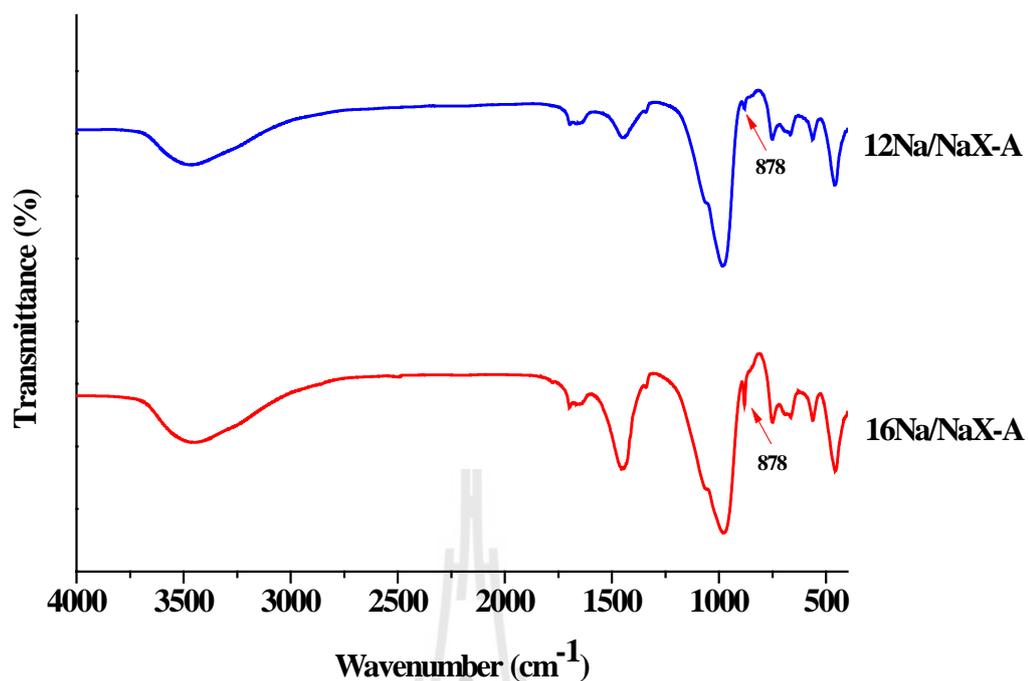
Figure 4.4 FTIR spectra of 12Na/NaX-A and 16Na/NaX-A (B)

The FTIR spectra of all catalysts are shown in Figure 4.5A. The spectra of Na/NaX-B with sodium loading of 4 and 8 wt% calcined at 500 °C were not different from the spectra of the catalysts calcined at 400 °C (Figure 3.7A in Chapter III) that the peaks corresponding to acetate related species were not observed. Furthermore, the 12Na/NaX-B and 16Na/NaX-B (Figure 4.5B) did not show the band at 1251 cm^{-1} which was assigned to C-C vibration and the symmetric stretching band at 1709 cm^{-1}. The asymmetric vibration peak at 1407 cm^{-1} corresponding to COO$^-$ of CH$_3$COONa were not observed after calcination at 500 °C. This indicated that CH$_3$COONa decomposed completely after calcination at 500 °C. In addition, the 12Na/NaX-B and 16Na/NaX-B showed bands at 1657, 1447 and 1439 cm^{-1} attributing to sodium carbonate. According to Liu et al. (2011) investigated the functional groups in the carbonate catalyst. There were two strong bands at 1457 cm^{-1}

and 1385 cm^{-1} attributed to carbonate species. However, these bands were not observed in the spectra of 4Na/NaX-B and 8Na/NaX-B. The FTIR results were in a good agreement with the XRD that carbonate species was not observed in 4Na/NaX-B and 8Na/NaX-B catalysts. Thus, the main basic sites which could contribute to transesterification reaction are the new-formed active sites of metal oxide species and Al-O-Na groups.
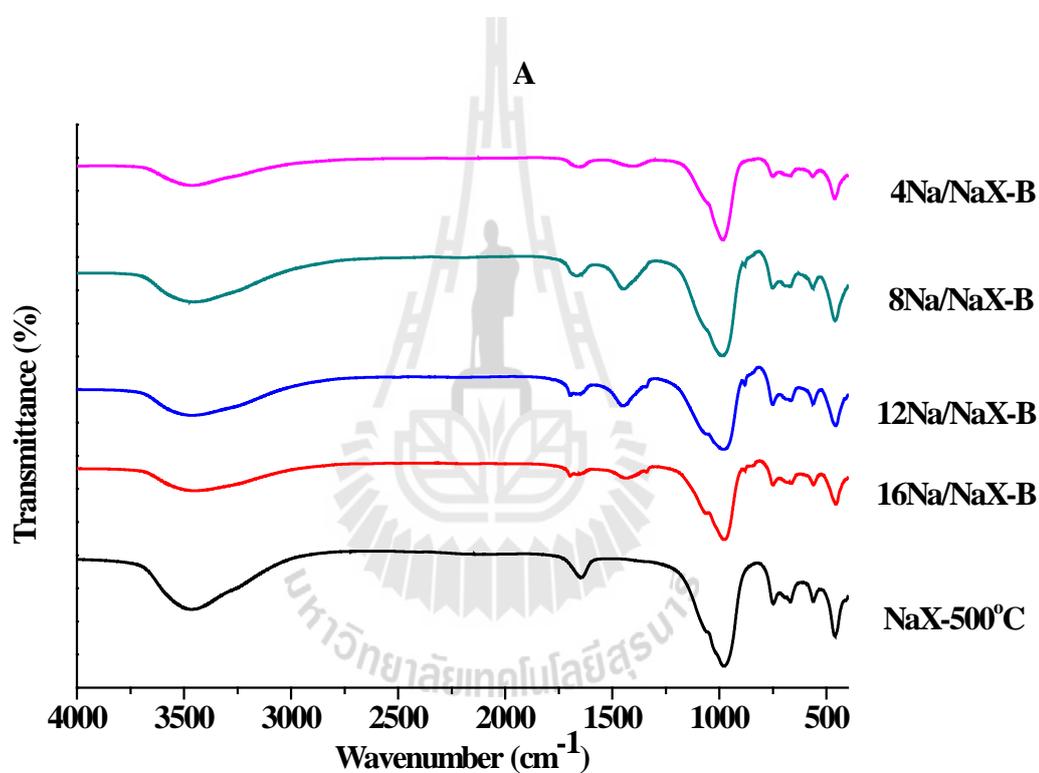
Figure 4.5 FTIR spectra of zeolite NaX and xNa/NaX-B (A)

B
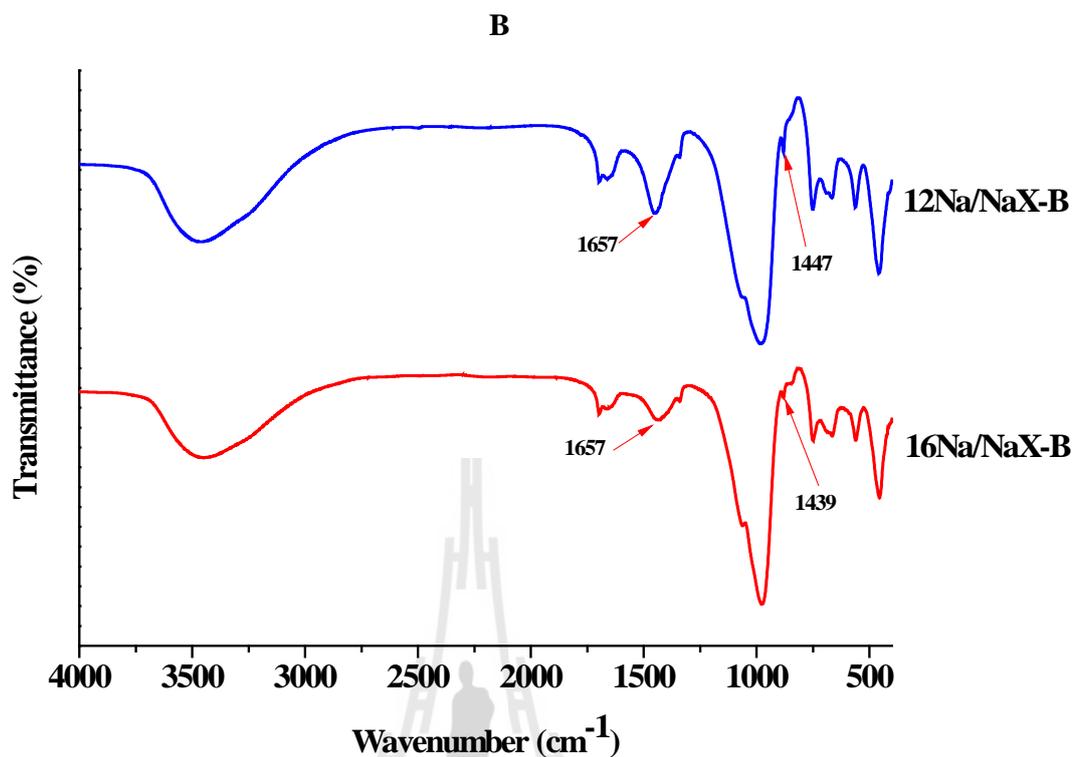
Figure 4.5 FTIR spectra of 12Na/NaX-B and 16Na/NaX-B (B).

4.3.4 Catalysts characterization by N_2 adsorption-desorption

The BET surface area and pore volume of zeolite NaX, xNa/NaX-A and xNa/NaX-B are listed in Table 4.1. The surface area and micropore volume of zeolite NaX from this work was in the same range as the results reported in literatures. The surface areas and pore volume of xNa/NaX-A and xNa/NaX-B decreased as amount of Na loading increased indicating that the resulting sodium oxide dispersed on surface of zeolite and occluded in the zeolite cavities. The large decrease in surface area could also also from the change of zeolite structure to amorphous phase. Similar results were obtained by Ramos et al. (2008) who suggested that impregnation of zeolite NaX with sodium acetate solution at 4.2 wt% resulted in the decrease in BET

surface area (from 711 to 186 m^2/g) and pore volume because sodium oxide resided in the zeolite cavities.

Table 4.1 Surface area of zeolite NaX, xNa/NaX-A and xNa/NaX-B catalysts.

Sample	BET surface area (m^2g^{-1})	Micropore volume (cm^3g^{-1})	External surface area (m^2g^{-1})	References
Zeolite NaX	591	0.27	-	Suppes et al., 2004
Zeolite NaX	432	0.17	52	Diaz et al., 2008
Zeolite NaX	711	0.29	-	Ramos et al., 2008
4.2 Na/NaX	186	0.10	-	Ramos et al., 2008
Zeolite NaX	650	0.27	72	This work
4Na/NaX-A	253	0.11	52	This work
8Na/NaX-A	187	0.07	28	This work
12Na/NaX-A	127	0.05	22	This work
16Na/NaX-A	120	0.05	21	This work
4Na/NaX-B	267	0.22	69	This work
8Na/NaX-B	236	0.15	56	This work
12Na/NaX-B	142	0.04	58	This work
16Na/NaX-B	118	0.03	50	This work

4.3.5 Catalysts characterization by CO_2-TPD

Figure 4.6 shows CO_2-TPD profiles of zeolite NaX. The peak in the temperature range of 100-200 °C and a broad peak at 200-400 °C attributed to weak basic sites. Borges, Diaza, Alvarez and Brito. (2011) reported that the KOH/pumice

catalysts possessed basic sites of weak, medium and high strength corresponding to OH^- groups, K–O and surface O^{2-} ions, respectively. The OH^- groups are Brönsted base sites while the others are Lewis basic sites. Ramos et al. (2008) suggested that the peak at approximately 150 °C was attributed to the interaction between CO_2 and weak basic site on the surface of zeolite NaX. In addition, only one type of adsorption site for CO_2 on zeolite NaX was reported by Diaz et al. (2008) at the temperature range of 200-400 °C. The parent zeolite NaX in the first cycle shows very low adsorption capacity, with a total capacity slightly higher than 2 mg g^{-1} (0.05 mmol g^{-1}). From this work the CO_2 desorption on NaX in all temperature range corresponded to the basicity of 0.8 x 10^5 mol g^{-1}.

Total basicity = 0.8 x10^5 mmol g^{-1}
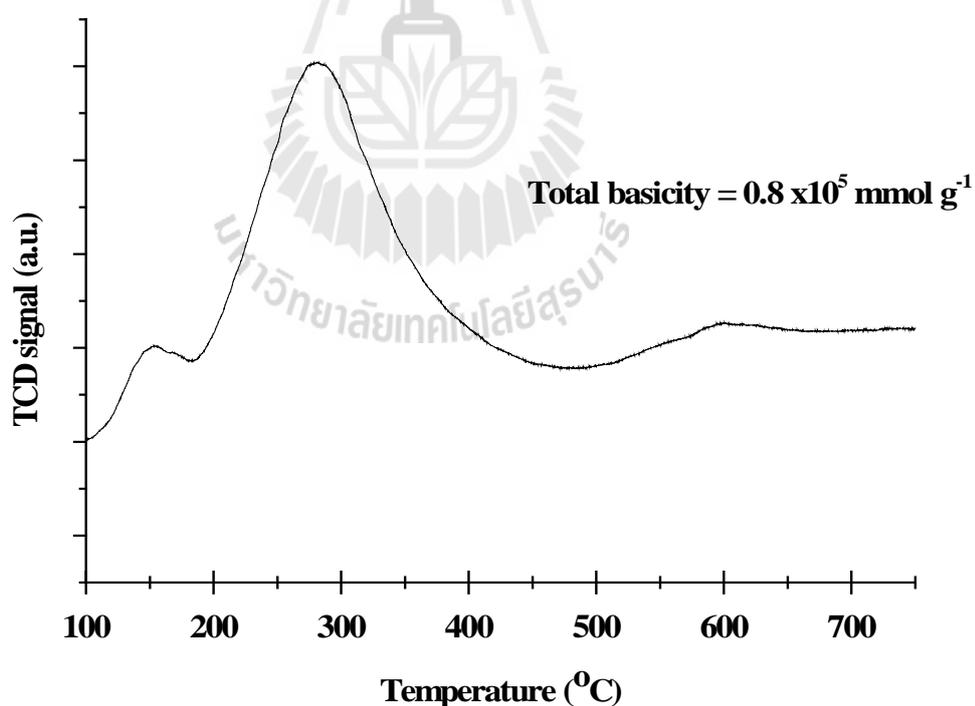
Figure 4.6 CO_2-TPD profiles of zeolite NaX.

