# CHICOREUS BRUNNEUS SEASHELLS AS A CATALYST IN RICE BRAN BIODIESEL PRODUCTION

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FACULTY OF ENGINEERING UNIVERSITY OF MALAYA KUALA LUMPUR

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# CHICOREUS BRUNNEUS SEASHELLS AS A CATALYST IN RICE BRAN BIODIESEL PRODUCTION

### ABSTRACT

Environmental pollution and the declining global supply of accessible fossil fuels are the key drivers to search for alternative energy sources. This study focused on developing a "green" and sustainable heterogenous calcium oxide (CaO) catalyst from Chicoreus Brunneus shells for biodiesel production from rice bran oil (RBO). Coastal people frequently collect these shells for food and shell crafts. Thus, by using seashell wastes, cost-efficient catalysts can be achieved for the biodiesel industry. The shells were calcinated, washed and dried to produce pure CaO catalyst. After that, CaO was converted into calcium methoxide  $(Ca(OCH_3)_2)$  and followed by loading onto zeolite support with wet impregnation to produce the hybrid catalyst. Both pure and hybrid catalysts along with methanol were used for the transesterification of RBO. The properties of the biodiesel were further evaluated. The tribological characteristics of biodiesel were assessed. Analytical tools have determined the formation of catalysts from C. brunneus. The surface of Ca(OCH<sub>3</sub>)<sub>2</sub> increased to 84.67 from 3.30 m<sup>2</sup>/g upon impregnation with zeolite. BET properties, average pore diameter and pore size of C. brunneus shell were also greater than that of commercial CaO catalyst. Both catalysts manifested relatively appreciable stability during the transesterification reaction with pure and hybrid catalysts presented the FAME yield of 93 and 98% respectively. However, FAME yield decreased significantly after the fifth transesterification reaction, and this was coincident with changes in the surface morphology of the catalysts. The fuel properties of biodiesel were within the ASTM D6751 and EN 14214 standards for biodiesel. The acid value of the biodiesel using the hybrid catalyst was 0.29 mg KOH, which was lower than the acid value obtained by the pure catalyst (0.5 mg KOH). The tribological examination suggested that 10% of biodiesel known as RBOB10 has a significant capacity as a mineral lubricant due to presenting the least wear scar diameter (462.3 µm) and lowest friction coefficient (0.085). From the results, the C. brunneus catalyst has the potential to be applied as industrial CaO nanocatalyst due to its large surface area and high stability which could increase the total yield of FAME. From the economic aspect, it is possible to recover C. brunneus derived catalysts in a facile way and to reuse them up to five cycles. They can be used frequently in the production cycles with constant catalytic activity and can potentially reduce the capital production cost. Further, the use of these catalysts simplifies the purification process, leading to reduced energy consumption and waste minimization. Overall, an efficient Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst was developed from a novel type of seashell, *i.e.*, *C. brunneus* which showed to be a prominent catalyst over the other sources of Ca(OCH<sub>3</sub>)<sub>2</sub>. Moreover, the produced catalyst resulted in a FAME yield of 98% within 120 min, having a higher yield in reduced reaction time, comparing with other synthetic catalysts. Therefore, the capacity of C. brunneus shell based-Ca(OCH<sub>3</sub>)<sub>2</sub> as a potential renewable source of CaO-based nanocatalyst for biodiesel production has been studied and approved.

Keywords: Rice bran oil, Heterogeneous catalysts, *C. brunneus*, Calcium methoxide, Zeolite Na-A

# CANGKERANG CHICOREUS BRUNNEUS SEBAGAI PEMANGKIN DALAM PENGHASILAN BIODIESEL DARIPADA DEDAK PADI

#### ABSTRAK

Pencemaran Alam Sekitar dan kemerosotan bekalan bahan api fosil global adalah pemacu utama kepada pencarian sumber alternatif tenaga. Kajian ini memberi tumpuan kepada pembangunan pemangkin kalsium oksida (CaO) yang "hijau" dan mampan sebagai sejenis pemangkin heterogen daripada kerang bronneus Chicoreus bagi pengeluaran biodiesel daripada minyak dedak padi (RBO). Kerang tersebut sering dikumpulkan oleh orang pesisir untuk makanan dan hasil seni kraf. Oleh itu, dengan menggunakan sisa-sisa buangan, pemangkin dengan keberkesanan kos yang tinggi juga dapat dihasilkan untuk industri biodiesel. Cangkerangnya dikalsin, dihidrasi, dan dikeringkan untuk menghasilkan pemangkin CaO iaitu pemangkin tulen. Selepas itu, CaO ditukar kepada Ca(OCH<sub>3</sub>)<sub>2</sub> dan diikuti oleh pemuatan pada zeolit dengan menggunakan kaedah penyerapan basah untuk menghasilkan pemangkin hybrid. Pemangkin CaO tulen dan hibrid yang dihasilkan daripada kulit C. brunneus dan metanol digunakan untuk transesterifikasi RBO. Ciri-ciri biodiesel berasaskan minyak dedak padi telah dinilai selanjutnya mengikut. Selepas itu, ciri-ciri tribologi biodiesel RBO dinilai. Pembentukan kedua-dua pemangkin daripada C. brunneus telah disahkan oleh alat analisis. Analisis kawasan permukaan mengesahkan bahawa peningkatan berlaku pada keluasan permukaan Ca(OCH<sub>3</sub>)<sub>2</sub> dari 3.30 m<sup>2</sup>/g hingga 84.67 m<sup>2</sup>/g setelah digabungkan dengan zeolit. Kawasan permukaan per jisim unit, purata diameter pori dan jumlah liang cecair C. brunneus lebih besar daripada CaO komersial. Akibatnya, lebih banyak atom pemangkin yang terdedah kepada reaktan, lalu menghasilkan hasil reaksi yang tinggi. Kemudian, biodiesel telah berjaya dihasilkan dengan cara pemangkin yang berasal dari C. brunneus. Kedua-dua pemangkin tulen dan hibrid menunjukkan kestabilan yang baik

semasa reaksi transesterifikasi dengan hasil FAME sebanyak 93% dan 98%. Walau bagaimanapun, hasil FAME berkurangan dengan ketara selepas tindak balas transesterifikasi ke-5 dan ini bertepatan dengan perubahan dalam morfologi permukaan pemangkin. Sifat bahan bakar biodiesel berada di dalam standard biodiesel ASTM D6751 dan EN 14214. Nilai asid biodiesel yang menggunakan pemangkin hibrid adalah 0.29 mg KOH, dimana ianya lebih rendah daripada biodiesel yang dibentuk dengan bantuan pemangkin tulen (0.5 mg KOH). Pemeriksaan tribologi mencadangkan bahawa 10% biodiesel minyak dedak padi atau dikenali sebagai RBOB10 mempunyai kapasiti yang sangat baik untuk pelincir mineral kerana menunjukkan diameter parut haus yang paling rendah (462.3 µm) dan pekali geseran terendah (0.085) di antara bahan api yang lain. Keputusan kajian ini mengenalpasti cangkerang C. brunneus mempunyai potensi sebagai sumber industri pemangkin-nano CaO disebabkan oleh kawasan permukaan dan kestabilan yang tinggi yang meningkatkan jumlah penghasilan FAME. Dari segi keuntungan ekonomi, adalah mungkin untuk memulihkan pemangkin C. brunneus yang dihasilkan dengan cara yang mudah dan menggunakannya semula sehigga lima kitaran. Mereka boleh digunakan dengan kerap dalam kitaran pengeluaran dengan aktiviti pemangkin yang berterusan dan berpotensi mengurangkan kos pengeluaran biodiesel. Selanjutnya, penggunaan pemangkin ini mempermudah proses pemurnian, yang menyebabkan pengurangan penggunaan tenaga dan pengurangan sisa. Secara keseluruhannya, pemangkin Ca(OCH<sub>3</sub>)<sub>2</sub> yang cekap dikembangkan dari jenis kerang baru iaitu C. brunneus yang menunjukkan peningkatan berbanding sumber Ca(OCH<sub>3</sub>)<sub>2</sub>. Pemangkin ini menghasilkan hasil FAME 98% dalam 120 minit, mempunyai hasil yang lebih tinggi dalam masa tindak balas berkurang, dibandingkan dengan pemangkin sintetik lain. Sebagai kesimpulan, ia telah disahkan bahawa cangkerang C. brunneus adalah sumber pemangkin-nano CaO yang boleh diperharu untuk pengeluaran biodiesel.

Kata kunci: Minyak dedak padi, Pemangkin heterogen, C. brunneus, Kalsium methoksida, Zeolit Na-A

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## LIST OF SYMBOLS AND ABBREVIATIONS

| AAS                                | : | Atomic absorption spectroscopy              |
|------------------------------------|---|---|
| Al                                 | : | Aluminium                                   |
| Al <sub>2</sub> O <sub>3</sub>     | : | Aluminum oxide                              |
| BaO                                | : | Barium oxide                                |
| BET                                | : | Brunauer-Emmett-Teller method               |
| С                                  | : | Carbon                                      |
| °C                                 | : | Degree Centigrade Celsius                   |
| cm <sup>-1</sup>                   | : | Centimeter (for energy unit)                |
| CaO                                | : | Calcium oxide                               |
| CaCO <sub>3</sub>                  | : | Calcium carbonate                           |
| CO <sub>2</sub>                    | : | Carbon dioxide                              |
| Ca(OCH <sub>3</sub> ) <sub>2</sub> | : | Calcium methoxide                           |
| CaMnO <sub>3</sub>                 | : | Calcium manganite                           |
| CeO <sub>2</sub>                   | : | Cerium oxide                                |
| C.brunneus                         | : | Chicoreus Brunneus                          |
| CaTiO <sub>3</sub>                 | : | Calcium titanate                            |
| CaZrO <sub>3</sub>                 | ÷ | Calcium zirconate                           |
| Cu                                 | : | Copper                                      |
| DMC                                | : | Dimethyl carbonate                          |
| DW                                 | : | Distilled water                             |
| EDX                                | : | Energy-dispersive X-ray spectroscopy        |
| FAME                               | : | Fatty acid methyl ester                     |
| FC                                 | : | Friction coefficient                        |
| FESEM                              | : | Field emission scanning electron microscopy |

| FFA                            | : | Free fatty acid                         |
|--------------------------------|---|---|
| FPC                            | : | Filter press cake                       |
| FTIR                           | : | Fourier transform infrared spectroscopy |
| g                              | : | Gram                                    |
| GC                             | : | Gas chromatography                      |
| g/m <sup>2</sup>               | : | Gram per square meter                   |
| h                              | : | Hour                                    |
| Κ                              | : | Degree Kelvin                           |
| K <sub>2</sub> CO <sub>3</sub> | : | Potassium carbonate                     |
| КОН                            | : | Potassium hydroxide                     |
| 1                              | : | Liter                                   |
| La                             | : | Lanthanum                               |
| La <sub>2</sub> O <sub>3</sub> | : | Lanthanum oxide                         |
| Li                             | : | Lithium                                 |
| MgO                            | : | Magnesium oxide                         |
| μm                             | : | Micrometer                              |
| ml                             | : | Milliliter                              |
| NaOH                           | : | Sodium hydroxide                        |
| RBO                            | : | Rice bran oil                           |
| RBOB                           | : | Rice bran oil biodiesel                 |
| RBOB10%                        | : | 10% RBOB+90% diesel                     |
| RBOB30%                        | : | 30% RBOB+70% diesel                     |
| RBOB50%                        | : | 50% RBOB+50% diesel                     |
| RBOB100%                       | : | Pure biodiesel                          |
| RPM                            | : | Rotations per minute                    |
| Si                             | : | Silicone                                |

- SiO<sub>2</sub> : Silicon dioxide
- SrO : Strontium oxide
- Sr/Ca : Strontium/calcium
- S/m : Siemens per meter
- TEM : Transmission electron microscopy
- TPD-CO<sub>2</sub> : Temperature-programmed desorption of carbon dioxide
- WSD : Wear scar diameter
- wt % : Weight percent
- XRD : X-ray diffraction
- Zn : Zinc
- ZnO : Zinc oxide

#### **CHAPTER 1: INTRODUCTION**

#### 1.1 Research background

The increase in energy demand, the fast declining supply of the world's available fossil fuels, global warming as a consequence of greenhouse gasses emission, and environmental pollution due to increasing carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere are the significant reasons that lead to the global search for alternative sources of energy (Phwan et al., 2019). Some of the most significant alternative energy sources that can be feasible substitutes for fossil fuels are the wind power, solar energy, hydropower and bioenergy (Izadyar et al., 2016). The predominant types of biofuels generated from biomass are in three forms, namely solid (bio-char), liquid (biodiesel and bioethanol), and gaseous (bio-hydrogen, biogas, and biosynthetic gas) (Thanh et al., 2012). Biodiesel has been categorized within the sustainable fuels due to its distinctive benefits such as being non-toxic, biodegradable, renewable, and eco-friendly which has become the research focus of attention (Quah et al., 2019).

The role of biodiesel is not to replace petroleum diesel, but to establish a balance energy supply between both finite and renewable resources. One of the finite fuels is petroleum diesel typically generated from the fractional distillation of crude oil in between 200 and 350 °C at atmospheric pressure, leading to the formation of carbon chain mixtures consist of 8 to 21 carbon atoms per molecule (Yoon, 2011). Differences between biodiesel and petroleum diesel in terms of physicochemical properties are also listed in Table 1.1.

| Property                 | Pure biodiesel                               | Petroleum diesel        |  |
|--------------------------|--|-------------------------|--|
| Exhaust emissions        | Low  | High                    |  |
| Renewable supply         | Renewable                                    | Non-renewable           |  |
| Biodegradability         | Biodegradable                                | Poor biodegradable      |  |
| Toxicity                 | Non-toxic                                    | Toxic                   |  |
| Brake thermal efficiency | Low  | High                    |  |
| Lubricity                | Improved                                     | Poor                    |  |
| Combustion degree        | Improved                                     | Incomplete              |  |
| Carbon monoxide          | Less   | More                    |  |
| emissions                |  |                         |  |
| Sulphur and aromatic     | Free of sulphur and aromatics                | Contains sulphur and    |  |
| content                  |  | aromatics               |  |
| Explosively              | Non-explosive                                | Explosive               |  |
| Flash point (°K)         | 423  | 337                     |  |
| Cetane number            | 45-70  | 40-52                   |  |
| Chemical structure       | C12, C14, C16, C18 and C22 fatty acid esters | C12 to C25 hydrocarbons |  |
| Chemical structure       | Straight chain hydrocarbon esters            | Ring structures         |  |
| Oxygen content (%)       | 11   | 0                       |  |
| Cold flow properties     | Rapid  | Gradual                 |  |
| Conductivity             | >500 pico siemens per meter                  | Low                     |  |
|                          | (S/m).                                       |                         |  |

Table 1.1: Differences between biodiesel and petrodiesel

Adopted from Saifuddin et al. (2015)

First and foremost, biodiesel shows no metal contents, crude oil residues, sulfur aromatics. Moreover, biodiesel emits negligible amount of greenhouse gasses to the atmosphere; thus, it is being referred as clean fuel (Gebremariam & Marchetti, 2018). Due to the high oxygen content in its composition, biodiesel can be combusted with higher efficiency and therefore produces less carbon monoxide (Silitonga et al., 2013). They also pointed out that biodiesel usage might decrease carcinogenic and toxic aerosols by 95 and 90% respectively, leading to safer and better environmental conditions. Furthermore, biodiesel can be utilized in a combined form with petroleum diesel, owing to their similar physicochemical characteristics (cetane number, viscosity, heating value, *etc.*) and directly used in any diesel engine without alteration. Biodiesel density and viscosity also exert certain influence on the fuel injection system of the engine. The low density and viscosity characteristics of biodiesel can result in a more enhanced fuel atomization and mix properties. Therefore, biodiesel could be a favourable alternative to

petroleum diesel as it possesses significant advantages over conventional petroleum diesel. Biodiesel can be used either as unblended and direct fuel or mixed form; however, its testing parameters are critical and must comply with stringent standards such as European Union (EN 14214) and American standards (ASTM D6751) for guaranteed properties in fuel applications.

## 1.1.1 Biomass feedstock

Compared to other forms of energy, one of the essential factors for biodiesel generation is that it can be generated through a broad diversity of existing and renewable feedstock which are available in large quantities and at low cost. Some examples are illustrated in Figure 1.1.



Figure 1.1: Potential feedstock for biodiesel production

Biodiesel can be classified according to their sources of feedstock. For instance, biodiesel produced from edible oil is known as first-generation biodiesel, and the group which comes from non-edible oil sources are termed as second-generation biodiesel. Third generation biodiesel is mainly produced from microalgal biomass (Ahmad et al., 2011). First-generation

biodiesel produces a high yield of biodiesel thanks to their lower free fatty acids (FFA) content, leading to a simpler and easier transesterification process. However, due to the 'food versus fuel' debate which emphasizes insufficient human food supply in the future and therefore leading to starvation as well as the overuse of the existing land on growing crops for fuel, there is a huge concern regarding the use of edible vegetable oils (Chhetri et al., 2008). On the contrary, non-edible vegetable oils are considered as prospective feedstock for biodiesel production because they have no conflict with the stability of food supply (Silitonga et al., 2013). Rice bran oil (RBO) is one of the non-edible vegetable oils as a promising choice due to its low cost as compared to fresh vegetable oil.

RBO is a non-edible oil produced from hard outer layers of the rice grain. To date, China and India lead the global production of RBO with annual production rates of 6,000,000 and 1,000,000 tonnes, respectively. Typically, the oil contens in the rich bran vary in between 16–32 wt% depending upon the variety of rice and degree of milling. Moreover, because of the presence of active lipases in bran, the FFA content in rice bran oil is comparable with other edible oils. Therefore, there is huge potential for significant global expansion of RBO production and for the application of RBO as a feedstock in biodiesel production.

## 1.1.2 Catalysts used in the transesterification process

Up to date, one of the most prevalent methods to generate biodiesel is the transesterification of oil triglycerides using alcohol and catalyst. The general equation of this reaction is illustrated in Figure 1.2. Catalyst has a crucial impact on the transesterification process; therefore, the selection of an appropriate catalyst is vital.



Figure 1.2: The transesterification reaction (Cesarini et al., 2015)

Catalysts are generally categorized into three groups such as homogeneous (alkalis and acids), heterogeneous (solid base or acid), and biocatalyst (lipases). During transesterification reaction, a homogeneous catalyst remains as the same phase (liquid) to that of the reactant, while heterogeneous catalysts can exist in different phases (*i.e.* solid, immiscible liquid or gaseous) to that of the reactant. Recently, enzyme catalysts have been gaining significant attention since they can hinder the formation of soap, leading to an easier subsequent purification procedure. Nonetheless, due to a long transesterification reaction time and high unit pricing, the usage of enzyme catalysts has been less commonly applied in commercial sectors.

Alkali homogeneous catalysts, including potassium hydroxide (KOH) and sodium hydroxide (NaOH), are common commercially used catalysts in the transesterification. To date, alkali-based homogenous catalysts are considered as the most viable choices for mass production since the transesterification process using alkaline catalysts is performed under low pressure and temperature conditions, and the conversion rate is outstanding with no intermediate steps. Nevertheless, the alkaline homogeneous catalysts are significantly hygroscopic and able to absorb water from the air throughout the storage. Besides, they also produce water when dissolved in the alcohol reactant and exert an undesirable influence on yield. Moreover, some other drawbacks that may occur by using homogenous catalysts include the washing process of biodiesel for catalyst removal, which leads to the subsequent loss of biodiesel and the further cleaning process. All those steps will make the overall biodiesel process to be more expensive. Further, the method used to remove the catalyst is arduous, which causes the process to less economical. Thus, heterogeneous catalysts can be used to reduce the cost of biodiesel production (Hassani et al., 2014) and act as promising candidates for the production of biodiesel from vegetable oils (Endalew et al., 2011).

Compared to other types of catalysts, solid heterogeneous catalysts are desired choices for being non-corrosive and can be utilized in a fixed-bed reactor, resulting in protected, inexpensive, and more environment-friendly processes. Furthermore, these forms of catalysts are highly recyclable and feasible for continuous mass production. When compared to biodiesel production using homogeneous catalysts, heterogeneous catalytic processes produce less contaminated water whereby the cost of sewage treatment can be reduced. Solid heterogeneous catalysts can catalyze the transesterification and esterification reaction simultaneously. Therefore solid heterogeneous catalysts can potentially eliminate the pre-esterification stage, especially for feedstock with high FFA contents (Leung et al., 2010). Like other forms of catalysts, heterogeneous solid catalysts are categorized into two groups which include acid and base forms. In terms of reaction rate, heterogeneous basic catalysts are 4000 times faster and more active than acid catalysts (Saifuddin et al., 2015). However, solid heterogeneous catalysts have some disadvantages such as catalyst leaching issues and complicated catalyst preparation, which should be taken into consideration (Dimantopoulos et al., 2015). As alkaline catalysts have higher catalysis activity than acid catalysts in transesterification reaction, they are better choices for pure oil feedstock with a low FFA content. By applying a solid heterogeneous base catalyst in a continuous flow, packed bed reactors for biodiesel production, both separation of catalyst and co-production of high pure glycerol processes

are made easier, hence leading to a decrease in production costs and higher feasibility of catalysts being re-used (Hebbar et al., 2018).

Currently, several groups of heterogeneous basic catalysts received attention owing to their active basic sites. Alkaline earth metal oxides, supported alkaline earth metal oxides, supported alkali metals, alkali, and alkaline earth mixed, zeolites and modified zeolites, hydrotalcite or layered double hydroxides, rare earth/lanthanide-based, ion exchange resin, and zirconia-based are some of prominent examples (Lee et al., 2014). Lately, there has been a great interest in the application of alkaline earth metal oxides in biodiesel generation, including magnesium oxide, barium oxide and strontium oxide (Nisar et al., 2017). After thermal pre-treatment, these metal oxides become effective in transesterification due to their improved alkalinity functions. The presence of M<sup>2+-</sup>O<sup>2-</sup> ion pairs in various coordination environments is one of the core reasons why these alkali earth oxides are basic. Among alkaline earth metals, CaO has been receiving much more attention recently due to its reasonable price, low solubility in methanol, low toxicity and high availability from natural resources (Yin et al., 2016). The preparation of CaO is straightforward, unlike other solid catalysts. Moreover, its catalytic activity is augmented by applying thermal calcination. There are different precursor salts for CaO preparation, including carbonate, hydroxide, oxalate and acetate monohydrate (Zamberi et al., 2016). When using CaO as a catalyst, it should be noted that its exposure to air even for a few seconds can deactivate the catalyst; however, reactivating the catalyst by calcination in a furnace at high temperature is possible.

Figure 1.3 shows the mechanism of transesterification by using CaO as a catalyst. Firstly, methoxide anion forms as a result of proton removal from methanol by basic sites. Secondly, alkoxy carbonyl intermediate assembles due to the effect of methoxide anion on the carbonyl carbon of triglyceride. Transformation of alkoxy carbonyl into a firmer structure: fatty acid methyl ester (FAME) and anion of diglyceride; methoxide cation draws the anion of diglyceride, which results in the development of diglyceride. The sequence is repeated twice for  $R_2$  and  $R_3$  (Kesić et al.,2016).



Figure 1.3: Mechanism of CaO in transesterification (R1, R2, R3: carbon chain of fatty acid and R4: alkyl group of the alcohol) (Kesić et al., 2016)

The neat (commercial or natural), supported, and mixed forms of CaO are the most frequently CaO-based catalysts applied in transesterification. It can also be obtained from different kinds of seashells. Normally, these catalysts will be active after thermal calcination in high temperatures. Sometimes, the activity of the pure CaO will be increased by increasing the number of basic sites by doping with other basic compounds or mixing with metal oxides like zinc (Zn), lanthanum (La), and cerium oxide (CeO<sub>2</sub>). To enhance the stability of the catalyst, CaO can be loaded onto several potential carriers to form supported CaO, which is suitable for continuous application. The challenges that accompany the use of CaO-based catalysts encompass minimum reusability and leaching. Overcoming these challenges necessitates environmentally benign CaO-based catalyst that does not cause high leaching. In this regard, recent advances in nanoparticle technology have opened new prospects for using nano CaO. Moreover, applying catalysis supports are sufficient to maintain the CaO-based catalyst to be more stable during the transesterification process.

### **1.2 Problem statement**

Around 45,000 tonnes of shells from crustaceans and shellfish are produced annually by the seafood industry. These seashells are discarded as waste products from the marine aquaculture and hence presents a significant disposal problem and waste management. These shells are typically burnt and buried in landfills which are considered to be a process that has high environmental and economic costs. There have been few studies using the waste seashell as a source of CaO catalyst for catalyzing the transesterification in the process of biodiesel generation. Jindapon et al. (2016) used mixed shells of *Meretrix meretrix, Amusium pleuronectes, Pernaviridis, Anadaragranosa* as a source of CaO. In another study, Ismail et al. (2016) prepared CaO from mud clamshell and subsequently applied it in the transesterification of castor oil. In terms of the number of reusability cycle, the authors reported that the catalyst could be reused up to five cycles while maintaining 96.7% biodiesel yield. The calcined mixed wastes of mussel, clam and oyster shells effectively catalyzed the transesterification of *camelina sativa* oil into biofuel (Perea et al., 2016).

