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BIODIESEL PRODUCTION VIA HETEROGENEOUS BASE CATALYST
FROM SEASHELLS IN CONTINUOUS FIXED BED REACTOR

Mr. Wayu Jindapon

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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วายุ จินดาพล : การผลิตไบโอดีเซลผ่านตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดเบสจากเปลือกหอยในเครื่องปฏิกรณ์เบดนิ่งแบบต่อเนื่อง. (BIODIESEL PRODUCTION VIA HETEROGENEOUS BASE CATALYST FROM SEASHELLS IN CONTINUOUS FIXED BED REACTOR) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร. ชวลิต งามจรัสศรีวิชัย, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร. ประพันธ์ คุชฌราธา, 99 หน้า.

งานวิจัยนี้ศึกษาการขึ้นรูปตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดเบสจากเปลือกหอยเหลือทิ้งสำหรับทรานส์เอสเทอร์ฟิเคชันของน้ำมันปาล์มกับเมทานอลในเครื่องปฏิกรณ์แบบเบดนิ่งด้วยวิธีการละลาย-การตกตะกอน (dissolution-precipitation method) โดยนำเปลือกหอยที่ผ่านการเผามาผสมกับซิงค์ไนเตรทที่ใช้เป็นตัวเพิ่มความแข็ง อะลูมินาที่ใช้เป็นตัวรองรับ และไฮดรอกซีเอทิลเซลลูโลส (hydroxyethyl cellulose) ที่เป็นสารเสริมสภาพพลาสติก (plasticizer) ในสารละลายกรดไนตริก ปัจจัยที่ศึกษาในการขึ้นรูปตัวเร่งปฏิกิริยาแบบเส้น ได้แก่ ชนิดของเครื่องอัดรีด ปริมาณไฮดรอกซีเอทิลเซลลูโลส และอุณหภูมิในการเผาตัวเร่งปฏิกิริยาต่อลักษณะทางกายภาพและสมบัติในการเร่งของตัวเร่งปฏิกิริยา สมบัติของตัวเร่งปฏิกิริยาถูกศึกษาด้วยการใช้เทคนิคต่างๆ ได้แก่ เอกซ์เรย์ฟลูออเรสเซนซ์สเปกโตรมิเตอร์ การเลี้ยวเบนรังสีเอกซ์ สแกนนิ่งอิเล็กตรอนไมโครสโคปี การสลายตัวด้วยความร้อน การวัดการดูดซับไนโตรเจน และการคายคาร์บอนไดออกไซด์แบบโปรแกรมอุณหภูมิ ภาวะที่เหมาะสมในการเตรียมตัวเร่งปฏิกิริยา คือ อัตราส่วนโดยน้ำหนักของเปลือกหอย/อะลูมินา เท่ากับ 1:1 ปริมาณของไฮดรอกซีเอทิลเซลลูโลสเป็นร้อยละ 3 โดยน้ำหนักของแข็งทั้งหมด ชนิดของเครื่องขึ้นรูปคือ เครื่องอัดรีดแบบสกรูเดี่ยว (single screw extruder) และอุณหภูมิในการเผาตัวเร่งปฏิกิริยาเท่ากับ 300 องศาเซลเซียส ตัวเร่งปฏิกิริยาแบบเส้นที่เตรียมให้ผลได้ของเมทิลเอสเทอร์ที่สูงและคงที่จากปฏิกิริยาทรานส์เอสเทอร์ฟิเคชัน ภาวะในการทำปฏิกิริยาถูกดำเนินการที่ อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันเป็น 30 ต่อ 1 อุณหภูมิในการทำปฏิกิริยาเท่ากับ 60 องศาเซลเซียส ผสมเมทิลเอสเทอร์เป็นร้อยละ 30 โดยน้ำหนักของตัวเร่งปฏิกิริยา อัตราการป้อนสารตั้งต้นเท่ากับ 2.0 มิลลิลิตรต่อนาที

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The present thesis was studied by formulation of heterogeneous base catalysts from waste mixed seashells for transesterification of palm oil with methanol in a fixed bed reactor. The catalysts were prepared by dissolution-precipitation method. Typically, the calcined seashells were mixed with zinc nitrate as a strength component, aluminium oxide as a supported material and hydroxyethyl cellulose (HEC) as a plasticizer in a solution of nitric acid. Effects of the formulation conditions in extrudates catalyst, including extruder type, amount of HEC and calcination temperature on the physicochemical and the catalytic properties were investigated. The properties of the catalysts were studied by X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric/ differential thermal analysis (TG/DTA), N₂ adsorption-desorption measurement and CO₂-pulse chemisorption analysis. The suitable condition for the catalyst preparation is the weight ratio of seashells/Al₂O₃ with 1:1, the amount of HEC with 3 wt.% of total solid, single screw extruder and calcination temperature of 300 °C. The extrudate catalysts attained gave the highest and stable FAME yield (95 wt.% and 24 h, respectively) attained from the transesterification under the suitable transesterification condition at methanol/oil molar ratio, 30; temperature, 65 °C; premixing with methyl esters, 30 wt.% of catalyst extrudates and total flow rate, 2.0 mL min⁻¹.

Field of Study: Petrochemistry and Polymer Science Student's Signature.....

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barret, Joyner, and Halenda
°C	Degree Celsius
g	Gram (s)
h	Hour (s)
cm	Centimeter
µm	Micrometer (s)
mL	Milliliter (s)
min	Minute (s)
M	Molarity
nm	Nanometer (s)
%	Percentage
SEM	Scanning Electron Microscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy
TGA	Thermogravimetric analysis

CHAPTER I

INTRODUCTION

1.1 Statement of Problems

Most of petroleum diesel affects on current energy situation and environmental constrains. Searching for green and renewable fuels has been made worldwide. Biodiesel is made from renewable sources such as edible oils (rapeseed, sunflower, palm and soybean) and non-edible oils (jatropha, fats, bacteria, used cooking oil and microalgae) with small alcohols via transesterification. The advantages of using biodiesel are a renewable fuels available, non-toxic and biodegradable [1].

Industrially, the transesterification has been carried out homogeneous base catalysts such as sodium hydroxide, potassium hydroxide and sodium methoxide. The homogeneous base catalysts have higher catalytic efficiency, and lower cost, reaction temperature and pressure. However, the using of homogeneous base catalysts requires extensive condition and purified steps for the reaction products, i.e. fatty acid methyl esters (FAME) and glycerol, to separate the soluble catalysts [2]. For this problem, heterogeneous base catalysts is investigated. The heterogeneous base catalysts are easily recovered from the products, reducing the amount of wastewater discharged. Moreover, these can be reusability [3].

Recently, Zn–Al mixed oxide is used as the heterogeneous catalyst developed by French Institute of Petroleum (IFP). The catalyst oxide is packed into two fixed-bed reactor located in a stream of the continuous flow system. However, the system requires high temperature and high pressure conditions [3].

Calcium oxide (CaO) is one of the active heterogeneous base catalysts in the transesterification. The advantages of the CaO are high basicity, low solubility in methanol and low cost. The CaO is formed by a thermal decomposition of calcium carbonate (CaCO₃) at high temperatures (>825 °C). Sources of the CaCO₃ can be natural rocks (limestone and dolostone) and animal organs (seashells and cuttlebone) [4]. In the continuous flow system, the CaO must be formed before packed into the fixed-bed reactor. Since the using of CaO in any form such as pellets, pills, rings, spheres, granules and extrudates can reduce problems relating to reactor blockage and

pressure drop [5]. Commonly, the CaO is a hard and brittle material. Binder (alumina, bohemite and clay) and plasticizer (hydroxyethyl cellulose, methylcellulose and MgO) are used to increase mechanical strength and formulating of the catalyst, respectively. When the catalyst is shaped in any form, a surface area, pore volume and number of active sites is reduced by binder blockage [6]. The dissolution-precipitation method was selected to help the problems. In the method, the CaO active site is dissolved in acid solution. Subsequently, the binder was added. The calcium compounds are precipitated into the added binder. CaO was found, as active sites, after calcination.

In the present study, we prepared and formulated heterogeneous base catalysts from waste mixed seashells as a source of CaO via dissolution-precipitation method. The binder and plasticizer were alumina and hydroxyethyl cellulose, respectively. The formulation of catalyst used two types of extruders including manual extruder and single screw extruder. Moreover, effects of addition of FAME were studied to find suitable conditions. Characterization of the catalysts was determined by various techniques including XRF, XRD, TG/DTA, SEM, CO₂-chemisorption analysis and N₂ adsorption-desorption measurement. Finally, the extrudate catalysts were investigated in the fixed-bed reactor for biodiesel production. The reaction condition was carried out at reaction temperature of 65 °C, methanol/oil molar ratio of 30, total flow rate of 2.0 mL min⁻¹ and reaction time of 8 h.

1.2 Objectives

1. To study preparation and formulation of heterogeneous base catalyst from waste mixed seashells for biodiesel production.
2. To study transesterification of palm oil with methanol over the heterogeneous base catalysts prepared from waste mixed seashells under batch and continuous conditions.

1.3 Scopes of work

1. Literature survey
2. Preparation and formulation of heterogeneous base catalysts from waste mixed seashells by dissolution-precipitation method in 2 parts:

2.1 The first one is the preparation of heterogeneous base catalysts from mixed seashells by dissolution-precipitation method in powdery form:

- Raw material of catalyst preparation
- Calcination temperature of powdery form: 300-800 °C
- Weight ratio of seashells/ Al_2O_3 : 1:0.4 and 1:1

2.2 The second part is the study on extrudates characteristics and mechanical testing of extrudates from:

- Amount of HEC: 0-5 wt.% of total solid
- Calcination temperature of the extrudates catalyst: 300-800 °C
- Extruder type for extrudates catalyst: manual extruder and single screw extruder
- Premixing the extrudate catalyst with methyl esters

3. Characterization of the raw material and the catalysts by following techniques:

- X-ray fluorescence spectrometry (XRF)
- X-ray diffraction (XRD)
- Scanning electron microscopy (SEM)
- Thermogravimetric and differential thermal analysis (TG/DTA)
- CO_2 -pluse chemisorption
- Crush strength: ASTM D-4179-82

4. Evaluation of the catalysts activity on the FAME yield attained from the transesterification of palm oil with methanol under condition of batch and continuous reaction

5. Investigation stability of the catalysts

6. Characterization of the FAME yield by using a gas chromatography technique

7. Summation of the results and write thesis

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Biodiesel production [7-9]

2.1.1 Background of biodiesel

Heavy consumption of petroleum diesel affects to global warming and concerns of energy security. Biodiesel is another diesel fuel. It is made from renewable biological sources for example edible oils (rapeseed, sunflower, palm and soybean) and non-edible oils (jatropha, fats, bacteria, used cooking oil and microalgae). Biodiesel is a much cleaner fuel than conventional fossil-fuel petroleum diesel. The advantages of using biodiesel are a renewable fuels available, non-toxic and biodegradable. Biodiesel production has four techniques such as direct use and blending, micro emulsion, thermal cracking (pyrolysis), and transesterification. The commonly method is the transesterification of vegetable oils or animal fats with small alcohols.

2.1.2 Method of biodiesel production

2.1.2.1 Direct use and blending

Direct use and/or blending of vegetable oils have commonly been considered to be not satisfactory and unworkable for both direct and indirect diesel engines. However, vegetable oil can be directly used as diesel fuel without any changes to engine. Advantages of direct use of vegetable oils are fluid nature and portability, high heat content (80% of diesel fuel), ready availability and renewability. The very first engine (by Rudolf Diesel) was tested using vegetable oil as fuel. It is high viscosity and leads to problem in the long run. Therefore, the problems perform only after long period. Various of common problem are coking and trumpet formation on the injects to such as extent that fuel atomization become difficult, carbon deposits, oil ring sticking, thickening and gelling.

2.1.2.2 Micro-emulsions

Vegetable oils have high viscosity. Solving of the problem is micro-emulsions method. It is mixed by solvents for example methanol, ethanol and 1-butanol. Definition of a micro-emulsion is colloidal equilibrium dispersion of optically isotropic fluid microstructures. The commonly dimension of a micro-emulsion is range of 1-150 nm. It can increase spray characteristics by explosive vaporization of the low boiling constituents in the micelles.

2.1.2.3 Pyrolysis or thermal cracking

Pyrolysis or thermal cracking is the transformation of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen. Chemical bonds of oil are broken to yield small molecules. The commonly material is used in pyrolysis such as vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis process is simple and effective compared with other cracking processes. Figure 2.1 shows the mechanism of thermal decomposition of triglycerides.

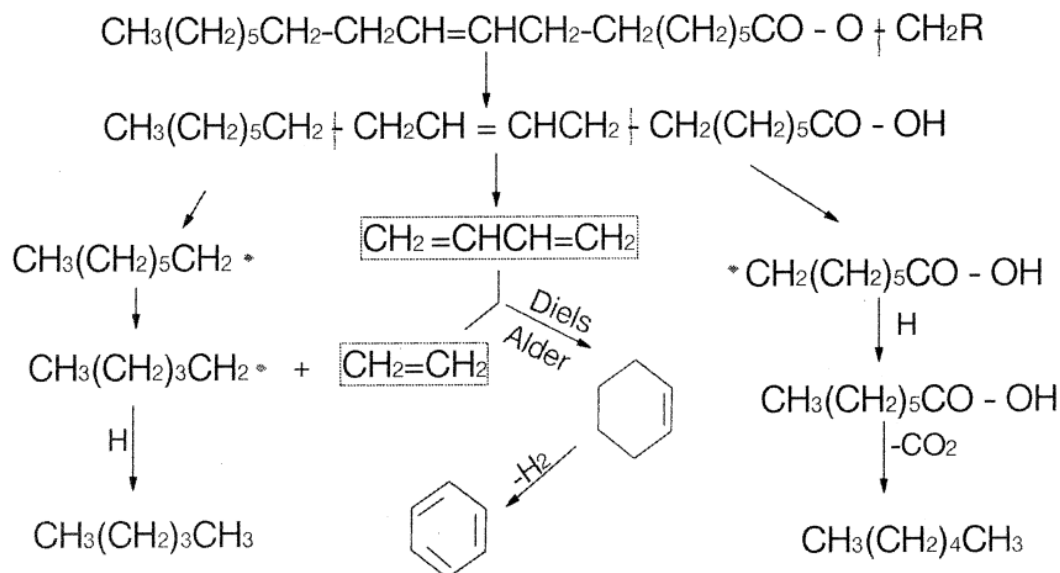


Figure 2.1 The mechanism of thermal decomposition of triglycerides [7].

2.1.2.4 Alcoholysis

Alcoholysis or transesterification is the reaction of triglyceride such as fat or oil with an alcohol to form esters and glycerol. The commonly equation is shown in Figure 2.2. A catalyst is generally used to increase the reaction rate and conversion. Alcohol is excessively used to shift the equilibrium to the products side because the reaction is reversible. Varieties of the alcohols are generally used in the transesterification process such as methanol, ethanol. Especially methanol is low cost and physical and chemical advantages (polar and shortest chain alcohol). NaOH is easily dissolved in methanol which can fast react with triglycerides. Follow stoichiometry, a 3:1 molar ratio of alcohol to triglycerides is needs for complete a reaction. However, the higher ratio is importantly to drive the equilibrium to a maximum ester yield. Transesterification can be catalyzed by alkalis (NaOH, KOH and NaOCH₃), acids (H₂SO₄, R-SO₃H and HCl), or enzymes (Lipases). Transesterification by alkali catalyst is much faster than acid catalyst. Alkali catalyst is most often used commercially.

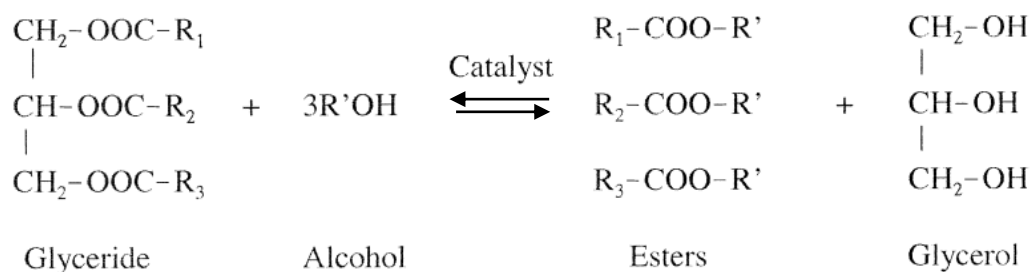


Figure 2.2 Transesterification of triglycerides with alcohol [7].

Figure 2.3 shows transesterification reaction. It includes a number of consecutive and reversible reactions. The first step is the conversion of triglyceride to diglyceride (Eq. (2.1)). Subsequently, the diglyceride is successively convert to monoglyceride (Eq. (2.2)), and glycerol (Eq. (2.3)). In each step, an alkyl ester is generated and thus three ester molecules are produced from one molecule of triglyceride. Finally, three ester molecules are generated from one molecule of triglyceride [8].

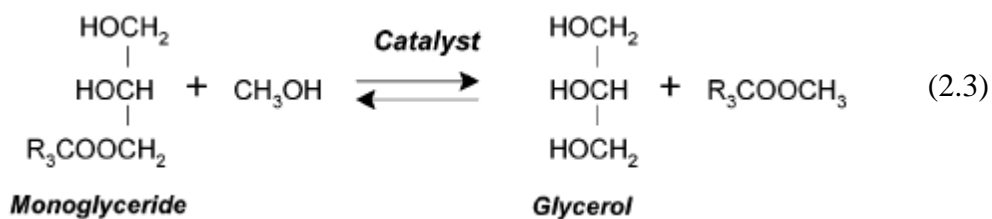
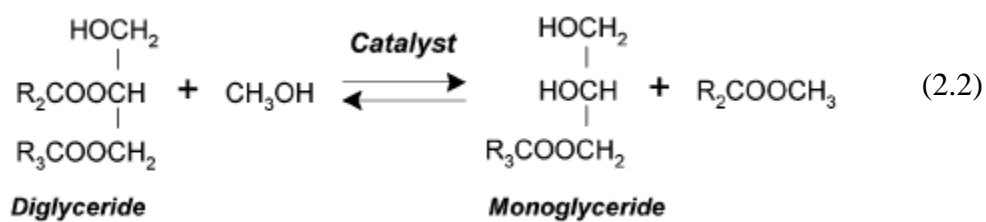
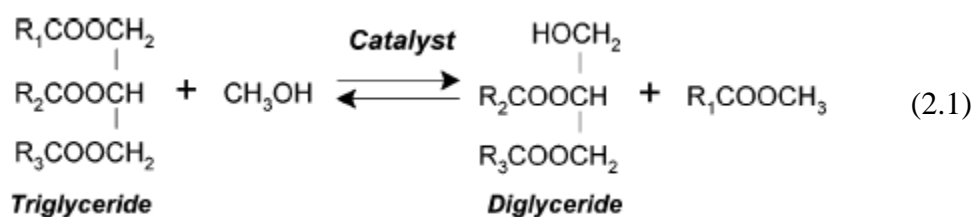


Figure 2.3 Three consecutive transesterifications of triglyceride [8].

The conversion of monoglyceride to alkyl ester is believed to be the rate determining step. Since the monoglycerides are the most stable intermediate compound.

Table 2.1 Comparison of methods of production of biodiesel [9].

Methods	Definition	Advantage	Disadvantage
Pyrolysis or thermal cracking	Method of conversion of one substance into another by application of heat with the aid of the catalyst in the absence of air or oxygen	1. Lower processing costs, compatibility with infrastructure, engines and fuel standards, and feed stock flexibility 2. The final products are similar to diesel fuel in composition	Energy intensive
Micro-emulsions	A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures.	1. Fuel viscosity is lowered 2. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles	Lower cetane number and energy content
Direct use and blending	Either use vegetable oil directly or is blended with diesel	Liquid nature and portability Heat content (~80% of diesel fuel) readily available; renewability	1. Higher viscosity 2. Lower volatility 3. The reactivity of unsaturated hydrocarbon chains
Alcoholysis	Alcoholysis is the reaction of a fat or oil with an alcohol to form esters and glycerol	Renewability; higher cetane number; lower emissions; higher combustion efficiency	Glycerol disposal and waste water problem

2.1.3 Conventional biodiesel production process [10-11]

2.1.3.1 Batch vs continuous process

- **Batch process.** Batch process is simple process for biodiesel production. Range of 4:1 to 20:1 of the methanol to oil molar ratio is generally used in the process. The reactor may be equipped or sealed with a reflux condenser. The operational temperature is commonly about 65 °C. The catalyst is generally catalyzed such as NaOH, KOH and NaOCH₃. The amount of catalyst is loaded in range of 0.3 to 1.5 wt.%.

The reactant (oil and methanol) is thoroughly mixed at the initial period of the reaction. To the end of the reaction, a reduced mixing can help increase the extent of reaction by allowing the inhibitory product (glycerol) to phase separate from the ester - oil phase. Using a two-step reaction in some groups, glycerol is removed between

steps to increase the final reaction extent to >95 %. Higher temperatures and higher alcohol/oil ratios also can increase the percentage of final product.

A process flow diagram for a typical batch system is shown in Figure 2.4. The first, triglyceride is added to the system, followed by the catalyst and methanol. The mixing is heavily stirred in the stirred tank reaction during the processing time. Subsequently, the stirring is stopped. In some processes, the mixing is extensively settled in the reactor for initial separation of the esters and glycerol. In other processes, the mixing is pumped into a settling vessel, or is separated using a centrifuge. The alcohol is removed from both the glycerol and ester tank using an evaporator. In ester tank, the neutralized esters are washed gently using warm. The finished biodiesel is transferred to product storage. In the case of glycerol tank, the glycerol is neutralized and washed with soft water. The glycerol is transferred to the glycerol refining section.

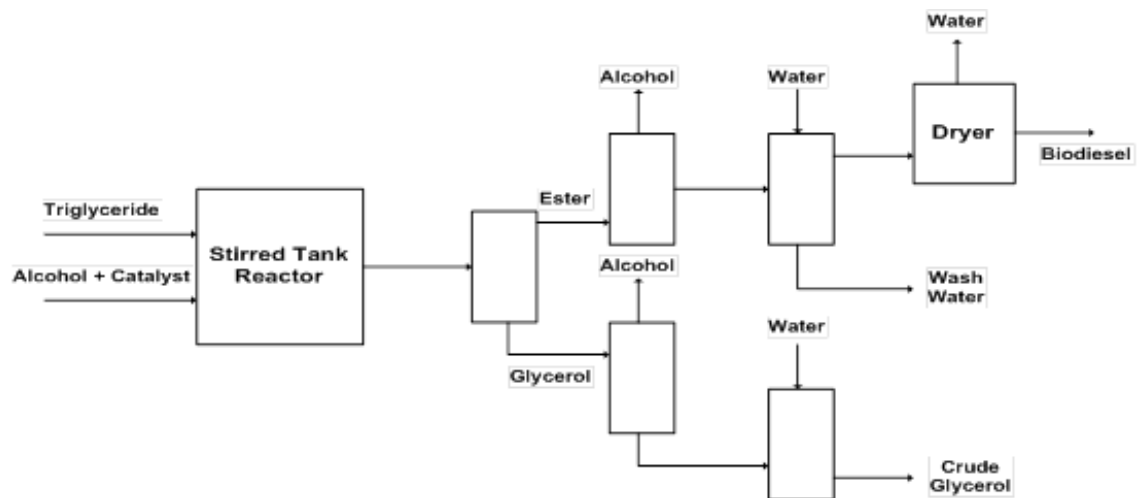


Figure 2.4 Batch reaction systems [10].

- Continuous process.** Continuous process is a flow production method used to manufacture, produce, or process materials without interruption. The continuous process rather allows short of residence times as 6 to 10 minutes for near completion of the reaction. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. Figure 2.5 shows a PFR system. The reaction rate is increased when increasing pressure and temperature.

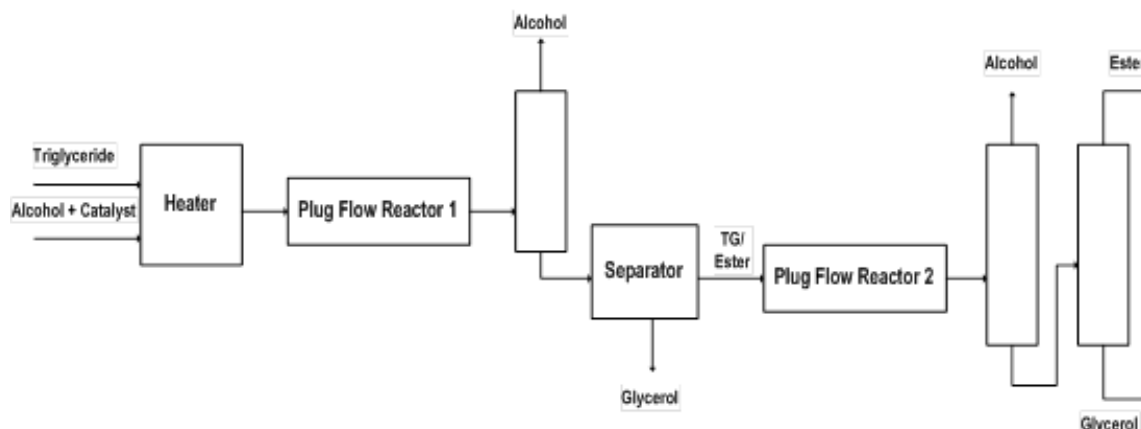
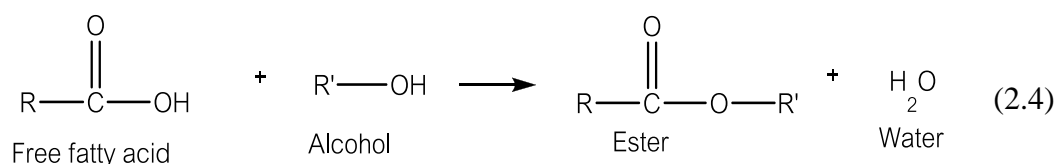


Figure 2.5 Plug flow reaction system [10].