Figure 4.7 shows CO_2-TPD profiles of xNa/NaX-A with Na loading of 4, 8, 12 and 16wt% after calcination. The main desorption peaks from all catalysts occurred at the temperature higher than 500 °C and the area of the peaks increased with sodium loading (see Table 4.2). Diaz et al. (2008) reported that CO_2 desorption peak from Na-loaded NaX located around 500-600 °C associated with the decomposition of sodium carbonate. In addition, the shift of the desorption peak to a slightly higher temperature in catalysts 8Na/NaX-A, 12Na/NaX-A, and 16Na/NaX-A implied a slight increase in basicity of these catalysts. Man et al. (2005) suggests that the higher of sodium loading may have forced sodium oxides to occupy small cages of the zeolites (i.e. double-six or -four ring cages) rather than in the channel systems. A slightly higher energy is needed to desorption the CO_2 in the small cages and thus, resulting in higher desorption temperature for these samples. However, the overall of 16Na/NaX-A catalysts had the desorption peak at around 500-800 °C larger area than that of other catalysts indicating higher basic sites. Ramos et al. (2008) reported that the strong basic sites on zeolite NaX loaded with Na by impregnation was the peak at 700 °C which may be attributed to the interaction of CO_2 with occluded sodium oxide species. Yagi, Tsuji and Hattori, (1997) suggested that alkali-added zeolite X possessed stronger basic sites, presenting desorption peaks of CO_2 above 400 °C. Furthermore, the strength of the basicity of xNa/NaX-A catalysts was slightly lower in which the maximum desorption temperature occur at slightly lower temperature than xNa/NaX-B catalysts (see below). This may be due to the fact that the framework structure of zeolite NaX impregnated with sodium acetate solution may have collapsed causing the sodium oxides to dislocate on to the amorphous surface of SiO_2 and Al_2O_3 (Man et al., 2005).
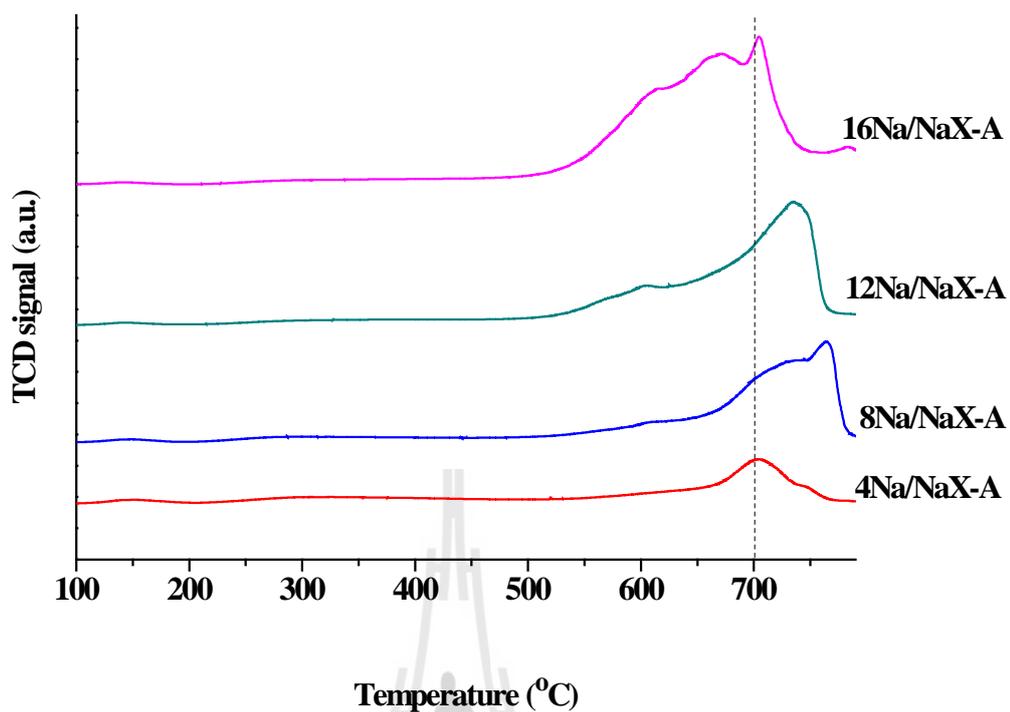
Figure 4.7 CO_2-TPD profiles of NaX and xNa/NaX-A with Na loading of 4, 8, 12 and 16 wt%.

Table 4.2 Total peak area of xNa/NaX-A catalysts.

Sample	Peak area
4Na/NaX-A	2.6×10^5
8Na/NaX-A	3.9×10^5
12Na/NaX-A	5.1×10^5
16Na/NaX-A	6.6×10^5

Figure 4.8 shows the CO_2-TPD profiles of NaX and xNa/NaX-A with Na loading of 4, 8, 12 and 16 wt% after the calcination. The amount of desorbed CO_2 increased with sodium loading (see Table 4.3) suggesting that the basicity increased with sodium loading. The main desorption occurred around 500-800 °C in all catalysts attributing to the strong basicity from Na_2O species generated after calcination. Doscocil and Mankidy (2003) reported that when sodium loaded on zeolites NaX, a new species of higher strength on NaX was formed by occlusion of sodium metal clusters or sodium oxide clusters. Increasing the loading of Na, the occluded species resulted in an increase in the number of CO_2 adsorption sites but did not significantly increase the highest strength of the sites formed on the catalyst. In addition, the result would apparently indicate that the sodium species (Na_2O) was responsible of the high catalytic activity of 16Na/NaX-B. Moreover, the peak area of the CO_2-TPD profile for xNa/NaX-B was higher than that for xNa/NaX-A, suggesting that the catalyst prepared from the acetate buffer solution had a higher basicity.
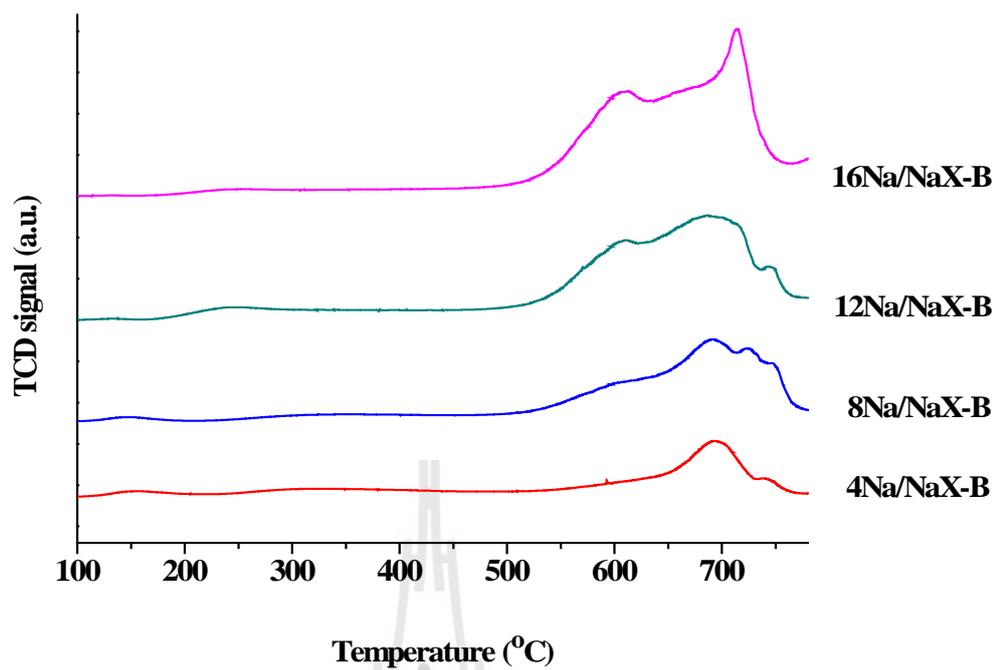
Figure 4.8 CO_2-TPD profiles of NaX and xNa/NaX-B with Na loading of 4, 8, 12 and 16 wt%.

Table 4.3 Peak area of xNa/NaX-B catalysts.

Sample	Peak area
4Na/NaX-B	2.8×10^5
8Na/NaX-B	4.1×10^5
12Na/NaX-B	5.4×10^5
16Na/NaX-B	8.1×10^5

4.4   Transesterification

4.4.1   Effect of Na loading in Na/NaX-A

The effect of Na loading in xNa/NaX-A on the conversion of Jatropha seed oil was preliminary determination by TLC. The results after transesterification for 3 h on these catalysts are shown in Figure 4.9. According to the spot size of crude Jatropha seed oil and biodiesel, the conversion increased with Na loading. This correlation was also observed by Ramos et al. (2008) who suggested that the increase in activity of NaX zeolite with increasing of Na loading associated to the basicity of the samples. Occlusion of oxide clusters in zeolite cages via decomposition of impregnated Na resulted in a further increase in the basicity of these samples. This factor would confirm that the presence of strong basic sites could influence on the catalytic activity of the transesterification of Jatropha seed oil. The 16Na/NaX-A provided the highest conversion but the reaction was not complete because the spot corresponding to crude Jatropha seed oil was still observed.
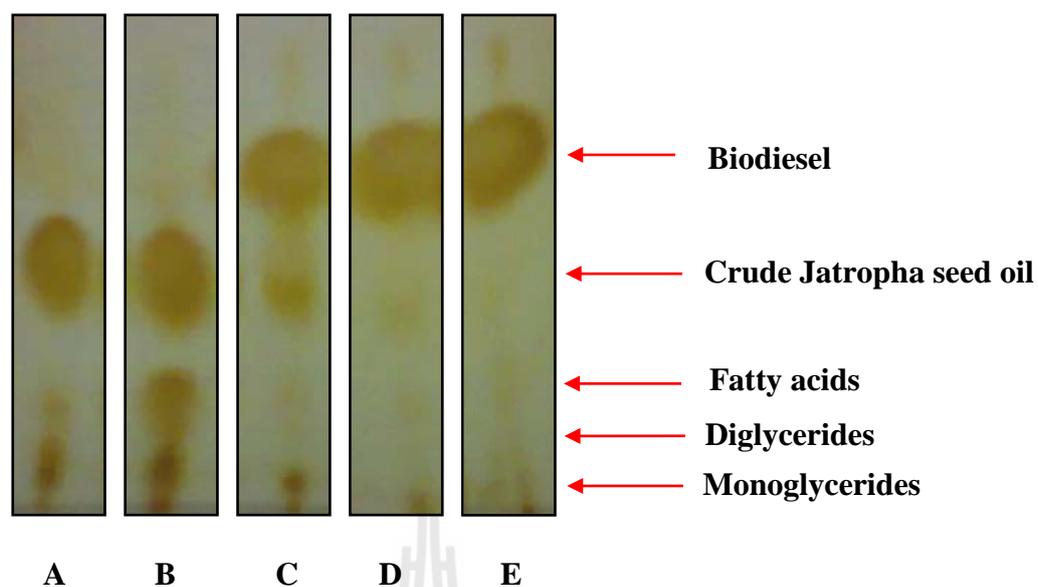
Figure. 4.9 TLC plate of product from transesterification with xNa/NaX-A; Crude Jatropha seed oil (A), (B) x = 4, (C) x = 8, (D) x = 12, (E) x = 16 wt% of Na loading. Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time = 3 h.

4.4.2 Effect of Na loading in Na/NaX-A on biodiesel yield

The transesterification products from the catalysts giving a complete conversion (by TLC analysis) were further analyzed by GC. The yields of biodiesel and basicity of 4, 8, 12 and 16 Na/NaX-A are shown in Table 4.4. The biodiesel yield of the transesterification and basicity of catalysts were increased with increased of Na loading. The yield from this work was lower than Na/NaX reported by Ramos et al. (2008). They loaded NaX with sodium acetate (4.2 wt%) and calcined at 500 °C before using as a catalyst for transesterification of sunflower oil to get biodiesel yield of 95.1wt%. Their higher yield could be attributed from the difference in the oil properties. Acid value of Jatropha seed oil was 4.11 mg KOH/g-sample where as that

of the sunflower oil was 0.09 mg KOH/g-sample. Acid value or neutralization number is a measure of mineral acids and free fatty acids contained in a fuel sample. The biodiesel yield decreased with high free fatty acids. Moreover, Ramos et al. (2008) suggested that the active species (Na_2O) from the highest concentration leached out to the reaction. In addition, the result from Di Serio et al. (2006) reported that the alkali metal oxide species occluded in zeolite cages, via decomposition of impregnated alkali metal salts were responsible for the high activity in the transesterification of sunflower oil. In addition, the results for the biodiesel yield using 8Na/NaX-A and 12Na/NaX-A were not significantly different because the basicity for these catalysts was not different. The 16Na/NaX-A catalyst was more active than other catalysts because it had the highest basicity. Suppes et al., (2004) reported the zeolite NaX impregnated with sodium azide at 1, 3 and 4 wt% had increased conversions of soy bean oil with Na loading due to increase of basicity and basic site. The increased incorporation of excess sodium oxide per supercage was found to be proportional to the conversion for the transesterification suggesting that the reaction was enhanced by the incorporation of additional basicity in the zeolite cages.