The conversion of waste shells into heterogeneous inorganic catalysts is one of the principal approaches to reduce both the amount of waste being disposed of in the landfill, and to increase the commercial value of seafood production. *C. brunneus* is frequently collected by coastal people for consumption. As a feedstock for biodiesel production, RBO as an unconventional oil offers significant potential as an alternative low-cost material. However, RBO with its high viscosity can contribute to the formation of carbon deposits in the engines and incomplete fuel combustion, which can result to a shorter

lifespan of an engine. To overcome such disadvantages, the viscosity of RBO can be decreased through transesterification, and the physicochemical characteristics of its biodiesel were found to be within the American Society for Testing and Material (ASTM) standard range for biodiesel (Kumar, 2007). The same study has also demonstrated that sulphur in RBO-based biodiesel was significantly lower as compared to diesel, which is a key feature in reducing SO<sub>2</sub> from the exhaust emission. Furthermore, biodiesel blends of B20 and B40 generated from RBO were applied as an alternative to diesel fuel without any modification on the compress ignition engine (Jayaprabakar et al., 2015). Another research has reported the favourable characteristics of RBO-based biodiesel which include the kinematics viscosity at 40 °C of 4.68 mm<sup>2</sup> s<sup>-1</sup>; flashpoint of 88 °C; pour point of 11 °C; and cloud point of 10 °C with no sulphur content. The authors mentioned that fuel properties of biodiesel blends B5, B10, B20, and B50 were much closer to high-speed diesel (Ahmad et al., 2011).

The current research investigated the efficiency of the *C. brunneus* seashell as a catalyst in biodiesel production using RBO as feedstock. In order to improve the catalytic activity of the seashell derived catalyst, Na-A zeolite was used as a support for the catalyst. Several sources have been reported for calcium methoxide (Ca(OCH<sub>3</sub>)<sub>2</sub>) development, such as calcium granules, quicklime and synthetic catalysts; however, to the best of the authors' knowledge, Na-A-Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst from seashell has never been used in the catalysis of transesterification for biodiesel production. Therefore, the purpose of this study was to determine the effects of as-synthesized catalysts on biodiesel yield from RBO. Furthermore, the pure and hybrid catalysts were characterized by notable techniques, and their properties were tested. Ultimately, the fuel properties, as well as the tribological attributes of the RBO-biodiesel catalyzed by these shell-derived catalysts were evaluated and compared against international standards. Furthermore, as a

part of the research development, the reusability and structural change after each reuse cycle study were assessed.

## **1.3** Objectives of the research

The overall aim of this research was to produce a novel seashell derived Ca-based catalysts, including CaO and Ca(OCH<sub>3</sub>)<sub>2</sub> and their supported forms on zeolite for the transesterification of RBO to produce biodiesel. The specific objectives for research work were to:

- 1. Produce and characterize *C. brunneus* seashell derived catalysts (pure and supported catalysts).
- 2. Evaluate the fuel properties of biodiesel generated from RBO, catalysed by *C*. *brunneus* seashell derived catalysts.
- 3. Measure the tribological characteristics of biodiesel, including friction and wear using four-ball testing.
- 4. Study the reusability of the catalyst through a regeneration cycle study on the FAME yield and the catalyst structural change.

### 1.4 Scope of research

This study revolves around determining the catalytic performances of *C. brunneus* derived catalysts for RBO transesterification. Two types of nanocatalysts have been investigated, *i.e.*, pure catalyst (CaO) and hybrid catalyst (Ca(OCH<sub>3</sub>)<sub>2</sub>) supported on zeolite). The catalysts have been implemented in the transesterification reaction to produce RBO-biodiesel (RBOB). The properties of biodiesel produced by the pure catalyst and hybrid catalyst have been tested according to ASTM D6751 and EN 14214 standards. Biodiesel produced by seashell catalysts were assessed in terms of tribological

performances by varying the blending ratio between RBOB and diesel as follows: RBOB10 (10% RBOB + 90% diesel); RBOB30 (30% RBOB + 70% diesel); RBOB50 (50% RBOB + 50% diesel); RBOB100 (100% RBOB + 0% diesel); and pure diesel RBOB0 (100% diesel)) to identify the minimum friction and wear losses. Field emission scanning electron microscopy (FESEM) was used to evaluate the reusability performance of seashell derived catalysts. The evaluation was based primarily on FAME yield and leaching studies. A comparison of the performance parameters related to the catalytic characteristics provided insight into the feasibility of *C. brunneus* derived catalysts for RBO transesterification.

#### **1.5** Layout of the thesis

This thesis is structured into five chapters, with the content and function of which are summarised as follows:

**Chapter 1** presents the background of this research, research aim and objectives as well as the scope of the research, which are addressed through the state-of-the-art research carried out in this thesis.

**Chapter 2** provides the literature review of research topics related to this research thesis, including a comprehensive literature review of different types of CaO catalysts as well as the application of zeolite as a catalyst support in biodiesel production. This chapter also includes a literature review of biodiesel as lubricating oil additives.

**Chapter 3** outlines the different materials and experimental methods employed in this work with their detailed sample preparation techniques, procedures, and testing conditions. Furthermore, it entails the development of *C. brunneus* shells derived

catalysts, including the detailed steps used to convert the seashell to different effective forms of catalysts. Moreover, the test set-ups, working principles, and illustrations of the characterization techniques such as Brunauer-Emmett-Teller method (BET), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Temperatureprogrammed desorption of carbon dioxide (TPD-CO<sub>2</sub>) constitute a major part of this chapter. The transesterification reaction has been explained and illustrated with relevant literatures. For biodiesel properties tests, the adopted procedures and the test equipment have been discussed for fuel properties such as viscosity, acidity, density, oxidation stability, flash point and calorific value. The catalyst reusability tests and the procedure to recover the catalyst have been explained. Tribology-testing procedures in controlled laboratory conditions are mentioned along with illustrations of testing rigs.

**Chapter 4** is dedicated to results and discussions based upon findings of experimental work. This chapter starts with the investigation of *C. brunneus* shell in terms of surface area, pore volume, pore diameter, size and morphology. Results obtained in the form of SEM micrographs, EDX spectra, FTIR spectra and surface topography have been discussed to understand and report the potential mechanisms for the considered seashell derived catalysts. The pure seashell derived catalyst was compared to the reference catalyst.

**Chapter 5** presents a summary of the key findings and concludes the main results and their significant contributions in the research. This chapter also puts forward some recommendations for potential areas of research for future studies.

#### **CHAPTER 2: LITERATURE REVIEW**

There have been numerous research and development projects conducted to improve biodiesel production and its properties by using a cost-effective catalyst. Thus, the formulation of a suitable catalyst is a function of its ability to control the FAME yield. For biodiesel production, the catalyst should provide effective performance throughout the transesterification reaction. Moreover, after the development of a potential catalyst, knowledge about catalyst reusability and leaching on the production yield of biodiesel is required. This chapter outlines literatures related to the biodiesel production by calcium oxide (CaO)-based catalysts. The potential and the challenges with regards to the use of seashell derived CaO as a catalyst have been also discussed in this chapter.

## 2.1 Calcium oxide-based catalysts in biodiesel production

In this study, CaO as a member of alkaline earth metal oxides was reviewed. CaO can be applied in transesterification reactions in different forms, namely neat, supported and mixed. Moreover, it can be obtained from different kinds of seashells. In the following sections, the use of different kinds of CaO in the transesterification reaction was reviewed. Further, the FAME yield and experimental condition were explained.

## 2.1.1 Pure calcium oxide catalysts

Pure CaO can be applied in the transesterification reaction effectively. Generally, pure CaO irrespective of its source can be tested by subjecting to high temperatures. In this part, the utilization of pure CaO either commercial or derived from other sources such as wastes along with their reaction conditions has been reviewed with the focus on the most recent published works (Table 2.1).

|  | Oil                                   | Catalyst          | Optimal                   | Yield | Reusability | Reference                        |
|--|---------------------------------------|-------------------|---------------------------|-------|-------------|----------------------------------|
|  |                                       | -                 | condition                 | (%)   | (cycle)     |                                  |
|  | Waste cooking                         | Commercial<br>CaO | Temperature(°C):<br>80    | 96    | -           | (Devaraj et al., 2019)           |
|  | -                                     |                   | Methanol-to-oil           |       |             |                                  |
|  |                                       |                   | molar ratio: 1.06         |       |             |                                  |
|  |                                       |                   | Catalyst amount           |       |             |                                  |
|  |                                       |                   | (wt%): 3                  |       |             |                                  |
|  |                                       |                   | Reaction                  |       |             |                                  |
|  |                                       |                   | time(min): 120            |       |             |                                  |
|  | Bombax                                | Nano CaO          | Temperature(°C):          | 96.2  | 5           | (Hebbar et al., 2018)            |
|  | ceiba                                 |                   | 65<br>Mathanal ta ail     |       |             |                                  |
|  |                                       |                   | melan ratio: 10.27        |       |             |                                  |
|  |                                       |                   | Catalyst                  |       |             |                                  |
|  |                                       |                   | amount(wt%).              |       | 3           |                                  |
|  |                                       |                   | 1.5                       |       |             |                                  |
|  |                                       |                   | Reaction                  |       |             |                                  |
|  |                                       |                   | time(min): 70.52          |       |             |                                  |
|  | Soybean                               | Nanocrystalline   | Temperature(°C):          | 89.89 | 3           | (Badnore et al.,                 |
|  |                                       | CaO               | 60                        |       |             | 2018)                            |
|  |                                       |                   | Methanol-to-oil           |       |             |                                  |
|  |                                       |                   | molar ratio: 6            |       |             |                                  |
|  |                                       |                   | Catalyst $amount(wt%): 4$ |       |             |                                  |
|  |                                       |                   | Reaction                  |       |             |                                  |
|  |                                       |                   | time(min): 80             |       |             |                                  |
|  | Palm oil                              | Hydrated CaO      | Temperature(°C):          | 97    | 4           | (Roschat et al., 2016)           |
|  |                                       | 2                 | 65                        |       | -           |                                  |
|  |                                       |                   | Methanol-to-oil           |       |             |                                  |
|  |                                       |                   | molar ratio: 15:1         | _     |             |                                  |
|  |                                       |                   | Catalyst                  |       |             |                                  |
|  |                                       |                   | amount(wt%): 6            | -     |             |                                  |
|  |                                       |                   | time(min): 120            |       |             |                                  |
|  | Waste                                 | Chicken           | Temperature(°C):          | 90    |             | (Maneerung et al                 |
|  | cooking                               | manure based      | 65                        | 70    | -           | (Wanteerung et al., 2016)        |
|  | e e e e e e e e e e e e e e e e e e e | CaO               | Methanol-to-oil           |       |             | 2010)                            |
|  |                                       |                   | molar ratio: 15:1         |       |             |                                  |
|  |                                       |                   | Catalyst                  |       |             |                                  |
|  |                                       |                   | amount(wt%):              |       |             |                                  |
|  |                                       |                   | 7.5                       |       |             |                                  |
|  |                                       |                   | Reaction                  |       |             |                                  |
|  | Canala                                | Wasta filtar      | Temperature(°C):          | 06    | 7           | (A ababarari fr                  |
|  | oil                                   | press cake        | 60                        | 90    | /           | (Agnabarari &<br>Martinez-Huerta |
|  | 011                                   | based CaO         | Methanol-to-oil           |       |             | Martinez-Huerta,<br>2016)        |
|  |                                       |                   | molar ratio: 12           |       |             |                                  |
|  |                                       |                   | Catalyst                  | 1     |             |                                  |
|  |                                       |                   | amount(wt%): 5            |       |             |                                  |
|  |                                       |                   | Reaction time             |       |             |                                  |
|  |                                       |                   | (min) 90                  |       |             |                                  |

## Table 2.1 continued

| Rubber<br>seed oil      | CaO                                 | Temperature(°C):<br>65<br>Methanol-to-oil<br>molar ratio: 15:1<br>Catalyst<br>amount(wt%): 9<br>Reaction time<br>(min): 180   | 97   | - | (Roschat et al.,<br>2017)      |
|-------------------------|-------------------------------------|---|------|---|--------------------------------|
| Canola<br>oil           | CaO from<br>dolomite                | Temperature(°C):<br>60<br>Methanol-to-oil<br>molar ratio: 9:1<br>Catalyst<br>amount(wt%): 5<br>Reaction<br>time(min): 90      | 97.4 | 4 | (Korkut &<br>Bayramoglu, 2016) |
| Palm oil                | CaO                                 | Temperature(°C):<br>60<br>Methanol-to-oil<br>molar ratio: 9:1<br>Catalyst<br>amount(wt%): 2<br>Reaction<br>time(min): 240     | 84.5 | 3 | (Poosumas et al., 2016)        |
| Palm oil                | CaO                                 | Temperature(°C):<br>65<br>Methanol-to-oil<br>molar ratio: 12:1<br>Catalyst<br>amount(wt%): 3<br>Reaction<br>time(min): 60     | 77.3 | - | (Mootabadi et al.,<br>2010)    |
| Waste<br>cooking<br>oil | CaO from<br>pulverized<br>limestone | Temperature(°C):<br>N/A<br>Methanol-to-oil<br>molar ratio: 12:1<br>Catalyst amount<br>(wt%): 0.2<br>Reaction<br>time(min): 60 | 93   | 2 | (Kouzu et al., 2008)           |

In one of the reported literatures, activated CaO could efficiently catalyze the conversion of waste cooking oil to biodiesel. The calcinated CaO activity was significantly increased after the catalyst activation with methanol, and under the optimized conditions at 3% (wt/v) catalyst concentration at 80 °C temperature, 1:6 of oil to methanol molar ratio, 120 min reaction time, and 400 rotations per minute (rpm)

showed 96% of biodiesel yield (Devaraj et al., 2019). CaO nanoparticles have been studied by Hebbar et al. (2018) in the transesterification reaction of bombax ceiba oil with methanol. A high FAME yield of 96.2% was obtained under the following reaction conditions: at 10.37 methanol-to-oil molar ratio with 1.5 wt% catalyst in 70.52 min at 65°C. The nanocrystalline CaO catalyst was developed by Badnore et al., (2018) by ultrasound-assisted emulsion-based method. The produced catalyst manifested 1.53 times higher surface area and 1.28 times smaller crystallite size and particle size comparing with commercial CaO catalyst. At optimal conditions, the synthesized catalyst exhibited 18.91% enhanced conversion of oil as compared to the commercial CaO catalyst.

The activity of original hydrated lime and hydrated lime derived CaO were examined by Roschat et al. (2016) in the transesterification reaction of palm oil with methanol. The biodiesel yield of 97% was achieved when hydrated lime derived CaO was used at 15:1 of methanol-to-oil molar ratio with 6 wt % catalyst in 2 h at 65 °C. Moreover, the hydrated lime-derived CaO presented greater BET surface area and pore volume than the synthetic one.

In recent years, the utilization of waste material as a catalyst has been of great research interest due to its low cost and abundant supply. However, very scant works have been reported on using waste-derived CaO catalyst in biodiesel production. In attempting towards a more reasonable and environmentally-friendly biodiesel production, Maneerung et al., (2016) reported the synthesis of an economical and profitable CaO catalyst derived from chicken manure for the first time. Chicken manure was subjected to calcination at 850 °C to obtain the active CaO. The obtained CaO catalyst exhibited high catalytic activity for biodiesel production from the transesterification of waste cooking oil and methanol. The optimum parameters for catalysts were 7.5 wt% catalyst, 15:1 of methanol: oil molar ratio, and 65 °C with a FAME yield of 90%.
In another study conducted by Aghabarari and Martinez-Huerta (2016), for the first time, CaO nanoparticles (FPC-NAC) were derived from waste filter press cake (FPC). FPC is the main waste of sugar-producing factories which could attract insects and also result in the pollution of water. Thus, managing such wastes is a big challenge for sugar-producing countries. Catalyst production from waste resources can exert influence on the environment by lowering the disposal of those wastes. The FPC was subjected to calcination at 900 °C for 2 h to convert it into an active CaO-based catalyst (FPC-HT). Further, the surfactant-hydration method was implemented to produce FPC-NAC. The yield of over 96% was reported when this catalyst used with canola oil and methanol (Aghabarari & Martinez-Huerta, 2016). Roschat et al., (2017) also investigated the extraction of rubber seed oil as a non-edible oil to produce biodiesel in the presence of CaO and methanol and, the FAME yield of more than 97% was obtained.

Ultrasonic assisted transesterification is an efficient method when using CaO as a catalyst because it can crush the catalyst into a smaller part which leads to higher availability of basic sites. As basic sites have the main role in CaO efficiency as a catalyst, therefore it improves the transesterification efficiency. Further, it also reduces the time needed for oil conversion to biodiesel. For instance, CaO obtained from dolomite was applied in the ultrasonic-assisted transesterification of canola oil for 90 min, which resulted in a biodiesel yield of 97.4% (Korkut & Bayramoglu, 2016). Poosumas et al., (2010) and Mootabadi et al., (2010) investigated the activity of CaO in the ultrasound-assisted transesterification of palm oil along with methanol. FAME yield of 84.5% was obtained when 2 wt% CaO was used at the temperature of 60 °C, 9:1 of methanol-to-oil molar ratio and reaction time of 4 h. Mootabadi et al. (2010) compared the catalysis activity of CaO, SrO, and BaO. CaO showed the moderate catalysis activity. The yields obtained in 1 h augmented from 5.5% to 77.3% (CaO), 48.2% to 95.2% (SrO), and 67.3% to 95.2% for barium oxide.

Calcination at high temperatures activates the CaO-based catalyst which can promote better catalytic effect. For instance, Kouzu et al. (2008) prepared CaO by calcination of pulverized limestone calcium carbonate (CaCO<sub>3</sub>) at 900 °C for 1.5 h, reaching 66% biodiesel yield when waste cooking oil was utilized as a feedstock. However, when CaO is used with waste cooking oil, oil pre-treatment must be done due to its high free acids to keep the catalyst in the active phase.

#### 2.1.2 Mixed oxides catalysts containing CaO

Many attempts have been made to use CaO mixed oxides in the past years to make the catalyst more basic and stable for the transesterification process. In this part, the utilization of mixed oxides containing CaO along with their reaction conditions, as well as their preparation method have been reviewed with the most focus on recently published works, and, illustrated in Table 2.2.

The Zn doped CaO nanocatalyst was prepared by Naveenkumar and Baskar (2019) and applied in transeterification of *Calophyllum inophyllum*. The catalyst demonstrated higher catalytic activity due to its large surface area. The maximum biodiesel yield of 89.0% was obtained at methanol: oil ratio of 9:1, catalyst concentration of 6% (w/v), the temperature of 55 °C, and reaction time of 80 min.

Barium-impregnated calcium oxide-zinc oxide (CaO–ZnO) catalyst has been produced by wet impregnation method. FAME conversion was obtained as  $98.94 \pm 0.45$ from microalgal oil under optimized condition (1:18 methanol-to-oil molar ratio with 2.5 wt % catalyst at 65 °C for 120 min). The catalyst was recovered and reused up to six cycles with 69.56% FAME conversion (Singh et al., 2019).

In the study conducted by Teo et al., (2015), highly basic bimetallic alkaline earth metal oxide (CaO–MgO) (750  $\mu$ mol g<sup>-1</sup>) was produced by using synergistic effects. The FAME yield of >99% was obtained under the optimal condition of 4 wt% catalyst at a

temperature of 60 °C and 6 h reaction time. Results showed that the basicity of mixed CaO–MgO (CM-1.0) was higher compared to the pure CaO catalyst. The atomic absorption spectroscopy (AAS) method was used to evaluate the leaching of the catalyst and its result showed that the catalyst was stable for 5 cycles. Strontium/Calcium (Sr/Ca) complex was prepared by Li et al. (2016) by using different preparation methods including wet impregnation, solid mixing, co-precipitation, and improved co-precipitation to compare their efficiency. The improved co-precipitation method was found to be the most excellent method due to the best interaction of CaO and Sr.

Magnetic materials have been a focus of attention lately as they can avoid other posttreatment processes, such as conventional filtration and purification. By using a synergistic effect, a novel magnetic nanoparticle catalyst was prepared by Liu et al. (2016) and subsequently applied in the transesterification reaction of soybean oil along with methanol. The FAME yield obtained by using (MgFe<sub>2</sub>O<sub>4</sub>@CaO) catalyst was 5.9% higher when using pure CaO. Additionally, (MgFe<sub>2</sub>O<sub>4</sub>@CaO) catalyst was found to be more active and more water and acid resistant than the neat CaO. In another study conducted by Fan et al. (2016), calcium oxalate and magnesium oxalate were used as precursors to generate Ca-Mg mixed oxide catalysts. The bimetallic catalyst showed a better surface area than the pure CaO. The FAME yield of 98.4% and 92.8% were reported for Ca-Mg and pure CaO respectively. The higher yield of mixed oxide catalysts could be attributed to the larger surface area.

Different types of mixed earth metal oxides (CaO-MgO, CaO-ZnO, CaO-Lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) and MgO-ZnO) were investigated in terms of catalysis by Lee et al. (2016). The results showed that mixed metal oxides have better activity in the transesterification of jatropha curcas oil than the single metal oxides, which could be due to the increased basic density and strength of the catalyst. Further, CaO based mixed metal oxides showed

the best catalytic activity. The biodiesel yield of 94% was achieved when CaO-ZnO was applied in the system to produce biodiesel.

The transesterification reaction of palm oil (high acid volume) and karanja oil (low acid volume) were evaluated by Syamsuddin et al. (2016) by using CaO–La<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> mixed-oxide catalyst, and FAME yields of 97.81% and 96.77% were obtained respectively. In this study, dimethyl carbonate (DMC) has been used instead of methanol due to its advantages, such as being non-toxic, non-corrosive and being active in the reaction. Further, it restrains the production of glycerol as products during the occurrence of reactions.

Ca-containing perovskites such as calcium titanate (CaTiO<sub>3</sub>), calcium manganite (CaMnO<sub>3</sub>) and calcium zirconate (CaZrO<sub>3</sub>) were prepared and used to catalyze the methanolysis of sunflower oil by Kesić et al. (2016). They found that the pure perovskite phase showed low or no catalytic activity. The FAME yield of 98.1% was reported after 10 h of reaction at 60 °C with CaTiO<sub>3</sub> catalyzing the transesterification reaction.

On the same subject of using mixed metal oxide for biodiesel production, transesterification of refined bleached deodorized palm oil with methanol using a new heterogeneous base catalyst was studied (Jindapon et al., 2016). A mixture of Ca, Zn, and Al compounds was prepared through dissolution–precipitation method by using *Meretrix meretrix* seashells as a source of CaO, in the presence of zinc nitrate and alumina as binder precursors. A FAME yield of 99.9% was achieved when 30:1 of methanol-to-oil molar ratio, 10 wt% of catalyst ratio, 3 h of reaction time and reaction temperature of 65 °C applied to the system (Jindapon et al., 2016).

