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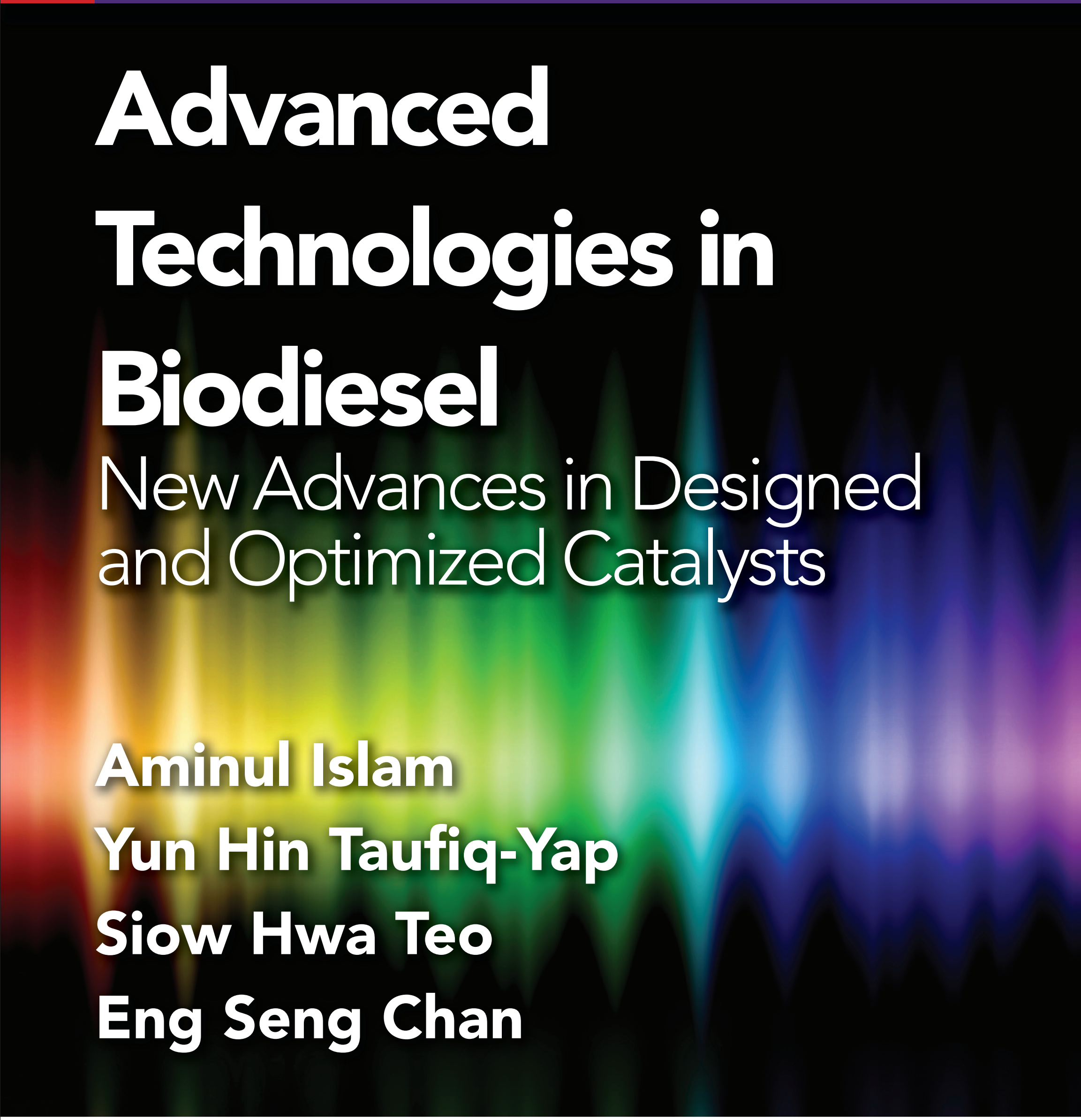

Advanced Technologies in Biodiesel

New Advances in Designed and Optimized Catalysts

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New Advances in Designed and Optimized Catalysts

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Dedication

Dedicated to my beloved father, Korban Ali, who showed me how to find the strength and wisdom to keep on reaching

Abstract

The inadequacy of fossil fuel is the main driving force of the future sustainable energy around the world. Interest in biodiesel is growing rapidly worldwide due to energy security, diversity, and sustainability as well as for greenhouse gas mitigation. Since heterogeneous catalysis is used in chemical industry for biodiesel production, achieving optimal catalytic performance is a significant issue for chemical engineers and chemists. Therefore, enormous attention has been placed in recent years on the selection of heterogeneous catalyst in biodiesel industry, where the catalyst could be facilitated highly selective toward desired products, easily handled, separated from the reaction medium and subsequently reused. This book stresses an overview on the contributions of tailored solid acid and base catalysts to catalytic biodiesel synthesis, and the influences of heterogeneous catalyst properties on biodiesel yield in order to develop a better understanding of catalyst design for the green production process as well as practical applications in the biodiesel industry. Coverage also includes the innovative and new techniques of biodiesel production processes currently used, illustrating the technological options and emphasizing the limitations factors for each technique, and the best choices available in a manner accessible to a general readership, biochemical engineers, academics, professionals, and industrial researchers.

Keywords

sustainable energy, energy security, biodiesel, heterogeneous catalysis

Contents

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CHAPTER 1

Solid Catalytic Biodiesel Production Approaches

An update on the advances in biodiesel production can reinforce the burning alternative fuel in the battle against global warming. The interest in alternative fuels has increased dramatically in recent years due to high demand of energy and the limitation of fossil fuel. Supplementing the petroleum consumption with renewable biomass resources might be one of the components of strategic approach to reduce dependence on petroleum-based fuels. Indeed, researches have been directed toward renewable, non-toxic, and carbon-neutral alternative fuel. Biodiesel is superior to diesel oil in terms of net atmospheric emission levels of CO, SOx, hydrocarbons, soot, particulate matter as well as safety, and biodegrability (Shahir et al. 2014). In general, biodiesel shows a number of characteristics that makes it more desirable than traditional petroleum-based diesel fuel as shown in Table 1.1. However, the improvement of its low-temperature flow characteristic still remains one of the major challenges while using biodiesel as an alternative fuel for diesel engines. Transesterification is the process of exchanging the organic group of an ester with another organic group of an alcohol. Methanol and ethanol are utilized most frequently, especially methanol because of its low cost and its physical and chemical advantages.

The transesterification reaction may be carried out using either high-temperature catalysts, usually acid, or low-temperature catalysts, normally basic. In general, alkali-based catalyzed processes are carried out at low temperatures and pressures (60 °C to 70 °C and 1.4 to 4.2 bar) with low catalyst concentrations (0.5 to 2 wt%) (Haas 2004). Contrary to alkali-based catalysts, solid acid catalysts would need high temperatures,

Table 1.1 The American Society for Testing and Materials (ASTM) standards of maximum allowed quantities in diesel and biodiesel

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC[a] (C10–C21)	FAME[b] (C12–C22)
Kin. viscosity (mm^2/s) at 401 C	1.9–4.1	1.9–6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (°C)	60–80	100–170
Cloud point (°C)	15–5	3–12
Pour point (°C)	35–15	15–16
Water, vol%	0.05	0.05
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen, wt%	0	11
Sulfur, wt%	0.05	0.05
Cetane number	40–55	48–60
HFRR[c], microns	685	314
BOCLE[d] scuff (g)	3,600	47,000

[a] Hydrocarbons.

[b] Fatty acid methyl esters.

[c] High frequency reciprocating rig.

[d] Ball-on-cylinder lubricity evaluator.

Source: Lotero et al. 2006.

high catalyst—loading to obtain reasonable biodiesel production rates (Li et al. 2007). However, the catalytic performance may differ in operational parameters, such as the use of co-solvents, reagents, temperature, pressure, batch, or continuous processing (Nakagaki et al. 2008). Moreover, the performance is dependent on the acidic/basic sites density involved in the catalysts (Kim et al. 2004; Liu et al. 2008a). Additionally, it has been mentioned that the differences in catalytic activity can be explained by the formation of a more electrophilic species (acid catalysis) or by the presence of a stronger nucleophile (base catalysis) species (Lotero et al. 2006). Nevertheless, both (acid and basic) of these types of catalysts suffer from deactivation due to the leaching of active species in the final biodiesel (Garcia et al. 2008; Furuta et al. 2006). Therefore, there is a challenge to prepare new types of catalysts which should reduce the disadvantages of both acid and basic catalysts.

To overcome the problems of catalyzed transesterification process, several researchers have proposed the non-catalytic process with supercritical alcohol (Saka and Kusdiana 2001). It was summarized by many workers that the problems associated with the two-phase nature of normal methanol/oil mixtures could be solved by forming a single phase using non-catalytic transesterification process (Deslandes et al. 1998; Madras et al. 2004). As a result, the reaction was found to be completed in a very short time. Compared with the catalytic processes, purification of products is much simpler and more environmentally friendly. However, the reaction requires temperatures of 350 °C through 400 °C and pressures of 450 through 650 bar, which are not viable in practice in industry (Han et al. 2005). Furthermore, such high temperatures and pressures lead to high production costs and energy consumption. The solid catalyst for biodiesel production should be non-toxic, inexpensive, and easy to produce along with their handling requirements, simplicity of process engineering, catalyst regeneration to allow the adoption of the technology for industrialization.

1.1 Process Prospective

In this section, the process prospective is split into two on the basis of the operating temperature since the temperature is the key parameter for transesterification reaction. The low-temperature approach aims to produce biodiesel that fulfills more than 95 percent alkyl esters content requirement for biodiesel, while the high-temperature approach proposes an alternative method to synthesize the biodiesel from acid-catalyzed transesterification.

1.1.1 The Low-Temperature Approach

The term low-temperature approach defines supercritical transesterification within a temperature range of 60 °C through 70 °C so as to avoid the thermal degradation of unsaturated fatty acids and to maximize the alkyl esters content in the product. Without the assistance of any co-solvent, catalyst or other process modification techniques, the low-temperature approach employs a high pressure, a high alcohol to oil molar ratio, and a long reaction time to achieve the >96.5 percent alkyl esters content required for biodiesel composition by the international standard.

The biodiesel product, which typically exceeds the 96.5 percent alkyl esters content of the international standard for biodiesel (EN14214), can be used as biodiesel. A great variety of solid basic catalysts such as alkaline-earth metals oxides and hydroxides, alkali metals hydroxides, or salts supported on alumina, zeolites, hydrotalcites as well as some acid solids have been evaluated to date at low-temperature reactions. Among the available catalysts, alumina loaded with $Ca(NO_3)_2$, KF, $LiNO_3$, and KI are effective and exhibit interesting results for the conversion of triglyceride to biodiesel as shown in Table 1.2.

Several supported basic catalysts have been reported in the literature—Na, K, Mg, Li, and Ca loaded on a support (alumina) and treated at high calcination temperature of 500 °C to 600 °C. The KNO_3, KCO_3, and KOH supported on Al_2O_3 catalysts showed good activities at low temperatures due to more basic sites forming either K_2O supported on Al_2O_3 species produced by thermal decomposition or Al–O–K groups formed by salt–support interactions (Xie et al. 2006a; Xie et al. 2006b). NaOH supported on Al_2O_3 gave low performance even though it produced catalytically active and strong basic sodium methoxide species after the calcination (Arzamendi et al. 2007). Moreover, leaching of sodium in the progress of the transesterification reactions has exhibited some chemical instability of the supported NaOH catalysts under reaction conditions. Therefore, the influence of the leached sodium on the overall performance of the $NaOH/\gamma Al_2O_3$ catalysts is expected to be of little importance. However, the $Na/NaOH/\gamma\text{-}Al_2O_3$ heterogeneous base catalyst showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst (Kim et al. 2004). It has been shown by Kim et al. (2004) that sodium aluminate as being formed by $Na/NaOH/\gamma\text{-}Al_2O_3$ catalyst upon calcination at 550 °C was originated from the strong basic sites of the catalysts, which might be the catalytically active species for the high yield of biodiesel.

Calcium methoxide catalyst has been tested as well with good results for the transesterification of oil. Besides, the recycling experiment results showed it had a long catalyst lifetime and could maintain activity even after being reused for 20 cycles (Liu et al. 2008c). The dissociation of methoxide gives rise to the catalytically active strong basic CH_3O^- species that might increase the reaction rates. However, results from Martyanov

Table 1.2 ***Summarization of biodiesel synthesis using heterogenious catalyst at low temperature (60 °C to 70 °C)***

Catalyst	Methanol/ Oil	Oil	RT (°C)	MFY	MFP	FY (%)	Calcination (°C)	References
KF/Al_2O3	15:1	Soybean	MR	0.0490	0.143	85.8	600	Xie et al. (2006a)
KCO_3/Al_2O_3	15:1	Soybean	MR	0.0274	0.08	48.0	600	Xie et al. (2006a)
KNO_3/Al_2O_3	15:1	Soybean	MR	0.0202	0.1643	87	600	Xie et al. (2006a)
KNO_3/Al_2O_3	12:1	Jatropha	70	0.0160	0.105	84	500	Vyas et al. (2009)
$NaOH/Al_2O_3$	12:1	Sunflower	50	0.4979	0.0366	88	500	Arzamendi et al. (2007)
$Na/\gamma\text{-}Al_2O_3$	6:1	Soybean	60	0.0400	0.35	70.0	550	Kim et al. (2004)
$Na/NaOH/\gamma\text{-}Al_2O_3$	6:1	Soybean	60	0.0446	0.39	78.0	550	Kim et al. (2004)
$NaOH/\gamma\text{-}Al_2O_3$	6:1	Soybean	60	0.0371	0.325	65.0	550	Kim et al. (2004)
$Ca(OCH_3)_2$	1:1	Soybean	65	0.0555	0.3266	98	105	Liu et al. (2008b)
CaO/MgO	12:1	Rapeseed	64.5	0.095	0.4	80	700	Yan et al. (2008)
CaO/ZnO	30:1	Palm cernel	60	0.0132	0.3116	93.5	900	Ngamcharussrivichai et al. (2008)
KOH/MgO	6:1	Canola	65	0.033	0.1066	96	500	Ilgen and Akin (2008)
$Ba(OH)_2$	9:1	Rapeseed	MR	0.20	3.91	97	–	Mazzocchia et al. (2004)
MgO/CaO (Mg:Ca=3.8)	12:1	Sunflower	60	0.0419	0.92	92	600	Albuquerque et al. (2008)
MgO/Al_2O_3(Mg:Al=5.8)	12:1	Sunflower	60	0.0296	0.65	65	600	Albuquerque et al. (2008)
Mg–Al hydrotalcite	6:1	Rapeseed	65	0.0629	0.226	90.5	800	Zeng et al. (2008)
ETS-10	6:1	Soybean	100	0.0105	0.3070	92	500	Suppes et al. (2004)

(continued)

Table 1.2 Summarization of biodiesel synthesis using heterogenious catalyst at low temperature (60 °C to 70 °C) (Continued)

Catalyst	Methanol/ Oil	Oil	RT (°C)	MFY	MFP	FY (%)	Calcination (°C)	References
KOH/NaX	6:1	Soybean	60	0.0090	0.034	82	500	Suppes et al. (2004)
KX	6:1	Soybean	60	0.0011	0.0042	82	500	Suppes et al. (2004)
KNO_3/CaO	6:1	Rapeseed	60	0.12	0.20	100	600	MacLeod et al. (2008)
$NaNO_3/CaO$	6:1	Rapeseed	60	0.12	0.20	100	600	MacLeod et al. (2008)
$LiNO_3/CaO$	6:1	Rapeseed	60	0.12	0.19	99	600	MacLeod et al. (2008)
Li-Al	15:1	Soybean	65	0.09	0.41	83	500	Shumaker et al. (2008)
$KF/\gamma\text{-}Al_2O_3$	12:1	Cottonseeded	65	0.31	0.186	93	600	Lingfeng et al. (2007)
KF/Al_2O_3	12:1	Palm	65	0.0212	0.3	90	600	Bo et al. (2007)
K_2CO_3/MgO	7:1	Soybean	70	0.495	0.0495	99	600	Liang et al. (2009)
Li/ZnO	12:1	Soybean	MR	0.02	0.20	96.3	600	Xie et al. (2007)
SrO	12:1	Soybean	70	0.0362	1.9	95.0	1200	Liu et al. (2007)
Li/CaO	14:1	Sunflower	60	0.3	0.5129	90	–	Alonso et al. (2009)
H_2SO_4/C^a	12:1	Castor	65	0.020	0.133	94	120	Yuan et al. (2009)
nano-MgO^a	1:4	Sunflower	70	0.294	0.6468	98	500	Verziu et al. (2008)
KF/Eu_2O_3	12:1	Rapeseed	MR	0.032	0.925	92.5	600	Sun et al. (2008)
eggshell	9:1	Soybean	65	0.316	0.0362	95	1000	Wei et al. (2009)
Oyster shell	6:1	Soybean	70	0.0033	0.1576	73.8	–	Nakatani et al. (2009)
$Ca(OCH_2CH_{3)2}$	12:1	Soybean	65	0.035	0.613	92	–	Liu et al. (2008b)

$Ca(MeO)_2$[b]	4.5:1	Rapeseed	MR	0.479	0.36	90	–	Gryglewicz (1999)
Mg/MCM-41	–	Frying oil	60	0.425	0.035	85	600	Georgogianni et al. (2009a)
MgAl hydrotalcite	–	Frying oil	60	0.485	0.0404	97	500	Georgogianni et al. (2009b)
Mesoporous K/ZrO_2	–	Frying oil	60	0.445	0.0370	89	500	Georgogianni et al. (2009b)
$CaTiO_3$	6:1	Rapeseed	60	0.0082	0.079	79	1050	Kawashima et al. (2008)
$CaMnO_3$	6:1	Rapeseed	60	0.0113	0.092	92	300	Kawashima et al. (2008)
$CaZrO_3$	6:1	Rapeseed	60	0.0092	0.088	88	300	Kawashima et al. (2008)
$CaCeO_3$	6:1	Rapeseed	60	0.0092	0.089	89	300	Kawashima et al. (2008)
$Mg(NO_3)_2/Al_2O_3$	65:1	Palm kernel	60	0.0014	0.0346	10.4	450	Benjapornkulaphong et al. (2008)
$Ca(NO_3)_2/Al_2O_3$	65:1	Palm kernel	60	0.0133	0.3143	94.3	450	Benjapornkulaphong et al. (2008)
KOH/Al_2O_3	15:1	Palm	60	0.0172	0.1458	87.5	500	Noiroj et al. (2009)
KOH/NaY zeolite	15:1	Palm	60	0.0179	0.300	91.07	–	Noiroj et al. (2009)
$K/KOH/\gamma\text{-}Al_2O_3$	9:1	Rapeseed	60	0.022	0.8452	84.52	500	Ma et al. (2008)
$(Al_2O_3)_X(SnO)_Y(ZnO)_Z$	1:4.6	Soybean	60	0.4	0.2	80	500	Macedo et al. (2006)
Na_2MoO_4	54:1	Soybean	MR	0.050	0.1456	87.4	–	Nakagaki et al. (2008)
$NaAlO_2$	12:1	Soybean	MR	0.0716	0.939	93.9	600	Wan et al. (2009)
KI/mesoporous silica	16:1	Soybean	70	0.0206	0.1126	90.09	600	Samart et al. (2009)
Mg/La mixed oxide	61:1	Sunflower	Room	0.0475	0.551	95	650	Babu et al. (2008)
MgO $MgAl_2O_4$[c]	15:1	Soybean	65	0.0855	0.057	57	900	Wang et al. (2008)

[a] Microwave condition.