Table 4.4 Catalytic activity of the xNa/NaX-A catalysts.

Samples	Basicity (mmol CO_2/g)	% Biodiesel yield
4Na/NaX-A	0.9	29
8Na/NaX-A	1.5	72
12Na/NaX-A	1.8	76
16Na/NaX-A	2.5	85

4.4.3 Effect of Na loading in Na/NaX-B

The effect of sodium content in xNa/NaX-B on transesterification was studied. The results from transesterification for 3 h of these catalysts are shown in Figure 4.10. The conversion increased with Na loading and the 16Na/NaX-B catalyst provided a complete conversion. The conversion increased because the basic strength and the number of basic sites of the parent zeolite NaX increased.
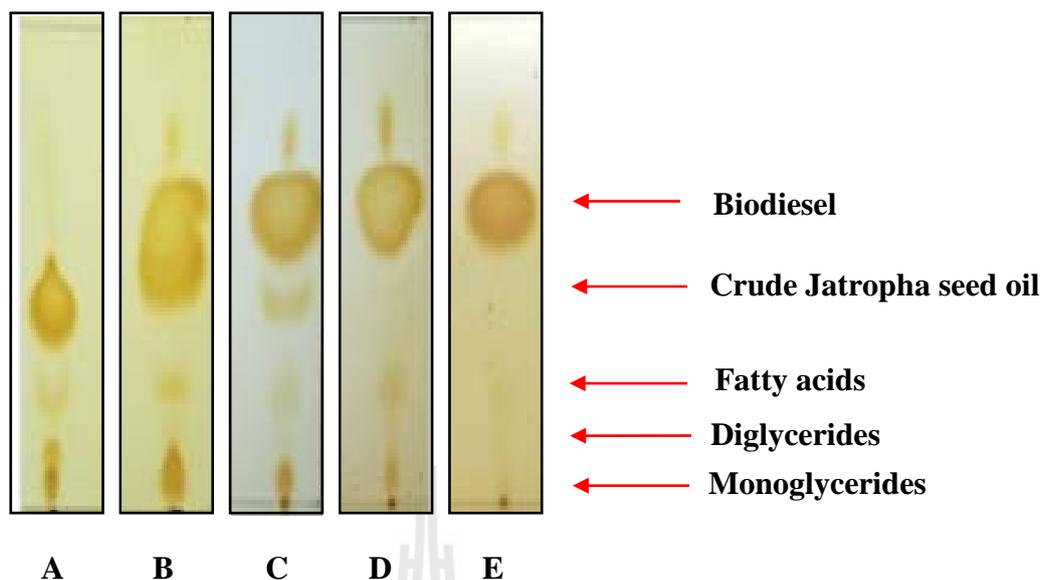
Figure 4.10 TLC plate of product from transesterification with xNa/NaX-B; Crude Jatropha seed oil (A), (B) x = 4, (C) x = 8, (D) x = 12, (E) x = 16 wt% Na loading. Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time = 3 h.

Thus, Na catalysts prepared from acetate buffer were more active than those prepared from acetate solution because the catalysts in latter case had lower surface area and crystallinity. Supamathanon et al. (2011) studied transesterification of Jatropha seed oil and methanol using a K/NaY catalysts prepared from potassium acetate buffer. The zeolite structure was not collapsed and it was possible to reuse the catalysts. Moreover, the 16Na/NaX-B was further tested for 2 h but a complete conversion was not obtained (Figure 4.11). Thus, the time for complete conversion is 3 h.
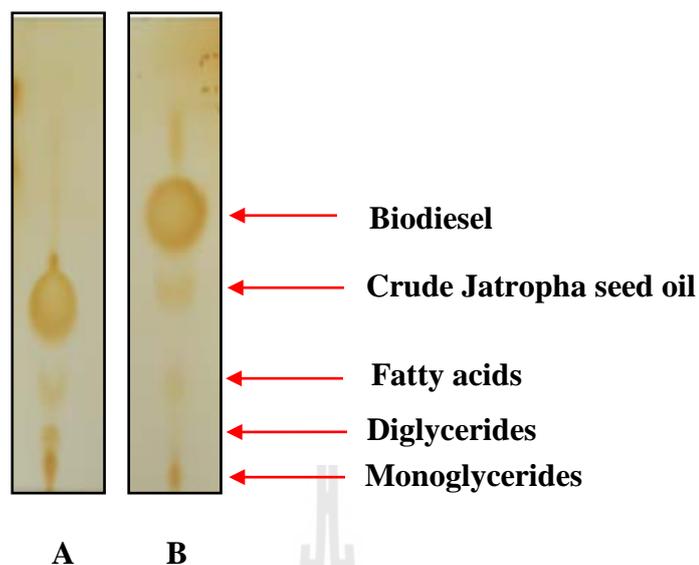
Figure 4.11 TLC plate of product from transesterification with 16Na/NaX-B comparing with the crude Jatropha seed oil. Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time in (A) = 2 h.

4.4.4 Effect of Na loading in Na/NaX-B on the biodiesel yield

The biodiesel yields from xNa/NaX-B determined by GC are shown in Table 4.5. The biodiesel yield increased with Na loading. The biodiesel yield from Na/NaX-B was higher than that from Na/NaX-A with similar Na loading. From TLC analysis, a complete conversion was obtained from 16Na/NaX-B which had the highest basicity. The biodiesel yield from this catalyst was 87%. Suppes et al. (2004) reported that presence of NaO_x/NaX as a catalyst obtained from sodium acetate or sodium azide precursor gave biodiesel yield of more than 80% because the occluded sodium oxide species increased the base strength and number of basic sites compared to the parent NaX zeolite.

Table 4.5 Catalytic activity of the xNa/NaX-B catalysts

Samples	Basicity (mmol CO_2/g)	% Biodiesel yield
4Na/NaX-B	1.2	37
8Na/NaX-B	2.1	75
12Na/NaX-B	2.2	78
16Na/NaX-B	2.6	87

4.5   Conclusions

Na/NaX-A and Na/NaX-B with Na loading of 4, 8, 12 and 16% were prepared from acetate and acetate buffer solutions of Na, respectively. Na resided mainly in the zeolite cavities resulted in decrease in surface area and micropore volume. High Na loading could result in partial collapse of the zeolite structure. With increase of Na loading, the basicity of catalysts was increased. The xNa/NaX-B had higher basicity than that of the Na/NaX-A with similar loading. In catalytic testing for biodiesel production, the catalytic activities increased with Na loading. A complete conversion and the highest biodiesel yield were obtained from 16Na/NaX-B which had the highest basicity.

4.6 References

Borges, M. E., Diaza, L., Alvarez, -G. M. C., and Brito, A. (2011). High performance heterogeneous catalyst for biodiesel production from vegetal and waste oil at low temperature. **Applied Catalysis B: Environmental**. 102: 310-315.

Diaz, E., Munoz, E., Vega, A., and Ordonez, S. (2008). Enhancement of the CO_2 retention capacity of X zeolites by Na- and Cs-treatments. **Chemosphere**. 70: 1375-1382.

Di Serio, M., Ledda, M., Cozzolino, M., Minutillo, G., Tesser, R., and Santacesaria, E. (2006). Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. **Industrial and Engineering Chemistry Research**. 45: 3009-3014.

Doskocil, E. J., and Mankidy, P. J. (2003). Effects on solid basicity for sodium metal and metal oxide occluded NaX zeolites. **Applied Catalysis A: General**. 252: 119-132.

Khemthong, P., Wittayakun, J., and Prayoonpokharach, S. (2007). Synthesis and characterization of zeolite LSX from rice husk silica. **Suranaree Journal of Science and Technology**. 14: 367-379.

Liu, H., Su, L., Liu, F., Li, C., and Solomon, U. -U. (2011). Cinder supported K_2CO_3 as catalyst for biodiesel production. **Applied Catalysis B: Environmental**. 106: 550-558.

Man, W. K., Ramli, Z., and Nur, H. (2005). Effect of loaded alkali metals on the structural, basicity and catalytic activity of zeolite Beta. **Jurnal Teknologi**. 42: 43-55.

Montalbo, K. D., De Leon, R. L., Sophiphun, O., Manadee, S., Prayoonpokarach, S., and Wittayakun, J. (2013). Characterization and catalytic performance of potassium loaded on rice husk silica and zeolite NaY for tranesterification of Jatropha seed oil. **Quimica Nova**. 36: 1116-1120.

Ramos, M. J., Casas, A., Rodriguez, L., Romero, R., and Perez, A. (2008). Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. **Applied Catalysis A: General**. 346: 79-85.

Supamathanon, N., Wittayakun, J., and Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. **Journal of Industrial and Engineering Chemistry**. 17: 182-185.

Suppes, G. J., Dasari, M. A., Doskocil, E. J., Mankidy, P. J., and Goff, M. J. (2004). Transesterification of soybean oil with zeolite and metal catalysts. **Applied Catalysis A: General**. 257: 213-223.

Yagi, F., Tsuji, H., and Hattori, H. (1997). IR and TPD (temperature-programmed desorption) studies of carbon dioxide on basic site active for 1-butene isomerization on alkali-added zeolite X. **Microporous and Mesoporous Materials**. 9: 237-245.

Yan, S., Kim, M., Steven, O., Salley, K.,Y., and Simon, Ng. (2009). Oil transesterification over calcium oxides modified with lanthanum. **Applied Catalysis A: General**. 360: 163-170.

Zhu, J., Chun,Y., Wang, Y., and Xu, Q. (1999). Attempts to create new shape-selective solid strong base catalysts. **Catalysis Today**. 51: 103-111.

CHAPTER V

CHARACTERIZATION AND CATALYTIC TESTING OF

POTASSIUM SUPPORTED ON ZEOLITE SODIUM X

Abstract

The aim of this chapter was to investigate properties of potassium catalysts supported on zeolite NaX (K/NaX) and their performance for biodiesel synthesis from Jatropha seed oil. The catalysts were prepared by impregnation NaX with a solution of potassium acetate buffer (B) to produce xK/NaX-B and potassium acetate (A) to produce xK/NaX-A where x is 4, 8, 12 and 16 wt% of K loading. The catalysts were characterized by XRD, FTIR, N_2 adsorption-desorption, and CO_2-TPD. Impregnation of the zeolite by both precursor solutions did not destroy the NaX structure but surface area and micropore volume decreased with increasing K loading. The basicity increased with the amount of K loading and lead to a better catalytic performance for biodiesel production. The best catalyst was 16K/NaX-B which gave the biodiesel yield of 95.2% when reaction was 3 h.

5.1   Introduction

This chapter involves an investigation on potassium supported on zeolite NaX (K/NaX) as catalysts for biodiesel synthesis from Jatropha seed oil. The results were compared with those in the previous chapters in which NaX was loaded with sodium. In addition, the results were compared with previous reports from literatures in which

potassium was loaded on zeolite NaY. In general, the catalyst activity depends on strength and amount of basic sites (Semwal, Arora, Badoni and Tuli, 2011). Between zeolite loaded with Na and K, the basicity of increased with increasing cation site (K > Na) because the electronegativity of cation site and the negative charge of oxygen atoms in the framework (Walton, Abney and Levan, 2006). Suppes et al. (2004) studied zeolite X modified by alkali metal as a solid base catalyst in biodiesel synthesis. Relatively weak basic sites and strong basic sites can be produced via alkali metal impregnation of basic components. It has been reported that the basicity of zeolite NaX can be increased by loading with larger cations such as K^+ (Martinez et al., 2011). The NaX loaded with K^+ is more effective than that loaded with other alkali ions, in terms of the basicity and transesterification activity, because the size of the larger ions affected the basicity associated with the framework oxygen. Xie et al., (2007) reported that zeolite NaX loaded with 10% KOH (KOH/NaX) was an effective base catalyst for transesterification of soybean oil. In their study zeolite NaX was first dried at 110 °C for 2 h then impregnated with aqueous solution of KOH for 24 h followed by drying and by heating at 120 °C for 3 h. The reaction was performed at reflux temperature (65 °C), 10:1 M ratio of methanol to oil and 3 wt. % catalysts and 85.6% conversion was achieved within 8 h.

The goal of this work was to prepare K/NaX catalyst by impregnation with a solution of potassium acetate buffer (B) or potassium acetate (A) to increase the basicity and hence, the reaction activity. The catalysts were characterized and tested for transesterification of Jatropha seed oil.

5.2 Experimental

5.2.1 Chemicals and materials

The chemicals for catalysts preparation were zeolite NaX, potassium acetate (CH_3COOK, 99% Unilab), glacial acetic acid (CH_3COOH, 100% BDH), and DI water.

5.2.2 Preparation and characterization of K/NaX catalysts

The xK/NaX catalysts were prepared with a method similar to that in Chapter IV. All catalysts were characterized by XRD, FTIR, N_2 adsorption-desorption, and CO_2 temperature programmed desorption (CO_2-TPD). The catalysts were characterized with techniques mentioned in Chapter III and IV. Powder XRD (Bruker axs D5005 diffractometer) was used to identify the crystal phase of the parent zeolites and the catalysts. FTIR (Perkin Elmer Spectrum GX spectrometer) was used to investigate the characteristic functional groups of the synthesized samples. The surface area of the catalysts was determined by N_2 adsorption-desorption analysis (Micromeritics ASAP 2010). The CO_2-TPD analysis was carried out using a BELCAT-B was used to obtain information on the basic sites of the catalytic samples.

5.2.3 Catalytic performance for transesterification

The catalysts were tested for biodiesel production with a procedure and conditions similar to those described in Chapter IV. The biodiesel obtained was monitored by TLC and the compositions of biodiesel from the reaction were determined by GC-FID.

