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Advancement in heterogeneous base catalyzed technology: An efficient production of biodiesel fuels

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Price fluctuation of petroleum-based diesel, climate change, emerging mandate obligations, availability of new feedstock and the upgrading of conversion technologies are expected to drive biodiesel market to grow robustly in the next coming 10 years. However, the current bottleneck in biodiesel production is the lack of economical sustainable conversion technologies. Generally, industrial production of biodiesel is greatly relied on alkaline homogeneous transesterification reaction. Limitation of the technology, such as multistep process which incur extra pre-step for high acid oil treatment and post-step for biodiesel purification and alkali washing as diminished the economic feasibility and low environmental impact of the entire biodiesel process. Heterogeneous catalysis offers immense potential to develop simple transesterification process, including one step reaction, easy separation, reusability of catalyst, and green reaction. Thus, the aim of this paper is to review the biodiesel production technologies such as blending, micro-emulsion, pyrolysis, and transesterification. Furthermore, recent studies on heterogeneous catalyzed transesterification were presented by discussing the issues such as catalytic performance on different types of biodiesel feedstock, transesterification reaction conditions, limitations encountered by heterogeneous catalysts, and reusability of solid catalysts. The heterogeneous catalysts presented in this review is mainly focused on solid base catalysts, which include single metal oxides, supported metal oxide, binary metal oxide, hydrotalcite, and natural waste shell-based catalyst. Furthermore, current perspectives on application of heterogeneous catalyzed technology in biodiesel industry were discussed herein. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4919082]

I. INTRODUCTION

The growth of global biodiesel industry is moving into a new phase determined by the policy of feedstock flexibility, product neutrality, and sustainability. Rising global concerns related to energy security, climate change, and economic immobilism are driving the rapid growth of renewable fuel mandates worldwide. Recently, approximately 38 nations from Europe, America, and Asia have executed blending mandates (B5 or B10) or aimed to expand the biodiesel market for transportation sector. This intention was expected to improve production and consumption of clean

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transportation fuels to reduce dependence on imported petroleum oil, while mitigating greenhouse gas (GHG) emissions, and to drive a cleaner and greener economy. Biodiesel is a potential alternative to petroleum-based fuels. It can be used in compression-ignition (diesel) engines without modification, including those in passenger cars, sport utility vehicles, light trucks, buses, ships, trains, off-road heavy equipment, and mining equipment, as well as for home heating fuel, power generation, and in two-stroke engines (as a mixing agent). Thus, in long term prospect, biodiesel usage will radically cover all types of consumer demand in ground transportation, aviation, and maritime fuel markets.[1]

Accessibility to inexpensive biodiesel feedstock and simple manufacturing process remains a challenge to biodiesel production in order to keep pace with new emerging mandates. Many studies are currently discussed on the intensification of biodiesel production by minimizing the production cost, including feedstock, technologies, and conversion pathways to improve competitiveness of biodiesel to fossil-based diesel.[2–5] Typical biodiesel feedstock, such as soybean oil, rapeseed oil, and palm oil, are the main edible oils, which are projected to underpin growth of biodiesel production over next decade. However, they are not fit to be included into the biodiesel feedstock policy in developing countries due to limited supply and high crop price. Thus, the emergence of low cost lipid, such as non-food oil (e.g., jatropha oil, algae oil, animal fats, and waste oil) could unleash considerable production potential of biodiesel throughout the world.[6]

A. Biodiesel demand in Malaysia and worlds

The demand of biodiesel is affected by global climate change, raise of petroleum-based fuel price, national economic stability, and awareness of energy conservation. Nevertheless, the main reason for increase of biodiesel demand is the increase in petroleum-based oil pricesdue to commodity scarceness.[7] Implementation mandatory regulation which requires fuel refinery to blend 5% biofuel in industrial diesel (also known as B5 regulation) would lead to increase of biodiesel production. In Malaysia, the B5 blending regulation stated in National Biofuel Policy (Feburary 2009, Government Vehicles, subsequent nationwide policy).[8]

Although execution of biofuel mixing policy would further propel biodiesel industry, the major difficulty in running a biodiesel plant is the cost of feedstock. Biodiesel plants running on palm oil are facing with fluctuating palm oil prices (averaged 2600 ringgit per tonne at January 2014) and this shall make the business to be risky and non-profitable. Biodiesel trader affirmed that biodiesel production will not be lucrative unless crude palm oil comes down to 2250 ringgit and crude petroleum oil is steady at $100. It is not sensible to buy crude palm oil feedstock at such a high price.[9] Therefore, some industry players utilize biodiesel (methyl ester) as alternative chemical building block which can be transformed to vegetable-based chemical surfactant such as fatty alcohol and sulphonated methyl ester.[10,11] Malaysia has exported 122 779 ton of biodiesel in 2013 according to Malaysian Palm Oil Board. This amount is virtually five times of the total biodiesel amount sold in 2012. The global demand for biofuel (palm-based) industry could rise by between 2×10^6 and 2.5×10^6 ton in 2013.[181] All the data indicated the potential of biodiesel/methyl ester's market and the feasibility of industry players. Figure 1 shows worldwide biofuel production from year 2000 to 2013 (different vegetable oils).[12]

B. Biodiesel production technologies

In the past 100 years, investigation on the usage of neat form vegetable feedstock as non-conventional transportation fuel including food-based or non-food based in internal combustion engine testing has been reported. Studies have shown that neat form vegetable feedstock transportation fuels may seem not significantly accepted with direct injection into diesel engines due to minor unfavorable physical properties. These include:[13,14]

(1) High viscosity of vegetable oil (about 11–17 times higher than diesel fuel) interfered with the injection process and led to poor fuel atomization.

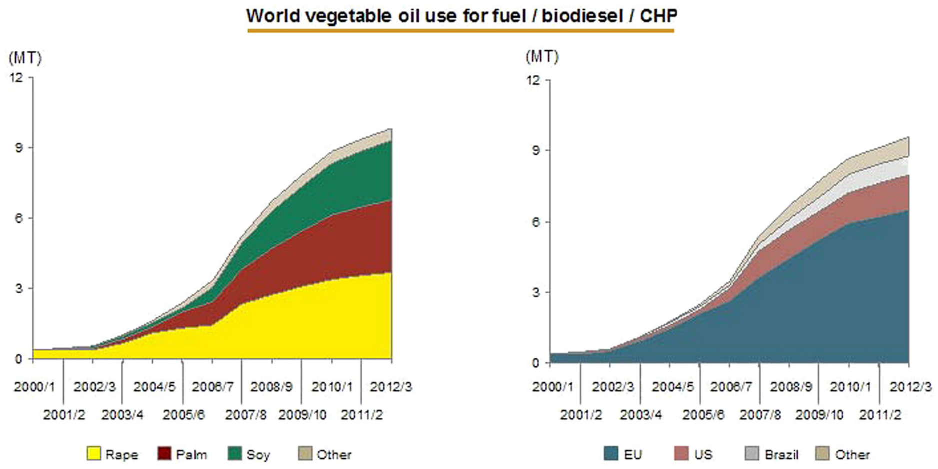

FIG. 1. Worldwide use of vegetable oil for biofuel production.

(2) The inefficient mixing of oil with air contributes to incomplete combustion and incorrect vaporization, leading to high smoke emission.
(3) Coking and trumpet formation on the injectors to an extent that fuel atomization does not occur properly or even stopped as a result of plugged orifices.
(4) The high flash point attributes to lower volatility characteristics.
(5) Lube oil dilution.
(6) Thickening or gelling of the lubricating oil as a result of contamination by vegetable oil.
(7) High carbon deposits.
(8) Oil ring sticking.
(9) Scuffing of the engine liner.
(10) Injection nozzle failure.
(11) Influence of different types and grade of oil to the local climatic conditions (high cloud and pour points may cause problems during cold weather).

The high viscosities, low volatilities, and polyunsaturated characteristic of vegetable oil accompanied by the presence of some contaminant (free fatty acids (FFAs), phospholipids, sterols, water, odorants, and other impurities) is a problem for direct usage in diesel engines. Therefore, it was known that vegetable oils (also known as triglycerides (TGs)) cannot be used directly as a fuel without any reaction modification and refining process. They must be refined to be compatible with existing vehicle engines (compression-ignition engine). In general, vegetable oils are consists of triacylglycerol (TAG) or TG, which is comprised of three esters of fatty acid chain (acyl group) attached to the glycerol backbone (glycerol group). If one and two acyl groups are replaced by hydroxyl groups (–OH), it is categorized as diacylglycerol (DAG) or diglyceride (DG) and monoaclyglycerol (MAG) or monoglyceride (MG), respectively. Naturally, the carbon chains of fatty acids are usually range from 10 to 24 carbon atoms.[15] The biodiesel may be affected by unsaturation, oxidative stability, ignition quality (i.e., cetane number), and cold-flow properties.[16] For example, oxidative stability is a critical parameter for biodiesel because it determines the ability to undergo oxidative degradation occurring not only during the storage but also during the engine combustion.[17] As reported by Kumar and Sharma, by-products of biodiesel results in the deposition of stable products in fuel lines and the injectors of diesel engine. As an example, soybean oil has a high content of linoleic acid, and a lower level of linolenic acid.[15] Although these fatty acids are essential for humans, they are also the cause of oxidative instability. However the quality of biodiesel is not only critically affected by the source of the feedstock, the process of producing this biodiesel also plays an important role.

Four primary biodiesel production techniques have been studied extensively in order to produce biodiesel with similar properties as of petroleum-based diesel fuel (Table I):[18]

TABLE I. Different techniques for biodiesel production.

Technique	Process	Advantages	Disadvantages
Direct use and blending	The oil use as diesel fuel or blend with conventional diesel fuel without chemical process	Liquid nature-portability Heat content (~80% of diesel fuel) Ready available; renewable	High viscosity Lower volatility Low reactivity of unsaturated hydrocarbon chain Low cetane number
Micro-emulsion	Synthesis of transparent, thermodynamically stable colloidal dispersion with dimensions generally in the 1–150 nm ranges formed spontaneously from two immiscible liquids such as methanol, ethanol and ionic or non-ionic amphiphiles	Reducing the high viscosity of oil by alcohol solvent Performance were similar to diesel fuel Better spray characteristic during combustion	Injector needle sticking Carbon deposits Incomplete combustion Increase lubricating oil's viscosity
Pyrolysis	Conversion of one substance into another high value substance by means of applying heat with temperature of 450–850 °C without presence of air or oxygen Cleavage of chemical bonds from long hydrocarbon chain to desired short hydrocarbon chain with the use of catalyst	Produce fuel similar physico-chemical properties of diesel and gasoline	High production cost due to the intensive energy usage Oxygen removal from the process decreases the products benefits of being an oxygenated fuel
Transesterification	Chemical reaction between oil and alcohol in the presence of catalyst to produce ester and glycerol	Physical properties close to diesel fuel Higher cetane number and combustion efficiency lower emission as compared to diesel fuel	Disposal of by-product (waste water during purification steps)
Supercritical process technology	Under critical point of 30 MPa and 300–500 °C, supercritical fluid produced with greatly changes of thermo-physical properties (dielectric constant, viscosity, specific weight, and polarity)	Avoid the use of catalyst Accelerate transesterification reaction and short reaction time	Energy intensive, high production cost

(1) Dilution or blending of vegetable oil with diesel fuel.
(2) Pyrolysis or thermal cracking and micro-emulsions with short chain alcohols.
(3) Esterification.
(4) Transesterification.

Transesterification of triglycerides to produce biodiesel is the most conventional method among all the proposed techniques. Biodiesel is a mono-alkyl long chain ester that can be synthesized from renewable triglycerides feedstock (such as vegetable oils or animal fats) via transesterification reaction with methanol. According to Feuge and Gros,[19] biodiesel manufacturing industries are located at many countries around the world from Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan to China since year 1920s and 1930s, whereas Germany and France being the largest producers of biodiesel fuels in the world. Biodiesel fuel is similar to conventional petro-based diesel fuel by looking at its main physical characteristics.[20] For instance, biodiesel can be used in compression–ignition (diesel) engine with little or no modification. Their physicochemical properties such as energy content, cetane number, and viscosity are equivalent to those petroleum-based diesel fuels. Furthermore, good combustibility performance of biodiesel in an unmodified diesel engine which resulted low deposit formation is another value adding feature that could make commercialization of biodiesel more viable.[21] Furthermore, surplus of by-product formed (glycerol) during biodiesel production could make glycerol an added value chemical which definitely promote commercial viability.[7]

C. Industrial-based biodiesel production via alkaline transesterification

Today, most of the biodiesel is produced by alkali-catalyzed process. The conventional transesterification process for biodiesel manufacturing process consists of four main principal steps (Figure 2):[7,18]

1. Acid esterification: Crude vegetable oil containing more than 4% of free fatty acids will go through acid esterification in order to remove the acid content and increase the yield of biodiesel. The presence of free fatty acid will generate soap during alkali-catalyzed transesterification process which is unfavorable to biodiesel production. Generally, sulfuric acid is used as acid catalyst for esterification process.
2. Transesterification reaction: The pretreated oils or fats (less than 4% of free fatty acid) are reacted with alcohol (normally methanol) to form mono-alkyl esters and its by-product glycerol. The catalyst used for transesterification process is typically potassium hydroxide (KOH).
3. Alkyl ester (biodiesel) purification: The excess methanol, residual catalyst, glycerol, and soaps are removed by water washing step. The biodiesel sometimes will further treat under distillation/evaporation processand later recycled into reactor for next reaction process.
4. Glycerol purification: The unreacted catalyst and soaps in glycerol phase are neutralized with acid to produce higher grade glycerol. Approximately 50%–80% of crude glycerol will be generated after extra water and alcohol was removed. The remaining contaminants such as unreacted oil (tri-, di-, mono-glycerides) can be further purified, to produce 99% purity glycerol, for pharmaceutical and cosmetic sectors.

D. Opportunities and challenges for biodiesel production

The overall cost of biodiesel included raw material (production and processing), catalyst, biodiesel processing (energy, consumables, and labor), transportation (raw materials and final

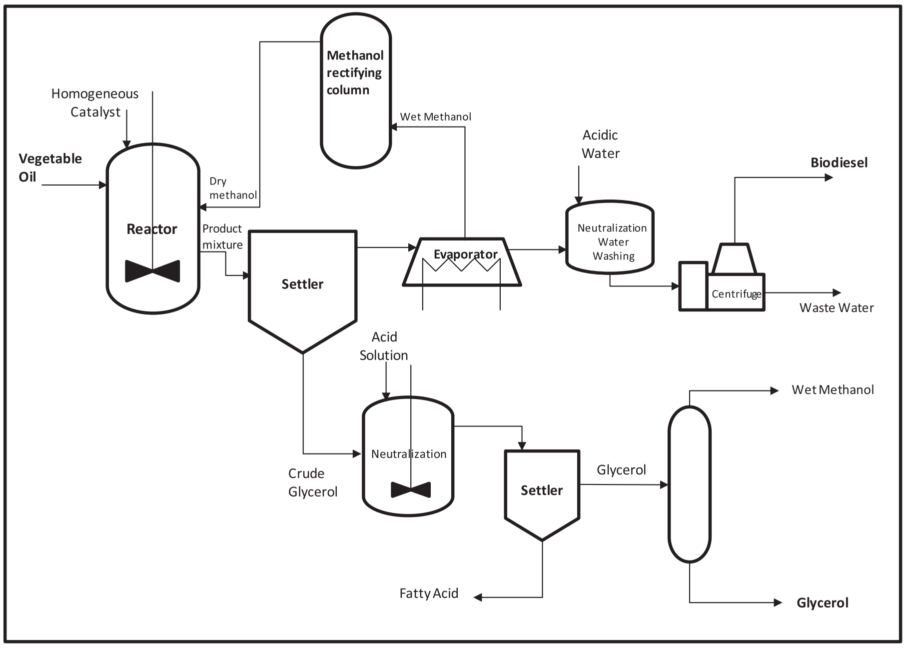

FIG. 2. Conventional continuous-flow process in homogeneous catalyzed transesterification reaction.

products), and local and national taxes (Figure 3). Currently, the greatest obstacle in biodiesel commercialization is the production cost, which involved raw material and production cost. Crude oil feedstock contributed the most in biodiesel production cost, which consisted 75% out of total operating costs. The raw materials used for biodiesel production generally consist of methanol and high quality vegetable oils.[18,22]