[b] THF as a co-solvent.

[c] n-hexene as a co-solvent.

Maximum FAME Yield (MFY) = FAME (g)/Oil (g).Catalyst (g), Maximum FAME Productivity (MFP) = FAME (g)/Oil (g). t (h), FAME Yield (FY) = FAME (g)/ Oil (g), Reaction temperature (RT), Methanol reflux (MR).

et al. (2008) were different in that the active homogeneous species calcium butyric acid derivatives were formed by the interaction of $Ca(OCH_3)_2$ with reaction products such as glycerol even if it was not deactivated over time.

Several supported oxide or hydroxide catalysts have also been reported in the literatures, i.e., KOH (Ilgen and Akin 2008), CaO (Yan et al. 2008) loaded on MgO in the transesterification with methanol. In the case of MgO, high concentration of strong basic sites were formed after calcination, which is responsible for higher FAME yields (>90 percent). Di Serio et al. (2006) found that the basicity increased the catalytic activity for the reaction conditions. However, the active sites of catalysts are poisoned by the O_2, CO_2, and H_2O, and the catalytic activities can be improved by thermal treatment before reaction. Barium hydroxide is more active than magnesium oxide under the same operating conditions which are now close to those used industrially with homogeneous catalysts, even though it acts as a homogeneous contribution during the reaction (Garcia et al. 2008).

Using commercial hydrotalcite MgO/Al_2O_3 (Mg:Al = 3) followed by calcination at 500 °C, Xie et al. (2006c) achieved oil conversions of up to 66 percent at methanol reflux temperature for the transesterification of soybean oil after a 9 hour residence time. It is interesting to highlight that the study carried out by Di Serio et al. (2006), the required temperatures at above 180 °C in order to achieve conversion yields at higher than 90 percent. In a similar approach, Albuquerque et al. (2008) have evaluated the MgCa and MgAl oxides catalysts in the transesterification of sunflower oil and have emphasized the influence of molar ratio of metal oxide on the yield of biodiesel. Highest activity was found for a Mg:Ca molar ratio of 3:8, with a FAME yield of 92 percent, for a methanol:oil molar ratio of 1:12, at a reaction temperature of 60 °C and 2.5 wt% of catalyst, whereas for Mg:Al at molar ratio of 5:8 the yield reaches a value of 60 percent. The best performance was observed for the series of MgCa oxides, which could be attributed to the presence of strong basic sites on the surface, mainly associated with Ca^{2+}-O^{2-} pairs and a surface area much higher than that of pure CaO (Albuquerque et al. 2008). The highest catalytic activity in the transesterification could be obtained using Mg–Al hydrotalcites with Mg/Al molar ratio of 3:0. Moreover, the catalyst could be suitable for its high catalytic activity by reason of easy separation of the catalyst through simple filtration, for possible recycling of the catalyst (Zeng et al. 2008).

In the zeolite family, zeolite X is widely accepted as one of the most basic zeolites, and ion exchange of the assynthesized Na-X with larger monovalent cations to either K-X or Cs-X which increases the zeolite basicity markedly (Barthomeuf 1996). Further increase in the zeolite basicity may also be achieved by impregnating the porous solids with cesium oxide (Hathaway and Davis 1989) and thus forming additional extra-framework basic sites. After 24 hours the conversion of soybean oil to methyl ester increased from 15.4 percent for NaX to 22.5 percent for KX and 18.7 percent for CsX. This decrease in the conversion for CsX compared to that of KX is unexpected and relates to the degree of ion exchange of these solids. The large size of cesium cations limits the exchange capacity compared to that for the smaller potassium, which affects the basicity associated with the framework oxygen. Similar phenomenon was observed in the case of the Engelhard titanosilicate structure-10 (ETS-10) zeolites as well. ETS-10 is potentially a very important new microporous inorganic titanosilicate framework material. The structure, which was first synthesized by Engelhard (Kuznicki 1989) and solved by Anderson et al. (1994), consists of corner sharing octahedral titanium (IV) and tetrahedral silicon. ETS-10 is one of a small group of zeolite or zeotype materials which contain a three dimensional 12-ring pore system. Owing to the high framework charge associated with the octahedral Ti, ETS-10 also exhibits a very high cation exchange capacity in which, the materials consists of 75 mol% sodium and 25 mol% potassium. The more basic sites produced remarkably higher conversions to methyl esters in the case of ETS-10 compared to NaX zeolite on an equal mass basis. Ion exchanging the parent zeolite with more electropositive metals produces stronger basic zeolites (Suppes et al. 2004). These stronger basic zeolites led to an increase of conversion and selectivity at the same reaction conditions in the transesterification of vegetable oil.

Several alkali-doped metal oxide catalysts were evaluated by MacLeod et al. (2008) for activity in the transesterification of rapeseed oil to biodiesel. Of those evaluated, $LiNO_3$/CaO, $NaNO_3$/CaO, and KNO_3/CaO exhibited greater than 99 percent conversion in a 3 hour test. The formation of active centers O^- by substitution of M^+ ion after calcination (600 °C) might have been responsible for the higher activity. There is also some degree of mass transfer limitation, possibly caused by the formation of a glycerol film limiting access to the active sites of the catalyst. Shumaker et al. (2008) have reported that the role of calcined (450 °C) in transesterification reactions of soybean oil with methanol was possibly due to their active basic Li-O and lattice O^- sites. Similar observation has been reported in the literature using $KF/\gamma\text{-}Al_2O_3$ as heterogeneous catalysts for the transesterification of cottonseed oil with methanol (Lingfeng et al. 2007). They claimed that the strongest basic sites (superbasic) would also promote the transesterification reaction at very low temperature (65 °C), while the basic sites of medium strength require higher temperatures to promote the same reaction. In a subsequent work, good results were obtained by Liang et al. (2009) with catalyst K_2CO_3 supported on MgO due to its strong basic sites, strong interaction of K_2CO_3 and MgO, and the high dispersion of active sites. In any case, K_2CO_3/MgO seems to be a promising catalyst because it gives high conversion (99 percent) in transesterification reaction and is stable under reaction condition (Liang et al. 2009).

Among the different solid basics MgO, Li/ZnO, SrO, Eu_2O_3/Al_2O_3, KF/Eu_2O_3 CaO/Al_2O_3, Li/CaO, and $CaCO_3$ have been studied for the transesterification of vegetable oil (Xie et al. 2007; Liu et al. 2007; Li et al. 2007; Alonso et al. 2009; Yuan et al. 2008; Verziu et al. 2008). Their success is based on the ability to prepare catalysts with strong basicity that can make the catalysts efficient for biodiesel production. In the supercritical state of methanol, good performances (up to 96 percent) can be obtained using Li/ZnO (Xie et al. 2007). High activity might be due to active species (Li_2O) formed after calcination of 600 °C. Despite indications of active species getting leached into the reaction medium thus causing rapid deactivation of the catalyst, further investigation could be necessary to quantify this aspect. These results are in good agreement with the experimental reactivity observed in the case of Li/CaO catalyst for the transesterification of triglycerides with methanol (Alonso et al. 2009).

Li et al. (2007) prepared a superbasic Eu_2O_3/Al_2O_3 (Eu content 6.75 wt%) catalyst that exhibited good activity at 70 °C for the transesterification of soybean oil. The other studies have also been reported on a higher conversion with methanol using KF/Eu_2O_3 catalyst for the transesterification of rapeseed oil (Sun et al. 2008). In particular, Al_2O_3/CaO has been found to be especially active for the transesterification of yellow green microalgae, *Nannochloropsis oculata*. Yield of 97.5 percent was obtained for Al_2O_3/CaO but deactivation occurred when the catalysts was reused (Umdu et al. 2009). It was proposed by Sun et al. (2008) that high basic site density were seen to be solely responsible for the transesterification of vegetable oil.

The catalytic activities of waste eggshell and oyster shell have been investigated for the transesterification of vegetable oil with methanol (Wei et al. 2009; Nakatani et al. 2009). CaO that is decomposed from waste eggshell ($CaCO_3$) and oyster shell ($CaCO_3$) at high temperature has been shown to exhibit the superior activity for the transesterification of soybean oil at 70 °C due to its superior basic strength. It is not clear if at moderate to high temperatures CaO might show some degree of solubility in methanol (Gryglewicz 1999). Related to CaO, SrO derived from thermal decomposition of $SrCO_3$ and nanocrystalline MgO has been shown to have applicability for transesterification reaction (Liu et al. 2007; Verziu et al. 2008). The conversion over nanocrystalline MgO was 98 percent compared with 95 percent over SrO. In the case of MgO, microwave energy could increase the reaction rate because of the microwave radiation that increases the catalyst's interaction with the reactant (Yuan et al. 2008). However, under microwave radiation, a leaching of the magnesium has been evidenced as a direct consequence of a saponification reaction. Therefore, from a practical point of view, further investigation should be done to intensify the stability and increase the lifetime of the catalyst.

High ester yields have also been obtained with Mg/MCM-41, Mg-Al hydrotalcite, and K/ZrO_2 using low frequency ultrasonication (24 KHz) (Georgogianni et al. 2009b). Particularly, Mg-Al hydrotalcite showed the highest activity (conversion 97 percent) due to the high basic strength. However, under ultrasound, magnesium might be leached as a direct consequence of a saponification reaction and further investigation is necessary to quantify this aspect. It would also be of great interest from a practical point of view to investigate the effect of co-solvent. The roles of co-solvent (THF) in the transesterification of waste cooking oil using K_3PO_4 catalyst were investigated by Guan et al. (2009a). Tri-potassium phosphate particles showed good catalytic reactivity; however, the catalytic activity could be reduced due to the formation of homogeneous phase in the presence of THF.

Noiroj et al. (2009) also compared the activities of KOH/Al_2O_3 and KOH/NaY catalysts in the transesterification of palm oil with methanol. It was found that the leaching of potassium in the final product consequently decrease in the catalyst activity even though high yield of biodiesel was produced at low temperature (Noiroj et al. 2009). Other results comparable with these findings using $K/KOH/\gamma\text{-}Al_2O_3$ catalysts for transesterification reaction are from Ma et al. (2008).

Stable and very active transesterification catalysts can be prepared by the co-precipitation of aluminum, tin, and zinc oxides (Macedo et al. 2006). $(Al_2O_3)_X(SnO)_Y(ZnO)_Z$ catalyst was still found to be in a high proportion (80 percent) of its original catalytic activity in the transesterification reaction and recycled it without apparent loss of its activity. It has been recently claimed that new sodium molybdate (Na_2MoO_4) was stable under reaction condition (Nakagaki et al. 2008). The activity of the catalyst was found to be completely restorable after being washed in the transesterification reaction. Indeed, similar to Na_2MoO_4, an active esterification catalyst can be prepared by the incomplete carbonization of natural products such as sugar, starch, or cellulose with their successive sulfonation (Lou et al. 2008). It was found that the sugar catalyst still retained a high proportion (93 percent) of its original catalytic activity in the methyl oleate formation reaction, even after more than 50 cycles of successive reuse. Wan et al. (2009) investigated the transesterification of the soybean oil using $NaAlO_2$ catalyst. The catalyst was found most promising which exhibited higher FAME yield of 94 percent; however, a small portion of $NaAlO_2$ leaching into methanol was also observed.

Attempts have been made to develop a mesoporous solid for the transesterification of vegetable oil at low temperature (65 °C to 70 °C), by testing different types of catalysts such as KI/silica, $MgO{\cdot}MgAl_2O_4$, NaCsX and evaluated the biodiesel production from vegetable oil (Samart et al. 2009; Wang et al. 2008; Leclercq et al. 2001). KI/silica catalyst was found to be the most active and stable catalyst. It was noticed that higher temperature enhanced the biodiesel yield. However, it has been observed that mesoporous catalyst could not resist the porosity collapse at the high temperature, resulting in low conversion (Corma et al. 1996). A new mesoporous $MgO{\cdot}MgAl_2O_4$ catalyst was synthesized by Wang et al. (2008) for biodiesel production. In this case, enhancement of catalytic activity toward the transesterification of soybean oil was explained by the higher specific surface area and strong basic properties of the catalyst. Other results consistent with this finding are obtained from Leclercq et al. (2001) using NaCsX catalyst for transesterification of rapeseed oil with methanol.

All of the basic catalysts reported above are overwhelmed by several disadvantages despite of their merits toward the transestrification of oils. In most of the experiments using heterogeneous catalysts, the transesterification reaction proceeds at a relatively slow rate compared to those conducted with homogeneous catalysts. The slow reaction rates are due to diffusion problems because these heterogeneous media behave as a three-phase system (oil/methanol/catalyst) and are not possessing strong basic sites required for transesterification. Therefore, new catalytic materials with a high reaction rate are extremely desirable for transesterification.

1.1.2 The High-Temperature Approach

The high-temperature approach uses acid-catalyzed transesterification at temperatures ranges from 120 °C to 300 °C. Temperature and pressure are important parameters as they allow the faster reaction kinetics and mass transfer rates in the transesterification reaction (Helwani et al. 2009). Indeed, the complete fuel properties need examining along with engine testing for the biodiesel product for the high-temperature approach (Boehman et al. 2005). On the other hand, the fine studies on the reactions pathways and/or chemical kinetics are also attractive works to better understand the high-temperature approach. The catalytic activity of some heterogeneous catalysts for the biodiesel production at temperature in the range of 120 °C to 450 °C is summarized in Table 1.3.

Table 1.3 ***Summarization of biodiesel synthesis using heterogenious catalyst at high temperature (120 °C to 300 °C)***

Catalyst	Methanol/ Oil	Oil	RT(°C)	MFY	MFP	FY (%)	P (bars)	Calcination (°C)	References
WZA	40:1	Soybean	250	0.22	0.044	88	1.013	800	Furuta et al. (2006)
TiO_2/ZrO_2	40:1	Soybean	250	0.21	0.042	84	1.013	800	Furuta et al. (2006)
WO_3/ZrO_2	40:1	Soybean	>250	0.0030	0.225	90	1.013	800	Furuta et al. (2006)
SO_4/ZrO_2	40:1	Soybean	300	0.0027	0.20	80	1.013	675	Furuta et al. (2006)
SO_4/ZrO_2	20:1	Soybean	150	0.0991	0.4335	86.7	–	600	Garcia et al. (2008)
ZrO_2/SO_4	12:1	cottonseed	230	0.04	0.10	80	–	550	Chen et al. (2007)
TiO_2/SO_4^{2}	6:1	Soybean	120	0.0053	0.25	2	–	300	De Almeida et al. (2008)
$SO_4^{2-}/TiO_2–SiO_2$	9:1	Cottonseed	200	0.0365	0.158	95	–	500	Peng et al. (2008)
SO_4^{2-}/SnO_2	6:1	Palm kennel	200	0.034	0.2256	90.3	50	500	Jitputti et al. (2006)
KNO_3/ZrO_2	6:1	Palm kennel	200	0.028	0.186	74.4	50	600	Jitputti et al. (2006)
SO_4^{2-}/SnO_2	6:1	Coconut	200	0.039	0.2014	80.6	50	500	Jitputti et al. (2006)
SnO^{2-}/ZrO_2	6:1	Coconut	200	0.0426	0.2157	86.3	50	500	Jitputti et al. (2006)
MgO/SBA-15	–	Vegetable	220	0.96	0.192	96	–	550	Li et al. (2009)
MgCoAl-LDH	16:1	Canola	200	0.543	0.2083	96	25.331	600	Li et al. (2009)
Al-MCM-41	60:1	Palmitic	180	0.4038	0.3105	60	–	480	Carmo et al. (2009)
Nano-MgO	36:1	Soybean	170	0.0373	0.539	98	240	–	Wang and Yang (2007)
s-MWCNTs	18.2:1	Cottonseed	260	0.5187	0.2999	89.93	–	700	Shu et al. (2009)

KNO_3 loading flayish	15:1	Sunflower	170	0.0199	0.1099	87.5	–	500	Kotwal et al. (2009)
Montmorillonite KSF	8:1	Palm	190	0.030	0.265	79.6	–	–	Kansedo et al. (2009a)
ZnO-La_2O_3	3:1	Palm oil	200	0.32	0.32	96	–	450	Yan et al. (2009)
ZS/Si	1:18	WC	200	0.27	0.081	81	–	110	Jacobson et al. (2008)
Fe-Zn-1PEG-4000	15:1	Sunflower	250	0.0366	0.241	96.5	–	180	Sreeprasanth et al. (2006)
VOP	27:1	Soybean	180	0.08	0.8	80	–	300	Di Serio et al. (2007a)
BMZ	32.7:1	Soybean	450	0.0025	0.463	92.6	172.369	444	McNeff et al. (2008)
V_2O_5/TiO_2	45:1	Palm	120	0.1484	0.0742	74	–	460	Ratanawilai et al. (2005)
Pb_3O_4,	7:1	Soybean	225	0.41	0.41	82	High	–	Singh and Fernando (2008)
MgO	55:1	Soybean	130	0.0186	0.1170	82	–	–	Antunes et al. (2008)
MgO	0.44:1	Soybean	>180	0.92	0.92	92	–	500	Di Serio et al. (2006)
MgO	39.6:1	Soybean	300	0.08	5.69	91	–	–	Tateno and Sasaki (2004)
ZHN	48:1	Palm	150	0.0186	0.475	95	–	–	Cordeiro et al. (2008)

Maximum FAME Yield (MFY) = FAME (g)/Oil (g).Catalyst (g), maximum FAME productivity (MFP) = FAME (g)/Oil (g). t (h), FAME Yield (FY) = FAME (g)/Oil (g), reaction temperature (RT), methanol reflux (MR); sulfonated multiwalled carbon nanotubes (s-MWCNTs), zinc stearate (ZS), vanadyl phosphate (VOP), base modified zirconia (BMZ), zinc hydroxide nitrate (ZHN).