CaO-La<sub>2</sub>O<sub>3</sub>, as another example of mixed metal oxides, was developed by Taufiq-Yap et al. (2014) by using the co-precipitation method. This catalyst was then utilized in the transesterification reaction of *Jatropha Curcas* along with methanol and the biodiesel

yield of 86.51% was reported under the following conditions: 4wt% of catalyst volume, 24:1 of methanol-to-oil ratio and temperature of 65 °C.

| Feedstock              | Catalyst | Preparation method                       | Optimal reaction<br>condition        | Yield<br>(%) | Reusability<br>(cycle) | Ref                          |
|------------------------|----------|--|--------------------------------------|--------------|------------------------|------------------------------|
| Calophyllum inophyllum | Zn-CaO   | Stirring- precipitation-<br>calcination  | Temperature(°C): 55                  | 89           | 4                      | (Naveenkumar & Baskar, 2019) |
|                        |          |  | Methanol-to-oil molar<br>ratio: 9:1  |              |                        |                              |
|                        |          |  | Catalyst amount (wt%):<br>6          |              |                        |                              |
|                        |          |  | Reaction time (min): 80              | -            |                        |                              |
| Spirutenla             | Ba-Ca-Zn | Wet impregnation followed by             | Temperature(°C): 65                  | 98.94        | 6                      | (Singh et al., 2019)         |
|                        |          | mechanochemical treatment                | Methanol-to-oil molar<br>ratio: 1:18 |              |                        |                              |
|                        |          |  | Catalyst amount (wt%): 2.5           | -            |                        |                              |
|                        |          |  | Reaction time (min):<br>120          | -            |                        |                              |
| Elaeis guineensis      | CaO–MgO  | Co-precipitation followed by calcination | Temperature (°C): 60                 | 99           | 5                      | (Teo et al., 2017)           |
|                        |          |  | Methanol-to-oil molar<br>ratio: 15:1 | -            |                        |                              |
|                        |          |  | Catalyst amount(wt%):<br>4           | -            |                        |                              |
|                        |          |  | Reaction time (min):<br>360          | -            |                        |                              |

# Table 2.2: CaO-mixed oxides used in biodiesel production

#### Table 2.2 continued

| Palm oil               | Sr/Ca                                      | Solid mixing, wet<br>impregnation, co-precipitation,<br>and improved co-precipitation    | Temperature (°C): 65<br>Methanol-to-oil molar<br>ratio: 9<br>Catalyst amount (wt%):<br>5<br>Reaction time (min): 80        | 98.3 | N/A | (Li et al., 2016)  |
|------------------------|--|--|--|------|-----|--------------------|
| Soybean oil            | MgFe <sub>2</sub> O <sub>4</sub><br>andCaO | Alkali precipitation with the<br>presence of sodium<br>dodecylbenzenesulfonate<br>(SDBS) | Temperature (°C): 70<br>Methanol-to-oil molar<br>ratio: 12:1<br>Catalyst amount (wt%):<br>1<br>Reaction time (min):<br>180 | 98.3 | 5   | (Liu et al., 2016) |
| Dehydrated soybean oil | Ca-Mg<br>mixed oxide                       | Oxalate precipitation  | Temperature (°C): 70<br>Methanol-to-oil molar<br>ratio: 12:1<br>Catalyst amount (wt%):<br>1<br>Reaction time: 120          | 98   | 5   | (Fan et al., 2016) |

| Jatropha Curcas oil | CaO-ZnO  | Co-precipitation   | Temperature (°C): 120   | 94              | N/A | (Lee et al., 2016)        |
|---------------------|--|--|---|-----------------|-----|---------------------------|
|                     |  |  | Methanol-to-oil molar<br>ratio: 25:1<br>Catalyst amount (wt%):<br>3<br>Reaction time 180                                |                 |     |                           |
| Karanj oil          | CaO–La <sub>2</sub> O <sub>3</sub> –<br>Al <sub>2</sub> O <sub>3</sub> mixed-<br>oxide | Co-precipitation followed by calcination                             | Temperature(°C): 150<br>DMC to oil molar ratio:<br>9:1<br>Catalyst amount(wt%):<br>5<br>Reaction time:180               | 96.77<br>-<br>- | N/A | (Syamsuddin et al., 2016) |
| Sunflower oil       | CaTiO <sub>3</sub><br>plus small<br>amount of<br>CaO                                   | Mechanochemical treatment<br>by ball mill<br>followed by calcination | Temperature(°C): 60<br>Methanol-to-oil molar<br>ratio: 6:1<br>Catalyst amount (wt%)<br>10<br>Reaction time(min):<br>600 | 98.1<br>-<br>-  | N/A | (Kesić et al., 2016)      |

# Table 2.2 continued

# Table 2.2 continued

| Palm oil Ca, Zn, a<br>Al mixed |                                    | Dissolution-precipitation | Temperature(°C): 65  | 99.9  | N/A | (Jindapon et al., 2016)   |
|--------------------------------|------------------------------------|---------------------------|--|-------|-----|---------------------------|
|                                | compounds                          |                           | Methanol-to-oil molar<br>ratio 30:1  |       |     |                           |
|                                |                                    |                           | Catalyst amount (wt%):<br>10   |       |     |                           |
|                                |                                    |                           | Reaction time(min):<br>180   |       |     |                           |
| Jatropha Curcas                | CaO-La <sub>2</sub> O <sub>3</sub> | Co-precipitation          | Temperature (°C): 65<br>Alcohol to oil molar<br>ratio: 24:1<br>Catalyst amount (wt%):<br>4<br>Reaction time(min):<br>N/A | 86.51 | N/A | (Taufiq-Yap et al., 2014) |
|                                |                                    |                           |  |       |     |                           |

#### 2.1.3 Supported and loaded CaO catalysts

To stabilize the CaO catalyst for the reaction process, the use of support or carrier can serve such purposes. In this way, CaO has the main role of catalysis but the carrier can make it more stable during the transesterification reaction and overcome its leaching problem. There are different methods for producing supported CaO including the wet impregnation method, precipitation and co-precipitation which are followed by calcination to activate the catalyst. Alumina (Quah et al., 2019), zeolite (Saifuddin et al., 2015) and silica (Dehkordi & Ghasemi, 2012) were reported to be among the common supports used for CaO in biodiesel production. An overview of supported CaO catalyzed transesterification and its different parameters have been listed in Table 2.3, with the focus on recently published works.

CaO supported with Al-MCM41 was prepared by using the sono dispersion and wet impregnation method and used in the transesterification reaction of sunflower oil. The authors found that the biodiesel conversion and quality increased by loading more CaO due to its basicity (Vardast et al., 2019).

Diatomite supported by CaO/MgO was generated by the impregnation method and then utilized in the transesterification reaction of waste cooking oil. Biodiesel yield of 96.47% was obtained under the following experimental condition: temperature of 90°C, methanol-to-oil molar ratio of 1:15, catalyst amount of 6 wt% and reaction time of 2 h (Rabie et al., 2019).

CaO supported with silica was successfully synthesized by using the wet impregnation method. After applying this catalyst in the transesterification reaction along with palm oil and methanol, the biodiesel yield of 87.5% was achieved which was higher than the yield achieved by using neat CaO (Lani et al., 2017). Structured catalyst reactors such as those based on the monolithic catalyst are a captivating method for biodiesel production. However, it should be noted that a high affinity between the support and catalyst could

lead to the deactivation of the catalyst (Reyero et al., 2016). In this regard, in the study conducted by Reyero et al. (2016), the metallic citrates decomposition method was used to prepare mixed CaO/CeO<sub>2</sub>, both in powder and structured shapes. Further, Ca-Ce mixed oxides deposited on structured catalysts using Fecralloy monoliths for their use in the transesterification of sunflower oil. KOH catalyst supported on CaO obtained from animal bones was synthesized by Nisar et al. (2017) and subsequently utilized in the transesterification reaction of *Jatropha Curcas* oil. CaO modification was done to enhance the surface area and alkalinity of the catalyst. The synthesized catalyst exhibited high performance and stability which therefore led to a high FAME conversion rate of 96.1% under the following reaction condition: methanol-to-oil molar ratio of 9:1, catalyst concentration of 6 wt% at a temperature of  $70 \pm 3$  °C in reaction time of 3 h.

In this regard, how hierarchical ZSM-5 supported CaO performs as a catalyst in biodiesel production from waste palm oil was investigated by Zein et al. (2016). The catalytic activity of CaO supported on H-ZSM-5 led to an improvement of FAME conversion from 93.17% to 95.40%. FAME yield of 95.40% was reported at 6 h reaction time, 3 wt% of catalyst amount, 12:1 of methanol-to-oil molar ratio and 65 °C of reaction temperature. On the same subject of zeolite utilization as catalyst support in biodiesel production, Wu et al. (2013) reported on the synthesize of supported CaO catalysts with NaY, KL, and NaZSM-5 zeolites by using microwave irradiation. These supported CaO catalysts were then applied in the transesterification of soybean oil and methanol and their functions were compared to that of pure CaO. Using zeolite as support for CaO boosted its catalysis performance due to basic sites, BET values, water resistance and acid resistance properties. Furthermore, it was found that CaO/NaY had the best activity and a biodiesel yield of 95% reported under the following experimental conditions: 3 wt.% of catalyst, methanol/ oil molar ratio of 9, reaction temperature 65 °C and the reaction time of 3 h.

Porous materials such as silica materials as carriers for CaO have gained much attention. In this regard, Witoon et al. (2014) prepared bimodal meso-macroporous silica material by the sol-gel method. CaO was then loaded on the prepared meso-macroporous material by using the incipient wetness impregnation method and applied in the transesterification reaction of palm oil with methanol giving FAME yield of 94.15%. Thus, porous materials are some other promising carriers for CaO to boost their stability. The high surface area may lead to the superior metal oxide dispersion and thus improve their catalysis activity. Nevertheless, low rate dispersion of massive triglycerides through the pores can decrease the activity of the CaO.

Wet impregnation method was used to make palm oil mill fly ash supported CaO for the generation of palm biodiesel. Characterization results revealed that this catalyst had a higher surface area and basic sites. The transesterification process was conducted at 45°C reaction temperature, 6 wt% of catalyst loading and 12:1 of methanol-to-oil molar ratio, 3 h of reaction time and stirring speed of 700 rpm. FAME conversion and biodiesel yield of 97.09% and 79.76% were obtained with the synthesis conditions above (Ho et al., 2014). The wet impregnation method was also used to make CaO–SnO<sub>2</sub> catalysts for the transesterification process. The biodiesel yield of 89.3% was achieved under reaction time of 6 h, catalyst dosage of 8 wt%, the methanol-to-oil molar ratio of 12:1 and temperature of 343 K (Xie & Zhao, 2013).

A modified single step method was applied to prepare Al<sub>2</sub>O<sub>3</sub> supported CaO by Umdu et al. (2009). The synthesized catalyst was further used in the transesterification reaction of *Nannochloropsis oculata* lipid along with methanol. The researchers discovered that CaO was not active; however, the Al<sub>2</sub>O<sub>3</sub> supported CaO showed the most catalytic activity. Furthermore, they showed that without changing the catalyst amount, only by increasing the methanol-to-oil molar ratio from 6:1 to 30:1; the biodiesel yield was enhanced from 23% to 97.5%. Al-Ca hydrotalcite loaded with potassium carbonate  $(K_2CO_3)$  was prepared by Sun et al. (2014) and subsequently employed in the transesterification reaction of soybean oil with methanol. Biodiesel yield of 95.1% was reported under the following reaction condition: alcohol-to-oil ratio of 13:1, temperature of 65 °C and catalyst volume of 2 wt%. Modified CaO by chemical loading of bromooctane onto the surface of CaO was prepared for biodiesel production. FAME yield of 99.5% was observed using soybean as a feedstock under experimental conditions of 15:1 of methanol-to-oil ratio, 3 h of reaction and temperature of 65 °C (Tang et al., 2013).

| Feedstock            | Catalyst   | Preparation<br>method                  | Optimal<br>reaction<br>condition   | Yield<br>(%) | Catalyst<br>reusability | Reference                    |
|----------------------|--|--|--|--------------|-------------------------|------------------------------|
| Sunflower oil        | CaO<br>supported<br>with Al-<br>MCM41  | Impregnation<br>and sono<br>dispersion | Temperature<br>(°C):70<br>Methanol-<br>to-oil molar<br>ratio: 12<br>Catalyst<br>amount<br>(wt%):<br>12<br>Reaction<br>Time -             | N/A          | 4                       | (Vardast<br>et al.,<br>2019) |
| Waste cooking<br>oil | Diatomite<br>supported by<br>CaO/MgO   | Impregnation                           | Temperature<br>(°C):90<br>Methanol-<br>to-oil molar<br>ratio: 1:15<br>Catalyst<br>amount<br>(wt%)<br>6<br>Reaction<br>Time (min):<br>120 | 96.47        | 5                       | (Rabie et<br>al., 2019)      |
| Palm oil             | CaO<br>supported<br>with silica  | Impregnation                           | Temperature<br>(°C):60<br>Methanol-<br>to-oil molar<br>ratio 20:1<br>Catalyst<br>amount<br>(wt%):3<br>Reaction<br>Time<br>(min):120      | 87.5         | 6                       | (Lani et<br>al., 2017)       |
| Sunflower oil        | Calcium<br>based<br>catalyst<br>supported on<br>(commercial<br>Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub><br>and CeO <sub>2</sub> ,<br>along with<br>in-house<br>prepared<br>CeO <sub>2</sub> | Metallic<br>citrates<br>decomposition  | Temperature<br>(°C):60<br>Methanol-<br>to-oil molar<br>ratio : 48<br>Catalyst<br>amount<br>(wt%): 2<br>Reaction<br>Time (min):<br>240    | 99           | N/A                     | (Reyero et<br>al., 2016)     |

#### Table 2.3: Supported and loaded CaO in biodiesel production

| Jatropha Curcas<br>oil | KOH<br>supported on<br>CaO   | Impregnation                         | Temperature<br>(°C): $70 \pm 3$<br>Methanol-<br>to-oil molar  | 96.1  | 4   | (Nisar et<br>al., 2017)  |
|------------------------|--|--------------------------------------|---|-------|-----|--------------------------|
|                        |  |                                      | Catalyst<br>amount<br>(wt%):<br>6<br>Reaction<br>Time (min):<br>180   | -     |     |                          |
| Waste palm oil         | ZSM-5<br>supported<br>CaO  | Impregnation                         | Temperature<br>(°C): 65<br>Methanol-<br>to-oil molar<br>ratio:12:1<br>Catalyst<br>amount<br>(wt%): 6<br>Reaction<br>Time (min):<br>360  | 95.40 | N/A | (Zein et<br>al., 2016)   |
| Soybean oil            | Supported<br>CaO<br>catalysts<br>with NaY<br>zeolites                                      | Microwave<br>irradiation             | Temperature<br>(°C): 65<br>Methanol-<br>to-oil molar<br>ratio: 9<br>Catalyst<br>amount<br>(wt%):3<br>Reaction<br>Time 3h                | 95    | N/A | (Wu et<br>al., 2013)     |
| Palm oil               | Bimodal<br>meso-<br>macroporous<br>silica<br>material as a<br>CaO<br>supported<br>catalyst | Incipient<br>wetness<br>impregnation | Temperature<br>(°C): 60<br>Methanol-<br>to-oil molar<br>ratio: 12:1<br>Catalyst<br>amount<br>(wt%): 9<br>Reaction<br>Time (min):<br>360 | 94.1  | 5   | (Witoon et<br>al., 2014) |
| Crude palm oil         | Palm oil mill<br>fly ash<br>supported<br>CaO   | Wet<br>impregnation<br>method        | Temperature<br>(°C): 45<br>Methanol-<br>to-oil molar<br>ratio12:1<br>Catalyst<br>amount<br>(wt%): 6<br>Reaction<br>Time (min):<br>180   | 97.09 | 3   | (Ho et al.,<br>2014)     |

#### Table 2.3 continued

| Soybean oil                      | CaO–SnO <sub>2</sub>   | Wet<br>impregnation<br>method                       | Temperature<br>(°C): 70<br>Methanol-<br>to-oil molar<br>ratio: 12:1<br>Catalyst<br>amount<br>(wt%): 8<br>Reaction<br>Time (min):<br>360  | 89.3 | 5   | (Xie &<br>Zhao,<br>2013) |
|----------------------------------|--|---|--|------|-----|--------------------------|
| Nannochloropsis<br>oculata lipid | CaO/Al <sub>2</sub> O <sub>3</sub>                                     | Modified<br>single step<br>sol–gel                  | Temperature<br>(°C): 50<br>Methanol-<br>to-oil molar<br>ratio: 30:1<br>Catalyst<br>amount<br>(wt%): 80<br>Reaction<br>Time (min):<br>360 | 97.5 | N/A | (Umdu et<br>al., 2009)   |
| Soybean oil                      | Al-Ca<br>hydrotalcite<br>loaded with<br>K <sub>2</sub> CO <sub>3</sub> | Co-<br>precipitation<br>followed by<br>impregnation | Temperature<br>(°C): 65<br>Methanol-<br>to-oil molar<br>ratio: 13:1<br>Catalyst<br>amount<br>(wt%): 2<br>Reaction<br>Time (min):<br>120  | 95.1 | 4   | (Sun et al.,<br>2014)    |
| Soybean oil                      | Bromooctane<br>modified<br>CaO   | Wet<br>impregnation                                 | Temperature<br>(°C)<br>Methanol-<br>to-oil molar<br>ratio:15:1<br>Catalyst<br>amount<br>(wt%):<br>5<br>Reaction<br>Time (min):<br>180    | 99.5 | N/A | (Tang et<br>al., 2013)   |

# Table 2.3 continued

#### 2.1.4 Recent novel CaO based catalysts

In this part, several novel catalysts derived from CaO have been listed in Table 2.4. Chemical stability and controllable structure are important criteria that enable the carbon materials to become efficient supports for catalyst.

Activated carbon (AC) powder was developed by using lotus leaves and then impregnate with CuFe<sub>2</sub>O<sub>4</sub> which resulted in the formation of AC/CuFe<sub>2</sub>O<sub>4</sub> nanoparticles, followed by encapsulation with CaO. FAME yield of 95.63% was obtained under the following experimental conditions: temperature of 65 °C, methanol-to-oil molar ratio of 12:1, reaction time of 4 h and catalyst amount of 3 wt% (Seffati et al, 2019). Activated carbon supported CaO was developed and applied in the transesterification reaction of waste cooking oil. The optimum reaction condition was at 5.5 wt% catalyst amount, 170 °C temperature, 15:1 of methanol-to-oil molar ratio and 2 h and 22 min reaction time. The predicted and experimental FAME content was found to be 80.02% and 77.32%, respectively (Wan et al., 2018).

Lately, the carbon nanotube-family has become a focus of attention to be used as a support . On this subject, carbon nanohorn supporting calcium ferrite was synthesized as a novel catalyst by Sano et al. (2017). The gas injected arc-in-water method was applied to prepare Fe-dispersed CNH (Fe-CNH). Further, to transform Fe nanoparticles dispersed in Fe-CNH to Fe<sub>3</sub>O<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub>, the oxidation treatment in diluted CO<sub>2</sub> in the air was conducted. Finally, co-calcination of Ca(NO<sub>3</sub>)<sub>2</sub> with Fe<sub>3</sub>O<sub>4</sub>-dispersed CNH (Fe<sub>3</sub>O<sub>4</sub>-CNH) or Fe<sub>2</sub>O<sub>3</sub>-dispersed CNH (Fe<sub>2</sub>O<sub>3</sub>-CNH) led to the formation of Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>-CNH. The results revealed that this hybridization avoided the formation of glycerol on the surface of the catalyst and therefore led to its better performance. The ferrimagnetic property of the catalyst could also be recovered by the magnetic field, giving tremendous reusability properties.

Nanomaterials, either natural or man-made having at least one dimension of 100 nm or less, have been extensively applied in the field of chemical catalysis. Gold nanoparticles are considered very important in the catalysis field owing to their exclusive attributes such as oxidation resistance and biocompatibility. In this regard, for the first time, Bet-Moushoul et al. (2016) tested CaO supported gold nanoparticles (AuNPs) catalyst for biodiesel production and these catalysts showed better catalytic activities than the CaO-based catalysts in the transesterification of sunflower oil with methanol. FAME yield of higher than 85 % was obtained after 10 times usage of the catalyst.

Glycerol as a by-product of transesterification reaction has been an oversupplied chemical in biodiesel production. Thus, attempts are conducted towards its removal or decrease. In this regard, no glycerol was found in the biodiesel production by Tang et al. (2016) work using CaO as a catalyst, dimethyl carbonate (DMC), methanol and rapeseed oil. CaO was further modified by ethyl bromoacetate which boosted the dispersion of DMC and triglycerides on the surface of the catalyst due to its ester group. The FAME yield of 98.8% was reported at the following conditions: 0.01% catalyst at the oil/DMC/methanol ratio of 1:1:8 under 65 °C in 6 h.

| Feedstock            | Catalyst                             | Preparation<br>method                     | Optimal reaction condition  | Yield<br>(%) | Catalyst<br>recovery<br>method | Reference              |
|----------------------|--------------------------------------|---|---|--------------|--------------------------------|------------------------|
| Chicken fat          | CuFe <sub>2</sub> O <sub>4</sub> CaO | Impregnation followed<br>by encapsulation | Temperature(°C): 64<br>Methanol/oil molar ratio: 12:1<br>Catalyst amount(wt%): 3<br>Reaction time(min): 240     | 95.63        | N/A                            | (Seffati et al., 2019) |
| Waste cooking<br>oil | Activated carbon<br>supported CaO    | Impregnation                              | Temperature(°C): 170<br>Methanol/oil molar ratio: 15:1<br>Catalyst amount(wt%): 5.5<br>Reaction time (min): 144 | 80.02        | N/A                            | (Wan et al., 2018)     |
|                      |                                      |   |   |              |                                |                        |

 Table 2.4: Recent novel CaO based catalysts in biodiesel production

# Table 2.4 continued

|               |  |   | Table 2.4 continued   |       |  |                             |  |  |  |
|---------------|--|---|---|-------|--|-----------------------------|--|--|--|
| Tricaprylin   | Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub> CNH | <ol> <li>Gas-injected arc-in-<br/>water</li> <li>Oxidation treatment</li> <li>Co-calcination</li> </ol> | Temperature(°C): 64<br>Methanol/oil ratio: 1<br>Catalyst amount (wt%): 0.012<br>Reaction time(min): 180               | 100   | Magnetic<br>field  | (Sano et al., 2017)         |  |  |  |
| Sunflower oil | CaO-supported gold<br>nanoparticles<br>(AuNPs)     | Impregnation  | Temperature(°C): 65<br>Methanol-to-oil molar ratio: 9:1<br>Catalyst amount(wt%): 3<br>Reaction time(min): 180         | 90-97 | Filtration,<br>washing with<br>methanol<br>followed by<br>drying | (Bet-Moushoul et al., 2016) |  |  |  |
| Rapeseed oil  | CaO modified by<br>bromoacetate                    | Impregnation  | Temperature(°C): 65<br>oil/DMC/methanol molar<br>ratio1:1:8<br>Catalyst amount(wt%): 0.01<br>Reaction time (min): 360 | 98.8  | N/A  | (Tang et al., 2016)         |  |  |  |
|               |  |   |   |       |  |                             |  |  |  |

#### 2.1.5 Seashell derived CaO catalysts

Among those aforementioned catalysts, seashell derived CaO catalysts are environmentally friendly and have no detrimental effect on the ecosystem (Ismail et al., 2016). CaO can be obtained from abundant natural CaCO<sub>3</sub> origins including mollusk shells, waste eggshells, ostrich eggshells, golden apple snail shells, capiz shell, meretrix venus shells, crab shell and clam shell (Viriya-Empikul et al., 2010). Therefore, the costeffective CaCO<sub>3</sub> can be obtained from these natural sources and then be converted to CaO by calcination (Roschat et al., 2016). According to Kesić et al. (2016), the application of natural sources of CaO instead of synthetic ones has been introduced as a novel way in catalyst preparation. Some of the seashell-derived CaO studies are shown.

| Type of oil                                      | Catalysts   | Reaction<br>time<br>(min) | Alcohol to<br>oil molar<br>ratio | Catalyst<br>concentrat<br>ion (wt%) | Temperature<br>(°C) | Biodiesel<br>yield<br>(%) | Reference                        |
|--|---|---------------------------|----------------------------------|-------------------------------------|---------------------|---------------------------|----------------------------------|
| Palm oil   | Riversnail shells<br>derived CaO  | 90                        | 12:1                             | 1                                   | 65                  | N/A                       | (Roschat et al., 2016)           |
| Chicken fat                                      | Turritella terebra  | 90                        | 1:12                             | 4                                   | 65                  | 94.03                     | (Mohiddin et al., 2020)          |
| Leather tanning waste                            | Waste capiz shell   | 360                       | 6:1                              | 3                                   | 60                  | 93.4                      | (Yuliana et al., 2020)           |
| Waste cooking oil                                | Waste oyster shell  | 180                       | 9:1                              | 6                                   | 65                  | 87.3                      | (Lin et al., 2020)               |
| <i>Calophyllum inophyllum</i> +waste cooking oil | Donax deltoides   | 129.3                     | 63.8                             | 7.5                                 | 65                  | 96.5                      | (Niju et al., 2019)              |
| Chlorella vulgaris biomass                       | CaO from chicken  | 180                       | 10:1                             | 1.39                                | 70                  | 92.3                      | (Pandit & Fulekar, 2019)         |
| Palm olein oil                                   | CaO from waste<br>shells of mollusk<br>and egg  | 120                       | 18:1                             | 10                                  | 60                  | >90                       | (Viriya-Empikul et al.,<br>2010) |
| Waste frying oil                                 | CaO from<br>Mereterixmereterixs<br>shell  | 180                       | 6.03:1                           | 0.1                                 | 60                  | >89                       | (Yin et al., 2016)               |
| Pongamiapinnata                                  | CaO from<br>eggshell  | 150                       | 8:1                              | 2.5                                 | $65 \pm 0.5$        | 95                        | (Sharma et al., 2010)            |
| Palm oil   | Cao from eggshell   | 120                       | 12:1                             | 0.03                                | 65                  | >98                       | (Cho & Seo, 2010)                |
| Palm oil   | Mixed seashells of<br>Pernaviridis,<br>Amusiumpleuronect<br>es, Anadaragranosa<br>and<br>Meretrixmeretrix | 180                       | 30:1                             | 10                                  | 60                  | 96                        | (Jindapon et al., 2016)          |
| Rapeseed oil                                     | Scallop shell   | 120                       | 12                               | N/A                                 | 60                  | 17                        | (Kouzu et al., 2016)             |

# Table 2.5: Seashell-derived CaO in biodiesel production

| Castor oil                       | Mud clam shell   | 120 | 14:1   | 3      | 60  | 96.7  | (Ismail et al., 2016)             |
|----------------------------------|--|-----|--------|--------|-----|-------|-----------------------------------|
| Palm oil                         | Dolomite and seashells   | 180 | 30:1   | 10     | 60  | >98   | (Jaiyen et al., 2015)             |
| Soybean oil deodorizerdistillate | Duck eggshell  | 80  | 10:1   | 10     | 60  | 94.6  | (Yin et al., 2016)                |
| Palm oil                         | Cyrtopleuracostata seashell  | 10  | 5:1    | 0.05   | 60  | 96.0  | (Indarti, 2016)                   |
| <i>Camelina sativa</i> oil       | Mussel, clam and oyster shells                                     | 120 | 12:1   | 1      | 65  | 95    | (Perea et al., 2016)              |
| Waste cooking oil                | Ba doped CaO<br>from waste shells of<br><i>Turbonillastriatula</i> | 180 | 6:1    | 1      | 65  | >98   | (Boro et al., 2014)               |
| Jatropha curcas                  | Polymedosaerosa<br>seashells                                       | 133 | 5.15:1 | 0.02:1 | 25  | 98.54 | (ANR et al., 2015)                |
| Palm oil                         | Waste obtuse horn shells   | 360 | 12:1   | 5      | N/A | 86.75 | (Lee et al., 2015)                |
| Waste cooking oil                | Scallop shell  | 120 | 6:1    | 5      | 65  | 86    | (Sirisomboonchai et al.,<br>2015) |
| Waste cooking oil                | Egg shells   | 660 | 6:1    | 5.8    | 25  | 97    | (Suwanthai et al., 2016)          |
| Soybean oil                      | Egg shells   | 660 | 6:1    | 5.8    | 25  | 98    | (Suwanthai et al., 2016)          |

# Table 2.5 continued

# Table 2.5 continued

| Microalgae oil   | Waste               | 120  | 150:1 weight | 9  | 65  | 84.11 | (Syazwani et al., 2015) |
|------------------|---------------------|------|--------------|----|-----|-------|-------------------------|
|                  | Cyrtopleuracostata  |      | ratio        |    |     |       |                         |
| Not specified    | Snail shell+KOH     | 210  | 9:1          | 6  | 65  | 96    | (Gupta & Agarwal, 2016) |
| Rubber seeds oil | Waste cockle shells | 2.81 | 15.57:1      | 9  | N/A | 88.06 | (Zamberi et al., 2016)  |
| Neem oil         | Snail shell         | 180  | 9:1          | 10 | 65  | 96    | (Mohan, 2015)           |

Before to a transesterification reaction, calcination was performed to convert  $CaCO_3$  to CaO (Nair et al., 2012). According to Nair et al., (2012), longer calcination time of CaCO<sub>3</sub> resulted in a shorter reaction time of transesterification, which could be an important factor in the transesterification process.