5.3   Results and Discussion

5.3.1 Catalysts characterization by XRD

The XRD patterns of zeolite NaX and K/NaX-A at various loading are shown in Figure 5.1. When the amount of K loading was increased, the peak intensity of zeolite NaX was more decreased because the ionic size of K^+ could scatter the X-ray more than Na^+ in cavity of the zeolite. This result agreed with the report by Pena et al. (2012) that the XRD intensity of zeolite NaX decreased with the amount of KNO_3 loading due to the collapse of the zeolite framework which depended on the type of cation. Joshi et al. (2003) explained that this effect was due to the variation in the charge to size ratio of different nonframwork cations which was responsible for the X-ray scattering. The XRD patterns were almost the same as the typical pattern of zeolite NaX and new phase of K_2O was not observed at 2-theta because of the good dispersion of K. Similar observation was reported by Noiroj et al. (2009) who explained that the phase of potassium at low KOH loading (5-10 wt%) on Al_2O_3 was not observed in the XRD patterns because of the good dispersion of KOH on Al_2O_3. When the K was increased to 7-15 wt%, the peak intensity decreased with KOH loading. Xie et al. (2007) reported that KOH/NaX with K loading of 4-14 wt% gave similar XRD pattern to the parent NaX. They explained that the KOH modification could maintain the pore structure of zeolite that is necessary for catalysis. Besides, Intarapong et al. (2011) found that the high amount of KOH loaded on NaY could change the zeolite structure to amorphous phase. Therefore, using KOH as a modifier has some intense interaction with the surface of the zeolite. Moreover, the decrease in peak intensity could be due to a decrease in zeolite crystallinity and secondary scattering of X-ray by K species.
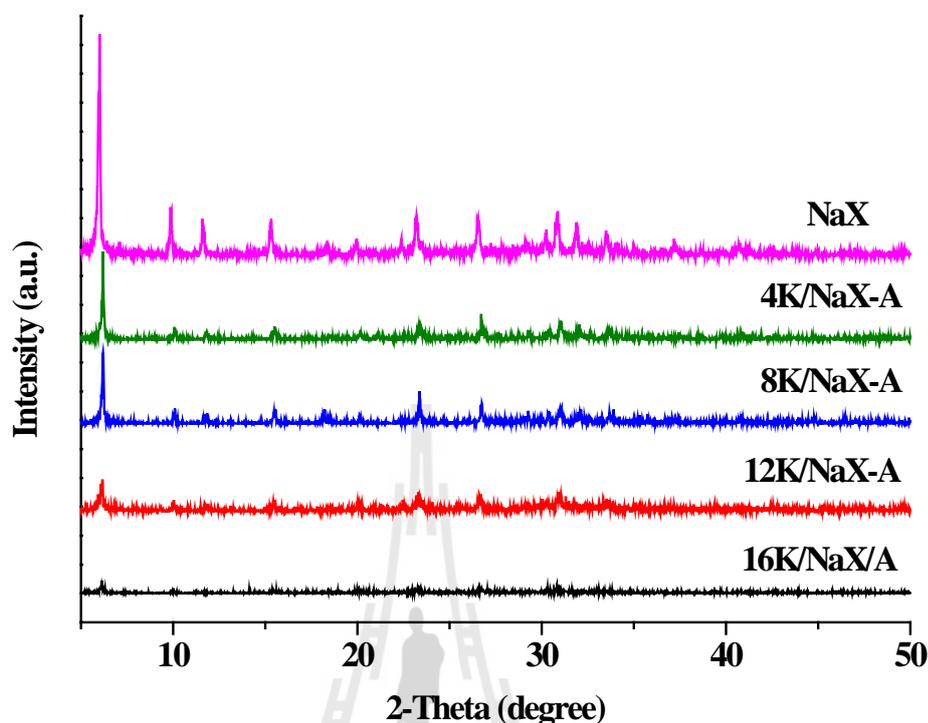
Figure 5.1 XRD patterns of the zeolite NaX and xK/NaX-A catalysts when x = 4, 8, 12 and 16 wt% K loading.

The XRD patterns of zeolite NaX and K/NaX-B with various K loading are shown in Figure 5.2. Characteristic peaks of NaX similar to those in the literature (Khemthong et al., 2007) were still observed in all catalysts indicating that impregnation with the buffer solution did not destroy the zeolite structure. This observation was similar to the work of Supamathanon et al. (2011) who observe the characteristic peaks of NaY when treatment with 4-12 wt% potassium acetate buffer solution was used. The results indicated that changing potassium precursor from KOH to potassium acetate buffer could better preserve the zeolite structure. The peaks intensity of the zeolite NaX decreased with an increase of K loading due to decrease

in zeolite crystallinity and secondary scattering of X-ray by potassium species. Xue et al. (2009) also stated that CH_3COOK on zeolite samples with loading of 9-47 wt%. The characteristic peaks for CH_3COOK or K_2O were not observed probably due to good dispersion of K^+ derived from CH_3COOK on zeolite NaX in the form of various compounds. In addition, the K_2O phase whose peaks are at 2-Theta of 31°, 39°, 51°, 55° and 62° were not detected by XRD because it may have dispersed on the zeolite NaX surface as a monolayer. The characterization results indicated that the active sites on the catalyst were K_2O derived from CH_3COOK, surface hydroxyl groups, and Al-O-K (or Si-O-K) groups.
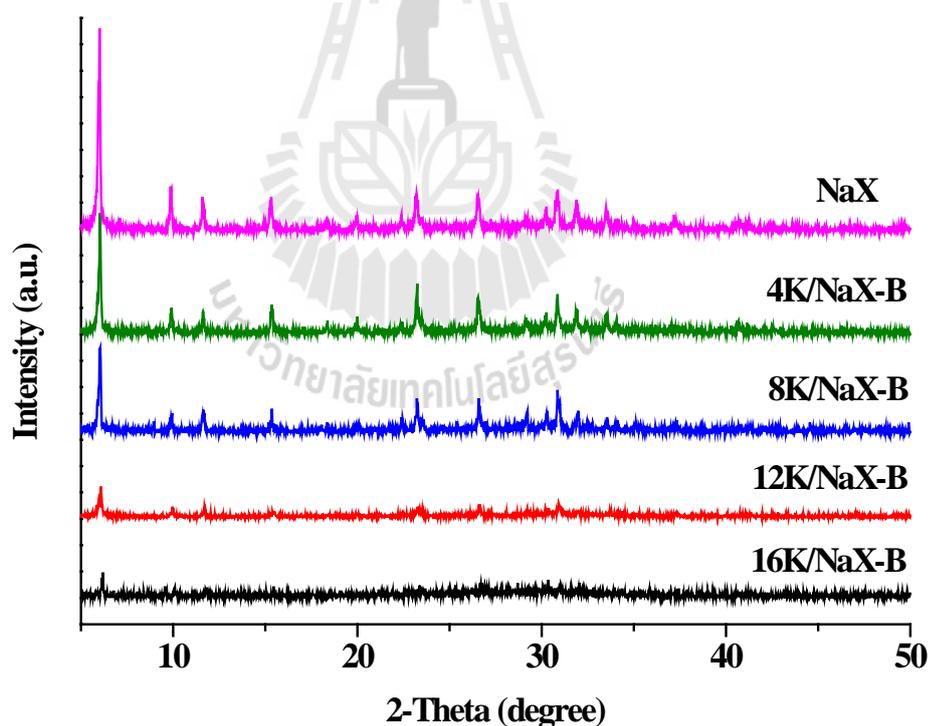
Figure 5.2 XRD patterns of the zeolite NaX and xK/NaX-B catalysts when x = 4, 8, 12 and 16 wt% K loading.

The XRD patterns of 12K/NaX-A, 16K/NaX-A, 12K/NaX-B and 16K/NaX-B are compared in Figure 5.3. The result showed that when the amount of K loading increased, the peak intensity got decreased. The change could relate to the decrease in the crystallinity from agglomeration of the oxide species in the zeolite cavity. The presence of the characteristic peaks of the zeolite after metal loading indicated the preservation of the zeolite structure. Moreover, the absence of K_2O peaks indicated a good dispersion of the metal oxide on the zeolite surface. This work agreed with Montalbo et al. (2013) who studied zeolite NaY loaded with potassium acetate buffer solution. The use of potassium acetate buffer solution could preserve the zeolite structure better than the use of potassium acetate solution due to the hydrolysis of Si-O-Al bonds by the alkali metal during the thermal treatment of the zeolite. Hydrolysis might occur at a greater extent when potassium acetate is used because it is more basic than the acetate buffer solution.
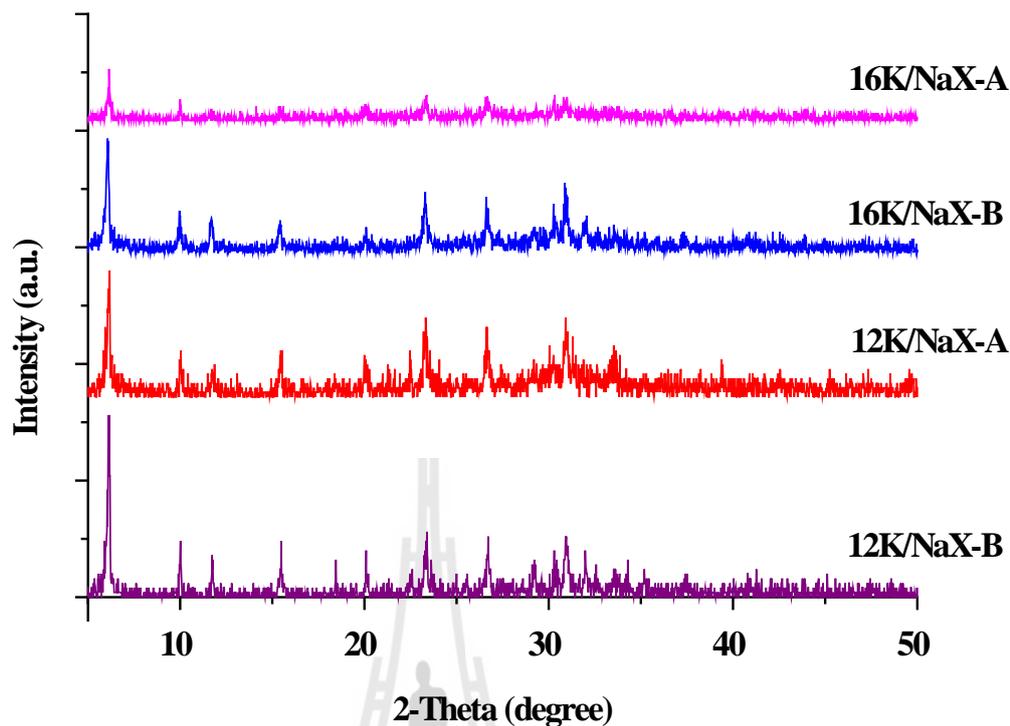
Figure 5.3 XRD patterns of the xK/NaX-A and xK/NaX-B catalysts when x = 12 and 16 wt% K loading.

5.3.2 Catalysts characterization by Fourier transformed infrared (FTIR) spectroscopy

The FTIR spectra of CH_3COOK are shown in Figure 5.4A. The characteristic spectra of CH_3COOK were observed at 1577 cm^{-1} assigned to asymmetric vibration peak of COO^- and band at 1407 cm^{-1} indicated to asymmetric stretching peak of COO^-. The band at 1653 cm^{-1} corresponded to stretching of C=O and band at 1340 cm^{-1} corresponded to C-C vibration. The bands at 1054 cm^{-1} and 1014 cm^{-1} were assigned to Si_2O vibration band. The bands at 923 cm^{-1} and 659 cm^{-1} corresponded to OH on surface and SiOAl, respectively. Cruz and Duro (1999) reported that the FTIR of kaolinite-potassium acetate. The bands at 1115 cm^{-1}, 1031