2.1.3.2 Esterification and transesterification

Using base catalysts in the transesterification have been controlled the amount free fatty acid content in triglycerides for protection of produced soap. Figure 2.6 shows a diagram of processing for eliminating free fatty acid in oil. Producing ester from free fatty acid and alcohol via esterification with water as the by-product is shown in Eq. 2.4.



The combined water and the catalyst are removed of reactor. Therefore, water from the reaction mixture is separated by evaporation. Consequently, the methyl esters produced and the triglycerides remaining are neutralized with base. In common, high ratios of alcohol to free fatty acid and large amount of acid catalyst are required to complete the reaction in 10 minutes to 2 hours. Subsequently, the triglycerides remaining and the methyl esters are dried and pumped to the transesterification reactor. Finally, the remaining of triglycerides is catalyzed completely by a base catalyst.

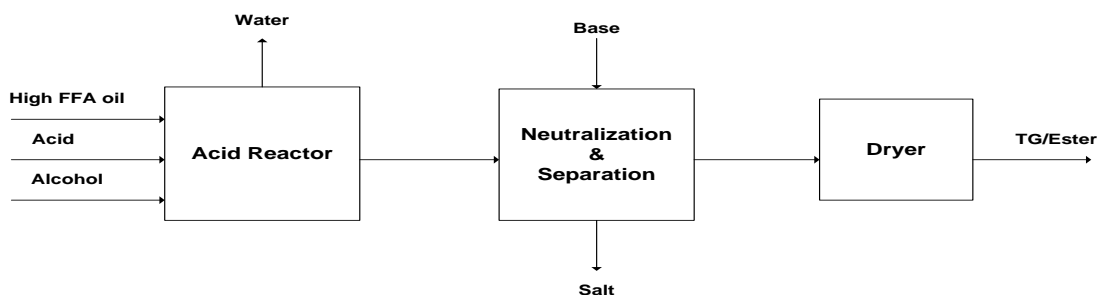
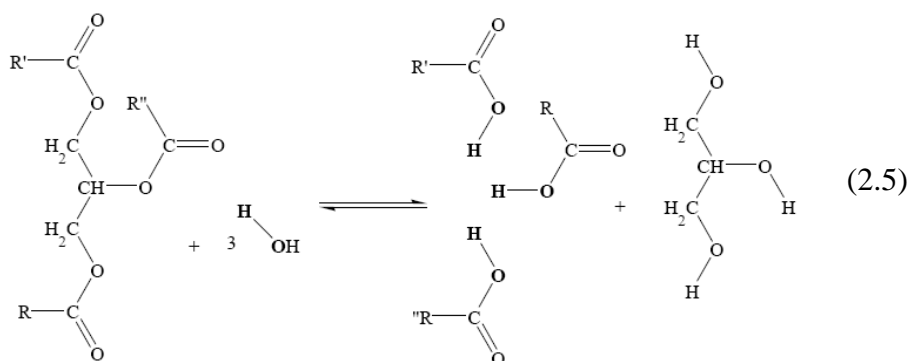


Figure 2.6 Diagram of processing for eliminating free fatty acid in oil [10].

2.1.3.3 Hydrolysis and esterification

Hydrolysis and esterification process is suitable at high amount of free fatty acid content. Eq. 2.5 shows hydrolysis reaction over acid catalysts from of high free fatty acid oil with water or by dilute acids. The occurred product is purified fatty acid and glycerol.



The reaction is technically carried on a counter-current continuous flow reactor as shown in Figure 2.7. Supplementary, the purified fatty acid is moved to another counter-current continuous reactor. It is further reacted by esterification with alcohol over acid catalyst to methyl esters.

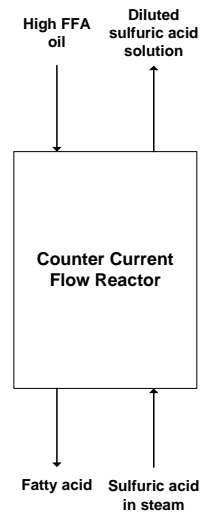


Figure 2.7 Hydrolysis of high free fatty acid oil in counter-current continuous flow reactor [10].

However, the reaction rate and catalyst activity are decreased due to dilution of the catalyst concentration by the water produced. The commercial process for biodiesel production includes using of alkali catalyst. Finally, the biodiesel product is removed of the soluble catalyst and the saponified products by water washing.

2.2 Biodiesel technology

2.2.1 Feedstock for biodiesel [12]

Feedstock for biodiesel composes of other oil such as edible oils (rapeseed, sunflower, palm and soybean) and non-edible oils (jatropha, fats, bacteria, used cooking oil and microalgae). The feedstock is the major factor affecting selling cost of biodiesel product. The feedstock is country depends on the availability and cost. The major feedstock composes of palm oil, soybean oil, rapeseed oil, sunflower seed oil, cottonseed oil and coconut oil. Table 2.2 shows other oil production and major country produced it. Palm oil is major oil for biodiesel production. Thailand is the top of the world for palm oil production. The major areas for palm plantation are Krabi, Surat Thani, Chumphon, Trang and Satun.

Table 2.2 Other oil production in other countries, year 2012 [13]

Other oil	Production (1000 MT)	Major country produced its
Palm oil	53,327	Indonesia, Malaysia and Thailand
Soybean oil	43,073	China, United States, Argentina Brazil, EU-27 and India
Rapeseed oil	23,493	EU-27, China, Canada and India
Sunflower seed Oil	13,260	Ukraine, EU-27, Russian and Argentina
Cottonseed oil	5,171	China, India and Pakistan
Coconut oil	3,522	Philippines, Indonesia and India

2.2.2 Biodiesel production technology [14]

2.2.3.1 Homogeneous catalysis

Definition of homogeneous catalyst is a same phase of catalyst in the substrate. Most generally, the homogeneous catalyst can be dissolved in a solvent with the reactants. The homogeneous catalysts for biodiesel production can be base catalysts (sodium hydroxide and potassium hydroxide), or acid catalysts (sulphuric, sulphonic, phosphoric, and hydrochloric acids). Base catalysts have higher catalytic efficiency, and lower cost, reaction temperature and pressure than acid catalysts. However, base catalysts are possibly reacted by free fatty acid to soap during transesterification. The formatted soap reduces efficiency of the catalysts.

2.2.3.2 Heterogeneous catalysis

Meaning of heterogeneous catalyst is a different phase of catalyst in the substrate. In heterogeneous system, the major phase of catalyst is solids in gases or liquids phase of substrate. It can be catalyzed in chemical reaction without them undergoing changes. The heterogeneous catalysts for biodiesel production can be solid acid catalysts (Amberlyst-15, zeolites and sulfated zirconia) or solid base catalysts (hydrotalcites, metal oxides, metallic salts and supported base catalysts).

Advantages of heterogeneous catalysts are higher biodiesel yield and glycerol purity, easier catalyst separation and recovery, lower cost and toxicity and lesser washing step. Furthermore, the heterogeneous catalysts are number one for biodiesel production. It can reduce side reaction such as saponification and hydrolysis.

2.2.3.3 Enzyme catalysis

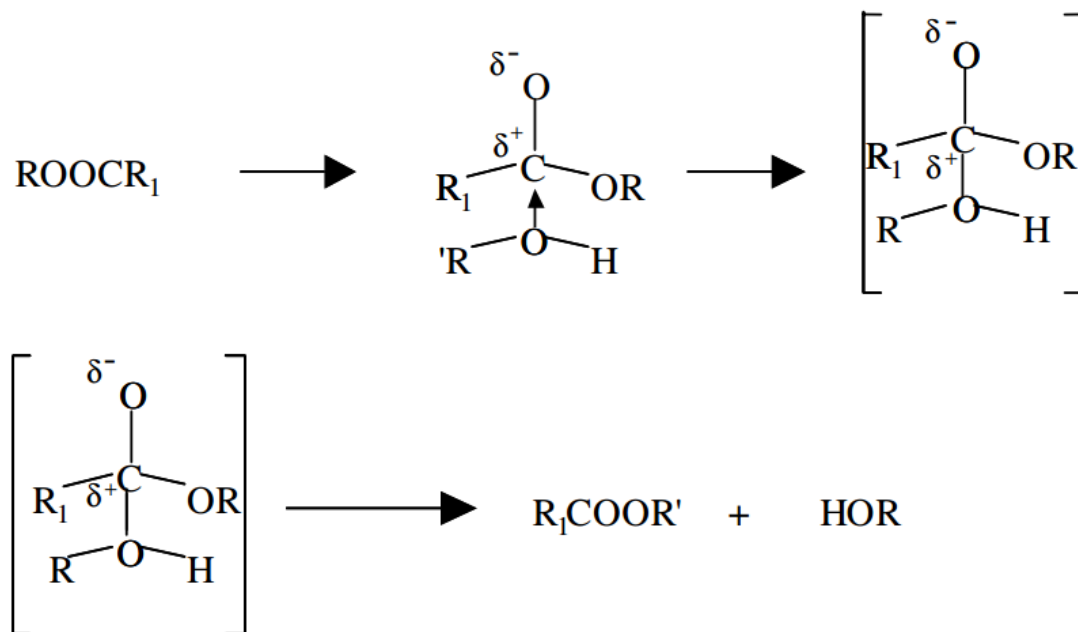
High free fatty acid of oils, the basic catalysts have the problem of saponification during the transesterification reaction. In the case of acid catalyst, it have slow reaction rate. Thus, enzyme catalysts are used for this problem. Advantages of enzyme catalysts avoid soap formation, works at neutral pH, lower reaction temperatures and thus can be economical. It can be immobilized on solid supports for reusability of enzyme catalysts. Several methods for immobilized enzymes are covalent bonding, cross-linking and micro-encapsulation. The main enzyme catalyst for transesterification is lipase. It can catalyze both hydrolysis and transesterification of triglycerides for biodiesel production.

2.2.3.4 Supercritical

Supercritical methanolysis is process to produce biodiesel without catalyst. It is forming a single phase of methanol/oil mixtures in the supercritical state. Therefore, the reaction is completely in very short time. Advantages of this technique are non-catalytic system, high purity of products, low reaction time and environmentally friendly. However, the reaction requires higher temperature (250-430 °C) and pressure (35-60 MPa). It is technically limited for production scale. Table 2.3 shows comparison of other biodiesel production technology.

Figure 2.8 shows mechanism of transesterification of vegetable oils in supercritical methanol. By assumption, alcohol molecule directly attacks the carbonyl atom of the triglyceride at the high pressure. In the supercritical state depends on pressure and temperature. Hydrogen bonding would be significantly decreased, which would allow methanol to be a free monomer. The transesterification is completed via a methoxide transfer. Therefore, the fatty acid methyl ester and diglyceride are formed. Subsequently, diglyceride is transesterified to form methyl ester and

monoglyceride. In the last step, the monoglyceride is converted to methyl ester and glycerol.



ROH: diglyceride

R₁: long chain hydrocarbon

R': alkyl group

Figure 2.8 Mechanism of transesterification of vegetable oils in supercritical methanol [15].

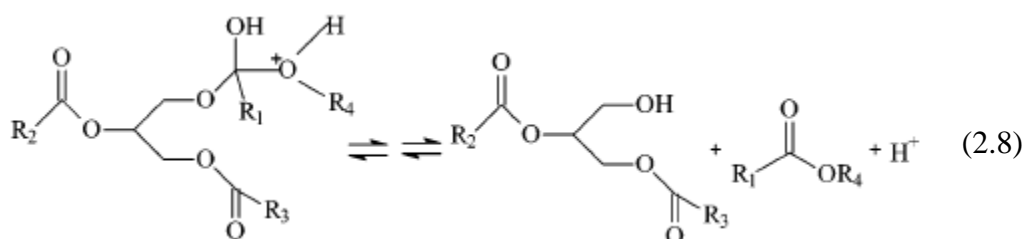
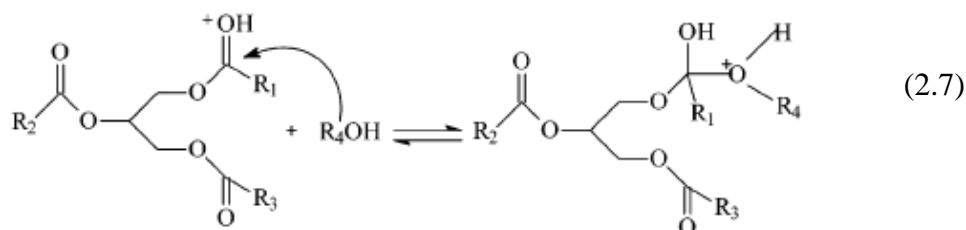
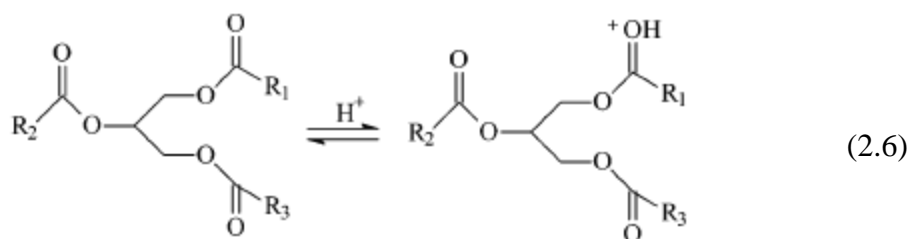
Table 2.3 Comparison of biodiesel production technology [16]

Technology	Homogeneous alkali catalysis	Metal oxide catalyst	Immobilized enzyme catalyst	Supercritical methanolysis
Contamination in glycerin	+	±	-	-
Reaction rate	++	-	-	+
Reaction condition	60 °C Atmospheric	60 °C Atmospheric	45 °C Atmospheric	350 °C 43 MPa
FFA pre-elimination	Required	Required	Unnecessary	Unnecessary
Conversion of FFA to FAME	Difficult	Difficult	Difficult	Possible
Other advantages/ disadvantages	Dated Process Alkaline waste	Short catalyst service life	Clean process Temperature control required	Higher plant construction/ maintenance cost

2.3 Catalysis system for transesterification

2.3.1 Acid catalyzed transesterification [17]

The mechanism of acid-catalyzed transesterification of vegetable oils is shown in Figure 2.9. In the first step, the proton from acid catalyst protonates on the triglyceride carbonyl group (Eq. (2.6)). Subsequently, an oxygen atom from alcohol molecule attacks on the activated carbonyl group (Eq. (2.7)). It forms a tetrahedral intermediate. Solvent as assisted proton migration gives rise a leaving group, promoting the cleavage of the tetrahedral intermediate and yielding a protonated alkyl monoester and a diglyceride molecule (Eq. (2.8)). The transfer of proton then regenerates the acid catalyst. Theoretically, 1 molecule of triglyceride gives 3 molecules of alkyl monoesters and 1 molecule of glycerol as the final products.



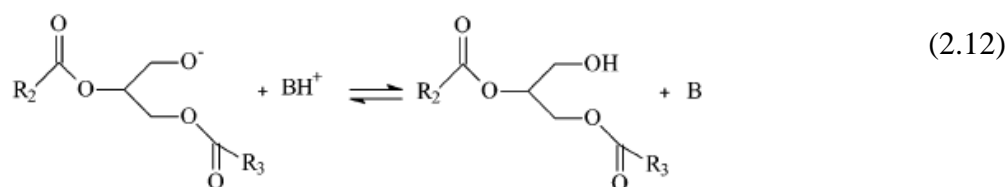
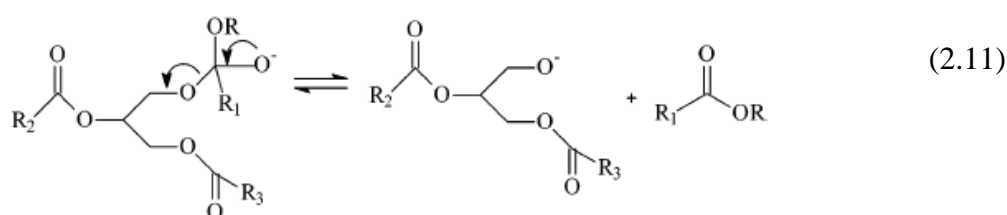
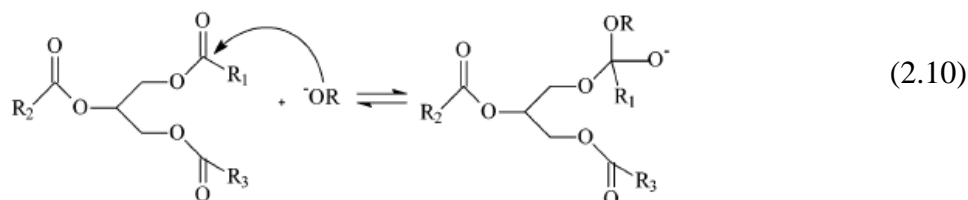
$\text{R}_1, \text{R}_2, \text{R}_3$: carbon chain of the fatty acids

R_4 : alkyl group of the alcohol

Figure 2.9 Mechanism of the transesterification of vegetable oils catalyzed by acid [17].

2.3.2 Base catalyzed transesterification [18]

Figure 2.10 shows the mechanism of base-catalyzed transesterification of vegetable oils. The first step, an alkoxide and the protonated catalyst are produced by base with alcohol (Eq. (2.7)). The alkoxide ion is a strong nucleophile and attacks the carbonyl group of triglyceride, generating a tetrahedral intermediate (Eq. (2.8)), from which the alkyl ester and the corresponding anion of diglyceride are formed (Eq. (2.9)). Finally, the deprotonation of the catalyst make to regenerate of active species (Eq. (2.10)). The regenerated catalyst is repeatedly used with alcohol for another catalytic cycle. In this mechanism, Diglyceride and monoglyceride are transformed to a mixture of alkyl esters and glycerol.



B: base catalyst

R₁, R₂, R₃: carbon chain of the fatty acids

R₄: alkyl group of the alcohol

Figure 2.10 Mechanism of the transesterification of vegetable oils catalyzed by base [18].

2.4 Heterogeneous catalyst preparation [19]

Heterogeneous catalyst preparation is composed two general methods such as bulk catalysts or supports and impregnated catalysts. The methods are based on the catalytic active phase generated as a new solid phase and the active phase introduced or fixed on a pre-existing solid. Physical and chemical properties of heterogeneous

catalysts are strongly affected by catalyst preparation. The properties are the desired final composition.

2.4.1 Method of catalyst preparation [20-21]

2.4.1.1 Bulk catalysts and support

- **Precipitation.** Precipitation is one of the generally method for catalyst preparation. It is prepared both single component catalysts and supports. Precipitation is usually understood as obtaining a solid from a liquid solution. The first step is mixing of two or more solutions or suspensions of materials, causing the precipitation of an amorphous or crystalline precipitate or gel. The formation of the precipitate from a homogeneous liquid phase may occur as a result of physical transformations (change of temperature or of solvent, solvent evaporation) but most often is determined by chemical processes (addition of bases or acids, use of complex forming agents).

It is generally desirable to precipitate the desired material in such a form. The counterions of the precursor salts and the precipitating agent can be occluded in the precipitate during the precipitation. It can easily be removed by a calcination step. The precipitation is induced by two methods such as physical means and addition of a precipitating agent. The physical means are cooling or evaporation of solvent to reach supersaturation of the solution. Addition of a precipitating agent, ions introduce into the system via this route also have to be considered. Favorable ions are nitrates, carbonates, or ammonium.

- **Co-precipitation.** Co-precipitation is the combination of trace element into mineral structure during solid solution formation and recrystallization of minerals. In the synthesis of multicomponent systems, the problems are even more complex. Co-precipitation allows one to obtain good macroscopic homogeneity. The term co-precipitation is usually reserved for preparation of multicomponent precipitates. It often is the precursors of binary or multimetallic compound. The composition of the

precipitate depends on the differences in solubility between the components and the chemistry occurring during precipitation.

2.4.1.2 Supported catalysts [19-20]

- **Ion exchange.** Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. Supported catalysts is importantly used an ability in ion exchanger (cation or anion). The esteemed ion exchangers are zeolites, montmorillonite, and clay. The support containing ions A is plunged into an excess volume (compared to the pore volume) of a solution containing ions B. Ions B slowly penetrate into the pore space of the support. As the ions A pass into the solution. Until, the equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution.

- **Impregnation.** Impregnation is general method for catalyst preparation. It is the permanent solution to the porosity networks without impacting the functional or dimensional characteristics of the supports. A certain volume of solution containing the metal precursor is contacted with the solid support, and then it is aged, usually for a short time, dried and calcined. The impregnation composes five methods such as adsorption, pore filling, incipient wetness, evaporation to dryness and spray. Diagram of catalyst preparation by impregnation methods is shown in Figure 2.11.

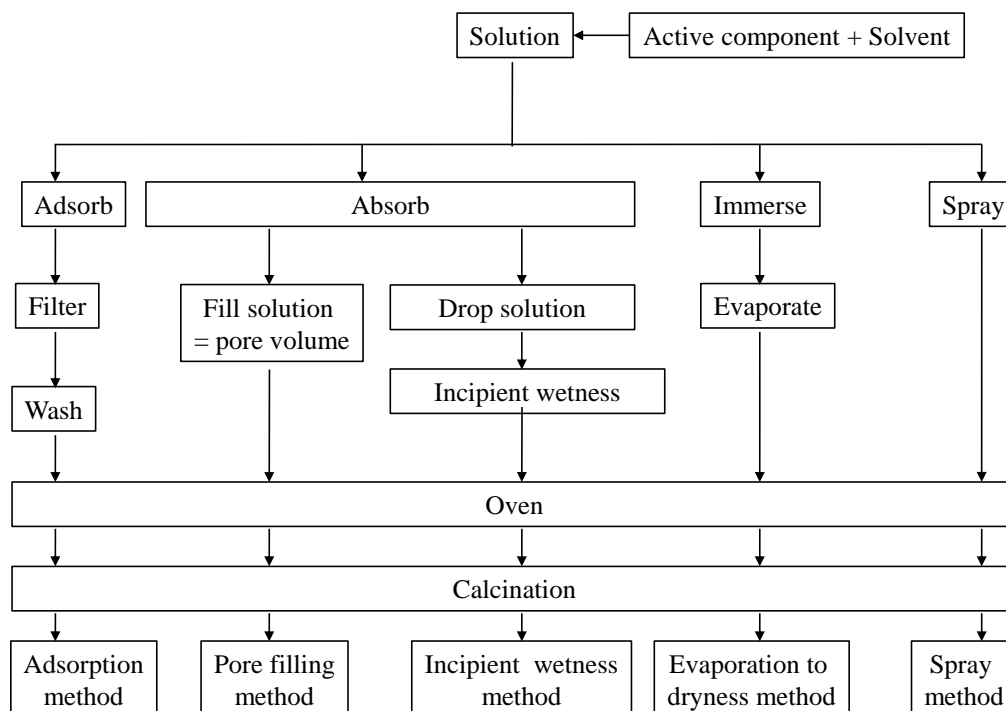


Figure 2.11 Diagram of catalyst preparation by impregnation method.

- Dissolution-precipitation.** Dissolution-precipitation method mainly composes two steps such as dissolved metal precursor and metal precipitated on the support [20]. The metal precursor is dissolved by acid solution for metal ion. A support material is subsequently added into the slurry. The metal ion precipitates on support material. Subsequently, the catalyst is evaporated to dryness for removed excess water. Finally, it is calcined for generated a new phases. Loading of metal precipitated on the support is determined by pH of the acid solution, the amount of metal precursor, and the temperature during the dissolution. In some cases, a supporter is accordingly required a type of added metal precursor in the acid solution.

2.4.2 Catalysts activation

After catalyst preparation, drying step removes of excess water in the catalyst using oven at 100 °C overnight. Subsequently, the catalyst is burned out any undesirable materials such as binder and organic material in the catalyst using muffle furnace. The catalyst is calcined for generating a new phases at various temperature. The used temperature is very important to generate crystallographic structure that should not high over that lead to sintering.

2.4.3 Catalyst formulation [23]

Generally, catalyst formulations compose of other methods such as extrudates, pellets, spheres, or monoliths. It is sometimes the final process in catalyst manufacture. It may be an intermediate step including formulation of the catalyst carrier before deposition of the active component.

The using of homogenously powdery catalyst in a fixed-bed reactor has problems of reactor blockage and pressure drop. The catalyst should be formed by formulation process before using in fixed-bed reactor. In the case of catalyst formulation, the major components are active sites, binder and plasticizer. A binder such as alumina, silica and clay is used for maintaining the formulated shape and improving strength of the enlarged particle. Also, a plasticizer is sometimes required to aid the catalyst formulation.