The temperature plays a significant role in the acid-catalyzed synthesis of biodiesel. For instance, in the transesterification of cottonseed oil with the methanol at 260 °C, sulfonated carbon-based solid acid catalysts were examined (Shu et al. 2009). It was reported that the catalyst was more active due to their high-acid site density, though the acid sites may have been involved in important side reactions, such as the double dehydration of glycerol to produce acrolein at reaction temperatures of above 250 °C, involving the condensation of glycerol molecules to produce glycerolethers (Clacens et al. 2002). In a similar approach, the effect of temperature is even more noticeable at higher temperatures for the transesterification of vegetable oil using Mg_2CoAl catalyst (Li et al. 2009). In particular, the accumulation of diolein content at lower temperatures substantially decreases the conversion of diolein to monoolein reaction steps.

Kotwal et al. (2009) reported that flyash when loaded with KNO_3, a solid-base catalyst, in the transesterification of sunflower oil to methyl esters and glycerol, resulted in higher conversions at higher temperatures. A conversion of 87.5 percent was obtained at 170 °C with an 8 hour reaction time. Although the catalyst showed a considerable initial activity for the reaction, a decrease in catalytic activity was observed when the recovered catalyst was reused. However, the reaction rates in montmorillonite KSF catalyzed transesterification may also be increased by the use of larger amount of catalyst (Kansedo et al. 2009b). They used different amount of catalysts in the transesterification of palm oil with methanol. In these studies, a rate enhancement was observed with the increased amount of catalyst and the FAME yield went from 50 percent to >93 percent as the catalysts concentration increased from 2 to 4 wt%. Therefore, high transesterification conversions can be obtained at 180 °C in the absence of high pressure. In this case, the enhanced catalytic performance was explained by increased active sites provided by high concentration of catalysts. Future research on this catalyst is still required to investigate the deactivation of the catalyst to commercialize this technology.

The activity of several acid catalysts using different ratio of TiO_2/SO_4 synthesized via sol-gel technique in the transesterification of soybean oil with methanol at 120 °C has been ranked in reference to their ratio of TiO_2/SO_4 such as $TiO_2/SO_4(5:1) > TiO_2/SO_4(10:1) > TiO_2/SO_4(20:1)$ (Almeida et al. 2008). The low activity of TiO_2/SO_4 (20:1) must be related to its low amount of Brönsted acid on its framework, probably due the insufficient amount of sulfuric acid used in its preparation. The results are in good agreement with the experimental reactivity observed in case of SO_4^{2-}/TiO_2 and SO_4^{2-}/ZrO_2 catalysts (Jitputti et al. 2006). Other findings have been reported by Peng et al. (2008). They observed that the catalytic activity of $SO_4^{2-}/TiO_2–SiO_2$ catalyst is the same in both transesterification and esterification reactions. However, the maximum inconvenience of the catalysts lies toward the deactivation owing to leaching of active species to the biodiesel. Further, it is not clear up to what extent the active site of catalyst is responsible for high conversion, though it has potential for industrial scale biodiesel production. The way of the reducing deactivation of the catalysts has been suggested by Yadav and Murkute (2004). They proposed that the catalyst prepared from chloro sulfonic acid precursor dissolved in an organic solvent, instead of the conventional impregnation of H_2SO_4 could reduce the leaching of sulfate under reaction condition.

Supports, such as MCM-41, have been used to increase the surface area and availability of base sites in catalysts. In particular, Li et al. (2009) prepared MgO/ MCM-41, MgO/KIT-6, and MgO/SBA-15 catalysts for transesterification reaction of blended vegetable oil. MgO-impregnated SBA-15 exhibits the highest activity for the production of biodiesel, achieving a conversion as high as 96 percent within 5 hours at 220 °C. Other results consistent with this finding are from Carmo et al. (2009). Their study shows that low conversion of palmitic acid with methanol, ethanol, and isopropanol in the presence of Al-MCM-41 mesoporous molecular sieves with different Si/Al ratios was obtained from transesterification at 180 °C. The conversion was 60 percent for 2 hours of reaction. However, at high temperature, high conversion was achieved within short intervals. For example, in 33 minutes, 98 percent conversion was obtained at 250 °C using nano-MgO. But there might be an undesirable thermal decomposition reaction taking place (Wang and Yang 2007). Though the high conversion rate was obtainable with nano-MgO, the handling of such nano-particles in large quantities from the practical point of view, however, is difficult.

It has been claimed by Yan et al. (2009) that a catalyst, $ZnO\text{-}La_2O_3$ is the most effective in simultaneously catalyzing the transesterification of triglycerides and esterification of free fatty acid (FFA) to methyl esters. In particular, these authors noted that it was highly tolerant to FFA and water and their activity in both transesterification and esterification reactions was significantly influenced by the strong interaction between zinc and lanthanium species. Similar to ZnO-$La_2O_{3,}$ the ZS/Si catalysts is equally effective in simultaneously catalyzing the transesterification of triglycerides and esterification of FFA to methyl esters, which could help in the processing of low-quality feedstocks (generally high in FFAs) (Jacobson et al. 2008). The investigation of resistibility test indicated that the catalyst retained high yield of biodiesel (98 percent) after four cycles of successive reuse. However, the catalysts (ZS/Si) should investigate first the characteristics of catalyst and then look for the reaction for which characteristics are appropriate to effectiveness of both transesterification of triglycerides and esterification reaction.

Attempts to prepare the heterogenious catalysts on mesoporous supports and their conversion rate at different operating parameter have also been reported. In particular, Brito et al. (2007a) designated zeolite Y with impregnated Al_2O_3 and Na_2O at different concentrations for transesterification of frying oil with methanol. According to the authors, under a good thermally stable reaction condition, catalysts were obtained with good reactivity and selectivity to methylester. However, the use of the catalysts still needed high temperatures (200 °C to 476 °C) in order to be effective. The same group investigated transesterification of fried oil with methanol over zeolite Y with CsCl and KOH at different concentrations (Brito et al. 2007b). The catalytic effect has been tested within a temperature range 60 °C to 476 °C and conversion was reported to be at 98 percent for the zeolite Y interchanged with KOH catalyst. In particular, these catalysts presented an appreciable activity for reactions when n hexane and THF were used as co-solvents. However, the regenerated zeolite was less deactivated over time than fresh catalyst even though the zeolite structure was stabilized. Further, deactivation test should perform at long time reactions in a larger scale reactor.

The catalytic activities of vanadium salts have been investigated for transesterification of soybean oil at temperature 120 °C to 200 °C. Among the catalysts tested, the vanadyl phosphate showed the highest activity under optimized reaction condition (Santacesaria et al. 2007). This type of catalysts exhibit varied activities depending on the formation of active species (V^{3+}, V^{4+}, V^{5+}) and reaction temperature where, V^{3+}, V^{4+} and V^{5+} were active, intermediate and inactive species respectively (Di Serio et al. 2007b; Li et al. 2008). It was reported by Di Serio et al. (2007b) that the activity of these catalysts slightly increased with increasing the reaction time. However, longer reaction time increases the production cost of biodiesel.

The active transesterification catalysts can be prepared by the Fe-Zn double-metal cyanide complexes (DMC). The DMC catalyst has higher activity in sunflower oil transesterification most likely because of higher concentration of acid sites on the surface and surface hydrophobicity (Sreeprasanth et al. 2006). It was found that the DMC catalyst's activity still retained a high proportion (96.5 percent) of its original characteristics of catalytic activity in the methyl ester formation reaction, even after many cycles of successive reuse. The use of another base catalyst was disclosed in a recent paper (McNeff et al. 2008). A modified base consisting of zirconia, titania, and alumina catalysts were used in the continuous rapid esterification and transesterfication reactions under high pressure (172 bar) and elevated temperature (300 °C to 450 °C). Moreover, the catalysts recycling showed that the catalysts was maintained a high yield of biodiesel (90 percent) over the course of 10 hours of continuous operation. This catalyst is very important from the view point of stability of catalyst; however, the active sites of the catalyst responsible for high activity is unknown and further investigation is necessary to find out this aspect.

Singh and Fernando (2008) compared the activities of a series of metal oxides MgO, CaO, PbO, PbO_2, Pb_3O_4, Ti_2O_3, and ZnO with methanol/oil ratio 7:1 at 225 °C to find the most suitable candidate for the transesterification of soybean oil. The reaction rate showed dependency on the base strength and surface area of each catalyst. Among the catalyst tested, the most active was Pb_3O_4 and found to be most favorable toward the transesterification and resulted in more than 89 percent of the biodiesel yield. However, side reactions such as alcohol esterification could occur in the transesterification reaction at 240 °C (Lotero et al. 2006). In this case, working with hydrated ethanol brings about additional advantages. For instance, zinc hydroxide nitrate (ZHN) showed high activity for the transesterification of palm oil with hydrated ethanol showing the conversion 95 percent (Cordeiro et al. 2008). However, the performance of the catalysts deteriorated with repeated use suggesting that some leaching of the catalysts took place, even if the catalyst could be activated by mineral acid treatment and reprecipitation process.

1.2 Properties of Catalyst Affecting on Biodiesel Production

The effectivity of transesterification reaction is controlled by several properties of heterogeneous catalyst. Catalysts allow reactions to proceed by a different pathway involving a lower energy transition state. By lowering the energy of this transition state, which is rate-limiting steps, catalysts reduce the required energy of activation to allow a reaction and in the case of reversible reaction, reach equilibrium more rapidly (Fig. 1.1). The transesterification reaction of oil to diesel fuel can be significantly improved by improving the physical properties of catalysts such as acidity, basicity, hydrophilic/hydrophobic character, the specific surface area, and mean pore size of catalysts (Xiao 2004).

The density of the base site is of key importance in determining the solid catalyst's activity and selectivity. Solid-base catalysts have a higher activity and faster reaction rate as compared to solid acid catalysts (Lotero et al. 2006). However, solid-base catalysts are very sensitive to the presence

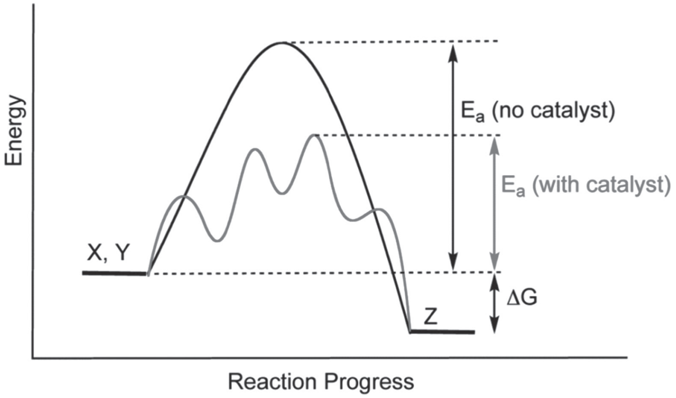


Fig. 1.1 Catalyst speeds up a reaction by lowering the activation energy required for the reaction to proceed (Adapted from Gutfreund 1995)

of water and FFA. Consequently, they need feedstock with low FFA to avoid deactivation. A great variety of solid basic catalysts such as alkaline-earth metals oxides and hydroxides, alkali metals hydroxides or salts supported on alumina, zeolites as well as hydrotalcites have been studied to date at different reaction conditions. The most widely applied molecular probe is carbon dioxide to measure basic sites of the catalyst. The temperature programmed desorption (TPD) of adsorbed CO_2 has also been used to characterize the basicity of alkali metal and alkaline earth-modified metal oxide catalysts (Doskocil et al. 2000). Several reaction mechanisms have been proposed to describe transesterification reaction on base catalyst surface. The most cited model for transesterification reaction is Eley-Rideal mechanism, in which an alcohol adsorbs on a surface basic site and forms an adsorbed alkoxide that attacks a carbonyl carbon of an ester in liquid phase; then, a tetrahedral intermediate is formed and then rearranged to produce another ester (Fig. 1.2).

Zhang et al. (2014) studied the influence of basicity and wettability of the catalyst in catalytic performance. The results showed that the catalyst $CaO/CoFe_2O_4$ had better catalytic activity than $CaO/ZnFe_2O_4$ and

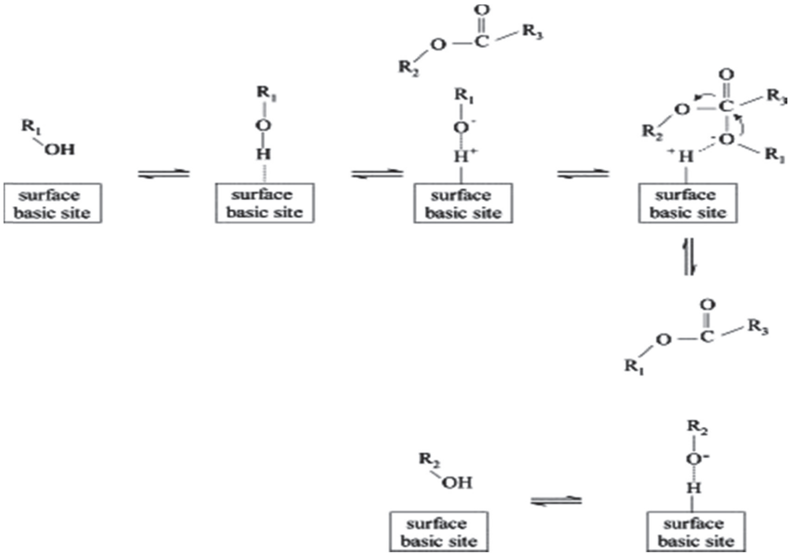


Fig. 1.2 Schematic representation of possible mechanism of transesterification of soybean oil with methanol over Zn, Al-mixed oxides (Adapted from Veiga et al. 2014)

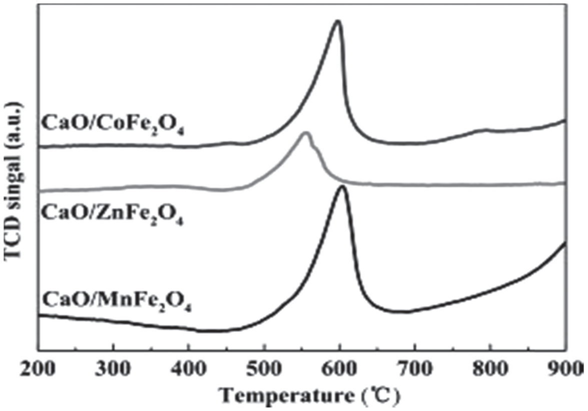


Fig. 1.3 CO_2-TPD profiles of the three magnetic catalysts

CaO/MnFe$_2$O$_4$ with a biodiesel yield of 87.4 percent due to the higher basicity of the catalyst (Fig. 1.3). Veiga et al. (2014) reported the Zn-Al-mixed oxides with different Al/(Al+Zn) molar ratios as catalysts for the transesterification of soybean oil with methanol. The determination of basicity showed that these materials have predominantly basic sites. The catalytic behavior of Zn/Al-mixed oxides could be related to the density of basic sites measured by TPD of CO_2. Similarly, the KI, KF, and KNO_3 catalysts supported on alumina showed good activities at low temperatures due to more basic sites forming either K_2O species produced by thermal decomposition or Al–O–K groups formed by salt-support interactions (Xie and Li 2006; Xie and Huang 2006; Vyas et al. 2009).

Tessonnier et al. (2009) in a recent work used N-bases grafted to multiwalled carbon nanotubes (MWCNTs) as a solid base. Various amino groups (1°, 2°, and 3°) were grafted onto the surface of MWCNTs using the scheme shown in Fig. 1.4. The amino-grafted multiwalled carbon nanotubes (N-MWCNTs) were used as an effective base catalyst in transesterification of triglycerides (glyceryl tributyrate). In their studies, all the amino-grafted nanotubes were found to be basic in nature ($pH > 7$). The nanotubes grafted with 3° amines were found to be the most basic (basic site density of 1.00 mmol/g and $pH = 10.30$), and hence the most active in the transesterification of triglycerides.

Several explanations for the formation of basic sites on supported catalyst have been proposed in the literature. (a) The solid-state reaction

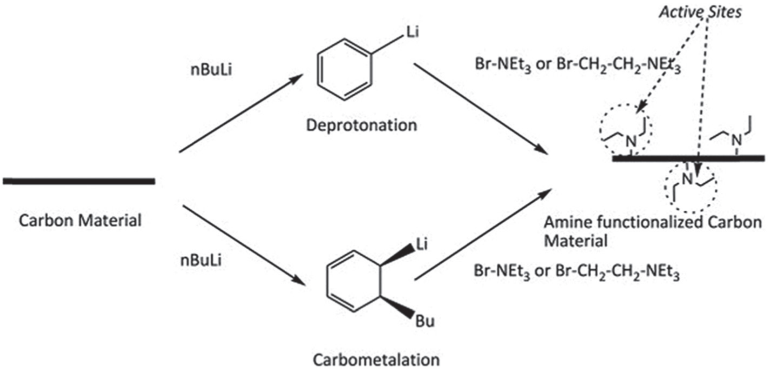


Fig. 1.4 Grafting of amines onto carbon surface (Adapted from Konwar et al. 2014)

between the guest compound and the surface of the support in the activation process is favorable for the catalysts basicity. The metal ion of catalyst could insert in the vacant sites of support, accelerating dissociative dispersion and decomposition of catalyst to form basic sites in the activation process (Xie and Li 2006); (b) The more catalyst are loaded on the support, the more free vacancies decrease, which results in the surface enrichment of metal species that is probably considered to be the active sites for base-catalyzed reactions (Xie and Huang 2006; Xie and Li 2006); and (c) When the amount of metal ion loaded on support was above the saturation uptake, it could not be well dispersed and, for this reason, not all but only a part of the loaded catalyst could be decomposed. As a result, the number of basic sites together with the activities of the catalysts would decrease (Xie and Huang 2006; Xie and Li 2006; Vyas et al. 2009). Thus, the basic sites could be proportional to the decomposed amount of catalyst, instead of the loaded amount of catalyst. As a general conclusion, it is possible to say that a large variety of solid-base catalysts are now available. However, it is not possible with any of the catalysts presented in this review to possess at the same time very strong basic, high surface area, inexpensive catalyst production and catalysts stability. Certainly, a compromise needs to be reached in each case.

The acidity of a material is defined relative to a base used in acid–base interaction. In the case of Brönsted acidity, the solid acid is able to donate or at least partially transfer a proton which becomes associated with surface anions. From the point of view of Lewis definition, the

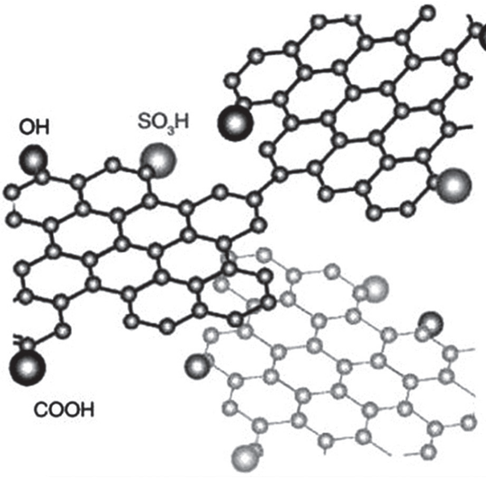


Fig. 1.5 Proposed schematic structure of the sulfonated carbon materials. (Adapted from Okamura et al. 2006)

solid acid must be able to accept an electron pair. Thus, when the acid surface reacts with a Lewis base molecule, a coordinate bond is formed. In heterogeneous Lewis acid catalysts favors the formation of electrophilic species that determine the rate of desorption followed by rate of transesterification reaction (Huber et al. 2006; Islam et al. 2013a; Di Serio et al. 1998, 2006).