Market analysis and researches have been conducted in order to overcome the problem of high production cost. Therefore, it is suggested that taking concern in raw materials selection especially to biodiesel feedstock, catalyst, and alcohol. The oil feedstock must be highly available at the lowest price with good specifications which includes high oil content (>99.5 wt. %), favorable fatty acid composition, low agriculture inputs (water, fertilizers, soils, and pesticides), controllable growth and harvesting seasons, consistent seeds maturity rates and potential market for agricultural by-products.[23] The second substrate for the synthesis of biodiesel is acyl-acceptor (alcohol and acetate). Methanol is the most common acyl-acceptor and it is used in both laboratory and industry due to its high availability, suitability, and low cost factor. Third, the potential catalysts for industrial biodiesel production process should include these characteristics: (1) FFAs and water content tolerance, (2) resistant to catalyst poisoning and leaching, (3) ability to catalyze transesterification and esterification, (4) stable, high activity in water and leach proof, (5) low activation conditions, (6) high selectivity and conversion rate, (7) enhance the availability and type of active sites (both Lewis acid–base sites and Bronsted acid–base sites have the ability to catalyze oil transesterification reaction, catalyst activity is closely related to the acid/base strength), (8) good texture properties (it influences catalyst's activity, such as specific surface area, pores size, pore volume, to minimize mass transfer limitations), and (9) high reusability.[24]

II. HETEROGENEOUS BASE CATALYSTS FOR TRANSESTERIFICATION REACTION

This review paper is mainly focused on the evolution and transformation of solid base catalyst which is highly potential to be employed in transesterification of biodiesel. The common base heterogeneous catalysts (single metal oxide, supported metal oxide, binary metal oxide, and hydrotalcite) and the latest green, renewable and natural waste shell base catalyst are discussed herein. Below is the simplified outline:

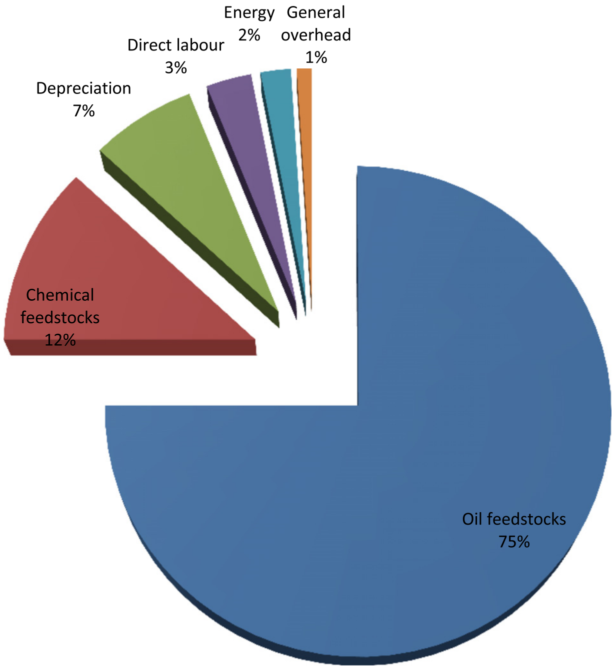

FIG. 3. General cost breakdown for biodiesel production.

Single metal oxide

- Alkaline-earth metal oxide
- Transition metal oxide
- Rare earth metal oxide

Supported metal oxide

- Alumina support
- Silica support
- Aluminosilicate support
- Zeolite support
- Alkaline-earth metal oxide support
- Transition metal oxide support (*titanium oxide, zirconium oxide, and zinc oxide*)

Binary metal oxide

- Calcium-based mixed metal oxide (calcium-based with alkaline metal oxide, calcium-based with aluminium oxide, calcium-based with transition metal oxide, calcium-based with lanthanide oxide)
- Magnesium-based mixed metal oxide (magnesium-based with transition metal oxide, magnesium-based with lanthanide oxide, and other mixed metal oxides catalyst)

Hydrotalcite

- Mg/Al hydrotalcite
- Li/Al hydrotalcite
- Zn/Al hydrotalcite
- Ca/Al hydrotalcite

Natural waste shell (*quail eggshell, chicken eggshell, oyster eggshell, fly ash, cockle shell, crab shell, and others*).

A. Single metal oxide

1. Alkaline-earth metal oxide

In earlier studies, most of the researchers produced biodiesel via single metal oxide catalyzed transesterification reactions. Among these single metal oxide catalysts (alkaline-earth metal oxide, transition metal oxide, lanthanide oxide, or rare earth metal oxide), alkaline-earth metal oxide catalyzed reaction obtained much attention since early 2006 for biodiesel production due to the presence of super basicity in Group II metal oxide. Most of the researcher believed that the basic properties of metal oxide seemed to be a major determinant for the catalytic transesterification activity. As shown in Table II, the catalytic activity is parallel to the basic strength of Group II metal oxide catalysts as in the following order: $MgO < CaO < SrO < BaO$. According to Hattori,[25] the basic strength of alkaline-earth metal oxide is related to the electronegativity of the conjugated metal cation. By going down Group II elements (Mg, Ca, Sr to Ba metal cation), increased ionic radius resulted decrement of the element's electronegativity, which reduced the attractive force of electrons for the conjugated metal cation. This has improved the basic characteristic of the attaching oxygen anion on the alkaline-earth metal oxide.[25]

This fact was proven in several studies. Patil *et al.*[26] investigated the catalytic activity of alkaline-earth metal oxide by microwave-assisted heating transesterification of *Camelina sativa* oil. Their findings showed transesterification activities increased in the order of $MgO < CaO < SrO < BaO$. It was found that microwave heating improved the reaction constantly by two orders of magnitude to that of conventional heating method. Furthermore, the study summarises that BaO and SrO produced higher biodiesel yields, although having lower surface area. It should be noted that the catalytic order was in reverse sequence to surface areas

TABLE II. Metal oxide catalysts used for biodiesel production.

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Alkaline-earth metal oxide							
MgO	*Camelina sativa*	3	100	n/d	n/d	22	26
CaO						30	
BaO						83	
SrO						80	
CaO[a]	Palm	1	Reflux and ultrasonic heating 50%	9	3	77.3	27
SrO[a]						95.2	
BaO[a]						95.2	
BaO[a]	Palm	<50 min	Reflux and ultrasonic heating (70%–80%)	9	2.8	>95	28
SrO[a]						>95	
SrO	…	0.5	65	12	3	>95	29
Calcium oxide							
CaO	Sunflower	2	60	6	1	98	30
CaO	Sunflower	5.5	80	6	1	91	31
CaO	Sunflower	0.17	252 (supercritical condition)	41	3	100	32
CaO	Sunflower	100 min	60	13	3	C = 94[b]	33
CaO	Waste cooking oil 5.1 mg/KOH/g	2	n/d	n/d	n/d	>99	34
CaO	Soybean (2.03% water)	3	65	12	8	>95	36
CaO-acetate	Tributyrin	…	60	6	0.06	68	38
CaO-carbonate						38	
CaO-hydroxide						82	
CaO-nitrate						<1	
CaO-oxalate						60	
CaO-$CaCO_3$	Palm olein	1	60	-	7	75.5	39
CaO-hydroxide		1				93.9	
CaO-carbonate		1				~0.8[c]	40
CaO-acetate						~0.7[c]	
CaO-oxalate						~0.45[c]	
CaO-nitrate						~0.05[c]	

TABLE II. (*Continued.*)

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
CaO-hydroxide						~0.6[c]	
CaO	Jatrophacurcas	2.5	70	9	1.5	C = 93[c]	41
$Ca(OCH_3)_2$	Rapeseed	3	60	0.26 mass ratio	0.7	90	42
CaO	Soybean	2	Reflux	n/d	n/d	93	43
Other metal oxide							
MgO	Soybean	2	215	7:1	2.0 g	>70	46
CaO							
PbO							
PbO_2							
Pb_3O_4							
Ti_2O_3							
ZnO							
ZrO_2	Rapeseed	10 min	270, 151 bar	40	1	~60	47
TiO_2						>70	
ZnO						>90	
CaO						>90	
SrO						>90	
Rare earth oxide							
La_2O_3	Rapeseed	2	200	27.5	10	91	48
CeO_2							
Pr_6O_{11}							
Nd_2O_3							
Sm_2O_3							
Y_2O_3							

[a] Ultrasonication heating.
[b] C is the conversion of oil.
[c] FAME formation (mol h^{-1} g^{-1}).

as a result from this study. This implies that surface area is not akey factor in promoting the transesterification rate.

Mootabadi *et al.*[27] also reported that ultrasonic-assisted transesterification of palm oil by using alkaline-earth metal oxide catalysts (CaO, SrO, and BaO) increased biodiesel yield sharply from conventional heating to within 60 mins. Increment from 5.5% to 77.3% (CaO), 48.2% to 95.2% (SrO), and 67.3% to 95.2% (BaO) was observed during ultrasonication heating. BaO catalyzed reaction showed the highest activity while CaO catalyzed reaction is the poorest. The authors concluded that the basic strength of catalyst is the key determinant in the reaction rate. In addition, Salamatinia *et al.*[28] stated that ultrasonic wave energy greatly influences transesterification reaction. The ultrasonic wave heating improved the reaction by reducing the reaction time to within 60 min. However, findings showed that the effect of ultrasonic wave also increases the solubility of BaO during reaction which resulted in high amount of residual elements in biodiesel product, despite the fact that BaO rendered higher activity than SrO.

Although alkaline-earth metal oxide rendered higher activity than other type of metal oxide, however, some researchers noticed the solubility of active metal cation increased in the sequence of $CaO < SrO < BaO$. Although BaO is active in transesterification reaction, however, it is highly dissolve in methanol compared to CaO and SrO which is less soluble in methanol. The loss of active component will reduce the catalytic activity of repeated use of Group II metal oxide and consequently decreases biodiesel production yield.

For SrO catalyst, it capable to deliver high transesterification yield of 95% which is closely associated with its high basicity and less solubility in methanol. However, the strong basicity of SrO promoted the reaction between CO_2 and water in the air and produced inactive $SrCO_3$ and $Sr(OH)_2$ phases. Unfortunately, high calcination temperature (>1200 °C) is required to transform $SrCO_3$ to its active oxide form.[29]

2. Calcium oxide

CaO catalyst is more cost effective, low toxicity, easy in preparation, and highly available. It would be the most potential solid base catalyst to be utilized in biodiesel synthesis. As a result, CaO was chosen as a potential heterogeneous catalyst in the biodiesel synthesis research and it is vital to improve and expand its physicochemical and activity studies.

As shown in Table I, many studies had been conducted by using CaO catalyst for transesterification of vegetable oil especially soybean and sunflower. Generally, the CaO catalyzed transesterification reaction followed the pseudo-first order reaction kinetics, in which the mass transfer and chemical reaction of triglyceride are main control keys in the process kinetics. The reaction showed that 98% of biodiesel yield was obtained with the used of CaO in 1 wt. %, 6:1 methanol/oil ratio, 2 h reaction time at 60 °C.[30] Another study showed that increment of reaction temperature to 100 °C with the pressure of 100 bar, using 1 wt. % of catalyst loading, 6:1 methanol/oil ratio, and stirring at 200 rpm resulted in an approximate of 91% of biodiesel yield.[31]

An optimization study was investigated by Demirbas,[32] where they concluded that CaO catalyzed methanolysis of sunflower oil is strongly depend on the reaction temperature and methanol/oil ratio. The study showed that transesterification was completed within 6 min at 252 °C, 41:1 of methanol/oil molar ratio with 3 wt. % catalyst amounts under supercritical condition.

Granados *et al.*[33] also reported that the high activity of CaO (94% of conversion) within 100 min in the transesterification of sunflower oil at 60 °C, 30:1 methanol/oil molar ratio, and 3 wt. % of catalyst content. Besides, CaO maintaining its biodiesel yield at >80% after eight consecutive reactions. However, the authors implied that the surface of CaO was active in H_2O and CO_2 chemisorptions when exposed to the atmosphere. The active surface sites of CaO were poisoned by both H_2O and CO_2 in carbonation and hydroxylation processes, in which CaO will be transformed to $Ca(OH)_2$ and $Ca(CO)_3$. Therefore, the exposure of CaO to the atmosphere shall be prevented and poisonous species must be removed by using thermal treatment at calcination temperature >700 °C.

The effect of hydroxylation and carbonation of CaO was compared with pure CaO by study the transesterification of soybean oil under reflux within 1 h reaction time. Results showed that 93% of biodiesel yield was obtained from CaO, 12% for $Ca(OH)_2$ and no catalytic activity for $CaCO_3$ catalyzed reaction. The authors found that CaO is tolerant to low FFA content (5.1 mg KOH/g of acid value) in waste cooking oil with 99% of biodiesel yield. However, the neutralization reaction between leached Ca active species and FFA has led to the formation of calcium soap and deactivation of the catalyst activity.[34] This finding was compatible with Gryglewicz's study,[35] where the catalytic reactivity for transesterification of rapeseed oil were increased in the order of $Ca(OH)_2 < CaO < Ca(CH_3O)_2$, which corresponding to the order of Lewis basicity of the catalysts.

Investigation on $Ca(OH)_2$ catalyst was further study by Liu *et al.*[36] They affirmed that the CaO catalyzed transesterification rate was accelerated by the presence of 2.0% water content in the oil feedstock. This was due to the generation of $Ca(OH)_2$ phase on the surface of CaO, which provided active basic sites to drive the formation of methoxide anions for the transesterification reaction. However, the authors stated that excessive water content in the oil (2.80%) has hydrolyzed the biodiesel product to fatty acid and resulted undesirable saponification reaction when the fatty acid reacted with CaO. Interestingly, CaO in nanocrystalline structure was found to render superior catalytic activity for transesterification. Venkat Reddy *et al.*[37] discovered high performance of nano-CaO (>99% of conversion) in the methanolysis of soybean oil or poultry fat within 24 h at room temperature. In order to further improve characteristic of CaO for enhance reactivity, different types of calcium sources were used for CaO catalyst synthesis. Cho *et al.*[38] investigated the catalytic activity of CaO prepared by thermal treatment of different precursors (calcium acetate, carbonate, hydroxide, nitrate, and oxalate). The finding showed that calcium hydroxide delivered the highest tributyrin conversion and methyl butyrate yield. This is due to the presence of high basic strength, formation of large crystal with smooth surface and generation of nano-sized pores at relatively low calcination temperature compared to other precursors. Besides, it was found that CaO derived from thermal treatment of $Ca(OH)_2$ (CaO refluxed with water) is an efficient technique to improve the transesterification of palm olein.[39] This result implied that decomposed-hydrated CaO is able to provide more porosity with high specific surface area, less crystallinity structure and high basicity as compared to CaO derived from calcium carbonate and commercial CaO. However, both findings from Cho and Yoosok was in contrast with the Alonso's study.[40] Alonso reported that the activities of CaO derived from various precursors are in the following order: CaO-carbonate > CaO-acetate > CaO/OH-A (precipitation of calcium acetate) > CaO-Oxalate > CaO/OH-N (precipitation of hydroxide) > CaO-nitrate. CaO derived from $CaCO_3$ showed maximum transesterification rate with highest specific area and exhibited strong basic sites. On the other hand, CaO derived from nitrate precursor produced lowest reaction rates. These studies indicated that syntheses of CaO via thermal decomposition of different calcium salts render significant effect in its physicochemical properties. It should highlight that the parameter of synthesis such as different calcination temperature for CaO activation influence the surface density of base sites (a combination of surface area and overall number of base sites). The studies showed straightforward relationship between surface basicity (directly related to the surface area) and the catalytic activity.

Zhu *et al.*[41] successfully improved the catalytic activity of CaO by chemical treatment, in which CaO was immersed into ammonium carbonate solution and calcified at 900 °C to produce superbasic strength in CaO material. The chemical treated CaO showed high catalytic efficiency when reacted in methanolysis of *Jatrophacurcas* oil to biodiesel. However, leaching of calcium ions was observed during the reaction, thus decalcifying agent (water, oxalic acid, citric acid, and ethylene-diamine-tetra-acetic acid (EDTA)) was used to wash off the leached calcium ion in biodiesel. Citric acid washing medium produced the highest yield of biodiesel at 95.5%, followed by EDTA (92.3%), oxalic acid (90.7%), and the least is water (69.5%).

Although CaO showed high catalytic activity in the transesterification reaction, however, the soluble active substance easily leached away from solid catalyst during reaction. It was found that the soluble substances were rather active in the transesterification reaction. This finding is paralleled with Kawashima,[42] the author reported that the CaO-methanol and

CaO-glycerine complex catalyzed transesterification of rapeseed oil exhibited a higher activity than non-activated CaO. Hence, researchers further investigated the active phase present in CaO and the leaching of CaO through examination of the active site of used CaO.[34,43] It was found that calcium diglyceroxide was produced during the transesterification reaction, the calcium diglyceroxide was the result of reaction between CaO catalyst with by-product glycerol. The authors reported that leaching process occurred in two pathways. As shown in Figure 4, the major leaching route (process 1) attributed to the formation of calcium diglyceroxide derived from CaO (generation of moisture at the beginning of reaction), which hydrolyzed the dissolved calcium diglyceroxide and resulted serious leaching of calcium cations and hydroxide anions. The creations of couple ion improved the catalyst basicity and thus enhanced the formation of methoxide ion in the transesterification reaction. The minor leaching route (process 2) was due to the formation of soluble calcium cation from dissociation of CaO during the reaction with methanol.[44] This scenario is similar to the finding by Granados *et al.*,[45] the authors reported that CaO is more soluble in the mixture of glycerol-methanol and biodiesel-glycerol-methanol medium than in pure methanol medium.