2.4.3.1 Catalyst shape [23-24]

Catalyst particulates are solids of relatively small dimension (a few microns to about 2-3 cm in diameter at most). It includes pellets, pills, rings, extrudates, spheres, granules, and powders for packed, slurry, and fluidized bed reactors. The catalyst manufacture of each forming is discussed separately below.

- **Pellets, pills and rings.** This process is formed by compressing catalyst or carrier powders in cylindrical dies at pressure ranging from 100-4000 atm. It causes grain boundaries to flow together, producing a uniform, high-strength pellet of moderate porosity and sometime of lower activity than original powder. The capability of forming strong pellets depends on its tensile strength, mesoporosity, and moisture content. This process has strong and uniformly-sized catalyst particles. Forming pellets is the most tedious, expansive method for producing particulate catalysts. However, the advantages of pellets are using in vapor or liquid applications requiring hard.

- **Extrudates.** Extrudates are formed by a heavy slurry or wet powder of catalyst or carrier. The material is extruded by mean of a hopper to a screw driver. This forces the material through holes of the desired shape. The shape of extrudates is formed by the description of dies holes such as circles, cogs, rings, ovals, lobed, circles or stars. The emerged material has shape solid ribbon. The ribbon is cut into the preferred lengths by a rotating knife or allows breaking into roughly uniform lengths. Subsequent, it is transferred to a dried section. Extrudates have lower strengths, higher porosities, and less regular shapes than pellets. However, the process of extrudates is significantly less expensive to make and produced at high rates.

- **Spheres.** Spheres are formed by a variety of methods on including (i) settling drops of hydrogel through oil, (ii) dropping hydrogel onto an inclined rotating pan containing a fine layer of moistened powder of the carrier, (iii) rolling extruded on material on a rotating wheel, and (iv) spaying large droplets down through the heated air space of a large tower to form prills.

- **Granules.** Granules are production of crushing and screening to specific mesh size such as 8-14, 6-8, 4-10, 4-6 and 2-4 mesh. Although these particles may have high bed porosity due to their irregular shapes. There is in some cases a tendency for small particles to pack into the interstices of larger ones. Therefore, it decreases bed porosity and increasing pressure drop.

- **Powder and microspheres.** Powder and microspheres used in fluidized bed and slurry reactor. The catalysts have particle diameters of 50-500 microns. It is produced by spray-drying process.

- **Monolithic catalyst.** Monoliths are defined here as honeycomb substrates having a cellular structure. Monoliths have body diameters of 2.5-50 cm and lengths of several centimeters to a few meters. Cell or channel densities range from 1.4 to 93 square cells/cm² (9-600 cells per in²). Although channel geometry may be square, triangular, hexagonal or sinusoidal. The square channels are most generally used.

Generally, commercial catalysts are available in any form such as pellets, spheres, granules, beads and extrudates. The each form of catalyst is used in different reactor. Table 2.4 shows guideline of commercial catalysts.

Table 2.4 Shapes of catalyst [25]

Form of catalysts	Diameter	Reactor
Spheres	$d = 1-10$ mm	Fluid bed reactor, moving bed reactor
Granules	$d = 1-20$ mm	Fluid bed reactor
Beads	$d = 1-5$ mm	Fluid bed reactor
Pellets	$d = 3-15$ mm	Fluid bed reactor
Extrudates	$d = 1-50$ mm	Fluid bed reactor

2.4.3.2 Paste extrusion [24]

Table 2.5 shows stages of forming a product by paste extrusion. The each stages of paste extrusion are discussed separately below.

- **Dry mixing.** Dry mixing stage has a purpose to uniformly mix all of solid components. It difficulty achieves for homogeneous solid components. Therefore, an addition of binder is used to help a mixing more distributed.

- **Wet mixing.** Wet mixing stage has a purpose to homogeneously distribute particles in liquid. During this stage, the mixing of the solid components also continues stirring. The stage may be made high viscosity of the mixture. The mixture is adheres by wet powder to the rotors or excessive entrapment of air. This problem can avoid by adding of clay or powder polymer.

- **High- shear mixing.**

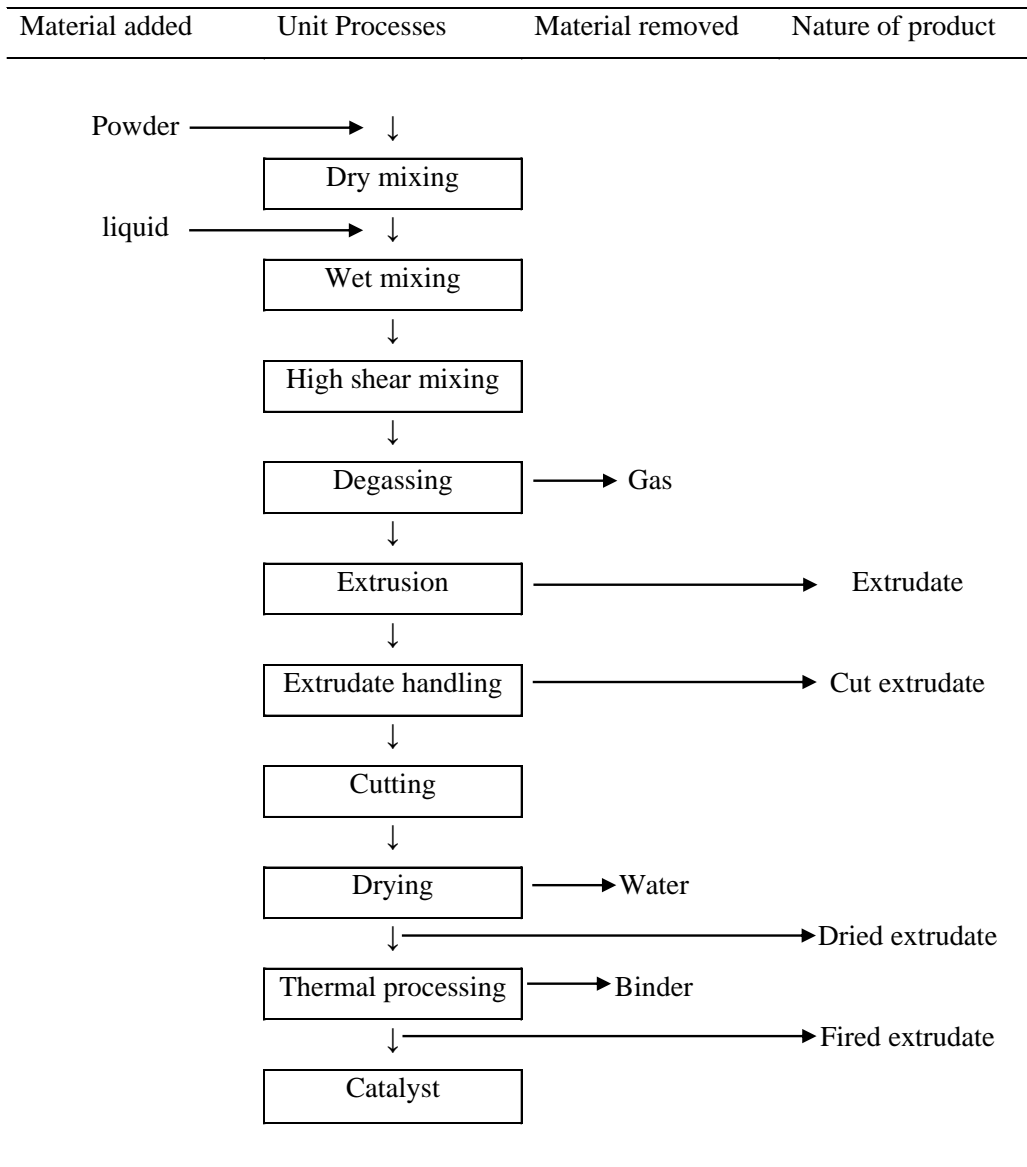
High-shear mixing stage is breaking down the agglomerates forming a liquid layer around individual particles. It is pleasing to secure the formation of single particles with a liquid layer or film covering the whole surface of each particle. In this process, the mixture importantly has a high viscosity. Therefore, the liquid leakage is not needed. An effect is promoted by the imposition of high stresses.

- **Degassing.** Degassing is a stage for removing of entrapped gas. It prevents of creation of voids in the structure during later processing stages.

- **Extrusion.** Extrusion is a stage to convert of shape and size of paste. The character of catalyst is carried by size and cross-section shape of die.

- **Extrudate handling and cutting.** Extrudate handling is a stage for removing the product. Subsequently, the product is formed by cutting stage for short units of the extrudate.

- **Thermal processing.** Thermal processing is a stage to burn out any undesirable materials such as binder and organic material in the extrudate. Also, it develops mechanical strength of the extrudate. The strength can be controlled by the relationship between temperature and time settle during calcination process. The stage should be used at high temperature to generate crystallographic structure. However, the temperature is not high to lead sintering of structure.

Table 2.5 Paste extrusion stages [25]

2.5 CaO as solid base catalyst for biodiesel production [26-31]

Heterogeneous base catalyst of solid base for biodiesel production is extensively interesting. CaO is the best choice for the solid base catalyst. The advantages of the CaO are low cost, high basicity and low solubility in methanol. Commercially, CaO is produced via a thermal decomposition at high temperatures of type of material source such as calcite, limestone, dolomite, seashells and egg shell. The types of material source have been studied on the transesterification of vegetable oils with methanol catalyzed by CaO.

Kouzu *et al.* [26] studied different calcium-based catalysts for biodiesel production via the transesterification of edible soybean oil with refluxing methanol. The reaction conditions are carried at the methanol/oil molar ratio of 12, amount of catalyst of 0.8 wt.% and reaction temperature of reflux methanol. CaO was obtained after calcination of pulverized lime stone. Moreover, Ca(OH)₂ prepared by hydration of CaO and CaO-air exposed by air was investigated. The FAME yield of CaO, lime stone, CaO-air and Ca(OH)₂ are 99 (1 h), 0 (4 h), 12 (4 h) and 99 wt.% (4 h), respectively. As the result, the CaO had high activity. However, CaO was also rapidly poisoned by the moisture and carbon dioxide in the ambient atmosphere.

Ngamcharussrivichai *et al.* [27] prepared CaO catalyst from dolomite, calcite, cuttlebone, hydroxyapatite, and dicalcium phosphate via a thermal decomposition at high temperatures. The transesterification of palm kernel oil (PKO) with methanol over the CaO was performed at the methanol/oil molar ratio of 30, amount of catalyst of 6 wt.%, reaction temperature of 60 °C and reaction time of 3 h. At 3 h of the reaction, the FAME yield of CaO catalyst from dolomite, calcite, cuttlebone, hydroxyapatite, and dicalcium phosphate are 98.6, 46.8, 24.1, 2.6 and 1.3 wt.%, respectively. As the result, the dolomite calcined at 800 °C was the most active catalyst. In the case of AR grade, the CaO give 92.8 wt.% of FAME yield.

Cho *et al.* [28] prepared CaO catalyst from calcium precursor such as calcium nitrate, -oxalate, -acetate, -carbonate and -hydroxide. Calcium carbonate is the major source of CaO used in a variety of industrial field. Calcium hydroxide is proper for preparation of highly pure CaO. Calcium acetate and -nitrate are convenient for preparing the supported CaO catalyst due to their large solubility in water. In

preparing of CaO catalyst, the calcination temperature of calcium nitrate, -oxalate, -acetate, -carbonate and -hydroxide was 600, 800, 800, 700 and 900 °C, respectively. The transesterification of tributyrin with methanol over the CaO was performed at the methanol/oil molar ratio of 6, amount of catalyst of 0.1 wt.%, reaction temperature of 60 °C and reaction time of 2 h. As the result, the calcium nitrate precursor gave the least product yield. Since the CaO catalyst from the calcium nitrate precursor was largest particles. On the other hand, the most active CaO catalyst was prepared from the hydroxide precursor. Since the CaO catalyst from the calcium hydroxide precursor had largest surface area. Among calcium carbonate, -acetate and -oxalate, there was no appreciable difference in the catalytic potentiality.

Viriya-empikul *et al.* [29] studied CaO catalyst derived from waste shells of egg, golden apple snail, and meretrix venus. It was employed to produce biodiesel from transesterification of palm olein oil. The shell materials were calcined in air at 800 °C to generate CaO catalyst. The condition of transesterification was methanol/oil molar ratio of 6, amount of catalyst of 18 wt.%, reaction temperature of 60 °C and reaction time of 2 h. The order of the catalytic activity over the waste shells catalysts was as follows: eggshell > golden apple snail shell > meretrix venus shell. The eggshell had the highest Ca content and highest surface area with smallest particle size. It could be the reason of highest biodiesel yield.

Experimental data from a variety of research papers on preparation of active CaO catalyst are shown in Table 2.6.

Table 2.6 Experimental data from a variety of research papers on preparation of active CaO catalyst [30]

Material source	CaO catalyst		Feedstock	Catalyst (wt%)	Transesterification		FAME (wt.%)
	Cal.	S _{BET}			Ratio ^a	Temp.	
Limestone	None	13.0	Soybean	0.8	12	Reflux	93 (1 h)
	900	10.0	Soybean	0.8	12	Reflux	10 (4 h)
CaO	None	n.d.	PKO	6.0	30	60	92 (2 h)
Dolomite	800	20	PKO	6.0	30	60	98 (2 h)
Calcite	800	n.d.	PKO	6.0	30	60	47 (2 h)
Cuttlebone	800	n.d.	PKO	6.0	30	60	92 (2 h)
Hydroxyapatite	800	n.d.	PKO	6.0	30	60	3 (2 h)
Dicalcium phosphate	800	n.d.	PKO	6.0	30	60	1 (2 h)
Calcium nitrate	600	n.d.	Tributyryn	0.1	6	60	50 (2 h)
Calcium oxalate	800	15	Tributyryn	0.1	6	60	80 (2 h)
Calcium acetate	800	21	Tributyryn	0.1	6	60	80 (2 h)
Calcium carbonate	900	11	Tributyryn	0.1	6	60	80 (2 h)
Calcium hydroxide	700	25	Tributyryn	0.1	6	60	95 (2 h)
Eggshell	800	1.1	Palm olein	10	18	60	90 (2 h)
Snail shell	800	0.9	Palm olein	10	18	60	90 (2 h)
Meretrix venus shell	800	0.5	Palm olein	10	18	60	90 (2 h)

^a methanol/oil molar ratio.

“n.d.” means not analyzed.

Boey *et al.* [31] reviewed reaction mechanism for CaO-catalyzed transesterification of many researchers. The mechanism is shown in Figure 2.12. In first step, the methoxide ion on catalyst surface attacks the carbonyl group of triglyceride (Eq. (2.13)). Subsequently, tetrahedral intermediate is formed (Eq. (2.14)). A diglyceride anion and a mole of methyl ester are formed by the rearranged intermediate. Moreover, a proton from the catalyst surface stabilized the charged-anion (Eq. (2.15)). The cycle continues until, 1 molecule of triglyceride gives 3 molecules of alkyl monoesters and 1 molecule of glycerol as the final products.

Calcium diglyceroxide compound can be formed from the reaction between calcium oxide and glycerol. However, the calcium diglyceroxide has also been recognized as a catalyst.

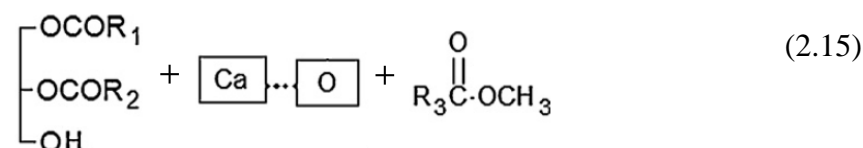
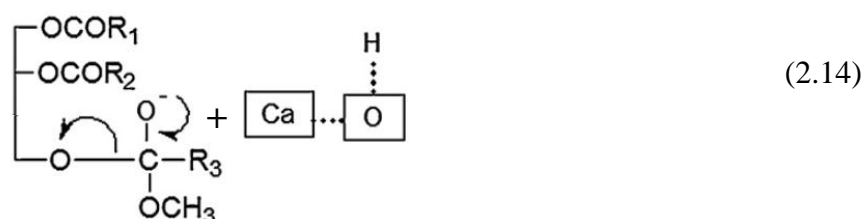
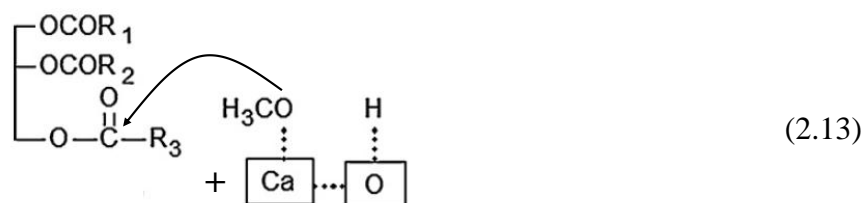


Figure 2.12 Mechanism of CaO-catalyzed transesterification [31].

2.6 Seashells [29]

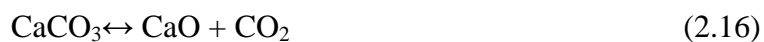
2.6.1 Definition

A seashell or sea shell, also known simply as a shell, is a hard, protective outer layer created by an animal that lives in the sea. In Thailand, the seashell is the waste of the agricultural and food industries. In the market, the seashell is used for animal feed and fertilizer. The seashell is mainly composed of calcium carbonate (CaCO_3). However, the seashell may have mixing of organic compound such as chitin. Before using for that, the seashell is washed, boiled, ground, sieved and calcined.

2.6.2 Thermal decomposition of seashell

A variety of research papers, the seashell exhibits one major decomposition of 42%, ranged 575–800 C, with centered temperature around 750 C. The decomposition can be attributed to the evolvment of CO_2 and the weight loss matched to the

stoichiometrical weight loss of 44% when CaCO_3 transforms to CaO . The phenomenon occurring during the thermal decomposition of seashell could be as follows:



2.6.3 Sources of seashells in Thailand

Actually, the agricultural and food industries are the large private sectors. The seashell is waste from food industries. The waste seashell from that is used to increase of cost using in agricultural industries such as chemical and animal food. In Thailand, the waste seashells mainly are *perna viridis*, *anadara granosa*, *amusium pleuronectes* and *meretrix meretrix* from those industries were produced several tons a day. Sources of seashell have been generally found in every region of Thailand such as following.

Agricultural industries	: Amphoe Donsak in Surat Thani Province
	: Amphoe Tha Muang in Kanchanaburi Province
	: Amphoe Na Thawi in Songkhla province
	: Muang Samut Sakhon in Samut Sakhon Province
Food industries	: Amphoe muang in Samut Sakhon Province
	: Amphoe muang in Songkhla province
	: Amphoe Klaeng in Rayong province
	: Amphoe Kabin Buri in Prachin Buri province

2.6.4 Applications of seashell on transesterification

Commonly, $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{OH})_2$ or CaCO_3 are the raw material to produce CaO. For instance, eggshell, mollusk shell, and bone are several natural calcium sources from wastes. Many researchers studied using seashell to produce CaO for biodiesel production. Recently, the using CaO from seashell (oyster shell, eggshells and mud crab shell) catalyzed in transesterification. Distinction of activity of the CaO from the commercial and seashell material is not significantly. The advantage of using CaO from seashell is a low-cost catalyst for biodiesel production. Searching for the alternative resource for low-cost catalyst synthesis is very attractive.

2.7 Literature review

Liu et al. [32] studied using CaO as a solid catalyst for transesterification of soybean oil with methanol. The BET surface area of the CaO was $0.56 \text{ m}^2/\text{g}$. The condition of transesterification was methanol/oil molar ratio of 12, amount of catalyst of 8 wt.% and reaction temperature of $65 \text{ }^\circ\text{C}$. At 3 h of the reaction, the biodiesel yield are 95.0 wt.%. Comparative activity of CaO with $\text{K}_2\text{CO}_3/\gamma\text{Al}_2\text{O}_3$ and $\text{KF}/\gamma\text{Al}_2\text{O}_3$ catalysts is investigated. Preparation of the impregnated catalysts on alumina support was carried out by an impregnation method. The impregnated catalysts were activated by calcination at $550 \text{ }^\circ\text{C}$ for 5 h. As the result, the CaO can be repeatedly used more than 20 repetitions with the retention of the biodiesel yield. However, the impregnated catalysts were not able to maintain activity and biodiesel yield after every use. Since the alkali metal compounds dissolved in methanol. It reduced the active ingredients and thereby decreasing biodiesel yield in the subsequent experiments. In this study, the presence of water is investigated. If in small amount of the water (less than 2.8 by wt.% of soybean oil), it acted as promoter. In the case of high amount of the water (more than 2.8 by wt.% of soybean oil), it hydrolyzed FAME under basic conditions and also induced soap formation.

Albuquerque *et al.* [33] loaded Ca salts on surface of SBA-15, which is one of mesoporous silica-based materials. SBA-15 was not collapsed at the temperature required for transforming the loaded Ca salts into CaO. On surface of SBA-15, the CaO particles were formed into aggregates in range of $0.5\text{--}3.0 \text{ }\mu\text{m}$. It couldn't

generate the nano-sized CaO dispersed on the surface of SBA-15 after calcination. However, the SBA-15 helps of the porosity of the catalyst which it may provide the stability against the leaching for CaO catalyst. In the leaching test, the solid base catalyst was preliminarily stirred into methanol solution. Subsequently, the solid base catalyst was removed by filtration. Finally, the test reaction was carried out in the presence of the methanol solution, instead of its original solid form. As the results, the methanol solution did not catalyze the test reaction. They concluded that the solid base catalyst did not leached Ca species in the methanol solution.

Meng *et al.* [34] studied effect of calcination temperature on the activity of solid Ca/Al composite oxide-based alkaline catalyst for biodiesel production. The Ca/Al composite oxide had composition of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and CaO phase. It was prepared by chemical synthesis from NaAlO_2 solution and $\text{Ca}(\text{OH})_2$ emulsion. Finally, the catalyst was calcined at temperature ranging from 120 to 1000 °C for transesterification. The reaction condition was carried at the methanol/oil molar ratio of 15, amount of catalyst of 6 wt.%, reaction temperature of 65 °C and reaction time of 3 h. The catalyst calcined at 600 °C showed the highest activity. Moreover, the Ca/Al composite was compared with CaO and NaOH. At 3 h of the reaction, the FAME yield of the Ca/Al composite, CaO and NaOH was 94.3, 92.6 and 96.0 wt.%, respectively. The advantage of Ca/Al composite catalyst was easy to separate from the reaction mixture and apparently stable.

Müller *et al.* [35] prepared the formulation of Cu/ZnO extrudates for the single-stage gas-phase processing of dimethyl maleate to tetrahydrofuran. In dry mixing step, the copper/zinc carbonate precursor was mixed with boehmite. In wet mixing step, the liquid phase (22 wt.%) was added. The mixture was mixed with high shear force in a rheo-kneader at a constant temperature of 20 °C and a rotor speed of 40 min^{-1} . In extrusion step, the paste was converted to cylindrical shape with a diameter of 2 mm and a length of about 400 mm. In drying step, the extrudates were dried at room temperature. In cutting step, the dried extrudates were cut into pieces of about 5 mm length. In thermal processing step, the extrudates particles were calcined in air for 3 h at 550 °C. Finally, the extrudate particles were formed the metal oxides by decarbonation of metal carbonates. Moreover, the binder particles were converted to a strong matrix of γ -alumina. The mercury porosimetry analysis of extrudates

indicated the presence of mesopores that are voids in between the catalyst particles and binders. Moreover, increasing of boehmite enhanced mechanical strength of extrudates. However, the active surface area and the catalytic activity were decreased.

Serrano *et al.* [36] investigated the mechanical strength of catalyst extrudates of TS-1 zeolites for propylene epoxidation. The catalyst paste was prepared by three different methods. In method I, the catalyst paste was mixed in two steps. Firstly, the TS-1 powder, clay (sepiolite) and methylcellulose were mixed by dry mixing method. Subsequently, distilled water (200 wt.% of solid) was added. In method II, TS-1 powder was suspended in water (200 wt.% of solid). Subsequently, clay was added in it. In method III, the catalyst paste was prepared from method II but using ultrasound and addition of water amount (240 wt.% of solid). In extrusion and cutting step, the catalyst paste was formed with a diameter of 3 mm and a length of 2 mm. In drying step, the extrudates particles were dried at 80 °C. In thermal processing step, the extrudates particles were calcined at 550 °C with a lower temperature ramp rate under air flow. As the result, method III was optimal extrusion procedure at higher mechanical strength. Since the used ultrasound could help to form a small particles and distribution in extrudates. The catalytic test of the extrudates particles was investigated in a fixed bed reactor. The evaluation of catalytic activity indicated that the conversion and the selectivity were close to 97% and 80%, respectively, which decreased slightly along the reaction time.

Ngamcharussrivichai *et al.* [37] investigated the effects of binder addition on the preparation of catalyst extrudates from limestone. The extrudates from heterogeneous catalysts from limestone using manual extruder can be conducted as followed: (i) add calcined limestone and/or metals oxide, hydroxide and carbonates (Ca, Mg and Al), (ii) add an NH_4^+ -based (NH_4OH and $(\text{NH}_4)_2\text{CO}_3$) caustic solvent or deionized water, (iii) change a powdery mixture into a uniform paste, (iv) shape into a continuous rod with a cross-sectional diameter of 2 mm by using a manual extruder, (v) dry at 100 °C and calcined in a muffle furnace at 800 °C. As the result, the addition of NaAlO_2 was a key to attain the dense and hard extrudates by inducing the formation of the mixed Ca and Al phases. The catalyst can be regenerated and used repeatedly. The catalytic test of the catalyst extrudates in the continuous-flow using fixed-bed reactor suggested the good activity and stability in the transesterification.