Almeida et al. (2008) tested the activity of several acid catalysts using different ratio of TiO_2/SO_4 in the transesterification of soybean oil with methanol at 120 °C, and the following order of reactivity was obtained: TiO_2/SO_4(5:1) > TiO_2/SO_4(10:1) > TiO_2/SO_4 (20:1). The low activity of TiO_2/SO_4 (20:1) could be related to its low amount of Brönsted acid on its framework, probably due the insufficient amount of sulfuric acid used in its preparation. Researchers (Hara et al. 2004; Okamura et al. 2006; Konwar et al. 2014) have also proved that sulfonated-ACs contain Ph-OH, –COOH, and $–SO_3H$ groups (Fig. 1.5), and therefore exhibit better catalytic performance during liquid-phase acid-catalyzed reactions compared to other solid acids. Due to the formation of such groups on the carbon material during carbonization process, they end up in the final product, i.e., sulfonated-ACs. Their presence enhances catalytic performance by increasing overall acid density and by acting as sites for the attachment of substrates such as triglycerides and fatty acids.

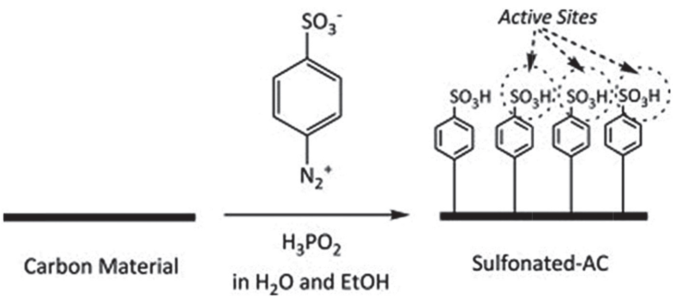
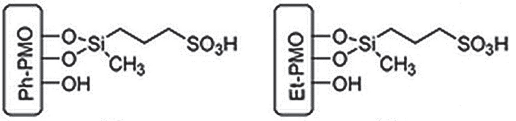


Fig. 1.6 Covalent attachment of Ph-SO_3H on carbon surface (Adapted from Konwar et al. 2014)

Sulfonation of carbon surfaces by reductive alkylation/arylation of sulfonic acid-containing aryl radical has been used exclusively by researchers to prepare sulfonated-ACs using various carbon sources such as ordered mesoporous carbon (OMC), nanotubes, graphite, and graphene according to Fig. 1.6 (Wang et al. 2007; Li and Dai 2005). Covalent attachment of sulfonic acid-containing aryl radicals on the surface of OMC (CMK-5) leads to a solid acid catalyst with a high-acid density. These materials exhibit high surface area, narrow pore size distribution, and large pore volume. Thus functionalization of OMCs with sulfonic acid groups is expected to allow high densities of functional groups and ensure good accessibility to active sites. The material exhibits high surface area, uniform pore size distribution, high activity and good stability for acid-catalyzed reactions, such as transesterification and esterification.

The hydrophilic/hydrophobic characters of the catalyst's surface have received a great deal of attention on the mesoporous surface reactivity of the catalysts. The appropriate surface modification (lipophilic–hydrophilic balance) allows catalyst's design to meet the requirements of the transesterification reaction (Melero et al. 2006). Novel water tolerant sulfonic acid-based periodic mesoporous organosilicas (PMOs) having either phenylene or ethyl as bridge and methylpropyl sulfonic acid as functionalized group have been reported by Karimi et al. (2012). The materials were then employed in efficient biodiesel production *via* direct transesterification of sunflower oil, canola oil, corn oil, refined olive oil, and extracted oil from olive sludge with methanol. By comparing the catalytic performance of these acids with well-known SBA-15-PrSO_3H, it was revealed that catalyst bearing an ethylbridging group is a more reactive catalytic system in biodiesel production (Fig. 1.7).

The mechanistic steps during the esterification reaction catalyzed by SO_3H-bearing solid acid has been proposed by Chang et al. (2013), as shown in Fig. 1.8. In step 1, the proton of $–SO_3H$ is transferred to the carbonyl of aliphatic acid to form a positive carbon ion, which is subsequently transformed to a tetrahedral intermediate (a) by the nucleophilic attack of methanol in step 2. Meantime, the proton of methanol hydroxyl is rearranged and transferred to the hydroxyl oxygen of aliphatic acid (step 3). The tetrahedral intermediate (b) is dehydrated (step 4) and then transfers the proton of the hydroxyl group to $–SO_3^-$ (step 5), finally



1a 1b

Fig. 1.7 Sulfonic acid-based PMOs having either (a) *phenylene or* (b) *ethyl (Adapted from Karimi et al. 2012)*

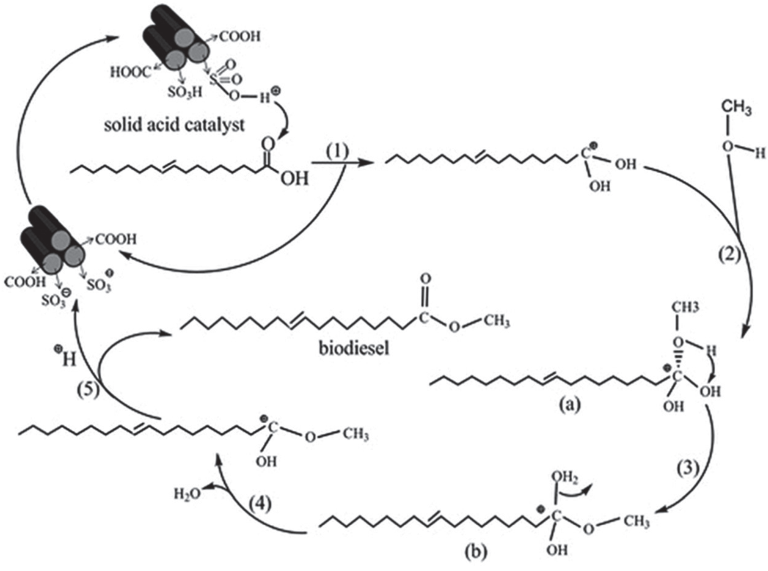


Fig. 1.8 Mechanism of SO_3H-bearing solid acid-catalyzed esterification of aliphatic acid (Adapted from Chang et al. 2013)

resulting in the formation of biodiesel products of methyl esters and the recovering of active sites of $–SO_3H$.

Recently another approach for the formation of hydrophobic catalyst through sulfonation of incompletely carbonized carbohydrate was reported by Lou et al. (2008). They mentioned that the catalyst derived from starch leads to their successful application for transesterification reaction from waste cooking oils containing high FFAs. A similar approach for the preparation of fatty acid alkyl esters (biodiesel/biolubricants) from waste cooking oils as well as non-edible oils has been proposed by Sreeprasanth et al. (2006). The strength of acid sites can be increased by incorporating functionalized group either by grafting on the silica surface or by post-synthesis route process (Fig. 1.9).

The Ar-SO_3H-10 catalyst was functionalized with methyl silyl groups to modify its surface hydrophilicity–hydrophobicity balance with an attempt to improve its catalytic performance. Methyl groups were incorporated into the catalyst by capping with methoxytrimethyl silane using a post-synthetic method (C-Ar-SO_3H-10) and methylation with methyltriethoxy silane using a one-step synthetic method (M-Ar-SO_3H-10). The organic–inorganic hybrid materials have received considerable attention as a consequence of their wide application potentials in versatile fields. In this regard, sulfonic acid functionalized SBA-15 with high acidity has shown excellent activity in transesterification reactions. Hexagonal structure, large pore size, high surface area, great pore wall thickness, and high thermal stability are significant properties of this catalyst.

The catalyst activity can be restored and the catalyst performance can be improved by calcination. The calcination temperature is crucial for the generation of catalytic activity. Since calcination temperature was found

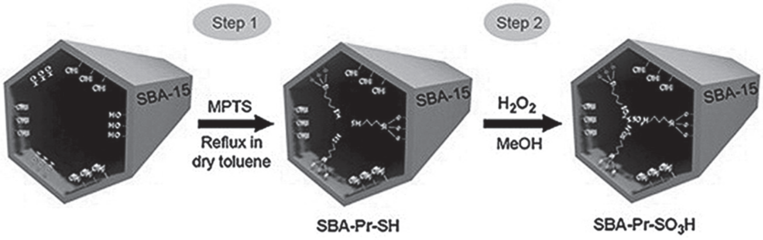


Fig. 1.9 Schematic illustration for the preparation of SBA-Pr-SO_3H (Adapted from Ziarani et al. 2014)

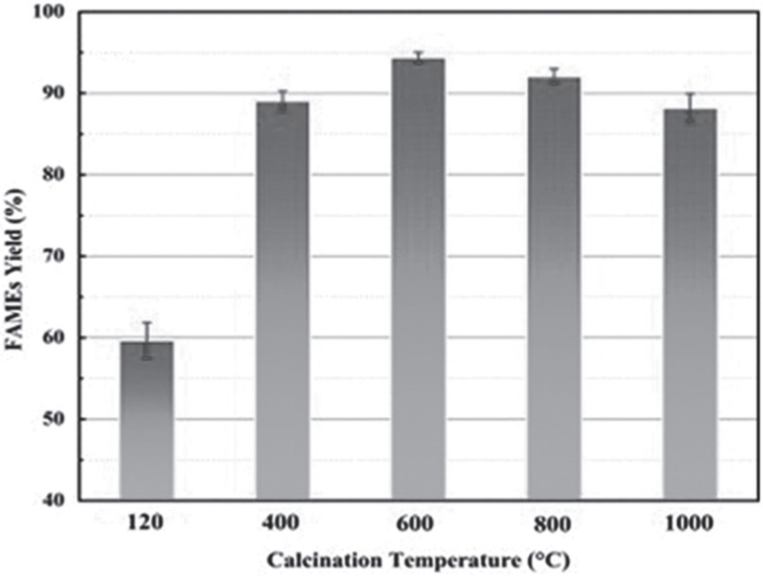


Fig. 1.10 FAME yields achieved with Ca/Al composite oxide catalysts calcined at different temperature

to affect the structural and catalytic properties of catalysts, researchers have been treated the catalysts at various temperatures to attempt to optimize this. The effect of calcination temperatures ranging from 120 °C to 1000 °C on activity of the catalyst was investigated by Meng et al. (2013). The catalyst calcined at 600 °C showed the highest activity with >94 percent yield of fatty acid methyl esters (i.e., biodiesel) when applied to the transesterification of rapeseed oil at a methanol:oil molar ratio of 15:1 at 65 °C for 3 hours (Fig. 1.10).

Feyzi et al. (2013) carried out a series of experiments to investigate the performance of Cs/Al/Fe_3O_4 catalyst with the variation of reaction time in the range of 60 through 240 minutes, at the optimal reaction conditions (methanol/oil = 14/1, T = 58 °C and the stirring rate of 300 rpm). It was reported that the reaction time of 120 minutes gave an optimum condition with 96.2 percent yield of biodiesel (Fig. 1.11).

Kawashim et al. (2008) performed a detailed comparison study of the calcium-containing catalysts—$CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and CaO-CeO_2 in the transesterification at 60 °C with a 6:1 molar ratio of methanol to oil for 10 hours. In this case, the enhanced catalytic

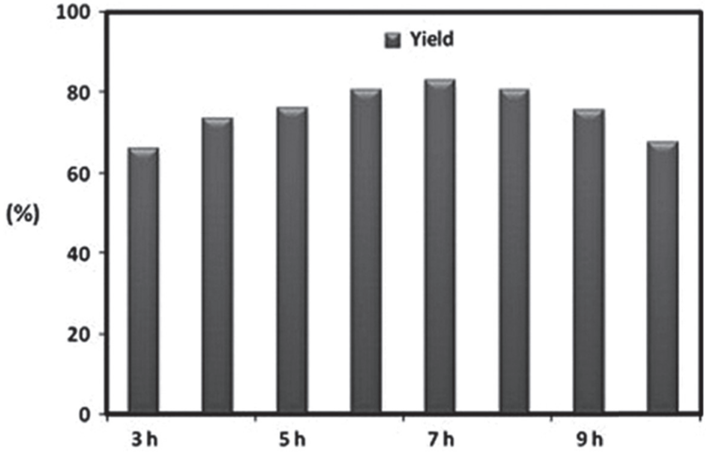


***Fig. 1.11** Effect of calcinations time on the catalytic performance of Cs/Al/Fe_3O_4 catalyst (Adapted from Feyzi et al. 2013)*

performance was explained by improved accessibility of active calcium methoxide species formed after calcination at 900 °C. However, the transesterification reaction in the presence of CaO/ZnO and KF/ZnO catalysts have been reported to be inactive catalysts as the calcination temperature increased beyond 800 °C (Ngamcharussrivichai et al. 2008). The inactivity toward the transesterification reaction might be due to the sublimation or penetration of the active species of CaO/ZnO and KF/ZnO catalysts into the subsurface of support at 800 °C, which latter would in turn, reduces the catalytic activity.

Leaching of heterogenious catalysts during the transesterification of vegetables oil has been reported in the literature (Ma et al. 2008; Alonso et al. 2007). In particular, it has been shown that deactivation is due to the progressive reduction of activity due to the leaching of active species of catalyst in the biodiesel. The high yield of biodiesel (93 percent to 98 percent) was obtained after 4 hours of reaction in the transesterification of rapeseed oil using lithium modified lime catalysts (Puna et al. 2014). However, the Li doped catalysts presented a faster deactivation than the bare CaO. The formation of the Ca-diglycerol phase could be attributed to promote the Ca leaching and thus contributes to catalysts deactivation. Similarly, the deactivation of the TiO_2/SO_4 catalysts was attributed to the leaching of active sulfate species (Almeida et al. 2008).

In particular, Corma (1997) noted that SO_3 functional groups are sensitive to water vapor. For instance, the SO_3 moeties on the surface gave rise to sulfate species such as SO_4^{2-}, HSO_4^{-}, and H_2SO_4. In a liquid-phase system, these sulfate species in the form can easily leach out from the catalysts. In any case, it appears quite clear that the presence of sulfate will always be a problem or at least a limitation for the practical use of this type of catalyst. Indeed, systematic research tackling these questions has to be conducted in order to more precisely emphasize the true catalytic nature of leaching for FAME yield.

Several authors (Sercheli et al. 1999) have reported that the presence of small pore size (>1 nm) limits the diffusion of oil molecules to the catalytic sites situated inside the porous channel and thereby reduces the conversion of biodiesel. Mesoporous calcium methoxide, H_3PO_4/Al_2O_3 catalysts have been used in the transesterification reaction with alcohol obtaining more than 96 percent yield in biodiesel (Liu et al. 2008c). The high yield of biodiesel could be demonstrated that large part of surface area is occupied by pores of relatively large size between 100 and 1400 nm. For smaller pore materials, the accumulation of methanol and water around the hydrophilic sites may have hindered the access of fatty acid ester (FFA) molecules to catalyst giving rise to a diffusion controlled reaction. Thus, porous solid catalyst offers advantages over traditional solid catalysts in high yield of biodiesel because of their potential for controlling the catalytic domains at the molecular scale. For reactions catalyzed by solid particles, transport of reagents through the stagnant boundary layer surrounding the particles (Region 1 in Fig. 1.12) and transport within the pore network (Region 2 in Fig. 1.12) can potentially limit the observed reaction rate. Thus, researchers need to ensure that artifacts in kinetic studies resulting from transport limitations involving the catalyst particles are minimized. It may be reasonable to state that the triglyceride molecule can be diffused into catalyst having pore diameter of more than 5 nm shown in Fig. 1.13. The diffusion of the triglyceride molecule could be restricted when the diameter of the catalyst was less than 5 nm and this would, in turn, decrease the catalytic activity (Santacesaria et al. 2007). Besides, the catalyst with high mechanical strength is essential, which could be decisive for long-term stability of catalyst.

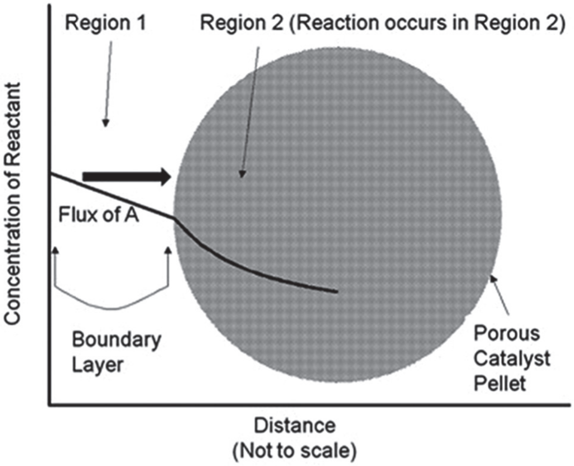


Fig. 1.12 Concentration profile of a reactant A in the vicinity of a porous solid catalyst particle. Region 1 depicts the stagnant boundary layer surrounding the particle, and Region 2 depicts the porous interior of a catalyst particle where active sites are located (Adapted from Davis 2013)

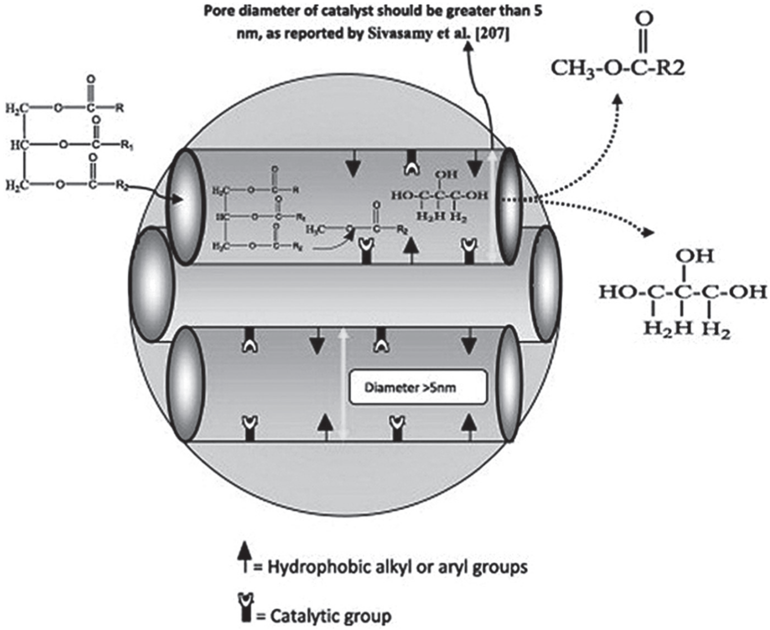


Fig. 1.13 Schematic of mesoporous hydrophobic group for FA esterification with alcohol (Adapted from Mbaraka and Shanks 2005)

A great deal of effort has been devoted in recent years to obtain catalysts with high surface area owing to its wide application potential in the field of petrochemical industries. Chen et al. (2007) studied the influence of surface area of TiO_2, ZrO2, TiO_2-SO_4^{2-}, and ZrO_2-SO_4^{2-} catalysts in the transesterification of cottonseed oil with methanol at 230 °C. It was shown that the specific surface areas of TiO_2 and ZrO_2 were increased by incorporation of sulfate to both of TiO_2 and ZrO_2 structure. Consequently, the large accessible surface area could provide an advantageous platform to improve the catalytic performance. Therefore, the suitable catalysts with high surface area could make the reactions to proceed at rates high enough to permit their commercial exploitation on a large scale efficiency of the transesterification (Corma 1997; Chen et al. 2007).