B. Transition metal oxide

Some of the researchers attempted to utilize the metal oxide from transition metal group or lanthanide group in the production of biodiesel (Table I). Singh and Fernando[46] studied the transesterification of soybean oil with different single metal oxide (MgO, CaO, PbO, PbO_2, Pb_3O_4, Ti_2O_3, and ZnO) at different temperatures with high pressure conditions. It was observed that more than 89% of biodiesel yield was achieved from PbO and PbO_2 catalyzed reaction. In addition, the catalytic activity and solubility of metal oxide (CaO, SrO, ZnO, TiO_2, and ZrO_2) were investigated by performing transesterification of rapeseed oil in supercritical or subcritical methanol condition. The findings showed that ZnO (transition metal oxide) was selected as the optimum catalyst owing to its excellent activity with minimum weight loss during transesterification reaction. Approximately 95% of biodiesel yield was achieved by using 1.0 wt. % ZnO catalyst, 40:1 of methanol/oil molar ratio within 10 min of reaction time. Although CaO and SrO showed high basicity and high catalytic activity in mild conditions, most of these catalysts were tend to dissolve more in biodiesel and glycerol layers compared to transition metal oxide (ZnO, TiO_2, and ZrO_2).[47] As refer to the studies of transition metal oxide catalyzed reaction, it is summarized that high reaction condition are require as compared to alkaline earth metal oxide catalyst.

C. Rare earth metal oxide

Rare earth elements are not rare and it is not only restricted to lab-scale research. It has been vastly utilized in researches by scientist in the recent decades. The series of lanthanides

Process 1: Formation of calcium diglyceroxide

$$CaO + 2C_3H_8O_3 \rightleftharpoons (C_3H_7O_3)_2 + H_2O$$

Process 2: Formation of Ca^{2+} ion

(i) Hydrolysis of soluble substance

$$Ca(C_3H_7O_3)_2 + H_2O \rightleftharpoons Ca^{2+} + 2OH^- + 2C_3H_8O_3$$

(ii) abstraction of proton from methanol by hydroxide anion

$$OH^- + CH_3OH \rightleftharpoons H_2O + CH_3O^-$$

Or

(i) Combination with methanol, and the following dissociation

$$CaO + 2CH_3O \rightleftharpoons Ca^{2+} + 2CH_3O^- + H_2O$$

FIG. 4. Process for activation of soluble substance leached away from solid base catalyst.

group offer the unique opportunity to infinitely tune and optimize the basicity of heterogeneous catalysts. One of the research groups had studied the rare earth oxides (REO) of the lanthanides group from La to Sm and Yb for the transesterification of crude and refined palm oil.[48] From their findings, the activity of lantanides oxide series from La to Sm and Yb was decreased corresponded to the decrement of cation radius and basicity. La_2O_3 converted refined palm oil to 90.6% of FAME yield, while crude palm oil (5.0% FFA) at even higher FAME content at 97.2%. However, the results indicated insufficient catalyst stability and a partial homogeneous catalysis by the formation of basic soaps.

Table II showed the list of metal oxide catalysts for transesterification reaction. As a conclusion alkaline-earth metal oxide was observed with highest activity compared to transition metal oxide, lanthanide oxide, and rare earth oxide. This was due to the presence of high basicity of Group II metal oxide. However, Group II metal oxide exhibited higher solubility amongst other metal oxides. The active metal cation will leach into the reaction medium and generate saponification reaction with the presence of water and FFA in oil feedstock.

D. Supported metal oxide

Catalyst support is vital in chemical reaction to minimize mass transfer limitation of heterogeneous catalytic liquid reaction. The standard supports (microporous, mesoporous, metal oxide support, and aluminosilicate layers) provide high surface area through the presence of pores where active metal particles anchor for reaction. The support may be inert and it might as well participate in the catalytic reaction. Different types of supports provide different interaction and stability between active metal and support.[49] Thus, catalytic activity varies with even with the same active metal attached on different type of catalyst supports.

1. Alumina support

Aluminum oxide (Al_2O_3) is an amphoteric oxide which is commonly referred as alumina. Porous γ-alumina, $\acute{\eta}$-alumina and nonporous crystalline α-alumina are widely used as a catalyst support in chemical reaction such as biodiesel synthesis via transesterification reaction. The superior properties of alumina support such as extreme thermal and mechanical stability, high specific surface area (as high as 300 m^2/g), mesopore size (5–15 nm), high pore volume (0.6 cm^3/g), and its ability to be extruded and pelletized[50] which make it a good catalyst support of active species with high catalytic activity in industrial process.

Alumina support was used as a basic solid catalyst by doping with active metal (alkali metal and alkaline-earth metal group) in biodiesel production (Table III). Alkali metals are the metal generally used for super-basicity characteristic and frequently selected as active species for supported catalysts in biodiesel production.[51] Alkali metals like Li, Na, K, and Cs are normally used in metallic form or in various forms in ionic salts (halide, carbonate, hydroxide, and nitrate). Some studies reported that different kinds of alkaline salts were applied on the supports to prepare basic catalysts, such as NaOH,[52] $LiNO_3$, $NaNO_3$, and KNO_3,[53] KOH,[54] K_2CO_3,[55] KI,[56] KF,[57] KNO_3,[58] LiF, KF, and CsF,[59] NaN_3,[60] and CsF.[61] In the case of alkaline-earth metal (Mg and Ca), the metal salts normally present in the form of acetate or nitrate ($Ca(NO_3)_2/Al_2O_3$ and $Mg(NO_3)_2/Al_2O_3$).[50,53,62]

The common method used to produce supported catalyst (alkali metal and alkaline-earth metal affix on alumina support) is wet impregnation method. In such method, a suspension of the alumina powder support is treated with aqueous solution of active metal salt, and the resulting material is then thermally activated to convert the precursor (often a metal salt) to a more active state (metal oxide). Rooney *et al.*[61] synthesized sunflower based biodiesel via CsF/α-Al_2O_3 catalyzed reaction. The synergy effect between solubilized CsF and α-Al_2O_3 promotes an active phase which favors triglyceride transesterification. The research group found that the oxide surface (probably surface hydroxyl) was the rate-limiting factor as α-Al_2O_3 has low surface area (5.48 m^2/g). In the other way, the use of high surface area γ-Al_2O_3 (26.0 m^2/g) resulted an even greater reaction rate with FAME productivity of 28 ml h^{-1} g^{-1}, in which higher than α-Al_2O_3 (1.1 ml h^{-1} g^{-1}). The reusability of CsF/α-Al_2O_3 catalyst was performed

TABLE III. Alkali metal and alkaline-earth metal supported alumina catalyst for biodiesel production.

Catalysts	Feedstock	Time (h)	Tempe-rature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Alkali metal group							
$K_2CO_3/\gamma\text{-}Al_2O_3$	Sunflower	1	Reflux	n/d	n/d	99%	55
$NaOH/\gamma\text{-}Al_2O_3$	Sunflower	4	50	24.10	0.4/20 g	100	52
$LiNO_3/Al_2O_3$	Palm kernel	3	60	65	10	92	53
$NaNO_3/Al_2O_3$						25	
KNO_3/Al_2O_3						35	
NaN_3/Al_2O_3	Sunflower	15 min	60	27	1 g	60	60
KF/nano-γ-alumina	Canola	8	65	15	3	98	57
$CsF/\alpha\text{-}Al_2O_3$	Sunflower	5	65	n/d	1 g	100	61
KOH/Al_2O_3	Palm	2–3	60	15	3	91	54
KNO_3/Al_2O_3	Jatropha	6	70	12	6	C = 84	58
KI/Al_2O_3	Soybean	8	65	15	2.5	C = 96	56
LiF/Al_2O_3	Sunflower	2	Micro-wave heating	4	0.3 g	<80	59
KF/Al_2O_3						<70	
CsF/Al_2O_3						>80	
Alkaline-earth metal group							
$Ca(C_2H_3O_2)_2/Al_2O_3$	Palm	5	65	12	6	99	50
$Mg(NO_3)_2/Al_2O_3$	Palm kernel	3	60	65	10	10.4	53
$Ca(NO_3)_2/Al_2O_3$						94.3	

using four consecutive runs with 4 h reaction. No catalytic activity was observed after the first run. The elemental analysis revealed that Cs concentration had decreased from 7.36 wt. % to 0.38 wt. % after utilization, indicating the leaching of Cs into methanol medium. According to Semwal *et al.*,[63] the catalytic activity for different type of metal salts was depending on the basic strength of active sites. In comparison of alumina loaded with KI, KF, KOH, K_2CO_3, KBr, or KNO_3, the order of oil conversion reported by the authors was $KI/Al_2O_3 > KF/Al_2O_3 > KOH/Al_2O_3 > KNO_3/Al_2O_3 > K_2CO_3/Al_2O_3 > KBr/Al_2O_3$.

The effect of different precursor salt in the support interaction towards the basicity and reactivity has been investigated by a group of scientist.[56] It was found that dispersion of K^+ from halide showed better results than nitrate precursor. The results showed that metal iodide and metal fluoride gave better catalytic activity and basicity strength than other metal salts. In the case of alkaline fluoride deposition on alumina surface, the fluoroaluminates and aluminate species were present in the supported catalyst. Although the basicity of fluorine in catalyst is smaller than in parent fluoride but with the present of oxygen, which is stronger, the cooperation between fluorine and oxygen has made the active site available.[59] As mentioned by several research groups,[64,65] fluoride ions are able to promote methoxide formation by initiating the deprotonation of alcohol in the transesterification reaction. With the presence of fluoride, the nucleophilicity of oxygen in alcohol molecules increased through strong hydrogen bonding and at the same time it also activate carbonyl groups in triglycerides, facilitating reaction completion. The active metal fluoride/alumina supported catalyst provides lower basicity than parent alkaline precursor hence higher amount of fluorides is required to compensate the basicity loss from its original state. After thermal decomposition of the supported catalyst, the surface Al-O-K groups were exhibited characteristics as the active species for transesterification reaction.[59]

Although different metal salts influence the interactions between active metals and alumina supports towards its activities, the type of alkali metal cation remains as the key factor in generating basicity and to enhance the transesterification activity. Verziu *et al.*[59] examined the effect of alkali metal cation group (KF, LiF, and CsF/Al_2O_3) in alumina supported catalysts. The catalysts were prepared using alkaline fluoride compounds by wet impregnation of basic mesoporous MSU-type alumina with high stability surface area. Transesterification at 75 °C, 23 ml sunflower oil, molar ratio methylic alcohol:sunflower oil 4:1, 2 h, 0.25 g of catalyst, the catalytic activity of the catalyst was in the order of: $CsF/Al_2O_3 > KF/Al_2O_3 > LiF/Al_2O_3$. It was found that CsF-based catalyst showed higher transesterification activity and has more basicity compared to KF and LiF-based catalysts.

Some findings revealed that alumina supported alkali metal catalysts are facing problem of active metal leaching during transesterification reaction. Thus, most of these catalysts could not be reused.[57,61] In general, alkali metal oxide groups are water-soluble, thus the catalysis reaction over alkali metal oxides supported catalyst occurred through a homogeneous pathway rather than truly heterogeneous route. Oxide phase M-O-Al species (M = K, Na or Li) on the surface of the supported catalyst was leached into methanol medium and produced methoxide ion (CH_3O^-) which is responsible for the homogeneous reaction route (Figure 5).[55]

By drawing on this, introduction of alkaline-earth metal as active species into alumina support was investigated in order to reduce the solubility of active metal in methanol. With lower basicity in alkaline-earth metal group compared to the former group, high catalytic activity is still achievable by using suitable preparation methods and transesterification conditions. Benjapornkulaphong *et al.*[53] compared the catalytic performance of Al_2O_3-supported alkali ($LiNO_3/Al_2O_3$, $NaNO_3/Al_2O_3$, and KNO_3/Al_2O_3) and Al_2O_3-supported alkaline-earth metal ($Ca(NO_3)_2/Al_2O_3$ and $Mg(NO_3)_2/Al_2O_3$) for transesterification of palm kernel and crude coconut oil with methanol. They found that the supported alkali metal catalysts showed high biodiesel yield (>93%). However, the reactions were mainly occurred through homogeneous catalysis pathway with the presence of dissolute alkali oxides. The $Ca(NO_3)_2/Al_2O_3$ catalyst was found to be the most suitable catalyst for heterogeneously catalyzed reactions exhibiting 94% biodiesel yield with low leaching effect, whereas $Mg(NO_3)_2/Al_2O_3$ catalyst showed low catalytic activity due to the present of inactive magnesium-aluminate phase.

2. Silica support

Catalysts with small pores support (zeolite and metal oxide) are not suitable for biodiesel production because of the diffusion limitation of the large fatty acid molecules (triglyceride). The outstanding textural properties of mesoporous solids (relatively large pores which facilitate mass transfer and high surface area which allows high concentration of active sites per mass of material) has become an interesting option to be used as catalyst support in the development of new catalysts with well-dispersed active phases. Thus, the basic mesoporous catalysts normally obtained by incorporation of alkaline metal, alkaline-earth metal oxides or by anchoring basic organic molecules on the surface of mesoporous materials.[66,67] Silica is a mesoporous materials which includes SBA-15, MCM-41, fumed silica, and TLT-16 are usually used as a support catalyst in biodiesel production. Mesoporous SBA-15 is a mesoporous silicate with high surface area (600–1000 m^2/g) and uniform pore size (5–30 nm). This material is formed by a hexagonal array of uniform tubular channels with tunable pore and thick pore walls (3–6 nm).[68] SBA-15 has strong hydrothermal stability, greater than MCM-41, which promises great opportunity for the application as catalysts or catalytic supports.[69] The large pore silica support would facilitate the diffusion of high molecular weight reactants involved in transesterification reactions to the active sites within the catalyst prior to the reaction. Thus, the overall reaction would be accelerated.[67]

Abdullah *et al.*[67] investigated the catalytic activity of K/SBA-15 for transesterification of palm oil to biodiesel. K/SBA-15 was prepared by impregnating the mesoporous SBA-15 with KOH solution. It was found that the basicity of catalyst increased due to the incorporation of superbasic potassium species into the support and thus increased the transesterification activity. Besides, the large Brunauer-Emmett-Teller (BET) surface area (539 m^2/g) with large pore

$$MAlO_2 + CH_3OH \longrightarrow AlOOH + M^+ + CH_3O^-$$

FIG. 5. Leaching reaction from alumina supported metal oxide with methanol.

diameter (5.63 nm) and high pore volume (0.63 cm^3/g) provided the high molecular weight reactant a relatively easy diffusion route for the reaction. K/SBA-15 catalyst obtained 87.3% biodiesel yield with reaction conditions of 70 °C, 11.6:1 of methanol/oil molar ratio, 3.91 wt. % of catalyst loading and 5 h of reaction time. Other research groups[70,71] had studied the transesterification activity of KI/mesoporous silica and CaO/mesoporous silica that prepared via incipient wetness impregnation method. The authors reported the mesoporous silica catalyst had large surface area and pore volume with uniform pore size. These properties enabled the potassium and calcium species to disperse well on the silica surface and fill in the pores of the support appropriately. Both catalysts yielded >90% of conversion rate using soybean oil at optimum conditions of 60–70 °C, 5 wt. % of catalyst loading, 8 h reaction time, and 16:1 of methanol/oil ratio.

While Albuquerqueet[66] compared the transesterification activity of different types of siliceous supports (fumed silica and two mesoporous silica-based materials: MCM-41 and SBA-15 with high surface area) loaded with active CaO species via impregnation method. CaO/SBA-15 showed high stability in its hexagonal support structure after impregnation and thermal activation steps. However, structure of MCM-41 and fumed silica has collapsed. This indicated that the interaction between CaO and SBA-15 support was strong and CaO active species was well distributed and stabilized on the surface of SBA-15. The CaO/SBA-15 showed 95% conversion rate after 5 h of transesterification using sunflower oil at 60 °C and methanol/oil molar ratio of 12. Rudolph[72] also studied the performance of three different mesoporous silicas (MCM-41, SBA-15, and KIT-6) loaded with MgO. The catalysts were synthesized via two different methods: (1) *in situ* coating and (2) impregnation methods. MgO/SBA-15 prepared by impregnation showed highest activity (96% in 5 h reaction time; 220 °C) compared to other supports with different synthesis techniques. The surface analysis (X-ray photoelectron spectroscopy (XPS)) showed lower attachment of MgO over the surface of SBA-15 catalyst by *in situ* coating method compared to impregnation method. According to Suarez *et al.*,[73] catalytic systems with Bronsted base or Lewis acid could minimize soap formation during biodiesel production process. The use of organic compound with Bronsted base properties (guanidines, amidines, and triamino-(imino) phosphoranes) showed high reaction activity as comparable to mineral base (KOH or NaOH) in homogeneous conditions.[74,75] Faria[76] studied the organic base (tetramethylguanidine) catalyst supported on silica gel for solid base catalyzed transesterification of soybean oil with methanol. High catalytic efficiency was achieved with 86.73% biodiesel conversion at 3 h of reaction time. The catalyst showed excellent recyclability with nine times reusability with catalyst efficiency maintained up to 62%. This finding indicated that the covalent bond between tetramethylguanidine and silica gel enhanced the catalyst's stability and solved the organic base leaching problem. Kazemian *et al.*[77] tested a highly ordered mesoporous silicate catalyst (SBA-15) which was impregnated with cesium in transesterification of canola oil to biodiesel. The optimized biodiesel yield of 25.35% was obtained at operating conditions of 135 °C (pressurized reactor), methanol to oil ratio (40:1), reaction time (5 h), and 2 wt. % of catalyst. It is found that cesium impregnated silicate catalyst is not a good base catalyst with its low biodiesel yield. Table IV shows the list of silica supported catalysts for biodiesel production.