*Turritella terebra* was used in the transesterification of chicken fat with methanol. Biodiesel yield of 94.03% was obtained under the following experimental conditions: 4 wt% of catalyst amount, methanol-to-oil ratio of 1:12 and reaction time of 90 min (Mohiddin et al., 2020).

Yuliana et al. (2020) developed a CaO catalyst from waste capiz shells. They reported that high yield (> 90 %) can be achieved by reusing this catalyst until the third reaction cycle. The optimum reaction conditions for obtaining maximum conversion were 4 h of reaction time, 6:1 of methanol-to-oil molar ratio, 3 wt% catalyst amount and 60 °C of reaction time.

Lin et al. (2020) prepared a potential catalyst by using the waste oyster shell and utilized it with waste cooking oil along with methanol in the transesterification reaction. They reported that 87.3% of FAME yield was obtained at 3 h reaction time with 9:1 methanol-to-oil molar ratio at 65 °C.

*Donax deltoides* shells (DDS) was utilized as a source of CaO for *Calophyllum inophyllum* biodiesel production. Biodiesel conversion of 96.5% was achieved with catalyst concentration of 7.5 wt%, methanol-to-oil volumetric ratio of 63.8% and reaction time of 129.3 min (Niju et al., 2019).

CaO was obtained from chicken eggshell waste and examined as a catalyst for the production of biodiesel from *Chlorella vulgaris* biomass. The optimum reaction conditions were observed at 70 °C, 10:1 of methanol: dry biomass ratio, 1.39% of catalyst loading and 3 h of reaction time, which resulted in 92.03% biodiesel yield (Pandit & Fulekar, 2019).

On the other hand, Roschat et al. (2016) prepared CaO derived from river snail and observed that by increasing the calcination temperature, the FAME conversion yield was also increased. About 95% of biodiesel yield was obtained in the study conducted by Sharma et al. (2010) when 2.5% catalyst obtained from eggshell was used. Cho and Seo (2010) used eggshell, as a CaO source to produce biodiesel using palm oil as a feedstock for transesterification. High biodiesel yield was obtained at an alcohol-to-oil molar ratio of 12:1, and temperature of 65 °C.

Jindapon et al. (2016) used mixed shells of Meretrix meretrix, Amusium pleuronectes, Pernaviridis, Anadaragranosa as a source of CaO, zinc and aluminium compounds via the dissolution precipitation method and subsequently applied it in a transesterification reaction. They found that 10 wt% of the catalyst with 5 cycles of reusability maintained the FAME yield conversion of 96%. They also concluded that higher calcination temperature made the catalyst more active and basic. Shell-derived CaO was compared with limestone derived in terms of efficiency in biodiesel production. The basic-MgCO<sub>3</sub> reagent was added to CaO obtained from a seashell. It was concluded that seashellsderived CaO was less active (Kouzu et al., 2016). Ismail et al. (2016) prepared CaO from mud clamshell and subsequently applied it in transesterification along with castor oil, obtaining a biodiesel yield of 96.7 % under the following experimental conditions: 14:1 of alcohol-to-oil molar ratio, temperature of 60 °C and reaction time of 2 h. The yield percentage remained the same after 5 times the usage of the catalyst. Jaiyen et al., (2015) compared waste mixed seashells and natural dolomitic rock as CaO sources and they found that the catalyst obtained from dolomitic rock led to a faster reaction. Moreover, it was more stable and basic than the seashell derived catalyst. Yin et al. (2016) investigated the potential of duck eggshell as a source of CaO and reported a biodiesel yield of 94.6% when reaction time of 80 min and a temperature of 60 °C was employed. In another study, Yin et al. (2016) employed about 10 wt% of catalyst on soybean oil deodorizer distillate as a feedstock in an experimental reactor. Microwave-assisted transesterification was performed by Indarti (2016), and in a short reaction time of 10 min, palm oil with the methanol-to-oil molar ratio of 5:1 was successfully converted to biodiesel (yield of 96 %). The calcined waste mussel, clam, and oyster shells effectively catalyzed the transesterification of camelina sativa oil (Perea et al., 2016). Nair et al. (2012) and Kouzu et al. (2008) applied CaO with waste frying oil to synthesis FAME, with high biodiesel yield of > 89% and 66% obtained, respectively.

Boro et al. (2014) developed barium (Ba) doped CaO obtained from waste shells of Turbonillastriatula. They reported that alkalinity extremely affected catalyst performance. The optimum reaction conditions for obtaining maximum conversion (>98 %) were 3 h of reaction time, 6:1 of methanol-to-oil molar ratio, 1 wt% of catalyst amount and 65°C reaction time. CaO nanocatalyst from polymedosaerosa seashells was prepared using calcination, hydration, and dehydration method and was compared with the synthetic one (ANR et al., 2015). The transesterification process was performed using Jatropha curcas oil as a non-edible feedstock under the following conditions: reaction time of 133.1 min, at room temperature, and methanol-to-oil ratio of 5.15:1, which led to the biodiesel yield of 98.54 %. In terms of reusability, six cycles out of nine cycles showed consistent catalysis process with the biodiesel yield maintained at an average of 95.8%. In another investigation, CaO from waste obtuse horn shells was used as a catalyst in transesterification (Lee et al., 2015). In terms of reusability, the conversion rate of FAME was more than 70 % after 3 times. These researchers also reported that FAME conversion was 86.75% under 12:1 methanol-to-oil molar ratio, 5 wt% catalyst amount, and reaction time of 6 h. Sirisomboonchai et al. (2015) investigated scallop shell as a potential catalyst. Biodiesel yield of 86% was reported under 6:1 molar ratio of methanol-to-oil, reaction time of 2 h and temperature of 65 °C. They reported that the prepared catalyst can be reused several times, but FAME yield decreased from 86 % to 66 % after the 4th cycle.

Waste cooking oil and soybean oil were used as a feedstock for transesterification which led to the FAME yield of 97 % and 98 %, respectively (Piker et al., 2016). Eggshell was used as a catalyst in this study under the reaction time of 11 h and methanol-to-oil molar ratio of 6:1 at room temperature. In terms of reusability, the catalyst could be used up to 5 cycles for waste cooking oil and 10 cycles for fresh soybean oil transesterification, respectively. FFA of waste cooking oil had a negative effect on the catalyst reusability.

Syazwani et al. (2015) prepared a potential catalyst by using waste cyrtopleura costata and utilized it in the transesterification with microalgae oil along with methanol. They reported that 84.11% of FAME yield was obtained at 1 h reaction time and 150:1 weight ratio of methanol-to-oil at 65 °C. The authors reported that the catalyst was efficient for more than 3 times, showing FAME yields of more than 65%. Gupta and Agarwal (2019) developed a catalyst combining snail shells and KOH. They demonstrated that a biodiesel yield of 96% was achieved when 6 wt% of the catalyst was used with 9:1 of methanolto-oil molar ratio at 65 °C under 3.5 h reaction time. Zamberi et al. (2016) tested the waste cockle shell as a catalyst and reported that 88.06% biodiesel yield was obtained by using rubber seeds oil as the feedstock. The transesterification was carried out under the following conditions: reaction time of 2.81 h, methanol-to-oil molar ratio of 15.57:1 and catalyst amount of 9 wt%. Meanwhile, Mohan (2015) used snail shells as a catalyst in biodiesel production and reported a higher yield compared to when waste cockleshell was used as a catalyst. The biodiesel yield obtained was 96% under conditions of methanolto-oil molar ratio of 9:1, catalyst amount of 10% and at 65 °C. In conclusion, CaO was obtained successfully from seashells source through calcination at high temperature. Calcination temperature and calcination time were the most effective parameters that influenced the CaCO<sub>3</sub> conversion to CO<sub>2</sub>.

#### 2.2 Zeolite as support for biodiesel production

Zeolites are likely the most studied inorganic heterogeneous solid acid catalysts for the generation of biodiesel, as the acidic/basic and textural characteristics of these materials can be tailored according to the desired purpose (Sivasamy et al., 2009). Zeolites are widely used in oil refining and petrochemical production, but one of the frequent implementations of zeolite (inorganic solid catalyst) is for the synthesis of organic compounds such as the ester (Meissner & Rudnik, 2019). They are another group of solids used as popular industrial acid catalysts because of numerous advantages such as better controllability in an undesired impurity phase, lower cost, high catalytic activity, easy handling, reusability and being environmentally benign (Nasrollahzadeh et al., 2015). They are comprised of micro porous crystalline solids of different molecular sizes and shapes which consist of silicon (Si), aluminium (Al) and oxygen (O) (Kumar et al., 2012).

Zeolites have been widely used as carriers in biodiesel production in the past several years (de Vasconcellos et al., 2015; Pratap et al., 2015). Since zeolite with specific pore structure and surface hydrophobicity can be modified according to substrate's polarity and size, consequently only molecules with proper size are allowed to enter the zeolite cavity and diffusing through the pores (Lam et al., 2010). In Table 2.6, several transesterification reactions using zeolites as basic heterogeneous catalysts have been summarized.

| Type of oil  | Type of<br>zeolite | Modified by | Loading<br>method                   | Reaction condition   | Yield<br>(%)  | References            |
|--------------|--------------------|-------------|-------------------------------------|--|---------------|-----------------------|
| Rapeseed oil | MAP                | K and Cs    | Ion exchange                        | Methanol/oil molar<br>ratio: 1:1<br>Catalyst amount<br>(wt%): 5<br>Temperature (°C): 160<br>Reaction Time (min):       | N/A           | (Al-Ani et al., 2019) |
| Waste lard   | ZSM-5              | СаО         | Impregnation                        | N/A<br>Methanol/oil: 30:1<br>Catalyst amount<br>(wt%): 8<br>Temperature (°C): 160<br>Reaction Time<br>(min):1.25       | 90.89         | (Lawan et al., 2019)  |
| Castor oil   | NaY                | Li          | Co<br>precipitation                 | Methanol/oil molar<br>ratio: 18:1<br>Catalyst amount<br>(wt%):3<br>Temperature (°C): 75<br>Reaction time (min):<br>120 | N/A           | ( Li et al., 2019)    |
| Sunflower    | Mordenit<br>Beta X | Na          | Impregnation<br>and ion<br>exchange | Methanol/oil molar<br>ratio: 6<br>Catalyst amount<br>(wt%): 10<br>Temperature (°C): 60<br>Reaction time (min):<br>420  | 93.5–<br>95.1 | (Ramos et al., 2008)  |

# Table 2.6: Biodiesel production using zeolite as a catalyst

# Table 2.6 continued

| Sunflower | ZSM-5                      | Sr   | Impregnation | Methanol/oil mlar<br>ratio: 9:1<br>Catalyst amount<br>(wt%): 6<br>Temperature (°C): 60<br>Reaction time (min):<br>180   | 80.9 | (Feyzi & Khajavi, 2014)        |  |
|-----------|----------------------------|--|--------------|---|------|--------------------------------|--|
| Palm oil  | NaX                        | (Mn <sup>2+</sup> ,Cu <sup>2+</sup> ,<br>CO <sub>2</sub> , Zn <sup>2+</sup> , Ni <sup>2+</sup> ) | Ion exchange | Ethanol/oil molar<br>ratio: 4:1<br>Catalyst amount<br>(wt%): N/A<br>Temperature (°C): 40<br>Reaction Time (min):<br>48  | >94  | (de Vasconcellos et al., 2015) |  |
| Soybean   | Gismondine<br>Na-P zeolite | Cu <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup>   | Ion exchange | Methanol/oil molar<br>ratio: 5:1<br>Catalyst amount<br>(wt%): N/A<br>Temperature (°C): 37<br>Reaction Time (min):<br>72 | 56.2 | (de Vasconcellos et al., 2012) |  |
|           |                            |  |              |   |      |                                |  |

|                |                |                  | Table 2.                 | 6 continued   |      |                             |
|----------------|----------------|------------------|--------------------------|---|------|-----------------------------|
| Soybean        | NaY            | CaO              | Microwave<br>irradiation | Methanol/oil molar<br>ratio: 9<br>Catalyst<br>amount(wt%):30<br>Temperature (°C): 65<br>Reaction Time (min):<br>180       | 95   | (Wu et al., 2013)           |
| Jatrophacurcas | Clinoptilolite | Modified zeolite | Ion exchange             | Methanol/oil molar<br>ratio<br>Catalyst amount<br>(wt%): 5<br>Temperature (°C): 70<br>Reaction Time (min):<br>360         | 96.5 | (Kay & Yasir, 2012)         |
| Jatropha       | NaY            | K                | Impregnation             | Methanol/oil molar<br>ratio: 16:1<br>Catalyst amount<br>(wt.%): 12<br>Temperature (°C): 65<br>Reaction Time (min):<br>180 | 73.4 | (Supamathanon et al., 2011) |

| Palm oil             | NaY                      | КОН              | Impregnation | Methanol/oil molar<br>ratio: N/A<br>Catalyst amount<br>(wt.%): 15<br>Temperature (°C): 60<br>Reaction Time (min):<br>420          | 92.18 | (Intarapong et al., 2012) |
|----------------------|--------------------------|------------------|--------------|---|-------|---------------------------|
| Madhucaindica<br>oil | NaY                      | КОН              | Impregnation | Methanol/oil molar<br>ratio: 9:1<br>Catalyst amount<br>(wt.%): N/A<br>Temperature (°C): 54-<br>74<br>Reaction Time (min):<br>1440 | 98.9  | (Pratap et al., 2015)     |
| Oleic acid           | BEA type<br>Beta zeolite | Modified zeolite | N/A          | Ethanol/oil molar<br>ratio: 20:1<br>Catalyst amount<br>(wt%): 0.167<br>Temperature (°C): 78<br>Reaction Time (min):<br>600        | 70    | (K. Sun et al., 2015)     |

# Table 2.6 continued

| Waste sunflower | zeolite tuft | КОН | Impregnation | Methanol/oil molar     | 96.7 | (Al-Jammal et al., 2016) |
|-----------------|--------------|-----|--------------|------------------------|------|--------------------------|
| oil             |              |     |              | ratio: 11.5:1          |      |                          |
|                 |              |     |              | Catalyst size :33 5 um |      |                          |
|                 |              |     |              | Temperature (°C): 50   |      |                          |
|                 |              |     |              | Reaction Time (min):   |      |                          |
|                 |              |     |              | 120                    |      |                          |

Nano-crystalline gismondine modified via cation exchange was synthesized and then utilized in biofuel production. The catalyst showed high activity and selectivity due to its high surface area (Al Ani et al., 2019). Lawan et al., (2019) loaded CaO on ZSM-5 by using the impregnation method. A FAME yield of 90.89% obtained when 8 wt% of catalyst along with methanol-to-oil ratio of 30:1 were used. Li/NaY zeolite catalysts with different molar ratios of  $Li_2CO_3$  to NaY zeolite were synthesized from fly ash by hydrothermal and microemulsion-assisted co-precipitation method and then applied in the transesterification reaction of castor oil. FAME yield of 98.6% was obtained with the following synthesis conditions: catalyst amount of 3 wt%, ethanol/oil molar ratio of 18:1, reaction temperature of 75 °C and reaction time of 2 h (Li et al., 2019).

Three different zeolites: beta, X and mordenite were used to investigate their respective effects on the methyl ester production. Both impregnation and ion-exchange methods were used to carry out metal incorporation. When Na<sub>2</sub>O was incorporated into the zeolite, the BET surface area and the pore volume were reduced. Transesterification was performed under the following experimental conditions: reaction time of 7 h, zeolite weight of 10%, methanol/oil molar ratio of 6:1, reaction temperature of 60 °C and stirring rate of 500 rpm (Ramos et al., 2008). Feyzi and Khajavi (2014) developed strontium-ZSM-5 nanocatalyst by incipient wetness impregnation method. Transesterification was done to produce biodiesel using sunflower oil as a feedstock under the following conditions: methanol-to-oil molar ratio of 9:1 at 60 °C with mechanical stirring of 500 rpm for 180 min which was considered as the best condition. The zeolite-enzyme complexes were developed as heterogeneous catalysts for the transesterification of oil to FAME by de Vasconcellos et al. (2015) and de Vasconcellos et al. (2012). In the first research, modified zeolite (nanometer-sized by using hydrothermal crystallization) was used as a carrier for lipase immobilization. Zeolite (nanometer-sized) was modified by various transition metals (Cu<sup>2+</sup>, Mn<sup>2+</sup>, CO<sub>2</sub>, Zn<sup>2+</sup>, Ni<sup>2+</sup>) using ion-exchange method.

Lanuginosus enzyme immobilized on nanozeolitic supports ion-exchanged with Ni2 showed the most relevant results. In the second study, Gismondine (P) modified by Cu<sup>2+,</sup>  $Zn^{2+}$ , and Ni<sup>2+</sup> by using an ion-exchange method were used as solid supports for the immobilization of the lipase, Rhizomucormiehei enzyme. NaY, KL, and NaZSM-5 zeolites were modified by CaO via microwave irradiation to be used in the transesterification of soybean oil with methanol. The supported CaO catalyst revealed more catalytic activity than the pure CaO. The enhanced activity was due to the increase of BET values and basicity after loading on NaY zeolite. Among these three zeolites, CaO/NaY showed the best performance. By using the CaO/NaY catalyst with 30 wt% of CaO loading on NaY zeolite, methanol-to-soybean oil molar ratio of 9:1, reaction temperature of 65 °C, reaction time of 3 h and catalyst/oil mass ratio of 3%, a biodiesel yield of 95% was achieved (Wu et al., 2013). Kay and Yasir (2012) prepared modified zeolite by ion-exchange method and used it as a heterogeneous catalyst in transesterification. In this study, Jatropha curcas was utilized as a feedstock to generate biodiesel under the following experimental conditions: 20:1 molar ratio of methanol-tooil, 5 wt% of catalyst amounts, reaction temperature of 70 °C at 6 h reaction time which led to a biodiesel yield of 96.5 %. Modified natural zeolite catalyst revealed a long catalyst lifetime and high activity even after 3 cycles. Jatropha oil was applied in the system for biodiesel production using K supported NaY (K/NaY) catalyst with different K loading. The impregnation method was used to prepare the catalysts. The optimum biodiesel yield of 73.4 % was achieved under 16:1 of methanol-to-oil ratio, 3 h of reaction time and temperature of 65 °C (Supamathanon et al., 2011). Modified zeolite (KOH/NaY) was used as a basic catalyst to perform palm oil transesterification. It was observed that KOH/NaY had strong basic sites and the catalyst complex was enhanced tremendously by increasing the potassium quantity. The FAME yield of 92.18 % was achieved when 15 wt % of the catalyst was used at 60 °C for 7 h (Intarapong et al., 2012). Pratap et al.
(2015) prepared NaY loaded with 5-25% KOH as a basic catalyst. Biodiesel produced from Madhucaindica oil (MI-oil) containing a high percentage of FFAs by transesterification reaction under the following conditions: reaction temperature of 328-348 K and reaction time of 20-100 min. Sun et al. (2015) investigated the potential of BEA type of Beta zeolite as a catalyst in the transesterification of oleic acid and the biodiesel yield of 70% was achieved. The alcohol used in the reaction was ethanol with the molar ratio of 20:1 at a reaction temperature of 78 °C and a reaction time of 10 h. Doyle et al. (2016) prepared modified zeolite Y (low Si/Al ratio) by ion-exchange method from Iraqi kaoline and subsequently investigated its potential as a catalyst in transesterification. About 85% oleic acid conversion was obtained when ethanol-to-oil ratio of 6:1, 6 wt% of catalyst amount, reaction temperature of 70 °C and reaction time of 1 h was applied to the system. Al-Jammal et al. (2016) used the impregnation method to modify the zeolite with the origin of the tuft. The transesterification reaction was done under the following conditions: ethanol-to-oil ratio of 11.5:1, 335 µm catalyst, reaction temperature of 50 °C and reaction time of 2 h where biodiesel yield of 96.7% was obtained. Based on Table 2.5, it is obvious that zeolite, as one of the natural sources, has the potential to be applied in transesterification of different oils such as soybean, jatropha, and other feedstocks in the presence of ethanol or methanol. The surface of zeolite can be modified by certain materials to suit the reaction. Most of these modifications are made to make the zeolite to be more basic as a catalyst. All in all, it can be concluded that the catalytic activity of zeolite can be improved by changing the hydrothermal reaction time and also the zeolite surface.

### 2.3 Biodiesel properties

The application of low-quality biodiesel as a result of the incomplete reaction and the existence of contaminants in a diesel engine may result in different problems in the existing engine such as filter plugging and precipitation of fuel insoluble. Thus, biodiesel is necessary to meet ASTM D6751 and EN 14214 standards as the main assessments of biodiesel product's qualities.