Bournay *et al.* [38] reported about new heterogeneous process for biodiesel production that had been developed by French Institute of Petroleum (IFP). The Zn–Al mixed oxide is used as the heterogeneous catalyst. It is packed into two fixed-bed reactor located in a stream of the continuous-flow transesterifying system. However, the reaction condition is operated at high temperature ranging from 210 °C to 250 °C and high pressure between 3 and 5 MPa. Excess of methanol is evaporated after each reactor by partial evaporation. Subsequently, the esters and glycerol is separate in settlers. In this procedure, biodiesel and glycerol has high purity without any salt contaminants. The process was first used in an industrial context in 2006, by Sofiproteol in Sete.

Kouzu *et al.* [5] investigated the reusability of CaO catalyst particles for biodiesel production in a circulating stream reactor. The lime stone is crushed for size in ranged from 1.0 to 1.7 mm. The top and bottom spaces of the column reactor were filled with active carbon ranged from 2.0 to 3.4 mm. Subsequently, the precursor and the employed active carbon were turned into the practical catalyst by only calcination at 900 °C. The reaction condition is operated at temperature ranging from 210 °C under atmospheric pressure with contact time at 2 h. As a result, the FAME yield is 96.5 wt.% at 2 h of the reaction time. It is good reaction efficiency went on for the successive 10 repetition, without exchanging the catalyst. On and after the 11th repetition, the reaction efficiency was slowly deteriorated. After the transesterifying operation was successively repeated 17 times. The practical catalyst was removed from the column reactor in order to investigate its deactivation.

Di Serio *et al.* [39] used a commercial Mg/Al hydrotalcite (Pural[®] MG76) in biodiesel production in a continuous packed bed reactor. The hydrotalcite composed of Al₂O₃ (25.8 wt.%) and MgO (74.2 wt.%). The hydrotalcite was pellets form with a diameter of 2.99 mm and a length of about 5.10 mm. Before use as catalyst, the hydrotalcite was calcined at 400 °C for 18 h. The biodiesel production was carried out at the reaction temperature of 220 °C, pressure of 55 bars, residence time of 6 min and total flow rate of 5.0 cm³/min in a laboratory micropilot plant. In the first run, the fresh catalyst was observed some deactivation during the time. After 15 h, the FAME yield was decreased from 85–80 to 60–65 wt.%. In the run after 50 h, the FAME yield was 50–55% wt.%. However, the catalyst can be completely regenerated by washing

with acetone. Advantages of the catalyst are sufficient activation, slow deactivation and easy regeneration.

CHAPTER III

EXPERIMENTAL

3.1 Materials and chemicals

3.1.1 Chemicals for catalyst preparation

1. Waste mixed seashells of *Perna viridis*, *Anadara granosa*, *Amusium pleuronectes* and *Meretrix meretrix* (Thai Dolomite Company Limited)
2. Calcium carbonate (CaCO_3) (Al_2O_3 , 95%) (AR grade, Ajax Finechem)
3. Aluminum oxide (Al_2O_3 , 95%) (AR grade, Ajax Finechem)
4. Aluminum oxide (Al_2O_3 , 99.6%) (Commercial grade, Fuji Kasei)
5. Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.8%) (AR grade, Ajax Finechem)
6. Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98.0%) (Commercial grade, PPM Chemicals)
7. Nitric acid (HNO_3 , 50-70%) (JT. Baker)
8. Hydroxyethyl cellulose (2,960 cP at 1% aqueous solution) (Commercial grade, Thai Specialty Chemical Company)

3.1.2 Chemicals for transesterification reaction

1. Refined bleach deodorized palm oil (The Patum Vegetable Oil Company Limited)
2. Methanol (CH_3OH , 99.5%) (Commercial grade)
3. Sodium sulfate anhydrous (Na_2SO_4 , 99%) (AR grade, Ajax Finechem)

3.1.3 Chemicals for reaction products analysis

1. Methyl heptadecanoate ($C_{18}H_{36}O_2$, 99.5%) (Synthesis grade, Fluka)
2. *n*- Heptane ($n-C_7H_{16}$, 99.8%) (AR grade, Riedel- deHaën)

3.2 Instruments and equipments

1. Muffle furnace
2. Desiccator
3. pH meter
4. Overhead stirrer
5. Oven
6. Centrifuge
7. Rotary evaporator
8. Hot plate & stirrer
9. Manual extruder (Figure 3.1)
10. Single screw extruder (The Bonnot Company, Catalyst Extruders) (Figure 3.2)

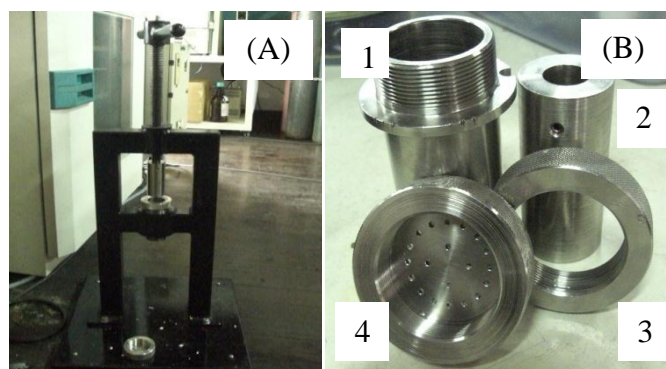


Figure 3.1 Manual extruder used for catalyst formulation: Extruder (A) and extruder components (B) (1= sample receptacle, 2 = pressing rod, 3= ring for locking the receptacle and 4 = 2-mm hole die).

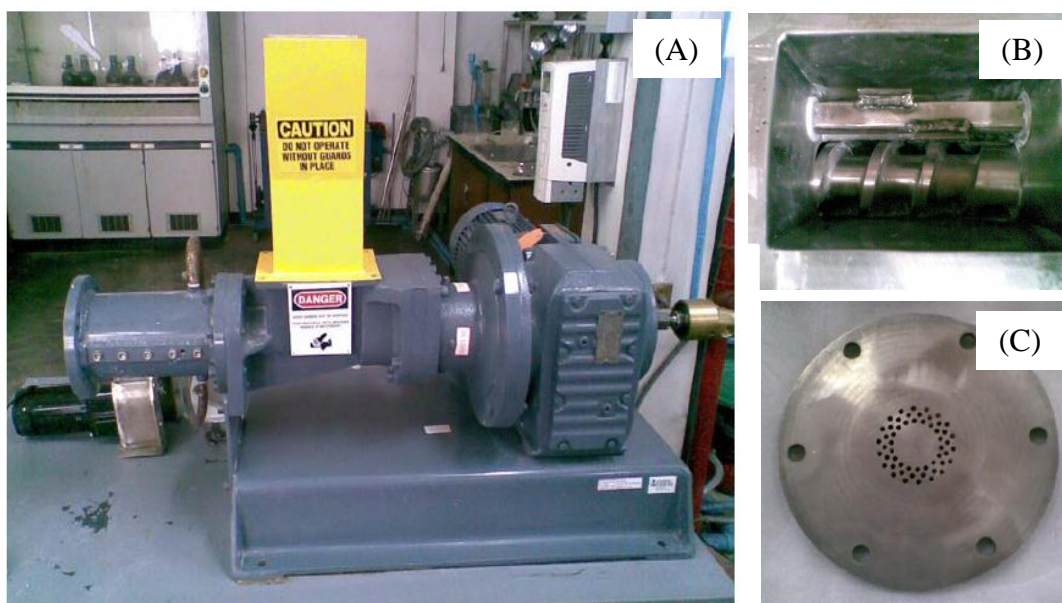


Figure 3.2 Single screw extruder used for catalyst formulation: Extruder (A), screw feeder (B) and 3.5-mm hole die (C).

3.3 Catalyst preparation by dissolution-precipitation method

3.3.1 Powdery catalyst

Raw seashells were received free of charge from the Thai Dolomite Company Limited in Surat Thani Province. They were mixture of several species of seashells, including *Perna viridis*, *Anadara granosa*, *Amusium pleuronectes* and *Meretrix meretrix*. It was ground and sieved to reduce particle size to $< 10 \mu\text{m}$ before being used. A seashell-derived catalyst was prepared by dissolution-precipitation method. Firstly, the raw seashell was calcined at $800 \text{ }^\circ\text{C}$, and then it was mixed with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution under acidic conditions using HNO_3 for pH adjustment. The slurry was vigorously stirred at ambient temperature to which Al_2O_3 was added. The resulting mixture was sonicated until dry. Finally, the catalyst paste was further dried in an oven at $100 \text{ }^\circ\text{C}$ for 24 h, crushed into powder and calcined in a muffle furnace at $300\text{-}800 \text{ }^\circ\text{C}$ for 2 h at a heating rate of $3 \text{ }^\circ\text{C min}^{-1}$. Hereafter, the catalyst in powdery form was designated as ZSA-P (Figure 3.3 (a)).

3.3.2 Extrudate catalyst

Firstly, the raw seashell was calcined at 800 °C, and then it was mixed with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution under acidic conditions using HNO_3 for pH adjustment. The mixing of the raw seashell and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution used overhead stirrer for vigorously stirred. After stirring for 2 h, Al_2O_3 was added into the mixture and further stirred for 1 h. Plasticizer (HEC) was then added and the resulting mixture was vigorously stirred and heated until forming catalyst paste. The solid paste was shaped to continuous rods by using extruder. There were two types of extruders used in the present work: Manual extruder (Figure 3.3 (B)) and single screw extruder (Figure 3.3 (C)). The extruded rods were dried at 100 °C and cut to 5-mm long length extrudates. Finally, the extrudates were calcined at 300-800 °C using a muffle furnace. Hereafter, the catalyst extrudates shaped by the manual extruder were denoted as ZSA-ME, while ZSA-SE was referred to as the extrudates formulated by the single screw extruder. Figure 3.3 shows the catalysts with different forms that were prepared in this work.



Figure 3.3 Photographs of the catalyst powdery ZSA-P (A) and extrudates ZSA-ME (B) and ZSA-SE (B).

3.4 Transesterification reaction

3.4.1 Batch system

The batch system was used initially to evaluate the transesterification activity of the catalysts prepared. The transesterification reaction was examined in a three-necked glass reactor (100 mL) equipped with a magnetic stirrer and a water-cooled condenser (Figure 3.4). The amount of catalyst was 10 wt.% based on the weight of palm oil. The methanol/palm oil ratio was 30:1. The reaction conditions were carried

out at 60 °C using a water bath for 3 h. The catalyst was separated by centrifugation at 5000 rpm for 30 min and the excess methanol was removed by rotary evaporator. Layer of FAME was washed by deionized water and dried with anhydrous Na₂SO₄. The FAME composition was determined by a gas chromatography (GC).



Figure 3.4 Experimental setup for the transesterification of palm oil with methanol under batch condition.

3.4.2 Continuous system

Figure 3.5 shows the simplified depiction of the continuous fixed-bed reactor system used for the transesterification of palm oil with methanol. The fixed-bed reactor was made of a glass column having 30-cm height and 3-cm diameter. Glass beads (average diameter = 3 cm) were used as ground bed materials which was packed at the top and the bottom of the catalyst bed. The height of catalyst bed was 22 cm. Peristaltic pumps were used for feeding reaction mixtures to the column reactor and controlled total flow rate of the reaction mixtures. The reaction was carried out at 65 °C using a heater band equipped with a thermocouple. After the reaction, the excess methanol was removed by evaporation, resulting in two-layer separation of liquid products. The composition of FAME containing in the upper phase was determined by a gas chromatography.

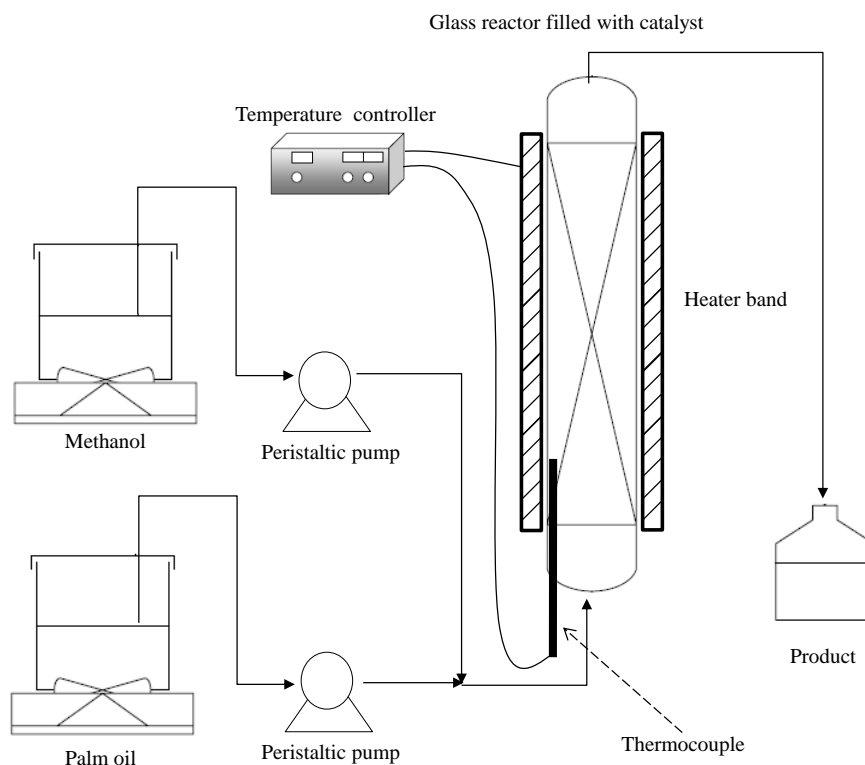


Figure 3.5 Schematic diagram of experimental setup for the transesterification of palm oil with methanol under continuous condition.

3.5 Analysis of FAME composition

The analysis of FAME product was carried out with a Shimadzu 14B gas chromatograph (GC) equipped with a flame ionization detector (FID) and a 30-m DB-Wax capillary column (Figure 3.6). The quantity of FAME produced was determined following the standard method EN 14103 using methyl heptadecanoate (99.5%, Fluka) as the reference standard. Table 3.1 shows the GC conditions for determining the FAME composition. The FAME yield was calculated according to the equation below:

$$\text{FAME yield (wt.\%)} = \frac{\text{Weight of FAME attained by GC}}{\text{Theoretical weight of FAME}} \times 100 \quad (3.1)$$



Figure 3.6 Shimadzu 14B gas chromatograph.

Table 3.1 The GC conditions for determination of FAME composition

Parameter	Value
Carrier gas (He) flow rate	1.0 mL min ⁻¹
Make up gas (He) pressure	100 kPa
Hydrogen pressure (for FID)	60 kPa
Air pressure (for FID)	30 kPa
Detector temperature	250 °C
Split ratio	1 : 100
Injection port temperature	250 °C
Inject volume	0.1 µL
Initial column temperature	180 °C
Ramp rate	8 °C min ⁻¹
Final column temperature	200 °C

3.6 Instruments and Equipments for Characterization of Catalyst

3.6.1 X-ray fluorescence spectrometer [41]

The X-ray fluorescence spectroscopy (XRF) was used to determine the elemental composition of seashells. The analysis was performed on an Oxford ED-2000 X-ray fluorescence spectrometer at the Scientific and Technological Research Equipment Centre of Chulalongkorn University.

The schematic drawing of the XRF process is shown in Figure 3.7. The XRF is an atomic spectrometric method based on the detection of emitted X-ray radiation from excited atoms. If the energy from the primary X-ray photon is enough to eject an inner electron (K-shell), the atom becomes unstable and the missing inner electron was replaced by an outer electron. When this happens, an outer electron with a higher energy level orbital will be transferred to an inner electron with the lower energy level orbital. During this transition a photon maybe emitted from the atom. The fluorescent radiation is termed the characteristic X-ray of the element. Characteristics of a transition between specific electron orbitals in a particular element have the energy of the emitted photon. The resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample.

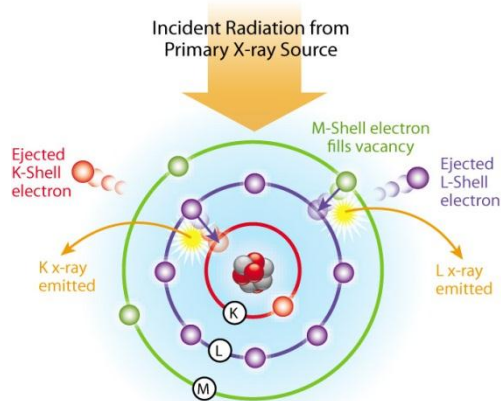


Figure 3.7 Schematic drawing of the XRF process.

3.6.2 X-ray diffractometry [42]

The X-ray diffractometry (XRD) was used to identify crystalline phase. The analysis was performed on a Bruker D8 Discover X-ray diffractometer equipped with Cu K α radiation.

XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. When an X-ray beam strikes a surface of crystalline sample at an angle θ , a portion of the radiation is scattered by the layer of atoms at the surface. A diffraction of the beam is the effect of scattering from the regularly spaced centers of the crystal. The diffraction of X-rays indicates that the spacing between layers of atoms and the scattering centers must be spatially distributed in a higher regular way (Figure 3.8).

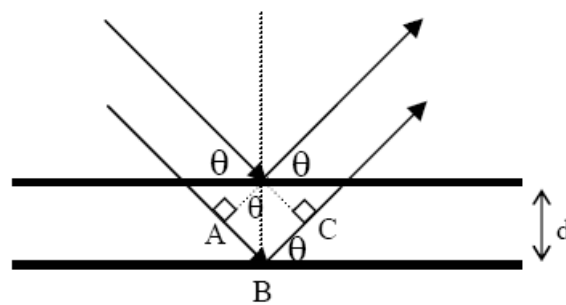


Figure 3.8 Diffraction of X-rays by a crystal.

The interaction of the incident rays with the sample produces constructive interference and a diffracted ray when conditions satisfy Bragg's Law with equation (3.2). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

$$n\lambda = 2d \sin \theta \quad (3.2)$$

Where n = An integer

d = Interplanar distance of the crystal (\AA)

θ = Angle between X-ray beam and crystal planes (degree)

λ = Wavelength of X-ray beam (\AA)

3.6.3 Thermogravimetric/differential thermal analyzer [43]

Thermal degradation of the raw seashells and the catalysts prepared was studied by the thermogravimetric/differential thermal analysis (TGA) using Perkin Elmer Pyris Diamond thermogravimetric/ differential thermal analyzer. A sample (~10 mg) was loaded into platinum pan on thermobalance and heated from 40 to 1,000 °C with a heating rate of 8 °C min⁻¹ under a dry nitrogen flow (50 mL min⁻¹).

In the thermogravimetric analysis, the mass of a sample in a controlled nitrogen atmosphere is recorded continuously as a function of temperature or time as the temperature of the sample is increased. This technique is commonly employed in research and testing to determine degradation temperatures, to determine characteristics of materials, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation. The data provided by thermogravimetric methods is more constrained than that obtained with differential scanning calorimetry (DSC) and differential thermal analysis (DTA), because here a temperature variation must bring about a change in mass of the analyze.



Figure 3.9 Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer.

3.6.4 Chemisorption analyzer [44]

The CO₂-pulse chemisorption analysis was applied to determine the amount of the basic sites in the catalysts using CO₂ as molecular probe. The analysis was performed on a Micromeritics AutoChemII 2920 chemisorption analyzer equipped with a thermal conductivity detector (TCD) (Figure 3.10). The experimental procedure started from loading some of sample in a U-shape tube after which the sample was pretreated at 300 °C under Ar flow (50 mL min⁻¹) for 1 h. Since the pretreating at low temperature protected the sample was changed to from a new phase. Subsequently, CO₂ diluted in Ar (10 vol.%) was pulsed into the tube until the sample was saturated with CO₂. The TCD was used to determine the amount of saturated CO₂ chemisorbed on basic sites.



Figure 3.10 Micromeritics AutoChemII 2920 Chemisorption analyzer.

3.6.5 Scanning electron microscopy [45]

Scanning electron microscopy (SEM) is used to study the morphology of catalysts. The SEM images were recorded on a JEOL JSM-5410 LV scanning electron microscope using a 15 kV electron beam with a magnification of 15 - 35,000. The sample was sputter-coated with gold before the observation.

The SEM technique relates rastering a narrow electron beam over the surface and detecting the yield of backscattered or either secondary electrons as a function of the primary electron beam. Contrast is occurred by the orientation: Parts of the surface facing the detector appear brighter than parts of the surface with their surface normal, pointing away, from the detector. The secondary electrons have mostly low energies (~5-50 eV) and originate from the surface region of the sample. Backscattered electrons come from deeper and carry information on the composition of the sample, because heavy elements are more efficient scatters and appear brighter in the image. A schematic diagram of the SEM instrument is shown in Figure 3.11.

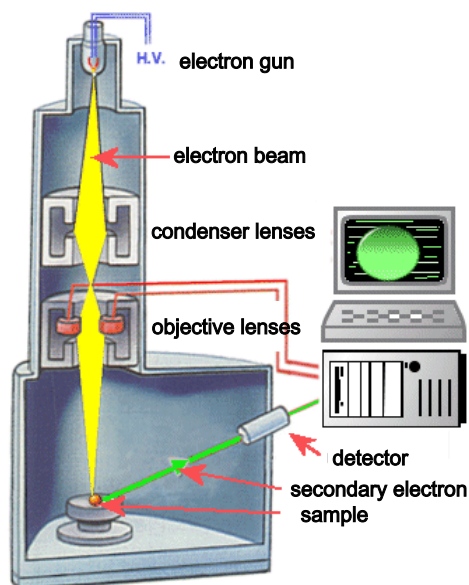


Figure 3.11 Schematic diagram of scanning electron microscope.

3.6.6 N₂ adsorption-desorption measurement [46]

Textural properties of the waste mixed seashells and the catalysts after the formulation were measured by a technique of N₂ physisorption using a Micromeritic ASAP 2020 surface area and porosity analyzer (Figure 3.12). Calculation of surface area was based on the BET equation using the linear-relationship data attained in the P/P₀ range of 0.02–0.2.



Figure 3.12 Micromeritic ASAP 2020 surface area and porosity analyzer.

The N₂ physisorption is a technique used to determine the specific surface area, pore size and pore volume of powders, solids and granules. Clean solid surfaces adsorb surrounding gas molecules and Brunauer-Emmett-Teller theory (BET) provides a mathematical model for the process of gas sorption. This physical adsorption of a gas over the entire exposed surface of a material and the filling of pores is called physisorption. The BET surface area measurement is crucial in understanding the behaviour of a material, as material reacts with its surroundings via its surface, a higher surface area material is more likely to react faster, dissolve faster and adsorb more gas than a similar material with a lower surface area.

3.6.7 Crushing strength [23]

The catalyst extrudates in a fixed-bed reactor is used to solve of reactor blockage and pressure drop. However, the catalyst extrudates necessarily has enough strength during the reaction procedure. Therefore, crushing strength is a technique used to determine the strength of catalyst extrudates.

The crushing strength for spheres (ASTM D-4179-82, 1988) is determined by simply crushing a several particles or single particle representative of the lot between parallel plates of a device capable of exerting compressive stress, while recording the force mandatory to crush the material. The crushing strength of extrudates, tablets or monoliths can also be characterized by a similar procedure; however, currently no standardized methods exist. A sample is emphasized within the plates so as to capacitate determination of either axial or radial crush strength in separate tests. Naturally, an enough number of particles must be tested to receive proper statistics. The method cannot be used reliably for granular or other materials with irregular shapes.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Waste mixed seashells as heterogeneous base catalysts for transesterification

4.1.1 Properties of waste mixed seashells

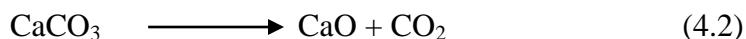
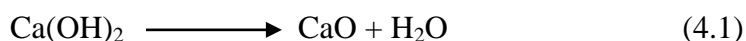
Table 4.1 shows the elemental composition of waste mixed seashells analyzed by XRF technique. The seashells were mainly composed of Ca with a trace amount of Mg, Al and Si.

Table 4.1 Elemental composition of waste mixed seashells analyzed by XRF spectroscopy

Material	Composition (wt.%)				
	CaO	MgO	Al ₂ O ₃	SiO ₂	Other ^a
Seashells	68.6	0.5	0.2	0.8	29.9

^aCO₂ as the major component.

Figure 4.1 shows that the raw seashells exhibited two-step weight loss. The weight loss at 444 °C corresponded to the dehydration of Ca(OH)₂ (weight loss = 7.4 wt.%), according to Eq. (4.1). The decarbonation of CaCO₃ occurred around 590-720 °C (weight loss = 27.2 wt.%), according to Eq. (4.2). The combination of the XRF and TGA results suggested that the quantities of Ca(OH)₂ and CaCO₃ in the as-received seashells were 24.7 and 61.8 wt.%, respectively.



