JIN, HAN. Synthesis of NaOH-impregnated Calcined Oyster shell for Transesterification Reaction. (Under the direction of Dr. Praveen Kolar.)

The goal of this dissertation research is to convert oyster shells into solid base catalysts for use in transesterification reactions. Specifically, the objectives were to: (1) synthesize a solid base catalyst by impregnating NaOH on the oyster shell (2) optimize the transesterification reaction parameters (3) study the kinetics of the transesterification and propose the underlying mechanism (4) elucidate the effects of preparation conditions on the surface structure and the activity of the catalyst.

This research was conducted in three phases. In the first phase, the catalyst was prepared by impregnating the waste oyster shell with 50 wt.% NaOH solution followed by calcination at 1000 °C for 3 h. The activity of NaOH-impregnated calcined oyster shell (Na-COS) was tested for transesterification of soybean oil and compared with the calcined oyster shell (COS) and conventional NaOH. Results indicated that Na-COS (> 87% yield in 1 h) was more active than COS (~ 70% yield in 3 h) and comparable with NaOH (~ 95% in 50 min). Reusability studies using Na-COS indicated that Na-COS could be applied to at least three consecutive batches of the transesterification reaction without any significant loss of activity. Additionally, batch experiments were carried out using Na-COS catalyst via a 4² factorial design at 62 °C, 800 rpm by selecting molar ratio of methanol to oil (MR) and catalyst loadings (CL) as factors. The levels of MR were set to 6, 12, 18, 24, while the levels of CL were set to 2%, 5%, 7%, 10%. Results indicated that MR = 12 and CL = 10% led to the highest fatty acid methyl esters (FAME) yield at 93.9%. Both MR and CL had significant effect on the FAME yield (p = 1.36 × 10⁻¹³ and 1.13 × 10⁻⁸, respectively), and a significant MR-CL interaction effect also existed (p = 6.08 × 10⁻⁷).

In the second phase, the surface of Na-COS was characterized to detect the active species on the surface. Based on XRD and XPS data it appeared that enhanced activity of
Na-COS was due to formation of Na$_2$O$_2$ phase and higher electron donating ability. Based on the characterization data, the mechanism of Na-COS-catalyzed transesterification was theorized to occur between adsorbed triglyceride and free methanol. Additionally, several mathematical models were developed to describe the transesterification process. To validate the models, batch experiments were carried out using Na-COS via a 3×4 factorial design at 62 °C, 800 rpm, volumetric ratio of hexane (co-solvent) to methanol = 1.83, wherein the levels of MR were set to 6, 12, 18, while the levels of CL were set to 2%, 4%, 6%, 8%. The most appropriate model was inferred to be the stepwise transesterification in which, transesterification of adsorbed triglyceride to adsorbed diglyceride was the rate determining step (RDS). The reaction rate constant of the RDS was estimated to be 0.0059 ± 0.0002 L mol$^{-1}$ min$^{-1}$ using the initial rate method. A reasonable fit was observed between the experimental and model predicted data (correlation of coefficient = 0.865).

In the third phase, effects of preparation conditions on catalyst structure and activity were investigated using the one-factor-at-a-time method. Firstly, various concentrations of NaOH and NaCl were chosen as the precursor chemicals for impregnation and tested in batch experiments (62 °C, 800 rpm). From the experimental results, the most feasible impregnation concentrations for NaOH and NaCl were found to be 6 mol/L and 2.43 mol/L, respectively. Subsequently, the effect of calcination temperature was investigated to observe that 800 °C was ideal for both precursors. All catalysts were studied via basicity tests, Brunauer–Emmett–Teller (BET) nitrogen adsorption method, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The data suggested that impregnated chemical and the calcination temperature determined the generated surface species that would affect the catalyst activity. Specifically, for NaOH$_{6}$/shell, higher calcination temperature facilitated the conversion of CaCO$_3$ and Ca(OH)$_2$ into CaO, and generation of Na$_2$O$_2$ on the surface, which resulted in consistent catalytic activity and higher durability.
For NaCl$_{2.43}$/shell, the synergistic effect of NaCl and CaO was observed when calcined at 800 °C, which enhanced the FAME yield, compared with those calcined at 1000 °C, in which no NaCl existed. Lower calcination temperature (600 °C) resulted in the limited amount of CaO formation and the high coverage of NaCl on the surface that led to almost no catalytic activity.

Overall, the results of this research suggested that the Na-COS is highly active and durable in transesterification that could potentially act as a substitute for NaOH. In addition, Na-COS catalyst could be employed in several organic reactions including: double bond isomerization of alkenes, hydrogenation of conjugated alkadienes, and cyanoethylation. Using wastes as precursors for catalysts will not only solve waste disposal problems but also add value to wastes.
Synthesis of NaOH-impregnated Calcined Oyster Shell for Transesterification Reaction

by

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DEDICATION

To my parents Yingji Jin & Qiuling Han.
BIOGRAPHY

Han was born in Wuhan, Hubei, China. He completed his B. Eng. in Biology Engineering at Xi’an Jiaotong University in 2012. In December 2012, he moved to North Carolina State University to pursue his Master degree in Biological and Agricultural Engineering. In January 2014, he was transferred to and started the doctorate degree.
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CHAPTER 1

Introduction

1.1 Background

Agricultural wastes refer to the wastes produced from various agricultural operations [1]. Due to their unique chemical composition and physical structure, agricultural wastes could be used as precursors for value-added products, such as biofuels [2], chemicals, and catalysts [3]. Since catalysts are widely used in the industrial manufacturing, there is a significant interest in developing catalysts from agricultural wastes.

Catalysts play an important role in transesterification reaction, which is the most commonly used method for biodiesel production [4]. The catalyst for transesterification reaction is either chemical or enzymatic. Because the enzymatic catalysts usually cost more, chemical catalysts are more widely chosen in industry [5]. The chemical catalyst used for transesterification reaction could be either an acid or a base [4]. The base catalyst catalyzes the reaction with a higher reaction rate, thus preferred over the acid catalyst [4].

Currently, NaOH is employed to catalyze the transesterification. Though highly active and efficient, the dissolved NaOH causes corrosion to the reactor and complicates the downstream processing of biodiesel, during which the neutralization and removal of NaOH produce large amount of wastewater. Moreover, NaOH is difficult to recover from the reaction system, therefore, the catalyst is non-reusable [6]. Hence this research focuses on the development of solid base catalyst for transesterification reaction.

Oyster shell, as one of the agricultural wastes, is produced in huge quantities from aquaculture industry in North Carolina and southeastern United States. Since oyster shell mainly consists of CaCO₃, it could be used as a cost-effective precursor for CaO, a strong solid base that can catalyze the transesterification reaction [7]. However, the major problem associated with the oyster shell-derived CaO is the relatively low catalytic activity,
compared with the homogeneous base catalyst, NaOH [7]. Hence, the improvement of the activity of the oyster shell-derived CaO is desired.

1.2 Hypothesis

NaOH-impregnation on oyster shell followed by calcination will enhance the catalytic activity of the oyster shell by modifying its surface structure. The NaOH-impregnated calcined oyster shell (Na-COS) will be highly active and durable in transesterifying soybean oil into fatty acid methyl esters (FAMEs).

The hypothesis was tested via studying the following objectives:

1.3 Objectives

(1) Synthesizing a solid base catalyst by impregnating NaOH on the oyster shell.

(2) Studying the effect of reaction variables on the transesterification of soybean oil.

(3) Determining the kinetics of the transesterification and proposing the underlying mechanism.

(4) Elucidating the effects of preparation conditions on the surface structure and the activity of the catalyst.

Based on the objectives above, this dissertation consists of six chapters. Chapter 2 summarized the recent research on developing solid base catalysts for transesterification reactions. This chapter aimed to report the various catalyst preparation methods and relevant results obtained from using those catalysts. The applications and limitations of the reviewed literature were discussed to help formulate the research questions that were addressed in chapter 3-5. Chapter 3-5 dealt with the development of a solid base catalyst, the kinetic study of the transesterification reaction, and the investigation on the effects of the preparation conditions on the surface structure and the catalytic activity of the catalyst,
respectively. Chapter 6 concluded the work and proposed the future directions for research on solid base catalyzed transesterification reaction.
References


CHAPTER 2

Literature review

2.1 Renewable energy

The decreasing storage of fossil fuels is compelling researchers to investigate other renewable energy sources. In addition, the usage of fossil fuels causes a series of environmental problems, including greenhouse effects, and acid rain due to excessive sulfur emissions [1]. Thus, there is an urgent need for alternative and renewable fuels.

Currently, a number of renewable energy sources are under consideration [2]. For example, solar, wind, tidal, wave and so forth are all green and renewable energy sources and have been playing a more and more significant role in today’s energy market. Nevertheless, several existing problems are limiting their potential to be used extensively. Firstly, many of those including, solar and wind energy, largely depend on the location and weather, which prevents them from being applied nationwide and worldwide. Secondly, the efficiency of the machines that are used for energy conversion and export is low. Hence, at this time, those energy sources are less economical to substitute fossil fuels.

Among all the renewable energy sources, energy generated from biomass shows a series of advantages over the others. Biomass refers to all the biological material derived from living, or recently living organisms, like wood, algae, and waste manure. In contrast to fossil fuels, biomass is generated from various bio-resources in a short-term cycle. Furthermore, since biomass uses sunlight and atmospheric CO$_2$, it is more environmentally friendly than fossil fuels. Currently, biomass is converted into other usable forms of energy, such as biogas [3], bioethanol [4], and biodiesel [5]. Those energy forms could be stored and transported easily. Although the current conversion method of biomass to any of the energy forms above remains inefficient and expensive, biomass has the potential to be a
major component of the future energy market due to its favorable features mentioned above.

Biodiesel or fatty acid methyl esters (FAME), refers to vegetable oil or animal fat-derived diesel fuel, [6]. Biodiesel has superb lubricating properties and cetane ratings compared with diesel fuels [7]. Despite possessing lower calorific value than diesel fuels, its better lubricity and a complete combustion could compensate for its lower energy density. Biodiesel can be used in pure form or blended with petroleum diesel at any concentration ratio. The fuel efficiency depends on the blend ratio and the type of combustion engine. Currently, biodiesel is being used for public transportation, including car, train, and aircraft.

There are four primary methods to produce biodiesel: direct use and blending, micro-emulsions, pyrolysis, and transesterification. Table 1 shows the advantages and disadvantages of each method [5]. In present, transesterification is the most efficient method to produce biodiesel with high quality.
Table 2.1 Comparison of four biodiesel production methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Definition</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct use and blending</td>
<td>Use pure vegetable oil or blended with diesel fuel.</td>
<td>High heat content; Renewability; Portability</td>
<td>High viscosity; Lower volatility; Active unsaturated hydrocarbon chain</td>
</tr>
<tr>
<td>Micro-emulsions</td>
<td>Liquid mixtures of oil, water, and surfactant that are clear, thermodynamically stable and isotropic</td>
<td>Lower viscosity</td>
<td>Lower energy content and cetane number</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>A thermochemical decomposition of one organic substance at high temperature in the absence of air or oxygen</td>
<td>Similar chemical properties to that of diesel fuels; Lower production cost</td>
<td>Energy-intensive</td>
</tr>
<tr>
<td>Transesterification</td>
<td>A chemical reaction between animal fat or vegetable oil and alcohol, which produces esters and glycerol</td>
<td>Renewability; Lower viscosity; High cetane number and energy content; Lower waste emissions</td>
<td>Higher cost of downstream processing; Large amount of wastewater produced</td>
</tr>
</tbody>
</table>
2.2 Transesterification

Transesterification is a chemical process of converting a carboxylic acid ester into another carboxylic acid ester [8]. In the case of producing biodiesel, the reactants are triglyceride and alcohol, usually methanol aided by an acid (H$_2$SO$_4$) or a base (NaOH) catalyst. The transesterification reaction for biodiesel production is shown in Figure 2.1:

$$\text{CH}_2\text{OOOCR}_1 \quad \text{CH}_2\text{OOOCR}_3 \quad \text{CH}_2\text{OH}$$

$$\text{CHOOCR}_2 \quad + \quad 3 \quad \text{CH}_3\text{OH} \quad \text{CH}_2\text{OOOCR}_2 \quad + \quad \text{CHOH}$$

$$\text{CH}_2\text{OOOCR}_3 \quad \text{CH}_2\text{OOOCR}_3 \quad \text{CH}_2\text{OH}$$

Figure 2.1 The transesterification between triglyceride and methanol for biodiesel production.

Although other alcohols could also be used, methanol is usually chosen due to economic considerations. In addition, methanol, due to its small size, yields FAME with lower viscosity, which is desired for the engine use.

The stoichiometry of this reaction suggests that the molar amount of methanol needed is three times as much as triglyceride. It is also worth noting that the reaction is reversible, and consequently, the triglyceride is only partially converted into FAMEs. To increase the yield of FAMEs, more than the stoichiometric amount of methanol is added into the reaction system to shift the chemical equilibrium towards the product. Generally, the methanol to oil ratio (MR) will largely exceed 3:1. The transesterification reaction between triglyceride and methanol consists of three consecutive reactions, wherein diglyceride and monoglyceride are formed as intermediates (Figure 2.2). Since the three consecutive...
reactions are all reversible, triglyceride, diglyceride, and monoglyceride all exist in the reaction mixture. The excessive methanol not only increases the conversion of triglyceride but also decreases the amount of those intermediates throughout the reaction period.

\[
\text{Triglyceride (TG)} + \text{CH}_3\text{OH} \xrightleftharpoons[k_1]{k_{-1}} \text{Diglyceride (DG)} + \text{CH}_3\text{OR}_1
\]
\[
\text{Diglyceride (DG)} + \text{CH}_3\text{OH} \xrightleftharpoons[k_2]{k_{-2}} \text{Monoglyceride (MG)} + \text{CH}_3\text{OR}_2
\]
\[
\text{Monoglyceride (MG)} + \text{CH}_3\text{OH} \xrightleftharpoons[k_3]{k_{-3}} \text{Glycerol (GL)} + \text{CH}_3\text{OR}_3
\]

Figure 2.2 The transesterification reaction of vegetable oil with methanol to esters and glycerol.

After completion of transesterification, the product mixture consists of three liquid phases, the methanol, the FAMEs-triglyceride (including diglyceride and monoglyceride) mixture, and the glycerol, from top to bottom. The (homogeneous) catalyst generally exists in the methanol and glycerol phase and could be washed away with deionized water. To obtain the FAMEs in the mixture, the downstream processing usually includes the removal of the unreacted methanol and glycerol followed by washing of FAMEs. Methanol could be removed by heating the mixture, while the glycerol could be separated by centrifugation as it has the highest density among all the compounds in this reaction. The washing of FAMEs is aimed to remove traces of methanol, glycerol and the ions resulting from the catalyst. Qualified biodiesel will be produced with the purified FAMEs through a series of further modifications and testing.

As with any chemical reaction, the catalyst is crucial to the transesterification reaction because it determines the reaction rate and affects the downstream processing of FAMEs. Diasakou et al. studied the kinetics of non-catalytic transesterification of soybean oil [9]. The reaction temperature was set at 220 °C and 235 °C, substantially higher than the
ambient temperature. Generally, non-catalytic transesterification requires a higher temperature, pressure, and MR to achieve a considerable reaction rate and oil conversion, and consequently, the process requires high energy input and expensive equipment that are temperature, pressure and corrosion resistant. The high production cost suggests that the non-catalytic transesterification is not favored by biodiesel industry. The catalytic transesterification reaction proceeds rapidly under mild conditions with the aid of catalyst that substantially lowers the activation energy. As described before, the catalyst could be either be a base or an acid, although, the catalytic mechanism is different for acids and bases. Generally, the base-catalyzed transesterification reaction occurs faster and requires lower MR than the acid-catalyzed one. However, base-catalyzed transesterification is less tolerant to the high free fatty acid (FFA) and water content in the feedstock. In the current biodiesel production industry, NaOH is chosen along with refined oils or fats to avoid any significant soap production. Although waste oil (with free fatty acids (FFA)) is an economical source to lower the production cost of biodiesel, esterification of FFA and the dehydration steps are required before it is applied to the transesterification.

NaOH can catalyze the reaction within 1 h, and as a homogeneous catalyst, the downstream processing includes centrifugation, neutralization of NaOH and washing to obtain clean FAMEs. The neutralization of NaOH implies non-reusability of NaOH and increased production of wastewater, suggesting that the NaOH-catalyzed transesterification reaction is somewhat uneconomical and non-environmentally friendly. To address the aforementioned problems, recent research has shifted towards development of heterogeneous catalysts for transesterification reaction. The advantages of heterogeneous catalysts are obvious; a catalyst could be regenerated easily because it is not dissolved in the liquid phase. The downstream processing of FAMEs is also simplified since the neutralization of the catalyst and the washing step are no longer needed if the leaching of
the solid catalyst is negligible. Finally, the catalyst could be used multiple times. However, a major shortcoming of a heterogeneous base catalyst, compared with a homogeneous base catalyst, is its relatively low catalytic activity. Unlike the homogeneous catalytic system where the reaction occurs ubiquitously, the reaction in a heterogeneous catalytic system only occurs on the surface of the solid catalyst. Thus, the reaction rate is substantially limited by the mass transfer rate of reactants to the catalyst surface. The mass transfer limitations could be alleviated by employing vigorous agitation and adding co-solvent, however, the agitation might affect the surface structure of the catalyst and the addition of co-solvent complicates the composition of the reaction system. In fact, several research studies have been conducted on optimizing the effect of stirring and co-solvent to maximize the FAMEs yield [10]. Another strategy to enhance the reaction rates is to increase the catalytic activity of the solid base catalyst. In a typical heterogeneous base-catalyzed transesterification reaction, the basic site facilitates the formation of methoxide, and further, adsorbs fatty acid long chains to form methyl ester. Stronger basic strength usually increases the affinity of methanol to the basic site, thus more methoxide is formed within a unit time. Ideally, the solid base catalyst is expected to acquire strong basic strength and higher basicity so that its reaction rate is comparable to that of the homogeneous catalysis.

The remaining part of this chapter summarized the recent research on developing solid base catalysts for transesterification reaction. For simplicity, the solid base catalysts were classified into categories consisting of alkaline earth metal oxide, mesoporous material supported base catalyst, natural source-derived base catalyst and superbase catalyst, and each category is discussed in detail.
2.3 Solid base catalyst

2.3.1 Alkaline earth metal oxide

The most commonly used solid base catalysts are derived from alkaline earth metal oxides. Alkaline earth metal commonly refers to beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). Their oxides typically have a strong basic strength. From Lewis theory of acids and bases, the basic strength of alkaline earth metal oxides is in the order of BeO < MgO < CaO < SrO < BaO < RaO [11]. Among all the alkaline earth metal oxides, MgO, CaO, and SrO have been extensively tested for the transesterification reaction because of their high accessibility and relatively low production cost.

2.3.1.1 Magnesium

MgO has one of the lowest basic strengths among alkaline earth metal oxides, and thus normal MgO is not an effective catalyst for transesterification. Ilgen selected dolomite as the catalyst source to transesterify canola oil [12]. Dolomite consists of MgCO$_3$ and CaCO$_3$, which decomposes into MgO and CaO under high temperature.

$$\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2$$

Their results showed that, at 500 °C and 600 °C, MgCO$_3$ decomposed into MgO while CaCO$_3$ remained uncalcined. The resulting solid exhibited almost no activity, suggesting that MgO derived from dolomite was an ineffective catalyst for transesterification reaction. Cantrell et al. tested the catalytic performance of MgO synthesized from Mg(NO$_3$)$_2$·6H$_2$O by the precipitation method, and a low reaction rate was observed [13]. To make MgO more efficient, the specific surface area and the density of basic sites need to be increased. Nano-MgO proved to be more active in transesterification reaction than conventional MgO. Verziu et al. synthesized three types of Nano-sized MgO using different methods [14].
Compared with the conventional microcrystalline MgO, the nanocrystalline MgO acquired higher surface area. Also, a low MR (4) was used under microwave conditions. In addition, Verziu et al. also concluded that the activity of nano-MgO depended on the activation temperature. A similar phenomenon regarding calcination temperature was also observed in another nano-MgO-catalyzed transesterification study conducted by Yacob et al. [15]. In their research, nano-MgO was synthesized from commercial MgO pretreated by the hydration-dehydration method. Based on their report, 600 °C was the optimal calcination temperature, and the resulting nano-MgO, however, converted 51.3% of the palm oil into biodiesel. So far, MgO or MgO-derived solid base catalysts exhibited only mild catalytic activity and the oil conversion remained low. Though many modification techniques have been utilized to improve their performance, the intrinsic low basic strength of MgO excluded its possibility of being effective in transesterifying oil into FAMEs.

