Synthesis of mesoporous calcium titanate catalyst for transesterification of used cooking oil: A review of the synthesized potential

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A B S T R A C T

Biodiesel is a promising alternative for conventional diesel fuel due to the unsustainable feature of the resources and unstable price of the fuels. However, the production cost is higher compared to the conventional ones and is significantly contributed from the feedstock. Realizing that a large portion of used cooking oil (UCO) is generated daily, this review aims to investigate and explore the production of biodiesel from UCO. In the production reaction process, undoubtedly, the catalyst plays an important role. It has been shown that calcium oxide (CaO) is one of the best heterogeneous basic catalysts in the transesterification reaction for biodiesel production. However, the catalyst has a low surface area which restricts the active basic sites to disperse on the catalyst surface. Moreover, CaO catalyst faces leaching problem, poor stability, and porosity which hinder its catalytic activity and reusability. Therefore, in this study, it is aimed to review the potential of titanium as a support catalyst to modify CaO supported titanium with a mesoporous structure (mesoporous calcium titanate) by a sol-gel-hydrothermal method to overcome the limitations of CaO catalyst.

1. Introduction

The global scenario of biodiesel has recently received intensive attention due to the fact that biodiesel is an alternative to diesel fuel that can solve issues inherent in diesel fuel. Moreover, biodiesel has a significant influence on reducing engine emissions such as carbon monoxide (CO) (44 %), sulphur oxide (SO) (100 %), unburned hydrocarbons (UHCs) (68 %), polycyclic aromatic hydrocarbons (PAHs) (80-90 %) and particulars (40 %) (Talebian-Kiakalaieh et al., 2013), compared to diesel fuel. However, the cost of the biodiesel has hindered the widespread application of this source of renewable energy (Abbaszaadeh et al., 2012). The circumstances of biodiesel production and trade are illustrated in Fig. 1.

In general, the cost of biodiesel production could be broken down into feedstock or raw material costs, capital costs and operating costs. Aside from that, feedstock costs contribute to a major portion of the total cost of biodiesel production. In fact, the average cost of feedstock is nearly 70 % of the total production cost (Fig. 2). As a consequence, the high cost of feedstock has led to the production cost of biodiesel to be approximately 1.5 times higher than that of diesel fuel (Singh and Patel, 2015). In addition, for biodiesel to become commercially successful on a large scale, it requires favorable economics, especially in terms of feedstock production and feedstock logistics (Kumar and Chauhan, 2013). Used cooking oil (UCO) is among the readily available and low cost feedstock for biodiesel production. UCO can be obtained from the domestic sector, restaurants, hotels and the food industry (Tsoutsos et al., 2016). Specifically, UCO comes from the edible oil produced through conventional cooking methods, such as frying. Therefore, considerable quantities of UCO are continuously available at an insignificant cost (Math et al., 2010). The use of UCO as a feedstock for biodiesel production not only helps to reduce the cost of production but also reduces the associated environmental problems. The reason for this is that the inappropriate disposal of UCO may cause possible pollution of land and water resources

(Pukale et al., 2015). Although UCO is a promising feedstock for the reduction of the overall total cost of production, this type of feedstock has the problem of containing high free fatty acids (FFA) and water content. The contents come from storage and transportation matters, in which UCO encounters microbes which can transform the triglycerides in UCO into FFA, and the acid value (AV) of the oil increases beyond 100 mg KOH g^{-1}. Furthermore, in cooking processes, water from the food materials is introduced to the oil. However, the combination of the contents in the oil makes biodiesel production from UCO harder than that from refined oil (Anuar and Abdullah, 2016a; Fu et al., 2016).
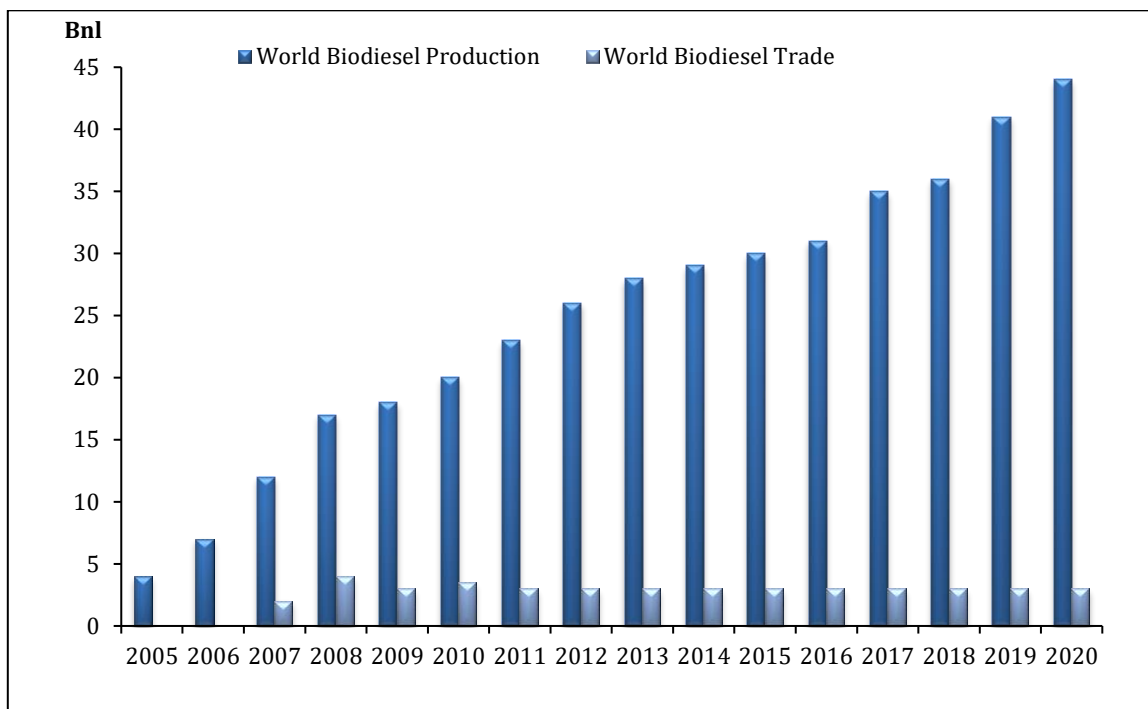

Fig. 1: Annually world biodiesel production and biodiesel trade (Hosseini and Wahid, 2012)
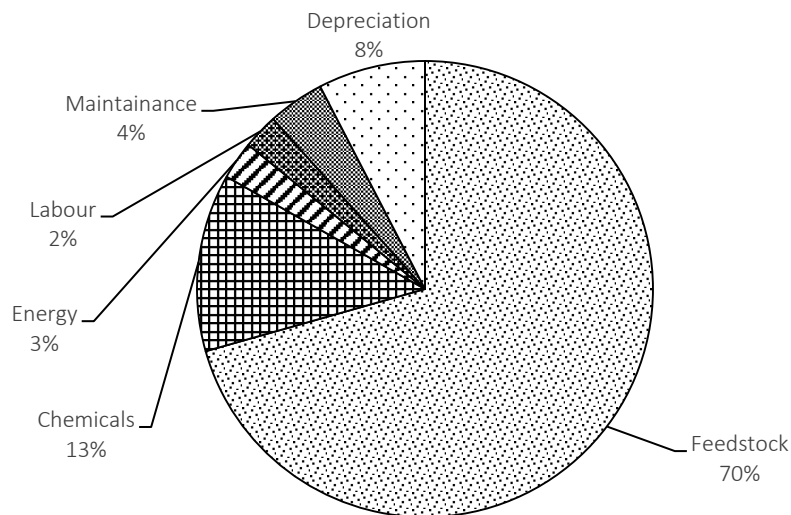

Fig. 2: General cost analysis of biodiesel production (Lim and Teong, 2010; Lin et al., 2011; Math et al., 2010)

As this oil encounters impurities that can lead to a decrease in the yield of biodiesel production caused by undesirable side reactions such as salt formation (soap) or esters saponification and hydrolysis, catalyst selection during the reaction of biodiesel production should be made wisely. Detailed work is worthy to be carried out to design a suitable catalytic reaction system that could address the contents at UCO. A heterogeneous catalytic reaction system has received great attention among researchers for biodiesel production. Thus, it is vital to develop a heterogeneous catalyst that can deal with this type of feedstock.

2. Biodiesel

In general, biodiesel is defined as a mixture of fatty acid alkyl esters (FAAE) derived from renewable feedstock's such as plant oil or animal fat through transesterification reaction (Liu et al., 2016;

Singh et al., 2016). The term "bio" indicates the biological source of biodiesel, in contrast with conventional diesel. Biodiesel appears as a clear liquid with light to dark-yellow color. It has a light musty or soapy odor, insoluble in water and has stable reactivity except towards strong oxidizing agents (Yaakob et al., 2013). There are similarities between the combustion properties of biodiesel and diesel fuel, and this makes the former among the most promising alternative for renewable and sustainable fuel (Abbaszaadeh et al., 2012; Kumar and Chauhan, 2013; Lin et al., 2011). Biodiesel also offers a number of technical and environmental benefits over conventional diesel fuel. Overall, biodiesel can be recognized as renewable, biodegradable, non-toxic, environmentally friendly and has better lubricity and ignition properties compared to conventional diesel fuel (Cao et al., 2016; Olutoye et al., 2016).