The XRD patterns of the as-received seashells and the seashells calcined at 600 and 800 °C are shown in Figure 4.2. The non-calcined seashells had CaCO₃ and Ca(OH)₂ phases (Figure 4.2(a)). After the calcination at 600 °C, the seashells were composed of CaCO₃ and CaO phases (Figure 4.2(b)). In this case, CaO phase was generated via the dehydration of Ca(OH)₂. However, CaO could be transformed to Ca(OH)₂ upon exposure with atmospheric moisture during the XRD analysis. The calcination of seashells at 800 °C decomposed all of CaCO₃ and Ca(OH)₂, generating CaO phase (Figure 4.2(c)).

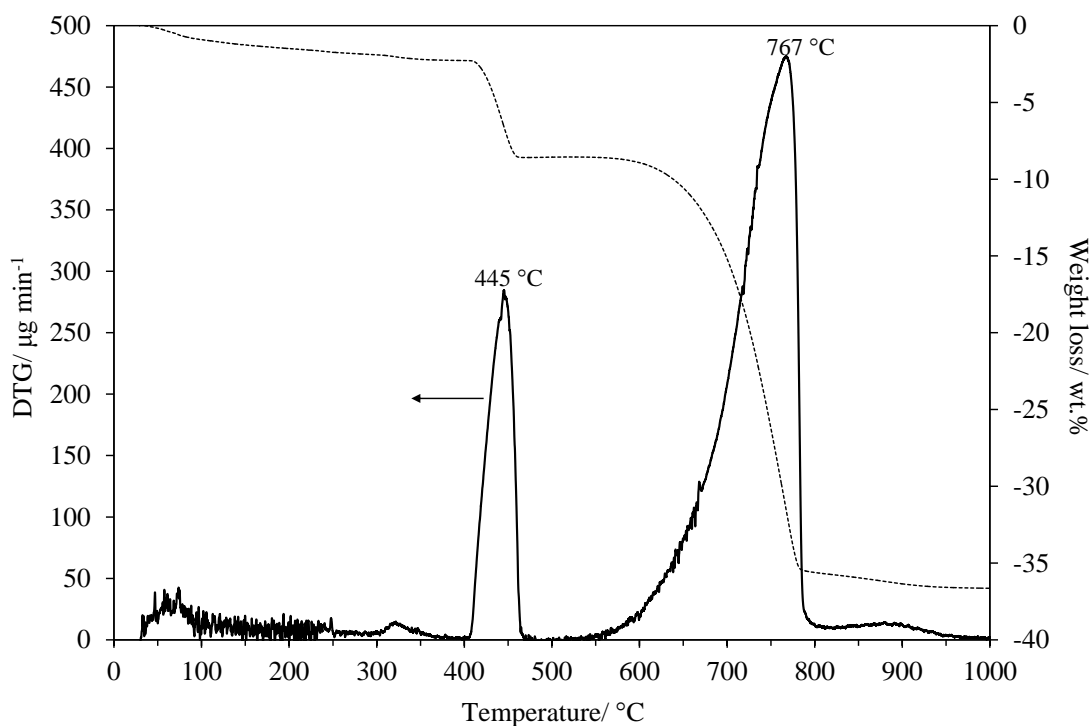


Figure 4.1 Weight loss and DTG curves of raw mixed seashells.

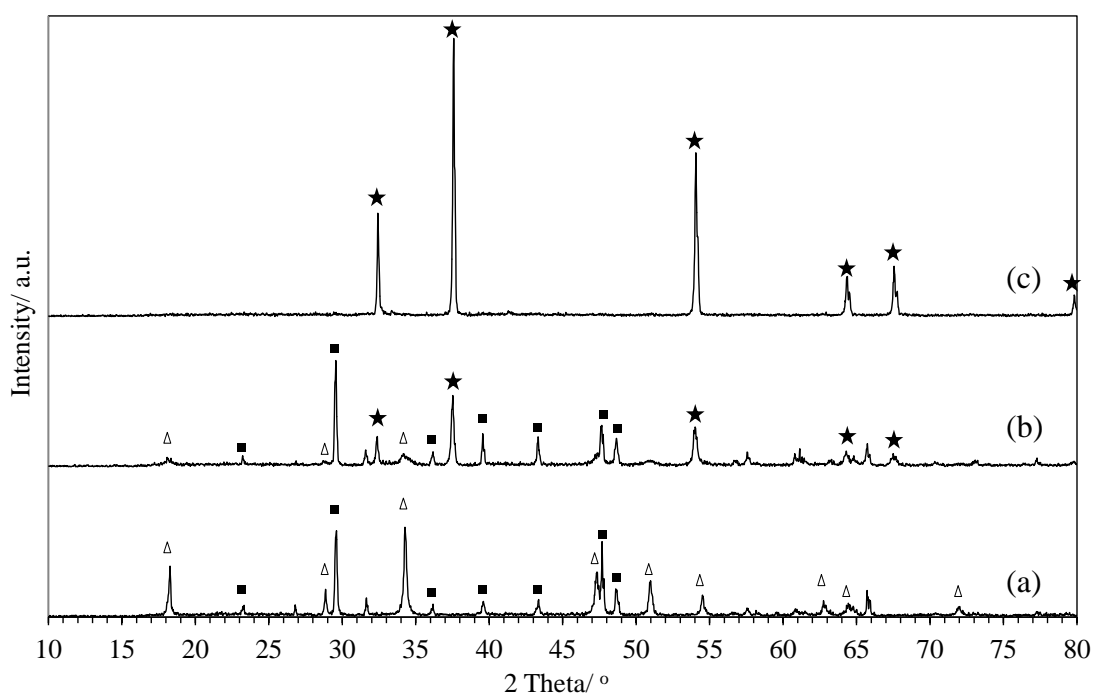


Figure 4.2 XRD patterns of raw mixed seashells (a) and mixed seashells calcined at 600 (b) and 800 °C (c). (Symbols: ■ = CaCO₃, Δ = Ca(OH)₂, ★ = CaO)

4.1.2 Transesterification over mixed seashells

4.1.2.1 Effect of calcination temperature of mixed seashells

Table 4.2 shows the effect of calcination temperature of waste mixed seashells on the FAME yield attained from the transesterification of palm oil with methanol. Using the raw seashells as the catalyst gave the lowest FAME yield of 24.4 wt.%. The FAME yield was increased to 34.2 wt.% when increasing the calcination temperature of seashells to 600 °C. These results should be due to the increase in the amount of CaO. In this case, CaO phase was generated via the dehydration of Ca(OH)₂ as evidenced by the weight loss and DTG curves (Figure 4.1) and the XRD results (Figure 4.2(b)). The FAME yield of 93.6 wt.% was achieved when the calcination of the mixed seashells was performed at 800 °C. Since the calcination at 800 °C, the seashells decomposed all of CaCO₃ and Ca(OH)₂, generating CaO phase (Figure 4.2 (c)).

Table 4.2 Effect of calcination temperature of mixed seashells on the FAME yield in the transesterification^a of palm oil with methanol under batch condition

Catalyst	Calcination temperature (°C)	FAME yield (wt.%)
Seashells	None	24.4
	600	34.1
	800	93.6

^aReaction condition: methanol/oil molar ratio, 30; temperature, 60 °C; time, 3 h; amount of catalyst, 10 wt.%.

4.1.2.2 Effect of amount of seashells catalyst

Effect of amount of seashells catalyst on the transesterification of RBD palm oil with methanol is summarized in Table 4.3. The as-received seashells were previously calcined 800 °C before being used in the reaction. It can be seen that the FAME yield increased from 53.4 to 93.6 wt.% when the amount of catalyst was

increased from 4 to 10 wt.%. This result implied that the increase in the methyl ester formation was due to the increase in the number of active basic sites.

Table 4.3 Effect of amount of seashells catalyst on the FAME yield in the transesterification^a of palm oil with methanol under batch condition

Catalyst ^b	Amount of catalyst (wt.%)	FAME yield (wt.%)
Seashells	4.0	53.4
	7.0	71.9
	10.0	93.6

^aReaction condition: methanol/oil molar ratio, 30; temperature, 60 °C; time, 3 h.

^bCatalyst preparation condition: calcination temperature, 800 °C.

4.2 Preparation of heterogeneous base catalysts from mixed seashells by dissolution-precipitation method

4.2.1 Effect of raw material of catalyst on the transesterification under batch condition

The batch system was used to evaluate the transesterification activity of the powdery catalysts prepared. However, for the continuous fixed-bed reactor system, much larger amount of the catalysts must be prepared. The grade of raw materials affects the catalyst cost. Therefore, effect of calcium source and raw chemical grade are investigated. In this part, the experiment of catalyst preparation and reaction condition was referred by the best condition from Jaiyen *et al.*

Effect of calcium source used in the catalyst preparation of catalyst on the FAME yield attained from the transesterification of palm oil with methanol in batch system are summarized in Table 4.4. The ZCA-P was prepared with CaCO₃ (AR grade) calcined 800 °C whereas ZSA-P was prepared with waste mixed seashells. The ZCA-P gave FAME yield of 98.3 wt.% whereas 97.9 wt.% was catalyzed by ZSA-P. The source of calcium from waste mixed seashells did not affect the FAME yield due to the composition of waste mixed seashells was similar as CaCO₃.

Table 4.4 Effect of source of calcium of catalyst on the FAME yield in the transesterification^a of palm oil with methanol under batch condition

Catalyst ^b	Calcium source	FAME yield (wt.%)
ZCA-P	CaCO ₃	98.3
ZSA-P	Seashells	97.7

^aReaction condition: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; temperature, 60 °C; time, 3 h.

^bCatalyst preparation condition: calcination temperature of calcium source, 800 °C; calcination temperature of catalyst, 400 °C.

Table 4.5 shows the FAME yield from the methanolysis of palm oil over ZSA-P was prepared at various grades of chemical. The ZSA-P (AR grade) gave FAME yield 98.3 wt.% whereas 96.9 was found in ZSA-P (commercial grade). In the case of cost of ZSA-P, using chemical with AR grade gave a higher cost than using commercial grade. Therefore, the Zn(NO₂)₃·6H₂O and Al₂O₃ from commercial grade were used in the next study.

Table 4.5 Effect of chemical grade of catalyst on the FAME yield in the transesterification^a of palm oil with methanol under batch condition

Catalyst	Zn(NO ₂) ₃ ·6H ₂ O		Al ₂ O ₃		FAME yield (wt.%)
	Grade	Cost (Baht/kg)	Grade	Cost (Baht/kg)	
ZSA-P	AR	1,500	AR	2,600	97.7
	Comercial	90	Comercial	42	96.9

^aReaction condition: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; temperature, 60 °C; time, 3 h.

^bCatalyst preparation condition: calcination temperature of catalyst, 400 °C.

4.2.2 Effect of calcination temperature of catalyst

The combination of the TGA and XRD results (Figures 4.3 and 4.4) suggested that the quantities and the quality of the catalyst. Figure 4.3 shows the weight loss and DTG curves of as-synthesized ZSA-P. The weight loss occurred in fifth steps. In the first step, the weight loss in range of 120-220 °C was related to the decomposition of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ to ZnO (3 wt.%) [47]. The second step at 280 °C (2 wt.%) related to dehydration of $Al(OH)_3$ [49]. The third step at 410 °C (10 wt.%) corresponded to dehydration of $Ca(OH)_2$ in form of $CaZn_2(OH)_6 \cdot 2H_2O$ and pure $Ca(OH)_2$ [28,48]. The decomposition of $Ca(NO_3)_2$ occurred in the third step at 517 °C which had weight loss of 9 wt.% [28]. Finally, the weight loss at 665 °C (5 wt.%) corresponded to the decarbonation of $CaCO_3$ [28].

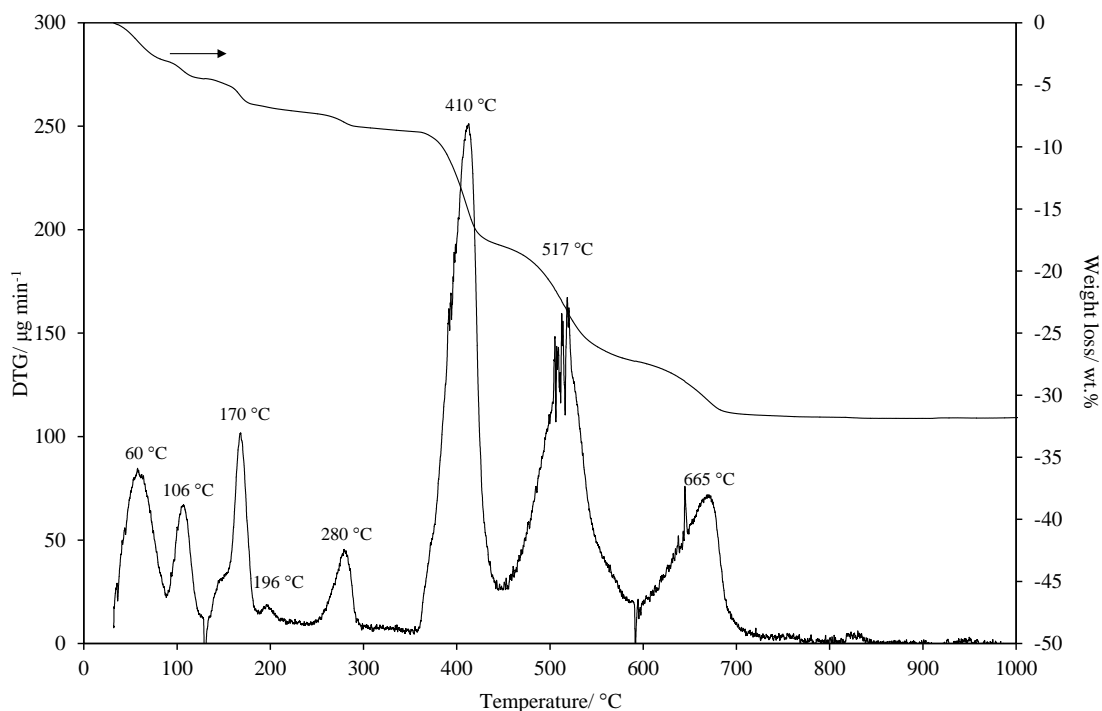


Figure 4.3 Weight loss and DTG curves of as-synthesized ZSA-P.

Table 4.6 shows the phase composition of as-synthesized ZSA-P as determined by the TG/DTG technique (Figure 4.3). The calculation of amount of each phase was demonstrated in Appendix C. The moisture physisorbed on the as-synthesized ZSA-P was 3.5 wt.%. The amount of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, $Al(OH)_3$, Al_2O_3 , $Ca(OH)_2$, $Ca(NO_3)_2$ and $CaCO_3$ were calculated to be 5.1, 7.8, 4.8, 16.8, 36.4,

14.0 and 10.1 wt.%, respectively. The total amount of each phase estimated from the TGA result was close to 100 wt.%.

Table 4.6 Phase composition of as-synthesized ZSA-P analyzed by TG/DTA technique

Catalyst	Decomposition temperatures (°C)	Phase	Composition (wt.%)
ZSA-P	0-100	H ₂ O (moisture)	3.5
	100-160	Zn ₅ (OH) ₈ (NO ₃) ₂ ·2H ₂ O	5.1
	160-220	CaZn ₂ (OH) ₆ ·2H ₂ O	7.8
	220-340	Al(OH) ₃	4.8
	-	Al ₂ O ₃ ^a	16.8
	340-450	Ca(OH) ₂	36.4
	450-590	Ca(NO ₃) ₂	14.0
	590-760	CaCO ₃	10.1
		Total	98.5

^aCorresponding to the quantity added in the synthesis mixture.

The XRD patterns of the seashells catalysts (ZSA-P) before and after the calcination at 300, 400, 500, 600 and 800 °C are shown in Figure 4.4. Before the calcination (Figure 4.4(a)), the major phases were Ca(OH)₂ and CaZn₂(OH)₆·2H₂O with a small amount of Zn₅(OH)₈(NO₃)₂·2H₂O [20,28,48,47]. CaCO₃ should be generated by CaO being exposed with CO₂ in atmosphere during the catalyst preparation. The ZSA-P calcined at 300 °C had ZnO and ZnAl₂O₄ as new phases, whereas Zn₅(OH)₈(NO₃)₂·2H₂O disappeared (Figure 4.4(b)) [20,47]. In the case of ZSA-P calcined at 400 °C (Figure 4.4(c)), CaO was generated from Ca(OH)₂ via dehydration, according to Eq. (4.1) [20,28]. The Ca(OH)₂ phase was completely transformed to CaO, when ZSA-P was calcined at 500 °C (Figure 4.4(d)) [20,28]. The increased amount of CaO phase was caused due to decarbonation of CaCO₃ at higher temperatures, according to Eq. (4.2) [20,28]. However, the amount of CaO was decreased, when the catalyst was calcined at 800 °C. It should be due to transformation of CaO to Ca₁₂Al₁₄O₃₃ (Eq. (4.3)) [34].

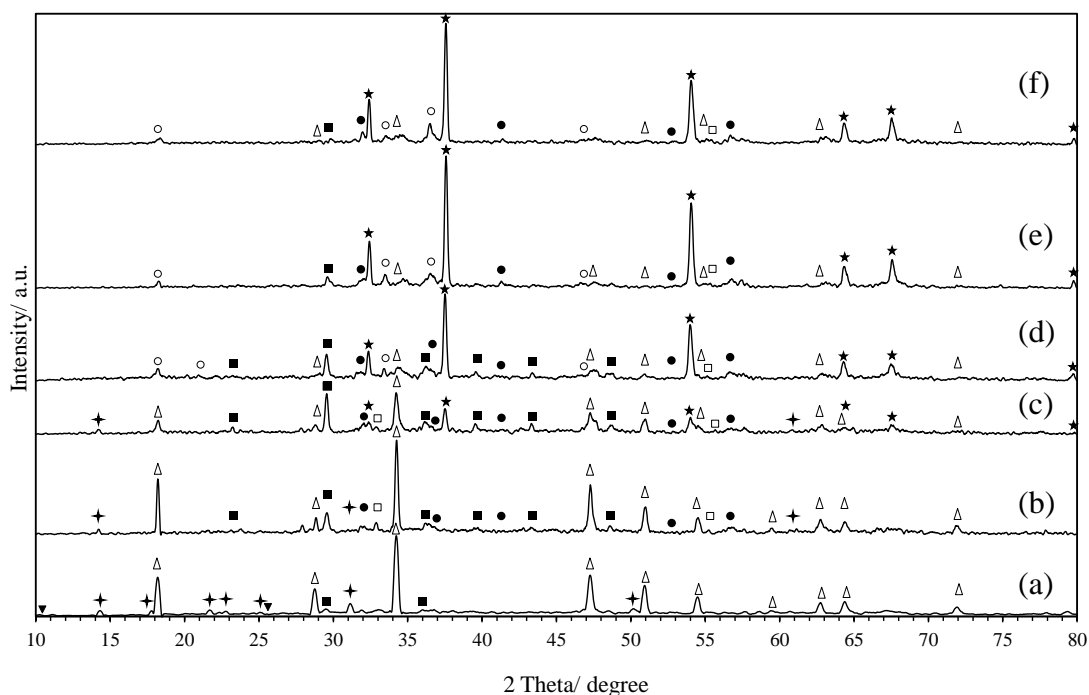
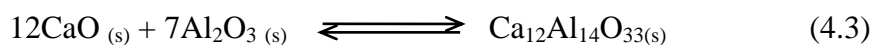


Figure 4.4 XRD patterns of as-synthesized ZSA-P (a) and ZSA-P calcined at 300 (b), 400 (c), 500 (d), 600 (e) and 800 °C (f). (Symbols: ■ = CaCO₃, ★ = CaO, ● = ZnO, Δ = Ca(OH)₂, □ = ZnAl₂O₄, † = CaZn₂(OH)₆·2H₂O, ▼ = Zn₅(OH)₈(NO₃)₂·2H₂O and ○ = Ca₁₂Al₁₄O₃₃)

The effect of calcination temperature of ZSA-P on the transesterification of palm oil with methanol is shown in Table 4.7. The highest FAME yield was achieved over ZSA-P calcined at 400 °C. These results are in agreement with those reported by Jaiyen et al. (2007). However, the FAME yield decreased from 97.9 to 85.9 wt.% when the calcination temperature was extended to 800 °C. As evidenced by the TGA and XRD results, the phase of the ZSA-P calcined at low temperatures (300-400 °C) was Ca(OH)₂, whereas the phase was mainly CaO in the ZSA-P calcined at high temperatures (500-800 °C). The increased amount of Ca₁₂Al₁₄O₃₃ phase at higher temperature caused less activity in the transesterification [34].

Table 4.7 Effect of calcination temperature of ZSA-P on the FAME yield attained from the transesterification^a of palm oil with methanol under batch condition

Catalyst	Calcination temperature (°C)	FAME yield (wt.%)
ZSA-P	300	94.9
	400	97.9
	500	95.2
	600	87.5
	800	85.9

^aReaction condition: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; temperature, 60 °C; time, 3 h.

4.2.3 Effect of weight ratio of seashells/Al₂O₃

The effect of seashells/Al₂O₃ weight ratio used in the preparation of ZSA-P on the FAME yield attained from the transesterification of palm oil with methanol under batch condition is expressed in Table 4.8. The weight ratios of 1:0.4 and 1:1 were studied. When the catalysts were calcined at 300-400 °C, the ZSA-P prepared with both seashells/Al₂O₃ ratios gave the similar FAME yield. The catalytic phases of both catalysts were Ca(OH)₂ and CaZn₂(OH)₆·2H₂O which were not strongly interacted with Al₂O₃ as support. In the case of ZSA-P calcined at 500 and 600 °C the weight ratio of 1:1 were higher FAME yield than the weight ratio of 1:0.4. When ZSA-P was calcined at 500 and 600 °C, the Ca(OH)₂ was transformed to CaO. However, both FAME yields were not significantly changed. The calcination temperature was increased to 800 °C, the FAME yield of the weight ratio of 1:1 (34.8 wt.%) was lower than the weight ratio of 1:0.4 (85.9 wt.%). These results should be due to the weight ratio at higher amount of Al₂O₃ caused conversion of CaO to Ca₁₂Al₁₄O₃, which it is less active in the transesterification [34].

Table 4.8 Effect of weight ratio of seashells/ Al_2O_3 at various calcination temperature of ZSA-P on the FAME yield attained from the transesterification^a of palm oil with methanol under batch condition

Catalyst	Calcination temperature (°C)	FAME yield (wt.%)	
		The weight ratio of 1:0.4	The weight ratio of 1:1
ZSA-P	300	94.9	95.6
	400	97.9	97.9
	500	95.2	99.9
	600	87.5	94.7
	800	85.9	34.8

^aReaction condition: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; temperature, 60 °C; time, 3 h.

4.2.4 Study on stability of the catalyst: Effect of air exposure

The basic sites of the catalyst can be deactivated easily upon exposing to H_2O and CO_2 in atmosphere. The desiccator was used to minimize the exposure of the catalyst to air before loading it into the reactor. In the industrial scale, avoiding the air exposure is difficult. The effect of air exposure of ZSA-P catalysts calcined at various temperatures (300-800 °C) on the structural change was investigated by the XRD technique. As shown in Figure 4.5(a), the ZSA-P calcined at 300 °C was mainly composed of $\text{Ca}(\text{OH})_2$ and $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ with a small amount of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and CaCO_3 . Interestingly, the catalytic phases were not changed after the air exposure (Figure 4.5(b)). CaO was generated when the calcination temperature of ZSA-P was increased to 400 °C (Figure 4.6(a)). In this case, the air exposure decreased the amount of CaO phase concomitantly with increasing of $\text{Ca}(\text{OH})_2$ phase (Figure 4.6(b)). The ZSA-P calcined at 500 °C also exhibited the transformation of CaO to $\text{Ca}(\text{OH})_2$ after the air exposure (Figure 4.7(a) and (b)). The diffraction peaks corresponding to $\text{Ca}(\text{OH})_2$ at 34, 46.5, and 51° were broad. In the case of the calcination temperatures at 600 and 800 °C, CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ were found as the major phases (Figures 4.8(a) and 4.9(a)), respectively. In this case, the CaO was transformed to $\text{Ca}(\text{OH})_2$ after air exposure (Figures 4.8(b) and 4.9(b)).

However, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ was not changed to new phase as the intensity of the peak at about 36.5° was not disturbed.