2.3.1.2 Calcium

In the past decades, CaO and its derived compounds have been tested for transesterification of vegetable oil. The stronger basic strength of CaO than MgO and its abundant existence allowed it to serve as an active precursor for the solid base catalyst. Liu et al. used commercial CaO as the catalyst for transesterification of refined soybean oil [16]. The biodiesel yield exceeded 95% after 3 h reaction under the optimal conditions (MR = 12, CL = 8%, temperature 65 °C, water content 2.03%). It was worth noting that the presence of water enhanced the catalytic performance of CaO. It was reported that CaO extracted the proton from H₂O to form OH⁻, which further extracted the proton from methanol to form methoxide. The presence of water in the reaction system increased the formation rate of methoxide, thus accelerated the reaction rate. In contrast, homogeneous base catalyst, NaOH, requires water and fatty acid-free system during transesterification.
Thus, NaOH does not favor the waste cooking oil as the triglyceride source, and the removal of water and free fatty acids are needed prior to the transesterification reaction if waste cooking oils are used. From Liu et al.’s results, however, the removal of water seemed to be unnecessary if CaO is employed as the catalyst. Given that the major production cost of biodiesel is from the triglyceride source, CaO has potential to lower the production cost of biodiesel by catalyzing waste cooking oils, instead of refined oils.

The proposed mechanism of CaO-catalyzed transesterification of oil by Liu et al. concluded that the real catalyst was Ca(OCH$_3$)$_2$ other than CaO [16]. To test the catalytic activity of Ca(OCH$_3$)$_2$, Liu et al. then used Ca(OCH$_3$)$_2$ to catalyze the transesterification [17]. The result indicated that Ca(OCH$_3$)$_2$ is superior to CaO in transesterifying oil into FAMEs. The optimal reaction required lower MR (6) and CL (2%), and a comparable yield (98%) was obtained. A desirable result was also achieved by Liu et al., wherein the Ca(OCH$_2$CH$_3$)$_2$ was used as the catalyst (MR = 12, CL = 3%, temperature = 65 °C, biodiesel yield 95% at 1.5h) [18]. The preparation method for these catalysts was dispersing Ca into the corresponding alcohol solution for a certain period under the stirring condition and being separated by filtration. In a different study by Kouzu et al., the real catalyst for transesterification switched to calcium diglyceroxide as the reaction proceeded [19]. CaO started to extract protons from the produced glycerol, forming calcium diglyceroxide to catalyze the reaction.

Some adjustments have been applied to CaO-catalyzed transesterification to increase its yield. Demirbas used supercritical methanol to increase the yield of CaO-catalyzed transesterification reaction [20]. The optimal result from Demirbas’s research showed a FAME yield between 80% and 90% within just 6 min (MR = 41, CL = 3%, temperature = 252 °C). However, this reaction system required a substantially higher MR and reaction temperature, which imposed strict demands on the production equipment. In this research,
the amount of oil used was in the range of 20 - 30 g. Considering the strict requirements imposed on the equipment, the scale-up problems regarding reactor design might arise if it applied to the industry. With no economic analysis, the chance of applying supercritical methanol to biodiesel production remained unknown. Another strategy is to improve the catalyst by combining it with other compounds to generate more active surface species. Ngamcharussrivichai et al. synthesized a mixed catalyst of CaO and ZnO by co-precipitation method from their nitrate solutions [21]. This CaO-ZnO mixed catalyst led to a FAME yield over 94% with MR = 30, CL = 10% at 60 °C in 1 h. The only problem with this CaO-ZnO catalyst was that it required high MR to obtain the high biodiesel yield. To address this problem, Rubio-Caballero et al. changed the preparation method by using calcium nitrate as the precursor to derive CaO-ZnO [22]. After the calcination at 400 °C, the resulting solids contained a high specific surface area and pore volume. The yield exceeded 90% within 45 min under milder reaction conditions (MR = 12, CL = 4%, temperature = 60 °C). The MR had been dramatically reduced, while the yield remained comparable. Yan et al. modified CaO by doping lanthanum on the surface and had successfully increased its basic strength, basicity, and specific surface area [23]. An optimal FAME yield of 94.3% was obtained in 1 h (MR = 20, CL = 5%, temperature = 58 °C). In addition, this catalyst showed a high tolerance to water and FFA, indicating its promising application to transesterifying waste cooking oils directly. Wang et al. reported another durable solid catalyst containing Ca_{12}Al_{14}O_{33} and CaO that led to 90% FAME yield in 3 h reaction under optimal conditions [24]. Based on the results of the characterization of CaO-modified catalysts, the addition of another metal element typically increased both basic strength and basicity, which improved the catalytic activity.

Some researchers focused on increasing the specific surface area of the CaO-derived solid catalysts to improve its catalytic performance. Zabeti et al. chose mesoporous Al_{2}O_{3}
as support and synthesized CaO/Al\(_2\)O\(_3\) by wet impregnation method [25]. Their study showed 98.64% FAME yield with the optimal conditions of MR = 12.14, CL = 5.97%, temperature = 64.29 °C after 5 h. Pasupulety et al. continued the study on Al\(_2\)O\(_3\) as the catalyst support for CaO by testing the activity of neutral, basic, and acidic Al\(_2\)O\(_3\) supported CaO [26]. Neutral Al\(_2\)O\(_3\) supported CaO exhibited the highest biodiesel yield due to its ability to form calcium diglyceroxide on its surface, which was the most active catalyst for transesterification reaction.

### 2.3.1.3 Strontium

Theoretically, SrO is more active than MgO and CaO in transesterification reaction because of its higher basic strength. Liu et al. first investigated the catalytic activity of SrO in the transesterification of soybean oil to FAME [27]. Characterization of SrO indicated that its basic strength was greater than 26.5, classified as superbase. Compared with CaO, SrO completed the reaction in a shorter time (30 min) with FAME yield exceeding 95%. In addition to the high catalytic activity, SrO also exhibited a high durability in that it could be applied to transesterification reaction for 10 cycles with only a slight decrease in FAME yields. Further, Koberg et al. improved the performance of SrO by replacing the conventional heating method with microwave irradiation method, which completed the reaction within 60 s [28]. However, this unconventional heating system was complicated to scale up for industrial applications.

### 2.3.2 Mesoporous material supported base catalyst

#### 2.3.2.1 Alumina-supported base catalysts

Alumina is the third most abundant element on the earth. Besides its high availability, alumina and its oxides also have a high specific surface area that can be used as the support
for dispersing catalytic material. In the past decade, alumina-supported base catalysts have been extensively evaluated for transesterifying oil into FAMEs. One of the most straightforward strategies is to adsorb a strong base onto the surface of the alumina materials to generate abundant surface basic sites. Arzamendi et al. loaded NaOH on γ-Al₂O₃ and investigated its performance on transesterification of sunflower oil [29]. The results indicated that its performance largely depended on catalyst/methanol ratio, and the alumina-supported NaOH dried at 120 °C performed better than those calcined at higher temperatures. Under optimal reaction conditions, the FAME yields obtained from this catalyst was comparable to homogeneous NaOH-catalyzed FAME yields. Another commonly used homogeneous catalyst, KOH, was also impregnated on Al₂O₃ and tested by Noiroj et al. [30] for transesterifying palm oil. The FAME yield reached 91.07% using an MR of 15, CL of 3% at 60 °C within 3 h. However, the problem associated with NaOH/Al₂O₃ and KOH/Al₂O₃ was significant leaching of Na and K species during the reaction, implying that these catalysts were not durable for repeated uses. In addition, the leached Na or K species lowered the quality of FAMEs and complicated the purification process of biodiesel.

Because, alkaline metal hydroxide-doped Al₂O₃ caused the undesired leaching of surface active species, researchers resorted to alkaline metal salts to generate active species on Al₂O₃ surface. Xie and Li selected a series of potassium salts and used them to modify Al₂O₃ [31]. The basic strength and transesterification reaction showed that KI loaded Al₂O₃ exhibited the highest basic strength and oil conversion (basic strength 15.0 < H_ < 18.0, conversion = 96%). In addition, they also studied the effect of support type on the activity of the catalyst, and Al₂O₃ supported KI led to the highest conversion than the other supports (ZrO₂, ZnO, NaX, KL), concluding that Al₂O₃ was the ideal support for KI adsorption. Boz et al. synthesized the KF/Al₂O₃ catalyst by using nano-sized Al₂O₃ [32]. Their optimization
study showed 97.7% ± 2.14% FAME yield with MR = 15, CL = 3% at 65 °C in 8 h. This high FAME yield was attributed to the formation of K₂O and Al-O-K groups on the surface of Al₂O₃. Since KF contains no oxygen atom, the formation of active site attributed to the oxygen of Al₂O₃, indicating new chemical bonding that may have occurred formed the impregnation-calcination process. Based on this mechanism, more potassium salts were tested by Vyas et al. [33] and Lukic et al. [34]. Vyas et al. [33] utilized KNO₃ as doping compound to modify Al₂O₃. Over 84% biodiesel yield was reported under optimal reaction conditions. However, the characterization of KNO₃ loaded Al₂O₃ catalyst was not performed, thus the formation of active site was not clarified. Lukic et al. [34] on the other hand, used K₂CO₃ as doping compound. An alumina/silica support was chosen and synthesized via sol-gel method, different from the alumina support used in other studies. The FAME yield of 93.5% was obtained within only 15 min, however, the reaction temperature was set to 120 °C, substantially beyond the usual reaction temperature range (50 - 70 °C). Besides, a significant leaching of potassium was observed, and the second transesterification run with the same spent catalyst only led to 25.4% FAME yield. The instability and high reaction temperature requirement suggested that this as-synthesized K₂CO₃/Al₂O₃ was unstable and needed further modification.

2.3.2.2 Zeolite-supported base catalysts

Zeolite refers to a series of naturally occurring microporous, aluminosilicate minerals that are usually used as catalysts and adsorbents. Natural zeolites usually contain high impurities and irregular shape, so they are rarely used in industry. Instead, the uniform and phase-pure synthetic zeolites are prepared via aqueous solutions of alumina and silica with sodium hydroxide. Because of the regular structure and the known composition, synthesized zeolites are easy to manipulate. Its porous structure favors the accommodation
of various types of cations, which is highly desirable for dispersion of catalytically active sites.

Suppes et al. investigated the catalytic performance of two types of zeolites, NaX faujasite zeolite and ETS-10 zeolite, loaded with various metal oxides [35]. Both of two zeolites were loaded with K and Cs via ion-exchange, while NaX zeolite was also loaded with various concentrations of Na. Results showed that aforementioned ion-exchanged zeolites exhibited higher catalytic activity after calcination at 500 °C. Reactions catalyzed by pure ETS-10, K-ETS10, and various Na/NaX zeolites (with different Na concentration) led to FAME yield above 90% at 120 °C and 150 °C. However, the reaction time was 24 h, substantially longer than the time required by most base catalysts. Besides, the reaction temperature was also higher than the temperature required by the NaOH (50 - 65 °C). In addition, the preparation method for these catalysts was complicated, and the reaction process required high energy input, which may not be commercially favorable. Similar results were reported by Leclercq et al., where the reaction time and temperature required by the Cs-exchanged NaX faujasite zeolite were significantly higher than other catalysts to obtain comparable yield [36]. Shu et al. chose zeolite-β as the support to load La to derive the solid base catalyst [37]. However, the optimal reaction condition only led to a 48.9% oil conversion. In addition, Brito et al. studied various types of zeolite Y loaded with different amounts of Al₂O₃ for transesterifying used vegetable oil [38]. A high reaction temperature (between 200 °C and 476 °C) was required to obtain a high biodiesel yield.

Some researchers reported encouraging results from using zeolite supported-solid base catalysts. Wu et al. investigated the performance of CaO modified NaY, K₃, and NaZSM-5 zeolite on transesterification of soybean oil [39]. Catalysts were prepared by mixing CaO and zeolite followed by microwave irradiation method. The results indicated that CaO modified NaY zeolite led to 95% FAME yield with MR = 9, CL = 3% at 65 °C in 3 h.
Kusuma et al. used KOH to modify the natural zeolite from Pacitan Indonesia by impregnation method [40]. The maximum FAME yield reached 95.09% after 2 h using 100 g/100 ml KOH-impregnated zeolite under the optimal conditions (MR = 7, CL = 3%, reaction temperature = 60 °C). In addition, the leaching of potassium species was also investigated, reported as 3.40% of the active site of the catalyst. The reusability test showed that the yield dropped down to 86.08% and 72.31% for the second and third run, respectively, with the same spent catalyst. The leaching of potassium species might have contributed to the decreasing yield.

2.3.3 Natural source-derived base catalyst

In the past decade, researchers have focused on deriving catalysts from natural sources other than commercial chemicals in order to lower production costs [41]. Among all the natural sources, natural shells tend to be the most feasible ones because of their high availability. Natural shells consist of CaCO₃ and, with a simple thermal conversion, could be decomposed into CaO. There are many advantages of using natural shells as the precursor of solid base catalysts. Firstly, natural shells, such as eggshell and oyster shell, are produced in huge quantities daily due to the large food consumption, thus making the catalyst supply potentially abundant. Secondly, the utilization of those shells tackles the disposal of agricultural wastes, alleviating the environmental pressure. It is, therefore, both economically and environmentally friendly to derive solid base catalysts from waste natural shells.

Calcination is the core step in the preparation of solid base from natural shells, where the CaCO₃ was converted into CaO [41]. The CaO produced in calcined natural shells is easy to absorb CO₂ and H₂O in the air. To protect the CaO site, inert gas, such as nitrogen and helium, is usually flown continuously into the furnace to remove the air. The calcined
shells are typically stored in a desiccator for further use. So far, many natural shells have been used to derive CaO to catalyze the transesterification reaction. Table 2 summarizes shell-derived catalysts used for biodiesel production.

However, unlike commercial CaO, the calcined natural shell is usually irregularly shaped, and the distribution of CaO is likely to be heterogeneous. This implies that the calcined natural shell is difficult to manipulate and does not possess uniformly distributed sites. When chosen as the support, the chemical interaction between surface CaO and loaded chemical species occurs heterogeneously and unpredictably. Besides, natural shells also contain various organic substances aside from CaCO₃. At 700 °C or above, organic substances are completely combusted and CaCO₃ starts to decompose into CaO. If the pretreatment method is intended to modify the surface of natural shells, then the removal of the surface organic matter is required beforehand to ensure the successful interaction between the loaded chemical and the surface CaCO₃. The most commonly used method is washing shells with deionized water and reducing their size. The residual organics could be removed by calcining the washed and cleaned shell particles at a temperature greater than the organics’ ignition point but lower than the CaCO₃ decomposition point.
Table 2.2 Summary of recently reported natural shell-derived catalysts for biodiesel production.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Source material</th>
<th>Calcination temperature</th>
<th>Calcination time</th>
<th>Oil type</th>
<th>Catalyst loadings</th>
<th>Molar ratio</th>
<th>Reaction temperature</th>
<th>Reaction time</th>
<th>FAME yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Eggshell</td>
<td>1000 °C</td>
<td>2 h</td>
<td>Soybean</td>
<td>3%</td>
<td>1:9</td>
<td>65 °C</td>
<td>3 h</td>
<td>95%</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800 °C</td>
<td>4 h</td>
<td>Palm olein</td>
<td>10%</td>
<td>1:12</td>
<td>60 °C</td>
<td>2 h</td>
<td>90%</td>
<td>[43]</td>
</tr>
<tr>
<td>2</td>
<td>Oyster shell</td>
<td>700 °C</td>
<td>3 h</td>
<td>Soybean</td>
<td>25%</td>
<td>1:6</td>
<td>65 °C</td>
<td>5 h</td>
<td>72.50%</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>KI/oyster shell</td>
<td>1000 °C</td>
<td>4 h</td>
<td>Soybean</td>
<td>3.50%</td>
<td>1:10</td>
<td>60 °C</td>
<td>4 h</td>
<td>85%</td>
<td>[45]</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$O/Mussel shell</td>
<td>900 °C; 600 °C</td>
<td>4 h; 3 h</td>
<td>Chinese tallow</td>
<td>5%</td>
<td>1:12</td>
<td>70 °C</td>
<td>1.5 h</td>
<td>90%</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>Mussel shell</td>
<td>1050 °C</td>
<td>2 h</td>
<td>Soybean</td>
<td>12%</td>
<td>1:24</td>
<td>60 °C</td>
<td>8 h</td>
<td>94.10%</td>
<td>[47]</td>
</tr>
<tr>
<td>4</td>
<td>Crab shell</td>
<td>700 °C</td>
<td>2 h</td>
<td>Palm olein</td>
<td>5%</td>
<td>1:12</td>
<td>65 °C</td>
<td>2.5 h</td>
<td>98%</td>
<td>[48]</td>
</tr>
<tr>
<td>5</td>
<td>Cockle shell</td>
<td>900 °C</td>
<td>2 h</td>
<td>Palm olein</td>
<td>4.90%</td>
<td>1:12</td>
<td>N.A.</td>
<td>3 h</td>
<td>97.48%</td>
<td>[49]</td>
</tr>
<tr>
<td>6</td>
<td>Pomacea sp. shell</td>
<td>900 °C</td>
<td>2 h</td>
<td>Palm olein</td>
<td>4%</td>
<td>1:7</td>
<td>60 °C</td>
<td>4 h</td>
<td>95.61%</td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>Material</td>
<td>Temperature</td>
<td>Time</td>
<td>Oil</td>
<td>Ratio</td>
<td>Time</td>
<td>Yield</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>--------------------------</td>
<td>-------------</td>
<td>------</td>
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<td>-------</td>
<td>------</td>
<td>---------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Turbonilla striatula shell</td>
<td>900 °C</td>
<td>4 h</td>
<td>Mustard</td>
<td>3%</td>
<td>1:9</td>
<td>65 °C</td>
<td>6 h</td>
<td>93.30%</td>
<td>[51]</td>
</tr>
<tr>
<td>8</td>
<td>Capiz shell</td>
<td>900 °C</td>
<td>2 h</td>
<td>Palm olein</td>
<td>3%</td>
<td>1:8</td>
<td>60 °C</td>
<td>6 h</td>
<td>93%</td>
<td>[52]</td>
</tr>
<tr>
<td>9</td>
<td>KF/Turtle shell</td>
<td>500 °C; 300 °C</td>
<td>N.A.</td>
<td>Rapeseed</td>
<td>3%</td>
<td>1:9</td>
<td>70 °C</td>
<td>3 h</td>
<td>97.50%</td>
<td>[53]</td>
</tr>
</tbody>
</table>

N.A. - not available
Many efforts have been made to increase the basic strength and basicity of the CaO derived from natural materials. Yoosuk et al. measured the basic strength of commercially purchased CaO, which was in the range of $9.8 < H_ < 12.2$ [54]. They also used fresh calcite as the precursor to generate CaO. Calcite was first calcined at $800 \, ^\circ\text{C}$ for 3 h, during which CaCO$_3$ was converted into CaO, and then pretreated with refluxing water, followed by recalcination at $600 \, ^\circ\text{C}$ for 3 h. The pretreatment with water caused the reaction between CaO and H$_2$O, forming Ca(OH)$_2$. Recalcination produced solid CaO again, however, with different textural properties, compared with the CaO generated from the first calcination. Table 3 is the summary of the structural properties of the solids at different stages of this pretreatment method [54]. The results showed that water-pretreated CaO solid acquired a higher basic strength and larger surface area than commercial CaO. A FAME yield of 95.7% was achieved under suitable conditions (MR = 15, CL = 7%, reaction temperature $= 60 \, ^\circ\text{C}$) within only 45 min. The hydration-dehydration of fresh calcite is an effective method to increase the basicity of CaO. Based on this idea, Hu et al. designed their experiment, in which the waste freshwater mussel shell, instead of fresh calcite, was chosen as the precursor of CaO [46]. Hu et al. develop a similar pretreatment, consisting of calcination, deionized water impregnation, and recalcination, to form the catalyst. Their catalyst also exhibited a largely increased surface area from $0.9 \, \text{m}^2/\text{g}$ of the raw shell to $23.2 \, \text{m}^2/\text{g}$ of the final catalyst [46]. Although the basic strength of the catalyst was not tested, this catalyst led to a FAME yield above 90% at the optimal conditions based on the statistical model, which was sufficient to conclude that the water impregnation and recalcination on calcined mussel shell was a promising strategy to produce an active catalyst for transesterification reaction.