3. Aluminosilicate support

Clay materials are ubiquitous in nature while heterogeneous in composition and particle size.[78,79] Utilization of clay material such as bentonite as catalyst or catalyst support for biodiesel preparation is scarce. Bentonite (silicataluminate) is a three-layer clay with a unique layer consisting of a sheet of octahedral alumina sandwiched between two sheets of tetrahedral silica.[50] Table V showed the list of aluminosilicate-based catalysts for transesterification process.

Rashtizadeh *et al.*[80] have done some comparison on the catalytic activity of KOH loaded on aluminosilicate layers (bentonite and kaolinite), microporous materials (zeolite Y and clinoptiloite), mesoporous materials (MCM-41 and Al-MCM-41), some oxides (Al_2O_3 and TiO_2), and silica gel surfaces via reactions of the OH^- groups or physical adsorption mechanisms. The series of KOH/support provides high catalytic activity with >80% oil conversion. The

TABLE IV. Silica supported catalyst for biodiesel production.

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Alkali metal							
KOH/SBA	Palm	5	70	11.61	3.91	93	67
KI/SiO_2	Soybean	8	70	16	5	90	70
$CsNO_3$/SBA-15	Canola oil	5	135	40	2	25	77
Alkaline-earth metal							
CaO/SBA-15	Sunflower	5	60	12	1	95	66
	Castor	1				66	
CaO/mesoporuous silica	Soybean	8	60	16	5	95	71
MgO/SBA-15	Blended vegetable oil	5	220	n/d	n/d	C = 96[a]	72
Other							
TMG/SiO_2 (tetramethylguanidine supported on silica gel)	Soybean oil	80	3	1.5/10	n/d	86.7	76

[a] C is the oil conversion.

exception goes to KOH/SiO_2 which showed low reactivity. This may due to insufficient Si-OH groups available in the silica structure compared to others catalysts. The results showed the correlation between catalyst basic strength and its activity. Partial transformation surfaces of Si–OH groups to Si–OK^+ was observed when potassium (K) species reacted with the supports. Potassium species exchanges with hydrogen of Si–OH groups available on support surfaces and produces some basic OK^+ sites. These basic sites promotemethoxide formation via deprotonation of CH_3OH, which was then increased the rate of transesterification process. The stability of active potassium metal with its support was performed in this study,[80] where potassium desorption trend for used catalyst was in the order of MCM-41 (5.64%) > silica gel (1.26%) > clinoptiloite (1.17%) > zeolite Y (1.00%) > Al_2O_3 (0.71%) > bentonite (0.66%) > kaolinite (0.60%) > Al-MCM-41 (0.46%) > TiO_2 (0.08%). Such behavior is contributed by leaching of basic sites on the support if potassium ions are not grafted to the support surface. Among other catalyst supports, bentonite and kaolinite as natural materials which is cheaper, higher catalytic activity (85% and 95% of oil conversion, respectively), and strong stability (potassium desorption of 0.66% and 0.60%, respectively) seem to be as good as solid supports with the optimized heterogenized characteristics.

Soetaredjo *et al.*[81] utilized bentonite clay as a catalyst support for biodiesel production because of its availability. The chemical composition in bentonite is Al 38.93%, Si 46.81%, Fe 3.24%, Ca 3.15%, Mg 0.41%, K 0.17%, Na 0.42%, and Mn 0.03%. The bentonite support from Pacitan was loaded with KOH via impregnation method. In transesterification conditions of 60 °C, 3 h reaction time, 3 wt. % of catalyst loading, and 6:1 of methanol/oil molar ratio, a total of 90.7% of biodiesel product was yielded. The reusability of KOH/bentonite catalyst was examined for at least four times, the biodiesel yield decreased gradually and was found less than 85% for second and third cycles. The authors suggested that the loss of activity was probably due to the poisoning of basic sites during the transesterification reactions.

TABLE V. Aluminosilicate supported catalyst for biodiesel production.

Catalysts	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
KOH/aluminosilicate layers							
Bentonite	Soybean	2.25	65	70	6.5	C = 85	80
Kaolinite						C = 96	
KOH/Bentonite	Palm	3	60	6	3	91	81

4. Zeolite support

Zeolites are microporous crystalline solids with well-defined edge structure. Generally, they are aluminosilicate minerals which are commonly used as catalyst supports for active species due to their unique pore system, high surface area, and high stability. The various chemical composition, pore size distribution, and ion-exchange abilities caused zeolite to carry varying catalytic properties. Different types of zeolites with different Si/Al ratio and ion-exchange cation technique were used to control the acid-base properties of zeolite. In order to study transesterification reaction with basic zeolite catalyst, the basicity of zeolite can be enhanced via ion-exchange with alkali metal ions or impregnation of basic components on the inner surface of the zeolite pores. The base strength of the zeolite can be improved by using alkali metal cation exchange technique or occlusion of alkali metal salts via impregnation technique.[82] Hattori[83] stated the impregnation method produces relatively strong basic sites rather than the ion-exchange method. The chemical composition and the nature of the interaction of the zeolite framework play a crucial role to influence its active sites. According to Ramos *et al.*,[84] the compensation of alkali metal cation into the negative charge framework of zeolite will enhance the electron density of the oxygen atom and thus act as basic active site.

Zeolite-(mordenite, beta and X), titanosilicates (ETS-4 and 10), and mesoporous zeolites (mesoporous silicates) are mostly used as catalyst support in biodiesel synthesis among zeolite family. NaX faujasites (FAU) zeolite ($Na_{82.8}K_{1.8}Al_{85.8}Si_{106.2}O_{384}$) is an aluminosilicate material with rigid framework structure which is remarkably stable with large void space amount about 50 vol. % of the dehydrated crystal.[82,85] ETS-10 (Engelhard titanosilicate structure (ETS) series zeolites) with chemical formula of $Na_{21.9}K_{7.5}Ti_{16.5}Si_{77.5}O_{208}$ has gained much interest in biodiesel synthesis due to the strong basic character than Na–X,[86] high cation-exchange capacity, and unique large pore structure.[82]

Most of the active metal used for the zeolite support is alkali metal with higher electropositivity characteristic such as sodium, potassium, and cesium. Suppes[82] studied the performance of zeolite loaded with alkali metal in biodiesel synthesis. Comparison between potassium and cesium-exchanged zeolite faujasite NaX and ETS-10 zeolite with impregnated sodium acetate or sodium azide inNaX zeolite cage has been done. ETS-10 catalysts (67.4%–71.9%) provided higher conversion than the Zeolite-X type catalysts (8.6%–10.3%). Philippou[86] reported that parent ETS-10 catalyst is approximately four times more basic than NaX zeolite. Nevertheless, the increased conversions were attributed to the higher basicity of ETS-10 zeolites and larger pore structures that improved intra-particle diffusion. The authors found that using impregnation method will improve the basicity instead of ion exchange method. Incorporation of occluded sodium species in zeolite-X catalyst (82%–84.2%) also helps to enhance the activity to the levels similar to ETS-10.

Ramos *et al.*[84] studied the catalytic effect of different zeolites: mordenite, beta, and X in transesterification of sunflower oil. It is found that the methyl ester content (wt. %) yielded by mordenite (12.7%) and beta zeolites (65.4%) was lower than those obtained with zeolite X (95.1%). The presence of super-basic sites in sodium acetate supported zeolite X which were not present in other zeolites has explained the superior performance of this catalyst. Metal incorporation technique was studied by using both impregnation and ion-exchange methods. Ion-exchanged catalyst showed lower catalytic activity compared to catalyst produced through impregnation method in transesterification reaction. The reusability test was performed for sodium acetate/NaX. The catalyst showed a significant drop from 95.1% to 4.7% in the third cycle. The author suggested that sodium acetate/NaX catalyzed reaction had occurred in conventional homogeneous pathway in which the sodium oxide has leached out into the reaction medium during transesterification.

The catalytic activity of NaX zeolite loaded with KOH reacted with soybean oil was studied. The conversion obtained from the reaction was 85.6% at 65 °C within 8 h reaction time.[87] The methyl ester content decreased to 48.7% for the second run has confirmed the leachate of KOH species from the supported catalyst as mentioned in other experiment.[84] Furthermore, the transesterification of palm oil using active KOH supported on NaY Zeolite via impregnation method was also performed.[54] The NaY Zeolite is composed of aluminosilicate materials with FAU structure together with its large pore openings and high surface area. The researchers stated that NaY has higher crystal stability than NaX with different Si/Al ratio. Biodiesel yield of 91.07% was achieved in the reaction conditions of 60 °C, 6 wt. % of catalyst, 3 h reaction time, and 15:1 methanol/oil ratio. The leaching test for KOH/NaY was studied and compared with KOH/Al_2O_3 for its reusability. The leached potassium species from alumina support was higher compared to that of zeolite Y support catalyst indicating that K in the NaY zeolite is strongly bound to the zeolite matrix. Supamathanon *et al.*[88] also synthesized the potassium supported on NaY zeolite and this catalyst was prepared via impregnation method using a buffer solution of CH_3COOK/CH_3COOH (as a potassium source) to prevent collapse of NaY structure. Biodiesel yield of 73.4% was obtained in the transesterification of jatropha seed oil with methanol under mild conditions. Recently, report showed that CaO/NaY exhibited the best performance among the supported catalysts of NaY, KL, and NaZSM-5 zeolites with CaO. 95% of biodiesel yield was achieved by using the CaO/NaY catalyst (30 wt. % of CaO loading on NaY zeolite catalyst by microwave radiation followed by calcination at a high temperature in air).[89] The transesterification was conducted at methanol/soybean oil molar ratio of 9, reaction temperature at 65 °C, reaction time of 3.0 h, and catalyst/oil mass ratio of 3%. The improved catalytic activity was attributed to the increase of BET values and the concomitant increase of basic strength and basicity after CaO was dispersed on NaY zeolite by using microwave irradiation during catalyst preparation.

Other studies[67] have reported that zeolite supported catalysts present severe limitation in transesterification reaction which involving large reactant molecules of vegetable oil. The zeolite catalyst with small pores (microporous structure) is not suitable for biodiesel production due to the mass transfer limitation of large sized triglyceride in oils. Hence, many efforts have been done by researchers to utilize mesoporous materials in instead of zeolites to be applied as the catalyst support to overcome this limitation. Table VI indicates the summary of Zeolite supported catalysts for biodiesel production.

5. Alkaline-earth metal oxide support

Some researchers have been showing strong interest in utilizing alkaline-earth metal oxide as a support that consists of basic properties to improve transesterification activity. Table VII depicted the list of alkaline-earth metal oxide support in biodiesel production. Wen *et al.*[90]

TABLE VI. Zeolite supported catalysts for biodiesel production.

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
KOH/NaY	Palm	3	60	15	6 g	91	54
Faujasite NaX	Soybean	24	60	6	n/d	10.3	82
KX	FFA = 2.6%					7.3	
CsX						8.6	
(Cs,K)X Titanosilicate-10							
ETS-10						71.9	
Cs-ETS10						67.4	
(Cs,K)-ETS-10							
K/NaY	Jatropha	3	65	16	0.04	73	88
KOH/NaX	Soybean	8	65	10	3	86	87
Na/NaX	Sunflower	7	70		n/d	95	84
Na/NaM[a]		7	70	n/d		13	
Na/NaB[a]	Soybean	7	70	9	3	65	89
CaO/NaY		3	65			>95	

[a] M is the modernite and B is the beta.

TABLE VII. Alkaline-earth metal supported catalysts for biodiesel production.

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount	Yield (%)	Reference
Alkali metal							
KF/CaO	Chinese tallow seed	2.5	65	12	4	96.8	90
$LiNO_3$/CaO	Rapeseed	3	60	6	0.2 g	99	91
$NaNO_3$/CaO						100	
KNO_3/CaO						100	
$LiNaO_3$/MgO						100	
KOH/MgO	Mutton fat	20 min	65	22	4	>98	93

prepared KF doped CaO support via impregnation method. The performance of KF/CaO was studied by transesterification of Chinese tallow seed oil with methanol. The results showed great catalytic activity (96% of biodiesel yield) and stability for the catalyst. The formation of porous structure with average pore size of 97 nm provided a good mixing contact between reactants and catalytic surface. On the other hand, formation of $KCaF_3$ active phase increased the catalytic effectiveness of KF/CaO. Fluorine has higher electronegativity than oxygen resulting Ca^{2+} ions in $KCaF_3$ (acting as Lewis acid) to form stronger attraction with CH_3O^- ion in methanol molecules during transesterification reaction. Besides, F^- ions (acted as Lewis base) formed attraction with H^+ in methanol easily. Hence, KF/CaO makes the deprotonation of methanol route easier and leads further increment of transesterification efficiency. The leaching test for bulk CaO and KF/CaO showed the presence of 150 mg and 31.6 mg of dissolved Ca^{2+} in the biodiesel product, respectively, indicating the existence of $KCaF_3$ phase has enhanced the stability of KF/CaO interaction system compared to CaO. Besides, the KF/CaO catalyst possesses a good anti-acidic ability and tolerance to fatty acid poisoning with improved saponification resistance than that of CaO. More than 80% of biodiesel content was yielded from acid oil (<7 mg KOH g^{-1}) using this catalyst. Therefore, the catalytic activity of KF/CaO for transesterification has been proved to be better than CaO.

According to MacLeod *et al.*,[91] a series of alkali metal ($LiNO_3$, $NaNO_3$, KNO_3) doped CaO and MgO support catalysts were prepared and evaluated for catalytic effectiveness in the transesterification of rapeseed oil to biodiesel. Among the catalysts tested, $LiNO_3$/CaO, $NaNO_3$/CaO, KNO_3/CaO, and $LiNO_3$/MgO exhibited >90% conversion in 3 h reaction time. These catalysts provided great catalytic effectiveness albeit low surface areas (1–2 m^2/g). The authors stated that it is useless to increase surface area by increasing porosity as the large size triglycerides are unable to diffuse into the pore structures, unless a mesoporous support was used. Furthermore, Meher *et al.*[92] reported that the basicity has more influence on the catalytic activity of solid base catalysts than the surface area. The finding showed clear correlation between the catalyst's basic strength and the catalytic activity. Formation of active O^- centre through the substitution of M^+ ions into the alkaline earth oxide lattice has enhanced the basic strength of the oxide. The catalysts have shown good reusability while maintaining the conversion rate of oil for five continuous cycles (with percentage of mass triglycerides in range of 0.1%–1.9%). However, the leaching of Ca^{2+} and Mg^{2+} has occurred and contributed to some of the activities in the reaction medium (14%–54% in biodiesel mass). Hence, these catalysts did not react in a truly heterogeneous pathway as the dissolved metals contributed actively in reaction.

Mutreja *et al.*[93] evaluated the effectiveness of KOH/MgO in transesterification of mutton fat with methanol. The reaction produced >98% conversion in the transesterification conditions of reflux temperature, methanol/oil ratio of 22:1 within 20 min of reaction time. The KOH/MgO was found to tolerate with 1 wt. % of moisture content and free fatty acids in the mutton fat. From this overall studies of alkaline-earth metal oxide supports, it is found that the alkali metal doped CaO or MgO basic metal oxide provide great catalytic activity in the transesterification. This is due to the enhancement of basicity and basic strength of the metal oxide support by promotion of alkali-metal species. However, CaO and MgO supports are less stable and are prone to leaching problem. This drawback would need to be resolved before mass production of biodiesel can be done.