Viscosity as one of the most important fuel properties plays a role in the ease of starting the engine, the spray quality and the size of particles. Kinematic viscosity is a measure of resistance to the flow of a liquid due to internal friction and high kinematic viscosity can result in damage to pumps, filter blockage, poor combustion efficiency and increased emissions. Moreover, the impact of biodiesel viscosity is exacerbated in cold weather because kinematic viscosity is inversely proportional to temperature. Density directly exerts influence on fuel performance, as some of the engine properties such as viscosity and cetane number are strongly connected to density. Further, density has an impact on the quality of atomization and combustion. The acid value is defined as the amount of KOH needed to neutralize the biodiesel acid moieties. A less than 0.5 mg KOH g<sup>-1</sup> acid value is considered safe for usage. Calorific value is defined as the energy content transferred to the chamber during combustion and indicates the available energy in fuel. High calorific value produces greater energy contained in the fuel which is achieved by the means of bomb calorimeter under specific conditions (ASTM D240). The calorific value of biodiesel is higher (39-41 MJ/kg) if compared with other liquid fuels. However, typically, it is lower than petrol (46 MJ/kg), diesel fuel (43 MJ/kg) or oil (42 MJ/kg), but higher than coal (32-37 MJ/kg). Biodiesel has a calorific value of about 12% lower than diesel. This property leads to greater consumer demand for biodiesel to achieve a yield equal to that of diesel (Oliveira & Da Silva, 2013). Oxidation stability is another important property as it may change the physical and chemical properties of fuel which

might damage the motors of vehicles. The flash point is the minimum temperature calculated to a barometric pressure of 101.3 kPa at which the fuel ignition may occur. The flash point is important in connection with the safety precautions involved in fuel handling and storage. Properties of biodiesel produced by conventional catalysts are illustrated in Table 2.7 (Sinha et al., 2008; Wakil et al., 2014; Lin et al., 2009).

| Properties                         | Unit                      | ASTM<br>standards<br>D6751 | En<br>standards<br>14214 | BD by<br>NaOH | BD by<br>NaOH | BD by<br>KOH |
|------------------------------------|---------------------------|----------------------------|--------------------------|---------------|---------------|--------------|
| Kinematic<br>viscosity (40<br>°C)  | $mm^2 s^{-1}$             | 1.9-6.0                    | 3.5-5.0                  | 4.65          | 5.29          | 4.12         |
| Density (15<br>°C)                 | kg m <sup>-3</sup>        | 880                        | 860–900                  | 886           | -             | 884          |
| Acid value                         | mg<br>KOH g <sup>-1</sup> | Max 0.5                    | Max 0.5                  | -             | -             | 0.4          |
| Calorific<br>value                 | MJ kg <sup>-1</sup>       | 35                         | 35                       | -             | 42            | 40           |
| Oxidation<br>stability (110<br>°C) | Н                         | 3                          | 6                        | 1.61          | -             | -            |
| Flash point                        | °C                        | >130                       | >101                     | 174           | 183           | 205          |

Table 2.7: Properties of biodiesel produced by conventional catalysts

Sinha et al. (2008) produced biodiesel using RBO as feedstock and NaOH as a catalyst. The properties of biodiesel met ASTM and EN standards with the exception of viscosity which was 5.29 mm<sup>2</sup> s<sup>-1</sup> and did not meet the EN14214 standards. In another study, RBO was also utilized to produce biodiesel. The oxidation stability of the biodiesel in the research conducted by Wakil et al. (2014) was 1.61 mm<sup>2</sup> s<sup>-1</sup> which was failed both EN standards and ASTM standards. Therefore, the oxidative stability is an extremely important property as this property also provides an estimation of the storage time of biodiesel.

### 2.4 Effect of parameters and their importance for transesterification

Temperature, alcohol-to-oil molar ratio, catalyst amount and reaction time are among the most effective parameters in transesterification reactions and the FAME conversion (Boro et al., 2014). In addition to those mentioned criteria, there are several specific criteria that should be taken into account when using CaO or CaO-derived catalysts. Catalyst reusability, calcination temperature, total basic sites, water content, using of support for the catalyst, and FFA are also among these effective parameters. In the following sections, literatures regarding the effects of these criteria were presented in a systematic manner.

# 2.4.1 Effect of catalyst loading amount

The presence of CaO catalyst leads to the presence of methoxide anion as a nucleophile, which further strikes the electrophilic carbonyl carbon of triglycerides and hence, resulting in the biodiesel molecule generation. According to Dehkordi and Ghasemi (2012), the biodiesel yield was enhanced with increasing the catalyst content from 5 wt% to 10 wt %. On the contrary, it was found that when the catalyst amount was more than 11 wt %, FAME yield would decrease due to the viscosity of reaction slurry (Piker et al., 2016). An excessive amounts of catalyst could result in the difficult of mixing due to high viscosity properties. In another case, it was found that when the catalyst activity (Boro et al., 2014). Following these previous studies, Ismail et al. (2016) concluded that the catalyst amount should be optimized to reach the efficient yield. Thus, finding an optimum catalyst amount is a significant factor that should be paid attention during transesterification.

# 2.4.2 Effect of alcohol/oil ratio

Another important parameter being studied in transesterification process is the alcoholto-oil ratio. Zamberi et al. (2016) reported that the alcohol-to-oil ratio had more effect on biodiesel yield than the catalyst loading amount. An increase of yield from 55.52% to 88.06% was observed when the alcohol-to-oil ratio was increased stepwise, whilst the excessive rise in the alcohol-to-oil ratio did not increase the biodiesel yield. Consequently, a higher amount of alcohol could minimize the interaction of the catalyst and oil resulting in a lower biodiesel yield. From the other point of view, the influence of impurity of source material on catalytic activity and the effect of storage conditions by FTIR, TGA, and DSC were respectively studied by (Kouzu et al., 2016; Piker et al., 2016). In another study, the influence of adding a co-solvent on FAME yield and reaction kinetics was examined. According to Roschat et al. (2016), by applying a suitable cosolvent during the production, the reaction time and biodiesel production expenses could be reduced greatly. Thus, alcohol-to-oil molar ratio could directly impact the biodiesel yield greatly.

# 2.4.3 Effect of reaction time

Sufficient reaction time is required to overcome the energy barrier required by the reactant to transform the oil and methanol into products (esters) (Boro et al., 2014). According to Indarti (2016), fatty acid conversion increased sharply with longer reaction times, reaching a maximum of 96.0%. However, further increasing reaction time resulted in a decrease in FAME yield. This trend could have been due to the solubility of biodiesel in glycerol. As excess reaction time also enhanced the hydrolysis of esters, this would result in a loss of FAME and causing more fatty acids to form soaps.

# 2.4.4 Effect of basicity

As discussed, basicity has an important role in catalyst productivity which can contribute to biodiesel production (Boro et al., 2014). In some studies, basic sites might decrease the BET surface area. To measure the basicity properties of a catalyst, Hammett indicator method can be employed as a reliable measurement. Generally, increased basic sites resulted in an increased yield of biodiesel. Nonetheless, Su et al. (2013) reported that catalyst activity hardly relied on basic sites of the catalyst. This might also be depending on the feedstock as well as the other factors, which requires further examination. Nonetheless, basicity factor of a catalyst should be evaluated a part of the characterisation studies.

### 2.5 Tribological behavior

With the development of technologies and fast modernization, energy generation is not exclusively depending on the fuel properties of biodiesel but greatly relies on lubricity of the biodiesel for wear purpose (Habibullah et al., 2015). As lubricity has an important effect on the quality of fuels to prolong the machine lifespan, it is important to consider the lubricity properties of biodiesel as it protects the moving surface against wear. Good lubricity will also result in reduced energy consumption as it decreases the friction of automotive parts (Mosarof et al., 2016). Lubricity is also very critical for some parts of the automobile including fuel injectors and pumps as they are lubricated by the fuel itself (Zayed et al., 2017). The temperature of the fuel inlet can reach above 60°C which can affect the lubricity leading to damage of fuel injectors and high-pressure fuel pumps (Dehkordi & Ghasemi, 2012). Furthermore, the lubricity of conventional diesel fuel is poor. It has been made known that neat biodiesel presents considerable lubricity than petrodiesel (Haseeb et al., 2010). Many studies have been carried out on the tribological characteristics of various biodiesels. In a study conducted by Habibullah et al. (2015), diesel was reported to have elevated friction coefficient and wear scar diameter of 16% and 40%, respectively. Furthermore, Fazal et al. (2013) examined the tribological attributes of palm oil-based biodiesel and they claimed that the increase of biodiesel concentration resulted in a decrease of wear and friction. When 5% of rapeseed biodiesel was mixed with 95% diesel, the friction coefficient of diesel dropped to 20% (Sulek et al., 2010). Thus, it is critical to discover such an approach which can overcome these concerns caused by lubricity issues. Thus, characterizing the lubricity in terms of wear and friction is an efficient method to check the efficiency of the biodiesel.

#### 2.6 Summary

The literature review highlights the studies showing the potential of CaO-based catalysts including pure, mixed, supported and seashell derived catalysts for biodiesel production. However, it has been found that CaO-based catalysts alone cannot give high catalytic performance for biodiesel generation. In this regard, the interesting catalytic behavior of zeolite makes them suitable carriers to improve catalytic performance.

For improved interaction of catalyst with other reactants including alcohol and oil, a variety of nanoparticles was used instead of conventional catalysts. Through CaO developed by using natural source of CaCO<sub>3</sub>, this approach offers a solution to catalyst recovery and washing costs problems associated with homogeneous catalysts. Significant improvement in terms of environmental conformity can be achieved by replacing the commercial catalysts by naturally-derived catalysts. As it has been discussed previously that seashell derived CaO has such characteristics to be used as a catalyst for biodiesel production, the environmental hazards can be reduced by replacing the homogeneous catalysts with heterogeneous catalysts. In this regard, the catalytic stability and tribological compatibility of a variety of biodiesel and diesel blends is required to be investigated. From the literature study, several sources have been reported for Ca(OCH<sub>3</sub>)<sub>2</sub>

development such as calcium granules, quicklime and synthetic catalysts. However, to the best of the authors' knowledge, Na-A-Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst from seashell has never been reported for the transesterification catalysis of biodiesel production. Therefore, the purpose of this study was to determine the effects of seashell derived  $Ca(OCH_3)_2$  on biodiesel yield from RBO as a feedstock.

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# **CHAPTER 3: RESEARCH METHODOLOGY**

This chapter outlines the different materials and experimental methods with their detailed sample preparation techniques, procedures, and testing conditions. It includes details about the development of *C. brunneus* shells derived catalysts as well as the steps used to convert the seashell to the most effective form of catalyst. The test set-ups, working principles, and illustrations of the surface analysis tools such as Brunauer-Emmett-Teller method (BET), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and temperature-programmed desorption of carbon dioxide (TPD-CO<sub>2</sub>) constitute a major part of this chapter.

In this chapter, the transesterification reaction was explained and illustrated. In order to evaluate the properties of the generated biodiesel, the adopted procedures and the test equipment were exploited for viscosity, acidity, density, oxidation stability, flash point, and calorific value to evaluate the produced biodiesel's fuel properties. Furthermore, the procedure for catalyst reusability tests and the catalyst recovery was discussed accordingly. Tribo-testing procedures in controlled laboratory conditions were mentioned with illustrations of testing rigs.

### **3.1 Preparation of materials**

RBO was purchased from Scienfield Sdn. Bhd, Selangor, Malaysia. Laboratory-grade chemicals included methanol (> 99 % pure) and distilled deionized water were purchased from Labchem Sdn Bhd, Kuala Lumpur, Malaysia. Commercial CaO (Sigma) was used as a reference catalyst (molar mass of 56.08 g mol<sup>-1</sup>, the boiling point of 2850 °C, and a density of 3.3 g /cm<sup>3</sup> at 25 °C). Zeolite was purchased from Sigma-Aldrich, Singapore, and nonadecanoic acid methyl ester and FAME mix (C4-C24) were purchased from IT Tech Research (M) Sdn. Bhd. Selangor, Malaysia.

# 3.2 Preparation of C. *brunneus* shell derived catalysts

#### 3.2.1 Calcination

CaCO<sub>3</sub> was converted to the active form of CaO through calcination. The calcination temperature and reaction temperature were set based on literature. The conversion of CaCO<sub>3</sub> to CaO could be performed at a calcination temperature of 900 °C. Some of the previous studies which used the temperature of 900 °C for the conversion of CaCO<sub>3</sub> to CaO and the temperature of 65 °C for the transesterification reaction were listed in Table 3.1.

| Catalyst                           | Calcination | Transesterification | FAME yield | References     |
|------------------------------------|-------------|---------------------|------------|----------------|
|                                    | (°C)        | (°C)                | (%)        |                |
| Ca, Zn, and Al                     | 900         | 65                  | 99.9       | (Jindapon et   |
| mixed compounds                    |             |                     |            | al., 2016)     |
| CaO-La <sub>2</sub> O <sub>3</sub> | 900         | 65                  | 86.51      | (Taufiq-Yap    |
|                                    |             |                     |            | et al., 2014)  |
| ZSM-5 supported                    | 900         | 65                  | 95.40      | (Zein et al.,  |
| CaO                                |             |                     |            | 2016)          |
| Cao from                           | 900         | 65                  | >98        | (Cho & Seo,    |
| eggshell                           |             |                     |            | 2010)          |
| Snail shell                        | 900         | 65                  | 96         | (Mohan,        |
|                                    |             |                     |            | 2015)          |
| Mussel, clam and                   | 900         | 65                  | 95         | (Perea et al., |
| oyster shells                      |             |                     |            | 2016)          |

Table 3.1: Some of the literature using the calcination temperature of 900°C and a reaction temperature of 65 °C

The heating rate of 20 °C/min was used for the decomposition of *C. brunneus* shell into the CaO. As higher heating rate, this would elevate the temperature of the reaction faster and hence, decrease the time taken for the reaction to complete. Therefore, the selection of suitable heating rates is rather critical for the calcination process.

# 3.2.2 Catalyst preparation

*C. brunneus* shells were collected from a local supplier at the Central market, Kuala Lumpur, Malaysia. CaO nanocatalyst was produced from the shells using calcination,

hydration, and dehydration (ANR et al., 2015). In brief, about 500 g of *C. brunneus* shell was washed with an aqueous solution of sulfuric acid (2 M) to remove the dirt and debris, rinsed in distilled water, and air-dried at 70 °C for 72 h. *C. brunneus* shells were crushed by mortar and pestle, and then ground using a PM 100 Planetary ball mill (using the lead balls) (Retsch, Germany) at 200 rpm for 2 h followed by passing it through an 80-micrometer ( $\mu$ m) mesh sieve (Retsch, Germany). The powdered shell was then calcinated in a furnace (Nabertherm, Germany) at 900 °C for 2.5 h. The decomposition of shell powder to CaO and carbon dioxide occurs via the following reaction:

$$CaCO_3 \stackrel{900^{\circ}C}{\to} CaO + CO_2 \tag{3.1}$$

*C. brunneus*-derived CaO was refluxed in the water at 60 °C for 24 h, the solid particles were filtered using a filter paper and then dried in an oven at 70 °C for 24 h. The resulting dry powder was ground in a PM 100 Planetary ball mill at 200 rpm for 3 h and dehydrated by calcination at different temperatures (800, 900, 1000, and 1100 °C) for 3 h to convert from the hydroxide form to the oxide form. The resulting CaO was then stored in a desiccator until required to prevent a decrease in catalyst activity from exposure to moisture. Commercial CaO was calcined at 900 °C for 2 h to eliminate any contamination from atmospheric carbonates and hydroxides, and the resulting catalyst was used as a reference. In order to provide an overview of this research study, the sequential details of major research activities are listed in the flow chart (Figure 3.1).



Figure 3.1: Flow diagram for the preparation of pure catalyst

In the following step of the research, a supported CaO catalyst (hybrid catalyst) was developed to compare with the pure catalyst. To produce the hybrid catalyst, first, the  $Ca(OCH_3)_2$  was synthesized by a direct reaction of CaO with methanol following a technique reported by Suwanthai et al (Eq. 2) (Suwanthai et al., 2016).

$$Ca0 + 2CH_3OH \rightarrow Ca(OH_3)_2 + H_2O \tag{3.2}$$

About 2 g of Ca(OCH<sub>3</sub>)<sub>2</sub> was added to 100 ml distilled water to prepare an aqueous solution. Afterwards, this solution was added to 4 g of zeolite and mixed vigorously using the wet impregnation method for 2 h at 65 °C. The catalyst was then filtered and dried in an oven for 24 h. An overview of this research study is illustrated in the flow chart, as shown in Figure 3.2.



Figure 3.2: Flow diagram for the preparation of hybrid catalyst

# 3.3 Characterization of the C. *brunneus* shell derived catalysts

Characterization of the catalysts was performed to identify and assess the physicochemical properties of the produced catalysts. Numerous methods applied in this study were summarized in the following section.

# 3.3.1 Scanning electron microscopy (SEM and FESEM)

Scanning electron microscopy (SEM) was utilized to study the morphology of worn surfaces in this work which helped in understanding the lubrication mechanisms engaged by biodiesel samples. The equipment used for the SEM analysis was a scanning electron microscope. The Field emission scanning electron microscopy (FESEM) was conducted to investigate the surface structure of both catalysts after development from seashells to confirm their structure, as well as the surface changes after reusability. FESEM functions by focusing electron beam passing across the sample surface. It could be used at different magnifications and high resolution. Qualitative information regarding the morphology of the samples can be obtained. FESEM (model ZEISS AURIGA) was used in studying the morphology of the catalysts.

# 3.3.2 Energy-dispersive X-ray spectroscopy (EDX)

EDX was used to measure the Al/Si ratio of the zeolite. Furthermore, EDX was used to investigate the chemical composition of the wear scars created on the balls. The working principle of this instrument is based on the emission of X-rays. By examining the energy spectra of X-rays emitted from the sample, the elemental composition of the sample was determined. The elemental information by EDX stems from approximately the first 1  $\mu$ m below the surface of the tested sample.

# 3.3.3 Transmission electron microscopy (TEM)

TEM utilizes energetic electrons to provide morphologic, compositional and crystallographic information on samples. In this study, the morphology and size of the catalysts were examined by TEM. Catalyst morphology was visualized using TEM (Libra 120, ZEISS, Germany).

#### **3.3.4 Brunauer–Emmett–Teller (BET) surface analyzer**

BET surface analyser (micromeritics, TriStar II) was used to measure the surface area, pore volume and pore diameter of the catalysts. Before any measurement, the sample was degassed in a vacuum at temperatures in between 50 to 60 °C to remove water and other contaminants. The highest temperature that does not damage the sample's structure is

usually chosen to shorten the degassing time. International Union of Pure and Applied Chemistry (IUPAC) recommends that samples should be degassed for at least 16 h to ensure that unwanted vapours and gases are removed from the surface of the sample. Generally, samples tolerating higher temperatures without structural changes have shorter degassing times. A minimum of 0.5 g of the sample was required for the BET to the surface area determination. Samples were situated in a glass cell (Hwang & Barron, 2011) and placed in the BET analyzer chamber. The surface area of the catalysts including CaO, reference CaO, Ca(OCH<sub>3</sub>)<sub>2</sub>, zeolite Na-A, and hybrid catalyst were studied using the BET (micromeritics, TriStar II).

# **3.3.5** Fourier transform infrared spectroscopy (FTIR)

The chemical structure of both developed catalysts, the RBO and biodiesel were examined by FTIR from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> using the FTIR spectrometer (Shimadzu FTIR- 8300). FTIR is the preferred method of infrared spectroscopy. When IR radiation passes through a sample, some radiation is absorbed by the sample and some passes through the sample. The resulting signal at the detector was a spectrum representing a molecular 'fingerprint' of the sample. The absorbance spectra for lubricant samples were analyzed for functional groups, and related absorbance peaks were determined.

### 3.3.6 X-ray diffraction (XRD)

The crystalline properties of the catalyst were examined by X-ray diffraction (XRD) test using a Shimadzu 6000 X-ray machine with nickel-filtered Cu K $\alpha$  ( $\lambda$  = 1.542 Å) radiation. XRD analysis was carried out at a temperature range of 20–80 °C at a rate of 2 °C min<sup>-1</sup> and a scanning angle of 20. Furthermore, the crystalline size of Ca(OCH<sub>3</sub>)<sub>2</sub>, zeolite, and the hybrid catalyst was determined from half of the width for a (200) diffraction peak using the Scherrer equation, equation below:

$$d = \frac{K\lambda}{\beta\cos\theta} \tag{3.3}$$

where K is the Scherer's constant (shape factor) which ranges from 0.9 to 1.0;  $\lambda$  is 1.5418 Å, which is the wavelength of the X-Ray radiation source;  $\beta$ 1/2 is the width of the XRD peak at half height; and  $\theta$  is the Bragg angle.

### **3.3.7 Temperature-programmed desorption (TPD)**

Temperature-programmed desorption of carbon dioxide (TPD-CO<sub>2</sub>) was evaluated by using temperature programmed desorption (TPD) (Thermo Electron, U.S). This test evaluated the basicity of the hybrid catalyst. TPD experiments were carried out in a flow apparatus with helium as carrier gas ( $30 \text{ cm}^3 \text{ min}^{-1}$ ) and at a pressure level of 1000 hPa.

### 3.4 Transesterification of RBO using the *C. brunneus*-derived catalysts

The most prevalent method to generate biodiesel is the transesterification of oil triglycerides using alcohol and catalyst. The general equation of this reaction is shown in Figure 3.3. CaO- and Ca(OCH<sub>3</sub>)<sub>2</sub>-based catalysts were applied in the transesterification reaction of RBO and methanol. Transesterification of RBO was conducted in a three-neck, round-bottom flask equipped with a thermometer, condenser and magnetic heating mantle. The mixture was then incubated at 65 °C for 2 h with continuous stirring at 150 rpm; the reaction temperature was selected based upon the observation in the literatures (Perea et al., 2016; Roschat et al., 2016). The product mixture was then allowed to settle under gravity overnight. Where required, catalyst separation was undertaken using centrifugation (Hettich ROTOFIX 46, Germany) at 2000 rpm for 7 min, followed by mechanical filtration. Methanol was removed by vacuum evaporator (IKA RV 10 Control, USA). Finally, the biodiesel was washed with distilled water.



Figure 3.3: The transesterification reaction (Degfie et al., 2019)

Gas chromatography (Agilent 7890, California, USA) equipped with FID (flame ionization detector) was used to determine the FAME yield. The FAME yield was calculated using the following equation:

$$FAME \ conversion(\%) = \frac{\sum A}{A_{EI}} \times \frac{Wt_{EI}}{m} \times 100\%$$
(3.4)

Where  $\sum$  A is the area of all peaks in the chromatogram (C<sub>6</sub>-C<sub>24:1</sub>), A<sub>EI</sub> is the area under the curve for the internal standard (C<sub>19</sub>), Wt<sub>EI</sub> is the weight of the C<sub>19</sub> internal standard (mg) and m is the sample weight (mg).

### 3.5 Biodiesel washing

The biodiesel was washed with distilled water several times to remove the glycerol. In this process, 50% (v/v) of distilled water at 50 °C was sprayed over the surface of the esters and stirred gently. The lower layer was discarded, and the upper layer was entered into a flask. The biodiesel was dried using CaCl<sub>2</sub> anhydrous and Na<sub>2</sub>SO<sub>4</sub> for 24 h and then 3 h, respectively. Finally, the biodiesel was further purified using a rotary evaporator with a vacuum pump at 60 °C for 1 h to remove the excess water from biodiesel.

# **3.6** Impact of process conditions on transesterification

The use of different loadings of catalysts (5, 10, 15 and 20 wt%), methanol-to-oil molar ratios (10:1, 15:1, 20:1 and 25:1), catalyst loading amounts (0.5, 1.5, 2.5 and 3.5 wt% based on the oil weight) and reaction times (30, 60, 120 and 150 min) and their effects on the reaction yield were studied in this research work.

### **3.7** Fuel properties analysis

The fuel properties of biodiesel produced by *C. brunneus* shell derived catalysts such as viscosity, calorific value, acid value, density, oxidation stability and flash point were tested and then compared with ASTM D6751 and EN 14214 standards, which are the common international standards referred to for the utilization of biodiesel in the engine. All experiment samples were in triplicates unless otherwise stated.

### 3.7.1 Viscosity

The kinematic viscosity was measured using ASTM D2270 at 15 °C and 40 °C. The experiments were carried out using an Anton Paar's Stabinger Viscometer<sup>TM</sup> SVM<sup>TM</sup> 3000. The test apparatus has a reproducibility of 0.35% and a repeatability of 0.1% for the viscosity measurements.

# 3.7.2 Density

DM40 densitometer was used to measure density. Approximately 2-3 ml of biodiesel sample was pushed into the cell by using a syringe. During the measurement, the current repeated deviation for density can be viewed. If the result of the first repetition is within limits for the density, the state changes to 'result valid', and the display will be frozen for data recording.

# 3.7.3 Acid value

3 g of oil/ biodiesel and 60 ml ethanol was poured into a volumetric bottle and titrated potentiometrically with alcoholic KOH using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings are plotted against the respective volumes of titrating solution and the end points are taken only at well-defined inflections in the resulting curve. When no definite inflections are obtained and for used oils, end points are taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions.

#### 3.7.4 Calorific value

The calorific value was measured according to the ASTM D240 standard. The equipment used to measure the calorific value was 6100 calorimeter (Parr). The Parr 6100 jacket calorimeter functioned in a location where it was not subjected to air draft and fluctuating temperature. The optimum frequency for checking the 6100 calorimeters was at least every tenth test. After the tenth test, it needed to be re-calibrated so that the precision classification could be taken as 0.1%. About 0.05 g of biodiesel was used to measure the calorific value.