2.1. Chemical composition of biodiesel

Free fatty acids (FFA) is a long chain acid that is not conjugated or attached to anything. Generally, biodiesel largely corresponds to the FFA profile of its origin feedstock. Therefore, biodiesel may be said to be a conversion of FFA with a different composition and values caused by the different parent oil or fat to the respective fatty acid alkyl esters (FAAE) (Abedin et al., 2016; Atabani et al., 2013; Kumar and Chauhan, 2013; Mardhiah et al., 2017; Sajjadi et al., 2016).

Since methanol is the favored alcohol to be used during the production reaction (Syazwani et al., 2017), all biodiesel composition is normally provided based on fatty acid methyl esters (FAME). Table 1 presents the straight chain hydrocarbons of FAME typically from C12 to C24 in biodiesel. FAME can further be grouped into two categories, which are the saturated and unsaturated ones. The saturated FAME comprises of single carbon bond, whereas the unsaturated FAME comprises of one or more carbon-carbon double bonds.

Generally, biodiesel with a higher unsaturated FAME content results in better fuel properties compared to biodiesel with high saturated FAME content. The unsaturated FAME is further divided to monosaturated and polysaturated FAME. By knowing the percentage of monosaturated and polysaturated FAME, the quality of the reaction conversion can be measured through the degree of unsaturation. Besides, the details of FAME are also important in determining the properties of biodiesel (Akbar et al., 2009; Ramos et al., 2009).

Table 1: Chemical composition of biodiesel (Banković-Ilić et al., 2014; Gardy et al., 2016; Lam et al., 2010; Taufiqurrahmi et al., 2011)

Common Name	Chemical Structure	Carbon Structure
Methyl laurate	$CH_3(CH_2)_{10}CO_2CH_3$	C12:0
Methyl myristate	$CH_3(CH_2)_{12}CO_2CH_3$	C14:0
Methyl palmitate	$CH_3(CH_2)_{14}CO_2CH_3$	C16:0
Methyl palmitoleate	$CH_3(CH_2)_5CH=CH(CH_2)_7CO_2CH_3$	C16:1
Methyl stearate	$CH_3(CH_2)_{16}CO_2CH_3$	C18:0
Methyl oleate	$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_3$	C18:1
Methyl linoleate	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7CO_2CH_3$	C18:2
Methyl linolenate	$C_2H_5CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7CO_2CH_3$	C18:3
Methyl arachidate	$CH_3(CH_2)_{18}CO_2CH_3$	C20:0
Methyl icosanoate	$CH_3(CH_2)_9CH=CH(CH_2)_7CO_2CH_3$	C20:1
Methyl behenate	$CH_3(CH_2)_{20}CO_2CH_3$	C22:0
Methyl erucate	$CH_3(CH_2)_7CH=CH(CH_2)_{11}CO_2CH_3$	C22:1
Methyl lignocerate	$CH_3(CH_2)_{22}CO_2CH_3$	C24:0
Methyl nervonate	$CH_3(CH_2)_7CH=CH(CH_2)_{13}CO_2CH_3$	C24:1

2.2. Properties of biodiesel

Knowing the properties of biodiesel is very important in evaluating the viability of the product towards its application as a fuel. Previous studies reported that the properties of biodiesel may vary significantly. This depends on their chemical compositions, which give a very measurable effect on engine performance and emissions (Issariyakul and Dalai, 2014; Sorate and Bhale, 2015; Yusuf et al., 2011). Therefore, its properties shall be measured when considering a specific. The properties of biodiesel which are commonly considered include density, acid value, saponification value, iodine value, kinematic viscosity, cetane number, calorific value, flash point, pour point, cloud point, cloud filter plugging point, free glycerol content, total glycerol content, ash sulphur content, sulphur content, phosphorus content, copper strip corrosion, oxidation stability, water and sediment content and carbon residue.

2.3. The quality standard of biodiesel

Quality standards of biodiesel are important to maintain the quality of the product and also to meet the consumers' expectations. At present, the ASTM D6751 (American Society for Testing and Materials) and EN 14214 (European Committee for Standardization) are the most referred standards (Syazwani et al., 2017; Abedin et al., 2016; Anuar and Abdullah, 2016b; Bokhari et al., 2016; Maneerung et al., 2016; Musa, 2016). Table 2 shows the properties of biodiesel with their limits.

Table 2: Physical and chemical properties of biodiesel with limits of US and EU standards (Asikin-mijan et al., 2015; Hajjari et al., 2017; Hassan and Kalam, 2013; Ho et al., 2014; Kostić et al., 2016; Mofijur et al., 2013; Mohamad et al., 2017)

Properties (Unit)	US (ASTM D6751)	EU (EN 14214)
Density (kg m^{-3})	860-894	860-900
Acid value (mg KOH g^{-1})	0.50 max	0.50 max
Saponification value (mg KOH g^{-1})	180-200	N.I
Iodine value	N.I	120 max
Kinematic viscosity at 40 °C (mm^2 s^{-1})	1.9-6	3.5-5
Cetane number	47 min	51 min
Calorific value (MJ kg^{-1})	42-46	35
Flash point (°C)	130 min	>110 min
Pour point (°C)	-15 to -16	N.I
Cloud point (°C)	-3 to -12	N.I
Cloud filter plugging point (°C)	19	5 max
Free glycerol content (mass %)	0.02 max	0.02 max
Total glycerol content (mass %)	0.24 max	0.25 max
Ash sulphur content (mass %)	0.02 max	0.02 max
Sulphur content (ppm)	0.05	10
Phosphorus content (ppm)	10	10
Copper strip corrosion (3 h, 50 °C)	Class 3 max	Class 1
Oxidation stability (h)	3	6
Water and sediment content (vol %)	0.05 max	N.I
Carbon residue (wt. %)	0.05 max	N.I

N.I-Not Include; Max-Maximum; Min-Minimum

2.4. Feedstock for biodiesel

One of the advantages of producing biodiesel as an alternative fuel lies in its wide range of available feedstock. The feedstock for biodiesel can be different from one country to another depending on their geographical locations and agricultural practices. Selecting the best feedstock is essential to ensure a low production cost. Feedstock supply and price alone covers more than 75 % of the overall production cost (Wu et al., 2014; Yin et al., 2016). To remain competitive compared to diesel fuel, the feedstock for biodiesel should be available at the lowest possible price and in aplenty. Other desirable properties for biodiesel feedstock include high oil content, favorable FFA composition, low agriculture inputs (water, fertilizers, soils, and pesticides), controllable growth and harvesting season, consistent seeds maturity rates and potential market for agricultural by-products. In addition, the biodiesel feedstock are edible oils (such as rapeseed, soybean, sunflower, palm and coconut oil), non-edible oils (such as jatropha, karanja, sea mango, algae and halophytes), microalgae, animal fats (for example tallow, yellow grease, chicken fat and by-products from fish oil) and used or recycled oil.

2.5. Used cooking oil

UCO is regarded as a promising low cost feedstock for biodiesel production (Gardy et al., 2016). This is due to the availability and considerable quantities of UCO all over the world. UCO is generated from the domestic sector, restaurants, hotels and food industry, and those existing in edible oil. In general, UCOs are usually produced through conventional cooking methods, such as frying, which are discarded after multiple uses. However, it should be noted that UCO contains a large amount of FFA, water content and other impurities. Nevertheless, the amount and the composition of FFA, water and other impurities content in UCO depend on the origin of the oil and cooking conditions. The high content of FFA in the oil is due to the presence of heat during the cooking process (Enweremadu and Mbarawa, 2009; Wong and Devi, 2014). Besides that, UCO comes into contact with microbes during storage and transportation, which can transform the triglycerides in UCO into FFA, and the AV of the oil can increase over 100 mg KOH g^{-1}. In addition, water from the food materials, and metal ions such as Na$^+$ and Fe^{3+} from cooking equipment, are both introduced to the oil. Further, during the cooking process, toxic compounds such as hydroperoxides, alkoxy radicals, and PAHs, are produced through oxidation or pyrolysis of oil molecules (Fu et al., 2016). All these limit UCO's wide application as a biodiesel feedstock. Moreover, an upper limit on the FFAs content in UCO can cause engine damage due to deposit formation (Haigh et al., 2013). In contrast, the application of UCO as a biodiesel feedstock may solve the problem of waste oil disposal as most of UCO is thrown as waste, that are then discharged to surface waters, leading to water pollution (Math et al., 2010; Tsoutsos et al., 2016). Table 3 shows the general chemical and physical properties of a UCO sample collected by various researchers (Kiss et al., 2014; Pukale et al., 2015; Yaakob et al., 2013).