The commercial exploitation of heterogeneous catalysts for biodiesel production could be the design of innovative chemical reactors to facilitate continuous processing of viscous bio-oils. Conventional plug flow reactors are ill-suited to slow reactions such as FFA esterification and TAG transesterification, since they require very high length: diameter ratios to achieve good mixing, and in any event are problematic due to their large

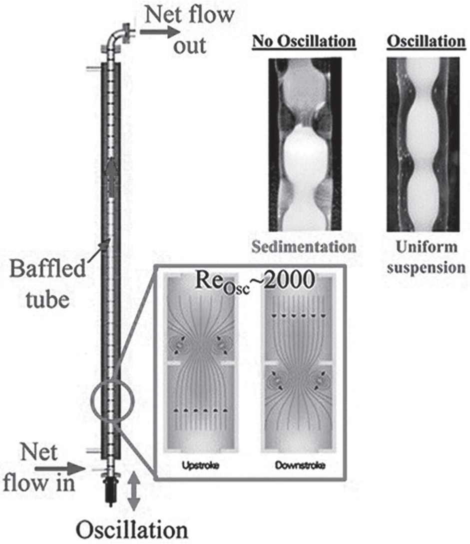


Fig. 1.14 Flow and mixing characteristics within an oscillatory baffled reactor (Adapted from Lee et al. 2014)

footprints and pumping duties, and control difficulties (Maddikeri et al. 2012). Oscillatory baffled reactors (Fig. 1.14) circumvent these problems by oscillating the reaction fluid through orifice plate baffles to achieve efficient mixing and plug flow, as proposed by Maddikeri et al. (2012) and Phan et al. (2012). However, there should be an additional work toward the preparation of a stable solid catalyst in which the active sites have the required strength to promote the transesterification reaction.

CHAPTER 2

Nano to Macroscopic Catalytic Progress in Biodiesel Production

The enormous worldwide use of diesel fuel and the rapid depletion of crude oil reserves have prompted keen interest and exhaustive research into suitable alternative fuel. Currently, attention is focused on human and environmental safety, in relation to the release of hydrocarbons into the environment. Petroleum derivatives contain benzene, toluene, ethylbenzene, and xylene isomers, the major components of fossil fuel, which are hazardous substances subject to regulations in many parts of the world (Serrano et al. 2006). As a consequence, the demand of green energy is increasingly gaining international attention. When green energy is used, the primary objective is to reduce air pollution, and minimize or eradicate completely any impacts to the environment (Burgess 1990). Among many possible sources, apparently, biodiesel is a viable alternative energy to conventional diesel fuel, which is of environmental concern and is under legislative pressure to be replaced by biodegradable substitutes. Four primary ways to make biodiesel are direct use and blending, micro-emulsions, thermal cracking (pyrolysis), and transesterification (Leung et al. 2010). The initial stage of hydrocracking triglycerides would be saturation of fatty acid chains and rapture of the ester group leading to the formation of free fatty acids (FFAs) (Fig. 2.1). In principle the latter can be further cracked, but in lower temperatures these rather undergo deoxygenetion and hydrogenation (hydrotreating) to produce suitable diesel-like hydrocarbons (C_{15}–C_{18}). Therefore, the process can employ less harsh conditions than conventional cracking over zeolites (Sivasamy et al. 2009). The transesterification reaction can be carried out using homogeneous, heterogeneous, or

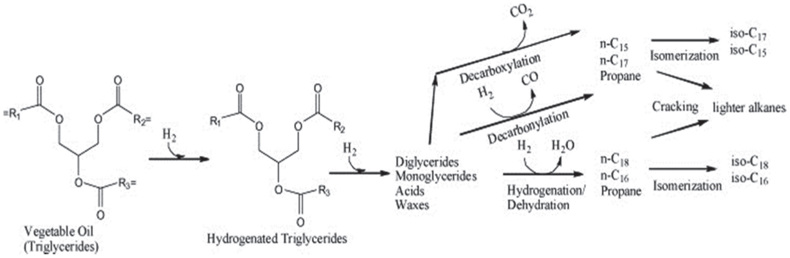


Fig. 2.1 General pathway of hydrotreatment of vegetable oils (Adapted from Huber et al. 2007)

enzymatic catalysts. Homogeneous catalysts (i.e., NaOH and KOH) are usually employed commercially for the preparation of biodiesel. Some of the shortcomings include the formation of an unwanted soap by-product in the presence of water and FFAs. From a process perspective, homogeneous catalysts, however, are corrosive, can be used only once, and require energy intensive separation operations that lead to waste formation and environmental pollution (Meher et al. 2006a).

On the contrary, the use of heterogeneous catalytic systems in the transesterification of triglyceride implies the elimination of several steps of washing of biodiesel, ensuring thereby, higher efficiency and profitability of the process as well as lowering the production cost, as summarized by Kawashima et al. (2008). However, the development of a stable catalyst with suitable particle size that can be recycled and reused to simplify the product separation and purification steps remains inadequately addressed. Therefore, a number of researches have been directed toward the development of heterogeneous catalyst for transesterification of triglycerides over the past decade. The aim of the preparation of catalytic materials is to prepare a product with high activity, selectivity, and stability (Pinna 1998). Although some catalytic materials are composed of single substances, most catalysts have different types of easily distinguishable components, active components, a support (Richardson 1989). Fig. 2.2 illustrates the various steps carried out for the preparation of supported catalysts using pre-shaped catalytic supports. The usual pathway (1, 3, 4, and presumably 5) involves impregnation of the support grains or pellets with an aqueous solution containing the species of the active element to be deposited followed by drying at low

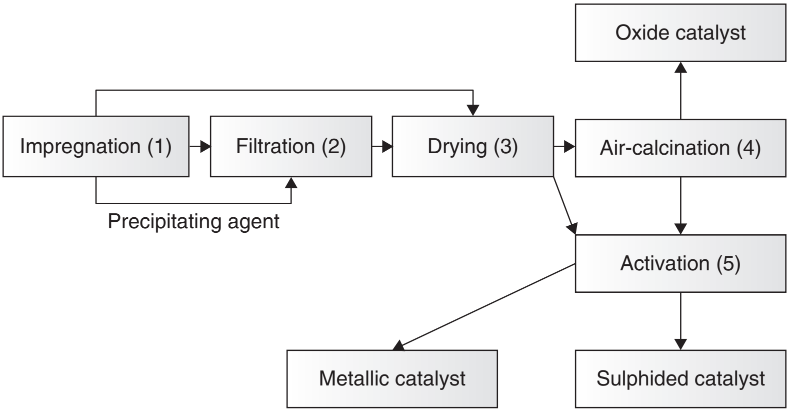


Fig. 2.2 General preparation scheme of supported catalyst (Adapted from Bourikas et al. 2006)

temperatures (20 °C to 100 °C) and then calcination at high temperatures (usually 300 °C to 1000 °C).

Supports can provide higher surface area through the existence of pores where metal particles can be anchored (Chorkendorff and Niemantsverdriet 2006). The active components are responsible for the principal chemical reaction. The active metal component is usually deposited on the surface of a porous or non-support support as shown in Fig. 2.3. The different methods which are usually used to prepare supported catalysts will be discussed in subsequent sections.

2.1 Methods for Preparation of Support Materials

2.1.1 Impregnation

Impregnation is a procedure whereby a certain volume of solution is contacted with the solid support, which, in a subsequent step, is dried to remove the imbibed solvent. Two methods of impregnation may be distinguished, depending on the volume of solution used: incipient wetness or dry impregnation and wet or soaking impregnation (Richardson 1989; Mul et al. 2005). In incipient wetness impregnation method, the volume of the solution is equal or slightly less than the pore volume of the support. The volume should be just sufficient to fill the pores and wet the outside of the particles. Although this volume may be determined from

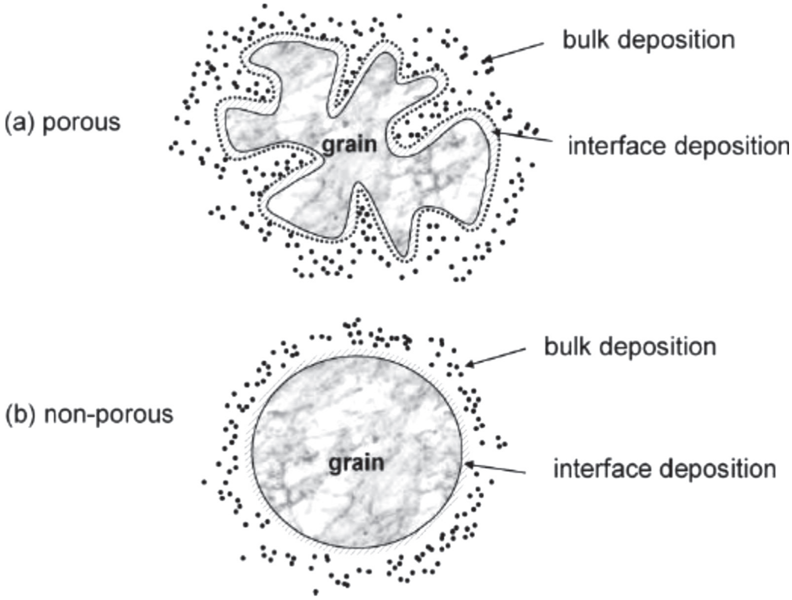


Fig. 2.3 Schematic representation of the supported catalytic particles; (a) porous support and (b) non-porous support (Adapted from Bourikas et al. 2006)

measured pore volumes, this is sometimes more reliably determined with preliminary test on aliquot samples (Richardson 1998).

The maximum loading is limited by the solubility of the precursor in the solution (Pinna 1998). When higher loadings are required, this limitation is overcome by carrying out consecutive impregnation steps. In wet impregnation, an excess of solution with respect to the pore volume of the support is used (Schwarz et al. 1995; Campanati et al. 2003). The system is left to age for a certain period under stirring; it is then filtered and dried. This procedure is applied when a precursor support interaction can be envisaged. Therefore, the concentration of the support will not only depend on the concentration of the solution and on the pore volume of the solution, but also on the type and/or concentration of the adsorbing sites existing at the surface. In general, wet impregnation is used for the preparation of low-loaded catalysts and, in particular, expensive precious metal catalysts, where the active metal phase should be highly dispersed in order to obtain high activity. The distribution of the metal precursor will be based on the density of the exchanging sites in the support. With low metal loading and high density of adsorbing sites on supports in granules, pellets, extrudates (where diffusion effects are encountered), the distribution of the precursor will be inhomogeneous (Pinna 1998). Deposition will mainly take place at the external layers of the particles.

2.1.2 Precipitation

Precipitation is another procedure where the solutions containing the metal salt and a salt of a compound that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxide and or/carbonates (Pinna 1998). After washing, these can be transformed to oxides by heating. Besides the above-mentioned methods, supported catalysts have also been prepared by grafting (Schwarz et al. 1995). It has also been discovered that metal oxides can be deposited on the surface of supports by physically mixing and heating the resulting mixture to spread the active component. However, this method applies only to active metal oxides that are volatile or have a low-melting temperature, such as rhenium oxide, molybdenum oxide, tungsten oxide, and vanadium oxide. The disadvantage of this method is the long calcination times required to achieve complete spreading of the active metal oxide over the support surface.

2.1.3 Drying

Drying is an important step in catalyst preparation since it can affect the distribution of the active species. The drying steps which follows the impregnation phase causes evaporation and flow of liquid in the pores, which can result in redistribution of impregnant in the pore volume. Drying of porous materials follows various stages characterized by drying rate, liquid phase distribution, and predominant mechanism of moisture transport (capillary flow or vapor deposition) (Morbidelli and Gavriilidis 2005). Two limiting regimes have been distinguished (Fig. 2.4): fast drying where vapor removal is much faster than capillary flow and slow drying in the opposite case. In the fast evaporation front is continuous and recedes toward the pellet center as drying progresses,

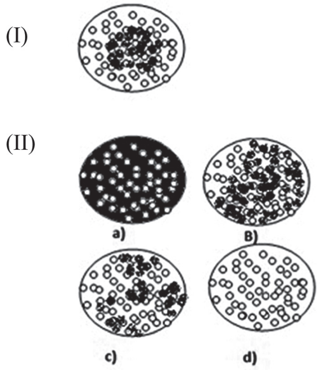


Fig. 2.4 Regimes of drying. (I) Fast drying, (II) slow drying (a–d) indicate the various steps (Adapted from Morbidelli and Gavriilidis 2005)

while in slow drying the evaporation front is initially located at the pellet surface, later portions of it move inward, and finally it breaks down so that isolated domain of liquid phase are formed (Morbidelli and Gavriilidis 2005).

During drying, the solution in the pores will become oversaturated and precipitation takes place (Mul et al. 2005). If not done properly, this step can result in irregular and uneven concentration distributions (Richardson 1998). Different variables such as the heating rate, final temperature and time of treatment, and type of atmosphere can influence the drying process and have to be selected according to different systems (Pinna 1998). In principle, rapid evaporation of the solvent is favorable because it causes rapid supersaturation of the solution in the pores and that is associated with a high dispersion of the active species (Mul et al. 2005). However, if the drying rate is too slow evaporation occurs at the meniscus, which retreats down the pore, some salt deposition occurs but most of the solute merely concentrates deeper in the pore (Richardson 1998; Pinna 1998). When finally crystallized, the salt is located at the bottom of a pore or at the particle center (Pinna 1998).

2.1.4 Calcination and Activation

Calcination is a thermal treatment process applied to solid materials in order to bring about a thermal decomposition or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials (Pinna 1998). The purpose of calcination is to decompose the metal precursor with the formation of an oxide and removal of the cations or the anion that have been previously introduced as gaseous products. Besides decomposition, during the calcination sintering of the precursor or of the formed oxide or a reaction of the formed oxide with the support can occur (Richardson 1998; Pinna 1998). When dealing with bimetallic catalysts, control of calcination temperature is required in order to avoid the formation of two separate oxides or segregation of one of the components. Other thermal treatments, such as reduction or sulphidation, which are performed in a special atmosphere, are called activation operations (Perego et al. 1997). Variables such as the rate of heating, the time of calcination have to be carefully chosen depending on the type of metal, catalytic system, and reaction type (Pinna 1998).

2.2 Advances in Supported Catalyst for Biodiesel Production

The significant step forward has come more recently with the discovery of the mesoporous M41S family in 1992 (Kresge et al. 1992), which offer many opportunities over microporous materials by being more accessible to reactants. Recently, the use of mesoporous catalysts such as zeolites (Sasidharan et al. 2004), SBA-15 (Ignat et al. 2010; Shah et al. 2004), Ti-HMS (Luo et al. 2007), MCM-41 (Pérez-Pariente et al. 2003), and Al-MCM-41 (Rashtizadeh et al. 2010) have been reported for the transesterification of vegetable oil. Some of these research findings had proven the potential application of catalyst for transesterification reactions; however, from a practical point of view, handling of small particles in large quantities is difficult and limits the possibilities to recover for reuse. Thus, the simplicity of catalyst reusability along with their handling requirements is a crucial prerequisite for designing a supported catalyst. A variety of supported porous catalysts for transesterification of vegetable oils have been investigated in laboratory scale, including K/SBA-15 (Abdullah et al. 2009), KNO_3/MCM-48 (Sun et al. 2009), KI/mesoporous silica (Samart et al. 2009), and CaO/mesoporous silica (Albuquerque et al. 2008; Bai et al. 2009).

Other inorganic oxides supported catalyst applied for transesterification of vegetable oil are NaN_3/mesoporous γ-Al_2O_3 (Bota et al. 2010), KF, CsF, and LiF supported on mesoporous alumina (Verziu et al. 2009). However, these catalysts preparation approaches are rather complicated, which limits their potentialities in a large-scale application. Concerning the catalyst properties, it has been reported by Pergo and Villa (1997) that the catalyst should have a high surface area and desirable mechanical strength to increase its stability under reaction condition and hence the catalyst life. In catalysis, gamma alumina is preferred because it can provide high surface area and thermal stability, which are suitable characteristics for the catalytic performance (Chuah et al. 2000).

Many heterogeneous catalysts for the transesterification of oils have been developed. For example, the transesterification reaction of soybean oil with KI/Al_2O_3 has been studied; conversion in excess of 90 percent was achieved at a temperature of 60 °C (Suppes et al. 2004). It has also been reported that the conversion to methyl ester reaches 87 percent with the potassium-loaded alumina catalyst, when a mixture with a molar ratio of methanol to oil of 15:1 is refluxed for a reaction time 7 hours (Xie et al. 2006a). Besides these, a great variety of γ-Al_2O_3 supported catalysts including $Mg(NO_3)_2/Al_2O_3$ (Benjapornkulaphong et al. 2009), $Na/NaOH/\gamma$-Al_2O_3 (Kim et al. 2004), $NaOH/Al_2O_3$ (Arzamendi et al. 2007), KNO_3/Al_2O_3 (Vyas et al. 2009), and $K/KOH/\gamma$-Al_2O_3 (Ma et al. 2008) have been investigated under various reaction conditions and with a variable degree of success. However, information on the catalyst reusability in transesterification reaction is still rather limited.

More recently, the utilization of Al_2O_3 supported KF catalyst having a particle size of nano-meter order for biodiesel production has been demonstrated by Boz et al. (2009) and reported that the catalyst can be effectively used in the production of biodiesel from vegetable oil. Wang et al. (2007a) reported that nano-MgO was used in the transesterification of soybean oil as a catalyst in supercritical and subcritical methanol. Furthermore, Wen et al. (2010) reported that high yield of biodiesel (97 percent) can be obtained in the transesterification of Chinese tallow seed oil at 65 °C after 2.5 hours of reaction using KF/CaO nanocatalyst. Besides, catalysts with *nano*-sized such as CaO.ZnO (Ngamcharussrivichai et al. 2008) and K_2O/Al_2O_3 (Ghasemi et al. 2014) have been demonstrated to be efficient heterogeneous catalyst for transesterification. Other workers (Montero et al. 2009, 2010) have discussed on the structure-sensitive biodiesel synthesis over MgO nanocrystal reported by Lee et al. (2014) correlations between the surface electronic structure and associated catalytic activity, revealing a pronounced structural preference for (110) and (111) facets (Fig. 2.5). In situ aberration corrected-transmission electron microscopy and XPS implicate the coplanar anion vacancies as the active sites in tributyrin transesterification with the density of surface defects predicting activity.