6. Titanium oxide support

A series of K-compound/TiO_2 catalysts were prepared by impregnation method. The catalytic activity of different types of potassium compounds (KI, $C_4H_4O_6HK$, K_2CO_3, KCl, $C_4H_4O_6KNa_4H_2O$, $KBrO_3$, or $C_8H_5O_4K$) loaded on TiO_2 support was studied in the soybean oil transesterification reaction. The catalytic activity was in the following order: $C_4H_4O_6HK/TiO_2 > C_4H_4O_6KNa_4H_2O/TiO_2 > K_2CO_3/TiO_2 > C_8H_5O_4K/TiO_2 \sim KBrO_3/TiO_2 \sim KCl/TiO_2 \sim KI/TiO_2 > TiO_2$. No catalytic activity was observed for the free potassium loaded TiO_2. However, promotion of active potassium species on TiO_2 support has increased the catalytic activity in the transesterification reaction. The presence of strong basic strength in $C_4H_4O_6HK/TiO_2$has made the catalyst to show distinctive transesterification activity (86%) compared to other catalysts.[94]

7. Zirconium oxide support

Qiu *et al.*[94] compared the catalytic effect of different supports (Al_2O_3, ZnO, SiO_2, ZrO_2, and TiO_2) loaded with potassium species ($C_4H_4O_6HK$). Although the basic strength of $C_4H_4O_6HK$ doped with different types of support was nearly the same, however, the activity of the catalyst has significant different. $C_4H_4O_6HK/ZrO_2$ was found to be the most active catalyst with 89.95% of conversion. This might due to the vacant site on the surface of ZrO_2 which the cations were easy inserted. Furthermore, ZrO_2 consists of granular and porous structures with particle sizes ranging from 10 to 40 nm, which is suitable to be used as a catalyst support. $C_4H_4O_6HK/ZrO_2$ catalyzed reaction is able to maintain biodiesel yield for five cycles with potassium leached from 15 to 4 ppm for the fresh and fifth used catalyst, respectively.

Georgogianni *et al.*[95] reported the production of soybean-based biodiesel with KNO_3/mesoporous ZrO_2 which was prepared by impregnation method. The transesterification was performed with mechanical stirring and frequency ulrasonification. 89% of biodiesel content was yielded by mechanical stirring within 24 h reaction time, whereas 83% yield achieved in 5 h reaction time with ultrasonication. The ultrasonic energy has led to the collapse of captivation bubbles which resulted in the formation of emulsion from the disrupted liquid phase boundary. This condition shall improve the mixing contact between reactant and catalyst for better catalytic efficiency. It is important to mention that the catalyst activity of ZrO_2 in the reaction also increased as it was enriched with the basicity enhanced active potassium cations.

At the same time, Hamad *et al.*[96] synthesized the alkaline metal cation (cesium ion) with zirconia support (ZrOCs) via cationic exchange technique. The ZrOCs catalyst was prepared by cationic exchange of zirconium hydroxide with Cs cations (form cesium carbonate) in a basic medium. The catalyst preparation method differs from that reported by Georgogianni[95] who prepared KNO_3/mesoporous ZrO_2 by impregnation, or by Sree[97] who synthesized the Mg-Zr by co-precipitation method. The ZrOCs catalyst showed high catalytic activity for methanolysis and ethanolysis of rapeseed oil in mild conditions (99.5% and 91% of biodiesel content, respectively), while no catalytic activity was observed for the non-loaded ZrO_2 catalyst. In order to prevent lixiviation of Cs species in the reaction medium, the weakly bonded Cs species were washed with two hot ethanol-leaching processes to ensure the exclusive contribution of heterogeneous basic catalysis.

ZrO_2 supported La_2O_3 catalyst for transesterification of sunflower oil was prepared via impregnation method. Sun *et al.*[98] reported that La^{3+} species has partially entered the ZrO_2 phase which resulted in the formation of La_2O_3-ZrO_2 solid solution phase. According to Sato,[99] REOs have similar basicity as CaO and thus La_2O_3 possess strong basic strength from the TPD-CO_2 analysis. As a result, presence of stronger basic strength in La_2O_3/ZrO_2 was due to the basic property of loaded La_2O_3 which has facilitated the synergy reaction between ZrO_2 and La_2O_3. The catalyst showed optimum biodiesel yield (85%) at reaction temperature of

200 °C. Table VIII illustrates summary of zirconia and titania supported catalysts for biodiesel production.

8. Zinc oxide support

Zinc oxide is a cheap, stable, re-usable, commercially available, and environmentally friendly catalyst which is used in many catalytic reactions. It has been reported that zinc oxide is widely used as catalyst support. Zinc oxide possesses basic properties, which makes impregnation with alkaline metals and alkaline-earth metals on ZnO support to promote a good basic solid characteristic which eventually improves the transesterification of vegetable oils.[100] Xie and Huang[101] loaded alkali metal salt on ZnO support for biodiesel production. The transesterification activities of different potassium precursor (KF, KOH, and K_2CO_3) on ZnO support were studied. It was found that the basicity of ZnO supported catalyst has increased significantly with the attachment of basic alkali metal. The transesterification activity of the catalysts was in the order of $KF/ZnO \geq KOH/ZnO > K_2CO_3/ZnO$. Both ZnO supported KF and KOH species exhibited more than 80% of conversion which is higher than K_2CO_3/ZnO (74%). The finding suggested a correlation effect between catalytic activity and catalyst's basicity in transesterification reaction. Higher catalyst basicity will directly improve the activity of the catalyst. According to some researchers,[102,103] O^{2-} species and coordinatively unsaturated F^- ions have major contributions in the catalytic activity of KF/Al_2O_3. The high activity of KF-type precursor loaded on ZnO support implied that association of F^- ion between the potassium and ZnO support showed better basicity than O^{2-} ion interaction.

The performance test of KF/ZnO also has been done by Hameed *et al.*[104] in the optimization study of palm oil transesterification reaction using response surface methodology (RSM) tool. RSM software provided more information per experiment than unplanned approaches and showed the interactions among the experimental variables within the studied ranges. Biodiesel yielded by the optimum transesterification was 89.23% at the conditions of 9.72 h of reaction time, 11.43:1 of methanol/oil ratio, and 5.52 wt. % of catalyst loading. A preliminary study was done by Yang and Xie[105] in the production of biodiesel using alkaline metal-doped zinc oxide catalyst. The catalytic efficiency of the catalyst was studied in terms of the conversion of soybean oil to methyl esters. The finding showed that ZnO does not contribute to any catalytic activity in the reaction. However, the addition of alkaline-earth metal species on ZnO support

TABLE VIII. Zirconia and titania supported catalyst for biodiesel production.

Catalysts	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	catalyst amount (wt. %)	Yield (%)	Reference
ZrO_2 Support							
$C_4H_4O_6HK/ZrO_2$	Soybean	2	60	12	6	86.65	94
Cs/ZrO_2 (cation exchange technique)							96
Ethanolysis	Rapeseed	5	79	18	4	91	
Methanolysis		5	60	18	4	99.5	
KNO_3/ZrO	Soybean	24	60	250	10	89	95
La_2O_3/ZrO_2	Sunflower	5	200	30	5	84.9	98
TiO_2 Support							
TiO_2	Soybean	2	60	12	6	0	94
KI/TiO_2						<10	
KCl/TiO_2						<10	
$KBrO_3/TiO_2$						<10	
$C_8H_5O_4K/TiO_2$						<10	
K_2CO_3/TiO_2						25.15	
$C_4H_4O_6KNa \cdot 4H_2O/TiO_2$						52.48	
C_4H_4HK/TiO_2						86.65	

exhibited high transesterification activity due to increase of basic strength on active sites. The catalytic efficiency of the catalysts was in the following order: $Sr(NO_3)_2/ZnO > Ba(NO_3)_2/ZnO > Mg(NO_3)_2/ZnO > Ca(NO_3)_2/ZnO$. $Sr(NO_3)_2/ZnO$ and $Ba(NO_3)_2/ZnO$ rendered highest conversion (>90%) with the presence of higher basicity than $Mg(NO_3)_2/ZnO$ and $Ca(NO_3)_2/ZnO$ catalysts. However, $Sr(NO_3)_2/ZnO$ catalyst showed weak reusability with only 15.4% conversion in the second run. Further study on calcination temperatures and doped Ba amounts on the efficiency of the catalysts for $Ba(NO_3)_2/ZnO$ in the transesterification reaction of soybean oil was reported.[106] The basicity of the catalyst was studied in different calcinations temperatures ranging from 400 to 800 °C. It was found that the catalyst showed highest basicity with improvement of catalytic activity at 600 °C. The presence of $BaCO_3$ and BaO phase in this temperature was expected to be the main catalytically active sites. However, the drop of basicity was observed above calcination temperature of 600 °C, it is due to the presence of perovskite $BaZnO_2$ phase which inhibited the activity of catalyst. The effect of different loading of Ba species on ZnO was studied. The authors found that increase of Ba loading above 2.5 mmol/g will lead to the drop of basicity. The culprit of reduced basicity and conversion was the overcoverage of ZnO support by monolayer of active component. The stability of Ba-ZnO was low as the catalyst provided low catalytic activity (43.2% of conversion) in the second cycle. A decrement in catalytic activity of the used catalyst may probably due to the leaching problem of Ba active species into the reaction medium.

Two types of ZnO (prepared via precipitation step and commercial scale) were used as a support for active phase CaO to catalyze transesterification reaction. The incorporation of CaO was carried out by impregnated calcium acetate aqueous solutions on ZnO support. Alba-Rubio's[100] study showed that the structural and textural properties of commercial ZnO (ZnO-com) and synthesized ZnO (ZnO-synt) were totally different. Although ZnO is a non-porous solid in both cases, small crystallite of ZnO-synt possesses higher specific surface area (24.1 m^2/g), pore volume ($0.162\,cm^3\,g^{-1}$), and large average pore diameter (23.5 nm in mesoporous region), thus improving the dispersion of active phase, while ZnO-com only consisted of micropores structure. The conversion of ethyl butyrate for CaO/ZnO-synt was found higher (41.2%) than CaO/ZnO-com with only 28.2%. Besides, the authors proved that the high stability of CaO/ZnO-synt with the absence of lixiviation in the reaction medium. This can be explained by the incorporation of CaO active particles into the mesopores and stabilized the CaO species on the support. The finding concluded that an alternative to stabilize these basic oxides against leaching is by using supports to facilitate the dispersion. The support-active phase interaction could prevent leaching. Table IX shows the list of ZnO supported catalysts for transesterification of oil with methanol:

E. Binary metal oxide

Studies on utilizing the alkali and alkaline-earth metal oxides that were unsupported over materials (alumina, magnesia, zirconia, and titania) to produce thermal activated hydrotalcites (Mg–Al, Ca–Al) or other binary metal oxides (Mg–Ca, Ca-Zr, Ca-Ti) has been done by researchers. The purpose is to improve the catalytic efficiency and basicity of the bulk metal oxide or undoped support in biodiesel production. Puna *et al.*[107] stated that catalytic behavior of triglycerides methanolysis can be enhanced by incorporating alkali metals and alkaline-earth metals in the sample composition, especially K, Li, Ca, and Sr. Mixed metal oxide catalyst is getting attention as potential solid catalyst for biodiesel synthesis. Mixed metal oxide is a combination of several metal or binary metal into mixed oxide forms via co-precipitation, solid state, or sol-gel techniques. These catalysts differ from the supported catalysts which are produced using wet-impregnation technique. As reported by other researchers, high loading of active components cannot be easily obtained using a wet impregnation method.[108,109] The physical mixing technique can produce mixed metal oxide catalysts with high loading of active components. However, the catalyst from physical mixing results in low specific surface area and low crystallinity which would reduce individual catalytic activity.[108,110,111] The preparation of binary metal oxide catalysts via co-precipitation and sol-gel method for transesterification

TABLE IX. Zinc oxide supported catalysts for biodiesel production.

Catalysts	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Alkali metal							
KF/ZnO	Palm oil	9.72	65	11.43	5.52	89.23	104
KF/ZnO	Soybean oil	9	65	10	n/d	C = 87[a]	101
KOH/ZnO						C = 82[a]	
K_2CO_3/ZnO						C = 82[a]	
Alkali-earth metal							
CaO/ZnO	Ethyl butyrate sunflower	2	60	12	1.2	90	100
		2	60	12	1.3	90	
$Mg(NO_3)_2$/ZnO	Soybean oil	5	65	12	5	25	105
$Ca(NO_3)_2$/ZnO						2	
$Sr(NO_3)_2$/ZnO						94	
$Ba(NO_3)_2$/ZnO						90	
$Ba(NO_3)_2$/ZnO	Soybean	1	65	12	6	C = 95[a]	106

[a] C is the conversion of oil.

has been studied by scientists. Some findings showed that the co-precipitation method is capable of increasing the concentration of catalyst active catalytic sites.[97,112]

1. Calcium-based with alkaline metal oxide

Ngamcharussrivichai *et al.*[113] performed a heterogeneously catalyzed transesterification of palm kernel oil (PKO) with methanol over metal doped dolomites and parent dolomite. The active metal doped dolomite was prepared by conventional precipitation method with alkaline-earth metal nitrate salts (Mg, Ca, and Ba) or trivalent metal nitrate salts (Al and La). The catalytic activity of the catalysts in reflux condition were as follows: DM-800 (parent dolomite) > Ca/DM-800 > Ba/DM-800 > Al/DM-800 > Mg/DM-800 > La/DM-800. The results showed that parent dolomite yielded the highest FAME (96.1%) followed by 95.0% (Ca-dolomite) and 89.2% (Ba-dolomite), other catalysts yield was less than 80%. This indicated that the amount of accessible CaO sites in the parent dolomiteis is the main key to improve the catalytic activity. The durability test revealed that Ca-dolomite survived three consequent cycles while maintaining the FAME content over 95%. The reduction of FAME content after 3rd run was due to the leaching of active species (9.3 wt. % loss of CaO species for fifth run catalysts).

The biodiesel synthesis via methanolysis of ethyl butyrate and sunflower oil using MgCa oxides was investigated. The MgCa mixed oxides was synthesized using co-precipitation method followed by thermal activation to obtain the corresponding metal oxides. Under optimum conditions, 45% of conversion for ethyl butyrate and 92% of FAME yield were achieved. The results showed the mixed metal oxide exhibited stronger basicity and resulted in better performance as compared to pure MgO and CaO.[114] In this study, isopropanol conversion test was applied to determine the acid and basic sites of the catalyst. The formation of propylene (from dehydration of isopropanol) or acetone (from dehydrogenation) provides information on the presence of acid and basic (or redox) centers. The formation of propylene is attributed to acid centers, whereas the formation of acetone is related to the presence of basic centers. From the results, MgCaO showed high selectivity towards acetone formation, indicating the presence of strong basicity in the catalyst.[114,115] Albuquerque *et al.*[115] continued the study on lixiviation of MgO/CaO in the transesterification process. The findings showed that MgCa catalyst exhibited high stability against lixiviation.

According to Wang *et al.*,[116] nano-catalyst with mesoporous structure exhibits larger surface area, pore size, and simple product-catalyst separation compared to conventional nano-size catalysts. The authors prepared a mesoporous nano-sized KF/CaO-MgO solid-base catalyst via co-precipitation method. The as-synthesized catalyst exhibited higher catalytic activity (95% of biodiesel yield) than pure CaO. The presence of newly formed $KCaF_3$ and $KMgF_3$ phases has improved catalytic activity, increased resistance to saponification and improved anti-poisoning of the catalyst. It is found that >80% of biodiesel was yielded when acid value in the oil feedstock was <10 mg KOH/g oil by using KF/CaO–MgO catalyst. Besides, KF/CaO-MgO is capable to maintain >90% of biodiesel yield for six cycles with low leachate.

Lee *et al.*[117] studied the optimization study of CaO-MgO catalyzed transesterification of jatropha oil by using response surface methodology technique. The reaction model statistically showed that the optimum biodiesel yield was 93.6% under best reaction condition of: (1) methanol/oil molar ratio: 38.67, (2) reaction time: 3.44 h, (3) catalyst amount: 3.70 wt. %, and (4) reaction temperature: 115.87 °C. In addition, the intensification of transesterification was due to the presence of synergetic effect of basicity between CaO and MgO which was shown in the physicochemical analysis.[118]

2. Calcium-based with aluminium oxide

The authors[119] synthesized mixed alkaline-earth metal with alumina oxide using single step sol-gel method. The catalytic activity of MgO/Al_2O_3 and CaO/Al_2O_3 was studied using transesterification of yellow green algae oil, *Nannochloropsis oculata* (preferred due to its high fatty acid content) to biodiesel. Among the mixed oxide catalysts, CaO/Al_2O_3 showed the highest activity in the transesterification reaction. The authors found that basic density (the number of basic sites per square meter) and basic strength generated during the sol-gel method has improved the activity of catalysts. Although the basic site density of pure CaO and MgO is higher than mixed oxides, it is believed that not only the basic site density but also the basic strength is very crucial in biodiesel yield. Besides, the increment in methanol amount has also contributed in the improvement of biodiesel yield from 23% to 97.5%. The CaO/Al_2O_3 mixed oxides showed high reusability with consistent biodiesel yield for second cycles, indicating that there was no coke formation or any other adverse effects of possible poisons on the catalyst activity.