In addition to the water impregnation method, various chemicals have been employed to impregnate natural shells to improve the catalytic performance. Xie et al. proposed a
carbonization-KF impregnation-activation method to modify the turtle shell [53]. Based on their proposed mechanism, the first carbonization step helped the organic matters of the shell decompose and evaporate, changing the original shell into a micro-nano-structural porous material with the ultrahigh surface area. The second KF impregnation step allowed the KF to be adsorbed on the surface of the shell, which was then further stabilized by the last activation step. More oxygen anion sites were formed due to the reaction between adsorbed KF and chitin of the shell, leading to a high catalytic activity. The biodiesel yield reached 97.5% in 3 h under optimal conditions. Somewhat similar research was conducted by Jairam et al., in which oyster shell and KI were chosen instead [45]. Largely increased specific surface area of the catalyst was observed as well. These studies indicated that the impregnation method followed by thermal conversion could increase the specific area of the shell. The thermal conversion temperature depended on the shell type. However, those studies did not determine the basic strength of the catalysts. Thus, whether this method was effective to increase the basic strength remained unknown. Jairam et al. impregnated oyster shell with KI, and the FAME yield reached 85%, higher than the yield (73.8%) reported by Nakatani et al., who used combusted oyster shell (no impregnation). The MR remained as 6 for both works, but the CL decreased from 25 wt.% to 3.5 wt.%, suggesting that the impregnation of KI had successfully improved the catalytic activity of calcined oyster shell [44, 45].
Table 2.3 Summary of various types of CaO derived from fresh calcite [54].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Fresh Calcite</th>
<th>CaO₆₀₀</th>
<th>CaO₆₀₀</th>
<th>CaO₆₀₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>0.4</td>
<td>12.4</td>
<td>25</td>
<td>2.1</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.01</td>
<td>0.19</td>
<td>0.25</td>
<td>0.02</td>
</tr>
<tr>
<td>Crystalline size</td>
<td>&gt;100.0</td>
<td>55.5</td>
<td>42.2</td>
<td>&gt;100.0</td>
</tr>
<tr>
<td>Basic strength</td>
<td>H_ &lt;7.2</td>
<td>12.2 &lt;H_ &lt;15.0</td>
<td>12.2 &lt;H_ &lt;15.0</td>
<td>9.8 &lt; H_ &lt;12.2</td>
</tr>
</tbody>
</table>

CaO₆₀₀ - Solids from fresh calcite calcined at 800 °C

CaO₆₀₀ - CaOs pretreated with hydration method then calcined at 600 °C

CaO₆₀₀ - commercially purchased CaO

2.3.4 Solid superbase catalyst

Superbase refers to a group of solid bases that possess basic strengths H_ > 26 [55]. Superbase catalysts have many advantages including, high activity, high selectivity, and ability to catalyze reactions at milder conditions. As a result, they are intensively applied in organic chemical synthesis [56]. There have been several studies on superbase-catalyzed organic reactions, such as isomerization of alkenes and alkynes, Michael addition, condensation reactions, anti-Markovniov hydroamination and hydroalkoxylation [57]. To take advantage of their excellent catalytic properties, superbases have recently been applied to the transesterification reaction, and many promising results have been obtained. Zhu et al. synthesized the superbasic CaO from commercial CaO by a simple impregnation-calcination method [58]. Commercial CaO usually has a low basic strength due to the adsorption of CO₂ and H₂O. In their research [58], 0.12 g/ml (NH₄)₂CO₃ solution was used to pretreat the commercial CaO, and the presence of H₂O led to a reaction between H₂O and CaO, forming Ca(OH)₂. Subsequent calcination converted the solid back into CaO, however, with a different structure. The XRD patterns and SEM images of commercially
purchased and modified CaO showed that the latter acquired the higher CaO content and more regular shape. These changes of chemical composition and surface structure contributed to the increase of its basicity, from normal base to superbase. However, how (NH$_4$)$_2$CO$_3$ affected the commercial CaO was not clarified. Yoosuk et al. used water to pretreat CaO calcined from fresh calcite, and an increased basic strength was observed, though not superbase [54]. Therefore, the superbase formation in Zhu’s research might either attribute to the presence of (NH$_4$)$_2$CO$_3$ in water or the source of CaO that was derived from. Another metal oxide superbase catalyst, SrO, was tested by Liu et al., [27] and the FAME yield exceeded 95% in 30 min with MR = 12, CL = 3%, at 70 °C, suggesting that SrO was comparable with the homogeneous catalyst, NaOH, in the transesterification reaction. However, the SrO was not characterized, thus the chemical nature of SrO was not clarified.

In addition to single-component metal oxides, a few superbases were derived from a combination of various chemical compounds. Eu$_2$O$_3$/Al$_2$O$_3$ was tested for transesterification of soybean oil by Li et al. [59]. Transesterification reaction was performed in a fixed bed reactor under atmospheric pressure, and the oil conversion reached 63% in 8 h (MR = 6, CL = 10%, reaction temperature = 70 °C). Eu$_2$O$_3$/Al$_2$O$_3$ led to a relatively low oil conversion, even though super basic sites were formed. The reason might be the low MR, the lower basicity or both, which was not investigated in their research. The durability of the Eu$_2$O$_3$/Al$_2$O$_3$ catalyst was not tested, either. Therefore, more work on this Eu$_2$O$_3$/Al$_2$O$_3$ catalyst is needed. Another solid superbase was prepared from K and KOH loaded Al$_2$O$_3$ by Ma et al. [60]. The characterization study verified that the Al-O-K was formed during the preparation method, which accounted for its high basic strength and activity. The optimal dosage of K and KOH was determined as 7.5 wt.% and 20 wt.% to
obtain the highest catalytic activity of the catalyst. The FAME yield reached 84.52% in 1 h (MR = 9, CL = 4%, reaction temperature = 60 °C).

2.4 Future perspective

Currently, most reported solid base catalysts for transesterification were derived from commercial chemicals. However, there are still two major obstacles to overcome in order to commercialize those catalysts: the preparation cost and the durability of the catalyst. Some of the catalysts contain relatively scarce elements, such as Sr [27] and Eu [59], that are more expensive than the homogeneous bases, NaOH or KOH. The alumina-supported solid base catalysts suffer from the significant leaching of active species, thus not favorable for the industry. To derive cost-effective and durable solid base catalysts, natural shells are more preferred to be used as precursors for the catalyst synthesis.

For natural shell-derived solid base catalysts, the major problem is associated with the low activity. The completion of transesterification reaction catalyzed by calcined natural shell requires higher MR and CL and longer time than the homogeneous base catalyst. Thus, the production cost is expected to increase due to the high material and energy input. Therefore, the activity of natural shell-derived solid base catalyst needs to be improved. Currently, most reported literature on developing solid base catalysts from natural shell only employ the high-temperature calcination as the preparation method. One possible way to improve its activity is to impregnate chemicals on the natural shell via wet impregnation method to form highly active and stable basic sites during calcination [44, 45]. Sodium and potassium-containing chemicals have been used to generate active basic sites on Al₂O₃. Those ideas and techniques may be extrapolated to natural shells (as support material) for the synthesis of highly active and stable catalysts.
References


CHAPTER 3

NaOH-impregnated oyster shell as a solid base catalyst for transesterification of soybean oil

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Abstract

There is significant interest in developing renewable solid base catalysts from agricultural wastes for use in the transesterification of fats into fatty acid methyl esters (FAME). In this study, an inexpensive base catalyst was synthesized by impregnating waste oyster shell with 50% sodium hydroxide solution, followed by calcination at 1000 °C for 3h. The resulting solid catalyst was used to catalyze transesterification of soybean oil. Transesterification using the catalyst was studied by systematically varying molar ratio (MR) (methanol to oil) and catalyst loading (CL). Results indicated that highest FAME yield was 93.9% using MR of 12 and CL of 10%. Reusability tests suggested that the catalyst could be used for at least three runs without any significant decrease in FAME yield.

Keywords: Fatty acid methyl esters, Biodiesel; Transesterification; Oyster shell; Reusability

3.1 Introduction

The decreasing production and environmental issues associated with fossil fuels are compelling researchers and scientists to explore other sources of energies that are renewable, practical, and easy to produce.

Biodiesel, or fatty acid methyl esters (FAMEs), is one such biomass-derived and renewable fuel. As a fuel, biodiesel has excellent lubricating properties and cetane ratings compared with diesel fuels [1]. Presently, biodiesel is being used as a fuel for public transportation, including cars, trains, and aircraft. Biodiesel may be produced via thermochemical (e.g., pyrolysis), biochemical (e.g., fungal fermentation), and catalytic (e.g., transesterification) processes [2], although transesterification is the most widely used method for biodiesel production in industry.
Transesterification is a chemical reaction that converts a carboxylic acid ester into a different carboxylic acid ester. In the case of biodiesel production, triglycerides from oil react with methanol or ethanol to produce glycerol and fatty acid methyl esters (FAMEs), which are further modified to biodiesel. A catalyst is usually needed for transesterification to ensure a high reaction rate since non-catalytic transesterification usually requires extremely high reaction temperature and methanol content [3]. Homogeneous base catalysts, such as sodium hydroxide or potassium hydroxide, are usually employed to catalyze the reaction. However, homogeneous base catalysts result in a series of problems, including issues with catalyst recovery, large wastewater production, and corrosion to operation facilities, all of which increase the production cost of biodiesel. Heterogeneous base catalysts can solve these problems because they are easily separated and reused, less corrosive to facilities, and reduce wastewater production [4]. Hence, alkaline earth metal oxides, such as MgO [5], CaO [6], and SrO [7], have been tested for transesterification of refined oil. Both CaO and SrO provided biodiesel yields of over 95%, while MgO provided a biodiesel yield of about 51.3%, perhaps due to its weaker basic strength [5]. Yacob et al. employed modified commercial nano-MgO to transesterify palm oil and achieved 51.3% biodiesel yield under optimal conditions [5]. Similarly, over 95% biodiesel yield was obtained by Liu et al. via CaO and SrO catalysts, respectively, for transesterification of soybean oil [6,7]. Mesoporous materials including Al₂O₃, was also used as the support to load various compounds to synthesize effective base catalysts [8-10]. Arzamendi et al. synthesized and tested NaOH-loaded Al₂O₃, for transesterification of sunflower oil in which about 95% fractional conversion of oil was reported [8]. Further, KOH and KF were also tested as the catalysts deposited on Al₂O₃ by Noiroj et al. and Boz et al., and the reported highest biodiesel yield were 91.07% for palm oil transesterification and 97.77% for canola oil transesterification, respectively [9, 10].
Nonetheless, these heterogeneous base catalysts are usually derived from commercial chemicals, and the preparation method sometimes consists of multiple complicated steps. As a result, those catalysts might become uneconomical, especially on a commercial scale. One possible way to address the problem is to synthesize catalysts from agricultural wastes, lowering the production cost and alleviating environmental pressure simultaneously. Shells derived from natural sources tend to be a suitable choice due to their high accessibility and non-toxic features [11]. A simple thermal conversion will convert natural shells into highly active CaO to catalyze transesterification. A modification step, like wet impregnation with other chemicals, could be combined with thermal conversion to improve the performance of shell-derived catalysts. Eggshell [12], crab shell [13], oyster shell [14, 15], mussel shell [16] and others have all been tested for transesterification. Recently, eggshell was tested as precursor for base catalyst by Wei et al. to transesterify soybean oil to obtain a biodiesel yield over 95% [12]. Similarly, crab shell and mussel shell were also chosen for base catalyst development by Boey et al. and Hu et al., respectively. Crab shell-derived catalyst led to a biodiesel purity of 98.8% during transesterifying palm olein, and mussel shell-derived catalyst provided a biodiesel yield over 90% by transesterifying Chinese tallow oil [13, 14]. Their results indicate a promising situation where those shell-derived base catalysts serve as the catalyst for biodiesel production.

In the eastern United States, oyster shells are produced in huge quantities. The major component of oyster shell, similar to other natural shells, is calcium carbonate [17]. Considering the chemistry of oyster shell, calcined oyster shells have been investigated for transesterification of oils. For example, Nakatani et al. used combusted oyster shells as the catalyst, and obtained a FAME yield of 73.8% under optimal conditions (catalyst loadings 25% wt.) from their statistical model [14]. Jairam et al. further enhanced calcined oyster shell by impregnating with KI, and reported an oil conversion of 85% using a molar ratio
of oil to methanol of 1:6, catalyst loading of 3.5%, and reaction temperature of 60 °C [15]. Based on the surface chemistry of oyster shell, we hypothesize that oyster shell could be chemically modified to enhance the conversion of oil into FAME. Hence the goal of this research is to enhance the catalytic activity of oyster shell via chemical impregnation of NaOH. Specifically, the objectives are to investigate the effects of catalyst loading and methanol and determine the durability of the catalyst.

3.2 Materials and methods

3.2.1 Catalyst preparation

Discarded oyster shells were collected from a local restaurant. The shells were washed with warm tap water to remove the dirt from the surface and dried at ambient temperature overnight. The washed shells were calcined at 500 °C for 2 h in a furnace (Paragon Industries) to remove the organic substances on the shell. Subsequently, the shells were crushed to a size of 1-2 mm and soaked in a 50% NaOH solution at 90 °C for 5 h. After NaOH impregnation, shell particles were filtered and calcined at 1000 °C for 3 h under a nitrogen environment to obtain the final catalyst.

3.2.2 Catalyst characterization

The catalyst was characterized via a FTIR analyzer to study the surface functional groups. In addition, the basic strength of the catalyst was determined via various Hammett indicator tests using bromothymol blue (H_= 7.2), phenolphthalein (H_= 9.3), 2,4-dinitroaniline (H_=15.0), and 4-nitroaniline (H_= 18.4) indicators. About 150 mg fresh catalyst was equilibrated with 2 mL of a Hammett indicator solution (diluted in methanol) for 2 h. The basic strength of the catalyst was determined as being stronger than the weakest indicator exhibiting a color change, but weaker than the strongest indicator exhibiting no
color change. The basicity was measured using Hammett indicator-benzoic acid (0.01 mol/L anhydrous methanol solution) titration method [18].

3.2.3 Transesterification

Transesterification reactions were performed in 250 mL three-neck glass reactor in triplicates. A typical reaction consisted of 20 mL of soybean oil mixed with a predetermined amount of methanol and catalyst on a process-controlled hot plate (Isotemp, Fisher Scientific, Pittsburgh, PA). Temperature and stirring rate were set to desired values according to specific reaction condition requirements. In this research, effects of molar ratio of methanol to oil (MR) and catalyst loadings (CL) on FAME yields were studied. The reaction temperature and stirring rate were set to 62 °C and 800 rpm, respectively. After completion of the reaction, the reaction mixture was transferred to 50 mL plastic tubes for centrifugation (5000 rpm for 8 min). The solid catalyst was removed, and the liquid mixture was washed with deionized water three times to remove excess methanol in the upper FAME phase. Washed samples were centrifuged again (5000 rpm for 12 min), and 1 mL of the upper FAME phase was collected for further gas chromatographic analysis.

3.2.4 Gas chromatography analysis

The FAME concentration was determined using a gas chromatograph coupled with a mass spectrometric detector (Agilent 7890/5975C VLMSD) and equipped with an HP-Plot Q column. Ultra-high pure helium (3 L min⁻¹) was used as a carrier gas. The instrument was set to an inlet temperature 250 °C while the oven temperature maintained at 100 °C for 2 min and was increased to 250 °C at a rate of 15 °C min⁻¹ and maintained at 250 °C. Methyl laurate was used as an internal standard for quantitative analysis of FAME concentration. The ratio of FAME peak area to internal standard peak area was calculated.
for each sample. FAME yields were calculated using the equation below, as proposed by Liu et al. and Chung et al. [6, 19].

\[
\text{Yield} = \left( \frac{\sum A - A_{IS}}{A_{IS}} \right) \times \frac{C_{IS}V}{m_{FAMEs}} \times 100\% = \left( \frac{\sum A}{A_{IS}} \right) \times \frac{C_{IS}V}{m_{oil}} \times 100\% = \left( \frac{\sum A - A_{IS}}{A_{IS}} \right) \times \frac{C_{IS}V}{\rho_{oil} \times \frac{1}{r} \times V} \times 100\% = \left( \frac{\sum A}{A_{IS}} \right) \times \frac{C_{IS}}{C_{oil}} \times 100\%
\]

where \( \sum A \) is the summation of peak areas of all methyl esters, \( A_{IS} \) is the peak area of the internal standard, \( C_{IS} \) is the concentration of the internal standard in the final diluted solution (g/ml), \( V \) is the volume of the final diluted solution (mL), \( m_{FAMEs} \) is the theoretical maximum mass of FAMEs (g), \( m_{oil} \) is the mass of pure soybean oil of volume \( V \) (g), \( \rho_{oil} \) is the density of soybean oil (g/mL), \( r \) is the dilution ratio of FAMEs sample, \( C_{oil} \) is the corresponding concentration of soybean oil (g/mL) in the final diluted solution if dilution ratio is \( r \).

3.2.5 Comparison with calcined oyster shell

Calcined oyster shell (control) was chosen as the reference to evaluate the performance of the catalyst. Both catalysts were tested in transesterification reactions at 62 °C (800 rpm) using MR = 12 and CL = 10%. Samples were drawn every hour and analyzed for FAMEs yield.

3.2.6 Experimental design and statistical analysis

A crossed, two-factor randomized design was employed, with the levels of one factor, MR, set to 6, 12, 18, and 24 and the levels of the other factor, CL, set to 2%, 5%, 7%, and 10%. All 16 factorial combinations were performed at 62 °C and 800 rpm. The FAME yields were determined and analyzed using SAS (SAS Institute Inc., Cary, USA). Factorial
effects of MR and CL on FAME yields were investigated using analysis of variance along and Tukey’s procedure to make pairwise comparisons of treatment combinations.

3.2.7 Reusability

Additional experiments were performed to determine the reusability of the catalyst. Based on the data obtained from the factorial experiments, conditions that provided the highest FAME yield was selected for catalyst reusability experiments. The catalyst was used for three successive runs. After each run, the FAME yields were recorded and the recovered catalyst was applied to the subsequent run without any treatment. The FAME data were analyzed via a Tukey’s HSD test.