# 3.7.5 Oxidation stability

The oxidation stability of biodiesel was measured using the EN14112 in Rancimat equipment model 743 (Metrohm, Herisau, Switzerland), which was operated under the following conditions: airflow rate of 10 l/h and a total of 3 g biodiesel sample. The sample was placed at a heating block with the temperature set from 100 to 120 °C, the vapors discharged to a flask containing 0.06 l of distilled water and the conductivity change was recorded by a computer simultaneously. The induction periods of biodiesel samples with

antioxidant concentrations from 0 to 10,000 ppm were determined by using Rancimat method.

# 3.7.6 Flash point

The flash point is the lowest liquid temperature at which the application of the ignition source causes the vapor of the sample to ignite. The flash point test was conducted according to ASTM D93, using a Pensky Martens flash point tester NPM 440 ASTM D93-88. 75 ml biodiesel sample was heated at a slow constant rate with continual stirring in a brass test cup off specified dimensions. An ignition source was directed into the test cup at regular intervals with simultaneous interruptions of the stirring.

The equipments and test methods were listed in Table 3.2. The figures of the equipments were also shown in Figure 3.4(A)-(F); A) viscometer, B) density meter, C) G20 compact titrator (acid value tester), D) calorimeter, E) 873 biodiesel rancimat, F) flash point tester.

| Properties          | Equipment              | Test method | Accuracy                           |  |
|---------------------|------------------------|-------------|------------------------------------|--|
| Kinematic viscosity | SVM 3000 viscometer    | D 445       | $\pm 0.01 \text{ mm}^{2}/\text{s}$ |  |
|                     | (Anton Paar)           |             |                                    |  |
| Density             | DM40 density meter     | D 127       | $\pm 0.01 \text{ kg/m}^3$          |  |
|                     | (Mettler Toledo)       |             |                                    |  |
| Acid value          | G20 compact titrator   | D 664       | $\pm$ 0.001 mg KOH/g               |  |
|                     | (Mettler Toledo)       |             |                                    |  |
| Calorific value     | 6100 calorimeter       | D 240       | ± 0.001 MJ/kg                      |  |
|                     | (Parr)                 |             |                                    |  |
| Oxidation stability | 873 biodiesel rancimat | EN 14112    | $\pm 0.01$ h                       |  |
|                     | (Metrohm)              |             |                                    |  |
| Flash point         | Pensky Martens NPM     | D 93        | ± 0.1 °C                           |  |
|                     | 440                    |             |                                    |  |

Table 3.2: List of equipment for physicochemical properties tests



Figure 3.4: Equipment used to test the biodiesel properties

# **3.8** Tribological assessment of biodiesel

The four-ball wear tester is the leading wear tester implemented by the oil industry for studying the lubricant chemistry (Zulkifli et al., 2013). In this study, four ball wear machine was used to investigate the friction and wear characteristics of RBO based biodiesel (see Figure 3.5). The experiment parameters in the current research were set according to ASTM D4172 standards. Details of the test conditions were reported in Table 3.3. RBOB was mixed with diesel to produce biodiesel blends. Three types of biodiesel blends were prepared, including RBOB10 (10% RBOB + 90% diesel), RBOB30 (30% RBOB + 70% diesel), RBOB50 (50% RBOB + 50% diesel), RBOB100 (100%RBOB + 0 diesel) and pure diesel RBOB0 (100% diesel). The mixture of biodiesel and diesel was prepared accurately using a magnetic stirrer at room temperature for 1 h. The fuel properties of the RBO-based biodiesels were tested and compared with the parameters set in both ASTM D6751 and EN 14214 biodiesel standards. As it could be observed from the schematic diagram of the four-ball wear machine, three balls were held in a steel cup (in a fixed position) and one ball in the upper chuck (rotating one). Approximately 10 ml of desired fuel was poured into the steel cup to cover the lower three balls.

| Test parameters   | Unit | Value              |
|-------------------|------|--------------------|
| Applied load      | kg   | 40                 |
| Rotation          | rpm  | 1200               |
| Fuel temperature  | °C   | 75                 |
| Test duration     | S    | 3600               |
| Balls diameter    | mm   | 12.7               |
| Surface roughness | μm   | 0.04               |
| Material          | -    | Chrome alloy steel |
| Hardness          | -    | 62                 |

Table 3.3: Conditions for the four-ball wear test



Figure 3.5: Schematic diagram of four ball tester

A computer was connected to the four-ball machine to record the friction torque. The conversion of friction torque to the friction coefficient was done through the following equation:

Coefficient of friction (
$$\mu$$
) =  $\frac{T\sqrt{6}}{3Wr}$  (3.5)

Where T is frictional torque (kg.mm), W is the applied load (kg) and r is the perpendicular distance from the rotational axis to the center of the contact surface of balls which is 3.67(mm). In order to measure the wear scar diameter of the balls, an optical microscope with a resolution of 0.01 mm (as per ASTM D4172) was used. Toluene was used to clean the ball bearing, followed by wiping using a tissue. After spotting the wear scar, the balls were placed on the stage with wear scar facing upwards. Acceptable magnification lens and focus were adjusted until the clear image was shown on the computer screen. The image was then captured and saved. The wear scar diameter from

the image was measured by using the software available in the computer. All these procedures were repeated for one bottom ball bearing from each test.

# 3.9 Reusability analysis of *C. brunneus*-derived catalysts

After each reaction cycle, the catalyst was separated from the product mixture by centrifugation and vacuum filtration. The catalyst was then washed five times with n-hexane (30 ml x 5), dried at 70 °C using the oven for 2 days, and then recalcined at 800 °C for 3 h before being used in the next reaction cycle.

FESEM was undertaken to assess any changes in the morphology of the catalysts after each reaction. Catalyst stability and capacity for recycling are two critical factors in the operation of commercial transesterification processes (ANR et al., 2015). *C. brunneus*derived CaO and Ca(OCH<sub>3</sub>)<sub>2</sub> catalysts were prepared using a calcination temperature of 1100 °C in seven transesterification reaction cycles. In order to evaluate the catalyst leaching in each cycle, AAS was used to measure the Ca content of the biodiesel.

# **CHAPTER 4: RESULTS AND DISCUSSION**

This chapter is dedicated to the results and discussions based upon findings of experimental work on the synthesis of pure and hybrid catalysts as well as their application in RBO-based biodiesel production and reusability performance. This chapter shows critical data on the investigation of *C. brunneus* shell in terms of surface area, pore volume, pore diameter, size and morphology. Results obtained in the form of FESEM micrographs, EDX spectra, FTIR spectra and surface topography were critically discussed to understand and report the potential mechanisms for the as-produced seashell derived catalysts. The seashell derived catalyst was also investigated in comparison to the reference catalyst.

In the next stage of experimentation, the compatibility of the *C. brunneus* shell as a catalyst in biodiesel production was investigated in terms of FAME yield by varying different loadings of catalyst, methanol-to-oil molar ratios, catalyst loading amounts and reaction times. The produced biodiesels were characterized for their fuel properties in terms of viscosity, acidity, calorific value, oxidation stability and flash point along with friction behavior and wear volume characteristics. The reusability and stability analysis of the catalysts were also covered in the final section of the chapter by correlating the cycle study with the changes of the catalysts.

#### 4.1 Characterization analysis of C. *brunneus* seashell derived catalysts

#### 4.1.1 FESEM analysis

Scanning microscopy has widely been used for the evaluation of the topology of catalyst surfaces. The physical and chemical properties of CaO nanocatalysts prepared from calcined *C. brunneus* shell were determined and compared to that of CaO prepared from commercial CaO. FESEM analysis (Figure 4.1) confirmed that calcination of CaO nanocatalyst prepared from *C. brunneus* shell changed the morphology of the CaO from

irregular shapes to a cluster of well-developed cubic crystal with obvious edges. Thus, it can be concluded that CaCO<sub>3</sub> converted to CaO successfully. The morphology of seashell derived CaO was similar to the morphology reported by Yin et al. (2016). In another study using waste shells of *T striatula*, a spherical structure of CaO with a non-uniform size was observed (Boro et al., 2014). Eggshells and crab shells were also used as a source of CaO. An irregular and heterogeneous distribution of crystal structure, and homogeneous distribution of well-developed pores were observed for the natural and calcined eggshells respectively. On the other hand, semispherical porous particles with different diameters, and particles with a larger pore structure were detected for uncalcined and calcined crab shell respectively (Correia et al., 2014). Furthermore, spongy and porous structure was noticed when CaCO<sub>3</sub> was converted to CaO indicating highly adsorbent surfaces. Uniform distribution of miniature agglomerates with irregular shapes indicated the formation of CaO upon calcination (Ho et al., 2014).



Figure 4.1: FESEM micrographs of A) CaO and B) CaCO<sub>3</sub> at 5.00 KX magnification, EHT of 1 KV and WD of 4.5 mm

The microscopic features of Ca(OCH<sub>3</sub>)<sub>2</sub>, zeolite and supported-Ca(OCH<sub>3</sub>)<sub>2</sub> were shown in Figure 4.2. As observed from Figure 4.2-A, the Ca(OCH<sub>3</sub>)<sub>2</sub> particles in the form of thin plates resembling the topology reported by Suwanthai et al. (2016) and Masood et al. (2012). However, this was different from the Ca(OCH<sub>3</sub>)<sub>2</sub> particles in the form of conglomeration which have been reported by (Liu et al., 2008). Particulate structures of Na-A zeolite from this study (Figure 4.2-B) were mostly in cubic which was in accordance with the morphology reported by Zayed et al. (2017) and Jha & Singh, (2016).

Thus, FESEM analysis confirmed that  $Ca(OCH_3)_2$  particles were dispersed on the surface of the zeolite. However, the quadrate crystal feature of the hybrid catalyst was not

changed obviously. It is indicated that zeolite modified by  $Ca(OCH_3)_2$  was not changed in terms of structure. A comparison of the two catalysts indicated that the morphology of CaO changed from a well cubic structure to thin plates. Thus, the conversion of CaO to the Ca(OCH\_3)\_2 was considered to be successful. Moreover, the structure of the Ca(OCH\_3)\_2 can be seen on the surface of zeolite indicating that it has been loaded.



Figure 4.2: FESEM micrographs of A) Ca(OH<sub>3</sub>)<sub>2</sub> B) zeolite C) hybrid catalyst at 10.00 KX magnification, EHT of 1 KV and WD of 4.5 mm

#### 4.1.2 **TEM analysis**

Figure 4.3 reveals the morphology of both pure and hybrid catalysts in a nanoscopic view. From the analysis, the majority of the CaO nanocatalyst prepared from calcined C. brunneus shell consisted of spherical particles or agglomerates of spherical particles with an average diameter of 66.2 nm. CaO derived from Polymedosa erosa (P. erosa) seashells with 66±3 nm diameter was reported by ANR et al. (2015). For small particle size of catalyst, the chemical reaction rate is increased since the diffusion forces would be able to carry the product away from the surface of the catalyst particle with better ease. The active surface, as the most important property of catalysts, increases when the catalyst size is decreased. So, with smaller particles, the surface to volume ratio and the reaction efficiency is greater and the required amount of catalyst for reaction decreases (Bankovic et al., 2017). Catalysts with a lower particle size and higher surface area accelerate the reaction rates. Other studies confirmed the spherical shape of CaO nanoparticles. The spherical morphology of CaO was validated after the conversion of Ca(OH)<sub>2</sub> to CaO (Mirghiasi et al. 2014). Further, Habte et al. (2019) reported the spherical morphology of nano CaO from waste eggshell by the sol-gel method which possessed high CaO mineral and a clay mineral. As evidenced by the findings, the morphology of catalysts would greatly affect its catalytic performance. The spherical morphology is significantly less sensitive to impact and friction. The TEM image of the hybrid catalyst showed the cubic structure of zeolite confirming the successful formation of a well-organized zeolitic framework. The cubic structure of Na-A zeolite was also confirmed by Selim et al. (2017). The structure of Ca(OCH<sub>3</sub>)<sub>2</sub> also could be seen as agglomerates on the surface of the zeolite. The structure of zeolite did not change after the loading, manifesting that catalyst loading did not affect the zeolite morphology.



Figure 4.3: TEM images of A) pure catalyst B) hybrid catalyst

# 4.1.3 **BET analysis**

The surface area, total pore volume, and average pore diameter of the calcined CaO, commercial CaO, Ca(OCH<sub>3</sub>)<sub>2</sub>, and hybrid catalyst were measured. By comparing the calcined seashell and commercial CaO, it was found out that the surface area per unit mass, average pore diameter, and pore volume of calcined *C. brunneus* shell was greater than that of calcined commercial CaO. It shows that the naturally prepared CaO manifests bigger surface area for catalysis; hence, when reactant particles collide, they have a greater chance of reacting with each other. But during a reaction, not all of the reactions would take place on the catalyst itself. Only those particles or reactants in contact with the

catalyst could be catalyzed. The average pore diameters for each nanocatalyst were between 2 and 50 nm, indicating that both catalysts were mesoporous. In addition, it confirms its suitability as a catalyst for biodiesel production (ANR et al., 2015).

The BET surface area of Ca(OCH<sub>3</sub>)<sub>2</sub> was found to be 3.30 m<sup>2</sup>/g. Upon impregnation with zeolite, an increase of the surface area to 84.67 m<sup>2</sup>/g was observed because the surface area of zeolite was considerably higher than that of Ca(OCH<sub>3</sub>)<sub>2</sub> (150.48 m<sup>2</sup>/g). Therefore, the newly synthesized catalyst was expected to improve the transesterification reaction by increasing the accessibility of the basic sites. The average pore volume and average pore diameter of Ca(OCH<sub>3</sub>)<sub>2</sub> were 0.01 cm<sup>3</sup>/g and 70.76 Å, respectively, while for the hybrid catalyst, these parameters were 0.41 cm<sup>3</sup>/g and 195.27 Å, respectively.

Reportedly, the higher average pore diameter decreases the diffusion limitations of reactant molecules. Consequently, the reaction elements could penetrate the catalyst, and more of the active sites would be available to the reactants during the transesterification reaction. Zeolites can accommodate new cations (mainly Na, K, Mg, and Ca), water molecules and even small organic molecules (Jha & Singh, 2016). However, in this study, as the size of the Ca(OCH<sub>3</sub>)<sub>2</sub> was found to be bigger than the average pore diameter of the zeolite, the Ca(OCH<sub>3</sub>)<sub>2</sub> particles should have been dispersed on both internal and external surfaces of the zeolite.

BET analysis indicated that the specific surface areas of zeolite decreased from 150.48 to 84.67 g/m<sup>2</sup>. The decrease in the surface area of zeolite is attributed to the incorporation of Ca(OCH<sub>3</sub>)<sub>2</sub> onto the zeolite surface. Many studies have confirmed that catalysts with a lower particle size and higher surface area accelerate reaction rates, due to an increased number of molecules that have the minimum required energy for the reaction to occur (ANR et al., 2015). Furthermore, the average pore diameter and pore volume decreased after loading the Ca(OCH<sub>3</sub>)<sub>2</sub> on the zeolite. This behavior was expected and could be explained by the presence of Ca(OCH<sub>3</sub>)<sub>2</sub> on the pore walls. However, the pores of the

zeolite were partially blocked by Ca(OCH<sub>3</sub>)<sub>2</sub>. The BET result of this study was in agreement with a study conducted by Wu et al. (2013) on the same subject of using zeolite as support. The BET values also decreased after loading CaO on the support; the specific surface areas of NaY zeolites decreased from 732 m<sup>2</sup>/g to 483 m<sup>2</sup>/g after loading 30 wt% CaO, while the total pore volume was reduced from 0.29 ml/g to 0.18 ml/g before loading. The BET values of Ba doped waste shells of Turbonilla striatula was higher than the unsupported catalyst itself. Authors reported that the surface area of catalyst increased from 8.359 m<sup>2</sup>/g to 11.56 m<sup>2</sup>/g after Ba loading. The surface area of catalyst decreased with increasing the loading amount of Ba. This decrease is associated to the addition of Ba on the CaO surface (Boro et al., 2014). In another study using quail eggshell and chicken eggshell, the surface area of 10  $m^2/g$  and pore volume of 0.15 ml/g were reported for eggshell, while the surface area of 13  $m^2/g$  and pore volume of 0.11 ml/g were reported for the quail eggshell (Cho & Seo, 2010). The surface area, total pore volume of Ca(OCH<sub>3</sub>)<sub>2</sub> reported in another study was found to be 38.6 m<sup>2</sup>/g and 0.24 ml/g respectively (Masood et al., 2012). Therefore, the surface area of Ca(OCH<sub>3</sub>)<sub>2</sub> in this study was relatively higher based on the findings. In short, the hybrid catalyst showed a greater surface area than the pure catalyst. Many studies also have confirmed that catalysts with a lower particle size and higher surface area accelerate the reaction rates, due to an increased number of molecules that have the minimum required energy for the reaction to occur.

| Sample                             | Surface<br>area (m <sup>2</sup> g <sup>-1</sup> ) | Average pore<br>volume (cm <sup>3</sup> g <sup>-1</sup> ) | Average pore<br>diameter (Å) | Crystal size<br>(nm) |
|------------------------------------|---|---|------------------------------|----------------------|
| Calcined seashell                  | 1.56  | 0.0044  | 112.54                       | 60                   |
| Commercial CaO                     | 1.34  | 0.0021  | 62.59                        | -                    |
| Ca(OCH <sub>3</sub> ) <sub>2</sub> | 3.30  | 0.01  | 70.76                        | 81.95                |
| Zeolite                            | 150.48  | 0.50  | 20.12                        | 57.29                |
| Hybrid catalyst                    | 84.67   | 0.41  | 195.27                       | 65.18                |

Table 4.1: Main pore properties of C. brunneus shell derived catalysts

### 4.1.4 FTIR analysis

The FTIR spectra of the uncalcined CaO, calcined CaO, Ca(OCH<sub>3</sub>)<sub>2</sub>, and zeolite were evaluated and illustrated in Figure 4.4 and Figure 4.5. The FTIR spectra of natural *C. brunneus* shell indicated the presence of the carbonates (859 centimeter<sup>-1</sup> (cm<sup>-1</sup>) and 713 cm<sup>-1</sup>) and methylene groups (1,456 cm<sup>-1</sup>) (Figure 4.4) which was in accordance with the result of previous studies (Selim et al., 2017; Yin et al., 2016). The FTIR spectrum of calcined *C. brunneus* shell exhibited a relatively strong broad absorption band at wave numbers < 600 cm<sup>-1</sup> which were attributed to Ca–O group stretching in CaO (ANR et al., 2015). Moreover, the appearance of peaks at 3,641 cm<sup>-1</sup> was attributed to the –OH stretching vibration of Ca(OH)<sub>2</sub> and most likely arose from adsorption of atmospheric water. Likewise, the appearance of absorption peaks at 1,072 cm<sup>-1</sup> and 1,489 cm<sup>-1</sup> was attributed to the stretching vibration of the CO<sub>3</sub> as a result of CO<sub>2</sub> chemisorption to the surface of the calcined *C. brunneus* shell. The conversion of the peaks from CaCO<sub>3</sub> to CaO-related peaks indicate that the conversion occurred successfully.



Figure 4.4: FTIR spectra of CaO and CaCO<sub>3</sub>

Comparing to natural crab shell, its FTIR evaluation showed bands characteristics of the acetyl groups of chitin (1650 cm<sup>-1</sup>), protein and carbohydrate (3275 cm<sup>-1</sup>, 3112 cm<sup>-1</sup>, 2958 cm<sup>-1</sup> and 2522 cm<sup>-1</sup>), hydroxyl group (3457 cm<sup>-1</sup>), carbonates group (870 cm<sup>-1</sup> and 715 cm<sup>-1</sup>) and methylene group (1414 cm<sup>-1</sup>). For calcined natural crab shell, bands were observed at 3650 cm<sup>-1</sup> for Ca(OH)<sub>2</sub>, 3456 cm<sup>-1</sup> (OH group), 1492 cm<sup>-1</sup> and 1051 cm<sup>-1</sup> for (CO<sub>3</sub>)<sup>2-</sup>. Moreover, symmetric stretching was noticed at 875 cm<sup>-1</sup> (CO group). Natural eggshell peaks were manifested at 3415 cm<sup>-1</sup> (OH), 1800 cm<sup>-1</sup>,1424 cm<sup>-1</sup>,875 cm<sup>-1</sup>, 713 cm<sup>-1</sup> (CO<sub>3</sub>)<sup>2-</sup>. Moreover, the C-H group of aliphatic compounds (2992 cm<sup>-1</sup>-2884 cm<sup>-1</sup>), and hydrides (2511 cm<sup>-1</sup>) were observed. Calcined eggshell groups at 3642 cm<sup>-1</sup> and 3458 cm<sup>-1</sup> were attributed to the OH stretching of Ca(OH)<sub>2</sub> and H<sub>2</sub>O respectively. These peaks presented might be due to humidity. Peaks at 1625 cm<sup>-1</sup>,1450 cm<sup>-1</sup>, 1062 cm<sup>-1</sup> and 876 cm<sup>-1</sup> were associated with stretching vibration of (CO<sub>3</sub>)<sup>2-</sup> due to chemisorption of CO<sub>2</sub> on the surface of material (Correia et al., 2014). In another study, uncalcined clam shell showed asymmetric stretching and bend vibration peaks at 1441 cm<sup>-1</sup>, 818 cm<sup>-1</sup>. 3652

cm<sup>-1</sup> and 3642 cm<sup>-1</sup> were associated to OH stretching band (presence of calcium hydroxide) (Nair et al., 2012).

For zeolite, the peaks with strong absorption at 465 and 970 cm<sup>-1</sup> were related to deformation bands Si-O-Si and the perpendicular Si-O vibration bands respectively which was in agreement with the previous study (Hassani et al., 2014). Further, peaks at 750-700 cm<sup>-1</sup> corresponded to the symmetric stretching vibration of SiO<sub>4</sub>, while the bands around 465 cm<sup>-1</sup> and 552 cm<sup>-1</sup> were related to the bending vibration of SiO<sub>4</sub>. For Ca(OCH<sub>3</sub>)<sub>2</sub>, the appearance of groups at 2922 cm<sup>-1</sup>, 2865 cm<sup>-1</sup> and 2813 cm<sup>-1</sup> were attributed to the C-H bond stretching. Regions around 1200-950 cm<sup>-1</sup> and 500-420 cm<sup>-1</sup> were due to the Si-O-Si and Si-O-Al vibrations (Figure 4.5) (Al-Jammal et al., 2016). The Ca–O group peaks did not form in the diffractogram of Ca(OCH<sub>3</sub>)<sub>2</sub>, suggesting that the CaO was converted to Ca(OCH<sub>3</sub>)<sub>2</sub>. According to Deshmane et al. (2013), calcium methoxide peaks at 2944 cm<sup>-1</sup>, 2865 cm<sup>-1</sup>, 2813 cm<sup>-1</sup> and 1470 cm<sup>-1</sup> were attributed to the C-H bond stretching vibrations. In addition, peaks at 1041 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> were assigned to the C-O bond stretching vibrations.



Figure 4.5: FTIR images of A) hybrid catalyst B) pure zeolite

# 4.1.5 XRD analysis

The XRD spectra of the uncalcined CaO, calcined CaO and reference catalyst were illustrated in Figure 4.6. Further, XRD spectra of Ca(OCH<sub>3</sub>)<sub>2</sub>, zeolite, and hybrid catalyst were illustrated in Figure 4.7. The XRD spectrum of natural *C. brunneus* shell (Figure 4.6-A) contained peaks at  $2\theta = 27.1^{\circ}$ , 46.4°, and 48.2° that were consistent with the presence of CaCO<sub>3</sub>. As expected, calcination at 1100 °C resulted in the conversion of CaCO<sub>3</sub> to CaO, as evidenced by the appearance of peaks at  $2\theta$  of  $32.30^{\circ}$ ,  $37.38^{\circ}$ ,  $53.8^{\circ}$ , and  $54.10^{\circ}$  (Figure 4.6-B) (Lee et al., 2015; Perea et al., 2016). The pattern of peaks in the XRD spectra of calcined *C. brunneus* shell (Figure 4.6-B) and commercially-available CaO calcined under the same conditions (Figure 4.6-C) were similar. Catalyst obtained from *mereterix mereterix* shells showed peaks at  $48.2^{\circ}$  characteristic of calcium carbonate, but the calcined catalyst showed peaks at  $37.4^{\circ}$ ,  $47.3^{\circ}$  and  $54.1^{\circ}$  indicative of CaO. Peaks at  $17.9^{\circ}$  and  $34.1^{\circ}$  were also associated to Ca(OH)<sub>2</sub>.  $32.3^{\circ}$ ,  $37.4^{\circ}$ ,  $53.8^{\circ}$  peaks were also characteristics of CaO (Nair et al., 2012; Massod et al., 2012).