3. Transesterification of oil

Transesterification or alcoholysis is a chemical reaction involving triglycerides (in which the fatty acids group attached to the backbone of triglycerides) and alcohol in the presence or without the presence of a catalyst to form fatty acid alkyl esters (FAAE) and glycerol (Poosumas et al., 2016). It involves three consecutive reversible reactions that starts from the conversion of triglycerides to diglycerides, which are then converted to monoglycerides. Then, the monoglycerides are converted to glycerol, giving one alkyl ester in each step. Different types of alcohols such as methanol,

ethanol, propanol, and butanol can be used to produce biodiesel. However, methanol and ethanol are the most widely used. Nonetheless, comparing both methanol and ethanol, methanol is the most commonly used due to its low cost and industrial availability (Syazwani et al., 2017).

Table 3: Chemical and physical properties of UCO

| Properties	Value		
	Sample 1	Sample 2	Sample 3
Fatty acid composition (%)			
Myristic (C14:0)	0.076	N.I	N.I
Palmitic (C16:0)	4.75	6.7	8.5
Stearic (C18:0)	1.496	1.6	3.1
Oleic (C18:1)	66.96	18.3	21.2
Linoleic (C18:2)	16.79	73.4	55.2
Linolenic (C18:3)	7.8	N.I	5.9
Others	2.13	N.I	4.2
Density (g/cm³)	0.91	0.93	0.91
Viscosity (mm²/s)	32.11	96.55	4.2
Calorific value (MJ/kg)	N.I	N.I	N.I
Acid value (mg KOH/g)	2.91	3.75	3.6
Water content (%)	0.01	0.7	1.9
Saponification value (mg KOH/g)	N.I	207.7	207
Peroxide value (meq/Kg)	N.I	N.I	23.1

N.I-Not Include

Commonly, transesterification reaction with the presence of a catalyst is more preferable compared to the absence of one. A catalyst is usually used to improve and enhance the rate of the reaction so that the reaction can be completed in shorter reaction time (Baskar and Aiswarya, 2016; Koh and Ghazi, 2011; Ramachandran et al., 2013). Numerous catalysts have been studied for transesterification reaction by many researchers. These include basic and acid types for both homogeneous and heterogeneous catalysts, as well as enzymes (Mutreja et al., 2014). However, it should be noted that the selection of suitable types of catalysts is very pivotal for the reaction because it significantly deals with the type of feedstock and quantity and quality of the outcome which corresponds to the performance of catalytic activity during the reaction (Issariyakul and Dalai, 2014). Fig. 3 shows the types of transesterification approaches.

3.1. Heterogeneous catalytic transesterification reaction for biodiesel production

The catalytic transesterification reaction is the most commonly used method for transesterification of oil to produce biodiesel as it is simple and has been widely studied and industrially used to convert edible, non-edible oil, microalgae, animal fats or UCO into biodiesel. Catalytic transesterification is the reaction of triglyceride molecules that are present in the feedstock with an alcohol in the presence of a catalyst to form alkyl esters (biodiesel) and glycerol (Doğan, 2016). Fig. 4 shows the catalytic transesterification reaction process of biodiesel production. Generally, the stoichiometry between the alcohol and the oil is a 3:1 molar ratio. However, excess alcohol is usually needed as the reaction is reversible to enhance biodiesel production. Generally, the production performance depends on the reaction process parameters such as alcohol to oil molar ratio, type of catalyst, amount of catalyst loading, reaction time, reaction temperature, FFA and water contents in the feedstock.
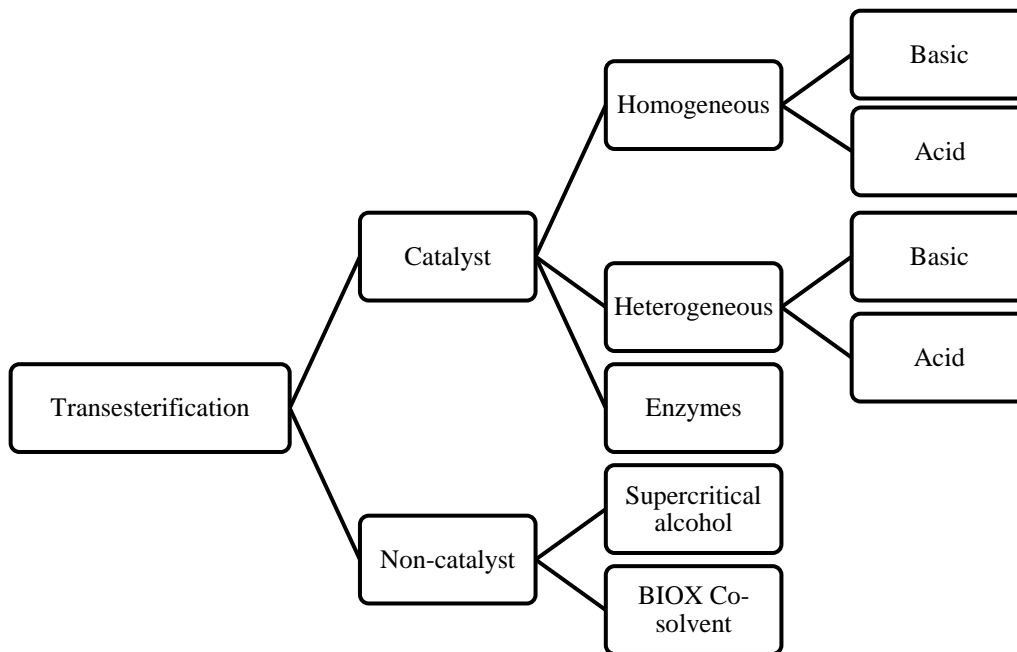
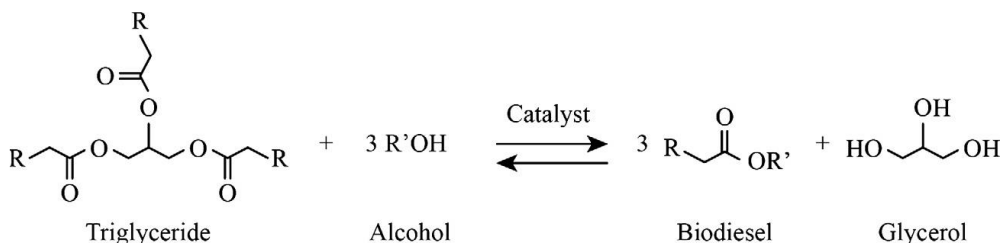**Fig. 3:** Types of the transesterification reaction process

Fig. 4: Catalytic transesterification reaction (Poosumas et al., 2016)

3.2. Heterogeneous catalyst

Heterogeneous catalysts, which were proposed to solve the homogeneous catalysts problems, have aroused great interest among researchers in the transesterification reaction for biodiesel production (Guldhe et al., 2017; Farooq et al., 2015; Li et al., 2015; Nasreen et al., 2015). These catalysts are considered for the improvement of the current biodiesel production process. The use of heterogeneous catalysts would result in a simpler and cheaper separation process, including reduction of the water effluent load and capital and energy costs. Besides that, heterogeneous catalysts can be reused and would not have to be continuously added. Heterogeneous systems operate in a continuous mode and are designed to give a longer lifetime and lowering associated costs (Deshmane and Adewuyi, 2013). Furthermore, heterogeneous catalysts are also claimed to be eco-friendly (Madhuvilakku and Piraman, 2013). However, this type of catalyst is restricted due to its complexity in the preparation process (Ma et al., 2016).

3.3. Heterogeneous acid catalyst

Heterogeneous acid catalysts have received considerable attention as a potential substitute for homogeneous acid catalysts because the former can be separated and reused and exhibit less corrosion, toxicity, and environmental problems than the latter (Cheng et al., 2016). Nevertheless, similar to homogeneous acid catalysts, heterogeneous acid catalysts may perform well in a high amount of FFA in the feedstock during the transesterification reaction in a high reaction temperature (Islam et al., 2014). But, this type of catalyst is commended for high methanol to oil molar ratio and amount of catalyst loading to obtained high catalytic activity performance (Wan and Hameed, 2014). Aside from that, Sharma et al. (2014) stated that heterogeneous acid catalysts suffer from a poor reusability performance compared to heterogeneous basic catalysts. The catalytic activity of recent studies of the heterogeneous acid catalysts in transesterification reaction are tabulated in Table 4 and Table 5 shows recent heterogeneous basic catalysts studied by researchers.

3.4. Heterogeneous basic catalyst

A basic catalyst in the heterogeneous form aims to overcome the constraints associated with the use of a homogeneous base catalyst, including the separation of product and by product and reusability. These catalysts have mostly shown high catalytic activity in the transesterification reaction under mild conditions (Mardhiah et al., 2017; Nayebzadeh et al., 2016). These catalysts are more preferable compared to the heterogeneous acid catalysts too, as they have non-corrosive and environmentally benign properties (Ofori-Boateng and Lee, 2013).