The HPW containing of Cs is more active in the transesterification, for instance, the $Cs_xH_{3-x}PW_{12}O_{40}$ with various content of cesium ($x = 0.9 - 3$) were found to be active catalysts in the transesterification of tributyrin (Narasimharao et al. 2007). On the other hand, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_2HPW_{12}O_{40}$ catalysts were found to be active catalysts for the transesterification of rapeseed oil (Hamad et al. 2008). This work investigated the effects of different weight percents of $H_3PW_{12}O_{40}$/(Fe–SiO_2), loading of Cs as a promoter and calcination

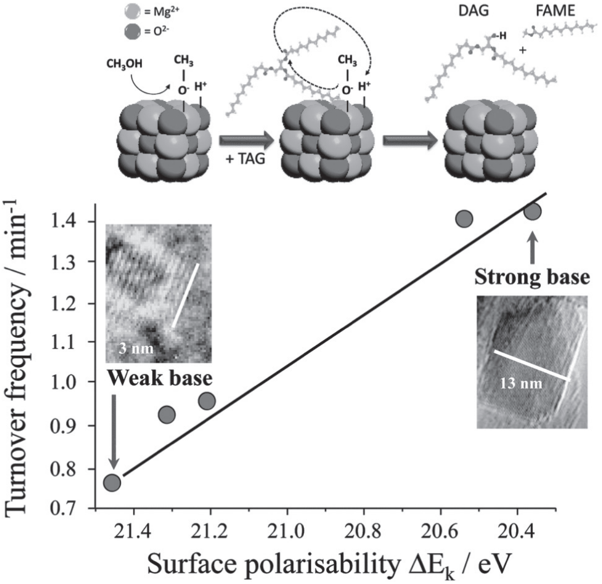


Fig. 2.5 Relationship between surface polarizability of MgO *nanocrystals and their turnover frequency toward tributyrin transesterifcation (Adapted from Lee et al. 2014)*

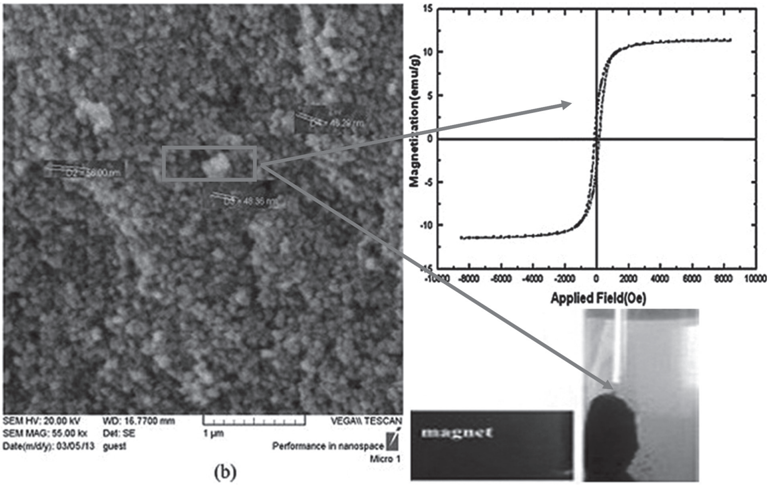


Fig. 2.6 The SEM images of $CsH_2PW_{12}O_{40}/Fe–SiO_2$ *nanocatalyst, (a) precursor and (b) calcined (Adapted from Feyzi et al. 2014)*

conditions on catalytic performance of $CsH_2PW_{12}O_{40}/Fe–SiO_2$ catalyst for biodiesel production. Feyzi et al. (2014) reported the results concerning the effects of operational conditions on the catalytic performance of $CsH_2PW_{12}O_{40}/Fe–SiO_2$ catalysts. It was highlighted that the recovery of the catalyst can be achieved easily with the help of an external magnet in a very short time (<20 seconds) with no need for expensive ultracentrifugation (Fig. 2.6). Recently, Zhao et al. (2013b) have investigated the catalytic activity and stability of two types of commercial nanopowder CaOs with different surface areas for the transesterification of canola oil with methanol at elevated reaction temperatures. It was reported that the nano-CaO catalysts exhibited high activity and stability for the production of biodiesel from canola oil.

2.3 Kinetic Approach Solid Catalyzed Biodiesel Production

A deeper study of heterogeneous catalysis biodiesel forming reactions was carried out by several researchers (Vujicic et al. 2010; Chantrasa et al. 2011; Birla et al. 2012) for more understanding of the reaction kinetics and mechanism using a previously reported kinetic and mass transfer model. To determine the kinetics of the reaction, the effect of reaction temperature and time were measured. A kinetic study was also conducted and the reaction rate constant (*k*) and activation energy (E_A) at various temperatures were determined. It was assumed that the catalyst was used in sufficient amount with respect to oil to shift the reaction equilibrium toward the formation of fatty acid methyl esters. Thus, the reverse reaction could be ignored, and the change in concentration of the catalyst during the course of reaction can be assumed to be negligible.

Transesterification reaction comprises three consecutive reversible reactions (Eq. 2.1), whereby 1 mol of ME is produced in each step, and diglycerides (DG) (Eq. 2.2) and monoglycerides (MG) (Eq. 2.3) are intermediate products (Birla et al. 2012).

Overall reaction

$$\mathrm{TG + 3R'OH \leftrightarrow 3R'COOR + GL} \tag{2.1}$$

Stepwise reactions

$$\mathrm{TG + R'OH} \xleftrightarrow[k_{1'}]{k_1} \mathrm{DG + R'COOR} \tag{2.2}$$

$$\mathrm{DG + R'OH} \xleftrightarrow[k_{2'}]{k_2} \mathrm{MG + R'COOR} \tag{2.3}$$

$$\mathrm{MG + R'OH} \xleftrightarrow[k_{3'}]{k_3} \mathrm{GL + R'COOR} \tag{2.4}$$

The following assumptions are used in this kinetic model: (i) k_{eq}. must be not depending on methanol concentration and the reaction is considered pseudo-first order (Vujicic et al. 2010; Chantrasa et al. 2011), (ii) production of intermediate species is negligible, and (iii) all chemical reactions only occurred in the oil phase. Therefore, first assumption (i) can be written (Eq. 2.5) as follows:

$$-\mathrm{r} = \frac{\mathrm{d[TG]}}{\mathrm{dt}} = \mathrm{k[TG][ROH]^3} \tag{2.5}$$

Then, based on the second assumption (ii) (Eq. 2.7) is obtained,

$$\mathrm{k' = k[ROH]^3} \tag{2.6}$$

$$-\mathrm{r} = \frac{\mathrm{d[TG]}}{\mathrm{dt}} = \mathrm{k[TG]} \tag{2.7}$$

$$\ln \mathrm{TG_o} - \ln \mathrm{TG} = \mathrm{k'.t} \tag{2.8}$$

According to the mass balance,

$$X_{ME} = 1 - \frac{[TG]}{[TG_o]} \tag{2.9}$$

$$[TG] = [TG_o][1 - X_{ME}] \tag{2.10}$$

$$\frac{dX_{ME}}{dt} = k'[1 - X_{ME}] \rightarrow -\ln(1 - X_{ME}) = k'.t \tag{2.11}$$

Based on the equations above and experimental data, first, the concentration of ME at various reaction times (based on the moles fraction) was obtained. Second, a graph with –ln (1 – X_{ME}) versus (T) was plotted (Fig. 2.7) using Eq. (2.11) and the rate constant at each temperature were measured.

Activation energy and pre-exponential factor are calculated via the Arrhenius equation (Eq. 2.12):

$$k = Ae^{-E_a/RT} \tag{2.12}$$

$$\ln K = \ln A - \frac{E_a}{RT} \tag{2.13}$$

$$\ln K = \left(\frac{-Ea}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{2.14}$$

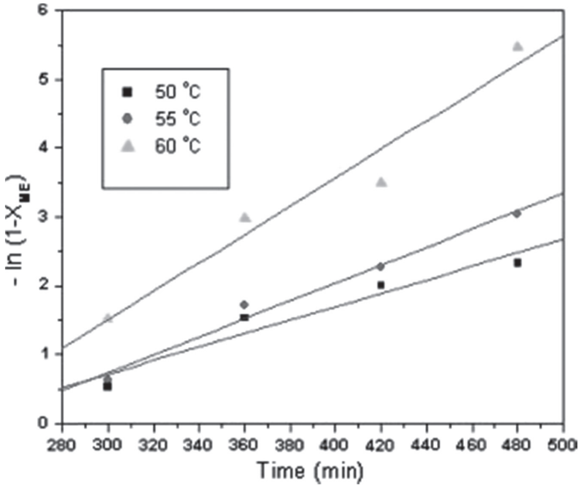


***Fig. 2.7** –ln(1 – X_{ME}) versus reaction time plot at different temperatures (Adapted from Birla et al. 2012)*

where k is the reaction constant, A is the frequency or pre-exponential factor, E_a is the activation energy of the reaction, R is the gas constant, and T is the absolute temperature. Therefore, plot of ln k versus $1/T$ (Fig. 2.8) are given from Eq. (2.14), then E_a and pre-exponential factor have been calculated.

The Eyring–Polanyi equation to calculate Gibbs free energy (ΔG) can be written as Eq. (2.15):

$$\mathrm{k} = \left(\frac{\mathrm{k_b T}}{\mathrm{h}}\right)\exp\left(-\frac{\Delta \mathrm{G}}{\mathrm{RT}}\right) \tag{2.15}$$

Taking the natural logarithm of Eq. (2.15) and substituting $\Delta G = \Delta H - T\Delta S$ where ΔH and ΔS are the enthalpy and entropy of activation respectively, Eq. (2.15) can be written as:

$$\ln\left(\frac{\mathrm{k}}{\mathrm{T}}\right) = \left(-\frac{\Delta \mathrm{H}}{\mathrm{RT}}\right) + \left[\ln\mathrm{k} + \ln\left(-\frac{\Delta \mathrm{G}}{\mathrm{RT}}\right) + \frac{\Delta \mathrm{S}}{\mathrm{R}}\right] \tag{2.16}$$

where k is the rate constant (min^{-1}), T is the absolute temperature (K), R, k_b, and h are the universal gas (8.314 J/mol/K), Boltzmann

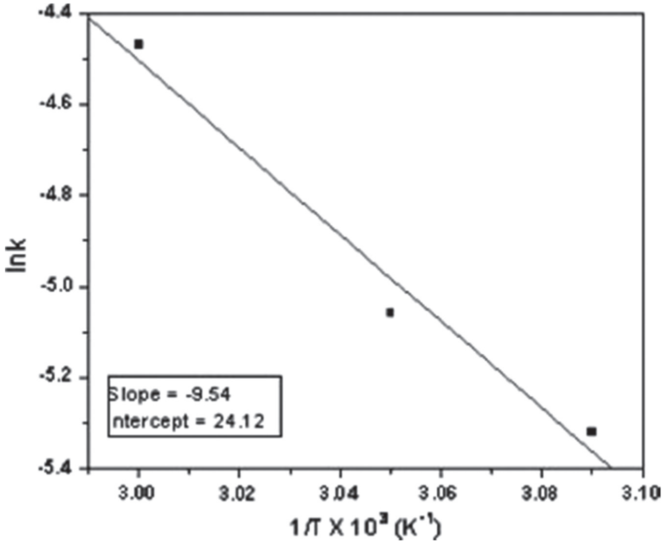


***Fig. 2.8** Arrhenius plot ln k versus 1/T × 10^3 for transesterification (Adapted from Birla et al. 2012)*

(1.38×10^{-23} J/K), and Plancks (6.63×10^{-34} J s) constants, respectively. The transmission coefficient, κ, is often taken as unity. Using Eq. (2.16) and the values of slope and intercept of the Erying plot (Fig. 2.9) between $1/T$ and ln k/T, the values of ΔG, ΔH, and ΔS can be calculated.

Deshmane and Adewuyi (2013) reported that the ultrasound enhances the transesterification reaction rates mainly by improving the mass transfer process without significantly changing the overall kinetics of the reactions. However, the values of ΔH and ΔS for algae biodiesel production from *S. platensis* differs from values for *Chlorella* algae (Ahmad et al. 2014) and leather tanning waste (Ong et al. 2013). The variation of values could be due to the difference of methods involved in biodiesel production changes the reaction parameters which affect the values of thermodynamic parameters. A positive value of ΔH shows that heat input is required to bring the reactants to the transition state so as to form the products. A negative value of ΔS indicates that the degree of ordered geometry/alignment of transition state is better as compared to reactants in the ground state. A positive value of ΔG indicates that the reaction was unspontaneous and endergonic in nature (Nautiyal et al. 2014).

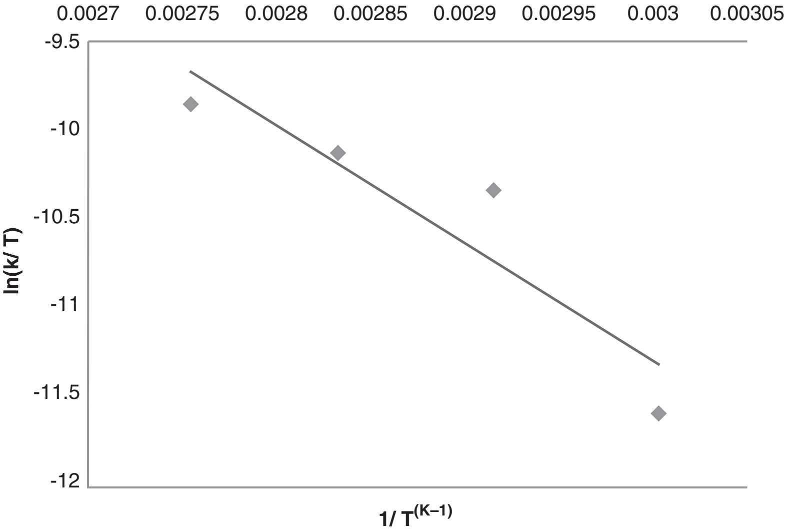


Fig. 2.9 The Erying plot of ln k/T vs 1/T (Adapted from Nautiyal et al. 2014)

2.4 Biodiesel Over Macroscopic Catalyst

Although a variety of solid catalysts have been studied with varying deree of success, these catalysts have been prepared in the form of powders with diameter ranging from nano- to micrometer. From the practical point of view, handling of small particles in large quantities could be difficult due to the formation of pulverulent materials. There are also possible health risks caused by inhalation of small particles. Utilization of powders in conventional catalytic reactions renders their recovery and purification difficult, and ultracentrifugation is needed for the subsequent separation. In particular, the use of powder catalysts gives rise to a number of problems on an industrial scale, including high pressure drops (Centi and Perathoner 2003); high diffusion resistance (Williams 2001); poor mass/heat transfer, and is not amenable to scale up (Meille 2006). The effect of pressure drop on particle size has been reported by Fjerbaek et al. (2009). Fig. 2.10 shows that the particle diameter must be above 4 mm for the pressure drop to be <1 bar/m reactor at a rapeseed oil flow velocity of 0.01 m/s, but also that this particle diameter is in the range of several commercial immobilized lipases. This problem can partly be alleviated either by increasing the size of the carrier or by adding a solvent that reduces the fluid viscosity. With increasing particle diameter, the pressure drop decreases as can be seen in Fig. 2.10, but internal mass transfer

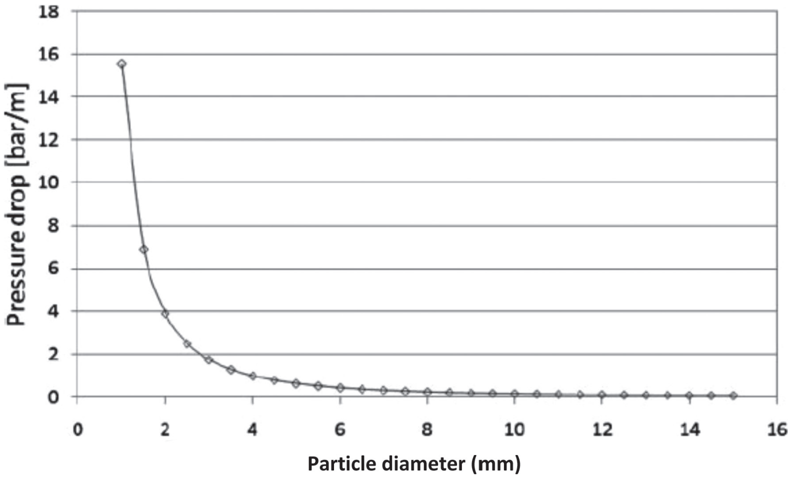


Fig. 2.10 Effect of pressure drop on the diameter of the catalyst (Adapted from Fjerbaek et al. 2009)

rate in the biocatalyst decreases. Further, the pressure drop in fluidized beds at minimum fluidization velocity as a function of pellet diameter is shown in Fig. 2.11. As seen, the pressure drop is at an acceptable level. Experiments using a fluidized bed for biodiesel production have been carried out by Shibasaki-Kitakawa et al. (2007) using an anionic ion exchanger as catalyst instead of enzymes. The main problem by using fluid bed reactors is that a relatively poor mixing of the fluid phase might be expected and that immobilized enzymes will be carried away by the product stream. The standard solution to the latter problem is to separate the pellets from the fluid phase using hydrocyclones, but this approach in the case of biodiesel production is yet to be tested.

The particles in the form of powder could be plugged in the reactor or form the aggregated cluster in the reaction medium which might reduce the mass transfer/heat transfer from the reactant to the active site of the catalyst (Meille 2006). In fact, the catalytic activity might be reduced. In addition, diffusion is the process, in which the ions move from the solution to the active surface of the catalyst particle. As reported by Williams (2001), the smaller the particle size, the greater will be the resistance against which an ion must flow inside the active surface of particle. In addition, the active phase of the catalyst may not be uniformly distributed on the support but rather form localized aggregates leading to low contact of active surface in

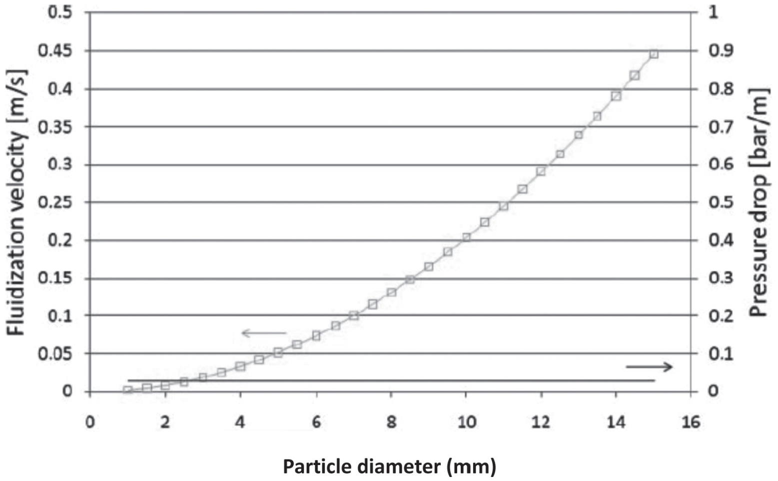


Fig. 2.11 Fluidized bed reactor velocities and pressure drop for the catalyst diameter (Adapted from Fjerbaek et al. 2009)

the catalyst (Wang et al. 2008). Thus, the efficiency of the catalyst and its feasibility at industrial scale might be reduced. Therefore, the design of a catalyst form at a macroscale (*millimeters in diameter*) is indispensable to avoid the problems in relation to the traditional catalysts.