3. Calcium-based with transition metal oxide

Kawashima *et al.*[120] initiated a study on the catalytic efficiency of solid base mixed metal oxides in transesterification process. The mixed oxide catalyst was prepared in A-B-O type metal oxides with A is an alkaline-earth metal (also known as alkaline metal/rare earth metal) and B is a transition metal which includes metal oxides of calcium, barium, magnesium, or lanthanum. The catalysts were prepared via conventional solid-state reaction (physical mixing), which involved mixing of metal oxides in desired proportions followed by calcination. The calcium-based catalyst showed higher activities (>90%) than Ba-, Mg-, and La-based catalysts (<1%) at the reaction condition of 60 °C, 6:1 of methanol to oil molar ratio, 10 wt. % of catalyst amount, and 10 h of reaction time. The impressive performance of Ca-based mixed metal oxides was due to the presence of stronger basic strength than other metals. Among other Ca-based catalysts, $CaZrO_3$ and $CaO\text{-}CeO_2$ rendered strongest catalytic durability, which is able to provide methyl ester yields greater than 80% for five times and seven times, respectively.

Ngamcharussrivichai *et al.*[121] produced biodiesel via transesterification of palm kernel oil with methanol using mixed CaO-ZnO oxides catalyst. The CaO-ZnO catalyst was prepared via conventional co-precipitation of the corresponding metal nitrate solution. This catalyst showed high catalytic activity (FAME yield > 94%) under optimum conditions of 60 °C, 10 wt. % of catalyst amount, 30:1 of methanol/oil ratio, and 1 h reaction time. The authors compared the catalytic activity of CaO-ZnO catalysts prepared using different type of precipitant agent (Na_2CO_3, $(NH_4)_2CO_3$ and urea hydrolysis). The finding showed that using Na_2CO_3 as the precipitant agent has resulted in more active CaO-ZnO catalyst with 93.5% FAME yield, which is higher than $(NH_4)_2CO_3$ (73.9%) and urea hydrolysis (27.6%). The low activity of CaO-ZnO using $(NH_4)_2CO_3$ and urea hydrolysis may due to incomplete precipitation between metal ions and CO_3^{2-} and thus led to the formation of mixed hydroxide.[122,123] This fact was in agreement with Ngamcharussrivichai's previous study in which CaO-ZnO derived from carbonate precursor rendered higher transesterification activity than that prepared through thermal dehydroxylation.[113] The catalyst can be reused for three times while maintaining the FAME yield >90% by washing the catalyst with mixture of methanol and 5 M NH_4OH solution after each cycle.

Lee *et al.*[124,125] studied the catalytic performance of CaZnO mixed thru transesterification of non-edible oil (*Jatropha curcas* oil) with methanol. Under reflux condition, the catalyst converted >80% of Jatropha oil to biodiesel product with catalyst amount (4 wt. %), methanol/oil molar ratio (15:1), and reaction time (6 h). According to Lee *et al.*, the bulk CaO contribute partial homogeneous catalytic pathway in the biodiesel synthesis in which the active Ca species leached into the reaction medium. The as-prepared mixed calcium-based oxide (CaZnO) was intended to stabilize the active phase to avoid the leaching process. The CaZnO catalyst is capable of maintaining biodiesel yield >80% for four cycles with low leaching of Ca species compared to CaO.

4. Calcium-based with lanthanide oxide

Yan *et al.*[126] have developed a calcium-lanthanum mixed oxide catalyst with high tolerance to water and FFA in oil feedstocks, unrefined oils and waste oils. The effect of FFA, water, and CO_2 on catalyst structure and catalytic activity was investigated. Under optimal conditions of 58 °C, 20:1 of methanol/refined soybean oil ratio, 5% of catalyst amount, and the FAME yield reached 94.3% within 60 min. Besides, CaO-La_2O_3 catalyst converted oils (crude palm oil, crude soybean oil, waste cooking oil, diluted crude palm oil, diluted crude soybean oil, and diluted waste cooking oil) which are high in water and FFA to 96% of biodiesel within 3 h. This has proven the ability of catalyst to tolerate high water and FFA content. CaO-La_2O_3 mixed oxide catalyst possessed mixture of Bronsted bases [$Ca(OH)_2$ and $La(OH)_3$ phases] and Lewis bases (CaO and La_2O_3 phases), which showed stronger base strength than bulk CaO and La_2O_3. Hence, the FAME yield was found to follow the trend of basicity: CaO-$La_2O_3 >$ CaO $>$ La_2O_3.

As reported by Lee *et al.*, La_2O_3 contributed both base and acid properties in the binary catalyst system. For metal oxides (like La^{3+}-O^{2-}), the surface lattice oxygen was attributed to Lewis base sites (favor for transesterification) whereas the metal ions are Lewis acid sites (favor for esterification). Integration of metal-metal oxide between Ca and La capable to enhance the catalytic activity for transesterification reaction due to well dispersion of CaO on composite surface and lead to increased of surface acidic and basic sites as compared to that of bulk CaO and La_2O_3 metal oxide.[127,128]

Since CaO-La_2O_3 mixed oxide catalyst provides a great potential to simplify the oil with high acid value and water content in transesterification reaction, Yan *et al.* have further studied the properties of this catalyst and its preparation method. Yan *et al.* have developed a multistep precipitation process to prepare CaO–La_2O_3 catalyst. This precipitation method utilized ammonia solution (as base precipitant), carbon dioxide (as acid precipitant), and ethanol (as neutral precipitant) in catalyst synthesis to facilitate a complete and uniform precipitation process and to improve the specific surface area, base strength, and basicity, which subsequently resulted in high transesterification activity. The calcium-based mixed oxide catalyst prepared by this novel method was compared with conventional techniques (physical mixing, impregnation, and co-precipitation methods). The Ca_3La_1 (multistep precipitation) showed highest FAME yield (95.3%) within 60 min, which is higher than CaO/La_2O_3 (wet impregnation), CaO–La_2O_3 (physical mixing), and La_2O_3·CaO (coprecipitation). This result was parallel with the study of catalyst's basicity followed the order of: $Ca_3La_1 >$ CaO/$La_2O_3 >$ CaO–$La_2O_3 > La_2O_3$·CaO. Ca_3La_1 has higher reusability within three cycles in batch reactor, but the activity dropped in the fourth cycle with less than 80% of FAME yield. In continuous fix bed reactor, FAME yield maintained at >92% for 14 days.[129] The list of calcium-based mixed metal oxide catalysts was depicted in Table X.

5. Magnesium-based with transition metal oxide

Mg/Zr mixed oxide catalyst (prepared via co-precipitation method) for the transesterification of both edible (sunflower, soybean, rice bran) and non-edible oils (Jatropha) to biodiesel at

TABLE X. Calcium-based mixed metal oxide catalysts for biodiesel production.

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
With alkaline metal group							
Dolomite							
DM-800	Refined palm kernel	3	60	50	10	96	113
Mg/Dm-800						<80	
Ca/DM-800						95	
Ba/DM-800						89	
Al-DM-800						<80	
La/DM-800						<80	
Mg:Ca(3.8)	Ehtyl butyrate	1	60	4	62 mg	$C = 45^a$	114
	Sunflower	180 min		12	2.5	$C = 92^a$	
MgCa15	Ethyl butyrate	1	60	4	62 mg	$C = 20^a$	115
MgCa9						$C = 32^a$	
$MgCa_3$						$C = 44^a$	
KF/CaOMgO	Rapeseed oil	3	70	12	3	95	116
With alumina group							
$MgO\text{-}Al_2O_3$	Lipid of yellow green microalgae, (*Nannochloropsis oculata*)	N/D		6	N/D	16	108
$CaO\text{-}Al_2O_3$						23	
With transition metal group							
Solid state mixing effect							
$CaTiO_3$	Rapeseed oil	10	60	6	10	79	120
$CaMnO_3$						92	
$Ca_2Fe_2O_5$						92	
$CaZrO_3$						88	
$CaCeO_3$						89	
Coprecipitation method							
CaO·ZnO (coprecipitation with Na_2CO_3)	Palm kernel	1	60	30	10	94	121
CaO·ZnO (coprecipitation with $(NH_4)_2CO_3$)						74	
CaO·ZnO (Urea hydrolysis)						28	

TABLE X. (*Continued.*)

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
CaZnO	Jatropha curcas	6	65	15	4	C = 83[a]	113
With lanthanide group							
Ca_3La_1 (ammonia–ethanol–carbon dioxide precipitation method)	Soybean oil	60 min	65	7.6 g met/10 g oil	5	95.3	129
CaO-La_2O_3 (physical mixing method)						~13	
CaO/La_2O_3 wet impregnation method)						~35	
La_2O_3·CaO (coprecipitation method)						<10	

[a] C is the conversion of oil.

room temperature and reflux condition was reported.[97] The catalyst showed high activity for both edible and non-edible oil within 1 h of reaction time. The performance of Mg/Zr mixed oxide was due to the presence of synergistic effect between basic sites of MgO and amphoteric nature sites of ZrO_2. The strong interaction between MgO and ZrO_2 has led to the transfer of electrons from metal oxide support (MgO) to ZrO_2 which results in strong basic strength.[130] The catalyst showed high reusability with maintained the FAME yield within four cycles.

Zirconia with amphoteric propertiesis now gaining popularity among researchers to produce supported catalyst which exposes both acid and basic sites. Another research group used basic mixed oxides of magnesium and zirconium for transesterification of tributyrin with methanol, a model reaction for biodiesel synthesis. Kozlowski *et al.*[131] evaluated the catalytic activity of Mg:Zr mixed oxide with different synthesis method (co-precipitation and sol-gel method). The co-precipitated mixed oxide (Mg:Zr-P) showed the presence of pure oxides crystal for both periclase MgO and tetragonal ZrO_2 phases. On the other hand, sol-gel synthesis (Mg:Zr-SG) showed better mix at atomic level with the absence of crystalline phase of ZrO_2 and low intensity of MgO phase. This indicated that no crystallization of the individual oxides has occurred during the synthesis. The catalytic activity of these catalysts was examined by determining the rate constant of tributyrin consumption (K_1). Mg:Zr-P showed higher activity than Mg:Zr-SG with the rate constant $k_1 = 0.50 \times 10^6$ and $0.32 \times 10^6\,\text{mol}^{-1}\,\text{m}^{-2}\,\text{s}^{-1}$, respectively. Mg:Zr-P was able to maintain the activity at 85% and 75% at its original activity and second cycles, respectively, with small amount of leaching occurred.

Wen *et al.*[132] studied the behavior of TiO_2–MgO mixed oxides catalyst (by sol-gel method) for biodiesel synthesis from waste cooking oil (WCO). The pure MgO showed higher catalytic activity than mixed oxides. The authors stated the high activity of MgO (89.6%) was due to the leaching of Mg^{2+} content (198 ppm) whereas no leaching was found for the TiO_2. This finding indicated that the high activity of MgO is likely attributed to the homogeneous magnesium methoxide from the metal leaching. The presence of $MgTiO_3$ mixed oxide phase showed the substitution behavior of Ti for Mg ions in the magnesia lattice, and this condition was found similar to the observations reported by Lopez *et al.*[133] The addition of Ti resulted in the formation of vacancies and induced defects on the catalyst surface that can improve the stability while maintaining an acceptable catalytic activity.[134] The TiO_2-MgO has tolerated highwater content in waste cooking oil for up to 1.9 wt. % with 85.3% of FAME yield. Further increment of water content shall lead to hydrolysis of methyl ester, thus reduced the FAME yield. The high stability of mixed oxides has maintained the FAME yield >80% for four cycles.

Olutoye *et al.*[135] studied the optimization conditions of transesterification of palm oil with methanol using KMgZnO heterogeneous catalyst. The mixed oxide KMgZnO catalyst (synthesized via co-precipitation method) showed the presence of synergetic effect of both MgO and ZnO which complimented each other to produce higher activity than its separate oxides. The interaction between the metal ions has led to the modification of electronic properties and thus resulted in synergetic effect. The same research groups[136] showed that increased Mg/Zn ratio formed more porous structure on the catalyst. The porous structure is believed to be induced by Mg^{2+} that formed MgO clusters surrounding the MgZnO complex. Under optimum conditions, 87% of FAME content was achieved by KMgZnO catalyzed reaction whereas the bulk MgO and ZnO produced lower FAME yield at 56% and 26%, respectively. Furthermore, Lee *et al.*[137] showed that MgO-ZnO mixed metal oxide catalysts are capable of performing in transesterification of high acid jatropha oil, which 83% of jatropha biodiesel was produced under 120 °C, 25:1 methanol:oil ratio, 3 wt. % of catalyst within 3 h.

6. Magnesium-based with lanthanide oxide

Mg/La-mixed oxide catalyst was prepared via co-precipitation method. Catalytic behavior of this catalyst was investigated using transesterification of edible (soybean and rice bran) and non-edible (jatropha) oils to biodiesel at two different reaction conditions, namely room temperature and reflux condition. All vegetable oils were completely converted to FAME under reflux condition within 20–30 min irrespective to the nature of the oil. The conversion of oil in room temperature took longer reaction time (120–140 min) to complete. The excellent performance of Mg/La mixed oxide is due to the presence of high basicity. The formation of La_2MgO_x solid solution phase resulted strong interaction between these oxides, thus creating strong basic sites on the catalyst. Besides, the presence of lanthanum hydroxide/carbonate species might be responsible for strong basic sites. Babu and his co-researchers found that the transesterification rate of edible oils was relatively higher than non-edible oil. Thus, this can be concluded that the reaction temperature, catalyst, and oil type greatly influence transesterification activity. This finding showed that the catalyst is tolerable to 10 wt. % of water content and 5 wt. % of FFA with 90% of conversion within 6 h reaction time. The reusability efficacy of the catalyst is tested up to five cycles with consistent activity together with marginal variation of conversion less than 5%.[138] Summary of magnesium-based mixed metal oxide catalysts for biodiesel production is shown in Table XI.

7. Other mixed metal oxides catalyst

Guo *et al.*[139] stated that sodium silicate ($Na_2O{\cdot}nSiO_2$) showed high catalytic activity in the transesterification of soybean oil to biodiesel. This catalyst possessed similar characteristic as supported-solid base catalysts. Almost 100% of biodiesel was yielded at the conditions of 60 °C, 3 wt. % of catalyst, and 7.5:1 methanol/oil ratio within 60 min of reaction time. Besides, catalyst tolerance experiment was conducted tooil contained 4.0 wt. % of water and 2.5 wt. % of FFA and interestingly conversion of 98% biodiesel was obtained. The tolerance of $Na_2O{\cdot}nSiO_2$ to water is related to its special crystal and porous structure. The presence of water would hydrolyzed the Si–O–Si bridges of $Na_2O{\cdot}nSiO_2$ and produce H_4SiO_4 monomers.[140] This catalyst can be reused for five cycles while maintaining biodiesel yield at 94%.

Yan *et al.*[141] developed a new class of mixed oxides catalyst ZnO-La_2O_3 (prepared by homogeneous-co-precipitation method) for the study of single-step biodiesel production from unrefined oil or waste oil. The ZnO-La_2O_3 was found to simultaneously catalyze the oil transesterification and fatty acid esterification reaction. Biodiesel yielded from waste cooking oil and unrefined oil (with high acid content) was 96% within 3 h reaction time at 200 °C. The ZnO-La_2O_3 consists of strong interaction between Zn-La species which are able to enhance the dispersion of ZnO on La_2O_3. This increased the surface amounts of acid and basic sites and thus improved the catalyst ability in both esterification and transesterification reactions.

TABLE XI. Magnesium-based mixed metal oxide catalysts for biodiesel production.

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Magnesium-based with transition metal oxide							
TiO_2-MgO	Waste cooking oil	6	150	30	5	80	132
Mg/Zr	Sunflower	45–75 min	65	2.5 ml/1g	0.1 g	>90	97
	Jatropha					>90	
	Soybean					>90	
	Ricebran					>90	
Mg:Zr (coprecipitate)	Tributyrin	n/d	60	30	0.5–1 g	0.5×10^6 [a]	131
Mg:Zr (solgel)						0.32×10^6 [a]	
KMgZnO	Palm oil	5	188	16	2.3	87	135
Magnesium-based with lantanide oxide							
Mg/La	Sunflower	30 min	65	2.5 mL/1 goil	0.05 g	>90	138
	Jatropha	or					
	Soybean	120–140 min	RT				
	Ricebran						

[a] Rate constant, $k1 = 0.5 \times 10^6$ (mol^{-1} m^{-2} s^{-1}).