cm^{-1} and 1009 cm^{-1} are due to in-plane Si$_2$O vibrations; bands at 912-939 cm^{-1} were attributed to OH deformation (inner surface and inner OH groups, respectively). The bands at 1586 cm^{-1} and 1410 cm^{-1} assigned from COO$^-$ asymmetric vibration of the symmetrical COO$^-$. All samples were calcinated at 400 °C the FT-IR spectra are shown in Figure 5.4B. The spectra of catalysts showed almost constant intensity of bands irrespective the amount of K loaded. These observations indicated that K loading had no distinct effect on the structure of NaX (Xie et al., 2007). The band at 1664 cm^{-1} was assigned to the Si-O-Si stretching vibrations (Intarapong et al., 2011) and band at 1422 cm^{-1} was assigned to the carbonate species of K$_2$CO$_3$. As reported by Yaki et al. (1997) that the carbonate group of K added on zeolite NaX were observed around 1400 cm^{-1} and 1550 cm^{-1}. Moreover, the broad band at 3432 cm^{-1} could be partly assigned to stretching vibrations of Al-O-K or Si-O-K groups. According to Xue et al. (2009) K$^+$ ions could replace the protons of OH groups on the support during activation to form Al-O-K or Si-O-K groups, and could be active basic species of this catalyst in transesterification.
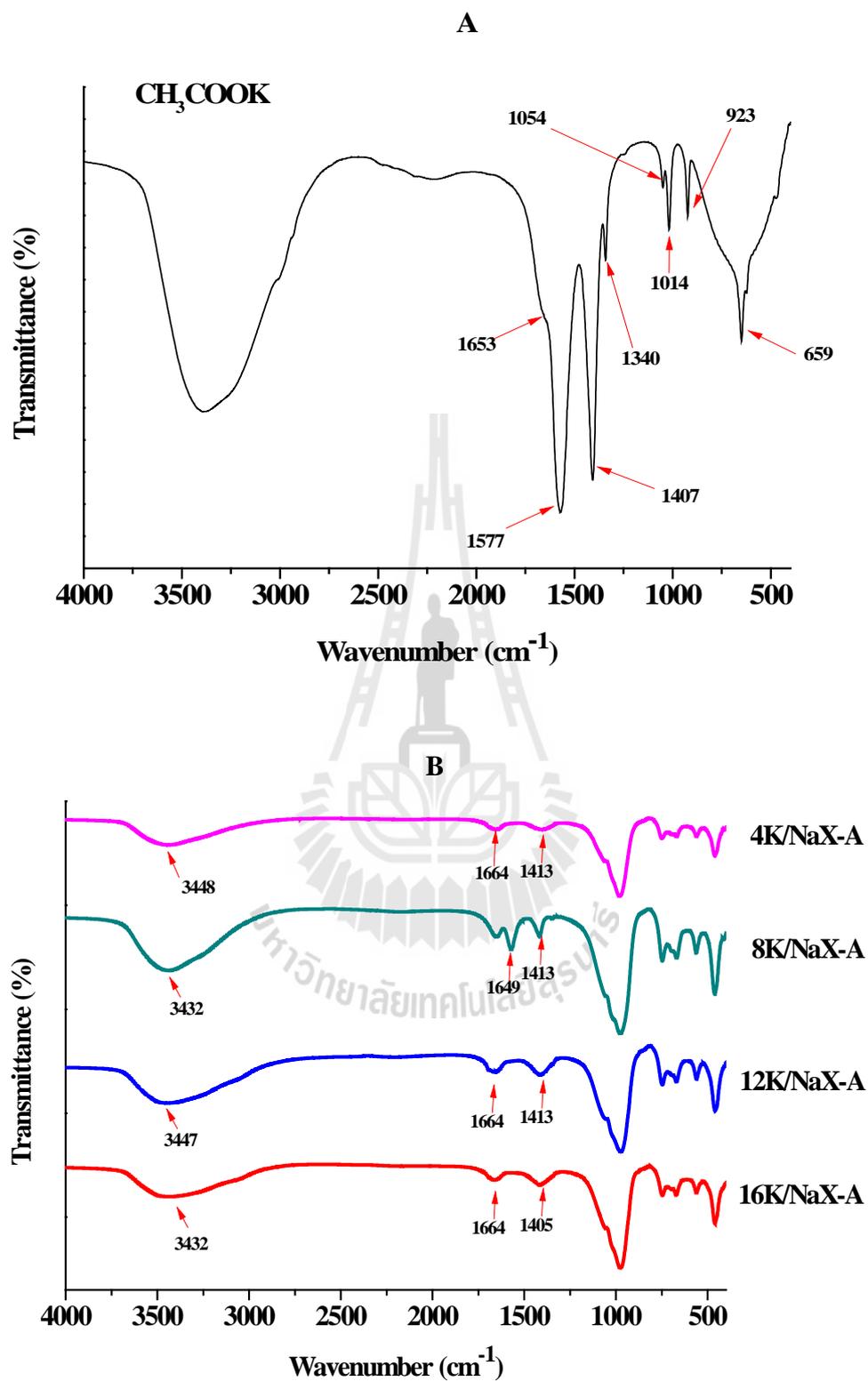
Figure 5.4 FTIR spectra of CH$_3$COOK (A), and xK/NaX-A (B).

The FTIR spectra of zeolite NaX with K loading are shown in Figure 5.5. The characteristic band at 1407 cm^{-1} was assigned to COO$^-$ asymmetric stretching. The bands at 1577 cm^{-1} and 1641 cm^{-1} attributed to COO$^-$ symmetric vibration bands of CH_3COOK were not observed. In addition, there were strong bands at 1457 cm^{-1} and 1385 cm^{-1} attributing to carbonate species of K_2CO_3. According to Liu et al. (2011) the band of T–O bond was weaker and shifted to 1119 cm^{-1} indicating that the T–O bond participated in the reaction between K_2CO_3 and support.
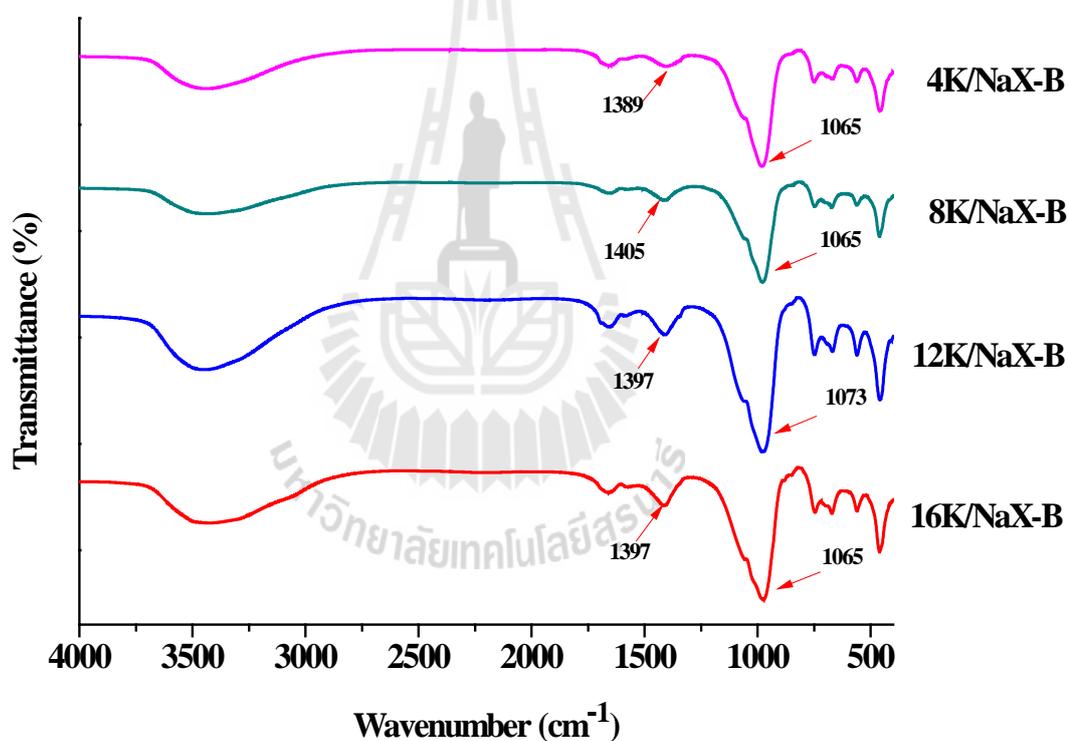
Figure 5.5 FTIR spectra of xK/NaX-B.

5.3.3   Catalysts characterization by N_2 adsorption-desorption

The BET surface area and pore volume of zeolite NaX and xK/NaX are listed in Table 5.1. The surface area and micropore volume of NaX decreased with the increase of the amount of K species. These results indicated that the K species were deposited mainly in micropores of the zeolite NaX as well as on external surface. Futhermore, 4K/NaX-A and 8K/NaX-A had a lower surface area than that of 4K/NaX-B and 8K/NaX-B, respectively because amorphization or collapse of the zeolite structure might occur during calcination. Man et al. (2005) studied the BET suface area of zeolite Beta with alkaline loading and found that the surface area decreased as the metal loading increased. These results were attributed to the dissolution of part of the framework during impregnation and pore filling by the potassium oxides. On the other hand, 12K/NaX-A and 16K/NaX-A had a higher surface area than that of the 12K/NaX-A and 16K/NaX-A catalysts. It was plausible that the part of the K species which was initially deposited on the catalyst surface was leached out from the zeolite. Liu et al. (2011) related the BET surface area of K_2CO_3 impregnated with high concentration. The less available base active points were induced by the decreased surface area and blockage of the inner pore or collapses of smaller pores. Beside, Noiroj et al. (2009) suggested that the loss of surface area in the catalyst had lesser impact than that of active species on the catalyst. The result of this present study implied that the support type strongly affects the chemical activity of the heterogeneous catalysts for the transesterification of Jatropha seed oil. The results also suggested that K species on the NaX zeolite was strongly bound to the surface area. Martin et al. (2007) recommended that the active species of heterogeneous catalysts must be not leached out from the solid-supporting materials

because the leached species in the reaction mixture could act as homogeneous types and reduced the efficiency of the heterogeneous catalysts. Importantly, the buffer solution could prevent the zeolite framework from collapses and improved the catalytic activity.

Table 5.1 Surface area of zeolite NaX, xK/NaX-A and xK/NaX-B catalysts were calcined at 500 °C.

Sample	BET surface area (m^2g^{-1})	Micropore volume (cm^3g^{-1})	External surfac area (m^2g^{-1})
Zeolite NaX	650	0.27	72
4K/NaX-A	537	0.23	52
8K/NaX-A	521	0.16	54
12K/NaX-A	387	0.16	69
16K/NaX-A	327	0.14	58
4K/NaX-B	567	0.25	57
8K/NaX-B	549	0.20	54
12K/NaX-B	325	0.15	34
16K/NaX-B	250	0.09	57

5.3.4 Catalysts characterization by CO_2-TPD

Figure 5.6 shows CO_2-TPD profiles of NaX and xK/NaX-A with K loading of 4, 8, 12 and 16 wt%. The profiles of xK/NaX-A consisted of main peaks in

the temperature range of 550-800 °C attributing to desorption from strong basic sites, namely, the interaction between CO_2 and Lewis basic site on the zeolite NaX. The peak area increased with K loading suggesting an increase in basicity. Furthermore, the basic site and basic strength in the zeolite increased with cation size. Thus, it could be expected that CO_2 would interact more strongly with K/NaX than with Na/NaX. Walton et al. (2006) studied the alkali metal cations (Li, Na, K, Rb and Cs) exchange into zeolite NaX. The Lewis basicity of oxygen atoms in the framework of alkali metal exchange zeolite increases with the cation size. There were several peaks in this range indicating various sites with different basicity. The peaks in the range of 500-600 °C refer to the moderate basic sites. Intarapong et al. (2011) studied the K loaded on zeolite NaY with various amount of K (5, 10, 15 and 20 wt%) and showed that the 10 wt% of K gave two desorption peaks at about 240 °C referring to weak basic site and at 400 °C referring to the moderate basic sites. Di Serio et al. (2006) reported the presence of these species of basic sites as super-basic sites at temperature of over 350 °C. The catalysts with K from 15-20 wt% had occluded K species which gave a peak at around 400 °C due to strong basic sites which were responsible for high activity of the catalysts.
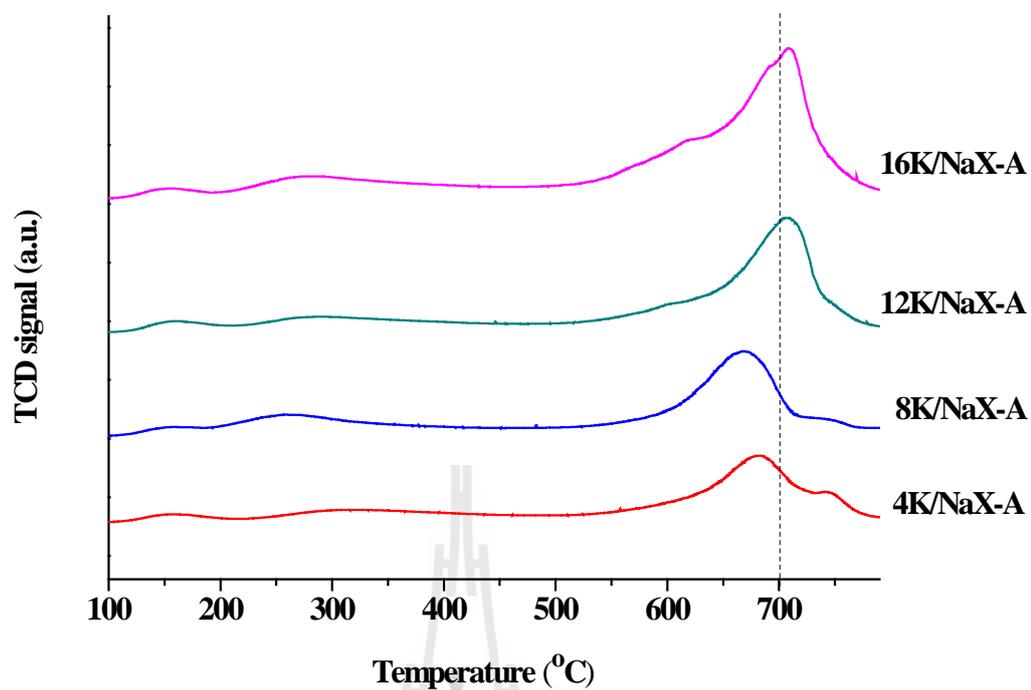
Figure 5.6 CO$_2$-TPD profiles of NaX and xK/NaX-A with K loading of 4, 8, 12 and 16 wt%.

Table 5.2 Peak area of xK/NaX-A.