3.3 Results and discussion

3.3.1 Catalyst characterization

![FTIR analysis of calcined oyster shell (control) and NaOH-impregnated calcined oyster shell.](image)

Figure 3.1 FTIR analysis of calcined oyster shell (control) and NaOH-impregnated calcined oyster shell.
The FTIR analysis of NaOH-impregnated calcined oyster shell displayed three significant major peaks at wavenumbers 1438 cm\(^{-1}\), 881 cm\(^{-1}\), and 704 cm\(^{-1}\), compared with the calcined oyster shell (control), which had no significant peaks at these positions (Figure 3.1). These three peaks represented the asymmetric stretch, out-of-plane bend, and in-plane bend vibration modes attributed to CO\(_3^{2-}\) group [20]. Because none of these peaks appeared for the calcined oyster shell (control), it implied that no CO\(_3^{2-}\) group existed in the oyster shell after calcination at 1000 °C, suggesting that all CaCO\(_3\) had been decomposed into CaO. In comparison, NaOH-impregnated calcined oyster shell acquired these peaks, probably due to the pretreatment with NaOH solution.

The basic strength of the catalyst was found to be in the range of 9.3 – 15.0 (Table 3.1) with a total basicity of 0.387 mmol/g suggesting that the catalyst surface acquired basic characteristics after impregnation with NaOH and subsequent calcination.

<table>
<thead>
<tr>
<th>Basic strength</th>
<th>Basicity (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_=) = 7.2 – 9.3</td>
<td>0.114</td>
</tr>
<tr>
<td>H(_=) = 9.3 – 15.0</td>
<td>0.273</td>
</tr>
<tr>
<td>Total</td>
<td>0.387</td>
</tr>
</tbody>
</table>

### 3.3.2 Comparison with calcined oyster shell

Calcined oyster shell was applied for transesterification of soybean oil by Nakatani et al., in which a FAME yield 73.8% (molar ratio of methanol to oil 6:1, catalyst loadings 25%, reaction temperature 65 °C) was predicted after 5 h from their statistical model [14]. In this work, calcined oyster shell was used as the reference catalyst and for evaluating the efficacy of NaOH-impregnated calcined oyster shell. Both types of catalyst were tested...
under the same conditions (MR=12, CL=10%, reaction temperature=62 °C, stirring rate=800 rpm). Performances of both catalysts are shown in Figure 3.2. For normal oyster shell, no FAMEs formation was detected at the first hour. After 3 h reaction, the FAME yield reached to about 70%. In addition, FAME yield at 4 h seemed to reach a plateau, suggesting that the reaction was completed. However, for NaOH-impregnated oyster shell, the reaction seems to occur rapidly and seems to be complete around 1 h with a final FAME yield about 90%. Compared with normal oyster shell, NaOH-impregnated calcined oyster shell led to a faster reaction rate and higher FAME yield, indicating that the NaOH solution pretreatment method had successfully improved the catalytic activity of oyster shell in soybean oil transesterification reaction.

![Figure 3.2 Comparison between calcined oyster shell (control) and NaOH-impregnated calcined oyster shell. MR=12, CL=10%, temperature=62 °C, stirring rate=800 rpm. Error bars represent standard error.](image)

### 3.3.3 Overall analysis of factorial design

The results obtained from factorial design experiments are summarized in Table 3.2 and 3.3. Both MR and CL showed significant effect on FAME yields. In addition, a significant MR-CL interaction effect was observed, suggesting that the effect of either
factor significantly depends on the specific level of the other. To interpret the effect of each factor, simple effects of MR and CL were analyzed.

Table 3.2 Results of factorial design experiment. The reaction temperature, stirring rate and reaction time were set to 62 °C, 800 rpm, 2 h, respectively. Standard error was calculated for each yield.

<table>
<thead>
<tr>
<th>Entry</th>
<th>MR</th>
<th>CL (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>5</td>
<td>86.4 ± 3.3</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>5</td>
<td>76.5 ± 2.8</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>5</td>
<td>71.4 ± 1.4</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>5</td>
<td>73.3 ± 1.6</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>10</td>
<td>93.9 ± 2.1</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>10</td>
<td>78.7 ± 1.8</td>
</tr>
<tr>
<td>7</td>
<td>18</td>
<td>10</td>
<td>86.2 ± 4.0</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>10</td>
<td>83.9 ± 4.5</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>2</td>
<td>55.4 ± 3.5</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>2</td>
<td>29.3 ± 1.3</td>
</tr>
<tr>
<td>11</td>
<td>18</td>
<td>2</td>
<td>71.6 ± 6.1</td>
</tr>
<tr>
<td>12</td>
<td>24</td>
<td>2</td>
<td>77.1 ± 4.0</td>
</tr>
<tr>
<td>13</td>
<td>12</td>
<td>7</td>
<td>88.9 ± 0.4</td>
</tr>
<tr>
<td>14</td>
<td>6</td>
<td>7</td>
<td>78.1 ± 4.3</td>
</tr>
<tr>
<td>15</td>
<td>18</td>
<td>7</td>
<td>90.2 ± 2.3</td>
</tr>
<tr>
<td>16</td>
<td>24</td>
<td>7</td>
<td>86.1 ± 3.1</td>
</tr>
</tbody>
</table>

Tukey’s LSD = 17.0%
Table 3.3 Analysis of variance of FAME yields.

<table>
<thead>
<tr>
<th>Sources</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean of squares</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR</td>
<td>0.621</td>
<td>3</td>
<td>0.207</td>
<td>63.760</td>
<td>1.36*10^{-13}</td>
</tr>
<tr>
<td>CL</td>
<td>0.251</td>
<td>3</td>
<td>0.084</td>
<td>25.796</td>
<td>1.13*10^{-8}</td>
</tr>
<tr>
<td>MR * CL</td>
<td>0.282</td>
<td>9</td>
<td>0.031</td>
<td>9.654</td>
<td>6.08*10^{-7}</td>
</tr>
<tr>
<td>Residual</td>
<td>0.104</td>
<td>32</td>
<td>0.003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.4 Effect of Methanol Ratio (MR)

Figure 3.3 summarizes the effect of MR on the FAME yield. The overall analysis of the factorial experiment indicated a significant interaction effect between MR and CL, suggesting that the effect of MR depended on the specific level of the CL.

![Figure 3.3 Effect of MR on FAMEs yield at various CLs. The reaction temperature, stirring rate and reaction time set to 62 °C, 800 rpm, 2 h, respectively. Error bars represent standard error.](image)

When CL was low (2%), increasing MR from 6 to 12 led to a significant increase in FAME yield from 29.3% to 55.4%. However, no significant increase in FAME yield was observed when MR was increased from 12 to 18 and 18 to 24. The increase in FAME yield
from low MR (6) to high MR (12, 18, and 24) might be attributed to the higher availability of methanol to the active catalytic sites. Based on Le Chatelier’s principle, an increase of reactant concentration will shift the equilibrium to product side, thus increasing FAMEs concentration in this case.

At higher CL, the effect of MR on increasing FAME yields became less significant. At CL of 5% and 10%, significantly different FAME yields existed between the highest and the lowest. At 7% CL, all four FAME yields for four MRs showed no difference between any two data points. At 5%, 7%, and 10% CL, the highest FAME yield appeared to be at MR of 12. In addition, overall mean yield at MR of 6 was less than that at MR of 12, which might be attributed to the lower concentration methanol leading to an equilibrium shift to the reactant direction. Interestingly, further increase of MR from 12 to 18 and 24, reduced the mean FAME yield as well, probably due to the relatively lower concentration of active catalytic sites resulting from an increase of methanol concentration. Thus, MR of 12 appeared to be an optimal level of the catalyst when CL was in the range of 5% to 10%. Our results are somewhat similar to Rezaei et al. [21], who investigated transesterification of soybean oil using calcined mussel shell as a catalyst. The authors reported an optimum yield of about 94% at a MR of 24 and 12% CL of at 60 °C. Similar results were reported by Hu et al. who employed water-impregnated calcined freshwater mussel catalyst for transesterification of Chinese tallow oil, wherein the authors observed an optimum FAME yield of 97.5% using 5.3% CL and MR of 13.4 [16].

### 3.3.5 Effect of Catalyst Loading (CL)

Figure 3.4 summarizes the effect of CL on FAMEs yield at various MR levels. A significant increase of FAME yield was observed between 2% CL and 5% CL at MR of 6 and 12, suggesting that 5% CL provided more active sites than 2% CL.
Figure 3.4 Effect of CL on FAMEs yield at various MRs. Reaction temperature, stirring rate and reaction time were set to 62 °C, 800 rpm, 2 h, respectively. Error bars represent standard error.

Further increase of CL did not increase the yield, probably because the total number of surface active site of catalyst was excessive for reactant adsorption, thus no improvement observed. At MR of 18 and 24, the increase of CL had no significant influence on the FAME yield. Tukey’s HSD indicated that there was no significant difference between any two FAME yields when MR reached 18 or 24.

Unlike the case for MR=6 and 12, MR=18 and 24 provided more methanol for transesterification, thus shifting equilibrium to FAMEs side, increasing the FAME yield. Therefore, the low CL level (2% and 5%) could still achieve comparable yields when compared to those of CL = 7% and 10%. The effect of CL was weakened in the case of high MR, in which the effect of MR became dominant. Hence, the effect of CL at low MR level (6 and 12) was more significant than that at high MR level (18 and 24). From Figure 3.4, it was apparent that for any MR level in this experiment, the effect of CL was not significant once it exceeded 5%.
3.3.6 Reusability

Additional experiments were performed to verify the reusability of the catalyst. Because Tukey’s HSD suggested no significant differences between several runs, experimental conditions based on highest FAME yield (MR=12, CL=10%) were selected to investigate the repeatability of the catalyst. Three experiments were performed using the same catalyst at 62 °C (800 rpm). Results indicated that no significant differences in FAME yields were observed between three runs (Figure 3.5).

![Figure 3.5 Reusability test of NaOH-impregnated calcined oyster shell (Reaction conditions: MR=12, CL=10%, temperature=62 °C, stirring rate=800 rpm, reaction time=2h). Error bars represent standard error.](image)

The FAME yields for all three runs were observed to be around 90%, suggesting that the catalyst was durable and possessed activity to catalyze transesterification for at least three times. Our results were somewhat similar to Hu et al. who investigated calcined freshwater mussel shell catalyst for transesterification of Chinese tallow oil [16]. The authors reported that the catalyst maintained activity for up to 7 cycles. Similarly, Boey et al. reported that activated cockle shell catalyst was able to maintain activity for at least three times for transesterifying palm oil [22]. However, the catalyst employed by Boey et
al. required washing with methanol recalcination at 900 °C (2 h) for removal of adsorbed impurities [22]. In our research, no visual impurities on the catalyst surface were observed. Similar results were reported by Wei et al. who investigated calcined eggshell for transesterification of soybean oil [12]. The authors reported no loss of activity even after the catalyst was reused 13 times and a simple calcination was expected to reactivate the catalyst. Based on our results NaOH-impregnated calcined oyster shell catalyst has the potential to serve as a solid base catalyst for transesterification of oils into FAMEs.

3.4 Conclusions

A highly active solid base catalyst was synthesized by wet impregnation of NaOH on oyster shell, followed by calcination. The basic strength of this catalyst was measured to be in the range 9.3 < H_ < 15.0. This catalyst was found to be highly active for soybean oil transesterification, with FAME yield exceeding 93% under the optimal conditions of MR=12, CL=10%, a reaction temperature of 62 °C, and a stirring rate 800 rpm. The catalyst was employed in soybean oil transesterification for at least three runs without any significant decrease of FAME yield, suggesting that it is suitable for biodiesel production.

Acknowledgments

The authors thank Rachel Huie, Lalitendu Das, Yane Ansanay and Yiying Zhu for laboratory help and the Department of Biological and Agricultural Engineering for funding support.
References


CHAPTER 4

Kinetics and mechanism of NaOH-impregnated calcined oyster shell catalyzed transesterification of soybean oil

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*This chapter “KINETICS AND MECHANISM OF NAOH-IMPREGNATED CALCINED OYSTER SHELL CATALYZED TRANSESTERIFICATION OF SOYBEAN OIL” is under revision in Energies
Abstract

The objective of this research is to develop a kinetic model to describe transesterification of soybean oil with methanol using NaOH-impregnated calcined oyster shell (Na-COS). Batch experiments were performed via two-factor randomized complete block design using molar ratios (MR) of 6, 12, and 18 and catalyst loadings (CL) of 2, 4, 6, and 8% to obtain fatty acid methyl ester yields (FAMEs). In addition, catalyst was studied by XRD, XPS, and TOF-SIMS to elucidate the role of catalyst in transesterification reaction. XRD and XPS analyses suggested formation of sodium peroxide (Na$_2$O$_2$) on the surface that contributed to catalytic activity. The Time-pf-Flight Secondary Ion Spectrometry (TOF-SIMS) analysis suggested that the transesterification occurred between adsorbed triglyceride and free methanol, similar to the Eley-Rideal mechanism. The transesterification of adsorbed triglyceride to adsorbed diglyceride was found to be the rate determining step with a rate constant of 0.0059 ± 0.0002 L mol$^{-1}$ min$^{-1}$.

Keywords: Oyster shell, Catalyst, Transesterification; Fatty acid methyl esters; Kinetics

4.1 Introduction

Biodiesel or Fatty acid methyl ester (FAME) is considered an alternative fuel for public transportation because of its favorable cetane rating, desirable lubricating properties, and low toxic emissions [1]. The most commonly employed method to produce biodiesel is transesterification, a chemical reaction that occurs between fat (usually vegetable oil) and an alcohol (usually methanol) catalyzed by an acid or a base to produce fatty acid methyl esters (FAMEs), which are further modified as qualified biodiesel [2].

Despite promising features, biodiesel production has a few practical challenges. One of the major drawbacks is the complicated downstream processing of the product that consists of FAMEs, unreacted methanol and NaOH and separation of these products
involve washing with large amounts of water, resulting in wastewater production [3]. In addition, NaOH is difficult to recover and for all practical purposes considered as a non-reusable catalyst [4]. Thus, usage of NaOH is therefore considered as non-environmentally friendly and non-economical. Hence, research has shifted towards the development of the heterogeneous base catalysts to replace the traditional homogeneous catalyst such as NaOH [4]. The heterogeneous base catalysts are insoluble in the reaction system and easy to regenerate, thus simplifying the downstream processing of biodiesel production [5].

Many solid base catalysts have been reported as potential substitutes for NaOH. Alkaline earth metal oxides, such as MgO [6], CaO [7], SrO [8], have proved to be active in transesterifying edible oils into FAMEs. Yacob et al. synthesized the nano MgO using the hydration-dehydration method for transesterifying palm oil and obtained the highest conversion of 51.3%. [6]. Similarly, Liu et al. used commercial CaO to catalyze the transesterification of soybean oil in the presence of water. The highest yield exceeded 95% with a molar ratio of methanol to oil (MR) at 12, catalyst loadings (CL) of 8%, a water content of 2.03%, at 65 °C in 1.5 h [7]. In addition, Liu et al. tested SrO as a superbase for transesterification of soybean oil, and the yield exceeded 95% at MR = 12, CL = 3%, at 65 °C [8]. Further, mesoporous material-supported solid base catalysts, such as KOH/Al₂O₃ [9] and KF/Al₂O₃ [10], were also tested for the transesterification reaction. Noiroj et al. used KOH/Al₂O₃ to catalyze the transesterification of palm oil. The 25% KOH loaded Al₂O₃ was suggested as the optimal loading for a yield of 91.07% with MR = 15, 3 g catalyst (300 rpm) at 60 °C in 2 h [9]. Boz et al. developed a series of KF/Al₂O₃ via wet impregnation methods to obtain a yield of 97.7% with MR = 15, CL = 3%, at 65 °C (8 h). The authors concluded that this high yield might attribute to the high surface to volume ratio of the nano-γ-Al₂O₃ that increased the basicity substantially [10].
In order to use those solid base catalysts to produce biodiesel in industry, the kinetic behavior of the catalyst needs to be studied. Understanding the kinetics of the solid base catalyzed transesterification reaction is crucial to the reactor design, process control, and scale-up. Based on the overall transesterification, it is intrinsic that the reaction rate depends on both the concentration of triglyceride and methanol. However, in most heterogeneous, base-catalyzed transesterification reports, methanol is usually provided in excess to achieve high oil conversion. Hence the concentration of methanol during the reaction is assumed to be constant throughout the reaction. As a result, most reported literature for solid base catalyzed transesterification reactions employed a pseudo-first-order model with respect to triglyceride [11-14]. Lukic et al. studied the kinetics of sunflower and used vegetable oil transesterification catalyzed by CaO/ZnO, and they proposed a pseudo-first order reaction for the overall process [11]. The pseudo-first-order rate constants were determined for different reaction temperatures which ranged from 0.043 min$^{-1}$ at 60 °C to 0.120 min$^{-1}$ at 96 °C. Similarly, Jairam et al. simulated the data from KI-impregnated calcined oyster shell catalyzed transesterification of soybean oil using pseudo-first-order kinetics. The pseudo-first-order rate constant was estimated as 0.4385 h$^{-1}$ [12]. Zhang et al. used a pseudo-first-order kinetics to model the transesterification of palm oil with dimethyl carbonate catalyzed by KOH. The activation energy and pre-exponential factor, $E_a$ and $k_0$, were determined as 79.1 kJ mol$^{-1}$ and $1.26 \times 10^9$ min$^{-1}$ [13]. Ramezani et al. also employed the pseudo-first order kinetics to describe the transesterification of castor oil with methanol. A good fit was observed, and the reaction rate constant was estimated to be $4.91 \times 10^{-3}$ min$^{-1}$ at 65 °C [14].

In addition to pseudo-first-order kinetics, other kinetics models have also been proposed. The pseudo-second order kinetics with respect to the triglyceride was used to describe the initial period of transesterification of sunflower oil with ethanol by Marjanovic
et al. The estimated activation energy, $E_a$, was reported to be in the range of 8.3 – 35.1 kJ mol$^{-1}$ at the reaction temperature ranging from 25 °C to 75 °C [15]. Issariyakul et al. modeled the transesterification of palm oil with methanol catalyzed by KOH as three consecutive reactions (triglyceride to diglyceride, diglyceride to monoglyceride, and monoglyceride to glycerol), each of which followed second-order kinetics with respect to triglyceride and methanol. The reaction rate constants of each stepwise reaction (forward and backward) were estimated, and the rate-determining step was found to be the step from triglyceride to diglyceride [16]. Xiao et al. used the Eley-Rideal mechanism to model the stepwise transesterification of palm oil with methanol catalyzed by KF/Ca-Mg-Al hydrotalcite solid base. The reaction was assumed to occur between free triglyceride and adsorbed methanol wherein the transessterification of triglyceride to diglyceride was the rate-determining step. The activation energy, $E_a$, was determined to be 111.6 kJ mol$^{-1}$ [17].

Further, Veljkovic et al. described a sigmoidal-type kinetic model, in which, the transesterification process was assumed to be mass transfer-limited during the initial period and reaction-limited during the completion of reaction between sunflower oil and methanol catalyzed via CaO [18]. The authors proposed a kinetic model with a rate constant that differs between the initial and ending periods, attributing to the different mass transfer/reaction approximation premises resulting in a sigmoidal FAME yield curve. The pseudo-first order rate constant was determined as 0.070 min$^{-1}$ for the terminal period of the reaction [18]. Miladinovic et al. also employed a sigmoidal-type model to describe quicklime-catalyzed transesterification of sunflower oil via a full factorial experimental design (MR set to 6, 12, 18 and CL set to 1%, 2.5%, 5%, 10%). Although, their model was found to be suitable, the underlying reaction mechanism was not elucidated [19].