The same research group[142] further reported on the transesterification activity of ZnO-La_2O_3 by using several types of inexpensive oils in different reactors (batch and continuous). Crude algae oil, corn oil, crude palm oil, crude soybean oil, crude coconut oil, waste cooking oil, food-grade soybean oil, and food-grade soybean oil with 3% water and 5% FFA addition were used for biodiesel synthesis. The ZnO-La_2O_3 successfully converted the oils into FAME within 3 h. In the durability test, the modified catalysts were reused for 17 times in batch stirred reactor with FAME yield maintained at 93.7%. Furthermore, the catalysts were also used continuously for 70 days in a fix bed continuous reactor with average FAME yield of 92.3%. Both reusability tests were performed without catalyst regeneration or washing steps. The findings concluded that ZnO-La_2O_3 possesses characteristics such as high catalytic activity, water and FFA content tolerance, long catalyst life and high stability with low leaching in biodiesel production.

Jin *et al.*[143] confirmed catalytic activity of ZnO/$La_2O_2CO_3$ heterogeneous catalyst are high with>95% biodiesel yield within 5 min in microwave heating and 20 min in conventional heating under mild reaction conditions (<100 °C). The catalyst with *in situ* precipitation method showed the presence of mixture of ZnO (zincite) and type II $La_2O_2CO_3$ layered structure, resulting in increase of strong basic sites of $La_2O_2CO_3$ material instead of weak basic site from ZnO. The catalyst can be reused for 3 times with biodiesel yield maintained >90%. The author found that transesterification reaction with microwave heating completed within a very short reaction time. This may due to the selective heating which took place on the internal and external surface of solid catalyst which could have accelerated the reaction.[144,145] Ding *et al.*[146] prepared a series of zirconia-based mixed oxide catalysts (M/Zr, with M = Li, Na, K, Mg, Ca) using sol-gel method. The catalytic activities of these mesoporous mixed oxide catalysts were evaluated using transesterification of soybean oil with methanol. Among the catalysts, alkali metal mixed with zirconia (Li- and K-modified ZrO_2) showed the highest yield with the presence of strong basic sites. On the other hand, formation of MgO–ZrO_2 and CaO–ZrO_2 solid solution phase was found in Mg–ZrO_2 and Ca–ZrO_2 catalysts with the presence of weak basic site thus reduce the catalytic activity. Li-ZrO_2 catalyst with the highest activity (98.2%) performed with 78.6% and 10.5% yield at second and third cycle, respectively, which is a symptom of Li leached into the reaction medium.

Kondamudi *et al.*[147] studied the behavior of Quintinite-3T (Q-3T) by performing transesterification reaction of soy, canola, coffee, and waste vegetable oil. Quintinite-3T ($Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$) is a natural mineral categorized in the layer double hydroxides (LDHs) group and this catalyst was prepared via co-precipitation method. Quinitnite consists of higher Al/Mg ratio (0.5) which makes it more suitable for acid catalyzed reaction than base catalyzed reaction. The catalyst showed the presence of BrØnsted acid sites (attributed to the presence of Mg–OH–Al bonds and Al–OH groups) and Lewis acidic sties (account for Al^{3+}). The introduction of alumina induced Lewis acid properties of the catalyst and accelerated the esterification process. From the findings, the catalyst showed excellent performance in converting FFA and triglyceride to >96% biodiesel. The catalysts showed high reusability with maintained yield of 95% for five cycles with structural integrity remained intact. Table XII summarizes the mixed metal oxide catalysts for biodiesel production.

F. Hydrotalcite

1. Mg/Al hydrotalcite

LDHs are gaining attention as a catalyst for vegetable oil transesterification. LDHs with general formula $[Mg_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125}{\cdot}0.5H_2O$ is the most well-known lamellar mixed hydroxides, which is also known as hydrotalcite (HT).[148,149] Hydrotalcite is a family of anionic clays with a brucite-like hydroxide layers ($Mg(OH)_2$) in which excess of positive charge originated from replacement of some Mg^{2+} ions by Al^{3+} ions in the octahedral sites of hydroxide sheets. Hydrotalcite's neutrality is attained by compensating negative charge of anions (${CO_3}^{2-}$) situated in the interlayer space.[148] The most interesting properties of hydrotalcite in LDHs

TABLE XII. Others mixed metal oxide catalysts for biodiesel production.

Catalyst	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Sodium silicate	Soybean	60 min	60	7.5	3	>95	139
$Na_2O{\cdot}nSiO_2$							
Zn_3La_1	Soybean	3 h	200 °C, 500 psi	1.42 mass ratio	2.4	94	142
	Coconut					91	
Zn_3La_1 (ammonia–ethanol–carbon dioxide precipitation method)	Refined soybean	60 min	58	20	5	94.30	126
	Crude palm oil	3 h				>80	
	Crude Soybean	3 h				>80	
	Waste Cooking Oil	3 h				>80	
Zn_3La_1 (homogeneous-coprecipitation)	Refined soybean	60 min	200	1.42 mass ratio	3g	>90	141
	Crude palm oil	3 h				>90	
	Crude soybean	3 h				>90	
	Waste cooking oil	3 h				>90	
Li/ZrO	Soybean	3	65	13	3	98.2	146
Na/ZrO						32.8	
K/ZrO						52	
Mg/ZrO						5	
Ca/ZrO						3.5	
$ZnO\text{-}La_2O_2CO_3$ (microwave heating)	Canola	5 min	85	n/d	5	99	143
$ZnO\text{-}La_2O_2CO_3$ (conventional heating)		20 min	65			95	
Quinitine-3T	Waste vegetable oil (15% FFA)	6	n/d	12	10	97.72	147
	Coffee oil (33% FFA)	4				96.6	
	Canola	2				97.28	

group is the tunable basicity (acid/base property could be easily controlled by varying their chemical compositions) and high surface area with well-dispersed mixed metal-oxides.[150,151]

In the past few years, several studies the usage of mixed oxides derived from hydrotalcite in biodiesel synthesis have been conducted.[114,152] Most of the researchers prepared hydrotalcite using co-precipitation method which involved sodium/ammonium bases or potassium salts as precipitant agent. Besides, other studies showed the relationship between composition and catalytic activity,[153,154] and the optimum ratio for desirable activity is $Al/(Mg + Al) = 0.25$.[155] Table XIII shows the list of different hydrotalcite catalyst for biodiesel production.

Cantrell *et al.*[155] utilized calcined hydrotalcites in promoting the transesterification of glyceryl tributyrate in methanol. 74.8% of oil conversion was obtained with 30:1 methanol/oil molar ratio at 60 °C in a 3 h reaction. The reaction rate increased steadily with Mg content and the most active $Al/(Mg + Al)$ ratio was 0.25, in which was more active than MgO. Xie[153] also obtained a maximum soybean oil conversion to biodiesel (67%) from calcined Mg/Al hydrotalcite catalyzed reaction with 7.5% catalyst dosage, 15:1 of methanol/oil molar ratio within 9 h. Besides, this group reported that the hydrotalcites, in the absence of calcinations, present no catalytic activity for transesterification reaction. Chen[156] employed the same catalyst under reaction condition of 230 °C, 12:1 methanol/oil molar ratio, and 2% catalyst dosage to achieve >90% FAME yield in 3 h reaction time. Xi and Davis[157] reported high catalytic activity in calcined Mg–Al hydrotalcite (Mg/Al molar ratio = 4) transesterification of tributyrin with methanol. The authors suggested that the activity of catalyst was mostly depended on the catalyst structure and CO_2 adsorption capacity with different pretreatment temperature. Trakarnpruk[158] improved the performance of calcined Mg-Al hydrotalcite by adding active species of potassium. The K loaded calcined Mg-Al hydrotalcite obtained 96.9% biodiesel yield in the conditions of 100 °C, 7 wt. % catalyst amount, 30:1 methanol/oil ratio in 6 h reaction time.

The effect of Mg/Al ratio in the methanolysis of soybean oil and catalytic activity of catalysts with different $Al/(Mg + Al)$ molar ratios of 0.20, 0.25, and 0.33 were studied.[159] It was found that >90% of biodiesel was yielded from catalyst with $Al/(Mg + Al)$ ratio of 0.33 in the presence of medium basic strength. The hydrotalcite catalyst showed low reusability with biodiesel yield reduced from 90.7% to 64% in the third cycle. Other than that, 85% of biodiesel yielded from crude oil (with acidity = 9.5%) indicated that this catalyst is active for both transesterification of triglycerides and esterification of free fatty acids. This activity is closely related to Lewis acid sites generated from calcination of hydrotalcites. The OH^- group of hydrotalcite is attributed to the weak basic sites, whereas both Mg^{2+}–O^{2-} and Al^{3+}–O^{2-} pairs were related to medium basic strength and isolated O^{2-} anion is corresponded to strong basic sites. Generally, Al is more electronegative than Mg; thus, the increase in $Al/(Mg + Al)$ ratio has led to the increase of catalyst electronegativity. Reduction of electron density in oxygen atoms directly reduced the total basicity of the catalyst by generating Lewis acid sites.

Study on doping of trivalent cations (such as transition metals) with hydrotalcite was tested in the transesterification of triacetin and soybean oil.[160] The incorporation of Fe^{3+} into Mg/Al layered double hydroxide lattice has created a catalyst with tunable basicity and high surface area with porous structure. The results showed that Fe-Mg/Al catalyst showed higher activity in shorter reaction time compared to Ga-Mg/Al catalyst. Fe-Mg/Al catalyst was repeatedly regenerated and consequently no degradation of catalyst performance was observed.

A new type of hydrotalcite with the presence of polymer membrane (poly(vinyl alcohol)) as a solid base catalyst was developed.[161] The catalyst was prepared by dispersing hydrotalcite in polymer solution to form a membrane and applied as a catalyst for transesterification of soybean oil with methanol to produce biodiesel. The effect of hydrophobic/hydrophilic properties of the membranes on the catalytic activity was investigated. The findings showed that the poly(vinyl alcohol) membranes loaded with hydrotalcite catalyst presented high catalytic activity for and it is 20 times higher than unsupported hydrotalcite catalysts. This is due to the presence of most hydrophililic membrane that has promoted the reaction with methanol to form methoxide which aids in transesterification of soybean oil. The poly(vinyl) membranes with a poly(vinyl alcohol) matrix is capable of totally or partially acetylated in order to increase

TABLE XIII. Hydrotalcite catalysts for biodiesel production.

Catalyst	Feedstock	Calcination temperature (°C)	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Mg/Al hydrotalcite								
Mg/Al hydrotalcite	Glyceryl tributyrate	450	3	60	30	n/d	C = 75[a]	155
Mg/Al HT	Soybean	450–500	9	n/d	15	7.5	C = 65[a]	153
Mg/Al	Cotton seed		3	230	12	2	>90	156
Mg-Al HT	Refined soybean oil	400	1	230	13	5	90	159
	Degummed soybean oil (9.5% acidity)						85	
Mg-Al/Ga	Triacetin	460	60 min	60	6	1	80	160
Mg-Al/Fe			40 min				>90	
PVA membrane loaded Mg-Al HT	Soybean	450	n/d	60	30	n/d	>80	161
Li/Al hydrotalcite								
Li-Ca HT	Soybean	450–500	1	65	15	1	53	162
Mg-Al HT						3	<3	
Li-Ca HT	Glyceryl tributyrate	450	2	65	15	1	>98	163
Mg-Al HT							32	
Mg-Fe HT							23.9	
Zn/Al hydrotalcite								
Zn/Al	Rapeseed	450	180 min	200, 2.5 MPa	42	2	84.53	167
KF/Zn-Al HT	N/D	500	3	65	6	3	95	168
Ca/Al hydrotalcite								
KF/Ca-Al HT	Palm	550	5	65	12	5	96	169
Ca-Al HT							8	
KF/Mg-Al HT							89	

[a] C is the oil conversion.

hydrophobicity or treated with succinic anhydride in order to increase hydrophilicity. This catalyst can be reused for several runs without any further reactivation.

2. Li/Al hydrotalcite

Shumaker *et al.*[162] revealed that Li-Al catalyzed reaction exhibited better activity than Mg-Al catalyst by achieving 53% biodiesel yield in 1 h compared to <3% by Mg-Al catalyst. Calcined Li–Al LDH produced from calcinations of $[Al_2Li(OH)_6](CO_3)0.5{\cdot}mH_2O$ showed the presence of $LiAlO_2$ and $LiAl_5O_8$ phases which resulted in formation of Lewis basic sites and strong Bronsted base sites. Catalyst recycling studies showed that the catalyst maintained a high level of activity over several cycles, albeit analyses indicated that a small degree of lithium leaching (3.6% of Li) from the catalyst. The findings suggested that catalytic activity of Li–Al catalyst was largely heterogeneous in nature. The same group[163] further expanded the study by comparing the activity of calcined Li–Al, Mg–Al, and Mg–Fe LDHs in transesterification reactions. Li-Al catalyst showed higher concentration of strong basic sites than other catalysts and this explained the higher performance of Li-Al catalyst compared to Mg–Al and Mg–Fe catalysts.

3. Zn/Al hydrotalcite

The mixed oxide of Zn and Al heterogeneous catalysts has been used as a heterogeneous catalyst in industrialized biodiesel manufacturing. French Institute of Petroleum (IFP) developed the only heterogeneous catalyzed biodiesel process—Esterfip-H process, which is capable of processing 160 000 t/year/plants in France and Sweden. This process involved the use of heterogeneous catalyst (Zn/Al mixed oxide) with high reaction conditions (higher temperature and pressure, with an excess of methanol).[164–166]

Furthermore, Jiang *et al.*[167] investigated the high transesterification activity of Zn/Al complex oxide (calcined hyldrotalcite like precursor $[Zn_{1-x}Al_x(OH)_2]_x{}^+(CO_3)_{x/2n}{\cdot}mH_2O$) with 84.25% of oil conversion under methanol sub-critical condition (200 °C, 2.5 MPa) in 90 min. The activity was higher than Mg/Al complex oxide. The strong alkalinity of Zn/Al complex oxide also aided in high catalytic activity of the transesterification reaction. Although alumina is weak acid and ZnO is weak base, the Zn/Al complex oxide catalyst exhibited higher alkalinity and tolerance to FFA (6%) and water (10%) content with >80% of oil conversion. However, the reusability of Zn/Al complex oxide catalyst was low, although there was no leaking of Zn and Al components. Further investigation is required since the basic strength and alkalinity of reused-catalyst decreased sharply over cycle.

Xu[168] synthesized the Zn-Al hydrotalcite-like compounds and doped with high alkaline active KF salt to improve the catalytic activity of unsupported Zn-Al complex oxide catalyst. KF/Zn(Al)O showed more excellent activity than Zn(Al)O with >95% of biodiesel produced under reflux condition, 6:1 methanol/oil ratio, 3 wt. % catalyst loading in 3 h reaction time. The high catalytic activity was due to the formation of new phase KF and KOH and enhanced alkalinity of Zn(Al)O support.

4. Ca/Al hydrotalcite

Other than Zn/Al hydrotalcite compound, another new catalyst with similar structure to Mg-Al HT was synthesized by Gao[169] for biodiesel synthesis. He explained that the incorporation of KF with Ca-Al mixed oxide has improved the catalytic activity of the palm oil transesterification reaction (95.6% FAME yield). KF/Ca-Al HT consisted of $KCaF_3$, $KCaCO_3F$, and $CaAl\text{-}F_4(OH)$ phases which created high basicity and better catalytic efficiency during transesterification process. During reusability test, the active species of KF/Ca-Al HT remained intact which has indicated its ability to be recycled. The catalyst maintained biodiesel yield at 95% for second use after post-treatment.

G. Natural waste shell

Researchers are focusing on reducing biodiesel manufacturing cost so it could compete with petroleum diesel. By drawing on this, researchers have made attempts to seek for cost-effective and eco-friendly catalyst for transesterification reaction. Using industrial waste, i.e., fly ash and natural calcium source from municipal waste, i.e., egg-shell, mollusk, bone, etc., as raw material for catalyst preparation would eliminate waste and simultaneously developed new low cost, highly efficient supported catalyst and alternative CaO source for sustainable green energy. In order to create an effective waste valorization avenue, preparation of a novel low cost heterogeneous catalyst from industrial and municipal wastes is a must to synthesis fuel grade biodiesel. Table XIV shows the natural waste shell used as solid catalyst for transesterification reaction.

For instance, the waste scale of Rohu fish (*Labeo rohita*) as a low-cost solid base catalyst was used to synthesis biodiesel from soybean oil.[170] *Labeo rohita* was found to be the largest fishery production which accounted for 23.9% of the total fish production in India.[171] Hydroxyapatite is abundantly available in the fish scale and it is widely available in fish farm waste. Under optimum transesterification condition, 97.73% of FAME yield was obtained at 6.27:1 methanol/oil molar ratio and 1 wt. % catalyst loading. The presence of β-$Ca_3(PO_4)_2$ as main active component after thermal activation made up the transesterification activity. The catalyst could be reused in 5 h reaction for six consecutive runs, creating a potentially applicable avenue in biodiesel synthesis.