Figure 4.6: XRD pattern of A) CaCO<sub>3</sub> (peaks at 2θ = 27.1°, 46.4°, and 48.2°), B) CaO (peaks at 2θ of 32.30°, 37.38°, 53.8°, and 54.10°), and C) commercial CaO ( peaks at 2θ of 32.30°, 37.38°, 53.8°, and 54.10°)

From Figure 4.7, XRD pattern of Ca(OCH<sub>3</sub>)<sub>2</sub> indicated that the CaO peaks were eliminated and the peak related to Ca(OCH<sub>3</sub>)<sub>2</sub> appeared proving that the success of the conversion process. In the diffractogram image of Ca(OCH<sub>3</sub>)<sub>2</sub>, the peak associated with Ca(OCH<sub>3</sub>)<sub>2</sub> was observed at  $2\theta$ =10.7° being responsible for the transesterification reaction. This result was comparable with other studies;  $2\theta$ =10.7° and  $2\theta$ =11° (Teo et al., 2015; Masood et al., 2012; Deshmane et al., 2013). Further, peaks at 10.19°, 12.48°, 16.13°, 21.68°, 24.01°, 26.15°, 27.15°, 29.96° and 34.21° corresponded to zeolite Na-A as indicated in other study (Selim et al., 2017). Furthermore, as it is evidenced in Figure 4.7-C, the intensity of the peak at  $2\theta$ =10.7° was increased to 2000 a.u comparing with Figure 4.7-B which the intensity was 1000 a.u. This increase in intensity could be explained as a indication that although Ca(OCH<sub>3</sub>)<sub>2</sub> and zeolite has coverage at  $2\theta$ =10.7°, the increase was because that Ca(OCH<sub>3</sub>)<sub>2</sub> has been loaded on zeolite.

The particle size of the catalyst is one of the most critical factors for their catalytic activity. As indicated in Table 4.1, the particle size of  $Ca(OCH_3)_2$  and zeolite were determined to be 81.95 nm and 57.29 nm, respectively based on the Scherrer equation. Vigorously loading process by using the wet impregnation method for 2 h at 65 °C slightly modified the less homogeneous morphology of the  $Ca(OCH_3)_2$  particles, and led to a reduction of particle agglomerations and particles size. The crystallite size of the hybrid catalyst using the Scherrer equation was 65.18 nm. With the reduced particle size, the catalytic chemical reaction rate is improved due to the higher surface area since the diffusion forces would only carry the products away from the surface of the catalyst particle (ANR et al., 2015).



Figure 4.7: XRD pattern of A) calcium methoxide (peak at 2θ=10.7°), B) zeolite (peaks at 10.19°, 12.48°, 16.13°,21.68°,24.01°,26.15°,27.15°,29.96° and 34.21°) C) hybrid catalyst; calcium methoxide (peak at 2θ=10.7°) and zeolite peaks at 10.19°, 12.48°, 16.13°,21.68°,24.01°,26.15°,27.15°,29.96° and 34.21°

# 4.1.6 **TPD-CO<sub>2</sub>** analysis

The TPD profile of the hybrid catalyst revealed a desorption peak at 872 °C. This desorption temperature is higher than that of pure Ca(OCH<sub>3</sub>)<sub>2</sub> (680 °C), suggesting that a higher desorption temperature is required to liberate CO<sub>2</sub> from a hybrid catalyst due to

the formation of very strong basic sites (see Figure 4.8). Basic properties of zeolite catalysts occur when alkali metal cations compensate for the negative charge of the framework. The presence of alkali cations enhances the electron density of the framework oxygen, therefore, acting as basic sites. Hence, the basicity of Ca(OCH<sub>3</sub>)<sub>2</sub> increased with zeolite support. As basic sites have the main role in CaO efficiency, therefore it improves the transesterification efficiency. Further, it reduces the time needed for oil conversion to biodiesel. As zeolite provides more surface area for catalyst as carrier, more basic sites available would be exposed to the reactants. Furthermore, the basic nature of the zeolite-based catalyst could also enhance the electron density of the framework of oxygen.

Brønsted and Lewis acid sites also occur in zeolites. Brønsted acid sites are associated to aluminium located in the frame-work of the zeolites while Lewis acid sites are related to the extra framework aluminium (EFAL) or distorted aluminium in the frame-work (Feyzi & Khajavi, 2014). Given that in terms of reaction rate, heterogeneous base catalysts are 4000 times faster than acid catalysts due to the more activity of base catalysts over acid ones, impregnation of Ca(OCH<sub>3</sub>)<sub>2</sub> as active metal phase were carried out to marginalize the acid activity of the zeolite. So, the activity of zeolite supported Ca(OCH<sub>3</sub>)<sub>2</sub> catalyst indicated that the modification with Ca(OCH<sub>3</sub>)<sub>2</sub> is very effective for increasing the zeolite performance to produce biodiesel.

In other study, the desorption peaks appeared at a temperature lower than 450 K which can be attributed to the interaction of CO<sub>2</sub> with weak basic sites and were observed for the catalysts with low CaO content (*i.e.*,Ca-to-Zr molar ratio 0.25). It has been proposed that these sites correspond to the weak basicity of ZrO<sub>2</sub>. The peaks that appeared from 450 to 750 K can be attributed to stronger basic sites. The desorption temperature of these peaks increases with increasing the Ca-to-Zr molar ratio (Dehkordi & Ghasemi, 2012).



Figure 4.8: TPD-CO<sub>2</sub> profiles of A) hybrid catalyst and B) Ca(OCH<sub>3</sub>)<sub>2</sub>

# 4.1.7 EDX analysis

Energy dispersive X (EDX) was conducted to measure the Al/Si ratio in the zeolite. The Al/Si ratio of the zeolite was estimated to be about 1 based on EDX analysis which is inconsistent with the chemical formula of pure Na-A zeolite (Selim et al., 2017) (see Figure 4.9). Na-A Zeolite ( $Na_{12}(AlO_2)_{12}(SiO_2)_{12}\cdot xH_2O$ ) is characterized by its three-dimensional cubic structure. The Si/Al ratio in zeolite A equals 1 and the numbers of mobile Na cations and Al atoms are equal. This means that comparing with other zeolites, zeolite A possesses relatively high exchange capacities owing to its chemical structure. In another study also the Na:Al:Si ratio was reported to be 1 which is consistent with chemical formula of zeolite Na-A (Selim et al., 2017).

A low silica sodium zeolite (Si/Al = 1, Na/Al = 1, *i.e.*, zeolite NA) possess an open cage within the lattice and a vast network of negatively charged open channels

(accommodating Na<sup>+</sup>cation) due to the presence of the common oxygen atom between Si and Al tetrahedra. In addition, the pores or channels are of microscopically small size as of molecular dimensions and hence they are also called the "molecular sieves" which facilitate cation exchange in the adsorption process.



Figure 4.9: EDX analysis of zeolite

# 4.2 Analysis of the impact of process conditions on transesterification

Several factors exert influence on the FAME yield throughout the transesterification reaction. Thus, the effect of parameters such as Ca(OCH<sub>3</sub>)<sub>2</sub>/zeolite loading amount, catalyst amount, methanol-to-oil molar ratio and reaction time were studied thoroughly.

#### 4.2.1 Effect of catalyst loading amount

The effect of the loading amount of Ca(OCH<sub>3</sub>)<sub>2</sub> on zeolite was investigated (from 5 wt% to 20 wt%) under the following reaction conditions: catalyst amount of 2.5 wt%, the methanol-to-oil molar ratio of 15:1 and reaction time of 120 min. As seen in Fig 4.10, FAME yield increased in correlation with Ca(OCH<sub>3</sub>)<sub>2</sub> loading over zeolite (depicted as CaM/zeolite in Figure 4.10-A) because the unmodified zeolite was not catalytically active due to the lack of basic sites. On the other hand, zeolite exposed the basic sites of the Ca(OCH<sub>3</sub>)<sub>2</sub> to the reactants due to its higher surface area. The highest FAME yield of 79.44% was obtained at a loading amount of 20 wt%. Thus, from the results, the catalyst activity strongly relies on its basicity for transesterification of RBO to biodiesel.

### 4.2.2 Effect of catalyst amount

Although a higher catalyst concentration accelerates the reaction, the reaction only moves forward until the reaction equilibrium is reached. After that, the catalyst concentration does not affect the reaction rate; however, the ability of reactants to access the available active sites influences the conversion. Boro et al. (2014) stated that the drop in catalytic activity can be attributed to the blockage of basic sites due to excess Ba loading and the subsequent obstruction would pose difficulty to the diffusion of reactants throughout the catalyst.

Excessive catalyst concentration can result in difficult mixing of the reaction reactants due to the increased viscosity, as mentioned by Piker et al. (2016). Further, when the catalyst concentration was execessively high, the catalyst became less basic, leading to reduced catalytic activity (Boro et al., 2014). Following these previous studies, Ismail et al. (2016) found out that the catalyst concentration should be optimized to increase yields. Thus, finding an optimum catalyst concentration is an important factor during transesterification reactions. In this study, transesterification was conducted by using different catalyst concentrations to evaluate their effect on the FAME yield. The catalyst concentrations used ranged from 0.5 wt% to 3.5 wt% under the following experimental conditions: Ca(OCH<sub>3</sub>)<sub>2</sub>/zeolite loading amount of 20 wt%, the methanol-to-oil molar ratio of 15:1 and reaction time of 120 min. As depicted in Figure 4.10-B, the FAME yield increased from 96.32% to 98.04% by increasing the catalyst concentration from 0.5 wt% to 2.5 wt%. As the amount of catalyst increased, the amount of zeolite with the high surface area also increased, which provided more available basic sites during the reaction. However, no further increase in FAME yield was observed when the amount of catalyst increased from 2.5 wt% to 3.5 wt%. In another study using zeolite as support, results showed that as the catalyst concentration increased, the biodiesel yield along with the ester content also increased. Increased amount of catalyst from 0.5% to 3% resulted in an increased yield of biodiesel from 40.5% to 94.6% (Wu et al., 2013). In another study using calcium methoxide, the results showed that the biodiesel yield increased with increasing the amount of catalyst (Liu et al., 2008). The highest yield was obtained when 4 wt% of catalyst was used. The result showed that the higher amount of catalyst resulted in the faster reaction rate the reaching the equilibrium. Theam et al. (2016) reported that the 0.5 wt% catalyst amount exhibited a very low FAME yield, and there was an observable increase in yield from 0.5 to 2%. This proves that the catalyst concentration exerts a significant influence on the transesterification reaction. The FAME yield was further increased to the optimum point, i.e., 80%, at 4% catalyst loading, above which the yield gradually decreased. This may probably be due to two reasons. First, excess catalyst in the reaction mixture may provide a greater chance for glycerol to cover catalyst's surface. High amount of catalyst may lead to a more viscous reaction mixture, hence affecting the mass transfer between reactants and products.

#### 4.2.3 Effect of alcohol/oil ratio

Another important parameter affecting the transesterification reaction is the methanolto-oil molar ratio. Stoichiometrically, three moles of methanol is needed for each mole of triglyceride. Therefore, a higher molar ratio is needed to complete the reaction. Zamberi et al. (2016) reported that the alcohol-to-oil ratio has a more significant effect on biodiesel yield than the catalyst loading amount. They also added that an increase of yield from 55.52 % to 88.06 % was observed when the methanol-to-oil molar ratio was increased stepwise, while the excessive increase in the ratio did not increase the biodiesel yield. In this study, different methanol-to-oil molar ratios (10:1, 15:1, 20:1, 25:1) were applied to the system under the following conditions: Ca(OCH<sub>3</sub>)<sub>2</sub>/zeolite loading amount of 20 wt%, catalyst concentration of 2.5 wt% and reaction time of 120 min. When the ratio was 25:1, the FAME yield reached 84%. It was observed that the FAME yield increased as the methanol-to-oil molar ratio increased. Theam et al. (2016) also reported a noticeable increase in the FAME yield when the methanol-to-oil molar ratio of 6 changed to 12. However, the FAME content in the products decreased slowly when higher methanol molar ratio was applied in the catalytic reaction. This trend can be explained that a greater volume of reaction mixture with a small amount of catalyst may lead to a low-yield reaction due to lower catalytic assistance from the catalyst.

## 4.2.4 Effect of reaction time

The effect of reaction time on the transesterification of RBO was studied at 30, 60, 120, and 150 min. As illustrated in Figure 4.10-D, the FAME yield increased with increasing reaction time. However, the FAME yield was reduced to 58.52 % during transesterification for 150 min. Under prolonged reaction time, the challenge for CaO-derived catalysts would be their tendency toward the formation of glycerol under transesterification reaction, and the formed complex of Ca–Gly would be less active in

terms of catalysis than the CaO. Thus, in this case, glycerol can cause the deactivation of the catalyst (Theam et al., 2016). Thus, the progress of reaction from 120 min to 150 min may have caused the catalyst to lose its effectiveness. Based on several studies, there could be few reasons behind the deactivation of the catalyst. A TG-DTA test conducted by Wen et al. (2010) showed the decomposition of organic species, indicating that the pores of the catalyst are filled by organic species, such as triglycerides and glycerol. Furthermore, Deng et al. (2011) found that the viscous liquid absorbed on the surface of the calcined hydrotalcite Mg/Al catalyst which was glycerol could deactivate the catalyst. The reaction time had a noticeable impact on the conversion of feedstock to FAME, which showed consistent to other study (Theam et al., 2016). As observed in their work, FAME yield was increased remarkably when the reaction time increased from 30 to 90 min, and it slowly increased to 88 % at 150 min, but there was an obvious decrease at 180 min, which might be due to the action of glycerol that deactivated the catalyst and induced saponification to take place.



Figure 4.10: Effect of the parameters such as (a) Ca(OCH<sub>3</sub>)<sub>2</sub>/zeolite loading amount, (b) catalyst amount, (c) methanol-to-oil molar ratio and (d) reaction time on FAME yield

# 4.3 Analysis of biodiesel produced by pure and hybrid catalysts

FTIR analysis allows a relatively rapid analysis of liquid samples and can differentiate between crude oil and biodiesel. Therefore, RBO-derived biodiesel produced using *C*. *brunneus* shell derived was evaluated using FTIR (Figure 4.11). Two peaks were present in the FTIR spectrum of RBO-derived biodiesel that was not present in RBO: (i) a peak at 1,435 cm<sup>-1</sup>, associated with an asymmetric stretch of  $-CH_3$  which was consistent with the result of Perea et al (2016), and (ii) a peak at 1,097 cm<sup>-1</sup> correspondings to asymmetric axial stretching of O-CH<sub>2</sub>.Ce-CH<sub>2</sub>.OH. Further, the peak 1,377 cm<sup>-1</sup> in the FTIR spectrum of RBO-derived biodiesel was found to be consistent with the presence of O-CH<sub>3</sub> in glycerol, a known by-product of biodiesel production. Based on the result obtained, RBO was converted to biodiesel successfully. Siatis et al. (2006) reported that the peaks at 1198 cm<sup>-1</sup>, 1363 cm<sup>-1</sup>, and 1436 cm<sup>-1</sup> were related to the methyl ester groups with a deformation vibration. Indarti et al. (2016) reported that peaks at 1435 cm<sup>-1</sup> and 1203 cm<sup>-1</sup> were associated with CH<sub>3</sub> asymmetric bending and O-CH<sub>3</sub> (methyl group) stretching.



Figure 4.11: FTIR spectra of RBO and its biodiesel

FTIR was used to analyze both *Ocimum basilicum* oil and its biodiesel. The peak at 1442 cm<sup>-1</sup>, associating with asymmetric stretch of–CH<sub>3</sub> was present in the spectrum of biodiesel but absent in the spectrum of crude oil. Likewise, the peak at 1197 cm<sup>-1</sup> associated with the stretching of O–CH<sub>3</sub> was present in the spectrum of biodiesel but absent in the spectrum of oil. Further, the spectral region between 1075 and 1100 cm<sup>-1</sup>, asymmetric axial stretching of O–CH<sub>2</sub>–Ce–CH<sub>2</sub>–OH, also discriminates between plant oils and biodiesel. A peak was observed at 1095 cm<sup>-1</sup> in the spectrum of crude oil but was not present in the respective biodiesel sample. The peak at 1375 cm<sup>-1</sup> observed in the spectrum of crude oil and attributed to O–CH<sub>3</sub> (glycerol group) was observed in the

spectrum from biodiesel, which indicates the residual glycerol in the biodiesel sample (Amini et al., 2017).

When introducing a novel catalyst for fuel production, it is essential to assess whether the properties of the new fuel derived from that product is equivalent to existing fuel. FAME concentration of RBO-derived biodiesel were analyzed by gas chromatography (GC) (Table 4.2). FAME yields of 93.5% and 98% was achieved by the pure and hybrid catalysts respectively, under the following condition: calcination temperature of 1100 °C, reaction temperature of 65 °C and reaction time of 120 min.

| FA/FAMF          | Formula Carbon                                     |       | Saturation      | FAME (%) |
|------------------|--|-------|-----------------|----------|
| ra/rante         | 1 01 mula  |       | Saturation      |          |
| D 1 '4'          | C IL COOCIL  | 016   | 0 / / 1         | 14.00    |
| Palmitic         | $C_{15}H_{31}COOCH_3$                              | C16   | Saturated       | 14.00    |
| acid/methyl      |  |       |                 |          |
| palmitate        |  |       |                 |          |
| Palmitoleic      | C <sub>15</sub> H <sub>29</sub> COOCH <sub>3</sub> | C16:1 | Monounsaturated | 0.11     |
| acid/methyl      |  |       |                 |          |
| palmitoleate     |  |       |                 |          |
| Stearic          | C <sub>17</sub> H <sub>35</sub> COOCH <sub>3</sub> | C18   | Saturated       | 1.38     |
| acid/methyl      |  |       |                 |          |
| stearate         |  |       |                 |          |
| (octadecanoat)   |  |       |                 |          |
| Oleic acid/cis-  | C <sub>17</sub> H <sub>33</sub> COOCH <sub>3</sub> | C18:1 | Monounsaturated | 38.76    |
| 9-oleic methyl   |  |       |                 |          |
| ester            |  |       |                 |          |
| Linoleic         | C <sub>17</sub> H <sub>31</sub> COOCH <sub>3</sub> | C18:2 | Polyunsaturated | 37.00    |
| acid/methyl      |  |       |                 |          |
| linoleate        |  |       |                 |          |
| Linolenic        | C <sub>17</sub> H <sub>29</sub> COOCH <sub>3</sub> | C18:3 | Polyunsaturated | 0.58     |
| acid/methyl      |  |       |                 |          |
| linolenate       |  |       |                 |          |
| Arachidic        | C <sub>19</sub> H <sub>39</sub> COOCH <sub>3</sub> | C20   | Saturated       | 0.55     |
| (Eicosanoic)     |  |       |                 |          |
| acid/methyl      |  |       |                 |          |
| arachidate       |  |       |                 |          |
| (icosanoic acid) |  |       |                 |          |

Table 4.2: FAME concentration and profile

Most of the feedstocks used for biodiesel production display a fatty acid profile ranging from caprylic (C8) to arachidic (C20) acids. Fatty acids exert a direct influence on the chemical and physical properties of biodiesel regardless of their origin. As predicted based upon the chemical composition of RBO, the relatively high proportion of unsaturated fatty acids in the source oil resulted in a less viscous biodiesel. According to Hoang et al. (2020), the average contents of monounsaturated fatty acids, polyunsaturated fatty acids and saturated fatty acids of RBO were 39.3%, 35.0%, and 19.7%, respectively. However, in the current study, those contents were detected to be 38.87%, 37.58% and 15.93% respectively. The variation in the fatty acid composition for the different RBO could also be due to varietal properties of the rice. The result of this study shows that RBO biodiesel has less saturated fatty acids comparing to the average contents of fatty acids, which therefore reduces the viscosity of the biodiesel. The impact of such a change in a large-scale production process would be reduction in the total cost, production time per unit volume and energy consumption. Moreover, the concentrations of saturated fatty acids were low, as follows; C16 (14%), C16:1 (0.11%) and C20 (0.55%). In other words, the concentrations of unsaturated fatty acids were high as follows: C18:1 (38.76%) and C18:2 (37%), which were the highest among other fatty acids of RBO. Thus, RBO can be classified as an unsaturated oil due to the presence of sufficient contents of oleic acid and linoleic acid. Oils with high content of oleic acid has been reported favourable for biodiesel production due to better oxidation stability and combustion attributes. Based on the fatty acid composition contents, RBO biodiesel produced by C. brunneus seashells is a reliable fuel.

The fuel properties of RBO, pure *C. brunneus* shell derived biodiesel and hybrid *C. brunneus* shell derived biodiesel were tested and compared with EN 14214 and ASTM D6751 standards specifications (Table 4.3). Further, the properties of biodiesel produced by *C. brunneus* seashells were compred to the properties of *Ceiba pentandra* biodiesel and neem biodiesel produced by conventional NaOH and KOH catalysts.

| Properties                      | Unit                         | ASTM<br>standards | En<br>standards | RBO   | RBOB<br>by pure | RBOB<br>by hybrid |
|---------------------------------|------------------------------|-------------------|-----------------|-------|-----------------|-------------------|
|                                 |                              | D6751             | 14214           |       | catalyst        | catalyst          |
| Kinematic                       | $mm^2$                       | 1.9-6.0           | 3.5–5.0         | 40.13 | 8.05            | 4.88              |
| viscosity (40 °C)               | $s^{-1}$                     |                   |                 |       |                 |                   |
| Density (15 °C)                 | kg<br>m <sup>-3</sup>        | 880               | 860–900         | 902   | 896             | 883               |
| Acid value                      | mg<br>KOH<br>g <sup>-1</sup> | Max 0.5           | Max 0.5         | 1.2   | 0.5             | 0.3               |
| Calorific value                 | MJ<br>kg <sup>-1</sup>       | 35                | 35              | 37.04 | 39.03           | 40.34             |
| Oxidation<br>stability (110 °C) | H                            | 3                 | 6               | 3     | 3.16            | 3.28              |
| Flash point                     | °C                           | >130              | >101            | 247   | 173             | 156               |
|                                 |                              |                   |                 |       |                 |                   |

Table 4.3: Physical characteristic of the RBO and associated biodiesel

As shown in Table 4.3, the kinematic viscosity of biodiesel produced by the pure catalyst could not fulfil the standards of ASTM D6751 and EN14214. Biodiesel with high viscosity could damage the engine and reduce its lifespan. The viscosity of biodiesel produced by the pure catalyst was  $8.05 \text{ mm}^2 \text{ s}^{-1}$  and this was reduced to  $4.88 \text{ mm}^2 \text{ s}^{-1}$  after using the as-produced hybrid catalyst. These result demonstrate that producing RBO biodiesel with favourable visocity is possible and can meet the standards' specifications. For example, in the study conducted by Silitonga et al. (2012), the kinematic viscosity of  $3.1578 \text{ mm}^2 \text{ s}^{-1}$  was reported for the *Ceiba pentandra* biodiesel when NaOH was used as a catalyst. In another study conducted by Inayat et al. (2020), the viscosity of neem biodiesel produced by KOH was  $4.8 \text{ mm}^2 \text{ s}^{-1}$ . Although the viscosity produced by NaOH and KOH in these studies was lower comparing to *C. brunneus* derived seashells, the problems of NaOH and KOH as homogeneous catalysts should not be neglected.

Density of respective RBO-biodiesels did not change significantly using pure catalyst (896 kg m<sup>-3</sup>) and hybrid catalyst (883 kg m<sup>-3</sup>). In general, both biodiesels were able to fulfil the standards. Comparing to other studies, the biodiesel density of 847 kg m<sup>-3</sup> and 888 kg m<sup>-3</sup> was reported using NaOH and KOH catalysts respectively. Higher density of

fuel bring out lower volatility and poor atomization during fuel injection causing incomplete combustion and carbon deposits in the chamber.

Both standards requires stringent acid value (max 0.5 mg KOH  $g^{-1}$ ) of biodiesel due to safe handling concern. Although RBO produced by the pure catalyst has a low acid value (0.5 mg KOH  $g^{-1}$ ), hybrid catalyst-generated biodiesel showed a lower acid value of 0.29 mg KOH  $g^{-1}$ , both within the standard value for both ASTM D6751 and EN 14214 standards limits. Through comparision, the acid value of *Cieba* biodiesel was reported to be 0.4 mg KOH  $g^{-1}$  which was more than the acid value obtained by the hybrid catalyst. The lower acid value makes the biodiesel more efficient in engine. Since the FFA content is corrosive in nature, this could corrode the automotive parts and limit the protection against vehicle engines and fuel tanks. Overall, the biodiesel produced by the hybrid catalyst showed better acid value among the catalyst studied.