Of late, there is a renewed interest using agricultural wastes as precursors for the synthesis of solid base catalysts. For example, naturally occurring shells, due to their high
content of CaCO$_3$, are considered excellent precursors for CaO that can catalyze transesterification reactions [20]. Wei et al. used calcined eggshell as the catalyst for transesterification of soybean oil, to obtain a maximum FAME yield greater than 95% with MR = 9, and CL = 3%, at 65 °C within 3 h [21]. Similarly, Rezaei et al. employed calcined mussel shell as the catalyst and reported a FAME yield of up to 94.1%, using an MR of 24, CL of 12% at 60 °C in 8 h [22]. Suryaputra et al. utilized the calcined capiz (Amusium cristatum) shell to catalyze the transesterification of palm oil. The maximum yield of 93% with a MR = 8, CL = 3% at 60 °C in 6 h was observed [23]. Xie et al. employed the turtle shell as the precursor, and prepared the catalyst via a tri-step procedure including incomplete carbonization followed by KF impregnation (25%) and activation (300 °C). When tested, FAME yield reached 97.5% with MR = 9, CL = 3% at 70 °C in 3 [24]. Recently, we prepared highly active solid catalysts from oyster shells by impregnating NaOH on the surface followed by calcination (Na-COS). When tested in batch systems, FAME conversions of up to 90% were obtained [25]. These results suggest that catalysts prepared from wastes could potentially make biodiesel production processes economically competitive. However, for scale-up and reactor design, reaction kinetics and understanding of reaction pathway is needed. However, at this time, there is limited data on the kinetics of transesterification for catalysts derived from animal and aquatic shells. Hence the objectives of this research are to (1) develop a kinetic model to describe the kinetics of transesterification and (2) elucidate how the reaction proceeded based on the observed experimental data.
<table>
<thead>
<tr>
<th><strong>Nomenclature</strong></th>
<th><strong>Definition</strong></th>
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<tbody>
<tr>
<td>a</td>
<td>Molar ratio of Methanol to oil (MR)</td>
</tr>
<tr>
<td>ΣA</td>
<td>summation of peak areas of all methyl esters</td>
</tr>
<tr>
<td>ΣA_{IS}</td>
<td>peak area of internal standard</td>
</tr>
<tr>
<td>C_{IS}</td>
<td>concentration of internal standard in the final diluted solution</td>
</tr>
<tr>
<td>C_{F}</td>
<td>Concentration of FAMEs (mol/L)</td>
</tr>
<tr>
<td>C_{M}</td>
<td>Concentration of methanol (mol/L)</td>
</tr>
<tr>
<td>C_{oil}</td>
<td>concentration of soybean oil (g/ml) in the final diluted solution</td>
</tr>
<tr>
<td>C_{tot}</td>
<td>Concentration of total basic site of the catalyst (mol/L)</td>
</tr>
<tr>
<td>C_{TG}</td>
<td>Concentration of triglyceride (mol/L)</td>
</tr>
<tr>
<td>C^{0}_{TG}</td>
<td>Starting concentration of triglyceride in the reaction (mol/L)</td>
</tr>
<tr>
<td>C_{TG*}</td>
<td>Concentration of adsorbed triglyceride (mol/L)</td>
</tr>
<tr>
<td>C_{*}</td>
<td>Concentration of vacant basic site of the catalyst (mol/L)</td>
</tr>
<tr>
<td>k</td>
<td>Overall transesterification reaction rate constant</td>
</tr>
<tr>
<td>k_{ad}</td>
<td>Triglyceride adsorption rate constant (L mol$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>k_{ad}</td>
<td>Triglyceride desorption rate constant (min$^{-1}$)</td>
</tr>
<tr>
<td>k_{1}</td>
<td>Reaction rate constant of transesterifying triglyceride to diglyceride (L mol$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>k_{-1}</td>
<td>Backward reaction rate constant of transesterifying triglyceride to diglyceride (L mol$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>k_{2}</td>
<td>Reaction rate constant of transesterifying diglyceride to monoglyceride (L mol$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>k_{2}</td>
<td>Backward reaction rate constant of transesterifying diglyceride to monoglyceride (L mol$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>------------</td>
</tr>
<tr>
<td>$k_3$</td>
<td>Reaction rate constant of transesterifying monoglyceride to glycerol (L mol$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>$k_{-3}$</td>
<td>Backward reaction rate constant of transesterifying monoglyceride to glycerol (L mol$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>$m_F$</td>
<td>Mass of FAMEs (g)</td>
</tr>
<tr>
<td>$m_0^{TG}$</td>
<td>Starting mass of triglyceride (g)</td>
</tr>
<tr>
<td>$M_F$</td>
<td>Averaged molecular weight of FAMEs (g/mol)</td>
</tr>
<tr>
<td>$M_{TG}$</td>
<td>Molecular weight of triglyceride (g/mol)</td>
</tr>
<tr>
<td>$r$</td>
<td>Fatty acid methyl esters (FAMEs) production rate (mol L$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>$t$</td>
<td>Reaction time (min)</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Volume of the reaction mixture (L)</td>
</tr>
<tr>
<td>$y$</td>
<td>Biodiesel yield</td>
</tr>
<tr>
<td>$z$</td>
<td>Dilution ratio</td>
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</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$\rho_{oil}$</td>
<td>Density of soybean oil (g/ml)</td>
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</table>

**Abbreviation**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL</td>
<td>Catalyst loadings (mass of catalyst/volume of oil) (%)</td>
</tr>
<tr>
<td>F</td>
<td>Fatty acid methyl esters</td>
</tr>
<tr>
<td>G</td>
<td>Glycerol</td>
</tr>
<tr>
<td>M</td>
<td>Methanol</td>
</tr>
<tr>
<td>MR</td>
<td>Molar ratio of methanol to oil</td>
</tr>
<tr>
<td>TG</td>
<td>Triglyceride</td>
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</table>
4.2 Materials and methods

4.2.1. Catalyst preparation

Waste oyster shells were collected from a local restaurant. The shells were washed with warm water to remove the dirt from the surface and dried at ambient temperature overnight. The washed shells were calcined at 500 °C for 2 h in a furnace (Paragon Industries) to remove the organic compounds from the shell. Subsequently, the shells were crushed to a size of 1-2 mm and soaked in the 50% NaOH solution at 90 °C for 5 h. After NaOH impregnation, the shells were filtered and calcined at 1000 °C for 3 h under a nitrogen environment to obtain the catalyst (Na-COS).

4.2.2. Catalyst characterization

X-ray powder diffraction (XRD) data were collected using a Rigaku SmartLab X-ray diffractometer with Cu Kα radiation (λ=0.15418 nm) in the 2θ range of 5° – 80°. The diffraction data were acquired using a step size and count time of 0.05° 2θ and 3 s/step, respectively.

X-ray photoelectron spectroscopy (XPS) studies were performed with a SPECS FlexMod system equipped with a hemispherical analyzer PHOIBIS 150 and a Mg Kalpha (1254 eV) X-ray source. High-resolution spectra were recorded at take-off-angle normal to surface. The X-ray incidence angle is ~ 30° from the surface and the X-ray source to the analyzer is ~ 60°. Energy calibration was established by referencing to adventitious Carbon (C1s line at 285.0 eV binding energy). The base pressure in the analysis chamber is in 10⁻¹⁰ mbar range.

The surface features of Na-COS and COS were studied using a Hitachi S-3200N SEM via a 20kV electron beam.
A time of flight-secondary ion mass spectrometer (TOF-SIMS) was employed to study the catalyst surfaces. A TOF SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a Bi_{n}^{m+} (n = 1-5, m = 1, 2) liquid metal ion gun, Cs⁺ sputtering gun and electron flood gun for charge compensation was used. Both the Bi and Cs ion columns are oriented at 45 with respect to the sample surface normal. The instrument vacuum system consisted of a load lock for rapid sample loading and an analysis chamber, separated by the gate valve. The analysis chamber pressure was maintained below 5.0 × 10⁻⁹ mbar to avoid contamination of the surface to be analyzed.

For high mass resolution spectra acquired in this study, a pulsed Bi³⁺ primary ion beam at 25 keV impact energy with less than 1 ns pulse width was used. The total accumulated primary ion dose data acquisition was less than 1 × 10¹³ ions/cm², an amount of ions which is within the static SIMS regime. The mass resolution on Si wafer is about ~8000m/Δm at 29 AMU. First, the fresh catalyst (Na-COS) was analyzed directly. Subsequently, to determine the adsorption of reactants on the catalyst surface, 0.1 g Na-COS was soaked into 2 ml soybean oil and 1 ml methanol, respectively, for 10 min. The catalyst was then separated and washed five times using hexane and dried at 70 °C in the oven and subjected to TOF-SIMS analysis.

4.2.3. Batch experiments

Transesterification reactions were performed in 250 ml three-neck glass reactor in duplicates. A typical reaction consisted of 24 mL of soybean oil mixed with a predetermined amount of methanol and catalyst on a process-controlled hot plate (Isotemp, Fisher Scientific, Pittsburgh, PA). A predetermined amount of hexane (based on the volumetric ratio of methanol to hexane equal to 1.83:1) was added to the reaction mixture as the co-solvent. Temperature and stirring rate were set to 62 °C and 800 rpm, respectively.
While the reaction was progressing, a 0.3 ml sample was withdrawn every 10 min for the first hour and every 20 min for the second hour. The reaction was stopped after 2 h. All samples were centrifuged at 14,000 rpm to remove the solids. The remaining liquid was placed in an oven at 70 °C for 30 min to remove methanol and then washed with DI water. Washed samples were centrifuged again at 14,000 rpm, and the supernatant liquid was analyzed using a gas chromatograph equipped with a mass spectrometer.

4.2.4. Gas chromatograph analysis

The FAME concentration was determined using a gas chromatograph coupled with a mass spectrometric detector (Agilent 7890/5975C VLMSD) and equipped with an HP-Plot Q column. Ultra-high pure helium (3 L min⁻¹) was used as a carrier gas. The instrument was set to an inlet temperature 250 °C while the oven temperature maintained at 100 °C for 2 min and was increased to 250 °C at a rate of 15 °C min⁻¹ and maintained at 250 °C. Methyl laurate was used as an internal standard for quantitative analysis of FAME concentration. The ratio of FAME peak area to internal standard peak area was calculated for each sample. FAME yields were calculated as proposed by Liu et al. and Chung et al. [7, 26].

\[
\text{Yield} = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V}{m_{\text{FAMEs}}} \times 100\% = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS} V}{m_{\text{oil}}} \times 100\% =
\]

\[
\frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V}{\rho_{\text{oil}} \times \frac{1}{Z} \times V} \times 100\% = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS}}{C_{\text{oil}}} \times 100\%
\]

4.2.5. Experimental design

A two-factor randomized complete block design was employed in which the levels of MR were maintained at 6, 12, and 18, while the levels of CL were maintained 2%, 4%, 6%, and 8%. All 12 experiments were performed at 62 °C and 800 rpm.
4.3 Results and discussion

4.3.1. Catalyst characterization

The X-ray diffraction (XRD) analyses were conducted to investigate the structure and crystallinity of the catalyst (Figure 4.1). The XRD pattern of the COS presented five major peaks ($2\theta = 32.35^\circ$, $37.5^\circ$, $53.95^\circ$, $64.3^\circ$, $67.5^\circ$), all of which are the characteristic peaks of CaO, indicating that the major component of COS is CaO. No characteristic peak of CaCO$_3$ was presented, suggesting that CaCO$_3$ in the oyster shell had been converted into CaO. The XRD pattern of the Na-COS showed a few additional peaks than those observed with COS. After impregnation of NaOH and subsequent calcination, the resulting catalyst acquired two new phases, Na$_2$O and Na$_2$CO$_3$, indicated by the newly generated peaks at $2\theta = 46.6^\circ$ and $2\theta = 30.45^\circ$, $34.5^\circ$, $35.1^\circ$, $39.9^\circ$, $41.3^\circ$, $41.6^\circ$, respectively.

Similar observations were reported by Xie et al, wherein KNO$_3$ impregnated Al$_2$O$_3$ was observed to acquire a newly generated K$_2$O phase [27]. The addition of alkaline metal on the oxide would facilitate the insertion of the alkaline metal ions into the vacant sites of the oxide, thereby enhancing the basicity during calcination.
The formation of Na$_2$CO$_3$ phase probably resulted from the abundant surface NaOH species, which perhaps reacted with the CaCO$_3$ to form Na$_2$CO$_3$ during the calcination process. Since Na$_2$CO$_3$ exhibited weak basic strength, the increased catalytic activity of the Na-COS may thus be attributed to the formation of Na$_2$O$_2$ on the shell surface.

![Figure 4.2 XPS spectra of COS and Na-COS](image)

The X-ray photoelectron spectroscopy (XPS) analysis showed the difference in surface species between Na-COS and COS (Figure 4.2). In COS, the Na might be the composition element of the original oyster shell [28]. The data also indicated that the proportion of Na increased while the proportion of Ca decreased in Na-COS, possibly due to adsorption of NaOH and subsequent calcination, which may have covered the Ca species. In addition, the percentage of oxygen in Na-COS decreased when compared to COS suggesting that carbonate had been converted into oxide.
Figure 4.3 presented C 1s, Ca 2p, O 1s, and Na 1s regions for COS and Na-COS. In the C 1s region, both COS and Na-COS exhibited two signals at 285.0 eV and 289.6 eV, due to C-H and carbonate groups, respectively [29]. The Ca 2p of COS and Na-COS exhibited a doublet with a separation of 3.5 eV, 2p1/2 and 2p3/2 components, whose binding energy (BE) values were 347.00 eV, 350.5 eV and 346.3 eV, 349.8 eV, respectively, suggesting that the Ca was associated with CaO [30,31]. In the O 1s spectra, both COS and Na-COS displayed doublet peaks, however, the intensity distribution was different. Both of COS and Na-COS showed the major O 1s peak at 531.5 eV, assigned to CaO [30]. However, the percentage of this major peak only contributed 69.8% to the total intensity in Na-COS, compared with the percentage, 96.8%, in COS. The minor O 1s peak, appeared at lower
BE (530.3 eV and 529.0 eV for Na-COS and COS, respectively), contributed 30.2% to the total intensity in Na-COS while only 3.2% in COS, suggesting that more surface oxygen in Na-COS had been shifted to lower BE. The Na 1s spectra also differed between COS and Na-COS, as COS only displayed a single peak at 1071.7 eV while Na-COS displayed doublet peaks at 1071.9 eV and 1071.0 eV, indicating that two different Na species existed on the Na-COS surface. For COS, the Na originated from the oyster shell that led to a substantially lower intensity compared with Na-COS. For Na-COS, the substantially higher amount of Na attributed to the impregnated NaOH, and the two Na 1s peaks at 1071.0 eV and 1071.9 eV might be assigned to Na$_2$CO$_3$ and Na$_2$O$_2$, respectively, based on the XRD results. Compared with the references, these two Na 1s peaks were both negatively shifted [32-34]. The negative shift in O 1s indicated that the surface oxygen atoms acquired higher effective negative charge, which led to an increase in the electron donating ability. The increased electron donating ability was attributed to the newly formed basic site, suggesting that the surface oxygen was more basic [35]. As shown in Figure 4.4, the increased electron donating ability may have facilitated the reaction between adsorbed triglyceride and methanol to form the tetrahedral intermediate, which further produced FAME under the structure rearrangement, during transesterification [7]. Because Na-COS contained more negatively shifted surface oxygen than COS did, it was more active in forming the tetrahedral intermediate and, further, increasing the FAME production rate.
Figure 4.4. Role of Na-COS surface basic site on the improved activity.

The scanning electron micrographs of morphologies of Na-COS and COS are shown in Figure 4.5. The surface of COS was nearly homogeneous and covered somewhat uniformly-sized CaO aggregates. However, on the surface of Na-COS, larger particles were generated due to the reaction between adsorbed NaOH and CaCO$_3$. In addition, the morphology of Na-COS was more irregular than COS, probably because of the adsorbed NaOH prevented the complete calcination of the surface CaCO$_3$ and led to the co-existence of both oxides and carbonates.
Figure 4.5 SEM images of COS (a) and Na-COS (b).

The results from the time of flight secondary ion mass spectrometry (TOF-SIMS) analysis are shown in Figure 4.6A and 4.6B. The positive ion TOF-SIMS spectra (Figure 4.6A) of Na-COS and soybean oil soaked Na-COS showed that the soybean oil soaked Na-COS contained surface species with the m/z value in the range of 590 – 610 while the fresh Na-COS did not. These surface species were plausibly generated from the triglyceride molecule, suggesting that the triglyceride molecule was adsorbed onto the Na-COS surface.

Figure 4.6B shows the negative ion TOF-SIMS spectra for Na-COS and methanol-soaked Na-COS. Unlike soybean oil, methanol did not seem to adsorb on the surface of Na-COS. Based on XRD analysis, Na-COS was found to contain CaO and Na₂O₂ on its surface. Adsorption of methanol on Na-COS surface would have resulted in the formation of large peaks of Ca(CH₃O)₂ and Na(CH₃O). However, in methanol-soaked Na-COS, the CH₃O⁻ peak intensity (5.8670 × 10⁻³) was even lower than the O₂⁻ peak intensity (1.0640 × 10⁻²). Considering that ionization of O₂⁻ is more difficult than the ionization of metal methoxide to negative methoxide ion, it is concluded that methanol molecule was not adsorbed on the Na-COS surface.
4.3.2 Batch experiments

Figure 4.7 and 4.8 show FAME yields obtained from transesterification reactions performed using different MRs and CLs. It appeared that the transesterification reaction started and progressed immediately from the beginning.
Figure 4.7 The FAME yield with the progress of the soybean oil transesterification catalyzed by Na-COS grouped by MR. Error bars represent standard error.
Our observations were different from the results reported by Veljkovic et al. and Miladinovic et al., where a slow initial reaction period existed due to the limited mass transfer rate of the triglycride to the catalyst surface [18,19]. In our research, because hexane was used as a co-solvent to improve the mixing condition, the transesterification reaction was not limited by the mass transfer of triglyceride to the catalyst surface. Another reason might be the generation of the new phase, Na$_2$O$_2$, which was perhaps more active than CaO in the transesterification reaction. In our previous research, transesterification reaction catalyzed by COS showed almost no FAMEs formation in the first 1 h, suggesting that the surface CaO phase required some time to initiate the transesterification reaction [18,19]. In contrast, the Na-COS, containing the more catalytic active basic sites (Na$_2$O$_2$), catalyzed the reaction immediately once added into the reaction mixture.

From the plots, the FAME yields for all Na-COS catalyzed transesterifications increased rapidly for the first 20 min. However, after around 20 min the reaction started to slow down, probably because of the decreasing triglyceride concentration. During the initial reaction period, the surface of Na-COS was saturated with triglyceride; however, as the triglyceride consumed, the Na-COS surface was only partially occupied by the triglyceride after the initial period.

During the initial period (0 - 20 min), the rate of FAMEs yields at high CL (6%, 8%) was higher than that at the low CL (2%, 4%) at each MR level. This is probably because of availability of a greater number of active sites at higher CL. However, at high MR (12, 18), yields of FAMEs at 6% and 8% in the initial period (0 - 20 min) showed no significant difference. Excess methanol in the system resulted in a decreased concentration of total triglycerides thereby impacting the rate of FAMEs yield.

In our research, a maximum FAME yield of 89.7% was observed in the group of MR = 18, CL = 8% in 80 min. Our yield was similar to the 87% yield obtained from Xie et al.
who employed KNO$_3$/Al$_2$O$_3$ catalyst for transesterification of soybean oil [27]. Similar results were reported by other groups as summarized in Table 4.1.
Figure 4.8 The FAME yield with the progress of the soybean oil transesterification catalyzed by Na-COS grouped by CL. Error bars represent standard error.