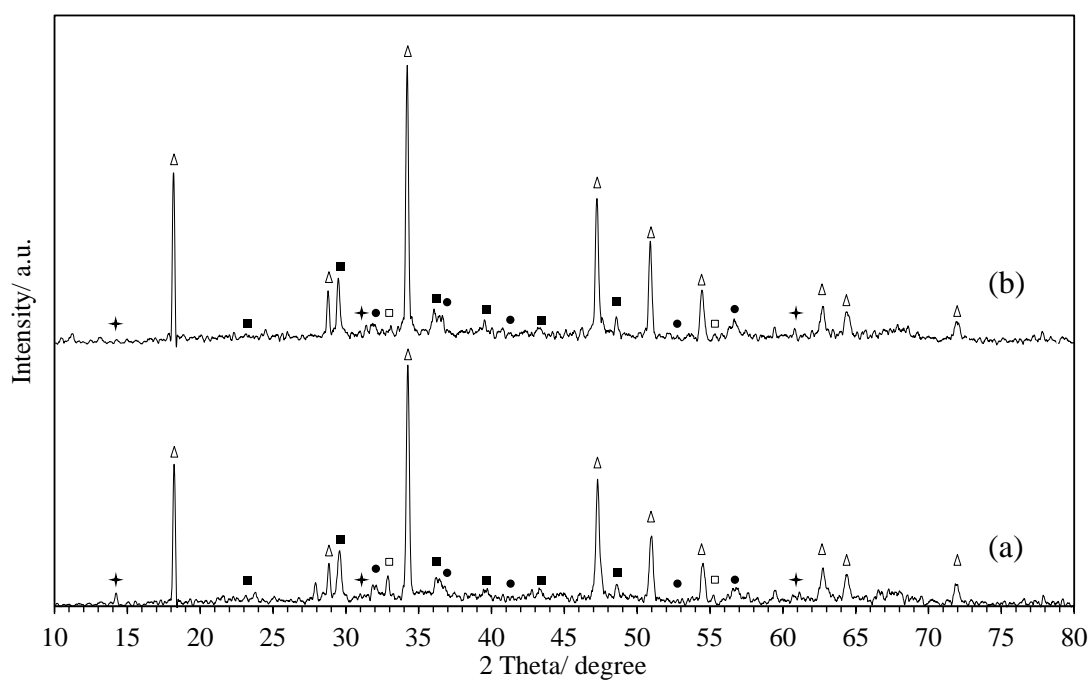


Figure 4.5 XRD patterns of ZSA-P calcined at 300 °C before (a) and after (b) the air exposure overnight. (Symbols: \blacksquare = CaCO_3 , \bullet = ZnO , Δ = $\text{Ca}(\text{OH})_2$, \square = ZnAl_2O_4 and \blacklozenge = $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$)

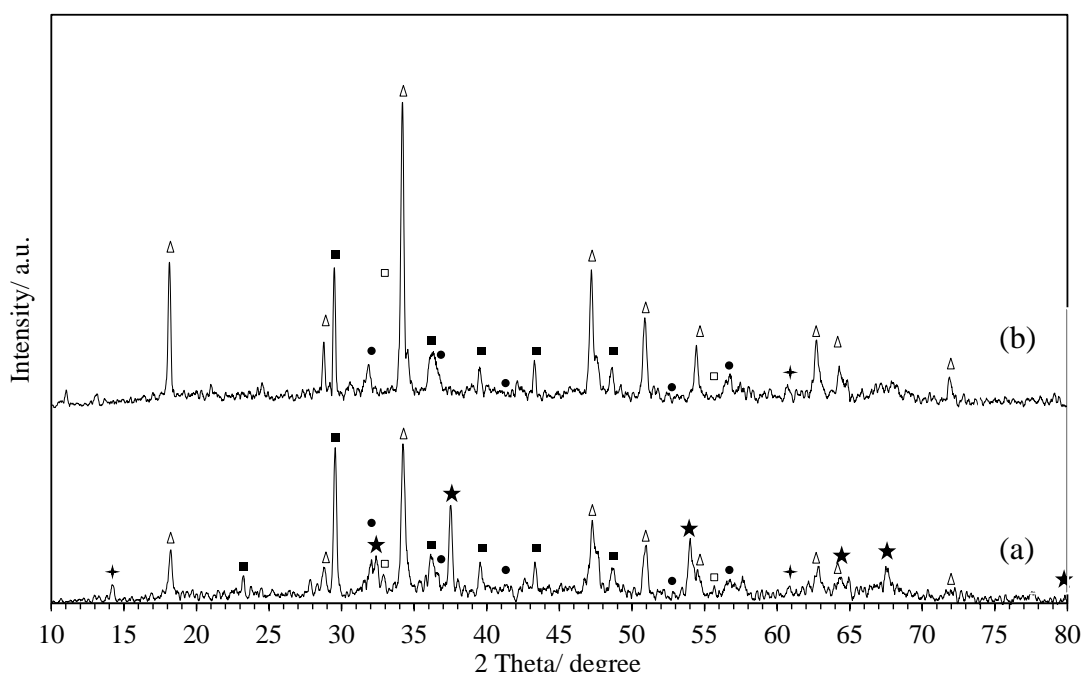


Figure 4.6 XRD patterns of ZSA-P calcined at 400 °C before (a) and after (b) the air exposure overnight. (Symbols: ■ = CaCO_3 , ★ = CaO , ● = ZnO , Δ = Ca(OH)_2 , □ = ZnAl_2O_4 and ★ = $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$)

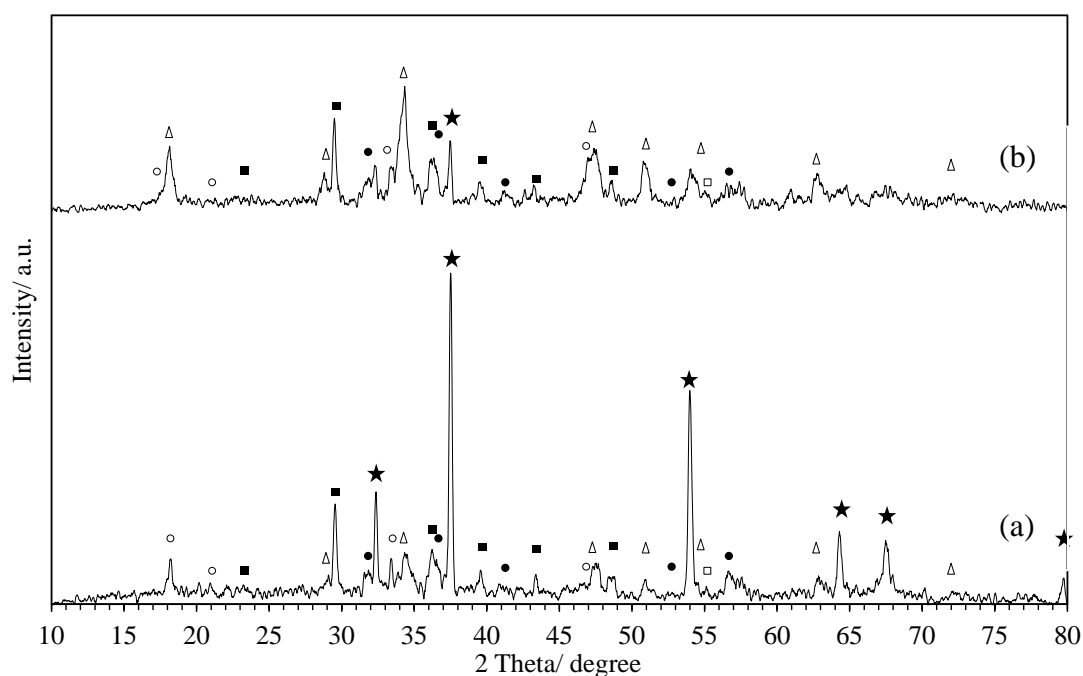


Figure 4.7 XRD patterns of ZSA-P calcined at 500 °C before (a) and after (b) the air exposure overnight. (Symbols: ■ = CaCO_3 , ★ = CaO , ● = ZnO , Δ = Ca(OH)_2 , □ = ZnAl_2O_4 , ★ = $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, and ○ = $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$)

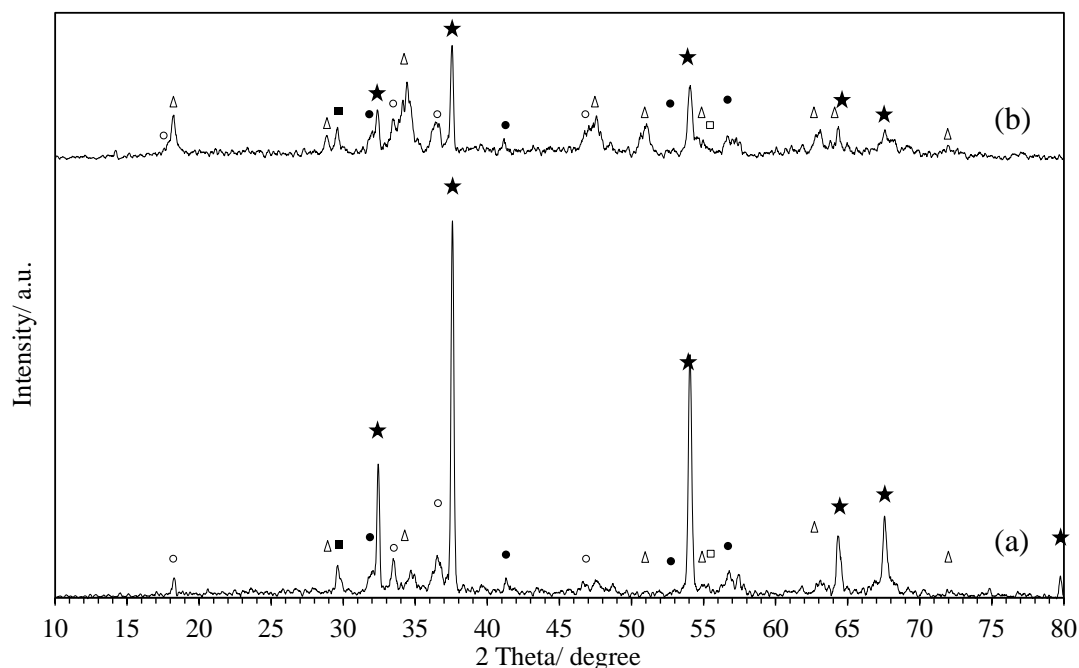


Figure 4.8 XRD patterns of ZSA-P calcined at 600 °C before (a) and after (b) the air exposure overnight. (Symbols: ■ = CaCO_3 , ★ = CaO , ● = ZnO , Δ = Ca(OH)_2 , □ = ZnAl_2O_4 , ★ = $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, and ○ = $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$)

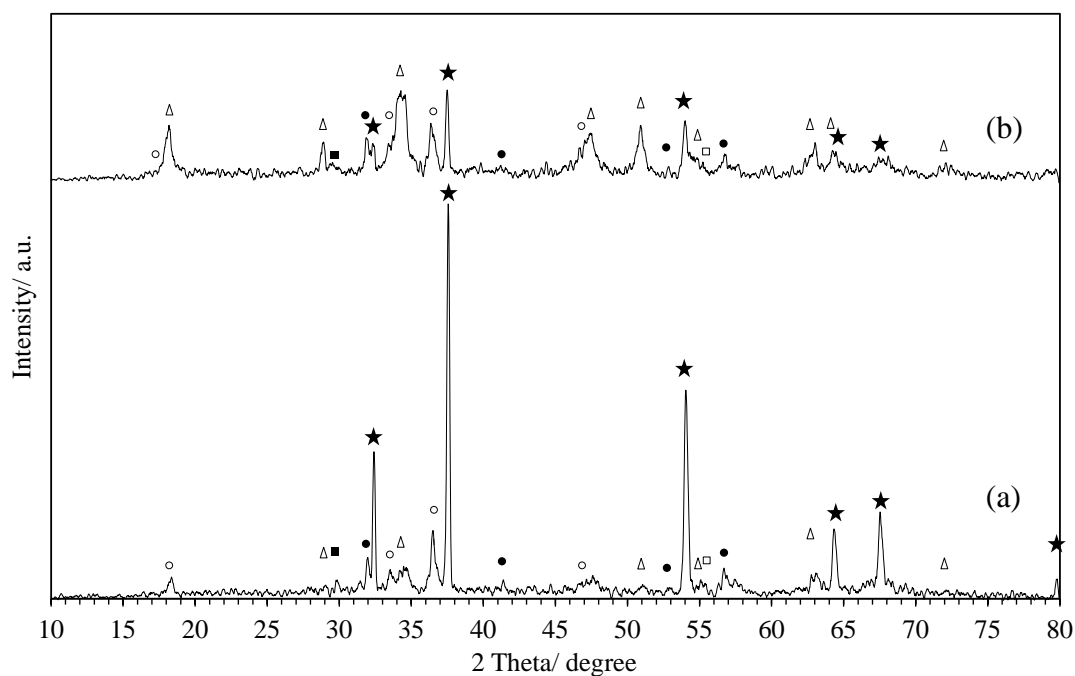


Figure 4.9 XRD patterns of ZSA-P calcined at 800 °C before (a) and after (b) the air exposure overnight. (Symbols: ■ = CaCO_3 , ★ = CaO , ● = ZnO , Δ = Ca(OH)_2 , □ = ZnAl_2O_4 , ★ = $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, and ○ = $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$)

Table 4.9 shows the effect of air exposure of ZSA-P catalysts calcined at various temperatures on the FAME yield attained from the transesterification of palm oil with methanol under batch condition. For the catalysts calcined at low temperatures (300 and 400 °C), the FAME yield was not significantly altered. The XRD results (Figures 4.4 and 4.5) indicated that the metal phases of the catalyst were mainly composed of Ca(OH)_2 and $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ with a small amount of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and CaCO_3 all of which were not changed after the air exposure. The ZSA-P calcined at 500, 600 and 800 °C exhibited a decrease in the FAME yield after the air exposure. From the XRD results (Figures 4.7, 4.8 and 4.9), the catalytic phase of these catalysts should be CaO. After the air exposure, the CaO was easily deactivated by H_2O and CO_2 to Ca(OH)_2 and CaCO_3 , respectively presenting in atmosphere as reverse reactions of the Eqs. (4.1) and (4.2). Consequently, the FAME yield was obviously decreased. Therefore, the ZSA-P catalysts were most stable against H_2O and CO_2 in atmosphere when the calcination was performed at 300 and 400 °C.

Table 4.9 Effect of air exposure of ZSA-P catalysts calcined at various temperatures on the FAME yield attained from the transesterification^a of palm oil with methanol under batch condition

Catalyst	Calcination temperature (°C)	FAME yield (wt.%)	
		Before the air exposure	After the air exposure
ZSA-P	300	94.9	95.0
	400	97.9	97.9
	500	95.2	82.0
	600	87.5	81.5
	800	85.9	66.6

^aReaction condition: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; temperature, 60 °C; time, 3 h.

4.3 Formulation of mixed seashells-derived heterogeneous base catalysts in extrudate form

4.3.1 Extrudate characteristics and mechanical testing of extrudates

4.3.1.1 Effect of the catalyst formulation

The effect of the catalyst formulation on the metal phases was investigated by the XRD technique (Figure 4.10). As evidenced by the XRD results, both of ZSA-P and ZSA-SE calcined at 400 °C had CaCO_3 , CaO , Ca(OH)_2 , ZnAl_2O_4 , $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ and ZnO phases. The higher intensity of CaCO_3 ($2\theta = 22.5, 29.5, 36.5, 39.5, 43.5$ and 49°) observed for ZSA-SE should be because the extrudate preparation spent long time for the active site to H_2O and CO_2 in the atmosphere. However, the metal phases in both catalysts were similar.

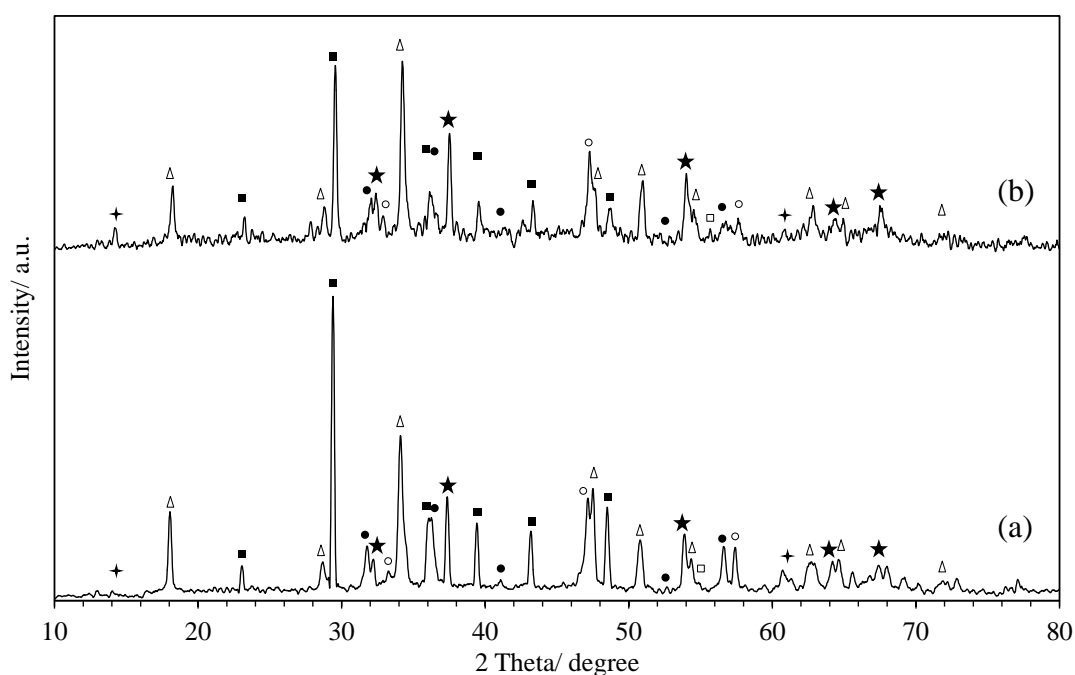


Figure 4.10 XRD patterns of ZSA-SE (a) and ZSA-P (b) both of which were calcined at 400 °C before the analysis. (Symbols: \blacksquare = CaCO_3 , \star = CaO , \bullet = ZnO , Δ = Ca(OH)_2 , \square = ZnAl_2O_4 and \blackstar = $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$)

4.3.1.2 Effect of amount of HEC on extrudate characteristics

The effects of HEC amount used in the preparation of catalyst extrudates on the extrudate characteristics are summarized in Table 4.10. Without the HEC addition, the catalyst could not be formulated into the extrudate form by using the manual extruder with low pressure during force. Therefore, the HEC as plasticizer was required when the formulation of catalyst extrudates was performed on the manual extruder. Before the calcination, the ZSA-ME extrudates were hard, suggesting that the HEC added enhanced the agglomeration of the raw material particles in the catalyst. After the calcination at 500 °C, the HEC containing in the extruded catalysts was decomposed. When the amount of HEC was increased to 5 wt.%, the extrudates shaped by the manual extruder could not retain their form (Figure 4.11). The HEC amount did not significantly affect the catalyst formulation when using the single screw extruder with high pressure shearing. The ZSA-SE extrudates were denser and harder than the extrudates of ZSA-ME catalysts. Similarly of the case of ZSA-ME, the calcination at 500 °C decreased the hardness of the ZSA-SE extrudates due to the extensive loss of HEC added.

Table 4.10 Effect of amount of HEC on extrudate characteristics

Catalyst	Amount of HEC (wt.%)	Extrusion	Extrudate characteristics	
			Drying at 100 °C	Calcining at 500 °C
ZSA-ME	0	Difficult	n.d.	n.d.
	3	Easy	Hard	Brittle
	5	Easy	Hard	Broken
ZSA-SE	0	Easy	Dense and hard	Hard
	1	Easy	Dense and hard	Hard
	3	Easy	Dense and hard	Hard
	5	Easy	Hard	Very brittle

“n.d.” means not analyzed

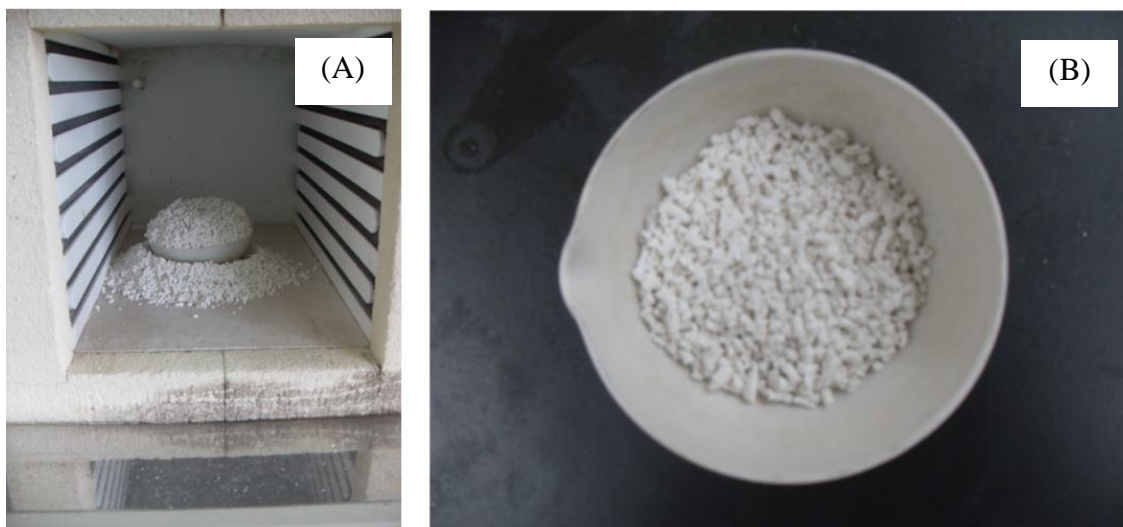


Figure 4.11 Extrudates of ZSA-ME prepared with 5% HEC after the calcination at 500 °C in muffle furnace (A) and cooling down to room temperature (B).

4.3.1.3 Effect of calcination temperature on crushing strength

Table 4.11 shows effect of calcination temperature of ZSA-SE extrudates on their crushing strength. Thus, the crushing strength according to ASTM D-4179-82 was used. When the calcination temperature was increased to 800 °C, the bulk density of ZSA-SE extrudates was decreased from 1.01 to 0.81 g cm⁻³. Similarly, the crushing strength was decreased from 1.15 to 0.02 MPa.

The weight loss and DTG curves of pure HEC are shown in Figure 4.12. The pure HEC had three-step weight loss. The first step occurred in the range of 45-100 °C was related to the physisorbed moisture. Secondly, the weight loss at 274 °C corresponded to the decomposition of polymer main chain of HEC. The weight loss at 650 °C as the final step was due to the combustion of remaining char. The crushing strength of the catalyst extrudates was decreased by the decomposition of HEC at higher temperature than 274 °C.

Table 4.11 Effect of calcination temperature of ZSA-SE extrudates on crushing strength^a

Catalyst ^b	Calcination temperature (°C)	Bulk density (g cm ⁻³)	Crushing strength (MPa)
ZSA-SE	None	1.01	1.15
	400	0.96	0.13
	800	0.81	0.02

^aASTM D-4179-82

^bPrepared with 3% HEC

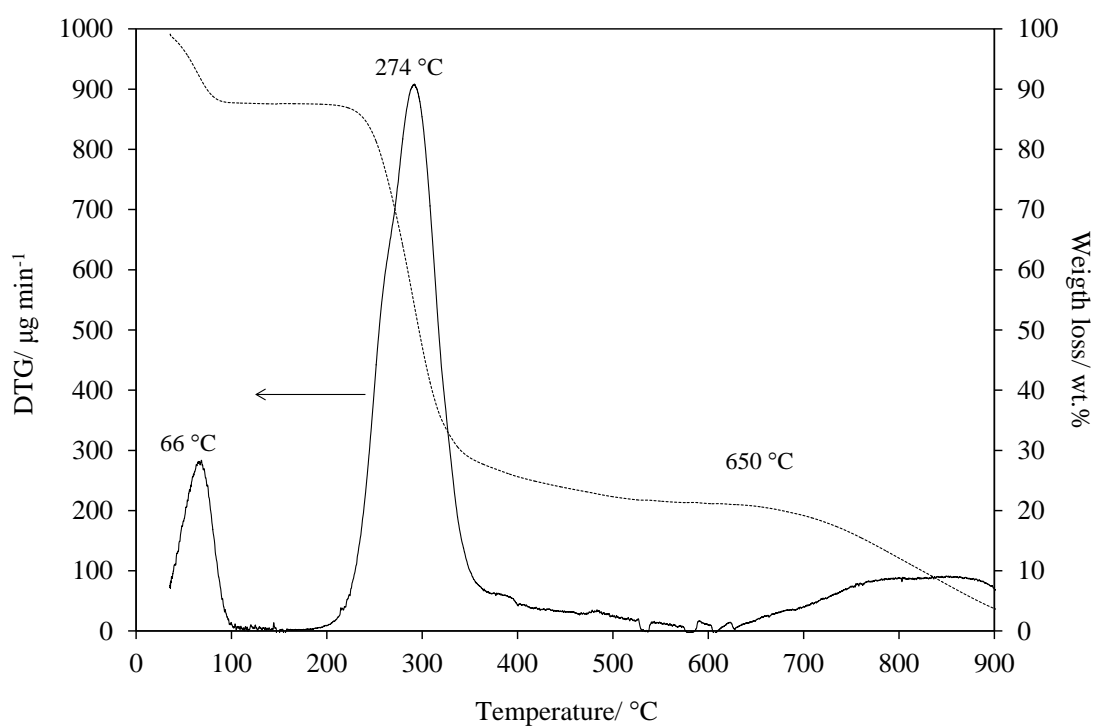


Figure 4.12 Weight loss and DTG curves of pure hydroxyethyl cellulose (HEC).

4.3.1.4 Morphological study of catalyst extrudates

When HEC was decomposed, it is interesting to investigate the surface morphology of the catalyst extrudates. Thus, the of the ZSA-SE extrudates studied by optical microscope (OM) (Figure 4.13). By considering both side view and cross-section of the extrudates, the surface of the non-calcined ZSA-SE were smoother than the surface of the calcined ZSA-SE. However, the detailed difference of the surface of catalyst extrudates could not be obtained by the OM technique. Thus, increasing of contrast, resolution and magnification by scanning electron microscopy was an effective way for investigation of the extrudate surface.