Table 4: Recent heterogeneous acid catalysts for transesterification reaction

Catalyst	Reaction conditions				Yield (%)	Reusability	References
	Methanol to oil molar ratio	Catalyst loading (wt. %)	Reaction time (h)	Reaction temperature (°C)			
$S_2O_8^{2-}/ZrO_2$	20:1	3	4	110	100	4	(Wang et al., 2016)
Sulfated zirconia	20:1	3	6	150	100	N.I	(Shi et al., 2016)
HZSM-5	5:1	1	3	200	74	5	(Alaba et al., 2016)
$SO_3H\text{-}ZnAl_2O_4$	9:1	1	1	120	94.7	8	(Soltani et al., 2016)
Carbon cryogel	20:1	5	5	65	91.3	N.I	(Zainol et al., 2015)
HZ/1.0/60	45:1	10	4	100	N.I	N.I	(Vieira et al., 2015)
(PW11)3/MCM-41	8:1	7	16	65	90	4	(Singh and Patel, 2015)
$SO_4^{2-}/C/Ce^{4+}$	12:1	1	5	66	N.I	6	(Shu et al., 2015)
$ACPhSO_3H$	20:1	10	2	65	N.I	7	(Malins et al., 2015)
TiSBA-15-Me-PrSO_3H	90:1	5	9	65	71	3	(Léon et al., 2015)
$Ce/ZrO_2\text{-}TiO_2/SO_4^{2-}$	6:1	5	1	65	N.I	5	(Kaur and Ali, 2015a)

N.I-Not Include

Table 5: Recent heterogeneous basic catalysts for transesterification reaction

Catalyst	Reaction conditions				Yield (%)	Reusability	References
	Methanol to oil molar ratio	Catalyst loading (wt. %)	Reaction time (h)	Reaction temperature (°C)			
Cs-Na$_2$ZrO$_3$	30:1	1	0.25	65	98.8	9	(Torres-Rodríguez et al., 2016)
40K/PA-550	12:1	5	3.5	65	97	8	(Shan et al., 2016)
35KOH/ZSM5	12:1	18	8	60	93.8	4	(Saba et al., 2016)
Sodium silicate	12:1	2.5	0.5	65	97	4	(Roschat et al., 2016a)
MgO/MgAl$_2$O$_4$	12:1	3	3	110	N.I	6	(Vahid and Haghighi, 2016)
KOH/calcium aluminate	12:1	3.5	4	65	96.7	3	(Nayebzadeh et al., 2016)
La/Mn oxide	12:1	3	1.5	180	N.I	11	(Nasreen et al., 2015)
20-Li/ZrO$_2$-700	12:1	5	1.25	65	99	10	(Kaur and Ali, 2015b)

N.I-Not Include

The disadvantageous feature of heterogeneous basic catalysts is its high affinity to moisture during storage and high FFA content in the feedstock (Issariyakul and Dalai, 2014). The high FFA feedstock would easily lead to saponification in the presence of a basic catalyst, which generates soap that will consume the catalyst and affecting the biodiesel yield.

3.5. Parameters in a heterogeneous catalytic transesterification reaction

Several parameters are generally considered during the transesterification reaction which will affect the quantity and quality of biodiesel production (Lee and Taufiq-Yap, 2015). The optimum value of each parameter will differ for each study due to the reaction factors such as the type of feedstock and catalyst used during the reaction.

3.5.1. Methanol to oil molar ratio

One of the most important variables affecting the percentage of biodiesel yield during transesterification is the methanol to oil molar ratio of methanol to triglycerides molar ratio as defined by some researchers. During transesterification, the required stoichiometric ratio is three moles of methanol and one mole of oil to yield three moles of FAME and one mole of glycerol. However, in practice, a higher feed mole ratio is employed to shift the transesterification reaction to the desired product (Tariq et al., 2012). Salinas et al. (2012) stated that the catalytic activity steadily increased with higher methanol to oil molar ratio. During the heterogeneous catalytic transesterification reaction, the higher amount of methanol facilitates the suspension of the catalyst which may eliminate the problem of mass transfer.

The lower methanol to oil molar ratio results in poor suspension of the slurry in the reaction solution, which possibly induces mass transfer problems, thus resulting in lower catalytic activity. Therefore, an excess of the methanol favors the formation of the products. Tariq et al. (2012) also claimed that higher methanol to oil molar ratio results in greater product conversion in a shorter time. In contrast, higher consumption of methanol

also increases the solubility of glycerol, and as a result, decreases the yield of biodiesel as some glycerol will remain in the FAME phase. Therefore, the ideal methanol to oil molar ratio needs to be established empirically according to the reaction system used.

3.5.2. Amount of catalyst loading

Heterogeneous catalyst influences the reaction by providing active surface sites for it to occur, whereby the increase of catalyst amount would increase the available catalytic sites. The ideal amount of catalyst loading will accelerate the reaction. However, an excess amount of catalyst loading can cause saponification which usually occurs to the homogeneous and heterogeneous basic catalysts (Silitonga et al., 2013). Besides that, Salinas et al. (2012) reported that an excess amount of catalyst can create catalyst accumulation on the wall of the reactor. This will possibly contribute to the diffusional problems during the reaction, which explains the lower catalytic activity. Furthermore, with an excess amount of catalyst, the slurry (a mixture of reactants and catalyst) becomes too viscous, which then gives rise to a problem of mixing and a demand of higher power consumption for adequate stirring (Qiu et al., 2011). Generally, the amount of catalyst loading pays respect to the amount of feedstock. The amount of catalyst loading will be expressed in the form of weight percentage (wt. %) based on the weight of the feedstock used.

3.5.3. Reaction time

On the other hand, reaction time would also affect the transesterification reaction process. Tariq et al. (2012) stated that the conversion rate increases with reaction time. In the heterogeneous catalytic system, a mass transfer limitation exists between the three different phases of oil-methanol-catalyst for the diffusion of molecules. Longer reaction time would allow sufficient contact time between the reactants and the catalyst surface (Wan and Hameed, 2014). In general, the reaction catalyzed through the heterogeneous catalyst requires a relatively long time compared to the homogeneous catalyst due to diffusion of reactants through the external surface

film and intra-particle pores (Lertpanyapornchai and Ngamcharussrivichai, 2015).

3.5.4. Reaction temperature

Transesterification reaction can occur at different temperatures, depending on the type of alcohol used during the reaction (Amani et al., 2014). The reaction temperature must be less than the boiling point of alcohol to ensure minimum vaporization (Tariq et al., 2012). Vaporization of alcohol will lessen product yield. Usually, the ideal reaction temperature ranges from 60 °C to 65 °C (if methanol is used as the alcohol). However, in several cases, high temperature is more favorable as it increases the solubility of oil in methanol and improves the methanol to oil contact. Besides that, the higher reaction temperatures speed up the reaction and shorten the reaction time. The increase in temperature causes the reactants molecule to gain more kinetic energy for collisions to occur and successfully react to form the product. Beyond the ideal reaction temperature, it may cause side reactions such as polymerization of fatty acid molecules which reduces the amount of reactants available (Wan and Hameed, 2014).

3.5.5. Free fatty acid content

The FFA content is a key parameter to determine the viability of the oil for the transesterification reaction. The acid value is an indicator of FFA content in the triglycerides (Hayyan et al., 2014), where a higher acid value shows that the feedstock contains a higher percentage of FFA. Numerous studies have been conducted to investigate the effect of FFA in the transesterification reaction. Theoretically, high FFA content will hinder the reaction with the basic catalysts through a saponification reaction (Talebian-Kiakalaieh et al., 2013). This situation results in a low yield of biodiesel and conversion of FAME (Verma and Sharma, 2016). Therefore, a pre-treatment step is needed to trans esterify the FFA before triglycerides can be converted into FAME.

3.5.6. Water content

Water content is a more critical variable in the transesterification reaction than FFA content (Tariq et al., 2012). All materials involved in the transesterification process should be waterless as water leads to hydrolysis of triglycerides and FAME which simultaneously contributes to the formation of soap which then increases the viscosity of the reaction mixture leading to the formation of a stable emulsion. This makes the separation process difficult. Additionally, Amani et al. (2016) stated that water contains in the feedstock for transesterification reaction affects the yield as it reduces the catalytic activity.

3.6. Mechanism of heterogeneous catalytic transesterification reaction

The study of mechanism in catalytic transesterification reaction is very critical in controlling reaction and designing the reactor to improve the biodiesel production process. Theoretically, the mechanism of heterogeneous catalytic transesterification follows the same principles to those of homogeneous catalytic transesterification as shown in Fig. 5. Generally, the mechanism of heterogeneous acid catalytic transesterification will start with the protonation of the carbonyl group, followed by a nucleophilic attack of alcohol which produces tetrahedral intermediate. Finally, the proton migration and the tetrahedral intermediate breakdown will omit glycerol to create a new ester and reforms the catalyst.

Fig. 6 shows the general reaction mechanism of heterogeneous acid catalytic transesterification. On the other hand, the heterogeneous basic catalyst transesterification mechanism deals with the formation of the alkoxide ion and then directly acts as a strong nucleophile (Fig. 7). Heterogeneous basic catalysis has a direct route compared to heterogeneous acid catalysis. The main difference between both catalysts' catalytic activity in transesterification reaction is the formation of electrophilic species versus stronger nucleophile formation (Talebian-Kiakalaieh et al., 2013).