Table 4.1 Comparison of various solid base catalysts for transesterification reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MR</th>
<th>CL</th>
<th>Reaction temperature</th>
<th>Reaction time</th>
<th>Yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>12</td>
<td>8%</td>
<td>65 °C</td>
<td>1.5 h</td>
<td>≥ 95%</td>
<td>[7]</td>
</tr>
<tr>
<td>CaO/Al₂O₃</td>
<td>12.14</td>
<td>5.97%</td>
<td>64.29 °C</td>
<td>5 h</td>
<td>98.64%</td>
<td>[36]</td>
</tr>
<tr>
<td>KNO₃/Al₂O₃</td>
<td>12</td>
<td>6%</td>
<td>70 °C</td>
<td>6 h</td>
<td>84%</td>
<td>[37]</td>
</tr>
<tr>
<td>KOH/Al₂O₃</td>
<td>15</td>
<td>3%</td>
<td>60 °C</td>
<td>2 h</td>
<td>91.07%</td>
<td>[9]</td>
</tr>
<tr>
<td>Eggshell</td>
<td>9</td>
<td>3%</td>
<td>65 °C</td>
<td>3 h</td>
<td>95%</td>
<td>[21]</td>
</tr>
<tr>
<td>Mussel shell</td>
<td>24</td>
<td>12%</td>
<td>60 °C</td>
<td>8 h</td>
<td>94.1%</td>
<td>[22]</td>
</tr>
<tr>
<td>Capiz shell</td>
<td>8</td>
<td>3%</td>
<td>60 °C</td>
<td>6 h</td>
<td>93%</td>
<td>[23]</td>
</tr>
<tr>
<td>Turtle shell</td>
<td>9</td>
<td>3%</td>
<td>70 °C</td>
<td>3 h</td>
<td>97.5%</td>
<td>[24]</td>
</tr>
<tr>
<td>Na-COS</td>
<td>18</td>
<td>8%</td>
<td>62 °C</td>
<td>1.33 h</td>
<td>89.7%</td>
<td>This research</td>
</tr>
</tbody>
</table>
4.3.3 Kinetics of the transesterification

In this section, several kinetic models were developed to fit the experimental data. From the proposed reaction mechanism, the reaction appeared to have occurred between adsorbed triglyceride and free methanol. However, for sake of completeness, few empirical models were also tested to provide a more comprehensive analysis regarding the Na-COS-catalyzed transesterification of soybean oil with methanol. The discussion will start with empirical models and conclude with models derived using rate determining steps (RDS).

The following assumptions were made to describe transesterification for all models based on the work reported by Veljkovic et al. and Miladinovic et al [18,19]. For each model discussed below, additional assumptions were added.

1. The initial reaction mixture was a three-phase system consisting of two immiscible liquids (triglyceride and methanol) and one solid (Na-COS). By using hexane as the co-solvent and vigorous stirring system (800 rpm), the mixture was considered perfectly mixed (two-phase system).

2. The transesterification reaction occurred only on the Na-COS surface. The homogeneous transesterification reaction was negligible and thus not considered.

3. The produced FAMEs did not neutralize the basic site of the Na-COS. Therefore, the total amount of basic site of the Na-COS did not change throughout the reaction.

4. There is no mass transfer limitation between reactant and the Na-COS surface. Therefore, the production rate of FAMEs only depended on the transesterification reaction rate.

In this work, the FAME concentration was converted into FAME yield for data visualization and modeling. Below are the mathematical expressions of various concentration variables in terms of the FAME yield, \( y \).
\[ C_{TG} = (1 - y)C_{TG}^0 \]
\[ C_F = 3yC_{TG}^0 \]
\[ C_M = (a - 3y)C_{TG}^0 \]

The data of the initial reaction period (0-20 min) was used to estimate the kinetic parameters in each model. The estimation was performed using Newton-Gauss algorithm via JMP software. The estimated kinetic parameter was formulated in the form as estimated value ± standard error.

### 4.3.3.1 Empirical models

Model 1: Pseudo-first order with respect to free triglyceride

\[ TG + 3M \overset{k}{\longrightarrow} G + 3F \]

The most frequently used kinetic model for transesterification was pseudo-first order with respect to the TG [12, 18]. The starting rate equation was formulated as below:

\[
\frac{dC_F}{dt} = 3kC_{TG}^0
\]

The above expression was re-formulated in terms of FAME yield, \( y \), as below:

\[
\frac{dy}{dt} = k (1 - y)
\]

The above equation was integrated, and with the initial condition \( t = 0, y = 0 \), the integrated form was derived as below:

\[ y = 1 - \exp(-kt) \]

The estimated reaction rate constant \( k = 0.0253 \pm 0.0020 \text{ min}^{-1} \) with sum of squared errors, \( \text{SSE} = 1.429 \).

Model 2: Pseudo-1st order with respect to adsorbed triglyceride

\[ TG^* + 3M \overset{k}{\longrightarrow} G + 3F \]
From the TOF-SIMS analysis, the adsorbed triglyceride, instead of free triglyceride, participated in the transesterification. Therefore, the pseudo-first order model was revised to accommodate for the adsorbed TG, TG*. The starting equation was formulated as below:

\[
\frac{dC_F}{dt} = 3kC_{TG}^*
\]

The adsorption/desorption process of TG was assumed to be fast and at equilibrium. By applying the basic site balance, TG* was expressed in terms of TG.

\[
C_{TG}^* = \frac{K_{ad}C_{TG}}{1 + K_{ad}C_{TG}} C_{tot} \quad ; \quad K_{ad} = \frac{k_{ad}}{k_{-ad}}
\]

The rate equation was re-expressed as below:

\[
\frac{dC_F}{dt} = 3k \frac{K_{ad}C_{TG}}{1 + K_{ad}C_{TG}} C_{tot}
\]

The TG was assumed to have high adsorption on the catalyst surface, suggesting that \( K_{ad} C_{TG} \gg 1 \). Hence,

\[
\frac{dC_F}{dt} \approx 3kC_{tot}
\]

\[
\frac{dy}{dt} = \frac{kC_{tot}}{C_{TG}}
\]

\[
y = \frac{kC_{tot}}{C_{TG}} t
\]

The estimated reaction rate constant \( k = 0.0384 \pm 0.00139 \text{ min}^{-1} \) with sum of squared errors, \( \text{SSE} = 0.538 \).

Model 3: Second order with respect to free triglyceride

\[
TG + 3M \xrightarrow{k} G + 3F
\]

The second-order kinetics with respect to TG was proposed by Darnoko and Cheryan [38]. The starting rate equation was formulated as below:
\[
\frac{dC_F}{dt} = 3kC_{TG}^2
\]

The above equation was re-expressed in terms of FAME yield, y, as below:

\[
\frac{dy}{dt} = kC_{TG}^0 (1 - y)^2
\]

\[
y = 1 - \frac{1}{1 + kC_{TG}^0 t}
\]

The estimated reaction rate constant \( k = 0.0517 \pm 0.0054 \text{ L mol}^{-1} \text{ min}^{-1} \) with sum of squared errors, \( \text{SSE} = 1.608 \).

Model 4: Second order with respect to adsorbed triglyceride

\[
TG^* + 3M \rightarrow G + 3F
\]

From the TOF-SIMS analysis, the adsorbed triglyceride, instead of free triglyceride, participated in the transesterification. Therefore, the second-order model was revised to accommodate for the adsorbed TG, TG*. The starting equation was formulated as below:

\[
\frac{dC_F}{dt} = 3kC_{TG^*}^2
\]

The adsorption/desorption process of TG was assumed to be fast and at equilibrium. By applying the basic site balance, TG* was expressed in terms of TG.

\[
C_{TG^*} = \frac{K_{ad} C_{TG}}{1 + K_{ad} C_{TG}}, \quad K_{ad} = \frac{k_{ad}}{k_{-ad}}
\]

The rate equation was re-expressed as below:

\[
\frac{dC_F}{dt} = 3k \left( \frac{K_{ad} C_{TG}}{1 + K_{ad} C_{TG}} C_{tot} \right)^2
\]

The TG was assumed to have high adsorption on the catalyst surface, suggesting that \( K_{ad} C_{TG} \gg 1 \). Hence,
The estimated reaction rate constant $k = 0.0797 \pm 0.0051 \text{ L mol}^{-1} \text{ min}^{-1}$ with sum of squared errors, $\text{SSE} = 1.423$.

### 4.3.3.2 Rate determining step (RDS)-based models

In RDS-based models, the transesterification consisted of consecutive reactions, including TG adsorption, transesterifying TG* to DG*, transesterifying DG* to MG*, transesterifying MG* to G [39]. The RDS was assumed to be irreversible. Any reaction occurs before the RDS was assumed to be reversible and at equilibrium while any step after the RDS were assumed to be irreversible. Each step was assumed to be elementary reaction [40]. The overall reaction was shown below:

$$TG^* + 3M \rightarrow G + 3F$$

Model 5: TG adsorption as RDS

$$TG + * \xrightarrow{k_{ad}} TG^*$$

$$TG^* + M \xrightarrow{k_1} DG^* + F$$

$$DG^* + M \xrightarrow{k_2} MG^* + F$$

$$MG^* + M \xrightarrow{k_3} G + F$$

Once triglyceride was adsorbed onto the catalyst surface, it was immediately consumed by the reaction. Hence, the triglyceride consumption rate was equal to the triglyceride adsorption rate. Because rate of TG adsorption = rate of TG consumption = $1/3 \times$ rate of FAME production, the starting rate equation was formulated as below:

$$\frac{dC_F}{dt} \approx 3k_{ad} C_{TG} C_\bullet$$
As the reaction is considered fast compared with the triglyceride adsorption, almost no adsorbed species existed due to its high consumption rate. Thus, it was reasonable to assume that the concentration of vacant basic site was equal to the concentration of the total basic site.

\[ C_* \approx C_{tot} \]

The rate equation was re-expressed as below:

\[
\frac{dC_*}{dt} = 3k_{ad} C_{TG} C_{tot} \\
\frac{dy}{dt} = k_{ad} C_{tot} (1 - y) \\
y = 1 - \exp(-k_{ad} C_{tot} t)
\]

The estimated reaction rate constant \( k_{ad} = 0.0847 \pm 0.0050 \text{ L mol}^{-1} \text{ min}^{-1} \) with sum of squared errors, SSE = 0.760.

Model 6: Reaction of transesterifying TG* to DG* as RDS

\[
\begin{align*}
TG + K_{TG} & \overset{k_{ad}}{\longrightarrow} TG^* \\
TG^* + M & \overset{k_1}{\longrightarrow} DG^* + F \\
DG^* + M & \overset{k_2}{\longrightarrow} MG^* + F \\
MG^* + M & \overset{k_3}{\longrightarrow} G + F
\end{align*}
\]

The starting rate equation was formulated as below:

\[
\frac{dC_F}{dt} = 3k_{C} C_{TG} C_{M}
\]

In this case, the catalyst is assumed to be covered by triglyceride (TG*) only, since once the diglyceride (DG*) or monoglyceride (MG*) was formed, it was immediately consumed due to its fast consumption rate. By applying the basic site balance, the TG* concentration was expressed as below:

\[
C_{TG^*} = \frac{K_{ad} C_{TG}}{1 + K_{ad} C_{TG}} \cdot C_{tot}, \quad K_{ad} = \frac{k_{ad}}{k_{-ad}}
\]
The rate equation was re-expressed as below:

\[
\frac{dC_F}{dt} = 3k_1 \frac{K_{ad}C_{TG}}{1 + K_{ad}C_{TG}} C_{tot}C_M
\]

The TG was assumed to have high adsorption on the catalyst surface, suggesting that 

\[K_{ad}C_{TG} \gg 1.\]

Hence,

\[
\frac{dC_F}{dt} \approx 3k_1C_{tot}C_M
\]

\[
dy = k_1C_{tot}(a-3y)
\]

\[y = \frac{a}{3} \left[1 - \exp(-3k_1C_{tot}t)\right]
\]

The estimated reaction rate constant \(k_1 = 0.0059 \pm 0.0002 \text{ L mol}^{-1} \text{ min}^{-1}\) with sum of squared errors, \(SSE = 0.459\).

Model 7: Reaction of transesterifying DG* to MG* as RDS

\[
\begin{align*}
TG + * & \xrightleftharpoons[k_{ad}]{k_{ad}} TG^* \\
TG^* + M & \xrightarrow{k_1} DG^* + F \\
DG^* + M & \xrightarrow{k_2} MG^* + F \\
MG^* + M & \xrightarrow{k_3} G + F
\end{align*}
\]

The starting rate equation was formulated as below:

\[
\frac{dC_F}{dt} = 3k_3C_{DG^*}C_M
\]

In this case, the catalyst is assumed to covered by triglyceride (TG*) and diglyceride (DG*), since once the monoglyceride (MG*) was formed, it was immediately consumed due to its fast consumption rate. By applying the basic site balance, the DG* concentration was expressed as below:
The TG was assumed to have high adsorption on the catalyst surface, suggesting that $K_{ad}C_{TG} \gg 1$. Hence,

$$C_{DG'} = \frac{K_1C_MK_{ad}C_{TG}}{1 + K_{ad}C_{TG}}$$

The rate equation was re-expressed as below:

$$\frac{dC_F}{dt} = 3k_2 \frac{K_1C_M}{C_F + K_1C_M}C_{tot}C_M$$

$$\frac{dy}{dt} = k_2 \frac{K_1(a-3y)}{3y + K_1(a-3y)}(a-3y)C_{tot}$$

The results of parameter estimation showed that $K_1$ was very large (much greater than $3y$, $0 \leq 3y \leq 3$), suggesting that it was reasonable to assume that $\frac{K_1(a-3y)}{3y + K_1(a-3y)} \approx 1$. Hence,

$$\frac{dy}{dt} = k_2(a-3y)C_{tot}$$

Apparently, this expression is similar to the expression obtained in model 6, only differing in the rate constant. The parameter estimation step was repeated on the above rate equation.

The estimated reaction rate constant $k_1 = 0.0059 \pm 0.0002$ L mol$^{-1}$ min$^{-1}$ with sum of squared errors, SSE = 0.459.
Model 8: Reaction of transesterifying MG* to G as RDS

\[ TG + \star \xrightarrow{k_{ad}} TG^\star \]
\[ TG^\star + M \xrightarrow{k_1} DG^\star + F \]
\[ DG^\star + M \xrightarrow{k_2} MG^\star + F \]
\[ MG^\star + M \xrightarrow{k_3} G + F \]

The starting rate equation was formulated as below:

\[ \frac{dC_F}{dt} = 3k_3 C_{MG} C_M \]

In this case, the catalyst is assumed to be covered by triglyceride (TG*), diglyceride (MG*), and monoglyceride (MG*). By applying the basic site balance, the DG* concentration was expressed as below:

\[ C_{TG} = K_{ad} C_{TG} \star \; ; \; K_{ad} = \frac{k_{ad}}{k_{-ad}} \]
\[ C_{DG} = \frac{K_1 C_M C_{TG}}{C_F} = \frac{K_1 C_M K_{ad} C_{TG}}{C_F} \; ; \; K_1 = \frac{k_1}{k_{-1}} \]
\[ C_{MG} = \frac{K_2 C_M C_{DG}}{C_F} = \frac{K_1 K_2 C_M C_{TG} K_{ad}}{C_F^2} \; ; \; K_2 = \frac{k_2}{k_{-2}} \]
\[ C_{tot} = C_{TG} + C_{DG} + C_{MG} + C_\star \]
\[ C_{MG} = \frac{K_{1} K_{2} C_M C_{TG}}{1 + K_{ad} C_{TG} + \frac{K_{1} K_{2} C_M C_{TG}}{C_F} + \frac{K_{1} K_{2} C_M C_{TG}}{C_F^2}} \times C_{tot} \]

The TG was assumed to have high adsorption on the catalyst surface, suggesting that \( K_{ad} C_{TG} \gg 1 \). In the initial period, the FAME concentration was low, and as a result, it was reasonable to assume that \( \frac{K_1 C_M}{C_F} \gg 1 \). Hence,
The starting equation was expressed as below:

\[
C_{MG} = \frac{K_1K_2C_M^2K_{ad}C_{TG}}{1 + K_{ad}C_{TG} + \frac{K_1C_MK_{ad}C_{TG}}{C_F} + \frac{K_1K_2C_M^2K_{ad}C_{TG}}{C_F^2}} C_{tot}
\]

\[
\approx \frac{K_1K_2C_M^2K_{ad}C_{TG}}{C_F^2} \frac{C_F}{K_{ad}C_{TG} + \frac{K_1C_MK_{ad}C_{TG}}{C_F} + \frac{K_1K_2C_M^2K_{ad}C_{TG}}{C_F^2}} C_{tot} = \frac{K_1K_2C_M^2}{C_F^2} \frac{C_F}{C_F + K_2C_M} C_{tot}
\]

The results of parameter estimation showed that \( K_1 \) was very large (much greater than \( 3y, 0 \leq 3y \leq 3 \)), suggesting that it was reasonable to assume that \( \frac{K_2(a-3y)}{3y + K_2(a-3y)} \approx 1 \). Hence,

\[
\frac{dy}{dt} = k_3 (a-3y) C_{tot}
\]

Apparently, this expression is similar to the expression obtained in model 6 and 7, only differing in the rate constant. The parameter estimation step was repeated on the above rate equation. The estimated reaction rate constant \( k_3 = 0.0059 \pm 0.0002 \) L mol\(^{-1}\) min\(^{-1}\) with sum of squared errors, SSE = 0.459.
4.3.3.3 Alternative model

Model 9: The overall transesterification as elementary reaction

\[ TG^* + 3M \rightarrow_k G + 3F \]

In this model, it was assumed that the overall reaction was elementary [41]. Hence, the starting rate equation was formulated as below:

\[
\frac{dC_F}{dt} = 3kC_{TG}C_M^3
\]

The adsorption/desorption process of TG was assumed to be fast and at equilibrium. By applying the basic site balance, TG* was expressed in terms of TG.

\[
C_{TG} = \frac{K_{ad}C_TG}{1 + K_{ad}C_{TG}}
\]

The rate equation was re-expressed as below:

\[
\frac{dC_F}{dt} = 3k \frac{K_{ad}C_TG}{1 + K_{ad}C_{TG}} C_{tot}C_M^3
\]

The TG was assumed to have high adsorption on the catalyst surface, suggesting that \( K_{ad}C_{TG} \gg 1 \). Hence,

\[
\frac{dC_F}{dt} = 3kC_{tot}C_M^3
\]

\[
\frac{dy}{dt} = kC_{tot} \left(a - 3y\right) C_{TG}^2
\]

\[
y = \frac{a^3 \left(6kC_{tot}C_{TG}^0\right)t - \sqrt{a^4 \left(6kC_{tot}C_{TG}^0\right)t + a^2 + a}}{3a^2 \left(6kC_{tot}C_{TG}^0\right)t + 3}
\]

The estimated reaction rate constant \( k = 0.000098 \pm 0.000007 \) L mol\(^{-1}\) min\(^{-1}\) with sum of squared errors, SSE = 1.379.
Table 4.2 Summary of models

<table>
<thead>
<tr>
<th>Entry</th>
<th>Kinetics</th>
<th>Estimated rate constant</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; to TG</td>
<td>( k = 0.0253 \pm 0.0020 \text{ min}^{-1} )</td>
<td>1.429</td>
</tr>
<tr>
<td>2</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; to TG*</td>
<td>( k = 0.0384 \pm 0.00139 \text{ min}^{-1} )</td>
<td>0.538</td>
</tr>
<tr>
<td>3</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; to TG</td>
<td>( k = 0.0517 \pm 0.0054 \text{ L mol}^{-1} \text{ min}^{-1} )</td>
<td>1.608</td>
</tr>
<tr>
<td>4</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; to TG*</td>
<td>( k = 0.0797 \pm 0.0051 \text{ L mol}^{-1} \text{ min}^{-1} )</td>
<td>1.423</td>
</tr>
<tr>
<td>5</td>
<td>TG adsorption as RDS</td>
<td>( k_{\text{ad}} = 0.0847 \pm 0.0050 \text{ L mol}^{-1} \text{ min}^{-1} )</td>
<td>0.760</td>
</tr>
<tr>
<td>6</td>
<td>TG* to DG* as RDS</td>
<td>( k_1 = 0.0059 \pm 0.0002 \text{ L mol}^{-1} \text{ min}^{-1} )</td>
<td>0.459</td>
</tr>
<tr>
<td>7</td>
<td>DG* to MG* as RDS</td>
<td>( k_2 = 0.0059 \pm 0.0002 \text{ L mol}^{-1} \text{ min}^{-1} )</td>
<td>0.459</td>
</tr>
<tr>
<td>8</td>
<td>MG* to G as RDS</td>
<td>( k_3 = 0.0059 \pm 0.0002 \text{ L mol}^{-1} \text{ min}^{-1} )</td>
<td>0.459</td>
</tr>
<tr>
<td>9</td>
<td>Overall elementary</td>
<td>( k = 0.000098 \pm 0.000007 \text{ L mol}^{-1} \text{ min}^{-1} )</td>
<td>1.379</td>
</tr>
</tbody>
</table>

Table 4.2 summarized the discussed models. The comparison indicated that Model 6, 7, 8 had the smallest SSE, suggesting that they were the best models among all to describe the kinetics of the reaction. Based on the reported literature, the reaction of transesterifying TG to DG was found to be RDS, with smallest reaction rate constant compared with the reactions from DG to MG and from MG to DG [39,42]. Therefore, Model 6 (Reaction of transesterifying TG* to DG* as RDS) was chosen as the best model to describe the Na-COS-catalyzed transesterification of soybean oil with methanol. Figure 4.9 suggested that the chosen model was a reasonable fit (correlation of coefficient = 0.865) to the data of the initial reaction period (0-20 min). The estimated reaction rate constant, \( k_1 = 0.0059 \pm 0.0002 \text{ L mol}^{-1} \text{ min}^{-1} \), was in the similar range as reported by Aransiola et al [39].
Figure 4.9 The FAME yield with the progress of the soybean oil transesterification catalyzed by Na-COS in the initial period (0 - 20 min) grouped by MR. Error bars represent standard error.
4.3.4 Proposed Reaction Mechanism

In the light of observations collected from catalyst characterization experiments, it appeared that oil molecules adsorbed on the surface of the catalyst and reacted with methanol in the bulk fluid, similar to the Eley-Rideal mechanism. As shown in Figure 4.10, the reaction seems to have occurred in steps. In the first step, triglyceride molecules adsorbed on the surface. Subsequently, in the second step, methanol reacted with adsorbed triglyceride molecule to form adsorbed diglyceride and FAME (RDS). In the third step, methanol reacted with adsorbed diglyceride to form adsorbed monoglyceride and FAME. In the last step, methanol reacted with adsorbed monoglyceride to form desorbed glycerol and FAME, and the vacant sites were available for next batch of reactants.