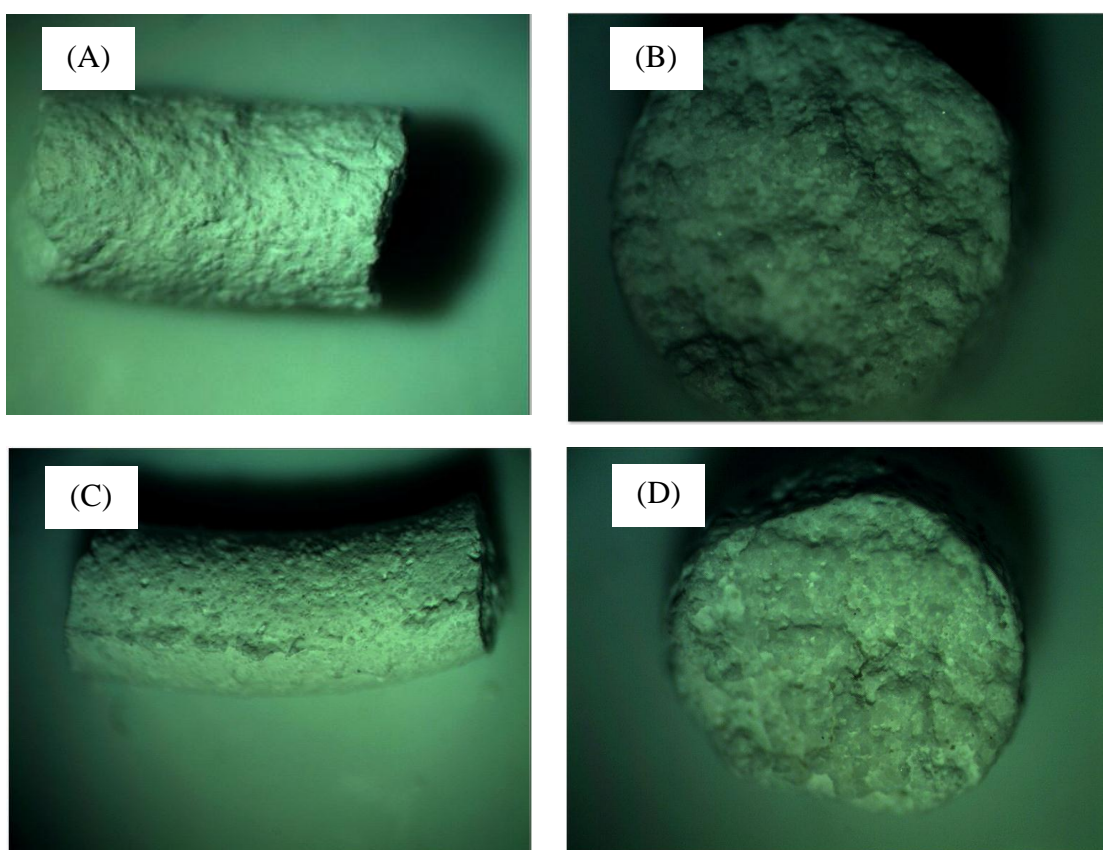


Figure 4.13 OM images of ZSA-SE prepared with 3 wt.% HEC before (A and B) and after (C and D) the calcination at 400 °C.

The side view images at various magnifications of $\times 30$, $\times 500$ and $\times 5,000$ obtained from the non-calcined and the calcined ZSA-SE with 3 wt.% of HEC are shown in Figure 4.14. At the magnification of 30 (Figure 4.14(A) and (B)), the non-calcined ZSA-SE had smoother surface than the calcined ZSA-SE. The calcined ZSA-SE exhibited the fracture of surface, which should be generated from the extensive losses of water and CO_2 during the decomposition of HEC in the catalyst extrudates. By increasing the magnification to $\times 500$ (Figure 4.14 (C) and (D)), the calcined ZSA-SE had very rough surface, whereas smooth surface was found on the non-calcined ZSA-SE. However, when the magnification was increased to $\times 5,000$, the non-calcined ZSA-SE showed a lot of secondary pores which were generated from the loss of water. The average diameter of the pore sizes was ca. $0.83 \mu\text{m}$ (Figure 4.14(E)). In the case of the calcined ZSA-SE, the surface was composed the pores with the sizes ca. $0.83 \mu\text{m}$ and the fracture with the widths ca. $5.41 \mu\text{m}$ (Figure 4.14(D) and (F)).

The cross-section images of the non-calcined and the calcined ZSA-SE at various magnifications of $\times 30$, $\times 100$ and $\times 5,000$ are shown in Figure 4.15. For the non-calcined ZSA-SE, the surface was composed of pores with the sizes between 0.47 to $47.50 \mu\text{m}$ (Figure 4.15(A), (C) and (E)). In the case of calcined ZSA-SE, the surface was composed the pores with the sizes between 20.0 to $50.0 \mu\text{m}$ and the fracture with the widths ca. $50.0 \mu\text{m}$ (Figure 4.15(B), (D) and (F)). Moreover, the combination of particles on the surface was observed when the ZSA-SE was calcined at 400°C .

From the SEM results (Figures 4.14 and 4.15), it can be concluded that the decrease in the hardness and bulk density of ZSA-SE after the calcination was resulted from the decomposition of HEC. However, the fracture appeared on the surface of the calcined ZSA-SE may be helpful for diffusion of triglyceride molecules to the active sites inside the extrudates [24].

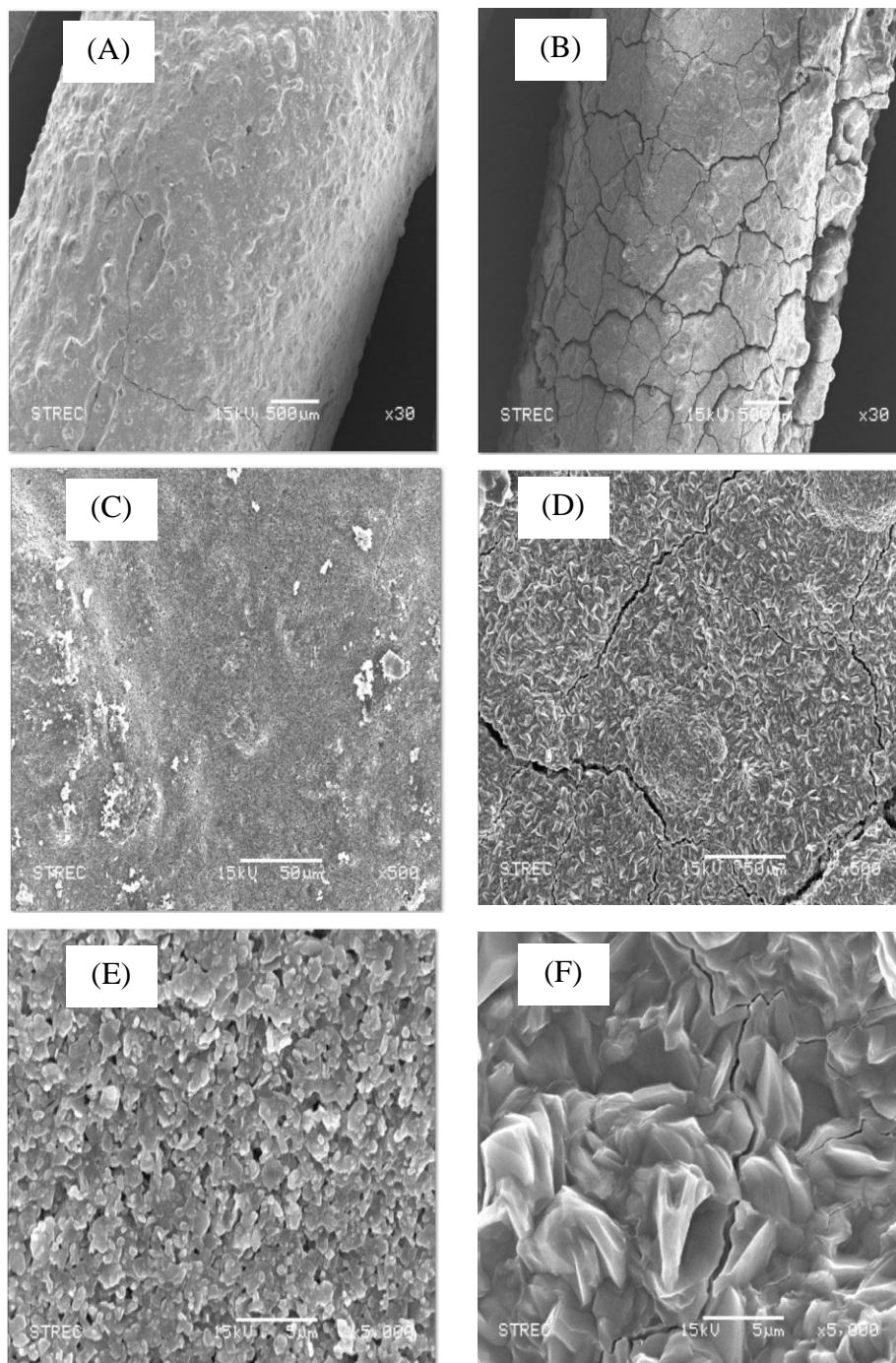


Figure 4.14 SEM images of side view of ZSA-SE prepared with 3 wt.% HEC before (magnifications of $\times 30$ (A), $\times 500$ (C) and $\times 5000$ (E)) and after (magnifications of $\times 30$ (B), $\times 500$ (D) and $\times 5000$ (F)) the calcination at $400\ ^\circ\text{C}$.

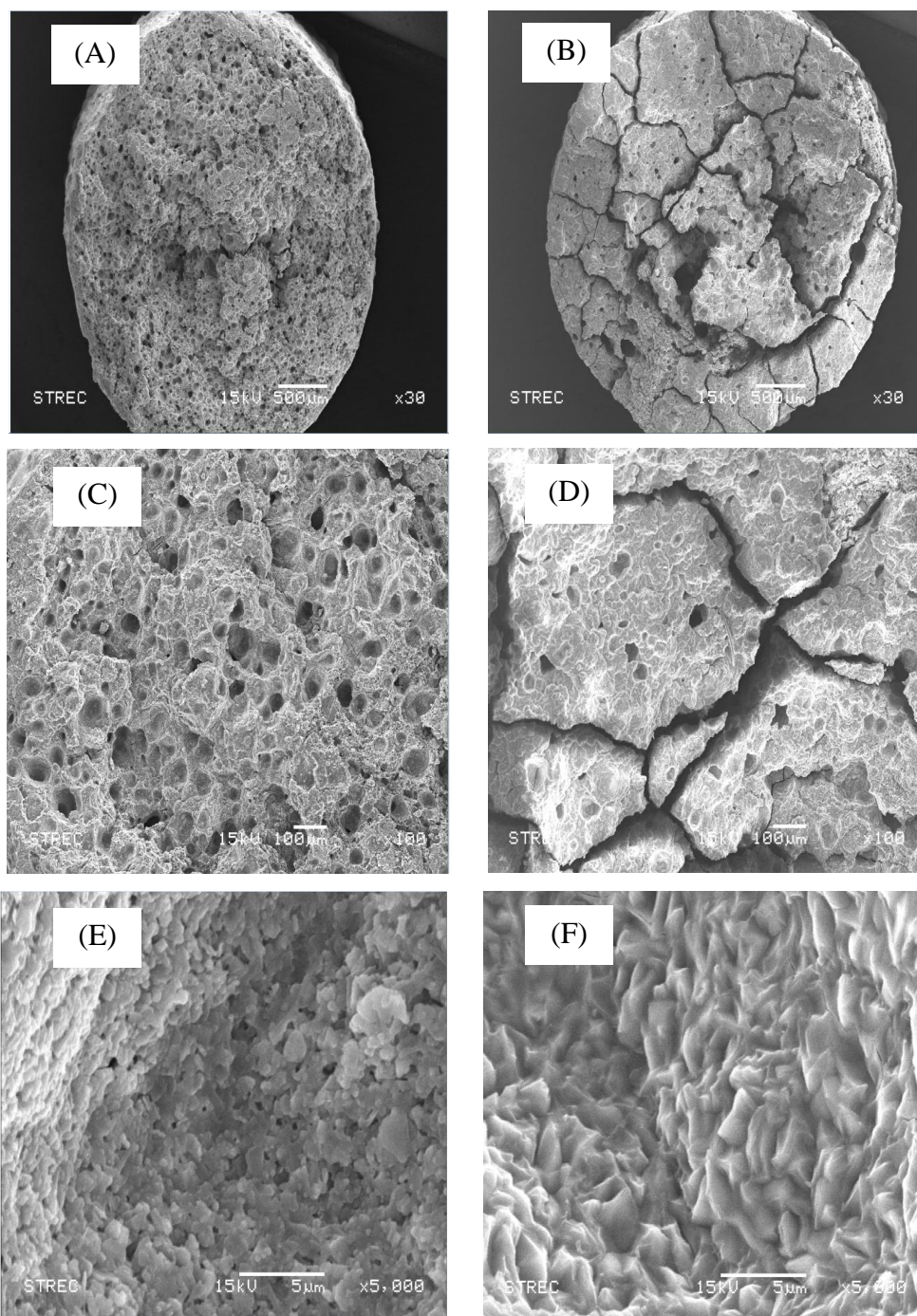


Figure 4.15 SEM images of cross-section of ZSA-SE prepared with 3 wt.% HEC before (magnifications of $\times 30$ (A), $\times 100$ (C) and $\times 5000$ (E)) and after (magnifications of $\times 30$ (B), $\times 100$ (D) and $\times 5000$ (F)) the calcination at 400 °C.

4.3.2 Catalytic activity of the extrudates catalyst

4.3.2.1 Effect of catalyst formulation on the transesterification under batch condition

Comparison between powdery catalyst and extruded catalyst on the transesterification under batch condition was initially studied to operation. Table 4.12 shows the effect of catalyst formulation on the FAME yield attained from the transesterification of palm oil with methanol under batch condition. ZSA-P, ZSA-ME and ZSA-SE gave a similar FAME yield. This result suggested that the catalyst formulation did not affect to catalytic activity under batch condition. Figure 4.16 illustrates the photographs of ZSA-ME and ZSA-SE before and after being used in the reaction in which they were stirred with the mixture of oil and methanol at 60 °C for 3 h. These photographs indicated that both ZSA-SE and ZSA-ME extrudates were broken after being used under the batch condition.

Table 4.12 Effect of catalyst formulation on the FAME yield attained from the transesterification^a of palm oil with methanol under batch condition

Catalysts ^b	Catalysts type	FAME yield (wt.%)
ZSA-P	Powder	97.9
ZSA-ME ^c	Extrudates	97.9
ZSA-SE ^c	Extrudates	97.6

^aReaction condition: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; temperature, 60 °C; time, 3 h.

^bCalcination temperature, 400 °C.

^cHEC amount, 3 wt.%.

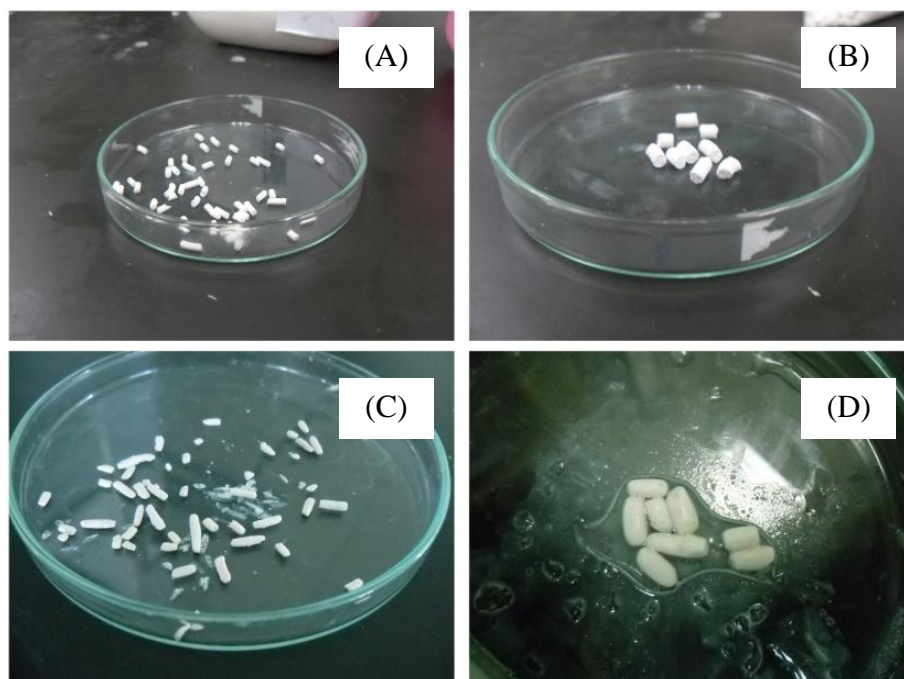


Figure 4.16 ZSA-ME and ZSA-SE prepared with 3% HEC and calcined at 400 °C before (A and B, respectively) and after (C and D, respectively) being used in the transesterification.

4.3.2.2 Effect of extruder type for catalyst extrusion on the transesterification under continuous condition

Figure 4.17 shows the FAME yield attained from the continuous transesterification of palm oil with methanol in the presence of ZSA catalysts formulated by different extruders. ZSA-ME was sized to 2 mm of cross-sectional diameter and 5 mm of length, whereas ZSA-SE was sized to 3.5 mm of cross-sectional diameter and 5 mm of length. Both the catalysts were calcined at 300 °C before being loaded into a fixed-bed reactor. The FAME formed over the calcined ZSA-ME was increased from 81.3 to 98.8 wt.% when the time on stream was increased from 5 to 8 h, whereas the calcined ZSA-SE gave the FAME yield less than 60 wt.% at 8 h. This result suggested that the distinction of catalyst size of extrudates each extruder may affect contact time between the catalyst and the substrate. Industrially, the single screw extruder was used due to the catalyst production needed in the large scale.

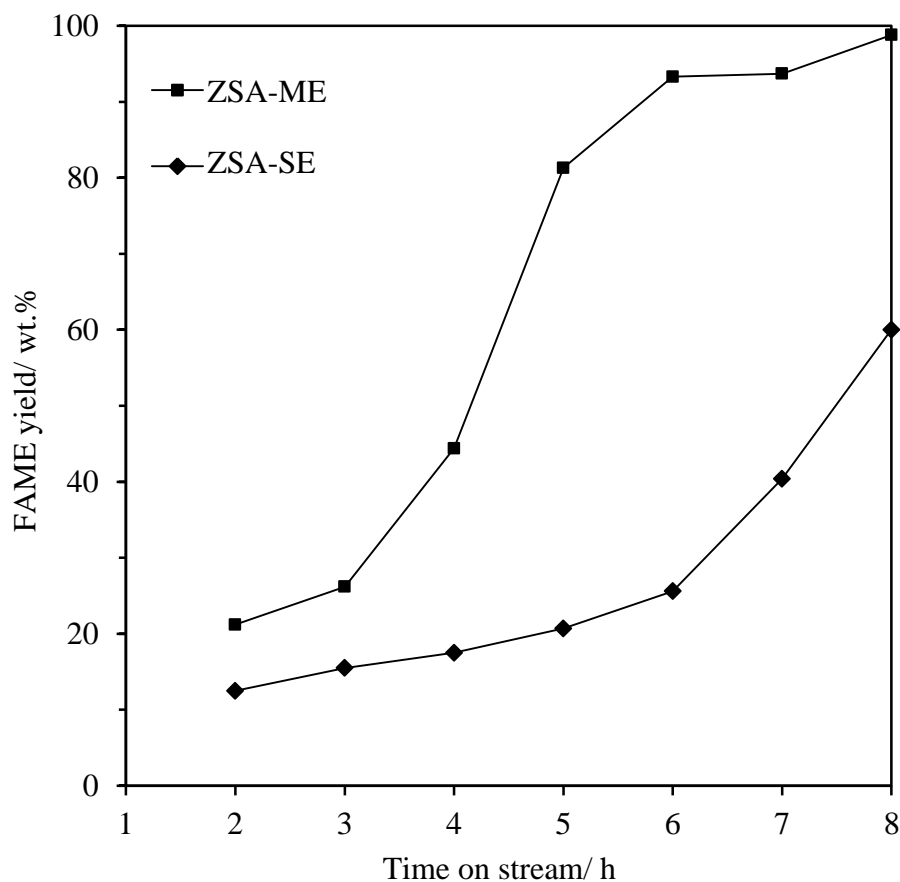


Figure 4.17 Effect of extruder type for catalyst extrusion on the FAME yield attained from the transesterification of palm oil with methanol under continuous condition. Catalyst preparation: HEC amount, 3 wt.%; calcination temperature, 300 °C. Reaction condition: methanol/oil molar ratio, 30; temperature, 65 °C; total flow rate, 2.0 mL min⁻¹; residence time, 1.00 h.

4.3.2.3 Effect of calcination temperature of extrudate catalyst on the transesterification under continuous condition

Figure 4.18 shows the effect of calcination temperature of ZSA-ME extrudates prepared with 3% HEC on the FAME yield attained from the transesterification of palm oil with methanol under continuous condition. Initially, the FAME yield was not stable due to the substances were not homogeneous. The highest FAME yield was achieved over ZSA-P calcined at 300 and 400 °C when the time on stream was

increased from 2 to 8 h. However, the FAME yield decreased to 25.5 wt.% when the calcination temperature was extended to 800 °C. As evidenced by the TGA and XRD results of the powder catalyst, the phase of the ZSA-P calcined at low temperatures (300-400 °C) was $\text{Ca}(\text{OH})_2$, whereas the phase was mainly CaO in the ZSA-P calcined at high temperatures (500-800 °C). The increased amount of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phase at higher temperature caused less activity in the transesterification [34].

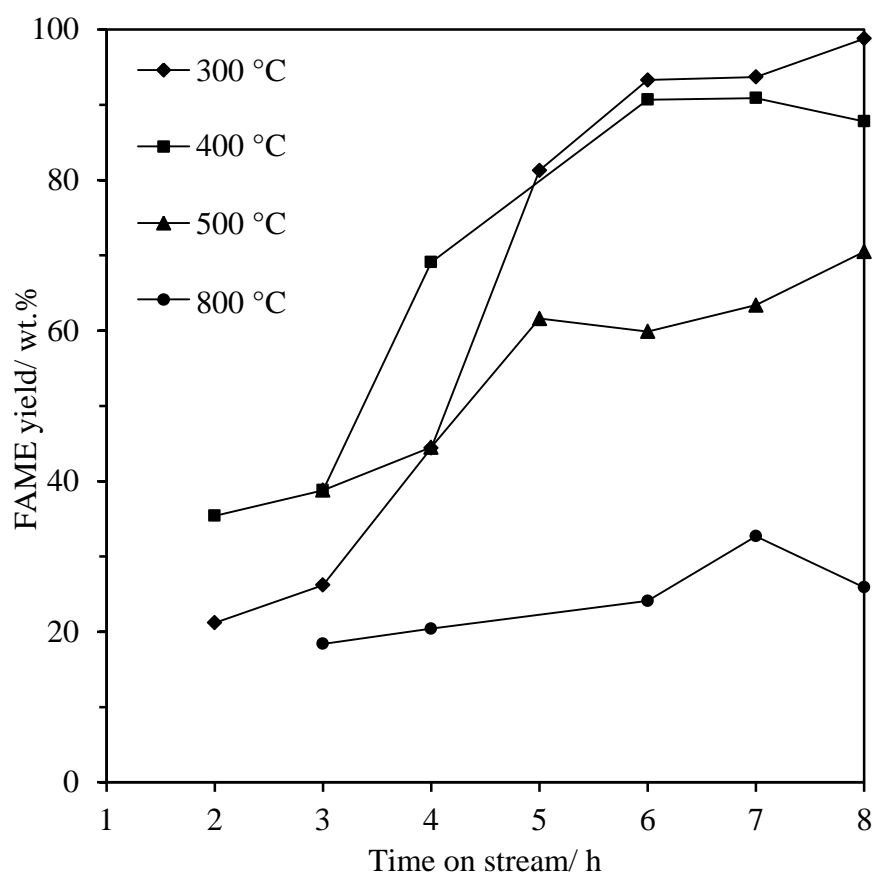


Figure 4.18 Effect of calcination temperature of ZSA-ME extrudates on the FAME yield attained from the transesterification of palm oil with methanol under continuous condition. Catalyst preparation: HEC amount, 3 wt.%; extrusion, manual extruder. Reaction condition: methanol/oil molar ratio, 30; temperature, 65 °C; total flow rate, 2.0 mL min⁻¹; residence time, 1.00 h.

4.4 Premixing the extrudate catalyst with methyl esters

4.4.1 Effect of type of fatty acid methyl esters on the transesterification under continuous condition

Premixing with methyl esters in the catalyst extrudates increased homogeneous of phase between palm oil and methanol [40,50]. Moreover, premixing with methyl esters could protect the catalyst extrudates with moisture and CO₂ in the ambient atmosphere. The effect of type of fatty acid methyl esters on the FAME yield attained from the transesterification of palm oil with methanol under continuous condition is shown in Figure 4.19. The methyl esters as a mixture of methyl laurate and methyl myristate (C₁₂-C₁₄) were previously mixed with the catalyst extrudates at the weight ratio of 30:70 and stored at room temperature overnight. Since the fatty acid composition of the palm oil feedstock, which was mainly composed of methyl palmitate (C_{16:0}), methyl stearate (C_{18:0}), methyl oleate (C_{18:1}), methyl linoleate (C_{18:2}), was different to the C₁₂-C₁₄ methyl esters, the amount of FAME produced by transesterification could be determined directly from the GC analysis. However, in the of premixing with the C₁₆-C₁₈ methyl esters, the amount of FAME determined by GC must be subtracted by 30 wt.% of the methyl esters added. For the effect of type of fatty acid methyl esters (C₁₆-C₁₈ and C₁₂-C₁₄), the FAME yield was not significantly altered. However, the reaction catalyzed by the extrudates premixed with the methyl esters gave higher FAME yield than the reaction without the methyl ester mixing. In the initial state of the reaction, the FAME yield was enhanced to 90 wt.%.