Consequently, the mechanism of heterogeneous catalytic transesterification moves further to the adsorption of reactants and desorption of products that takes place on the surface of the catalyst (Wu et al., 2017). Recently, the most widely used mechanism models in heterogeneous acid and basic catalysts are Eley-Rideal and Langmuir-Hinshelwood mechanisms (León-Reina et al., 2013). According to the Eley-Rideal mechanism, the reaction is performed by a direct pickup of species from the surface by a liquid phase molecule, whereas in the Langmuir-Hinshelwood mechanism the reactants are first adsorbs on the catalyst surface and then reacts, follows by the product desorption (Dange et al., 2014; Davison et al., 2013; Marinković et al., 2016). Table 6 demonstrates the difference in the Eley-Rideal and Langmuir-Hinshelwood mechanism in general.

3.7. Kinetic study in the catalytic transesterification reaction

Initially, when conducting a kinetic study for catalytic transesterification reaction, it is important to calculate the reaction rate constant (k) for the reaction. Usually, the rate constant is sensitive to temperature, which increases with the increase in reaction temperature for elementary reactions. This may be due to the enhancement of the energy required to induce the reactants to actively participate in the transesterification reaction (Parthiban and Perumalsamy, 2016). The reaction

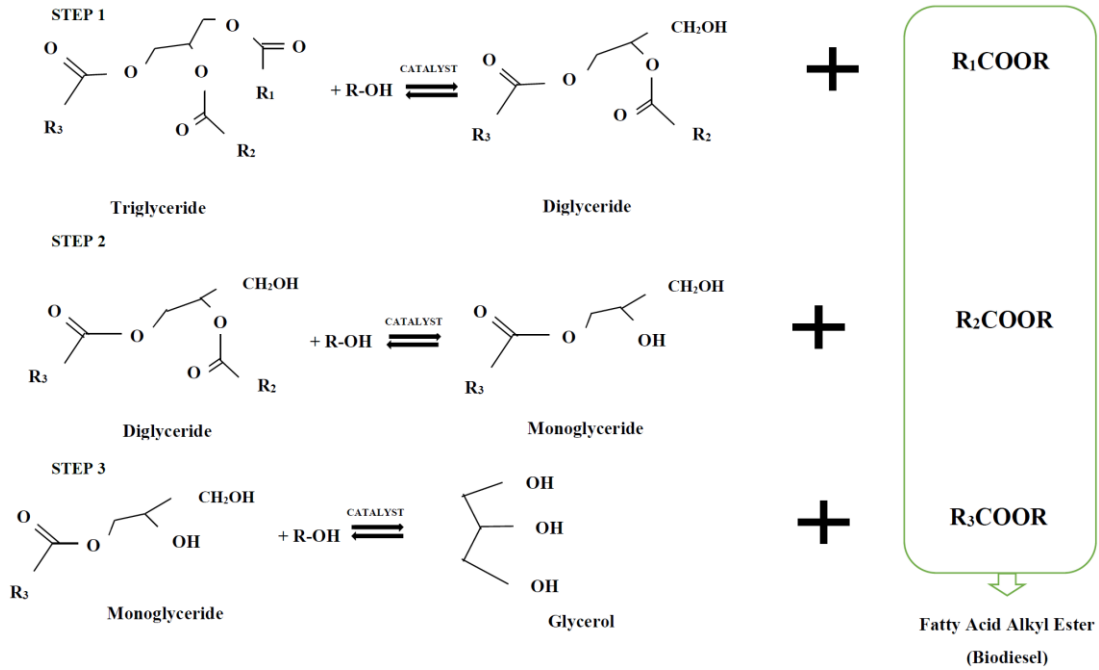rate constant is obtained from the slope of the linear plot of reaction temperature and time intervals.

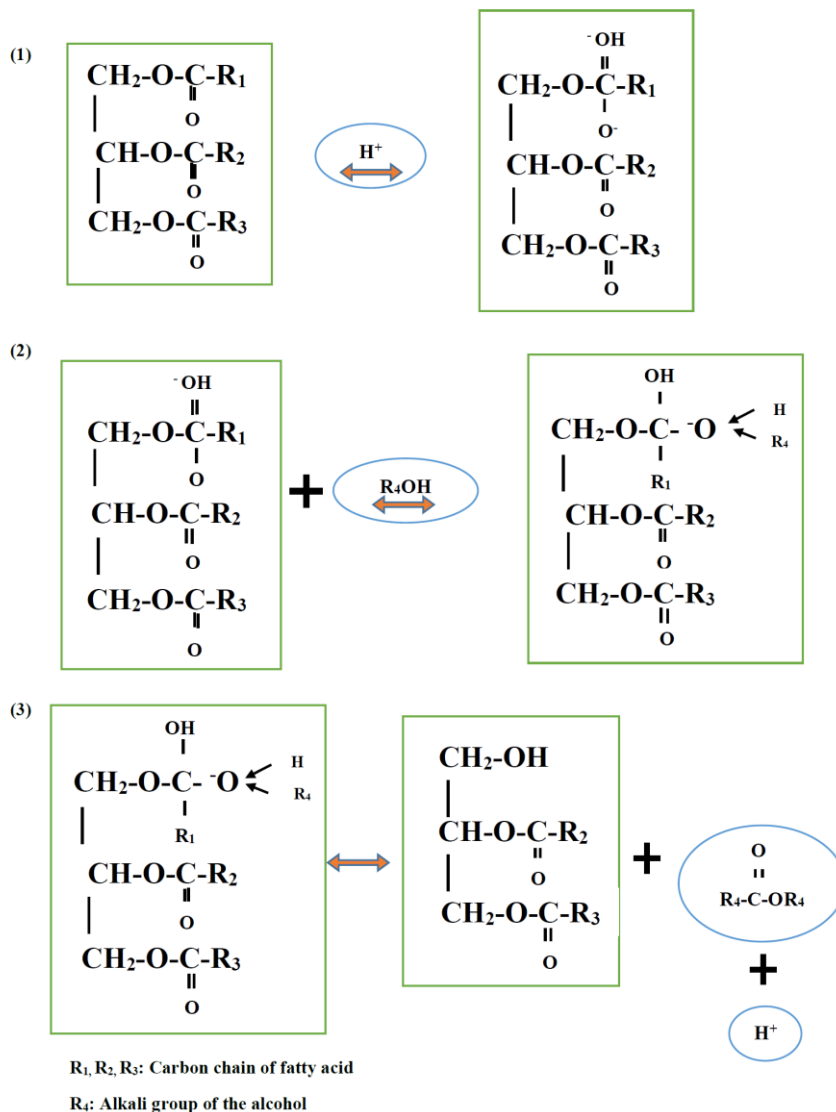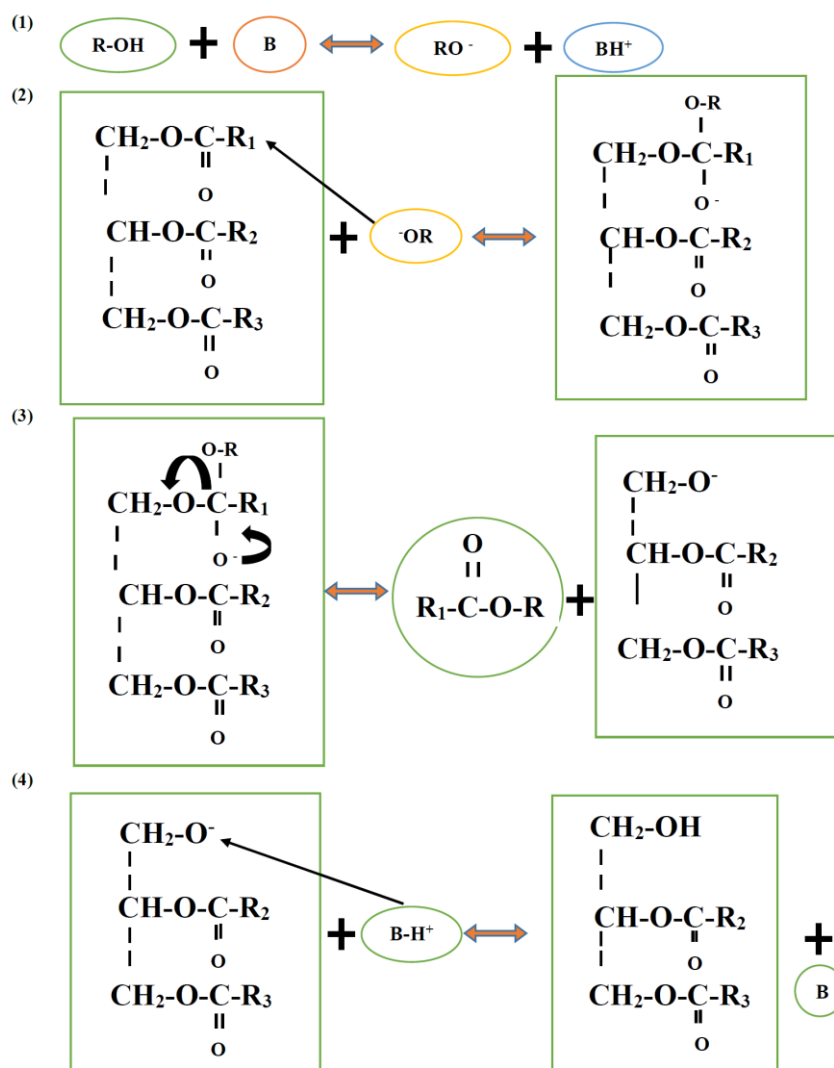**Fig. 5:** General mechanism of heterogeneous catalytic transesterification reaction (Avhad and Marchetti, 2015)