![Diagram of Reaction Mechanism](image)

Figure 4.10 The mechanism of Na-COS-catalyzed transesterification of soybean oil with methanol. TG, DG, MG, M, G, F represent triglyceride, diglyceride, monoglyceride, methanol, glycerol, and FAME, respectively.
4.4 Conclusions

In this research, a kinetic model for transesterification of soybean oil via sodium hydroxide impregnated oyster shell as a solid catalyst was developed. The experimental data and reported literature suggested that the stepwise transesterification reaction started between adsorbed triglyceride and free methanol similar to the Eley-Rideal mechanism with the step of transesterifying adsorbed triglyceride to adsorbed diglyceride as the rate determining step. MR and CL affected the initial reaction rates. Characterization of the catalyst suggested that the electron donating ability was strengthened after the impregnation, probably due to the newly generated phases (Na$_2$O$_2$ and Na$_2$CO$_3$) on the surface. Using wastes as precursors for the synthesis of solid catalysts is expected to make biodiesel processes more competitive.

Acknowledgments

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References


CHAPTER 5

Effect of preparation conditions on structure and activity of sodium-impregnated oyster shell catalysts for transesterification.

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Abstract

Catalyst preparation technique plays a significant role in its activity and durability. This research evaluated NaOH and NaCl as the impregnation precursors for waste oyster shell and studied the effects of precursor concentration and calcination temperature on the surface structure and the activity of the catalyst via the one-factor-at-a-time method. The optimal impregnation concentrations of NaOH and NaCl were determined as 6 mol/L and 2.43 mol/L, respectively. The optimal calcination temperature was determined as 800 °C for both 6 mol/L NaOH and 2.43 mol/L NaCl impregnated calcined oyster shell (NaOH<sub>6</sub>/shell and NaCl<sub>2.43</sub>/shell). The X-ray Diffraction and X-ray photoelectron spectroscopy analysis of NaOH<sub>6</sub>/shell calcined at 400 °C, 800 °C and NaCl<sub>2.43</sub>/shell calcined at 600 °C, 800 °C, 1000 °C indicated that different surface species and distribution of elements were formed. The impregnation precursor type and concentration and the calcination temperature determined the surface species that would influence the activity of the catalyst. This study can benefit the development method of solid catalysts.

Keywords: Oyster shell; Transesterification; Fatty acid methyl ester; Biodiesel; Wet impregnation

5.1 Introduction

Solid base catalysts have been extensively studied for their catalytic performance in the transesterification reactions [1]. CaO, as one of the solid base catalysts, was shown to be capable of transesterifying various oils to FAMEs. However, its activity is still lower than that of NaOH [2]. Hence, to increase the catalytic activity of CaO, wet impregnation methods have been employed to modify the surface of CaO to generate more active sites. The most frequently used impregnated species is alkaline metal (e.g., Li, Na, K) in that it could react with the oxygen present in CaO to produce defect sites on the surface, which
serve as the enhanced basic sites for transesterification reaction [3-8]. Watkins et al. impregnated the CaO with a series of LiNO$_3$ solutions ranging from 1 - 20 wt % [4]. Despite showing a continuous drop in the specific surface area with increasing Li content, all Li-impregnated CaO exhibited increased basic strengths compared with CaO. The transesterification results indicated that the initial reaction rate increased with the increased Li content and reached a maximum at 1.23 wt % Li content. Further, the characterization study indicated that the doped LiNO$_3$ helped the surface OH$^-$ formation, which increased the catalytic activity. However, the high concentration of LiNO$_3$ may have covered the surface OH$^-$ group, and thus lowered the catalytic activity.

In addition to the alkaline metal oxide and hydroxide groups generated from impregnation-calcination method, another group consisting of alkaline metal, calcium and halogen have been identified by many research groups as active species. Mar and Somsook used KCl to modify the surface of CaO by the wet impregnation method under microwave irradiation [5]. The as-synthesized catalyst was characterized to obtain KCaCl$_3$ on the surface, which contributed to the increased biodiesel yield during transesterifying soybean oil with methanol. A similar observation has been reported by Wen et al., in which the doped chemical was KF [6]. A new KCaF$_3$ phase was observed on the surface of the as-prepared catalysts, and the increased catalytic activity was attributed to the higher H$^+$ affinity for F. Liu et al. synthesized CsF/CaO catalyst by mixing CsF solution with Ca(OH)$_2$ solution followed by calcination [7]. The as-synthesized catalyst exhibited excellent activity in transesterification reaction in which about 98% biodiesel yield was obtained in 1 h under optimal reaction conditions. This highly improved activity was plausibly attributed to the formation of CsCaF$_3$ on the surface. Interestingly, somewhat different results were obtained when KBr was impregnated on CaO [8]. XRD analysis did
not show the KCaBr$_3$ phase on the surface perhaps because longer radius of Br failed to form the KCaBr$_3$ compound on the surface.

Some metals, other than alkaline metals, have also been tested for their ability to enhance the catalytic activity of CaO. Yan et al. synthesized a solid catalyst, Ca$_3$La$_{1}$, by mixing La(NO$_3$)$_3$ solution with Ca(Ac)$_2$ solution followed by ethanol precipitation and calcination [9]. The as-synthesized catalyst consisted of Ca(OH)$_2$ as the major phase on the surface, and the initial reaction rate and FAME yield at 2 h using Ca$_3$La$_{1}$ was close to the NaOH-catalyzed transesterification, indicating Ca$_3$La$_{1}$ as a potential substitute for transesterification reactions. Kuar and Ali synthesized Zr/CaO catalyst using wet impregnation by mixing CaO with ZrOCl$_2$•8H$_2$O solution followed by calcination [10]. The 15 wt.% Zr/CaO calcined at 700 °C exhibited highest reaction rate in transesterifying jatropha curcas oil. The authors attributed the activity of the catalyst to the relatively lower ratio of tetragonal to monoclinic ZrO$_2$ on the surface and decreased crystallite size.

Recently, waste natural shells have attracted attention, since they could serve as the economical precursors for CaO. Various natural shells have been tested for catalyzing transesterification reactions. For example, Wei et al. used waste eggshell as the precursor for the catalyst and reported a FAME yield of over 95% during transesterification of soybean oil using a methanol to oil ratio (MR) of 9, and catalyst loading (CL) of 3%, at 65 °C within 3 h [11]. Rezaei et al. employed calcined mussel shell to catalyze transesterification of soybean oil and observed a 94.1% FAME yield at MR of 24, CL of 12% at 60 °C in 8 h [12]. Suryaputra et al. utilized the calcined capiz (Amusium cristatum) shell to catalyze the transesterification of palm oil. The maximum yield of 93% with a MR = 8, CL = 3% at 60 °C in 6 h was observed [13]. However, the natural shell-derived CaO exhibited relatively lower activity compared to commercial CaO and NaOH [11-13]. Thus, to improve the activity, natural shells may be impregnated with chemicals. Additionally,
preparation conditions could be manipulated to enhance the activity of shells. Wei et al. investigated the effect of calcination temperature, and the results indicated that eggshells calcined at 800 °C or above showed high activity due to the formation of CaO [11]. Similar results were observed by Rezaeti et al. wherein the minimum calcination temperature was 950 °C for the formation of CaO [12]. Jaraim et al. improved the activity of calcined oyster shell by impregnating KI, and the optimal KI concentration was determined as 1 mmol/g [14].

In our previous work, NaOH-impregnated calcined oyster shell proved to be active and durable in transesterification of soybean oil [15]. However, the role of NaOH and calcination on catalyst activity was not clarified. By elucidating how calcination temperature and impregnation conditions affect the catalyst activity will not only improve catalyst syntheses processes, but also allow us to predict the performance of the catalyst. Hence, the goal of this research is to systematically investigate how the catalyst preparation conditions (precursor type, precursor concentration, calcination temperature) influence the structure and subsequent activity of the catalyst.

5.2 Materials and methods

5.2.1 Catalyst preparation

Discarded oyster shells were collected from a local restaurant. The shells were washed with warm tap water to remove the dirt from the surface and dried at ambient temperature overnight. The washed shells were calcined at 500 °C for 2 h in a furnace (Paragon Industries) to remove the organic substances on the shell. Subsequently, the shells were crushed to a size of 1 - 2 mm.

Two types of Na-based precursor solutions were employed in this research: NaOH and NaCl. Typically, 20 g of oyster shells were impregnated with 60 ml of precursor
solution of the predetermined concentration on a process-controlled hot plate (Isotemp, Fisher Scientific, Pittsburgh, PA) at 90 °C for 5 h. Subsequently, the impregnated shells were filtered and calcined at predetermined temperature for 3 h under nitrogen environment.

5.2.2 Catalyst characterization

The specific surface area of the catalyst synthesized was determined using Quantachrome Monosorb Surface Area Analyzer (Quantachrome Instruments, USA) based on the Brunauer–Emmett–Teller (BET) nitrogen adsorption method. Prior to the measurement, all catalysts were degassed at 120 °C overnight to desorb the volatiles (if any) from the surface.

The basicity of the catalyst was determined based on the method as described by Mo et al [16]. 0.1 g sample was soaked into 20 ml of the 0.1 N HCl solution for 20 min. The solution was then titrated using 0.15 N NaOH solution using Phenolphthalein as an indicator.

X-ray powder diffraction (XRD) pattern was collected using a PANalytical Empyrean X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm) in the 2θ range of 5° – 90°. The diffraction data were acquired using a step size and count time of 0.026° 2θ and 67 sec/step, respectively.

X-ray photoelectron spectroscopy (XPS) analysis was performed with an SPECS FlexMod system equipped with a hemispherical analyzer PHOBIS 150 and a Mg Kalpha (1254 eV) X-ray source. High-resolution spectra were recorded at take-off-angle normal to surface. The X-ray incidence angle is ~ 30° from the surface and the X-ray source to the analyzer is ~ 60°. Energy calibration was established by referencing to adventitious Carbon
(C1s line at 285.0 eV binding energy). The base pressure in the analysis chamber is in 10^{-10} mbar range.

5.2.3 Transesterification

Transesterification reactions were performed in 250 mL three-neck glass reactor in duplicates. A typical reaction consisted of 20 mL of soybean oil mixed with a predetermined amount of methanol and catalyst on a process-controlled hot plate (Isotemp, Fisher Scientific, Pittsburgh, PA). Temperature and stirring rate were set to 62 °C and 800 rpm, respectively. In this research, molar ratio of methanol to oil (MR) and catalyst loading (CL) were set to 12 and 10%, respectively. After a 2-h reaction, 3 mL of the reaction mixture was transferred to 15 mL plastic tubes for centrifugation (5,000 rpm for 5 min) to remove the catalyst. Subsequently, 800 μL of the supernatant liquid was drawn and washed three times with DI water from which a 300 μL sample was collected for further gas chromatographic analysis.

5.2.4 Gas chromatography analysis

The FAME concentration was determined using a gas chromatograph coupled with a mass spectrometric detector (Agilent 7890/5975C VLMSD) and equipped with an HP-Plot Q column. Ultra-high pure helium (3 L min⁻¹) was used as a carrier gas. The instrument was set to an inlet temperature 250 °C while the oven temperature maintained at 100 °C for 2 min and was increased to 250 °C at a rate of 15 °C min⁻¹ and maintained at 250 °C. Methyl laurate was used as an internal standard for quantitative analysis of FAME concentration. The ratio of FAME peak area to internal standard peak area was calculated for each sample. FAME yields were calculated using the equation below, as proposed by Liu et al. and Chung et al. [2,17].
In the equation above, \( \sum A \) is the summation of peak areas of all methyl esters, \( A_{IS} \) is the peak area of internal standard, \( C_{IS} \) is the concentration of internal standard in the final diluted solution (g/ml), \( V \) is the volume of the final diluted solution (ml), \( m_{FAMEs} \) is the theoretical maximum mass of FAMEs (g), \( m_{oil} \) is the mass of pure soybean oil of volume \( V \) (g), \( \rho_{oil} \) is the density of soybean oil (g/ml), \( r \) is the dilution ratio of FAMEs sample, \( C_{oil} \) is the corresponding concentration of soybean oil (g/ml) in the final diluted solution if dilution ratio is \( r \).

5.2.5 Experimental design

A two-factor randomized block design was employed for batch experiments. All experiments were performed in duplicates. For the synthesis of NaCl/shell catalyst, NaCl solutions of 2, 2.43, 3.64, 4, and 6 mol/L were employed. Similarly, for the synthesis of NaOH/shell catalyst, NaOH solutions of 2, 4, 6, 8, 10, and 12.5 mol/L were used. All catalysts synthesized were tested in batch reactors and the FAME yields were analyzed using SAS (SAS Institute Inc., Cary, USA).

The optimal conditions of each precursor type were chosen based on the FAME yield. The corresponding catalyst was then re-prepared but calcined at various temperatures. For NaCl-impregnated catalysts, calcination temperatures of 600 °C, 800 °C, 1000 °C and for NaOH-impregnated catalysts, calcination temperatures of 400 °C, 600 °C, 800 °C, and 1000 °C were used.
Additional experiments were performed to test the reusability of the various NaOH-impregnated calcined oyster shells. The same spent catalyst was used for five consecutive runs. After each run, the FAME yield was determined and the recovered catalyst was applied to subsequent run without any treatment. The data were analyzed via a Tukey’s HSD test.

5.3 Results and discussion

5.3.1 Effects of the precursor type and concentration

Figure 5.1 summarized the effects of precursor type and concentration. For both precursors, the calcined oyster shell was used as a control for comparison purposes. When low precursor concentration (2 mol/L) was used, there were no significant differences between the FAME yields obtained from control (COS) and NaCl/shell and NaOH/shell catalysts suggesting that no catalytically actives were formed on the surface of the oyster shells. When the precursor concentrations were increased, significant differences were observed. For NaOH/shell experiments, FAME yields increased with increased precursor concentration from 2 mol/L to 6 mol/L. However, for precursor concentrations beyond, 6 mol/L, FAME yields appeared to be similar. The results obtained from NaCl/shell exhibited a different trend. The FAME yield increased when the precursor concentration was increased from 2 mol/L to 3.64 mol/L and started decreasing when the precursor was further increased suggesting that presence of excess precursor may inhibit catalytic activity. Hence, precursor concentrations of 6 mol/L (NaOH) and 2.43 mol/L (NaCl) were selected for subsequent studies to investigate the effect of calcination of catalyst activity.
Figure 5.1 The FAME yield of the transesterification reaction catalyzed by various concentrations of NaOH and NaCl impregnated calcined oyster shell. Transesterification conditions: temperature = 62 °C, stirring rate = 800 rpm, MR = 12, CL = 10%. Error bars represent standard error.

5.3.2 Effect of calcination temperature

The effects of calcination temperature are summarized in Figure 5.2. For experiments with NaOH/shell, calcination temperature did not affect the yields of FAME.
Figure 5.2 The FAME yield of the transesterification reaction catalyzed by NaOH$_6$/shell and NaCl$_{2.43}$/shell calcined at various temperatures. Transesterification conditions: temperature = 62 °C, stirring rate = 800 rpm, MR = 12, CL = 10%. Error bars represent standard error.

However, since the stability of catalyst depends on the calcination temperature, further experiments were performed to test the reusability of the catalysts calcined at various temperatures (400, 600, 800, and 1000 °C). The catalysts were reused consecutively for five times using fresh batches of methanol and oil to determine the yields of FAMEs. As shown in Figure 5.3, catalysts calcined at 400 °C started losing activity after the second run and provided a FAME yield of 26.2% after the fifth run.
Figure 5.3 The FAME yield of the repeated transesterification reaction catalyzed by the same spent NaOH/shell calcined at various temperatures. Transesterification conditions: temperature = 62 °C, stirring rate = 800 rpm, MR = 12, CL = 10%. Error bars represent standard error.

However, when calcination temperature was increased, the stability of the catalyst appeared to increase. The catalysts calcined at 800, and 1000 °C exhibited similar FAME yields for all five runs whereas the catalyst calcined at 600 °C provided lower FAME yields after the third run, when compared to 800 and 1000 °C suggesting that calcination at higher temperatures allowed for adequate reaction between Na ions and oyster shell and string binding of active sites on the surface.

For NaCl/shell, no activity was observed at 600 °C. As the calcination temperature was increased to 800 °C, the yield of FAME increased to 88.4% and started to decrease with further increase in calcination temperature.

Overall, it appears that NaOH/shell and NaCl/shell, when calcined at 800 °C provided best FAME yields and stability. Hence to elucidate the role of calcination and effects of precursor concentrations, the surface properties of catalysts synthesized under various conditions were studied in detail.
5.3.3 Catalyst characterization

The specific surface areas and basicities of the catalysts synthesized are summarized in Table 5.1. The impregnation of NaOH or NaCl lowered the specific surface area of the oyster shell, probably because of blocking of the surface pores of COS by precursor. The basicity, however, showed no substantial difference between all types of catalyst, indicating that the precursor type and concentration calcination temperature did not affect the basicity of the catalyst.