There has been limited work to prepare alkali metal-based catalyst in macroscopic form to catalyze the transesterification reaction for biodiesel production. In a recent work, Wang et al. (2008) prepared a magnesia-rich magnesium aluminate spinel ($MgO{\cdot}MgAl_2O_4$) framework catalyst using γ-Al_2O_3 macrospheres (up to 1.0 mm in diameter) as a hard template. The process involves in situ growth of an magnesium–aluminum layered double hydroxides (MgAl-LDHs) precusor within the pore channels of the γ-Al_2O_3 template, followed by spinel formation and the selective removal of the template by leaching with alkali. The catalyst was used for methanolysis of soybean oil, and the biodiesel yield was also compared to that produced using $MgO/MgAl_2O_4/\gamma$-Al_2O_3 catalyst prepared by conventional impregnation of the γ-Al_2O_3 spheres with magnesium nitrate solution, followed by drying and calcination. However, the biodiesel yield obtained with both catalysts $MgO{\cdot}MgAl_2O_4$ and $MgO/MgAl_2O_4/\gamma$-Al_2O_3 were substantially low at 57 percent and 36 percent, respectively, after 10 hours of reaction. Furthermore, there has been no subsequent work to improve the biodiesel yield or to demonstrate the reusability of using macroscopic catalyst.

2.5 Preparation and Application of Macroscopic Catalyst in Biodiesel Production

Boehmite suspensions find wide applications as precursor materials for the preparation of macroscopic support (Islam et al. 2013b; Islam et al. 2012).The understanding on the rheological properties of the suspension is important for process control and optimization. Islam et al. (2012) and Tsai et al. (2007) studied the effect of aging time on rheology of alumina slurries, and Fauchadour et al. (2000) studied the peptization mechanism of boehmite suspension. Song and Chung (1989) studied the rheological properties of aluminum alkoxide in acid and basic solutions. In a similar approach, Moreno et al. (1997) and Schilling et al. (2002) studied the effect of additives on the rheology of alumina slurry.

One possible method involves the impregnation of a macroscopic support, such as a monolith of cordierite (a magnesium aluminosilicate with the formula $Mg_2Al_4Si_5O_{18}$) or silica fibers, with metal salts followed by calcination to give an oxide phase (Ogihara et al. 2007). One drawback of this approach, however, is that the active phase may not be uniformly distributed on the support but rather form localized aggregates. Furthermore, there may be a conflict between the properties of the active phase and the host, e.g., the acid–base characteristics of the host may alter the base catalyst properties of the metal oxide phase. Finally, the low porosity of the composite may limit the catalytic activity of the active phase. An alternative approach is to use a template to fabricate a continuous metal oxide phase; subsequent removal of the template affords a free-standing macroscopic metal oxide form with very high porosity (Davis 2002). The resulting materials have been employed in a variety of applications including as catalysts, catalyst supports, molecular sieves, and components of host–guest systems (Xia and Mokaya 2005). Both soft and hard templates have been employed in the synthesis of porous structures with various morphologies (Wakayama et al. 2001). Soft templates include surfactants (Kimura 2005) and biotemplates (Dong et al. 2007), which can subsequently be removed by combustion or extraction with an organic solvent. The hard template approach involves the fabrication of an inorganic framework from suitable inorganic molecular precursors in the pore channels of a material such as mesoporous silica or mesoporous carbon, followed by removal of the template by mineralization or combustion.

The millimetric particle was developed using two different approaches (Islam et al. 2012, 2013a); the integrative gelling process and the oil-drop granulation gelling process. The millimetric particle was prepared according to the method described by Prouzet et al. (2006). The apparatus for particles formation is depicted in Fig. 2.12. In a typical procedure, drops of the mixture suspension were progressively gelled and form particles that were left for aging in the gelifying solution consisting of $AlCl_3$ and $CaCl_3$ for 12 hours. The beads separated by simple filtration were subjected to the calcinations at different temperatures. It was reported by Islam et al. (2013a) that the spherical particles (sphericity

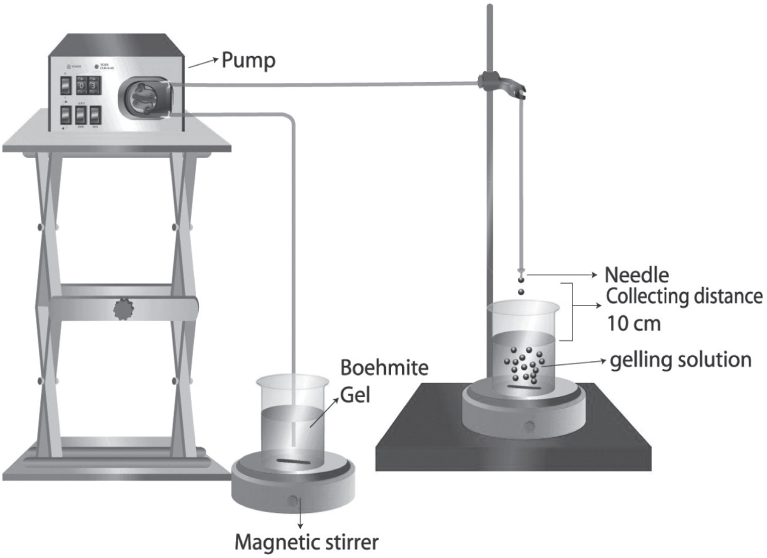


Fig. 2.12 Experimental set-up for production of boehmite-alginate particles (Adapted from Islam et al. 2012)

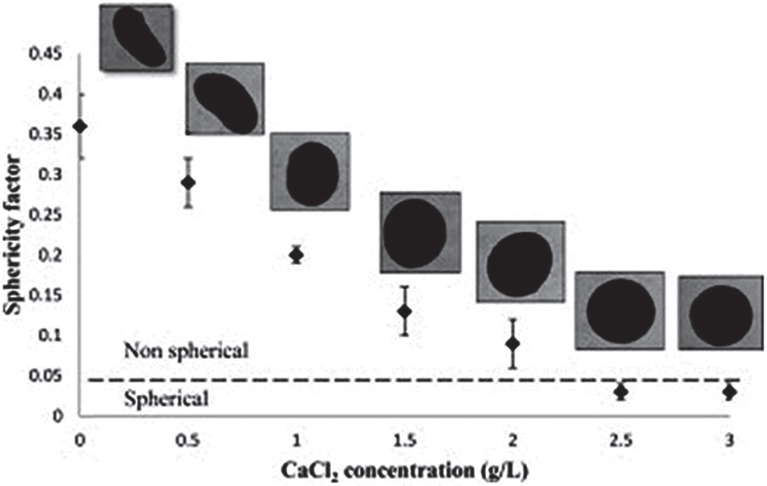


Fig. 2.13 Effect of sphericity of particle on the concentration of calcium chloride (Adapted from Islam et al. 2012)

factor = 0.03 ± 0.01) was obtained at the volume fractions of 2.5 g/L $CaCl_2$, followed by calcination at 800 °C, afforded a porous network of the particles (Fig. 2.13).

The size of a particle can be determined using Tate's law as described by Chan et al. (2009) from the following equation:

$$d_p = k k_{LF} (6 d_T \gamma / \rho g)^{1/3} = K (6 d_T \gamma / \rho g)^{1/3} \tag{2.17}$$

where, d_p is the overall diameter of bead (mm) and g is the gravitational force (m/s^2). γ and ρ are the surface tension (mN/m) and the density (kg/m^3) of the liquid, respectively.

The $k = k_g = k_a = k_c$ and k_{LF} defined as shrinkage factor and liquid lost factor, respectively, are calculated using Eqs. (2.18) to (2.20) and Eq. (2.21), respectively.

$$k_g = d_g / d_f \tag{2.18}$$

$$k_a = d_a / d_f \tag{2.19}$$

$$k_c = d_c / d_f \tag{2.20}$$

$$k_{LF} = 0.98 - 0.04 d_T \tag{2.21}$$

where, k_g, k_a, and k_c are the shrinkage factor of bead after gelling, after air-drying and after calcining, respectively. d_f, d_g, d_a, and d_c are the diameters of the bead while falling, after gelling, after air-drying, and after calcining, respectively. d_T is the dimensionless tip diameter (d_T) used in Eq. (2.21).

The progression of droplet injection at different stages was photographed by employing a digital camera (Canon, Japan) with a synchronized stroboscope light (Monarch, Nova-Strobe) having a frequency controller (100 to 14,000 flashes per minute). The resultant photographs of the bead were then transferred to image analyser software (SigmaScan Pro 5.0, SPSS Inc). Diameter of the beads at different stages was measured directly from the image analyser software, from which at least 100 measurements for each stage were analyzed to obtain an average value.

In the sol–gel processing, the granular γ-Al_2O_3 sorbents were prepared from the stable boehmite sols by the oil-drop method described in our previous publications (Wang et al. 1998). This established sol–gel CuO/γ-Al_2O_3 sorbent process consists of synthesis of boehmite sol from ALTSB or other precursor, doping the pseudo-boehmite sol with $Cu(NO_3)_2$, formation and shaping of wet-gel particles in oil, aging of the particles in ammonia solution, washing the particles, slow drying, and, finally, calcination to give the final granular sorbents. In the established synthesis process, the wet-gel particles extracted from the ammonia solution need to be sequentially washed with cold water, warm water, and alcohol to remove oil and ammonia, remnant of the dropping and aging steps. The washing step requires a large amount of washing solvent and also results in a loss of up to 25 percent of Al_2O_3. Elimination of this step is highly desired as this will minimize the generation of solvent waste, increase the efficiency of material utilization, simplify the process, and reduce the sorbent costs.

The granulation of the sorbents in the established process is performed in batch fashion, in which the sol drops are generated by manually squeezing the rubber head of a dropper. The wet-gel particles are collected in the bottom of the tank and removed batchwise from the bottom of the tank for subsequent washing, drying, and calcination. Practical application requires a continuous process that allows production of sorbents in a larger quantity, with better uniformity and high reproducibility (Buelna et al. 2001; Wang et al. 1998). This is usually accomplished by the conventional wet-impregnation method (Deng and Lin 1997; Centi et al. 1995). The wet-impregnation coating method involves (a) preparation of the support body, (b) bringing the support in contact with the liquid containing the active species precursor, (c) drying the coated support, and (d) calcination to convert the active species precursor to the final active species. Lin (2001) recently reported that the grain surface of sol-gel-derived ceramic membranes could be coated with metal oxides by a one-step solution–sol mixing method. Recently, millimetric gamma-alumina (γ-Al_2O_3) support was prepared using oil-drop granulation process. In brief, different amounts of boehmite powder (AlOOH) were suspended in water, followed by addition of acid to turn into gel. The resulting mix gel was then transferred drop wise by a peristaltic pump into a liquid column consisting of paraffin oil in the upper layer and ammonia solution in the bottom layer. The schematic presentation of the experimental system employed for the production of the particles is shown in Fig. 2.14.

Islam et al. (2012) had proposed oil-drop granulation method as an alternative approach to obtain porous structures of the millimetric

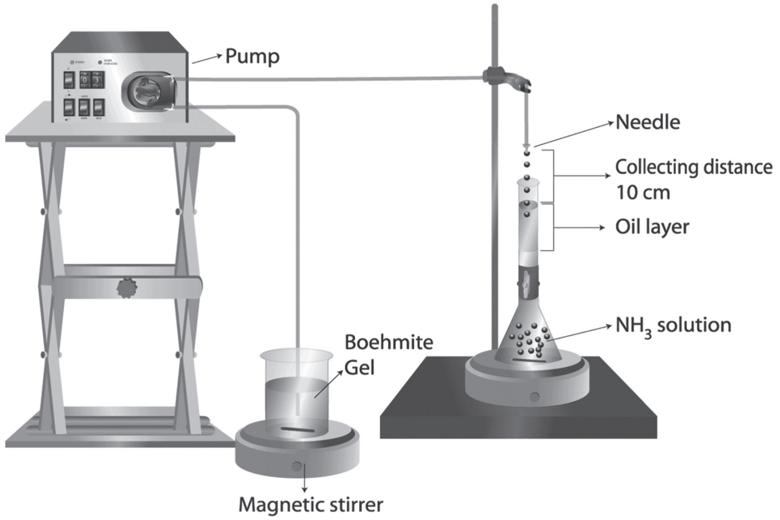


Fig. 2.14 Experimental set-up for production of boehmite-starch particles (Adapted from Islam et al. 2013c)

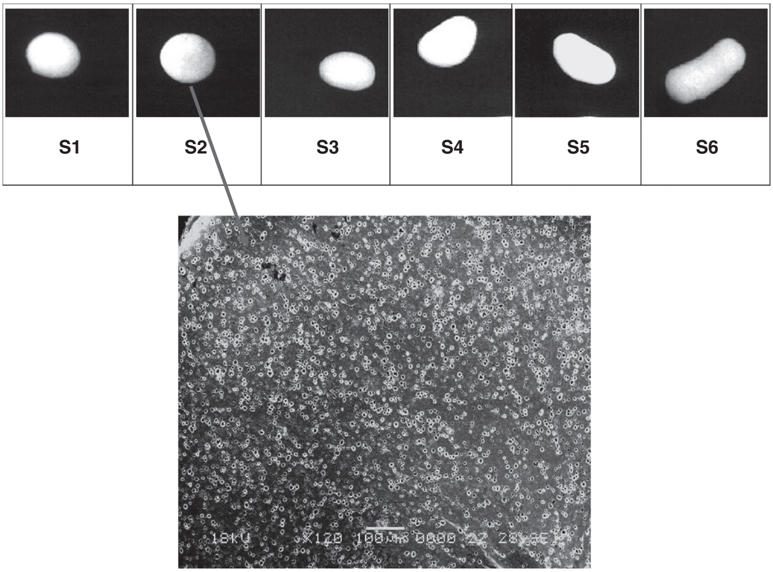


Fig. 2.15 Optical photograph shows the effect of boehmite concentration on sphericity factor of the particle (Adapted from Islam et al. 2012)

spherical particles (Fig. 2.15). The size of pore openings, also called cell windows or throats, often act as constrictions between connected pores to limit the flow of gas or fluid. A high degree of connected porosity and a hierarchical pore size distribution is typically required for catalysis applications to achieve high permeability, accessibility to the active surface area, and a low pressure drop (Čejka et al. 2007). More efficient catalytic processes require improvement in catalytic activity and selectivity. Both aspects will rely on the tailor-design of catalytic materials with desired structure and active site dispersion. Porous materials offer such possibilities with controlled large and accessible surface area (Čejka et al. 2007). It turns out this structure, a honeycomb of channels that run through the sphere, serves as a foundation for the development of tiny porous materials useful for a range of catalysis and biotechnological applications. Biodiesel production happens to be one of these applications, and the implementation of these tiny tools has been proven in the lab to alleviate several sticky points in the process.

The need for development of heterogeneous catalysts has arisen from the fact that homogeneous catalysts used for biodiesel development pose a few drawbacks discussed in previous sections. Easy separation, easy recovery, no problems in solubility, and miscibility are the strengths of a heterogeneous system in order to reduce the cost of production. Heterogeneous catalysis is thus considered to be a green process. Needless to say, because of these advantages, research on the transesterification reaction using heterogeneous catalysts for biodiesel production has increased over the past decade. Wang et al. (2008) reported the macrospherical spinel framework catalysts for methanolysis of soybean oil. According to authors, the enhancement of mechanical strength, specific surface area, pore volume, and pore size could be useful catalyst for biodiesel production (Fig. 2.16).

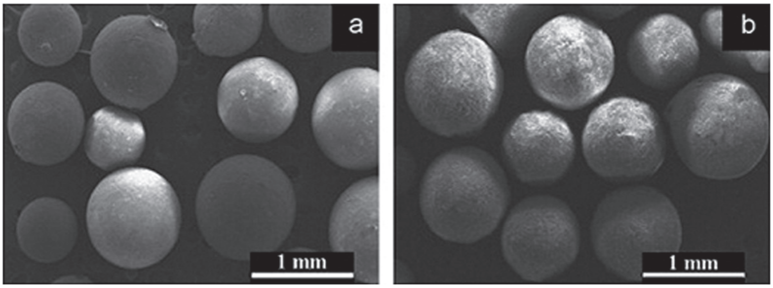


***Fig. 2.16** Typical SEM images of (a) γ-Al_2O_3 spheres and (b) spherical $MgO{\cdot}MgAl_2O_4$ frameworks (Adapted from Wang et al. 2008)*

During a catalytic reaction, reactants and products are transferred to and from the catalyst surface where the reaction occurs in an uninterrupted and repeated cycle of elementary steps such that the catalyst is regenerated to its original form in the last step. These steps as proposed by several researchers (Levenspiel 1972; Dumesic et al. 2008) given below:

1. Diffusion of reactants from the bulk fluid phase to the external surface of the porous catalyst particle.
2. Intraparticle diffusion of the reactants through the catalyst pores to the internal active sites.
3. Adsorption of reactants onto the active sites.
4. Reaction on the surface of the catalyst.
5. Desorption of products from catalyst surface.
6. Intraparticle diffusion of the products through the catalyst pores to the external surface of the catalyst particle.
7. Diffusion of the products from the external particle surface to the bulk of the fluid.