Fig. 6: General reaction mechanism of heterogeneous acid catalytic transesterification (Talebian-Kiakalaieh et al., 2013)

B: Base catalyst, R_1, R_2, R_3: Carbon chain of fatty acid, R_4: Alkali group of the alcohol

Fig. 7: General reaction mechanism of heterogeneous basic catalytic transesterification (Talebian-Kiakalaieh et al., 2013)

Table 6: General mechanism of Eley-Rideal and Langmuir-Hinshelwood (Ilgen and Akin, 2012)

Eley-Rideal mechanism	Langmuir-Hinshelwood mechanism
$M + S \Leftrightarrow M.S$	$M + S \Leftrightarrow M.S$
$TG + M.S \Leftrightarrow DG + E.S$	$TG + S \Leftrightarrow TG.S$
$DG + M.S \Leftrightarrow MG + E.S$	$TG + M.S \Leftrightarrow DG + E.S$
$MG + M.S \Leftrightarrow G + E.S$	$DG + M.S \Leftrightarrow MG + E.S$
$E.S \Leftrightarrow E + S$	$MG + M.S \Leftrightarrow G + E.S$
	$E.S \Leftrightarrow E + S$

TG-triglyceride; M-methanol; DG-diglyceride; MG-monoglyceride; G-glycerine; E-ester; S-catalytic surface

One of the useful parameters to understand the reaction is activation energy (E_a), which is defined as the amount of energy required for reactants to be overcome for the reaction to occur. Table 7 summarizes the previous activation energy from the kinetic studies on catalytic transesterification reaction using various feedstock for biodiesel production. Usually, lower activation energy is preferred during the reaction. This is to obtain less energy required to overcome the activation barrier for reaction completion, besides accelerating the rates of reaction. It is also important to understand whether the reaction rate is diffusion limited or mass transfer limited or is truly governed by the chemical step where the catalyst is being used to its maximum capacity. If the reaction rate is diffusion limited or mass transfer limited, the activation energy is usually as low as 10 to 25 kJ mol^{-1}. However, for reactions which rate are governed by a truly chemical step, the activation energy will show an excess of 25 kJ mol^{-1} (Patel and Brahmkhatri, 2013).

In addition, kinetic of various orders of the catalytic transesterification reaction can be described through the relationship between reaction temperature and time, which depends on the rate of reaction (Gurunathan and Ravi, 2015). Kinetic order is important in confirming and clarifying the reaction rate constant and the activation energy obtained from the reaction. Generally, in catalytic transesterification reaction, zero, first, pseudo-first and second order kinetic models will be determined to treat all the kinetic data for the reaction.

3.8. Thermodynamic study in the catalytic transesterification reaction

Commonly, thermodynamic parameters of catalytic transesterification reaction are studied

based on transition state theory and calculated using the Eyring-Polanyi equation based on the reaction rate constants from various temperatures (Mathiarasi and Partha, 2016; Wu et al., 2016). From the equation, the value of the changes in enthalpy, ΔH and entropy, ΔS of activation for the reaction system can be obtained. Usually, the value of ΔH is positive and the value of ΔS is negative. However, both parameters can be obtained in vice versa (Feyzi et al., 2017; Feyzi and Shahbazi, 2017). A positive value of ΔH shows that heat input is required to bring the reactants to the transition state to form the products. A negative value of ΔS indicates that the

degree of ordered geometry or alignment of the transition state is better than reactants in the ground state (Nautiyal et al., 2014). Another parameter that needs to be considered during the thermodynamic study is the Gibbs free energy, ΔG, where a positive value indicates that the reaction is unspontaneous and endergonic in nature (Wu et al., 2016) and a negative value indicates that the reaction equilibrium constant is big. That in itself is the evidence of further progress of the reaction towards the products. ΔG will be more negative with the increase of reaction temperature and that with the increasing of the equilibrium constant.

Table 7: Summary of activation energy and order of reaction of the catalytic transesterification reaction

Feedstock	Catalyst	Activation energy, Ea (kJ mol^{-1})	Order of reaction	Reference
Karanja oil	KOH	20.2	First	(Verma et al., 2017)
Sunflower oil	CaO-based PKSB	108.8	Pseudo first	(Kostić et al., 2016)
Palm oil	CaO	121.1	Pseudo first	(Roschat et al., 2016b)
Waste cooking oil	CaO	78.8	Pseudo first	(Maneerung et al., 2016)
Bitter almond oil	PA/AC	56.7	First	(Fadhil et al., 2016)
Soybean oil	NaOH	31	Pseudo first	(Wu et al., 2016)
Nannochloropsis oculata oil	Ca(OCH$_3$)$_2$	58.6	Pseudo first	(Teo et al., 2016)
Kusum oil	Ba(OH)$_2$	21.8	Second	(Sarve et al., 2016)
Rapeseed oil	KOH	21.9	Pseudo first	(Encinar et al., 2016)
Waste cooking oil	(PW$_{11}$)$_3$/MCM-41	64.1	First	(Singh and Patel, 2015)
Peanut oil	MWM-700	66.8	First	(Niu et al., 2015)
Neem oil	CZO	233.9	First	(Gurunathan and Ravi, 2015)
Jatropha oil	Zr/CaO	29.8	Pseudo first	(Kaur and Ali, 2014)

N.I-Not Include

4. Calcium oxide as a catalyst in the transesterification reaction

CaO catalyst is one of the most promising heterogeneous catalyst used in transesterification reaction for biodiesel production. It has good availability and causes less impact on environment, besides being non-toxic, low cost and easy to be handled (Bet-Moushoul et al., 2016; Esipovich et al., 2014; Ho et al., 2014; Joshi et al., 2015; Kouzu et al., 2016; Li et al., 2016; Liu et al., 2016). Thus, this catalyst has undergone a continuation study in the transesterification reaction for biodiesel production until the present.

4.1. Properties of calcium oxide

CaO is an alkaline earth metal oxide. CaO occurs through thermal decomposition of minerals such as limestone and calcite or from natural resources such as sea- and eggshells that contain calcium carbonate (CaCO$_3$) (de Sousa et al., 2016). The general physical and chemical properties of CaO are listed in Table 8. CaO has a very weak Lewis acidity of metal cation due to its small electronegativity (Kouzu and Hidaka, 2012). Hence, the conjugate anion (oxygen) displays strong basic properties for CaO (Bazargan et al., 2015). The basicity of CaO, as well as its other structural and textural characteristics, depends on the activation procedure and the starting precursor used. In addition, CaO is not stable in which its basic sites on the surface will spontaneously react with water and CO$_2$ from the surrounding to form calcium hydroxide (Ca(OH)$_2$) and CaCO$_3$.

Table 8: General physical and chemical properties of CaO (Marinković et al., 2016)

Properties	Description
Chemical structure	CaO
Molar mass (g mol^{-1})	56.08
Density (kg m^{-3})	3.34
Boiling point (°C)	2850
Melting point (°C)	2613
Color	White
Odor	Odorless

4.2. Catalytic activity of calcium oxide in the transesterification reaction

CaO is used in transesterification due to its high basicity, low solubility in methanol and biodiesel and excellence in biodiesel produced yield (Feyzi and Norouzi, 2016; Korkut and Bayramoglu, 2016). The catalytic activity of CaO in the transesterification reaction is based on the existence of basic active sites in the catalyst surface. The main advantage of this catalyst is its ability to perform in a mild transesterification reaction conditions as compared to heterogeneous acid catalyst. There are a number of previous and current studies of the catalytic activity performance of CaO in transesterification reaction for biodiesel production. Table 9 presents the catalytic activity performance of CaO in transesterification reaction at optimum reaction conditions from various CaO sources.

4.3. Modification of calcium oxide for transesterification reaction

CaO is superior to other heterogeneous basic catalysts in the catalytic performance for the transesterification reaction for biodiesel production

(Mahesh et al., 2015). However, this heterogeneous catalyst exhibits a much lower catalytic activity than the homogeneous catalytic activity which is applied to the existing biodiesel production (Chen et al., 2016a). This is due to the low surface area of CaO catalyst which lowers the amount of exposed active sites during the reaction (Asikin-mijan et al., 2015; Degirmenbasi et al., 2015). Therefore, a higher amount of catalysts and longer reaction time are often required, which would then increase the biodiesel production cost. Therefore, many researchers who take interest in utilizing CaO catalyst for biodiesel production strive towards raising the catalytic activity.

Furthermore, it is important to enhance the stability of the catalyst with high tolerance to the ambient water and CO_2, which poisons the catalytically basic sites. The poisoning may deactivate the active basic sites of the catalyst. Furthermore, the low stability of the catalyst also contributes to the leaching problem (Ezzah-Mahmudah et al., 2016; Liu et al., 2015; Reyero et al., 2016; Wong et al., 2015; Yan et al., 2016). Additionally, the bulky structure of CaO makes it a non-porous catalyst. This structure has limited the catalytic activity of CaO to catalyze a large triglycerides molecule. Thus, it increases the diffusion limitation of the reactant molecules.