Table 5.1 The specific surface areas and basicities of COS, NaOH$_6$/shell-400, NaOH$_6$/shell-800, NaCl$_{2.43}$/shell-600, NaCl$_{2.43}$/shell-800 and NaCl$_{2.43}$/shell-1000

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area / m$^2$ g$^{-1}$</th>
<th>Basicity / mmol g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>COS</td>
<td>2.15</td>
<td>11.9</td>
</tr>
<tr>
<td>NaOH$_6$/shell-400</td>
<td>0.43</td>
<td>13.5</td>
</tr>
<tr>
<td>NaOH$_6$/shell-800</td>
<td>0.56</td>
<td>12.7</td>
</tr>
<tr>
<td>NaCl$_{2.43}$/shell-600</td>
<td>0.31</td>
<td>11.9</td>
</tr>
<tr>
<td>NaCl$_{2.43}$/shell-800</td>
<td>0.31</td>
<td>13.4</td>
</tr>
<tr>
<td>NaCl$_{2.43}$/shell-1000</td>
<td>0.69</td>
<td>13.3</td>
</tr>
</tbody>
</table>

The XRD pattern of each catalyst is shown in Figure 5.4. For NaOH-impregnated shells, major phases formed on the surface of NaOH$_6$/shell-400 were CaCO$_3$, Na$_2$CO$_3$ and Ca(OH)$_2$. Since CaCO$_3$ and Na$_2$CO$_3$ are not catalytically very active for transesterification, it may be concluded that the catalytic activity of NaOH$_6$/shell-400 may be due to Ca(OH)$_2$. This result was similar to the result obtained by Kumar and Ali, who used KOH to modify the surface of CaO. The as-synthesized nanocrystalline 3.5% K-CaO showed newly generated Ca(OH)$_2$ on the surface that contributed to the increased basic strength from 9.8
< H_ < 10.1 to 11.1 < H_ < 15.0. The activity was also improved as the FAME yield reached 98% in 75 min. [18]. As the calcination temperature increased (from 400 to 800 °C), the type of surface species changed. The major phases formed on the surface of NaOH_6/shell-800 were CaO and Na_2O_2, both of which are catalytically active in transesterification. The formation of alkaline oxide (Na_2O_2) was also observed in the KNO_3 impregnated CaO-ZnO catalyst synthesized by Istabdi et al. The as-synthesized catalysts acquired K_2O on the surface, which might result in the improved activity on transesterifying soybean oil [19]. As shown in Figure 5.1, up to 90% FAME yields were obtained from the NaOH_6/shell-800.

It appears that calcination at higher temperature allowed for decomposition of carbonate and hydroxide to respective oxides that are active and stable.

The reusability experiments using NaOH_6/shell-400 and NaOH_6/shell-800 also supported the characterization data. NaOH_6/shell-800 provided 90% yield consistently even after five successive runs whereas the FAME yields for NaOH_6/shell-400 kept dropping down to 26.2% at the fifth run, indicating a substantial loss of activity.

The XRD patterns of NaCl_2.43/shell-600, NaCl_2.43/shell-800 and NaCl_2.43/shell-1000 are shown in Figure 5.4. At 600 °C, the major phases identified were CaCO_3 and NaCl and only traces of CaO. As a result, NaCl_2.43/shell-600 provided only 0.13% FAME yield after 2 h. As the calcination temperature increased to 800 °C, most CaCO_3 had been decomposed into CaO, thus the characteristic peaks of CaCO_3 disappeared, and the intensity of CaO increased. Because CaO is also an active catalyst, the FAME yield from NaCl_2.43/shell-800 increased up to 88.4%. Further increase of the calcination temperature to 1000 °C, however, decreased the yield to 58.3%. As seen from the XRD pattern for NaCl_2.43/shell-1000, only CaO was detected on the surface. The disappearance of NaCl in NaCl_2.43/shell-1000 might cause the FAME yield drop, which implied that a synergistic effect of NaCl and CaO on
the catalytic activity might exist. Because of this synergistic effect, the FAME yield of NaCl\textsubscript{2.43}/shell-800 was higher than the yield of NaCl\textsubscript{2.43}/shell-1000.

**Figure 5.4** The XRD patterns of NaOH\textsubscript{6}/shell-400, NaOH\textsubscript{6}/shell-800, NaCl\textsubscript{2.43}/shell-600, NaCl\textsubscript{2.43}/shell-800 and NaCl\textsubscript{2.43}/shell-1000.

The XPS analysis of NaOH-impregnated catalysts indicated different elemental distribution between NaOH\textsubscript{6}/shell-400 and NaOH\textsubscript{6}/shell-800 catalysts (Figure 5.5). The atomic percentage of Na in NaOH\textsubscript{6}/shell-400 was 42.6%, whereas the atomic percentage of Na dropped to 16.6% in NaOH\textsubscript{6}/shell-800 as the calcination temperature increased from 400 to 800 °C. The atomic percentage of Ca was found to be 1.4% in NaOH\textsubscript{6}/shell-400 but increased to 9.3% as the calcination temperature increased. Combined with the XRD results, the Na from the surface of NaOH\textsubscript{6}/shell-400 probably originated from Na\textsubscript{2}CO\textsubscript{3}. When the calcination temperature increased, the covered Na\textsubscript{2}CO\textsubscript{3} and CaCO\textsubscript{3} probably decomposed into Na\textsubscript{2}O\textsubscript{2} and CaO as was revealed from XRD spectra.

The XPS data obtained from NaCl-impregnated catalysts also revealed different elemental distributions between NaCl\textsubscript{2.43}/shell-600, NaCl\textsubscript{2.43}/shell-800 and NaCl\textsubscript{2.43}/shell-1000.
1000 (Figure 5.5). As the calcination temperature increased, the amount of Na and Cl decreased continuously from 32.4% and 15.0% (600 °C) to 10.0% and 2.1% (800 °C), and finally dropped to 1.2% and 0% (1000 °C), respectively, while the amount of Ca increased from 5.8% (600 °C) to 10.3% (800 °C), and finally reached 15.8%. This observation was consistent with the XRD results, in which the major phases of the catalyst, as the calcination temperature increased, changed from carbonate to oxide for the Ca, and the intensity of NaCl phase was attenuated continuously and disappeared finally at 1000 °C.

Figure 5.5 The XPS analysis of NaOH$_6$/shell-400, NaOH$_6$/shell-800, NaCl$_2$.43/shell-600, NaCl$_2$.43/shell-800 and NaCl$_2$.43/shell-1000.
Figure 5.6. XPS spectra of C 1s, Ca 2p, Na 1s, O 1s of NaOH/Shell-400 and NaOH/Shell-800. (bottom: NaOH/Shell-400; top: NaOH/Shell-800).

Figure 5.6. presented the C 1s, Ca 2p, Na 1s, and O 1s regions for NaOH/Shell-400 and NaOH/Shell-800. In the C 1s region, both catalysts showed doublet peaks (285.0 eV and 289.2 eV for NaOH/Shell-400, 285.0 eV and 289.5 eV for NaOH/Shell-800), suggesting that they contained C-H and carbonate groups on the surface, probably resulted from the air contaminants [20]. In the Ca 2p region, NaOH/Shell-400 showed two peaks at 346.5 eV and 350.1 eV, suggesting that the Ca originated from CaCO$_3$ [21]. NaOH/Shell-800 showed two peaks at 346.8 eV and 350.3 eV, suggesting that the Ca originated from CaO [22]. In the Na 1s region, both catalysts displayed doublet peaks. In
this analysis, the two peaks in both catalysts seemed to shift to lower BE by 1.0 eV compared with the references [23-25]. Combined with the details of the preparation method and the XRD results, the Na 1s peak at lower BE might have originated from Na$_2$CO$_3$, while the Na 1s peak at higher BE might be associated with NaOH and Na$_2$O$_2$ for NaOH$_6$/Shell-400 and NaOH$_6$/Shell-800, respectively [23-25]. In the O 1s region, NaOH$_6$/Shell-400 displayed doublet peaks at 530.3 eV and 531.2 eV, assigned to CaO and Ca(OH)$_2$, respectively [26,27]. Similarly, NaOH$_6$/Shell-800 exhibited doublet peaks at 530.3 eV and 531.5 eV, assigned to Na$_2$O$_2$ and CaO [28], respectively, based on the XRD analysis. This doublet feature indicated that some of the surface oxygen had been shifted to lower BE for both catalysts, acquiring higher effective negative charge. As shown in Figure 5.7, this would have increase the electron donating ability, suggesting that the surface oxygen was more basic [29]. This increased electron donating ability probably facilitated the reaction between triglyceride and methanol to form the tetrahedral intermediate, which further produced FAME under the structure rearrangement, during transesterification [2].
Figure 5.7. Role of NaOH/Shell-800 surface basic site on the improved activity.
Figure 5.8. XPS spectra of C 1s, Ca 2p, Na 1s, O 1s and Cl 2p of NaCl$_{2.43}$/Shell-600, NaCl$_{2.43}$/Shell-800, and NaCl$_{2.43}$/Shell-1000. (bottom: NaCl$_{2.43}$/Shell-600; middle: NaCl$_{2.43}$/Shell-800; top: NaCl$_{2.43}$/Shell-1000. For Cl 2p, bottom: NaCl$_{2.43}$/Shell-600; top: NaCl$_{2.43}$/Shell-800).
Figure 5.8. presented the C 1s, Ca 2p, Na 1s, O 1s and Cl 2p regions for NaCl₂₄₃/Shell-600, NaCl₂₄₃/Shell-800, and NaCl₂₄₃/Shell-1000. In the C 1s region, NaCl₂₄₃/Shell-600 and NaCl₂₄₃/Shell-800 showed triplet peaks while NaCl₂₄₃/Shell-1000 showed doublet peaks. In addition to peaks at ~ 289.4 eV and ~285.0 eV (assigned to C-H and carbonate groups, respectively) [20], NaCl₂₄₃/Shell-600 and NaCl₂₄₃/Shell-800 also displayed a third C 1s peak at ~ 292.4 eV, which might attribute to the existence of C-Cl [30]. NaCl₂₄₃/Shell-1000 did not contain Cl element, thus no such peak was detected. In the Ca 2p region, all three catalyst showed doublet peaks. The peaks at 346.6 eV and 350.1 eV in NaCl₂₄₃/Shell-600 were assigned to CaCO₃ [21]. The peaks at 347.1 eV and 350.6 eV in NaCl₂₄₃/Shell-800 and at 347.2 eV and 350.7 eV in NaCl₂₄₃/Shell-1000 were assigned to CaO [28]. In the Na region, NaCl₂₄₃/Shell-600 and NaCl₂₄₃/Shell-800 showed doublet peaks at ~1073.6 eV and ~1071.5 eV, assigned to NaCl [31] and Na₂CO₃ [24], respectively, while NaCl₂₄₃/Shell-1000 only showed single peak at 1071.6 eV, assigned to Na₂CO₃ [24]. The Na₂CO₃ in NaCl₂₄₃/Shell-600 might be attributed to adsorbed Na and undecomposed carbonate in the shell, while the Na₂CO₃ in NaCl₂₄₃/Shell-800 and NaCl₂₄₃/Shell-1000 might attribute to the air contaminant on the surface since no carbonate group was detected based on the XRD analysis. Because NaCl₂₄₃/Shell-1000 did not contain Cl element, it did not show the peak representing NaCl. In the O 1s region, all three catalysts showed single peak, the peak at 531.0 eV of NaCl₂₄₃/Shell-600 was assigned to CaCO₃ [22] and the peak at 531.5 eV of NaCl₂₄₃/Shell-800 and the peak at 531.6 eV of NaCl₂₄₃/Shell-1000 were assigned to CaO [28]. In the Cl 2p region, both NaCl₂₄₃/Shell-600 and NaCl₂₄₃/Shell-800 showed doublet peaks at 200.3 eV and 202.0 eV, for 2p3/2 and 2p1/2 components of Cl, respectively, with a separation of 1.7 eV that was also observed by Wu et al [32]. In addition, NaCl₂₄₃/Shell-800 also showed a third peak at lower BE, 198.4 eV. Comparing the FAME yields of NaCl₂₄₃/Shell-800 with NaCl₂₄₃/Shell-1000 suggested that
NaCl\textsubscript{2.43}/Shell-800 resulted in higher FAME yield than NaCl\textsubscript{2.43}/Shell-1000. Considering that the BE of O 1s for NaCl\textsubscript{2.43}/Shell-800 was comparable with NaCl\textsubscript{2.43}/Shell-1000, the enhanced activity of NaCl\textsubscript{2.43}/Shell-800 may have been due to the formation of surface Cl with lower BE (198.4 eV). As shown in Figure 5.9, the negatively shifted Cl probably behaved similarly as the negatively shifted O, increasing the effective negative charge that led to an increase in the electron donating ability to improve the FAME production rate by facilitating the formation of the tetrahedral intermediate between adsorbed triglyceride and methanol [2,29]. This synergistic effect between NaCl and CaO might depend on the calcination temperature and the NaCl concentration because NaCl\textsubscript{2.43}/Shell-600, with high surface NaCl concentration due to the lower calcination temperature, did not exhibit any improved activity.

![Diagram](image)

Figure 5.9. Role of NaCl\textsubscript{2.43}/Shell-800 surface basic site on the improved activity.
5.4 Conclusions

In this work, NaOH and NaCl were selected to modify the surface of oyster shell. The FAME yield of NaOH-impregnated shells increased as the NaOH concentration increased from 2 mol/L to 6 mol/L, but reached the plateaued (about 80%) once it exceeded 6 mol/L (up to 12.5 mol/L). The most feasible NaOH impregnation concentration was found to be 6 mol/L. In contrast, the FAME yield of NaCl-impregnated shells increased from 2 mol/L and reached the highest value (84.3%) at 3.64 mol/L. The further increase in NaCl concentration, however, decreased the FAME yield, with only 2.6% at 6 mol/L. The most feasible NaCl impregnation concentration was found to be 2.43 mol/L.

The calcination temperature for each impregnation chemical was studied based on the most feasible impregnation concentration. The most feasible calcination temperature for NaOH-impregnated shell was found to be 800 °C, as the FAME yield remained at about 80% for five consecutive runs. The most feasible calcination temperature for NaCl-impregnated shell was found to be 800 °C because of its highest mean FAME yield.

The impregnated precursor type and the calcination temperature determined the newly generated surface species that further influenced the activity of the catalyst. In general, higher calcination temperature could remove volatiles and convert more carbonates and hydroxides into oxides. Impregnating NaOH could form Ca(OH)$_2$ on the catalyst for the transesterification reaction at low calcination temperature (400 °C) and Na$_2$O$_2$ at high temperature (800 °C). The oxygen species of NaOH/shell calcined at low calcination temperature obtained higher electron donating ability than those from high calcination ability.

For NaCl/shell, when calcined at low temperature (600 °C), the catalyst mainly consisted of CaCO$_3$ and NaCl that were inactive for transesterification reaction. When the calcination temperature was above 600 °C, more CaCO$_3$ was converted into CaO, and the
activity was increased accordingly. At 800 °C, a synergistic effect of NaCl and CaO was found, since the FAME yield of NaCl/shell-800 was significantly higher than the yield of NaCl/shell-1000, which contained no NaCl. This synergistic effect was attributed to the existence of negatively shifted surface Cl species, which acquired higher electron donating ability.

In addition, for NaOH/shell, the calcination temperature also affected the durability of the active sites on the catalyst surface. High calcination temperature could help generate more durable basic sites (Na$_2$O$_2$), while (Ca(OH)$_2$) species generated at low calcination temperature were less durable during transesterification.

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References


CHAPTER 6

Conclusion and prospects

This project was conceived with a goal of adding value to oyster shells for use as solid base catalysts in transesterification reactions. Specifically, the research was focused on (1) synthesizing a catalyst by impregnating NaOH on oyster shell, (2) optimizing the transesterification reaction parameters, (3) studying the kinetics of the transesterification and propose the underlying mechanism, and (4) elucidating the effects of preparation conditions on the surface structure and the activity of the catalyst.

The objectives of this research were accomplished in three phases and relevant findings are listed below:

Phase One

- A novel solid base catalyst (Na-COS) was synthesized from waste oyster shell via 50 wt.% NaOH impregnation followed by calcination (1000 °C for 3 h).
- When tested with soybean oil, the FAME yields obtained from Na-COS catalyst were over 87% (1-h at 62 °C, 800 rpm) using a MR of 12 and CL of 10%. The catalytic activity of Na-COS was also comparable with NaOH, which catalyzed the transesterification to obtain 95% FAME yield in 50 min under the same conditions.
- The Na-COS was durable in that it could be applied to the transesterification reaction for three consecutive runs (with 90% yield) without any significant loss of activity.
- The factor study indicated that both MR and CL had significant effect on the FAME yield ($p = 1.36 \times 10^{-13}$ and $1.13 \times 10^{-8}$, respectively). The MR-CL interaction effect also existed ($p = 6.08 \times 10^{-7}$), suggesting that the effect of MR (CL) on the FAME
yield depended on the level of CL (MR). At low CL (2%), increasing MR from 6 to 12 would increase the FAME yield. Further increase in MR did not increase the FAME yield. At high CL (5%, 7%, 10%), the significant increase on FAME yield only existed between MR = 6 and 24 for CL = 5% and 10%. For CL = 7%, no significant difference on FAME yield existed between any two MRs. At low MR (6, 12), increasing CL from 2% to 5% increased the FAME yield. Further increase on CL did not increase the FAME yield. At high MR (18, 24), no significant difference on FAME yield was observed between any two CLs.

- The factor study (based on MR and CL) on the Na-COS-catalyzed transesterification of soybean oil with methanol suggested that the highest FAME yield of Na-COS-catalyzed transesterification reaction exceeded 93% under the conditions (MR = 12, CL = 10%, stirring rate = 800 rpm, temperature = 62 °C).

**Phase Two**

- The surface of the Na-COS was found to consist of newly generated Na$_2$O$_2$ and Na$_2$CO$_3$ phases compared with COS (control). The enhanced catalytic performance of Na-COS was attributed to the presence of the Na$_2$O$_2$ phases and the higher electron donating ability of surface oxygen.

- The mechanism of Na-COS-catalyzed transesterification of soybean oil with methanol was inferred to follow an Eley-Rideal mechanism wherein the stepwise transesterification started with adsorbed triglyceride and free methanol.

- Nine kinetic models were mathematically derived and tested for the initial period (0 – 20 min). The kinetic model that assumed that transesterification of adsorbed triglyceride to adsorbed diglyceride as the rate determining step (RDS) was chosen as the most appropriate model based on the experimental data and reported literature. The rate constant of the RDS, $k_1$, was estimated to be $0.0059 \pm 0.0002$ L mol$^{-1}$ min$^{-1}$.
A reasonable fit was observed between the experimental and predicted data (correlation of coefficient = 0.865).

- The effects of MR and CL on the initial reaction rate were investigated. Higher CL (6%, 8%) resulted in higher initial reaction rate at all MRs (6, 12, 18). At low CL (2%), there was no significant effect of MR on the initial reaction rate, while at high CL (4%, 6%, 8%), higher MR (12, 18) resulted in higher initial reaction rate.

**Phase Three**

- NaOH and NaCl were chosen as the precursor chemicals for oyster shell and the concentration effect on the FAME yield was investigated individually. For NaOH-impregnated oyster shell, increasing the precursor concentration from 2 mol/L to 6 mol/L increased the FAME yield. Further increase in precursor concentration did not increase the FAME yield. For NaCl-impregnated oyster shell, increasing the precursor concentration 2 mol/L to 3.64 mol/L increased the FAME yield. However, further increase in precursor concentration decreased FAME yield.

- The effect of calcination temperature on the FAME yield was also investigated. NaOH-impregnated oyster shell calcined at higher temperatures (> 800 °C) imparted stability to the catalysts which ensured sustained activity even after five consecutive runs. On the other hand, NaCl-impregnated oyster shell provided best activity at 800 °C (when compared to 600 and 1000 °C).

- It is theorized that for NaOH-impregnated oyster shell, calcination at higher temperature facilitated conversion of calcium carbonate and calcium hydroxide into calcium oxide, and a new phase, Na₂O₂ on the surface, which resulted in consistent catalytic activity. For NaCl-impregnated oyster shell, synergistic effect of NaCl and CaO was observed when calcined at 800 °C due to the negatively shifted surface Cl species.
NaOH-impregnated calcined oyster shell (Na-COS) had proved to be effective in transesterifying soybean oil with methanol into FAMEs. Some of the future directions are listed below:

1. The Na-COS could be tested on transesterifying waste cooking oils instead of refined vegetable oil (in this research) to lower the production cost.

2. The Na-COS has small specific surface area. By reducing the size of Na-COS and adsorbing it onto a mesoporous support, the as-synthesized catalyst might acquire more active sites, hence, higher production rate.