Sample	Peak area
4K/NaX-A	3.2 x 10^5
8K/NaX-A	5.1 x 10^5
12K/NaX-A	6.6 x 10^5
16K/NaX-A	7.3 x 10^5

The CO_2-TPD profiles of the K/NaX-B catalysts with K loadings of 4, 8, 12, and 16 wt% are shown in Figure 5.7. The CO_2 desorption peak was observed at high temperature attributing to the strong basic sites. The peak areas increased with the increase of potassium loading. In addition, almost all xK/NaX-B catalysts had higher peak area than the xK/NaX-A with similar K loading, suggesting that the catalysts prepared from the acetate buffer had higher basicity. Montalbo et al. (2013) studied K/NaY prepared by loading the potassium acetate buffer solution and potassium acetate as a precursor on zeolite NaY. From the CO_2-TPD profile, the desorption occurred between 550 °C and 800 °C, which corresponds to a strong basicity and clusters of oxides in the zeolite cavity. In addition, the peak area for 12K/NaY-B was larger than that for 12K/NaY-A, suggesting that the catalyst prepared by the acetate buffer solution had a higher basicity.
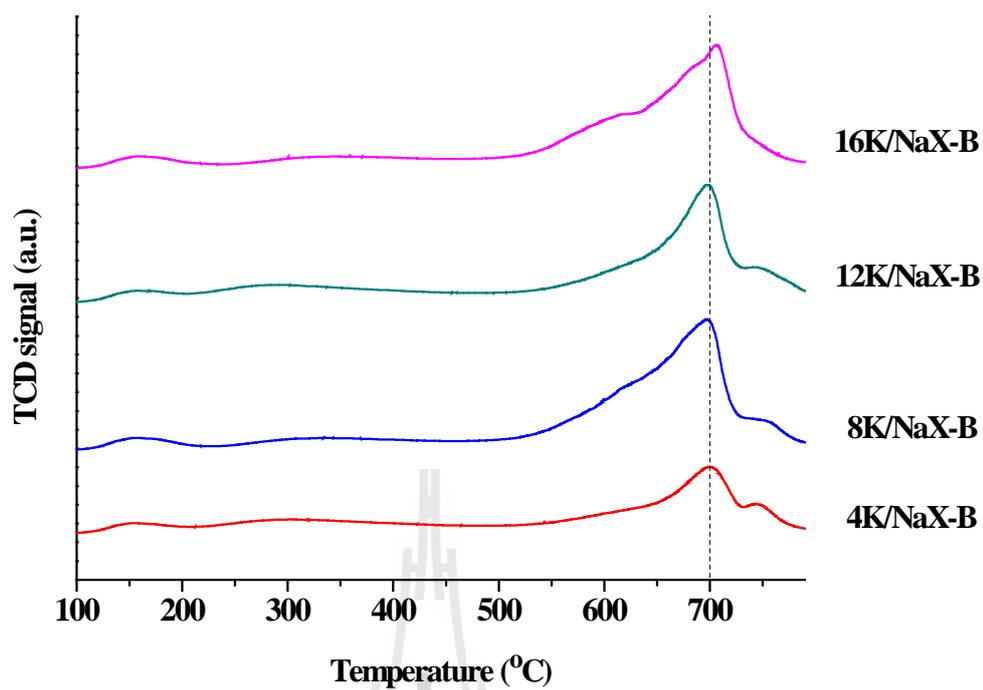
Figure 5.7 CO_2-TPD profiles of NaX and xK/NaX-B with K loading of 4, 8, 12 and 16 wt%.

Table 5.3 Peak area of xK/NaX-B.

Sample	Peak area
4K/NaX-B	3.4×10^5
8K/NaX-B	5.8×10^5
12K/NaX-B	7.3×10^5
16K/NaX-B	8.9×10^5

5.4   Transesterification

5.4.1   Effect of K loading in K/NaX-A

The effect of potassium loading in xK/NaX-A on transesterification was studied. The results are shown in Figure 5.8. The biodiesel yield increased with K loading but spot of crude Jatropha seed oil was still observed from all catalysts indicating an incomplete conversion. Vyas et al. (2009) indicated an increase in the conversion in the transesterification of jatropha oil using K loaded on Al_2O_3 as a catalyst. These catalysts showed the highest conversion because they were strong solid base catalysts. Besides, Noiroj et al. (2009) employed KOH/Al_2O_3 and KOH/NaY as the catalysts for transesterification of palm oil with methanol. Although both KOH/Al_2O_3 and KOH/NaY gave the highest biodiesel yield, the lower K weight in KOH/NaY made it a more active catalyst. Their results showed that the support type strongly affected the activity of the heterogeneous catalyst for the transesterification. Thus, zeolites are more suitable supports than alumina because potassium bound to NaY more strongly than to alumina. However, the potassium leached out from the surface of both NaY- and alumina-supported catalysts under the optimum conditions. The leached active species could then act as a homogeneous catalyst which was difficult to separate from the product mixture. Moreover, high loading of KOH could cause collapse of the zeolite crystalline structure.
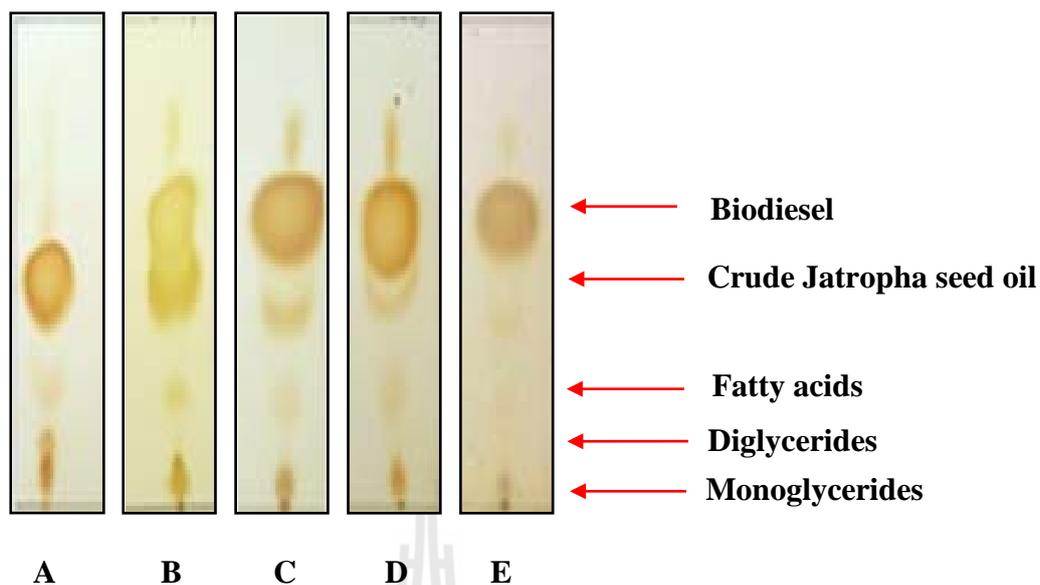
Figure 5.8 TLC plate of product from transesterification with xK/NaX-A; crude Jatropha seed oil (A), (B) x = 4, (C) x = 8, (D) x = 12, (E) x = 16 wt% K loading. Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time = 3 h.

5.4.2 Effect of K loading in K/NaX-A on the biodiesel yield

The biodiesel yields from xK/NaX-A were determined by GC. The results after transesterification for 3 h on these catalysts are shown in Table 5.4. The biodiesel yield increased with K loading and the 16K/NaX-A gave the highest biodiesel yield of 84%. This catalyst had more basic site and higher basic strength than other catalysts. Pena et al. (2012) reported biodiesel production from sunflower oil with methanol using zeolite NaX loaded with potassium nitrate. The amount of potassium oxide resulted in an increase in the basicity and the number of basic sites and therefore, an increased of biodiesel yield. Xie et al. (2006) concluded that the K_2O derived from decomposition of KNO_3 during calcinations was probably the main

active sites in the transesterification of soybean oil. Xie and Hung (2006) reported that the use of KOH-promoted zeolite NaX enhanced biodiesel yield to 85% in 8 h at 66 °C and the methanol to oil molar ratio of 10:1. Xie et al. (2007) studied transesterification of soybean oil and methanol using zeolite NaX loaded with KOH as a catalyst and found that the best catalyst was from the 10% KOH loading. The biodiesel yield was 85.6% but the reaction time was long (8 h) and the reaction temperature was high (120 °C). Broges et al. (2011) reported that the biodiesel yield of 80.8% was obtained from potassium acetate loaded on zeolite NaX at reaction temperature of 155 °C, methanol to oil molar ratio of 48:1 and the amount of catalyst of 6 wt%. In this study, the methanol to oil molar ratio 16:1 was used and this ratio was enough to complete the transesterification. Too much methanol would cause a flooding of available sites. The use of K species increased basicity because the electropositivity and size of the cation influenences the amount of negative charge on the oxygen atoms in the framework structure (Walton et al., 2006). In other studies, Di Serio et al. (2006) conducted a study using occluded NaO_x species in zeolite X which significantly increased the strength and concentration of basic sites and ultimately enhanced the reaction activity. The biodiesel yield from soybean oil increased from 22.7 to 94.2% when changing from NaO_x/NaX to K-X.

Table 5.4 Catalytic activity of the xK/NaX-A catalysts.

Samples	Basicity (mmol CO_2/g)	% Biodiesel yield
4K/NaX-A	1.0	35
8K/NaX-A	2.1	75
12K/NaX-A	2.2	79
16K/NaX-A	2.4	84

5.4.3 Effect of K loading in K/NaX-B

The effect of potassium loading in xK/NaX-B on the conversion of Jatropha seed oil was followed by TLC. The results after transesterification for 3 h on these catalysts are shown in Figure 5.9. According to the spot size of crude Jatropha seed oil and biodiesel, the conversion increased with K loading. The 16K/NaX-B gave a complete conversion because only a spot of biodiesel was observed. As mentioned earlier, the 16K/NaX-A which was prepared by impregnation of acetate solution showed an incomplete conversion of Jatropha seed oil to biodiesel. Thus, the catalysts prepared from acetate buffer solution were more active than those prepared from acetate solution. The K from buffer solution can be dispersed on zeolite NaX better than the K from acetate solution. The result from this work could be related to the work of Noiroj et al. (2009) which indicated that the agglomeration of the active K species or the covering of the basic sites from excess K led to less the surface area and activity.
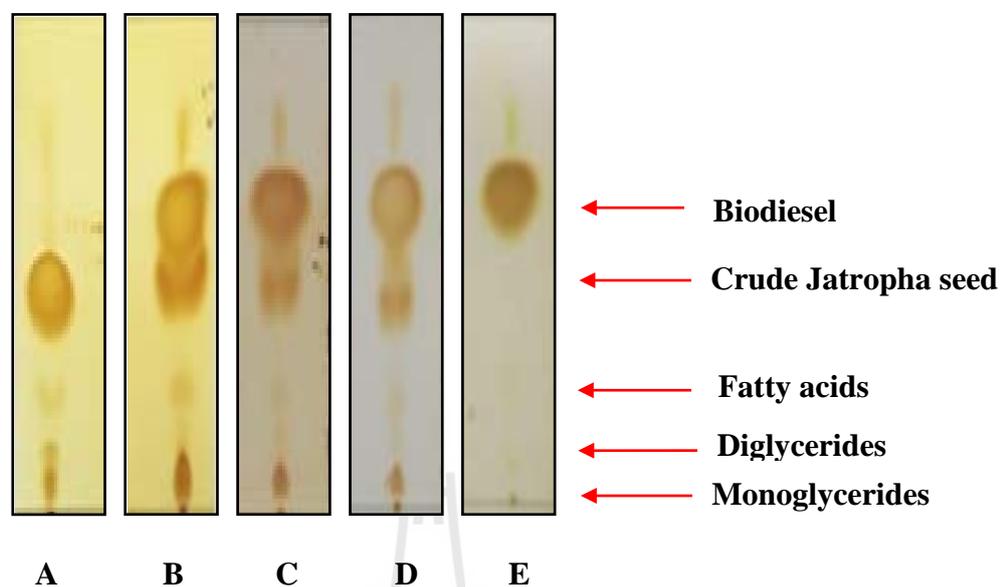
Figure 5.9 TLC plate of product from transesterification with xK/NaX-B; Crude Jatropha seed oil (A), (B) x = 4, (C) x = 8, (D) x = 12, (E) x = 16 wt% K loading. Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time = 3 h.

Because 16K/NaX-B gave the highest conversion, it was tested in the transesterification for 2 h. The result is shown in Figure 5.10. However, a complete conversion was not achieved within 2 h. Thus, it could be concluded that the time for complete conversion was 3 h.
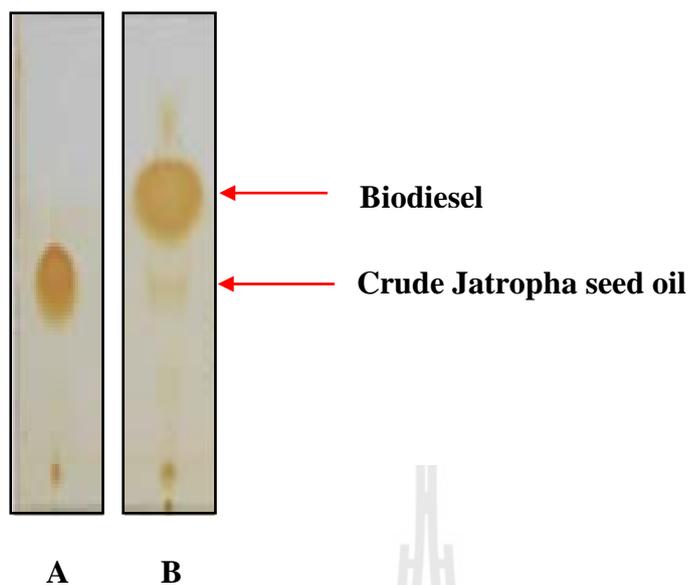
Figure 5.10 TLC plate of product from transesterification with 16K/NaX-B comparing with the crude Jatropha seed oil (A). Reaction condition: methanol to oil molar ratio = 16:1, temperature = 65 °C, and testing time = 2 h.

5.4.4   Effect of K loading in K/NaX-B on the biodiesel yield

The biodiesel yields from xK/NaX-B determined by GC are listed in Table 5.5. These results are consistent with the estimation by TLC that the biodiesel yield of catalysts for transesterification increased with K loading. Noiroj et al. (2009) studied the production of biodiesel from plam oil using KOH/NaY with the K loading from 7 to 15 wt%. They found that the biodiesel yield of 91.07% was obtained from the catalyst with K loading of 10 wt%, the reaction time 3 h, methanol to oil molar ratio of 15:1, reaction temperature at 60 °C, and the amount of catalyst at 6 g. Intarapong et al. (2011) studied the transesterification of plam oil by using K/NaY prepared from KOH with K loading of 5, 10, 15 and 20 wt%, a methanol to oil molar ratio of 15:1, a reaction time of 7 h. They found that the activity increased with the K

content and the biodiesel yield increased from 41.1 to 92.24%. The catalytic activity

is dependent on the basicity and the highest activity from 15%K/NaY corresponded to

its high number of basic sites. In this study, a methanol to oil molar ratio was 16:1,

reaction temperature was 65 °C and the amount of catalyst employed in this study was

6 g. The biodiesel yield from such condition from 16K/NaX-B was 95%.