In addition to the abovementioned problems, there are efforts on the modification of CaO to overcome the problems with excellent catalytic activity performance. According to the numerous studies on the use of this catalyst in transesterification reaction for biodiesel production, CaO can be modified through four different methods. Firstly, the modification of CaO can be done by enlarging the surface area and increasing the stability of the catalyst by doping CaO with active ingredients which are alkali and organic compounds. The final modified catalyst is denoted as the doped CaO catalyst. Most frequently, doping of CaO is prepared by incipient wetness, co-precipitation and impregnation method.

Besides that, the characteristic properties of CaO catalyst (especially surface area and stability) can also be improved by incorporation of this catalyst into various catalyst supports including metals, metal oxides, transition metal oxides, and non-metals. The synthesis of the catalyst frequently includes the deposition of CaO from precursor salts onto the catalyst support through precipitation, co-precipitation, wet impregnation or sol-gel method followed by calcination step which additionally defined as loaded or supported CaO catalyst. Furthermore, it should be noted that the amount of CaO used is higher than the modifier during that modification preparation (Abdulkareem-Alsultan et al., 2016; Witoon et al., 2014; Liu et al., 2012).

On the other hand, the properties and the catalytic activity of CaO catalyst can be enhanced by mixing the catalyst with metal oxides and transition metal oxides. A mixed oxide is an oxide with cations of more than one chemical element or with a single element in several states of oxidation. Mixed oxides-CaO is usually synthesized through solid state reaction, incipient wetness impregnation and co-precipitation, followed by thermal decomposition. In addition, CaO can be modified to porous (micro-, meso- or macro-) and nano-sized catalysts. These can be done by thermal activation treatment (calcination), varying the precursor salt (such as $CaCO_3$, $Ca(OH)_2$, etc.) and pre-treatment with methanol.

Based on previous studies, it can be concluded that the modification of CaO catalysts has increased the catalytic activity of CaO. Those modified CaO catalysts had achieved a high percentage of biodiesel yield which was higher than 90 %. However, those studies have shown that the catalysts still need a high reaction condition to achieve such a great catalytic activity performance.

In parallel, an ongoing study is still running actively as many areas need to be explored to enhance the performance of CaO with mild reaction conditions. Besides, the catalyst preparation method was mostly complicated and not cost effective. Finally, there is an increasing interest in using a large amount of FFA and water content feedstock. Therefore, the main challenge for the modified CaO catalyst will be how to achieve a good catalytic activity performance for that particular type of biodiesel feedstock during the reaction.

The reason is due to the saponification side reaction caused by the use of a basic catalyst which consumes the catalyst and can form an emulsion that makes separating the products difficult and reduces biodiesel yield. Therefore, it is expected that more emphasis will be given to the modification of CaO in the future. Despite those difficulties that remain to be solved, there is still a need for a study to modify CaO to perform in mild reaction conditions which uses simple and practical modification preparation methods, and that can tolerate well with a low grade of biodiesel feedstock.

5. Titanium as catalyst support in the transesterification reaction

The catalyst support is an important aspect to be considered in catalysis as it may give a significant effect on the performance of the catalyst such as providing larger surface area for better distribution of the active sites of catalyst and enhancing stability and durability of the catalyst as compared to the unsupported catalyst. To date, there has been an increasing study on titanium as catalyst support during transesterification reaction for biodiesel production. Titanium is well known to be a cheap, readily available and non-toxic element (Dai et al., 2017; Mallakpour and Dinari, 2012). Titanium possesses other unique combination of properties, such as tunable porous surface structure, relatively high surface area, high stability and with an available surface for adsorbing, dissociating and reacting which makes it an attractive potential catalyst support for transesterification reaction (Feyzi and

Shahbazi, 2015; Bagheri et al., 2014; Ye et al., 2013; Mallakpour and Dinari, 2012).

Various recent studies have shown that titanium owns an excellent performance as a catalyst support in the transesterification reaction for biodiesel production. Most recently, Dai et al. (2017) reported the use of titanium loaded lithium as a base catalyst for biodiesel production. The obtained catalyst proved to be more stable and the interaction between titanium and lithium was strong enough to have good recyclability of the catalyst with excellent catalytic activity performance. Besides that, potassium has been supported by titanium and shown remarkable performance towards the production of biodiesel from canola oil by the presence of highly strong basic sites associated with the interaction of both catalyst and catalyst support structure formed on the synthesized catalyst (Salinas et al., 2016).

In another study conducted by Chen et al., (2016b), a carbonaceous Ti-SBA-15 catalyst for transesterification of jatropha oil with methanol was successfully developed. The result showed that the catalyst gave excellent activity and durability in the synthesis of high-quality jatropha biodiesel, which fulfills the specification of international fuel standard. Kaur and Ali (2015c) have modified the titanium with sulfate group immobilization for the esterification of fatty acids. The catalyst was able to convert >98 % free fatty acids into respective esters. A study by Feyzi and Shahbazi (2015) demonstrated that Cs-Ca/TiO$_2$-SiO$_2$ catalyst was able to achieve a maximum biodiesel yield of 98 % under optimal reaction conditions. It is reported that effective factors on the catalytic activity are specific surface area, pore diameter, pore volume and active site concentration on the surface of the catalyst.

Table 9: Catalytic activity of calcium oxide from various resources in the transesterification reaction

Resource	Reaction conditions				Yield(%)	Reusability	References
	Methanol to oil molar ratio	Catalyst loading (wt. %)	Reaction time (h)	Reaction temperature (°C)			
Waste venus clam shell	15:1	5	6	65	97	5	(Syazwani et al., 2017)
Duck eggshell	10:1	10	1.33	60	94.6	8	(Yin et al., 2016)
Hydrated lime	15:1	6	2	65	97	5	(Roschat et al., 2016a)
Chicken manure	15:1	7.5	N.I	65	90	4	(Maneerung et al., 2016)
Crab shell	8:1	2.5	2	65	94	5	(Madhu et al., 2016)
Palm kernel shell	9:1	3	4	65	99	3	(Kostić et al., 2016)
Chicken bones	15:1	5	4	65	89.3	4	(Farooq et al., 2015)
Waste carbide slag	9:1	1	0.5	65	91.3	3	(Li et al., 2015)
Snail shell	6.03:1	2	7	60	87.3	N.I	(Birla et al., 2012)
Waste freshwater mussel shell	12:1	5	1.5	70	97.5	7	(Hu et al., 2011)

N.I-Not Include

Lertpanyapornchai and Ngamcharussrivichai (2015) and Sharma et al. (2014) included titanium as a catalyst support or promoter of their catalyst in preparing biodiesel through a transesterification reaction. Their study shows a good catalytic performance towards the production of this renewable fuel. Another study regarding the titanium as catalyst support was conducted by Takase et al. (2014) whereby the modified C4H4O6HK catalyst with the presence of titanium had granular and porous structures with high basicity and superior catalytic performance of 90.1 % of biodiesel yield at 30 minutes of reaction. Marciniuk et al. (2014) meanwhile prepared sodium titanate catalyst for the transesterification reaction under mild conditions. The study offers better light regarding titanium as catalyst support in the transesterification reaction.

There are many other studies that shows the ability and potential of titanium as a catalyst support or promoters for support catalyst in transesterification reaction for biodiesel production (Sani et al., 2016; Hernández-Hipólito et al., 2015;

Chen et al., 2013; Madhuvilakku and Piraman, 2013; Mguni et al., 2013; Yu et al., 2013; Mongkolbovornkij et al., 2010; Wen et al., 2010). This further strengthens the fact that the study of titanium as a catalyst support has a big potential especially in transesterification reaction for biodiesel production.

6. Mesoporous catalyst in the transesterification reaction

The introduction of porous materials in catalytic systems improves the overall life of the systems process and the yields of the reactions. attracting the interest of researchers to stimulate an intense activity aimed at the preparation of the materials. Specifically, porous materials are of great interest because of their ability to interact with atoms, ions, molecules, and nanoparticles, not only at their surfaces but also throughout the bulk of the materials. Therefore, the presence of pores in the structured materials can greatly promote their physical and chemical properties, as well as

extending their potential during the catalytic activity (Linares et al., 2014).

Among the available porous materials use for catalysis, mesoporous materials have attracted growing interest, owing to their fascinating properties such as tunable large pore sizes, large pore volumes, alternative pore shapes, high surface areas and controllable framework compositions (Feinle et al., 2015; Schmit et al., 2015; Yu et al., 2015). According to International Union of Pure and Applied Chemistry (IUPAC), mesoporous materials are materials possessing pore dimensions between 2 to 50 nm, that is between micro- pores and macro-pores in size. Taking into account the diffusional limitations when dealing with high molecular weight reactants, mesoporous materials may be advantageous over microporous materials because the mass transfer resistance and diffusion limitations can be significantly reduced (Tao et al., 2013).