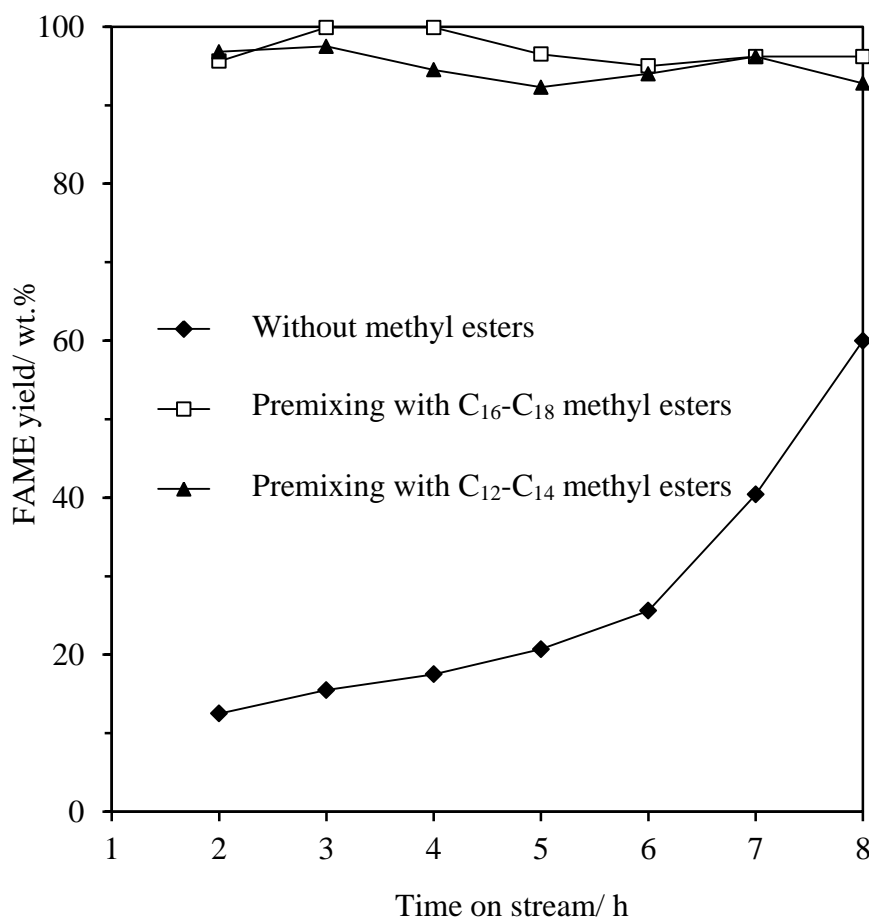


Figure 4.19 Effect of addition methyl esters on the FAME yield attained from the transesterification of palm oil with methanol under continuous condition. Catalyst preparation: HEC amount, 3 wt.%; extrusion, single screw extruder; calcination temperature, 300 °C. Reaction condition: methanol/oil molar ratio, 30; temperature, 65 °C; total flow rate, 2.0 mL min⁻¹; residence time, 1.00 h.

4.4.2 Effect of HEC amount used in the catalyst formulation on the transesterification under continuous condition

Figure 4.20 shows the effect of of HEC amount used in the catalyst formulation on the transesterification under continuous condition. From the SEM results (Figures 4.13 and 4.14), many fracture appearing on the surface of the calcined ZSA-SE may be helpful for increasing triglyceride molecules to the active sites inside the extrudates. ZSA-SE prepared with various HEC amount gave a similar FAME

yield. This result suggested that the HEC amount did not affect to catalytic activity under continuous condition.

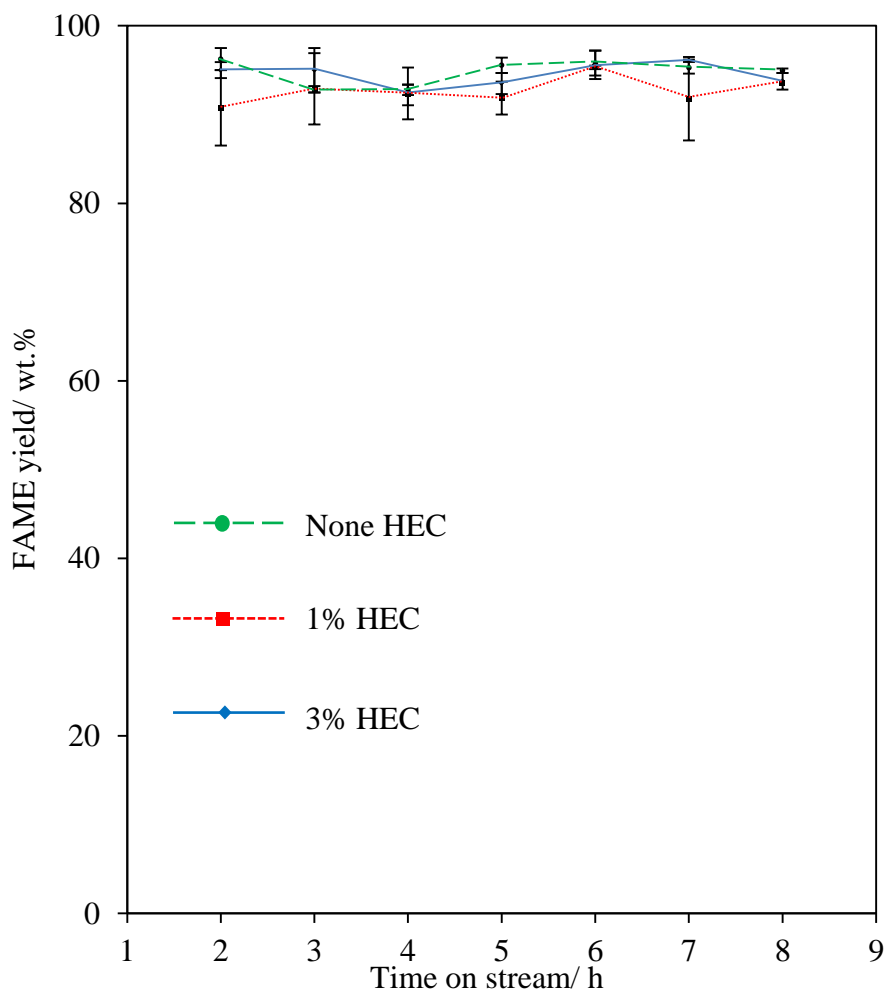


Figure 4.20 Effect of of HEC amount used in the catalyst formulation on the FAME yield attained from the transesterification of palm oil with methanol under continuous condition. Catalyst preparation: extrusion, single screw extruder; calcination temperature, 300 °C. Reaction condition: methanol/oil molar ratio, 30; temperature, 65 °C; total flow rate, 2.0 mL min⁻¹; premixing with 30 wt.% of the methyl esters (C₁₂-C₁₄); residence time, 1.00 h.

4.5 Stability of the extrudate catalyst in the transesterification under continuous condition

As evidenced by the reaction results (Figure 4.19), the ZSA-SE extrudates premixed with C₁₂-C₁₄ methyl esters gave high and stable FAME yield over 8 h. In this part, the spent catalyst extrudates at top and bottom of the fix-bed reaction were analyzed by the XRD technique to observe any sturtural change (Figure 4.21). Before the reaction (Figure 4.21(a)), the major phases of fresh catalyst were Ca(OH)₂, CaZn₂(OH)₆·2H₂O and CaCO₃. After the reaction (Figure 4.21(b) and (c)), the spent catalysts at the top and the bottom of the fixed-bed reactor retained their metal phases. The stability test of ZSA-SE premixed with C₁₂-C₁₄ methyl esters was investigated by performing the continuous transesterification for longer reaction time.

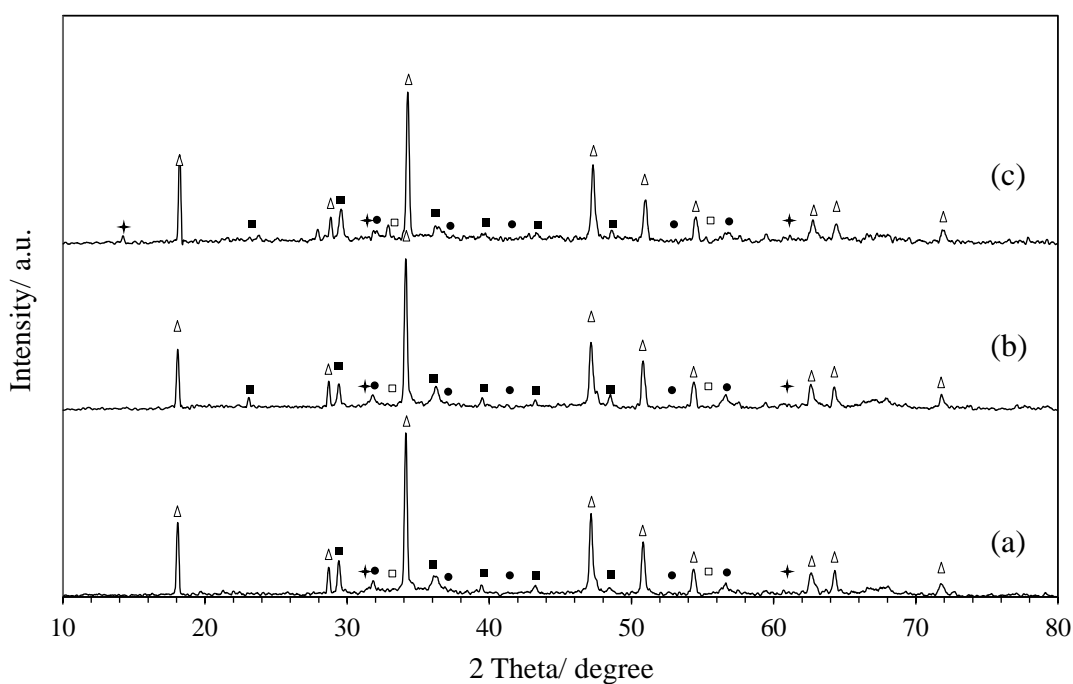


Figure 4.21 XRD patterns of fresh ZSA-SE calcined at 300 °C (a) and spent ZSA-SE extrudates at the top (a) and the bottom (c) of the fixed-bed reactor. (Symbols: ■ = CaCO₃, ★ = CaO, ● = ZnO, Δ = Ca(OH)₂, □ = ZnAl₂O₄ and ✦ = CaZn₂(OH)₆·2H₂O)

The stability testing of ZSA-SE extrudates calcined at 300 °C, prepared with 3% HEC and premixed with methyl esters on the FAME yield attained from the transesterification of palm oil with methanol under continuous condition is shown in Figure 4.22. The extrudate catalysts attained was stable in the transesterification over 24 h, giving the average FAME yield of 95 wt.%.

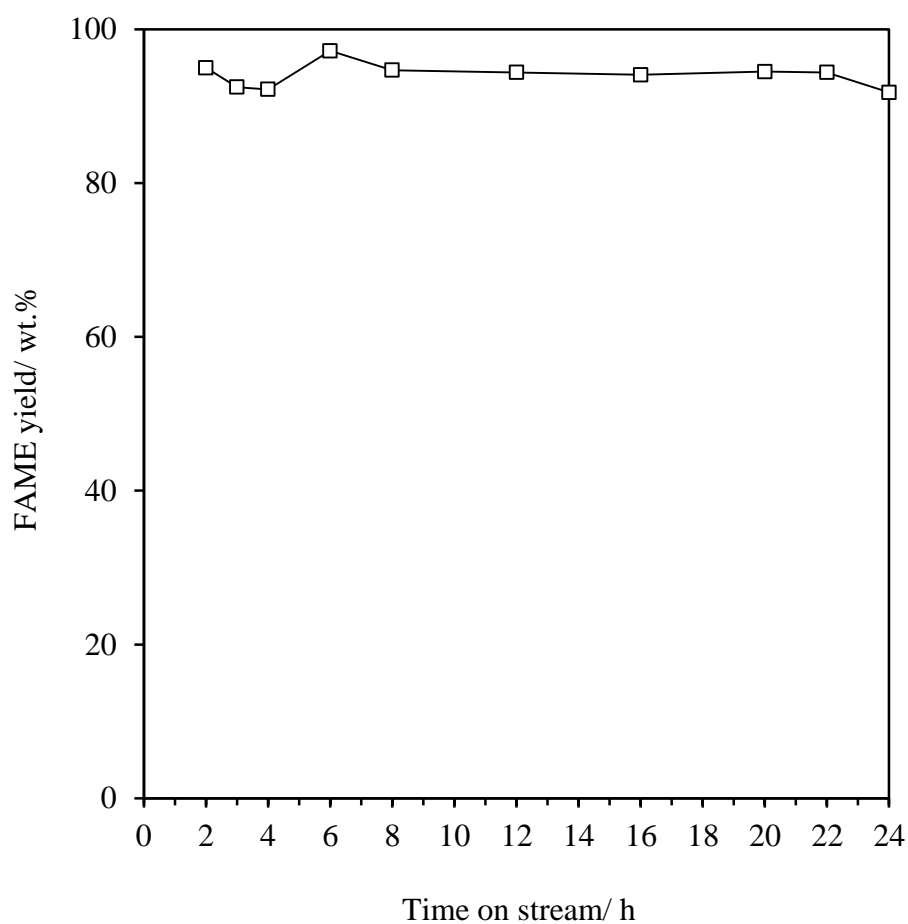


Figure 4.22 Stability of the ZSA-SE extrudates in the transesterification of palm oil with methanol under continuous condition. Catalyst preparation: HEC amount, 3 wt.%; extrusion, single screw extruder; calcination temperature, 300 °C. Reaction condition: methanol/oil molar ratio, 30; temperature, 65 °C; total flow rate, 2.0 mL min⁻¹; residence time, 1.00 h.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the present study on the preparation of the heterogeneous base catalysts from waste mixed seashells by the dissolution-precipitation method, the following conclusions can be made:

- The suitable conditions for preparation of powder catalysts is the weight ratio of seashells/ Al_2O_3 of 1:1 and calcination temperatures of 300 and 400 °C. The catalytic phases were composed of $\text{Ca}(\text{OH})_2$ and $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$. Under batch conditions, the catalysts gave the highest and stability FAME of 96 wt.% at the methanol/oil molar ratio of 30, amount of catalyst of 10 wt.%, reaction temperature of 60°C, reaction time of 3 h.
- The extrudate characteristics of the catalyst formulation with single screw extruder were harder than the catalysts formulated with manual extruder.
- The crushing strength and bulk density of the catalyst extrudates were decrease when HEC was decomposed by the calcination.
- The presence of premixing with methyl esters in the transesterification of palm oil with methanol under continuous conditions can enhance the FAME yield.
- The suitable condition for formulation the extrudate catalysts was carrier out at HEC amount, 3 wt.%; extrusion, single screw extruder; calcination temperature, 300 °C. The extrudate catalysts gave the high (95 wt.%) and stability (24 h) FAME yield attained from the transesterification of palm oil with methanol under continuous conditions. The continuous condition was methanol/oil molar ratio, 30:1; temperature, 65 °C; total flow rate, 2.0 mL min^{-1} ; residence time, 1.00 h.

5.2 Recommendations

- To improve the crushing strength of the catalyst extrudates, the formulation process should be done by using a twin screw extruder or using of new binder.
- To save the energy and cost in step of recovery methanol, the methanol/oil molar ratio should be decrease from 30:1.

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APPENDICES

Appendix A
Calculation of Cost of the catalysts

Table A1 Chemicals for catalyst preparation

Chemicals	Grade	Company	Cost (Baht / kg)
Seashells	-	Thai Dolomite Ltd	1.2
CaCO ₃	AR	Ajax Finechem	1160.0
(Zn(NO ₃) ₂ ·6H ₂ O)	AR	Ajax Finechem	1500.0
(Zn(NO ₃) ₂ ·6H ₂ O)	Commercial	PPM Chemicals Ltd	89.6
Al ₂ O ₃	AR	PPM Chemicals Ltd	42.1
Al ₂ O ₃	Commercial	Ajax Finechem	2600.0
HEC	Commercial	A.H.A. International	320.0

Calculation of powdery catalysts cost in 1 kg (Commercial grade)

$$\begin{aligned} \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} &= 0.3 \text{ kg (1 kg = 89.6 Baht)} \\ &= 26.8 \text{ Baht} \end{aligned}$$

$$\begin{aligned} \text{Waste mixed seashells} &= 0.5 \text{ kg (1kg = 1.2 Baht)} \\ &= 0.6 \text{ Baht} \end{aligned}$$

$$\begin{aligned} \text{Al}_2\text{O}_3 &= 0.2 \text{ kg (1kg = 42.12 Baht)} \\ &= 8.424 \text{ Baht} \end{aligned}$$

$$\begin{aligned} \text{Total of catalysts cost in 1 kg} &= \text{Zn(NO}_3)_2 + \text{Shells} + \text{Al}_2\text{O}_3 \\ &= 26.8 + 0.6 + 8.4 \text{ Baht} \\ &= 35.9 \text{ Baht} \end{aligned}$$

Calculation of powdery catalysts cost in 1 kg (AR grade)

$$\begin{aligned}
 \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} &= 0.3 \text{ kg (1 kg = 1500.0 Baht)} \\
 &= 450 \text{ Baht} \\
 \text{CaCO}_3 &= 0.5 \text{ kg (1kg = 1160.0 Baht)} \\
 &= 580 \text{ Baht} \\
 \text{Al}_2\text{O}_3 &= 0.2 \text{ kg (1kg = 2600.0 Baht)} \\
 &= 520 \text{ Baht} \\
 \text{Total of catalysts cost in 1 kg} &= \text{Zn(NO}_3)_2 + \text{CaCO}_3 + \text{Al}_2\text{O}_3 \\
 &= 450 + 580 + 520 \text{ Baht} \\
 &= 1550 \text{ Baht}
 \end{aligned}$$

Calculation of powdery catalysts cost in 1 kg (Commercial grade)

$$\begin{aligned}
 \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} &= 0.3 \text{ kg (1 kg = 89.6 Baht)} \\
 &= 26.8 \text{ Baht} \\
 \text{Waste mixed seashells} &= 0.5 \text{ kg (1kg = 1.2 Baht)} \\
 &= 0.6 \text{ Baht} \\
 \text{Al}_2\text{O}_3 &= 0.2 \text{ kg (1kg = 42.12 Baht)} \\
 &= 8.424 \text{ Baht} \\
 \text{HEC} &= 0.05 \text{ kg (1kg = 320 Baht)} \\
 \text{Total of catalysts cost in 1 kg} &= \text{Zn(NO}_3)_2 + \text{Shells} + \text{Al}_2\text{O}_3 \\
 &= 26.8 + 0.6 + 8.4 + 16 \text{ Baht} \\
 &= 51.9 \text{ Baht}
 \end{aligned}$$

Appendix C

Calculation of Methanol to Oil Molar Ratio

Example Calculation of methanol to oil molar ratio of 30

Molecular weight of palm oil = 847 g mol⁻¹

Density of palm oil = 1 g ml⁻¹

Molecular weight of methanol = 32.04 g mol⁻¹

Density of methanol = 0.792 g ml⁻¹

For 10 g of palm oil

From molecular weight of palm oil = 847 g

So, 10 g of palm oil = 10/ 847 = 0.0118 mol

From methanol to oil molar ratio of 30

So, mol of methanol = 30x 0.0118 = 0.354 mol

From molecular weight of methanol = 32.04 g mol⁻¹

So, methanol = 0.354x 32.04 = 11.34 g

From density of methanol = 0.792 g ml⁻¹

So, methanol = 11.34/ 0.792 = 14.32 ml

Therefore, the desired amount of methanol was 14.32 g

Appendix D

Calculation of Methyl Ester Content

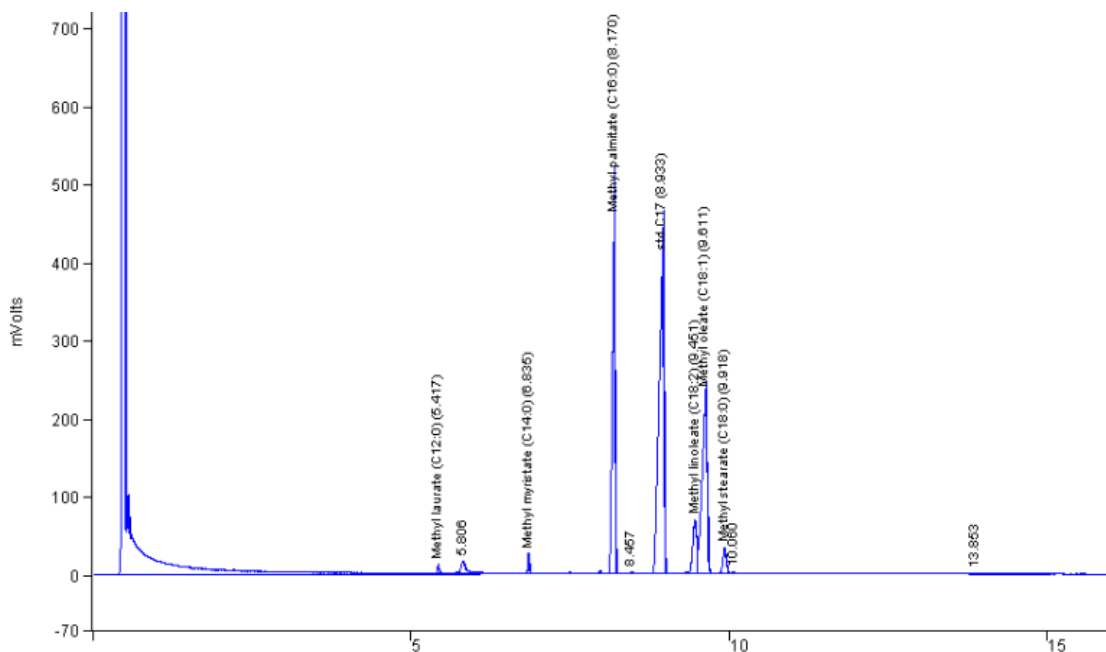


Figure D-1 The chromatograms of methyl ester product

The methyl ester content (wt.%) was calculate from the formula

$$\text{Wt.}\% = (\sum A_i \times W_{\text{std}}) / A_{\text{std}} \times W_s$$

Where $\sum A_i$ = The total area from methyl ester, from methyl caprylate (C8:0) to methyl stearate (C18:0)

W_{std} = The weight of methyl undecanoate

A_{std} = The area of methyl undecanoate

W_s = The weight of the sample

Example**Table D1** GC analysis of fatty acid methyl esters

Time/ min	Area
5.028	23223
6.803	56586
9.037	1489
9.415	21176
10.238	6669

The retention time at 5.028 is the retention time of C16

The retention time at 6.803 is the retention time of internal standard (C17)

The retention time at 9.037 is the retention time of C18:0

The retention time at 9.425 is the retention time of C18:1

The retention time at 10.238 is the retention time of C18:2

The weight of sample 0.0253 g

The weight of internal standard 0.0257 g

From, $Wt.\% = (\sum A_i \times W_{std}) / A_{std} \times W_s \times 100$

$$Wt.\% = ((23223+1489+21176+6669) \times 0.0257 / 56586 \times 0.0253) \times 100$$

$$Wt.\% = 94.35\%$$

Appendix E

Calculation of Residence time

Residence time, which is defined in the equation below:

$$\text{Residence time} = \frac{T \times 60 \text{ (min)}}{V_{\text{void}} \times 1 \text{ (h)}} \quad (\text{E-1})$$

where;

T = Total flow rate of reactant (mL/min)

V_{void} = Volume of liquid in packed column (ml)

$$V_{\text{void}} = V_{\text{void of Cat in}} + V_{\text{void of Cat out}} + V_{\text{void of bead}} \quad (\text{E-2})$$

where;

V_{void} = Volume of liquid in packed column

$V_{\text{void of Cat in}}$ = Volume of inner catalyst

$V_{\text{void of Cat out}}$ = Volume of outer catalyst

$V_{\text{void of bead}}$ = Volume of glass bead

VITAE

Mr. Wayu Jindapon was born on August 24, 1987 in Phang-nga, Thailand. He received a Bachelor's degree of Science, majoring in Polymer Science from Prince of Songkla University in 2009. He has pursued Master's degree in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2010 and finished her study in 2013.

Presentation

- 1-2 September 2012 Oral presentation "Shell-derived heterogeneous base catalyst for transesterification of palm oil" Congress on International Conference on Power and Energy Engineering (ICPEE 2012) at Radisson Blu Plaza Resort Phuket Panwa Beach, Phuket, Thailand