Eggshell is another solid waste produced from food processing and manufacturing plants. Most of this natural waste shell is disposed in landfills without any pretreatment because it was traditionally useless. The chemical component in eggshell mainly attributed to calcium carbonate ($CaCO_3$) (94%), and other elements such as magnesium carbonate (1%), calcium phosphate (1%), and organic matter (4%).[172] The calcified eggshell build up intrinsic pore structure and formation of CaO phase make it an active heterogeneous base catalyst for transesterification reaction. Hence, Wei *et al.*[173] studied the viability of waste eggshell derived CaO in soybean oil transesterification reaction. The authors confirmed the presence of $CaCO_3$ phase of eggshell and the appearance of CaO after thermal treatment (>700 °C). The eggshell-derived catalyst showed high activity with >95% of biodiesel content was yielded using 9:1 methanol/oil molar ratio, 3 wt. % catalyst amount, 65 °C reaction temperature in 3 h. The waste shell derived catalyst was reused for 17 times and degradation of catalyst's activity occurred after 17th run. This was due to the structural change of CaO phase to $Ca(OH)_2$ during the reaction with reactants (methanol and soybean oil) which consists of H_2O and CO_2.

On the other hand, Cho[174] also used quail eggshell derived catalyst for transesterification of palm oil with methanol. According to some researchers,[175–177] quail eggshell consisted of three layers: a thin cuticle outer layer, a thick palisade middle layer, and a thin mammillary inner layer. Majority of large pores are contained in the palisade layer. Cho found that using weak acid treatment followed by calcination at 800 °C to remove the dense cuticle layer from the eggshell had led to the generation of porous layer and strong basic sites in the quail eggshell derived catalyst. The porous structure has accelerated the diffusion of large oil molecule while the strong basic site improved the catalytic activity of the catalyst. From the results, quail eggshell derived catalyst showed higher catalytic activity compared to chicken eggshell derived catalyst. The quail eggshell catalyst is capable to be reused for five consecutive runs while maintained oil conversion rate at over 98%.

Boey *et al.*[178] discovered the new CaO source from waste mud crab shell (*Scylla serrata*) for the biodiesel synthesis. The mud crab, also known as mangrove crab or black crab, is commonly found in mangrove swamps nearby intertidal and subtidal muddy habitat. A recent rising trend in mud crab (*Scylla serrata*) aquaculture activities has intensified the supply of waste crab shell which is feasible to be used as a heterogeneous catalyst for transesterification reaction. In this preliminary study, mud crab shell derived catalyst exhibited high catalytic activity with >90% biodiesel yield and high reusability for up to 11 times in reflux condition, 0.5:1 methanol mass ratio, and 4 wt. % catalyst amount in 2 h reaction time. They[179] found that the

TABLE XIV. List of natural shell used as a catalyst for biodiesel production.

Catalysts	Feedstock	Time (h)	Temperature (°C)	Methanol/oil ratio	Catalyst amount (wt. %)	Yield (%)	Reference
Quail eggshell	Palm	2	65	12	1.5	C = 89	174
Chicken eggshell						C = 40	
CaO derived waste egg shell loaded on fly ash	Soybean	5	70	6.9	N/D	97	181
Combusted oyster shell	Soybean	5	70	6	25	98	186
KNO_3/flyash	Sunflower	8	170	15	15	C = 88	182
Eggshell	Plam olein oil	2	60	18	10	>90	183
Golden apple snail shell						>90	
Meretrix venus shell						>90	
Limestone calcite	Refined bleached deodorized PKO	3	60	30	6	46.8	190
Cuttle bone						24.1	
Dolomite						98.6	
Hydroxyapatite						2.6	
Dicalcium phosphate						1.3	
Cockle shell	Refined Palm	3	N/D	0.54[a]	4.9	97	187
Mixed crab and cockle shell	Chicken fat	3	Reflux	0.55[a]	4.9	98	188
Crab shell (schlla serrata)	Palm olein	N/D	65	0.5	5	97	179
Crab shell (schlla serrata)	Palm olein	2.5	65	0.5[a]	4	>90	178
Waste Rohu fish (Labeo rohita) scale	Soybean	5	70	6.27	1.01	98	170
Eggshell	Soybean	3	65	9	3	>95	173
Shrimp shell	Rapeseed	3	9		2.5	C = 89	184
Cocoa pod husks	Soybean	2	60	6	1	98.7	191

[a] Methanol/oil mass ratio.

non-calcined crab composed mainly of calcite-magnesia ($CaCO_3$–MgO). Thus, generation of active component (CaO and MgO) after thermal activation is feasible. Besides, the statistical analysis coupled with central composite design has been used to evaluate the effectiveness and interaction parameters in the basis of biodiesel purity.

Fly ash is one of the inorganic industrial residues from coal-based thermal power plant (via coal combustion processes). The chemical composition of fly ash is mainly composed of 55.19% SiO_2 and 30.01% Al_2O_3, while others corresponded to 4.58% Fe_2O_3, 2.12% Na_2O, 0.77% CaO, 1.91%MgO, 2.74% TiO_2, 1.28% BaO, and 1.40% K_2O.[180] This waste is potentially selected as low cost catalyst support due to the high amount of large pore silica and alumina. In view of this, an effort has been made to develop a fly ash-based heterogeneous catalyst for triglyceride transesterification to biodiesel.[181] Kotwal *et al.*[182] evaluated the catalytic activity of fly ash loaded with KNO_3 usingtransesterification of sunflower oil with methanol. The active species of K_2O derived from KNO_3 improved the basicity and catalytic efficiency of fly ash-based catalyst with maximum oil conversion of 87.5% at 170 °C, 15:1 methanol/oil molar ratio, 8 h reaction time, and 15% catalyst loading. However, the deposition of reactants/product with the loss of the active sites during the reaction resulted in low reusability for this catalyst.

Additionally, an active CaO derived from waste eggshell was loaded on waste fly ash support for the transesterification of soybean oil to biodiesel. A total of 96.97% biodiesel was yielded from the fly ash supported catalyst. This synthesized catalyst showed higher reusability characteristic (16 times repeated runs) and superior catalytic activity compared to bulk CaO catalyst derived from egg shell. This was due to the presence of mesoporous structure in the fly ash framework and intensified basicity from the interaction between CaO and fly ash components.[181]

Viriya-empikul *et al.*[183] compared the activity of waste mollusk shells (golden apple snail shell and *Meretrix venus* shell) with waste eggshell in the biodiesel synthesis. The findings showed that the catalytic activity was in the following order: eggshell > golden apple snail shell > *Meretrix venus* shell. The result was parallel to the descending order of Ca content in the catalyst, in which the highest Ca content was eggshell (99.21%) followed by golden apple snail shell (99.05%) and the last was *Meretriz venus* shell (98.59%). Hence, the highest biodiesel yield from eggshell catalyzed reaction was due to the highest Ca content, high surface area with smallest particle size of the catalyst.

The performance of shrimp shell supported KF catalyst for the transesterification of rapeseed oil to biodiesel was also reported.[184] Within 3 h reaction time, 89.1% of oil conversion was obtained at reflux condition with 2.5 wt. % catalyst and 9:1 methanol/oil molar ratio. The high catalytic activity of the prepared catalyst was due to the porous framework structure from shrimp shell with active sites formed by the incomplete carbonization of shrimp shell loaded with KF during activation process. The oyster production is one of the major marine aquacultures activities in Japan. However, due to the high demand of oyster, disposal of untreated oyster shell waste has created some environmental issues. Oyster shell is one of the selected low cost catalysts for the calcium oxide source. This is due to the dominant component of $CaCO_3$ (95%) or calcite in oyster shell,[185] and it is easy to transform to CaO by calcinations at high temperature (>700 °C). While other researchers[186] reported 95% of biodiesel content was yielded in 5 h transesterification of soybean oil with methanol.

The plentiful supply of cockles as protein source led to the abundant generation of cockles shell waste in Malaysia. Boey *et al.*[187] tried to utilize the cockles shell derived catalyst for the transesterification of palm olein. It was found that the cockles shell catalyst rendered high content of biodiesel yield (96.5%) under the optimized conditions of 4.9 wt. % catalyst loading and 0.54:1 methanol/oil mass ratio. The present findings of Boey *et al.* indicated that the high catalytic activity from crab shell and cockle shell derived catalyst in biodiesel synthesis. In the further study, they[188] compared the effectiveness of mixed crab and cockle derived shell with both individual crab and cockle shell catalysts in the transesterification of low FFA chicken fat (2.1% FFA as oleic acid and 0.14% moisture content). It was found that mixed shells performed equally in the reaction, as compared to individual shells. Furthermore, high availability of clamshell in Malaysia has led to another interesting material for CaO synthesis. Natural short necked clam shell was utilized as calcium oxide (CaO) source for transesterification of non-edible Jatropha curcas oil to biodiesel. 93% of biodiesel was successfully produced within 6 h of reaction with methanol in reflux temperature.[189]

Ngamcharussrivichai[190] investigated the catalytic activity of different type of natural calcium including calcite ($CaCO_3$), cuttlebone, dolomite ($CaMg(CO_3)_2$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), and dicalcium phosphate($CaHPO_4$)) in the methanolysis of palm kernel oil. Dolomite is naturally abundant carbonate rock which mainly composed of $CaCO_3$ and $MgCO_3$. The calcite is known as high purity $CaCO_3$ whereas hydroxyapatite and dicalcium phosphate are also natural calcium compounds. Among the natural calcium, activated dolomite with the presence of synergetic effect between CaO and MgO showed highest activity at 98% of ester content with 6 wt. % catalyst loading, 30:1 methanol/oil ratio, and 3 h reaction time.

Besides, the possibility of using potash from cocoa pod husks (CPHs) in transesterification of soybean oil into biodiesel was investigated.[191] Both supported (CPH/MgO) and unsupported (CPH ash) catalysts were tested. The yield obtained for CPH/MgO-catalyzed reaction with oil/methanol ratio of 1:6, 60 °C, 60 min, 1 wt. % of MgO doped CPH ash catalyst was 98.7%; and 91.4% of biodiesel yield achieved for CPH-catalyzed reaction at 60 °C, oil/methanol ratio of 1:6, 120 min, 1 wt. % of CPH ash. CPH is major agricultural wastes from the cocoa industries and has been found as a rich source of potassium carbonate therefore it will be another potential alternative catalyst source.

III. HETEROGENEOUS CATALYST IN BIODIESEL PLANT

Studies has been conducted to investigate acid or base solid catalysts that could be equipped in biodiesel manufacturing plant due to increase in biodiesel demands.[192,193] However, majority of biodiesel plant in Malaysia is using homogenous catalyzed technology (wet washing method) in producing biodiesel. Therefore, process modification is required in order to facilitate heterogeneous-catalyzed reaction technology.

For continuous solid catalyst catalyzed reaction process, biodiesel converted from vegetable oils without losing catalyst in a reactor (solid catalyst was loaded in reactor column with proper tray basket). Figure 6 shows an example of solid catalyst catalyzed reaction process flow diagram.[11,194] Generally, reaction could be carried out at lower pressure and temperature compared to those with a homogeneous catalysis. Excessive methanol usage and frequent catalyst loading

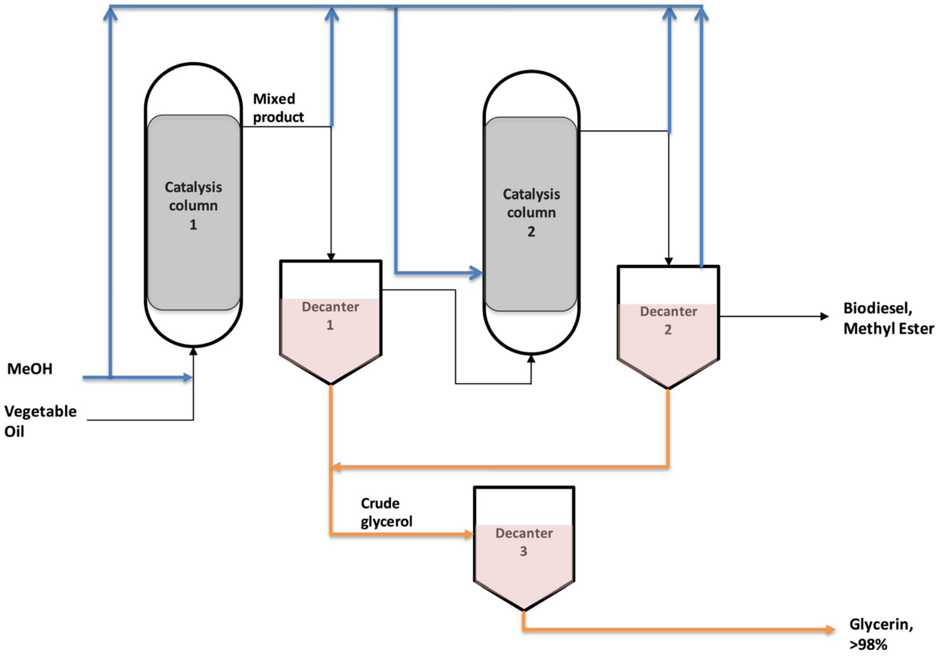

FIG. 6. Simplified process flow diagram for heterogeneous catalysed process.

is required because solid catalyst is only managed to survive in shorter reaction time while maintaining its reactivity.

The catalysis section consisted of two fixed bed reactors which are fed with vegetable oil and methanol in the given proportions (normally methanol in excess). The excessive methanol is removed after each reaction by partial evaporation and being fed into reactor 2 for reaction. Decanter was used to separate esters and glycerol. From the schematic, biodiesel was fed into the two successive reaction column and glycerol separation occurred in the decanter. The methyl ester purification section (outlet from decanter 2) vaporized of the methanol in vacuum followed by final purification step in an absorber to remove soluble glycerol. There is no massive waste water and soluble soap being generated in solid catalyzed process which eases in operation at lower production cost.[195]

To date, it is uncommon to make use of heterogeneous catalyzed process technology in biodiesel plant. However, several leading technology companies have started their plant commissioning. For example, Benefuel, Inc. has built an industrial-scale biodiesel refinery by using novel solid catalyst located in Seymour, U.S.[196] Besides, Axen has built the first solid catalyst plant in 2006 which is located in Sete, France (capacity is 160 000 tons per annum). Catilin Inc. introduced T300 solid catalyst to the biodiesel industry in year 2009 and it is anticipated that lower operating costs, ease of use and better safety to be achieved by the technology.[197] While in Malaysia, Biofuel, Ltd. (a wholly owned subsidiary of Green Energy Group, Ltd.) cooperated with Incbio (a leading Portuguese engineering company) to build a 8000MT per annum Biodiesel plant in Kuala Lumpur which consisted of ultrasonic reactors and solid catalyst acid esterification technology in 2013. Incbio, Ltd., stated that the catalysts can stay in column up to 3 years.[198] Texas BioDiesel reported that a 30×10^6-gal-a-year continuous flow solid-catalytic biodiesel process plants built was in Texas and was brought into production in 2006.[199]

IV. CONCLUSION AND FUTURE WORKS

Although several country (Brazil, the U.S., and the European Union) had successfully demonstrate the viability of conventional technology for biodiesel manufacturing process, the biodiesel industry is entering a new era of feedstock flexibility, product neutrality, and advanced conversion pathways. Thus, intensification of transesterification process by transforming from homogeneous catalyst to heterogeneous route is the current focus in biodiesel technology. In conventional process, homogeneous catalysts (NaOH or KOH) are unable to fit into biodiesel feedstock with high acidity such as non-edible based acid oil, which is a highly available feedstock for developing country. While strong acid (H_2SO_4) catalyzed reaction will lead to environmental issues and corrosiveness to reactor in long term usage. Transformation of homogeneous route to heterogeneous technology is a viable choice in biodiesel industry. The use of heterogeneous catalyst may require mild modification of existing biodiesel plant, which reduce the overall production cost, while improve the productivity and reusability of transesterification process. Heterogeneous base catalyst is the potential transesterification catalyst which emerged with high reactivity under mild reaction conditions, versatility to various types of biodiesel feedstock and lower catalyst cost. Main criteria of good transesterification catalyst are high surface area with large porous system together with high basicity and strong basic strength on the active sites. Furthermore, a catalyst with hydrophobic surface is important to improve the adsorption of feedstock and to prevent the deactivation of catalytic sites by the strong adsorption of polar by-products such as water and glycerol. Intensification of transesterification process can be manipulated by reaction temperature, reaction time, methanol/oil ratio, catalyst loading, stirring rate, reaction pressure, and physical treatment (ultrasonication, microwave heating, and supercritical condition) is another criterion for a good heterogenous catalyst. Most of the industry players are still using conventional step for biodiesel production, albeit researchers has proved that solid catalyst may render more profit in long term operation. More biodiesel workshop needed to be organized in order to provide more information on advantages of heterogeneous catalyzed system to biodiesel manufacturer.

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