The measurement of calorific value determines the chemical energy of the fuel and also indirectly specifies the combustion efficiency. Calorific value of biodiesel produced by pure catalyst was approximately 39.03 MJ kg<sup>-1</sup> which was quite similar with the value of biodiesel produced by the hybrid catalyst (40.34 MJ kg<sup>-1</sup>), which both met the standard limits (calorific value >35 MJ kg<sup>-1</sup>). The calorific value of biodiesel produced by *C*. *bruuneus* catalysts were then compared with the calorific value of biodiesel using conventional catalysts. Calorific value of *Ceiba pentandra* biodiesel was 40.490 MJ kg<sup>-1</sup> which was almost similar to the calorific value obtained by *C*. *brunneus* seashells. In another study conducted by Inayat et al. (2020), the calorific value of neem biodiesel produced by KOH was 36 MJ kg<sup>-1</sup>. Therefore, the RBO biodiesel could be applied as fuel based on the results.

The flash point is an indication of how easy a fuel may burn in this case. Materials with higher flash points are less flammable or hazardous than those with lower flash points. From the results, the flash point of biodiesel produced by pure catalyst was less flammable comparing to the biodiesel produced by hybrid catalyst. The flash point of biodiesel produced by *C. bruuneus* catalysts were then compared with the flash point of biodiesel using conventional catalysts. For example, the flash point of *Ceiba* biodiesel was reported to be 130 °C, which was lower than the value obtained by pure catalyst (173°C) and hybrid catalyst (156°C), respectively (Silitonga et al., 2012). Therefore, biodiesel produced by *C. brunneus* catalyst is potentially a safer fuel for transportation purposes as compared to most diesel oils with lower flash points.

The oxidative stabilities of the biodiesel produced by the pure catalyst and hybrid catalyst was determined to be 3.16 h and 3.28 h, respectively. Both RBO biodiesel could meet the minimum oxidative stability according to the ASTM D6751 standard (3 h) but not the En Standards 14214 (6 h). Nonetheless, both produced RBO biodiesels fulfilled most of the criteria set by the standards, which means they have the potential to be applied as biodiesel fuel in the industry.

### 4.4 Tribological assessment of biodiesel

#### 4.4.1 Friction and wear analysis on the biodiesel blend

As shown in Figure 4.12, the friction coefficient (FC) of diesel was higher than other blended biodiesel. The result showed that the addition of RBOB10 reduced the FC in comparison to diesel from 0.09 to 0.0855. RBOB10 showed the best performance in terms of reducing the FC among pure or blended fuels. Interestingly, the FC increased by addition of RBOB concentration which can be interpreted as the fatty acid present in the RBOB acting as an active surface material which is adequate for 10% contamination and above that, the fatty acid does not take part because the rubbing contact surface might cover fully by RBOB10. The result of this study is in agreement with the research conducted by Shahabuddin et al. (2013) who also found that the above 10% addition of the bio-lubricant adversely affects the quality of the lubricant. Practically, biodiesel also contains methyl ester, which can represent better scuffing protection compared to hydrocarbon of diesel, leading to the better FC (Mosarof et al., 2016; Tan et al., 2019). Furthermore, biodiesel consisting of more oxygen can diminish friction compared to diesel fuel (Reyero et al., 2016). According to Nisar et al. (2017), the formation of several compounds on the frictional surface of steel such as FeS, FeSO4 as well as organic compounds with C–C, -COH, and -COOH groups could play the main role in diminishing the friction. Results revealed that blending RBO biodiesel with pure diesel showed more appropriate tribological characteristics than when either biodiesel (RBOB100%) or pure diesel (RBOB0) alone was used. It is found that the decreasing trend of FC is not linear for the blends. This contradicts to study by Fazal et al. (2013) who found that the average FC decreased with the increase of biodiesel concentration. This is more likely attributed to the non-uniform availability of the concentration of heteroatom (*e.g.* oxygen, sulfur) in different blends which plays important role in creating the lubricating film (Fazal et al., 2013).



Figure 4.12: Change in friction coefficient (FC) in different fuels

Figure 4.13 shows the wear scar diameter (WSD) for various RBOB blended with diesel at the operating conditions of 3600 s with the constant temperature at 75 °C and constant sliding speed of 1200 rpm at a constant load of 40 kg. WSD varied from 498.7 to 691.1 µm. WSD also increased as the amount of biodiesel in the blended mixture increased. However, the WSD for the blended mixtures were lower than the pure diesel and pure biodiesel. It is observed that the maximum wear was occurred for the RBOB%100. Haseeb et al. (2010) showed that lubricity in terms of FC and WSD increased with increasing the concentration of palm biodiesel. From the resits, WSD decreased remarkably for B10 compared with diesel. It could be concluded that a mixture of diesel with lower biodiesel blends caused less wear than that in higher biodiesel blends or either pure diesel or pure biodiesel.



Figure 4.13: Effect of different biodiesel concentration on wear scar diameter

In term of percentage, the significant improvement in WSD was found for RBOB10, which was improved to 462.3% compared to RBOB0 (498.7%) and RBOB100 (691.1%). This could be explained that an increase in the number of ester groups led to the greater

binding of the molecules, which provided greater resistance to shear forces. However, increasing RBOB ester by more than 10% did not show any improvement in WSD. Thus, it can be concluded that RBOB10 has the greatest potential to replace mineral lubricant.

The result of this study was in agreement with a study conducted by Zulkifli et al. (2013) who found that increasing the TMP ester more than 3% did not show any improvement on WSD. They also added that this phenomenon can be attributed to the reason that more than 3% of palm oil-based TMP ester could not form the stronger lubrican. Fazal et al. (2013) also stated that the presence of aliphatic fatty acid of general formula  $CnH_2n+1COOH$ , such as stearic acid in POME could boost the lubricity. They control the friction and wear between the contact surfaces by developing the lubricating films. Thermal energy can be diminished by the protective films in sliding contact, which therefore improves the lubricity. According to Sharma et al. (2008), the ester end of the fatty acid chain were absorbed to the metal surfaces and therefore led to the monolayer film formation with the hydrocarbon end of fatty acids which was away from the metal surface. The fatty acid chain, therefore, offers a sliding surface that blocks the direct metal-to-metal contact.

## 4.4.2 SEM analysis

Figure 4.14 (A)-(E) shows the scanning electron micrographs of worn surfaces of the tested balls. The surface deformation was severe for diesel and RBOB100. Furthermore, the wear scar increased with the increase in biodiesel concentration. The particles that were removed from the worn surface were larger and created bigger cavities for the diesel and biodiesel, indicated in Figure 4.14 (D) and (E), respectively. By contrast, the particle size of worn surfaces was smaller and created small cavities for RBOB10, RBOB30 and RBOB50. Researchers reported that the removal of particles with sizes greater than 20 µm resulted in adhesive wear (Rabinowicz, 1984). Abrasive wear presented on the wear

surface due to the removal of smaller particles (less than 20  $\mu$ m) (Sperring & Nowell, 2005). Therefore, abrasive wear was observed on the wear surface for RBOB10, RBOB30 and RBOB50. The surface morphology indicated that the edge of the surface at the diesel fuel and biodiesel was elongated which resulted in the cracks and wear debris. Wears produced by diesel (RBOB0) and biodiesel (RBOB100) fell into the category of adhesive wears. RBOB10 displayed smaller worn surfaces than other diesel-biodiesel blends.



Figure 4.14: SEM characterization of wears on balls

In this study, the severity of the wear increased by increasing the biodiesel concentration. However, the wear produced by diesel and pure biodiesel was worse than the blends. The SEM result of this study was not in agreement with the study conducted by Fazal et al. (2013) whereby they found that the severity of the wear was reduced with the increase of biodiesel concentration. They showed that both wear and friction decreased with the increase of biodiesel concentration. The different observations are

more likely attributed to the presence of oxygenated moieties, degree of unsaturated molecules, free fatty acid components, *etc.* in RBO biodiesels.

# 4.4.3 EDX analysis

According to EDX analysis, diesel fuel (RBOB0) displayed minimum percentages of C and O; however, it exhibited highest atomic percentage of Fe compared with other diesel–biodiesel blends. The O content of RBOB10 was the highest among those blends and diesel. Lu et al. (2005) suggested that a high O content in the sample could be due to the high amount of iron oxide produced on the solid surface during the test; thus, enhancing the overall lubricity. Therefore, RBOB10 displaying great performances in terms of wear and friction is also supported by the results of the SEM/EDX analysis, as shown in Figure 4.15.



Figure 4.15: EDX analysis of the different fuel blends

The following conclusions can be drawn based on this tribological investigation. The FC generally diminished with the decrease of biodiesel concentration. WSD increased with increasing the biodiesel concentration. Thus, lubricity of the blend fuels decreased as a consequence of increasing biodiesel concentration. The least WSD of 462.3 µm was found for RBOB10 at the lowest FC of 0.085. Further increasing the blend percentages increased the WSD of the ball specimens. Therefore, it can be stated that the higher blend concentration degrades the lubricant film strength by increasing the FC. The findings suggested that RBOB10 exhibited the most suitable lubricating fuels against wear and friction which can be implemented in the automotive engines.

## 4.5 Reusability study of C. brunneus seashell derived catalysts

#### 4.5.1 FAME yield and FESEM analysis

The reusability of any catalyst is a central concern to its application in a commercialscale, industrial process. Many CaO catalysts derived from natural sources could be reused in multiple reaction cycles (with or without regeneration) in industrial processes (Mirghiasi et al, 2014; Zamberi et al., 2016) but the impact of *C. brunneus* shell derived catalysts reuse on the FAME yield from RBO transesterification was unknown. Therefore, *C. brunneus* derived catalysts prepared at 1100 °C was reused in eight sequential cycle with 120 min transesterification reaction time at a constant temperature of 65°C. The impact of catalysts reuses on FAME yield and the surface properties of the catalyst itself were determined (Figure 4.16, Figure 4.17 and Figure 4.18). Although the time duration that the catalyst was in contact with other reactants during the reusability test was about 120 min (*i.e.* 120 min for each cycle), but it was interrupted. Then, the catalyst would be recovered and engaged into the reaction again from the time 0 to 120 min only.



Figure 4.16: FAME yield during catalyst reusability cycle analysis

For both catalysts, FAME yield decreased significantly after the 5<sup>th</sup> transesterification reaction and this was coincident with a change in the surface morphology of the catalyst (*i.e.*, the disappearance of a cluster of well-developed cubic crystals with obvious edges in the pure catalyst and, the disappearance of the agglomeration of  $Ca(OCH_3)_2$  on cubic structures of zeolite in hybrid catalyst).

The reusability of pure *C. brunneus* shell derived catalyst for transesterification compares well with other CaO catalysts obtained from seashells for biodiesel production. CaO catalyst produced from duck shell was reported to result in 80% FAME yield after five transesterification reactions under optimal conditions, but after eight reactions, the FAME yield was reduced to only 60% (Yin et al., 2016). Likewise, CaO catalyst produced from the angel wing shell, which could be reused three times under optimum reaction conditions and still result in an FAME yield above 65% (Syazwani et al., 2015).

As for hybrid catalyst, its reusability for transesterification compares well with other Ca(OCH<sub>3</sub>)<sub>2</sub>-based catalysts (either pure or supported) for biodiesel production. Binary metal-doped methoxide catalyst was reported to result in a 59.2% FAME yield after ten transesterification reactions under optimal conditions. Catalyst deactivation was the main cause for FAME yield to drop (dos Santos et al., 2017). Likewise, Ca(OCH<sub>3</sub>)<sub>2</sub> could be reused up to three times under optimum reaction conditions and still result in FAME yield above 84.74%. The authors found that excess methanol does not enhance the catalyst's reusability. They also added that the deactivation of the catalyst was due to surface changes validated by XRD result (Suwanthai et al., 2016). Ismail et al. (2016) evaluated the biodiesel yield of mud clam shell synthesized CaO in transesterification of castor oil in 5 cycles. They found that the biodiesel yield reduced slightly even after 5 cycles with a decrement of 12.2%. The biodiesel yield after 5 times of reusing the catalyst was 84.5%. They declared that the reduced catalyst activity was due to the agglomeration of the catalyst particles after being reused in transesterification. The size of the agglomeration of the catalyst particles became bigger as the number of transesterification cycles increased. Thus, the biodiesel yield decreased when the number of cycles increased. The stability and reactivity of the synthesized CaO from mud clam shell were better than the synthetic CaO with a higher biodiesel yield for 5 cycles of transesterification. For both catalysts, the morphology of the catalysts changed after reuse of the catalysts. A cluster of well-developed cubic crystals with obvious edges and the agglomeration of Ca(OCH<sub>3</sub>)<sub>2</sub> on cubic structures of zeolite were disappeared in pure and hybrid catalysts respectively.



Figure 4.17: FESEM micrographs of the pure catalyst during eight reaction cycles



Figure 4.18: FESEM micrographs of the hybrid catalyst during eight reaction cycles

# 4.5.2 Leaching analysis

The leaching of CaO catalysts can cause catalyst deactivation. Interestingly, Kouzu et al. (2008) suggested that the leaching of CaO from recycled CaO nanocatalyst contributed to a reduction in FAME yield during transesterification. Therefore, the Ca ion concentration in the product mixture from each transesterification reaction cycle was measured using AAS. For pure catalyst, as shown in Figure 4.19, the leaching was

gradually decreased with the number of cycles. Comparing to other studies this catalyst could maintain its structure up to 5 cycles. In terms of leaching, this catalyst was better compared to other studies, although the Ca leached amount is not assessed as part of the standards. Compared to the work by Roschat et al. (2016), they reported the leaching amount of 121.7 ppm for the first catalyst reuse while the leaching of pure catalyst in the current study was 90.3 ppm which was relatively lower.



Figure 4.19: The leaching analysis of pure and hybrid catalysts

As can be seen from Figure 4.19, the leaching was highest in the product obtained from fresh catalysts and gradually decreased with the number of cycles. However, in the sixth reuse cycle, a remarkable drop occurred in the active Ca element content, which was coincident with a change in the surface morphology of the catalyst illustrated by FESEM. Such a decrease in Ca ion leaching was considered to be reasonable as the reaction mixture covered the catalyst surface. Thus, the loss of active sites was considered a significant factor in the reduction of catalyst activity during reusability studies. The result of this study was in accordance with the study conducted by Roschat et al. (2016). They claimed that both the Ca leaching and the covered catalyst surface were the main reasons for the catalyst deactivation.

For the hybrid catalyst, Ca leached from the catalyst during the reaction in the first five cycles was high; however, this leaching did not have a significant effect on its catalytic activity. This could be explained as a result of Ca being dissolved in the reaction medium; thus, biodiesel was produced by the leached species. As shown in FESEM micrographs (Figure 4.8), the structure of the catalyst was modified, indicating Ca washout from the surface of the catalysts. Therefore, Ca contents in the reaction mixture was lower from the sixth cycle. As there are less Ca elements on the catalysts surface, this resulted in a lower catalytic activity which eventually produced lower FAME yield. Thus, as observed, FAME yield also reduced considerably after the fifth cycle which corresponded to the surface change of the catalyst such as the disappearance of the agglomeration of Ca(OCH<sub>3</sub>)<sub>2</sub> on cubic structures of zeolite in line with the Ca leaching study results. Unlike hybrid catalyst, FAME yield decreased at the same rate when using the pure catalyst in the seventh and eighth cycles; this could be attributed to the improved attachment properties when supporting the catalyst by zeolite. Moreover, due to the washing and reuse process, the loss of active sites was considered a significant factor, which resulted in the permanent reduction of catalyst reactivity. Compared with homogeneous catalysts, an important advantage of heterogeneous catalysts is that they can be easily separated, making the process economically more viable. While many studies have focused on the development and evaluation of metal oxide-based catalysts, leaching of metal ions is still regarded as a great disadvantage of heterogeneous catalysts.

The reusability and stability of the hybrid catalyst for transesterification reactions were comparable to other Ca(OCH<sub>3</sub>)<sub>2</sub>-based catalysts for biodiesel production as the FAME yield remained greater than 90% during the first five cycles (Theam et al., 2016). The

degradation of catalytic activity throughout the reusability runs may have caused by three main reasons: (i) leaching of metal ion from active sites into the reaction medium, (ii) poisoning of the catalyst active sites by the reaction medium (oil, biodiesel, and glycerol) which reduced contact between basic sites and reactants, and (iii) catalyst structure collapsed (Lee et al., 2013).

Comparing the two catalysts in terms of leaching showed that the leaching of the pure catalyst was more than 5 ppm that does not meet the biodiesel standard limit, but the hybrid catalyst leaching ranged below 5 ppm which was in agreement with standards.

However, various studies on CaO and Ca(OH)<sub>2</sub> showed leaching of the active phase during the transesterification was inevitable. Kouzu et al. (2016) found that significant loss of CaO occurred during the first use of the catalyst. Yoosuk et al. (2010) found that the content of neat CaO dissolved into the biodiesel phase and glycerol-methanol phase was 0.456 mg CaO/ml and 0.975 mg CaO/ml respectively. Verziu et al. (2011) revealed that the leaching of Ca from microcrystalline CaO was 325 ppm after the second cycle and 825 ppm after the third cycle. The increase of the number of leached Ca in repeated cycles coincided with the decrease of both the conversion and the yield of the reaction. However, the yield reduction was explained by the effect of blocking a part of catalytic sites with organicmolecules from the reaction mixture. The contribution of homogeneous catalysis arising from leached species from CaO-based catalysts can be considered negligible. Leaching of CaO into the reaction medium can be significantly reduced by anchoring the catalyst onto a support or using its mixed oxides. Zabeti et al. (2009) revealed that the level of calcium leached from CaO/y-Al<sub>2</sub>O<sub>3</sub> catalyst into the reaction medium was only 31 ppm. Using a very similar catalyst for biodiesel production, Pasupulety et al. (2013) found that negligible concentration of active species was separated in the reaction solution. Campos-Molina et al. (2010) did not observe leaching of the mixture of CaO used in sunflower oil transesterification. In the case of mixed oxide CaO/ZnO, Kesic et al. (2016) determined a lower concentration of Ca in methanol (8.9 mg/l), compared to the solubility of neat CaO (96 mg/l). Taufiq-Yap et al. (2014) did not found significant leaching of mixed oxide catalyst CaO–La<sub>2</sub>O<sub>3</sub> into the reaction medium during three repeated runs (about 1.5 ppm in every run). A slight decrease in activity was attributed to the deposition of orgnanic compounds on the active sites of the catalyst. Based on the current literatures, the catalyst produced in this study especially the hybrid catalyst showed great potential for the RBO biodiesel production, as it showed higher resistance against leaching.

### **CHAPTER 5: CONCLUSION AND RECOMMENDATION**

#### 5.1 Conclusion

*C. brunneus* seashell was successfully converted to CaO, namely as a pure catalyst. The pure catalyst was then converted to a hybrid form by using zeolite Na-A as a support to improve the fatty acid methyl conversion. Analytical tools validated the production of the *C. brunneus* seashell derived catalysts and its conversion into hybrid form. The results of the FTIR, XRD, TEM, FESEM were comparable with other studies. Based on FTIR results, wave numbers < 600 cm<sup>-1</sup> which were attributed to Ca–O group stretching in CaO as detected in the pure catalyst. Whilst, the lack of Ca–O group peaks in the diffractogram of Ca(OCH<sub>3</sub>)<sub>2</sub> manifested that the CaO was successfully converted to Ca(OCH<sub>3</sub>)<sub>2</sub>.

According to XRD results, peaks at  $2\theta = 27.1^{\circ}$ , 46.4° and 48.2° indicating the presence of CaCO<sub>3</sub>, were converted to the CaO peaks at 2 $\theta$  of 32.30°, 37.38°, 53.8°, and 54.10°. Moreover, peaks at  $2\theta=10.7^{\circ}$  (Ca(OCH<sub>3</sub>)<sub>2</sub>) and 10.19°, 12.48°, 16.13°, 21.68°, 24.01°, 26.15°, 27.15°, 29.96° and 34.21° (zeolite Na-A) groups corresponded to the hybrid catalyst. TEM proved that the agglomerates of spherical particles formed for the pure catalyst. TEM image of the hybrid catalyst also revealed the cubic structure of zeolite with agglomerates structure of Ca(OCH<sub>3</sub>)<sub>2</sub> on its surface. Cluster of well-developed cubic crystals with obvious edges was observed by FESEM for the pure catalyst. Ca(OCH<sub>3</sub>)<sub>2</sub> particles were dispersed on the surface of the zeolite. However, the quadrate crystal feature of the zeolite did not change obviously.

Biodiesel was produced and optimized successfully by using both pure and hybrid forms of *C. brunneus* seashell derived catalysts. The hybrid catalyst exhibited improved FAME yield and fuel kinematic viscosity. The FAME yield increased from 93.5% to 98% by using the hybrid catalyst under the following conditions: calcination temperature of 1100 °C, reaction temperature of 65 °C and the reaction time of 120 min. Fuel properties such as viscosity, acidity, density, oxidation stability, flash point, and calorific value of both pure and hybrid catalysts met the ASTM standards except the kinematic viscosity of the pure catalyst. Kinematic viscosity of the biodiesel produced by the pure catalyst did not meet the ASTM and EN standards (8.05 mm<sup>2</sup> s<sup>-1</sup>) but the biodiesel produced by the hybrid catalyst manifested and improved kinematic viscosity of 4.88 mm<sup>2</sup> s<sup>-1</sup> which was commensurate with the international standards.

Tribological studies of biodiesel were performed with different biodiesel blends. Three types of biodiesel blends were prepared including RBOB10 (10% RBOB + 90% diesel), RBOB30 (30% RBOB + 70% diesel), RBOB50 (50% RBOB + 50% diesel). RBOB100 (100%RBOB + 0 diesel) and pure diesel RBOB0 (100% diesel). The FC diminished with the decrease of biodiesel concentration. WSD and lubricity increased with increasing the biodiesel concentration. The least WSD of 462.3  $\mu$ m was found for RBOB10 at the lowest FC of 0.085. RBOB10 exhibited perfect lubricating operation concerning wear and friction, and thus it can be implemented in the automotive engines.

*C. brunneus* derived catalysts prepared at 1100 °C was reused in eight sequential studies with 120 min transesterification reactions at a constant temperature of 65°C. For both catalysts, FAME yield decreased significantly after the 5<sup>th</sup> cycle, which was corresponded to the morphology changes as observed from the FESEM results. Furthermore, the biodiesel produced by the hybrid catalyst showed a higher FAME yield by the end of 8 cycles (79.3%). In terms of leaching, the pure catalyst manifested more than 5 ppm which did not meet the biodiesel standard limit of 5ppm. However, this was not for the case of hybrid catalyst, as its leaching contents were all below 5ppm. Thus, the hybrid catalyst manifested better catalytic activity in terms of leaching.

In overall, an efficient  $Ca(OCH_3)_2$  catalyst was developed from a novel type of seashell *i.e.*, *C. brunneus* which showed improvement over other sources of  $Ca(OCH_3)_2$ , such as calcium granules, calcium carbonate, quicklime, and synthetic catalysts. This catalyst resulted in a FAME yield of 98% within 120 min, having a higher yield in a reduced

reaction time, comparing with other synthetic catalysts. Biodiesel produced from RBO generally met the standards of biodiesel. Thus, the produced catalysts as well as its biodiesel show great potential to be applied in the industry due to their favourable performances.

#### 5.2 Recommendations

Based on the obtained results, the following actions are recommended to carry out related future studies. It is necessary to focus on establishing the catalyst costing study as a key research challenge. The need for the tools to guide catalyst development towards economical and commercially viable targets is essential. For example, the catalyst cost model (CCM) can be designed to estimate the cost of catalyst manufacturing, to compare the cost of different catalyst synthesize methods and materials. Further, investigation of different supports or mixing with other metals for the C. brunneus catalysts can be carried out to explore other options. The consistent dispersion of CaO on a suitable support or mixing it with other potential materials would further boost the stability and durability of the catalyst under severe reaction circumstances and, thus, overcome the leaching problems. In this regard, using the appropriate loading technique could be more effective and reduce the production cost of biodiesel. In comparison with conventional preparing methods such as ion exchange and impregnation, microwave irradiation is developing as a promising method to prepare supported catalyst thanks to its energy-saving, immediate drying and consistent distribution of active compounds. On the other hand, so far, there are scant works on using microwave-assisted transesterification, this method is highly recommended as it significantly reduces the reaction time compared to the conventional methods. Overall, essential advancements are still needed to design productive CaObased catalysts to use them at industrial scale.

In addition, exploring the *C.brunnes* derived biodiesel performance in real engine is suggested. The impact of poor-quality biodiesel will probably not be immediately noticeable in the operation of engine, but over time deposits, corrosion and damage can accumulate until the engine catastrophically fails. In this regard, various combinations of diesel and biodiesel can be explored. In addition, it is recommended to investigate the *C.brunnes* derived biodiesel with other non-edible feedstocks. It is reported that nearly 70-95% of the total cost of biodiesel production arises from the cost of raw material; *i.e.*, vegetable oil or animal fats. The cost of biodiesel can be reduced greatly if feedstock with high availability, cheap and unused biomass such as non-edible oils instead of edible oils were selected.

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