Despite the attractive properties of mesoporous materials, consequently, a new mesoporous catalyst is required to be designed to provide a higher available active surface which results in an enhancement in catalytic activity (Endo et al., 2015; Kumar et al., 2015). As for biodiesel production, the development of mesoporous catalysts has exhibited good catalytic activities during the transesterification reaction. The catalysts have allowed the catalytic activity to tolerate with high FFA content feedstock at mild reaction conditions during the reaction. Furthermore, the limitation of loading larger reactants molecules can be overcome and obtain the improvement of the catalytic activity performance. There are a number of mesoporous catalysts that have been developed to be used in the transesterification reaction for biodiesel production.

Alaba et al. (2016) have synthesized a promising solid catalyst for biodiesel production through desilication of conventional ZSM-5 with an aqueous solution of NaOH. The synthesized hierarchical mesoporous HZSM-5 catalyst attained an optimum biodiesel yield of 82.12 % using 1 wt. % of catalyst loading. The excellent performance of the catalyst was attributed to the matrix area, pore size, and mesopore volume of the catalyst. Helwani et al. (2016) had investigated mesoporous hydrotalcite as a catalyst for the transesterification of jatropha oil with methanol to produce biodiesel. The catalyst was capable of achieving high FAME yield (91.2 %) within a few hours of reaction time with relatively low methanol to oil molar ratio.

Studies by Léon et al. (2015) have demonstrated that mesoporous TiSBA-15-Me-PrSO3H organic-inorganic hybrid catalyst is successfully prepared through a direct P123-assisted sol-gel co-condensation-hydrothermal treatment route. It is reported that strong Brönsted and Lewis acidity, excellent porosity properties and hydrophobic surface have contributed to the high catalytic activity of the catalyst. In another study conducted by Xie et al. (2015), a novel heterogeneous base catalyst was prepared by anchoring 1,3-dicyclohexyl-2-octylguanidine (DCOD) onto the mesoporous SBA-15

silica. The DCOG-functionalized SBA-15 material (SBA-15-pr-DCOG) was demonstrated to be an efficient and recyclable heterogeneous catalyst for the transesterification of soybean oil with methanol. This heterogeneous base catalyst could be easily recovered and reused for several runs with a negligible loss of activity.

Another study regarding the mesoporous millimetric gamma-alumina bead supported KI (γ-Al$_2$O$_3$/KI) catalyst was conducted by Islam et al. (2015), whereby the highest FAME yield of 98 % was obtained when the transesterification reaction was carried out under the conditions of 14:1 methanol to oil ratio, 4 wt. %, of catalyst loading for 4 h of reaction time temperature at 60 °C. Furthermore, there is also a report that shows the deposition of CaO in mesoporous silica which gave rise to improved catalytic activity for the transesterification reaction of sunflower oil and castor oil with methanol. The catalyst also had shown no lixiviation of the active phase under the optimum reaction conditions, in contrast to commercial CaO (Linares et al., 2014).

Besides that, Narkhede et al. (2014) have synthesized a mesoporous catalyst based on the uniform dispersion of TSA inside the hexagonal channels of SBA-15. The catalyst has been investigated in the transesterification reaction of WCO with methanol. The catalyst also shows the potential of being used as recyclable material without notable loss. The finding justified that this catalyst has good stability. Additionally, Kazemian et al. (2013) reported the preliminary experiments of various catalysts for biodiesel production from canola oil. The results show that mesoporous ordered silicate SBA-15 impregnated with 2 wt. % of CsNO$_3$ has provided an excellent catalytic activity performance for biodiesel production.

Despite the advantages of the mesoporous catalyst, this catalyst is largely time-consuming, complicated, expensive, and difficult to scale up, therefore making them less industrially viable (Bastakoti et al., 2014; Lertpanyapornchai and Ngamcharussrivichai, 2015; Olsen et al., 2014; Ren et al., 2012). This statement can be justified through the previous studies conducted by many researchers (Konwar et al., 2016; Sahu et al., 2009; Xia et al., 2012; Yan et al., 2013; Zhang et al., 2015). Thus, the development of a novel one-step method for the synthesis of mesoporous catalyst is needed to make it an efficient yet economic catalysis system especially in the biodiesel production field.

7. Previous study regarding heterogeneous catalytic transesterification reaction of used cooking oil

Numerous studies have been conducted regarding the development of heterogeneous catalysts for the transesterification reaction of UCO to produce biodiesel. Both acid and basic catalysts have their own characteristics and catalytic activity performance, depending on the undesirable FFA and

water content at UCO. For instance, a novel, efficient and recyclable mesoporous $TiO_2/PrSO_3H$ solid acid Nano-catalyst was synthesized by the post-synthetic grafting of propyl sulfonic acid groups onto a mixed phase of a TiO_2 support on the biodiesel production from UCO. The synthesized catalyst shows that 98.3 % of biodiesel can be obtained with 15:1 of methanol to oil molar ratio using 4.5 wt. % of catalyst loading at 60 °C of reaction temperature after 9 h of reaction time. It was also found that the acid strength of the synthesized catalyst was enhanced, providing more acid sites for the reactants and improving the accessibility of methanol to the triglycerides or FFA by increasing the pore volumes or sizes of the synthesized catalyst. Further, the solid acid nano-catalyst can be re-used in four consecutive runs without significant loss of catalytic efficiency (Gardy et al., 2017). Gardy et al. (2016) conducted a study on solid acid nano-catalyst $(Ti(SO_4)O)$ used for biodiesel production from UCO. The study demonstrated 97.1 % yield of FAME can be achieved using the synthetized catalyst under a methanol to UCO ratio of 9:1, catalyst loading amount of 1.5 wt. %, reaction time of 3 h, at 75 °C reaction temperature. Other heterogeneous acid catalysts derived from sulfonic resins, such as Nafion NR50, sulfated zirconia and tungstate zirconia were synthesized and have characteristics such as an interconnected system of large pores, a moderate to high concentration of strong acid sites, and a hydrophobic surface that may catalyse well in transesterification reactions of UCO (Wong and Devi, 2014).

Besides that, the heterogeneous basic catalysts such as iron (III) oxide (Fe_2O_3) doped on natural CaO catalyst (Fe_2O_3/CaO) were prepared and utilized in biodiesel production from UCO. As a result, the optimum reaction parameters found were 15:1 methanol to oil molar ratio, 1 wt. % of the Fe_2O_3/CaO at 65 °C and 3 h of reaction time can be achieved over 90 % of reactant conversion (Ezzah-Mahmudah et al., 2016). Another study was done using CaO catalyst derived from wastes of both ostrich-eggshell and chicken-eggshell, where the biodiesel production from UCO showed that 1.5 wt. % of catalyst, 12:1 of molar ratio of methanol to oil, 65 °C reaction temperature with 2 h reaction time gave the best results (Tan et al., 2015). Meanwhile, Hindryawati et al. (2014) experimented with three alkali metals (Li, Na, and K) supported by rice husk silica as basic catalysts for biodiesel production from UCO. The optimum conditions for the process were: Methanol to oil molar ratio of 9:1; catalyst loading amount of 3 wt. %; reaction time of 3 h and reaction temperature of 65 °C. Another report was done by Muciño et al. (2014) which shows that sea sand which was made a source of CaO catalyst has performed 95.4 % of biodiesel from UCO at mild reaction temperature of 60 °C, 12:1 of methanol to oil molar ratio yet in a high amount of catalyst loading of 7.5 wt. %. Additionally, finding of biodiesel produced from UCO in transesterification with methanol using calcined layered double hydroxides (LDHs) as heterogeneous basic catalysts were reported by Sankaranarayanan et al. (2012). From the study, $CaAl_2$-LDH (hydrocalumite) showed the highest activity with >90 % yield of biodiesel using methanol: Oil molar ratio (<6:1) at 65 °C in 5 h. The activity of the catalyst was attributed to its high basicity of the synthesized catalyst.

8. Summary

The previous literature reported the importance of biodiesel production as an alternative to conventional diesel fuel. Commonly, biodiesel is produced from edible and non-edible oils. Alternatively, biodiesel can be produced from UCO. However, UCO contains a high level of FFA and water content, which hinders the reaction of biodiesel production. Aside from that, a review of recent studies reveals that the heterogeneous basic catalysts i.e. CaO may exhibit better properties and catalytic activity compared to others. Although CaO catalyst has been extensively studied, it may have several limitations related to its low surface area, stability and bulky structure. Therefore, those limitations led to the high operating conditions from a practical perspective. Thus, catalyst support such as titanium seems to be the best candidate to overcome the CaO limitations. The construction of mesoporous structure for the heterogeneous catalysts attracted great interest due to its ability to provide a high distribution of catalyst active sites in the catalyst surface to enhance the catalytic activity. Moreover, the study on the interaction of titanium supported CaO catalyst with a mesoporous structure for biodiesel production from UCO is yet to be reported. The properties of the catalyst are known to be strongly affected by the support and the mesoporous structure, which makes it very complicated to understand its catalytic activity during the reaction. Thus, a detailed investigation of this mesoporous supported CaO-based (mesoporous calcium titanate) catalyst for biodiesel production from UCO is very crucial.

Acknowledgment

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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