The effect of the reaction time on biodiesel yield was studied on

16K/NaX-B because it gave the highest biodiesel yield. From TLC results, the

conversion increased with time and only 16K/NaX-B gave a complete conversion.

The reaction time on the transesterification of Jatropha seed oil to biodiesel was

studied with 1, 2 and 3 h. The yields obtained from GC analysis of the products at

various reaction times were 74, 83 and 95%, respectively. The lowest biodiesel yield

from 1 and 2 h than 3 h might come from a mixing problem between the oil and

methanol as well as the dispersion of the catalyst in the mixture. Kusuma et al. (2012)

studied the effect of the reaction time between 1 and 4 h on the transesterification of

palm oil and methanol. The proposed reaction mechanism consisted of three steps. In

the first hour of reaction, only some triglycerides were converted to biodiesel.

Furthermore, the rate of reaction was relatively slow in the first hour due to the

problem of mixing and dispersion between palm oil and methanol. With a longer

reaction time, the amount of biodiesel produced increased and the yield of biodiesel

was essentially constant after 2 h. The equilibrium condition of transesterification

reaction of palm oil with methanol was reached after 2 h. Xue et al. (2009) prepared

the catalyst using the CH_3COOK loading in transesterification of Jatropha seed oil.

They found that the catalyst containing 18.7 wt% K gave the highest biodiesel yield

of 91% after the reaction time 4 h. The optimum time in this work was 3 h and the highest biodiesel yield was 95%.

Table 5.5 Catalytic activity of the xK /NaX-B catalysts.

Samples	Basicity (mmol CO_2/g)	% Biodiesel yield
4K/NaX-B	1.3	48
8K/NaX-B	2.0	73
12K/NaX-B	2.3	83
16K/NaX-B	2.9	95

5.5   Conclusions

Transesterification of Jatropha seed oil with methanol was carried out using K-loaded on zeolite NaX by impregnation method. With either acetate buffer or acetate solutions, the zeolite structure was not destroyed. For xK/NaX-B and xK/NaX-A the conversion increased with K loading but only 16K/NaX-B gave a complete conversion with the yield of 95.2%. The optimum reaction time was 3 h.

5.6   References

Borges, M. E., Diaza, L., Alvarez -G. M. C., and Brito, A. (2011). High performance heterogeneous catalyst for biodiesel production from vegetal and waste oil at low temperature. **Applied Catalysis B: Environmental**. 102: 310-315.

Cruz, M. D. -R., and Duro, F. I. -F. (1999). New data on the acetate kaolinite-potassium complex. **Clay Minerals**. 34: 565-577.

Di Serio, M., Ledda, M., Cozzolino, M., Minutillo, G., Tesser, R., and Santacesaria, E. (2006). Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. **Industrial and Engineering Chemistry Research**. 45: 3009-3014.

Intarapong, P., Luengnaruemitchai, A., and Jai-In, S. (2011). Transesterification of palm oil over KOH/NaY zeolite in a packed-bed reactor. **International Journal of Renewable Energy Research.** 1: 271-280.

Joshi, U. D., Joshi, P. N., Tamhankar, S. S., Joshi, V. V., Rode, C. V., and Shiralkar, V. P. (2003). Effect of nonframework cations and crystallinity on the basicity of NaX zeolites. **Applied Catalalysis A: General**. 239: 209-220.

Khemthong, P., Wittayakun, J., and Prayoonpokharach, S. (2007). Synthesis and characterization of zeolite LSX from rice husk silica. **Suranaree Journal of Science and Technology**. 14: 367-379.

Kusuma, R. I., Hadinoto, J. P., Ayucitra, A., Soetaredjo, F. E., and Ismadji, S. (2012). Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil. **Applied Clay Science**. 74: 121-126.

Liu, H., Su, L., Liu, F., Li, C., and Solomon, U. -U. (2011). Cinder supported K_2CO_3 as catalyst for biodiesel production. **Applied Catalysis B: Environmental**. 106: 550-558.

Man, W. K., Ramli, Z., and Nur, H. (2005). Effect of loaded alkali metals on the structural, basicity and catalytic activity of zeolite Beta. **Jurnal Teknologi**. 42: 43-55.

Martin, A. D., Mariscal, R., Moreno-Tost, R., Zafra Poves, M. D., and Lopez Granados, M. (2007). Potassium leaching during triglyceride transesterification using $K/g-Al_2O_3$ catalysts. **Catalysis Communications**. 8: 2074-2080.

Martinez, S. L., Romero, R., Lopez, J. C., Romero, A., Mendieta, V. S., and Natividad, R. (2011). Preparation and characterization of CaO nanoparticles/NaX zeolite catalysts for the transesterification of sunflower oil. **Industrial and Engineering Chemistry Research**. 50: 2665-2670.

Montalbo, K. D., De Leon, R. L., Sophiphun, O., Manadee, S., Prayoonpokarach, S., and Wittayakun, J. (2013). Characterization and catalytic performance of potassium loaded on rice husk silica and zeolite NaY for tranesterification of Jatropha seed oil. **Quimica Nova**. 36: 1116-1120.

Noiroj, K., Intarapong, P., Luengnaruemitchai, A., and Jai-In, S. (2009). A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. **Renewable Energy**. 34: 1145-1150.

Pena, R., Romero, R., Martinez, S. L., Natividad, R., and Ramirez, A. (2012). Characterization of KNO_3/NaX catalyst for sunflower oil transesterification. **Fule**. 110: 63-69.

Semwal, S., Arora, A., Badoni, R., and Tuli, D. (2011). Biodiesel production using heterogeneous catalysts. **Bioresource Technology**. 102: 2151-2161.

Supamathanon, N., Wittayakun, J., and Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. **Journal of Industrial and Engineering Chemistry**. 17: 182-185.

Suppes, G. J., Dasari, M. A., Doskocil, E. J., Mankidy, P. J., and Goff, M. J. (2004). Transesterification of soybean oil with zeolite and metal catalysts. **Applied Catalysis A: General**. 257: 213-223.

Vyas, A. P., Subrahmanyam, N., and Patel, P. A. (2009). Production of biodiesel through transesterification of Jatropha oil using KNO_3/Al_2O_3 solid catalyst. **Fuel**. 88: 625-628.

Walton, K. S., Abney, M. B., and Levan, D. M. (2006). CO_2 adsorption in Y and X zeolites modified by alkali metal cation exchange. **Microporous and Mesoporous Materials**. 91: 78-84.

Xie, W., and Hung, X. (2006). Synthesis of biodiesel from soybean oil using heterogeneous KF/ZnO catalyst**. Catalysis Letters**. 107: 53-59.

Xie, W., and Li, H. (2006). Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. **Journal of Molecular Catalysis A**: **Chemical**. 255: 1-9.

Xie, W., Huang, X., and Li, H. (2007). Soybean oil methyl ester preparation using NaX zeolite loaded with KOH as a heterogeneous catalyst. **Bioresource Technology**. 98: 936-939.

Xue, W., Zhou, Y. -C., Song, B. -A., Shi, X., Wang, J., Yin, S. -T., Hu, D. -Y., Jin, L. -H., and Yang, S. (2009). Synthesis of biodiesel from *Jatropha curcas* L. seed oil using artificial zeolites loaded with CH_3COOK as a heterogeneous catalyst. **Natural Science**. 1: 55-62.

Yagi, F., Tsuji, H., and Hattori, H. (1997). IR and TPD (temperature-programmed desorption) studies of carbon dioxide on basic site active for 1-butene isomerization on alkali-added zeolite X. **Microporous and Mesoporous Materials**. 9: 237-245.
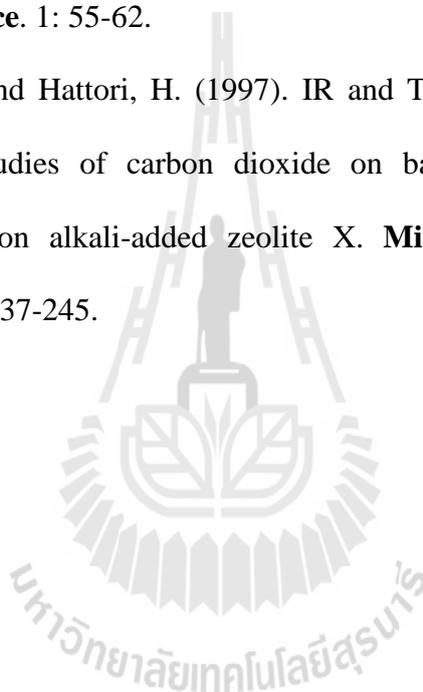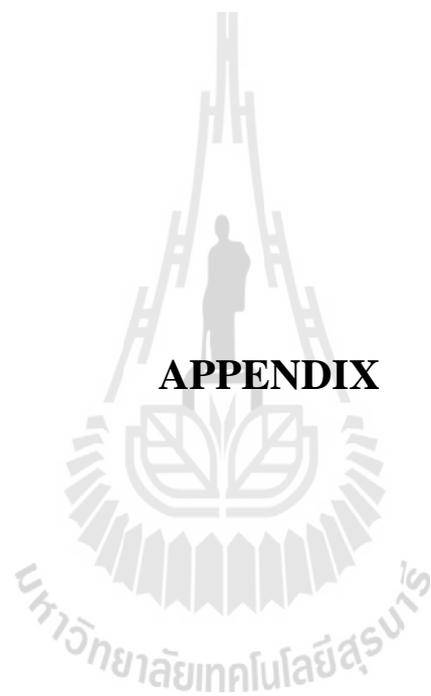
APPENDIX
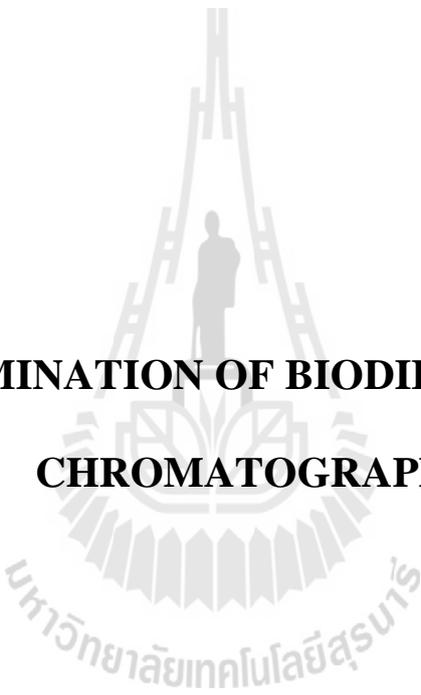
DETERMINATION OF BIODIESEL BY GAS

CHROMATOGRAPHY

1. Preparation of standard solutions for GC analysis

1.1 Preparation of internal standard

100 mg of methyl nonadecanoate (C19:0) was weighed, dissolved in chloroform and transferred to 5 mL volumetric flask. Chloroform was added to make up the solution volume.

1.2 Preparation of stock standard solution of methyl esters

Methyl ester standards as shown in Table A1 were weighed and dissolved in hexane. The solution was prepared in a 5 mL volumetric flask.

Table A1 Composition of methyl esters standard solution.

Methyl ester	Weight (mg)	Concentration (ppm)
C16:0	20	4,000
C16:1	10 (11.4 µL)	2,000
C17:0	10	2,000
C18:0	20	4,000
C18:1	50 (57.2 µL)	10,000
C18:2	50 (56.2 µL)	10,000
C18:3	10	2,000
C20:0	11.5	2,000

2. Preparation of calibration curve for GC analysis

2.1 Standard solutions of C16:0, C16:1, C17:0, C18:0, C18:1, C18:2, C18:3, and C20:0

A set of five 1 mL of volumetric flasks was labeled No. 1-5. 0.8, 0.5, 0.2, 0.1, and 0.05 mL of the stock standard solution were added into the labeled 1 mL of volumetric flasks, respectively. 50 µL of C19:0 as the internal standard was added into all flasks and hexane was added to make up the solution volume. The prepared solutions were transferred to 1 mL vial and septum capped. Table A2 presents methyl esters concentration in standard solutions.

Table A2 Concentration of the standard solution for calibration curve.

Standard solution	Concentration of methyl ester standard (ppm)							
	C16:0	C16:1	C17:0	C18:0	C18:1	C18:2	C18:3	C20:0
1	3,200	1,600	1,600	3,200	8,000	8,000	1,600	1,600
2	2,000	1,000	1,000	2,000	5,000	5,000	1,000	1,000
3	800	400	400	800	2,000	2,000	400	400
4	400	200	200	400	1,000	1,000	200	200
5	80	40	40	80	200	200	40	40

3. Preparation of sample for GC analysis

50 µL of sample (biodiesel) was added into 1 mL volumetric flask and added hexane to dissolve. Then 50 µL of C19:0 was spiked into the solution and hexane was

added to make up the solution volume. The prepared solutions were transferred to 1 mL vial and capped with the septum.

4. Chromatographic conditions

Instrument: Hewlett Packard (HP6890-Series)

Detector: Flame Ionization Detector (FID)

Column type: HP-INNOWax Polyethylene Glycol, 30 m x 0.32 mm

     ID, 0.15 µm

Parameter for the run:

  Injection temperature: 220 °C

  Detector temperature: 250 °C

  Temperature program:

   - Initial oven temperature: 140 °C

   - Initial time: 3 minutes

   - Heating Rate: 10 °C/ min

   - Final temperature: 240 °C/ min

   - Final time: 10 min

   - Run time: 20 min

  Injection volume: 1 µL

5. Calibration curve for fatty acid methyl ester standard FAME std. (C16:0)

$y = 0.001x + 0.2898$

$R^2 = 0.990$

FAME std. (C16:1)

$y = 0.0002x + 0.1408$

$R^2 = 0.991$

FAME std. (C17:0)

$$y = 0.0002x + 0.1525$$
$$R^2 = 0.990$$

FAME std. (C18:0)

$$y = 0.0004x + 0.2761$$
$$R^2 = 0.991$$
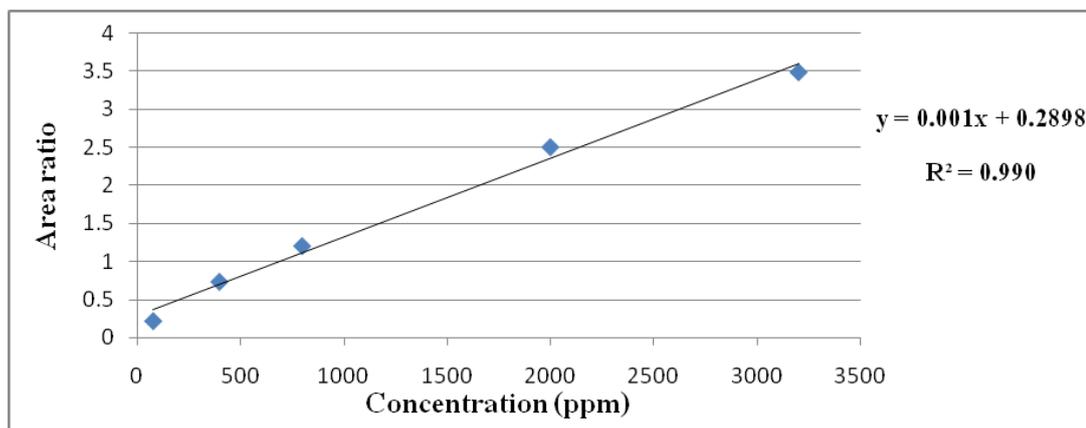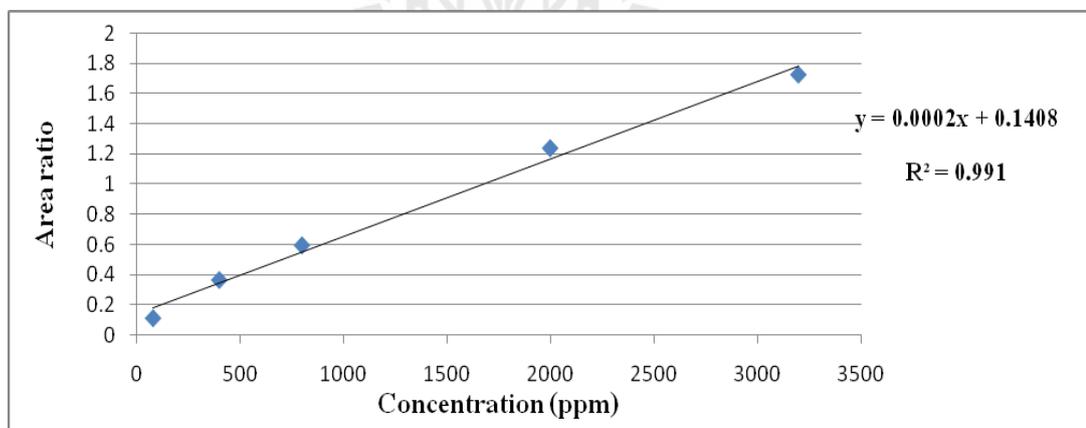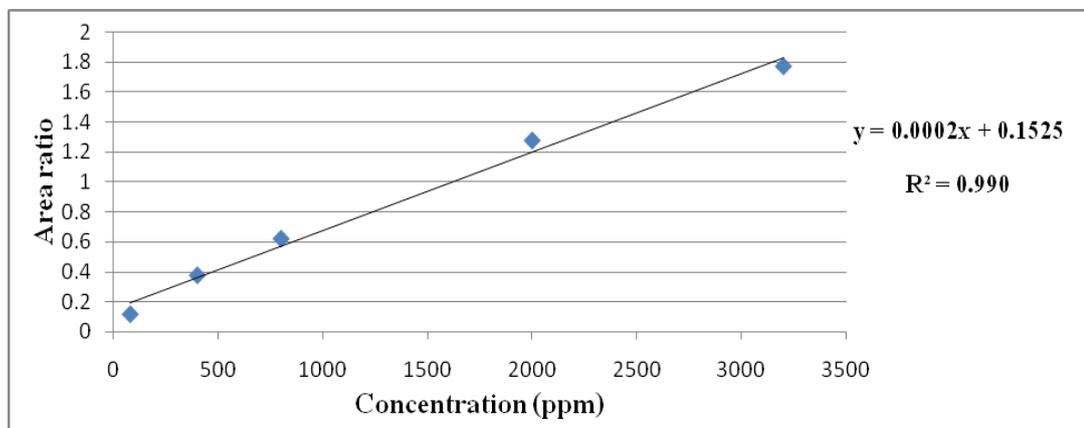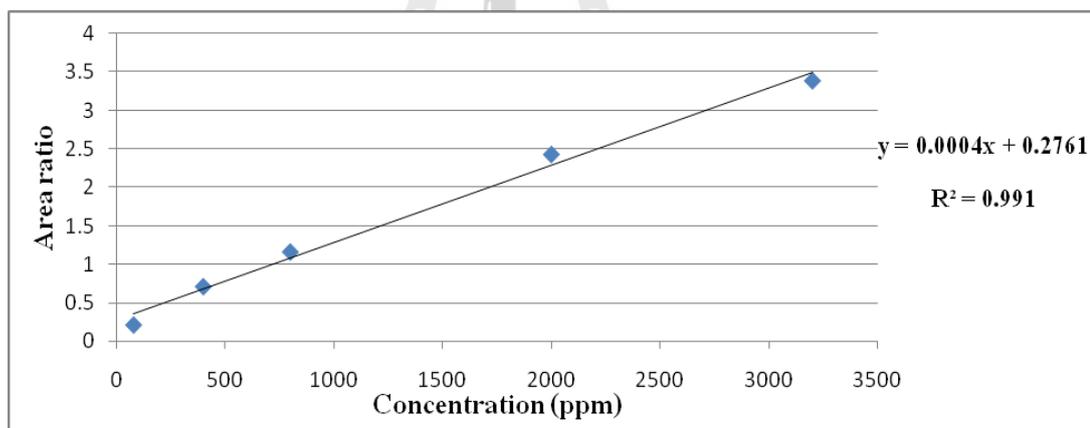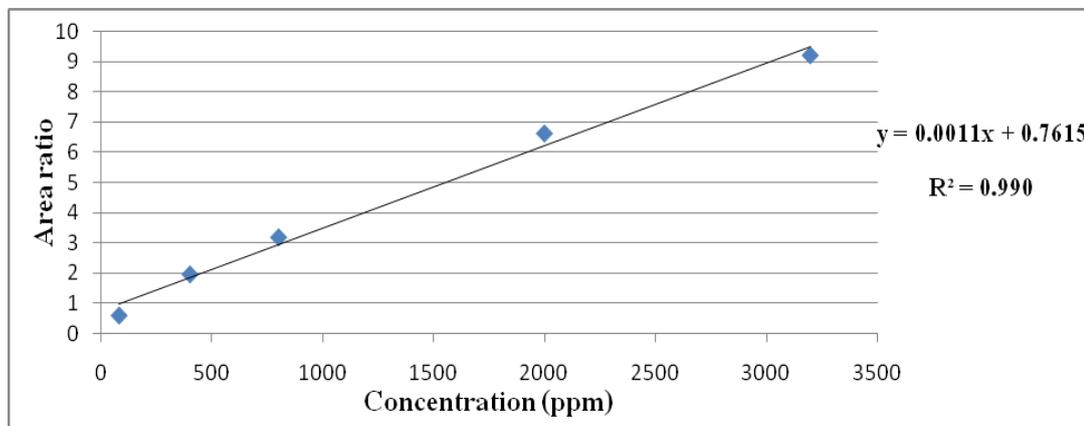
FAME std. (C18:1)

FAME std. (C18:2)

FAME std. (C18:3)

$y = 0.0007x + 0.0844$

$R^2 = 0.991$

FAME std. (C20:0)

$y = 0.0002x + 0.1432$

$R^2 = 0.992$
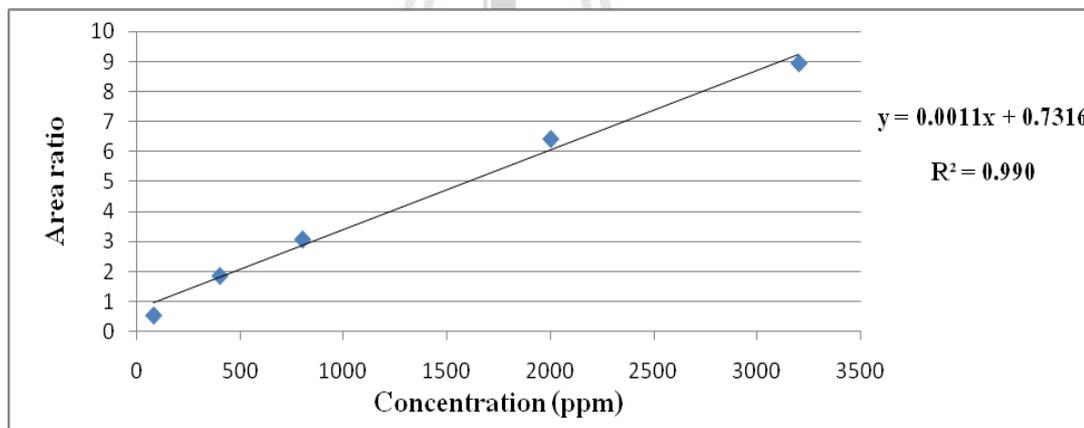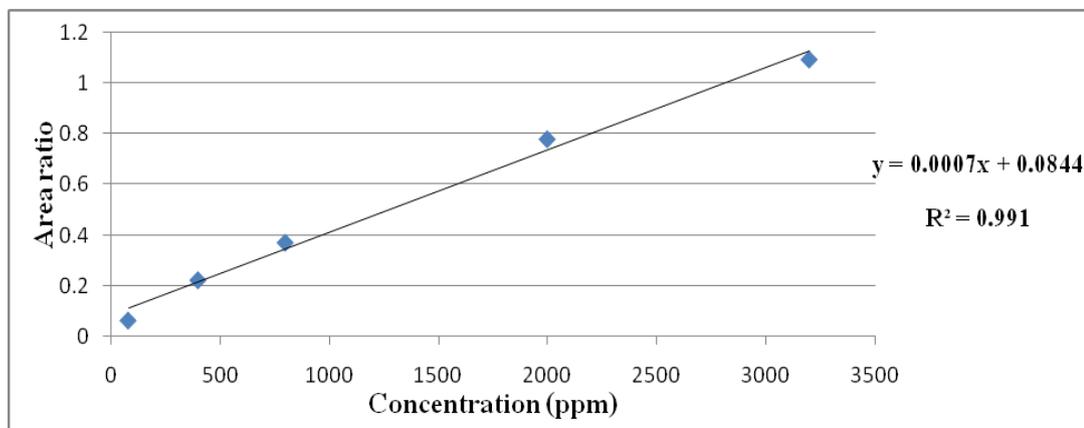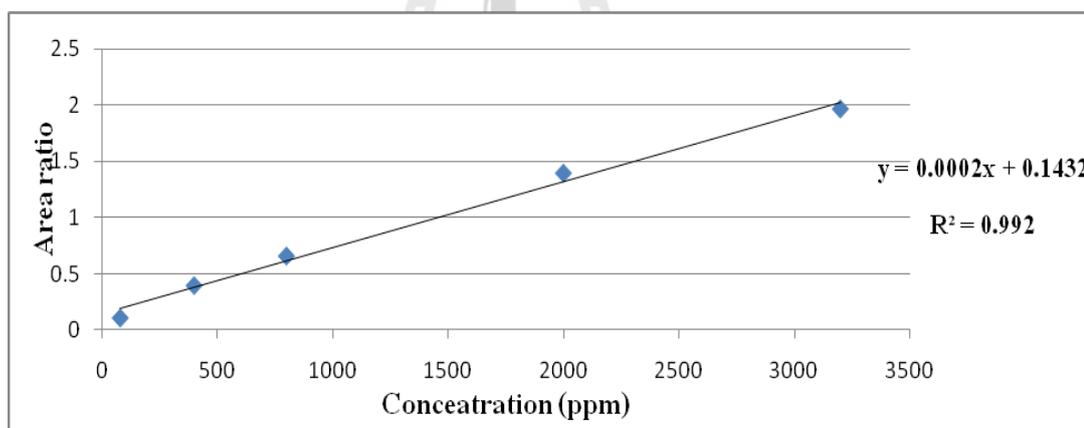
CURRICULUM VITAE

Name   Miss Saowanee Manadee

Education

2006-2009   B.Sc. (Chemistry) Mahasarakharm University, Mahasarakharm,

Thailand

2009-2013   Student in M.Sc. Program (Chemistry) Suranaree University of

Technology, Nakhon Ratchasima,Thailand

Publications

1. **Manadee, S.,** Supamathanon, N., Montalbo, K., D., Prayoonpokarach, S., Wittayakun, J. (2012). Catalyst preparation by addition of K and Na on zeolite NaX for transesterification of Jatropha seed oil. Proceeding (oral presentation). The Asian Conference on Sustainability, Energy & the Environment Official Conference. Japan. 3-6 June 2012, pp. 400-412.

2. Montalbo, K., D., De Leon, R., L., Sophiphun, O., **Manadee, S.,** Prayoonpokarach, S., and Wittayakun, J. (2013). Characterization and catalytic performance of potassium loaded on rice husk silica and zeolite NaY for tranesterification of Jatropha seed oil. Quimica Nova. 36: 1116-1120.