Enzyme catalyzed reaction using lipases provides a solution to the aforementioned problems as it is more efficient, highly selective, involves less energy consumption, and produces less waste (Hama and Kondo 2013). Glycerol recovery is easier in enzymatic process and high grade glycerol would be produced compared to an alkaline process (Gog et al. 2012). However, the drawbacks for the use of enzymes are: (a) low reaction rate (Zhang et al. 2003); (b) their cost (Meher et al. 2006b) for industrial-scale use 1,000 US$ per kg compared to 0.62 US$ (Haas et al. 2006) for sodium hydroxide. A comparative economics diagram of plant investment costs and manufacturing costs for one ton capacity of biodiesel by alkali, immobilized lipase, and soluble lipase-catalyzed transesterification has been reported by Jegannathan et al. (2011) as shown in shown in Fig. 2.17. The above results showed that the plant cost for biodiesel production using immobilized enzyme was 57.18 percent higher than the alkali catalyst process and 0.40 percent higher than soluble enzyme catalyst process. The high cost for both the soluble and immobilized catalyst process was due to the process time variation with respect to the alkali catalyst. Likewise, a marginal increase of plant cost for

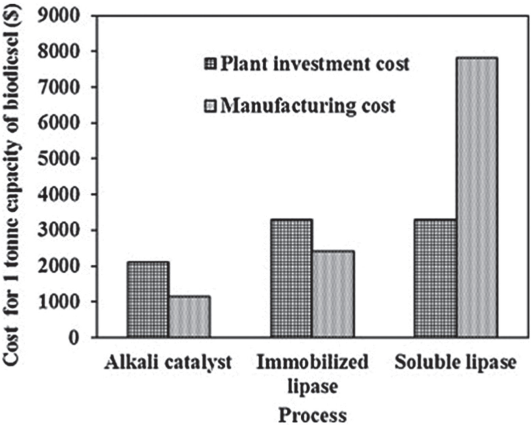


Fig. 2.17 Economic assessment of biodiesel production (Adapted from Jegannathan et al. 2011)

immobilized catalyst process over soluble enzyme process was due to the addition of encapsulation unit as reported by Jegannathan et al. (2011).

Extensive studies on transesterification reactions have been carried out using *C. Antarctica* lipase (Novozym 435), using a wide variety of substrates. The immobilized lipase by entrapment is much more stable than physically adsorbed lipase and unlike the covalent bonding method, this method uses a relatively simple procedure and at the same time the immobilized lipase maintains its activity and stability (Kennedy et al. 1990). A variety of methods have been used for trapping lipases in a polymer matrix (Bickerstaff 1997). Entrapment of enzymes in an inorganic polymer matrix is one method that has received a considerable attention in recent years. This method which was pioneered by Avnir et al. (1994) is based on sol–gel process. The application of the sol–gel material in the immobilization of lipases is well-documented (Reetz 1997). A substantial collection of research on the enzymatic transesterification of triglycerides has focused on free enzyme reactions with and without organic solvents. Alcoholysis of tallow with primary and secondary alcohols in the presence of solvents was first investigated using lipase from *C. Antarctica* by Nelson et al. (1996), and it was reported that the lipase was most suitable for transesterifing triglycerides with secondary alcohols for production of branched alkyl esters. Ultrasound assisted lipase-catalyzed reaction method witnesses a fast development. The enhancement of enzyme activity of Novozym 435 by ultrasound irradiation has been reported earlier (Yu et al. 2010). Yu et al. (2010) achieved a 96 percent yield of FAME from soybean oil in 4 hours with a combination of 50 percent of ultrasonic power and 50 rpm vibration. The improved reaction rate was attributed to the rapid emulsification by ultrasonic irradiation and sufficient contact between enzyme and substrate by vibration which caused accelerated transportation of reactants. Nasratun et al. (2009, 2010) immobilized *C. rugosa* lipase on chitosan beads to catalyze the transesterification of cooking oil with methanol which gave a FAME yield of 76.25 percent. Moreno-Pirajan and Giraldo (2011) immobilized *C. rugosa* lipase with activated carbon and used it for the enzymatic transesterification of palm oil with methanol and ethanol, which gave 70 and 85 mol% of methyl and ethyl esters, respectively. Jegannathan et al. (2010) reported that *Burkholderia cepacia* lipase encapsulated in κ-carrageenan by co-extrusion could be considered as a potential biocatalyst for eco-friendly biodiesel production, provided its reusability parameter could be increased to make it economically viable (Fig. 2.18).

Many types of lipases have been used, giving high yields with a large variety of oil, fats, and acylacceptors. High productivity, involving yield and numbers of reuse, as well as low reaction time, have been achieved, and further improvements such as pretreatment and reactor design can make industrial solvent free enzymatic biodiesel production an option for the future.

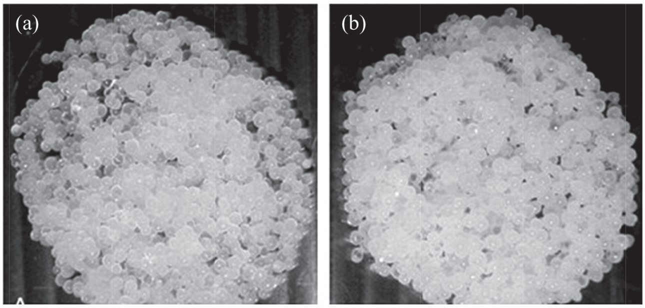


Fig. 2.18 Picture of κ-carrageenan encapsulated lipase before (a) and after (b) use in transesterification of palm oil with methanol (Adapted from Jegannathan et al. 2011)

CHAPTER 3

Intensification Process in Biodiesel Production

The breadth of biodiesel production technologies has exploded along with the expansive growth of the industry in the past several years. The biodiesel process continues to evolve as producers and researchers determine ways to refine production techniques. Occasionally, drastic design changes provide a new way of thinking about the transesterification process. As the process evolves there are opportunities for inventive technology. In the transesterification of vegetable oils, reaction rate can be limited by mass transfer between oil and alcohol because of the very poor mutual miscibility. Hence, some process intensification technologies have been developed and applied to improve mixing and mass/heat transfer between the two liquid phases in recent years. Reaction rate is greatly enhanced and thus residence time may be reduced. To reduce the limitations of mass and heat transfer in chemical reactions, literature indicates conducting these reactions in non-catalytic supercritical, ultrasound, or microwave conditions.

3.1 Non-Catalyzed Biodiesel Production

Biodiesel can be produced at a relatively fast rate without the presence of catalyst by heating up methanol to its supercritical stage. In a more recent development, non-catalytic supercritical transesterification with co-solvent provides a new way of producing biodiesel fuel from bio-based oils (triglycerides) (Gui et al. 2009). The supercritical method has the following advantages over other methods used for biodiesel production (Gui et al. 2009; Saka et al. 2001; He et al. 2007a):

a. Catalyst is not used in the reaction, and purification procedures are much simpler, since the separation process of the catalyst and the saponified product is not required;
b. The supercritical reaction requires shorter reaction time than the traditional catalytic transesterification, and the conversion rate is high. The catalytic transesterification requires, in some cases, hours to reach the reaction equilibrium, while supercritical method only minutes;
c. Low quality substrates can be used in the supercritical method, since high levels of free fatty acids (FFAs) and water do not have a negative effect on the reaction.

The reaction mechanism of supercritical transesterification was proposed by Kusdiana and Saka (2004a) as shown in Fig. 3.1. According to the mechanism, the alcohol molecule (methanol) directly attacks the carbonyl carbon of the triglyceride because the hydrogen bond energy is lowered, which would allow the alcohol to be a free monomer. In the case of methanol, the transesterification is completed via transfer of a methoxide

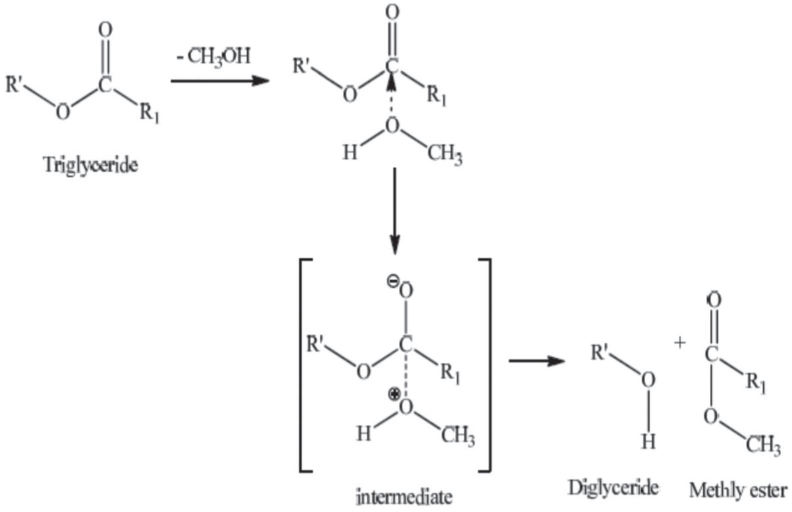


***Fig. 3.1** The proposed reaction mechanism of transesterification in supercritical methanol (R′ is a diglyceride group and R_1 is a fatty acid chain) (Adapted from Kusdiana and Saka 2004a)*

moiety, whereby fatty acid methyl esters (FAME) and diglycerides are formed. Consequently, the diglyceride reacts with other methanol molecules in a similar way to form the methyl ester and monoglyceride, the latter of which is further converted to methyl ester and glycerol in the last step. The same process is applicable to other primary alkyl alcohols, such as ethanol. Similarly, thermal cracking of unsaturated fatty acids, especially the polyunsaturated fatty acids, occurs at temperatures over 300 °C and reaction times over 15 minutes (Quesada-Medina and Olivares-Carrillo 2011). An example of the thermal cracking of a palmitic, oleic, and linoleic acid-based triglyceride is illustrated in Fig. 3.2. However, the glycerol may react at high temperature in different ways, as proposed by several researchers (Silva and Oliveira 2014; Markočič et al. 2013; Sanchez et al. 2014):

i. decomposition to produce products of lower molecular weight, such as acrolein, acetaldehyde, acetic acid, among others,
ii. polymerization to form polyglycerols, which occurs at high temperature conditions and
iii. etherification with methanol to produce ethers of glycerol, thus consuming the alcohol in the reaction medium.

A number of conversion pathways occur in the supercritical treatment of oils containing water and FFA (Fig. 3.3), as reported by Kusdiana and Saka (2004b). Many methods have been proposed for biodiesel production in supercritical (SC) technology, including SC methanol (He et al.

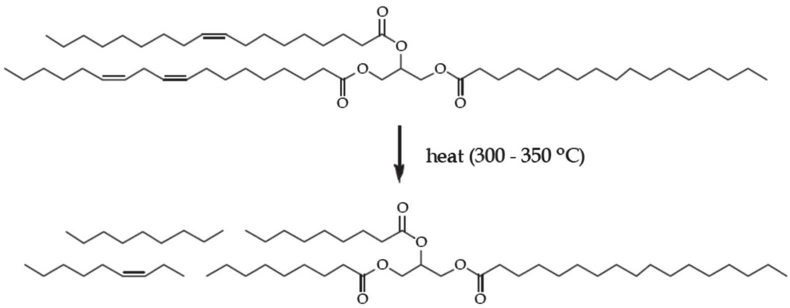


***Fig. 3.2** The thermal cracking reaction of a triglyceride under supercritical conditions at a temperature range from 300 °C to 350 °C (Adapted from Quesada-Medina and Olivares-Carrillo 2011)*

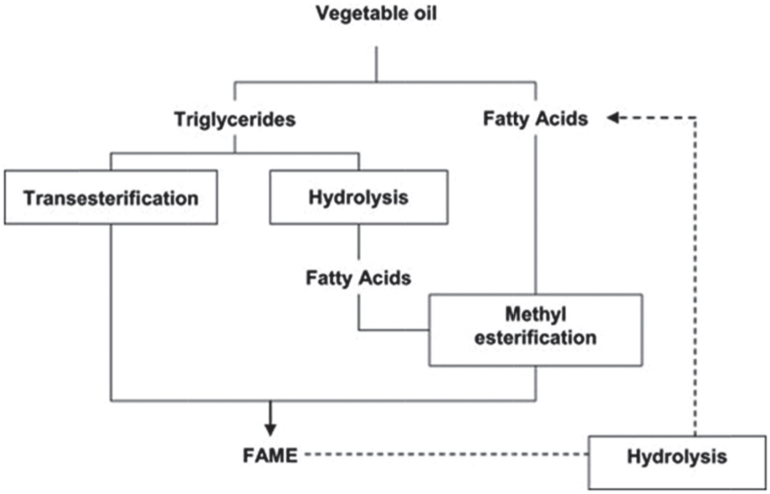


Fig. 3.3 Interactions between reactions in the supercritical treatment of oils containing water and FFA (Adapted from Kusdiana and Saka 2004c)

2007; Kasim et al. 2009; Hawash 2009; Kusdiana et al. 2001; Madras et al. 2004; Tan et al. 2009; Yin et al. 2008), SC ethanol (Gui et al. 2009; Madras et al. 2004), SC methanol with CO_2 as a co-solvent (Kasim et al. 2009), SC dimethyl carbonate (Ilham et al. 2009), SC carbon dioxide with enzyme (Madras et al. 2004), and SC with calcium oxide (Demirbas 2007a). The summarization of non-catalyzed biodiesel production is given in Table 3.1.

He et al. (2007) subjected soybean oil to transesterification process in the absence of catalyst with the supercritical methanol and found that the maximum biodiesel yield can be obtained at 310 °C. Lee et al. (2012), in the synthesis of biodiesel from waste canola oil, reported that side reaction was obtained by reacting glycerol and supercritical methanol at 543 K/10 MPa for 15, 30, and 45 minutes. The experimental results showed that these reactions could positively affect the overall biodiesel yield by providing oxygenated compounds such as 3-methoxy-1,2-propanediol, dimethoxymethane, and 2,2-dimethoxypropane as well methyl palmitate and methyl oleate. However, the side reactions of unsaturated FAME at reaction temperature above 300 °C lead to much loss of material (He et al. 2007a). It was

Table 3.1 ***Summarization of non-catalyzed biodiesel production***

Methanol/Oil	Oil	RT (°C)	MFP	FY (%)	P (bars)	SF	References
40:1	Sunflower	350	1.45	96	200	SCM	Madras et al. (2004)
41:1	Rapeseed	350	16	95	450	SCM	Saka and Kusdiana (2001)
40:1	Soybean	310	1.87	77	250	SCE	He et al. (2007)
41:1	Cottonseed	230	7.53	98	–	SCM	Demirbas (2008)
41:1	Cottonseed	230	5.76	75	–	SCE	Demirbas (2008)
42:1	Soybean	280	1.8	90	350	SCM	He et al. (2007a)
271:1	Rice bran oil	300	–	51.28	300	SCM	Kasim et al. (2009)
271:1	DDRBO	300	–	94.84	300	SCM	Kasim et al. (2009)
41:1	Linseed	287	1.992	99.6	–	SCM	Demirbas (2009)
42:1	Rapeseed	350	4.7	94	200	SDC	Ilham et al. (2009)
43:1	Jatropha	320	16.66	100	84	SCM	Hawash et al. (2009)
33:1	Palm	349	1.584	79.2	–	SCE	Gui et al. (2009)
41:1	Linseed	250	7.538	98	–	SCM	Demirbas (2009)
41:1	Sunflower	252	2.204	97	81	SCM	Demirbas (2007a)

FAME Yield (FY) = FAME (g)/ Oil (g), Reaction temperature (RT), Pressure (P), Supercritical fluid (SF), Supercritical Dimethyl Carbonate (SDC), Supercritical Ethanol (SCE), Supercritical Methanol (SCM), dewaxed-degummed rice bran oil (DDRBO).

pointed out that gradual heating procedure could effectively reduce the loss of materials caused by the side reactions of unsaturated FAME, but the high temperature is still very much energy intensive for biodiesel production (He et al. 2007a). To solve this problem, the use of methanol with CO_2 as a co-solvent has been suggested, since they are able to reduce supercritical temperature during production of biodiesel (Kasim et al. 2009). Since supercritical CO_2 is a good solvent for vegetable oil, it allows the reaction mixture to form a single phase which will accelerate the reaction rate at lower temperature (Pinnarat et al. 2008; Yin et al. 2008). Therefore, it could offer a potentially low cost method with simpler technology for biodiesel production. It was reported by Abbaszaadeh et al. (2012) that the CO_2 as a co-solvent provide in a single phase that takes only seconds at ambient temperature and pressure (Fig. 3.4). A somewhat related conclusion has been reached by Pinnarat and Savage (2008) who reported that the CO_2 is a good solvent to allow reaction mixture in a single phase at relatively lower temperature. This could be achieved through the presence of co-solvent molecules which enhanced the local density of the mixture homogeneity by attracting solvent around them (Marulanda et al. 2009). Thus, the supercritical method with co-solvent could provide improved phase solubility, decrease mass transfer limitations, and provide higher reaction rates.

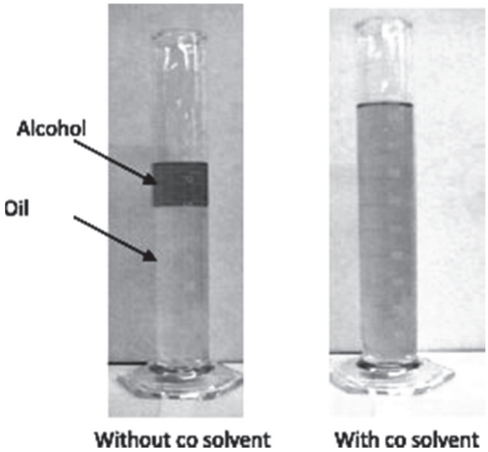


Fig. 3.4 Mixture of oil and alcohol with and without the use of co-solvent (Adapted from Abbaszaadeh et al. 2012)

The influence of process parameters has been investigated for non-catalytic transesterification to optimize the biodiesel content (Demirbas 2007b; Gui et al. 2009). Good results in transesterification of *Jatropha* oil were obtained by Hawash et al. (2009), using supercritical methanol in absence of a catalyst. They found that 100 percent yield of esters can be obtained using super critical methanol within 4 minutes only, at a temperature of 320 °C and under a pressure of 84 bar. Similar results have been reported by Ilham et al. (2009). After 12 minutes of reaction at 350 °C and pressure 200 bar rapeseed oil treated with supercritical dimethyl carbonate reached 94 percent yield of FAME. Likewise, the conversion was 96 percent in case of coconut oil and palm kernel oil over the same temperature range with molar ratio of methanol to oil 1:4 and the reaction time of 10 minutes (Bunyakiat et al. 2006). Other results consistent with these findings are from Silva et al. (2007) and Ilham et al. (2009). However, the conversion below the solvent critical temperature is very low (Silva et al. 2007). It should be noted that the critical temperatures of methanol and ethanol are 240 °C and 243 °C, respectively, and, therefore, the conditions at 200 °C represent a subcritical state of the medium (Madras et al. 2004). Consequently, above the critical temperatures, the results indicate that high transesterification can be obtained at supercritical conditions in the absence of added catalysts. According to Antoine's formula, pure methanol is no longer valid and predicts a higher pressure than that displayed by any of the mixtures tested. The effect of pressure–temperature on co-solvent was proposed by D'ippolito et al. (2007), shown in Fig. 3.5. It was reported that lower amount of co-solvent was needed for lower MeOH/TG ratios. The lower pressure of the MeOH–oil-co-solvent solutions is readily explained by the formation of true solutions in which the components do not exert their pressure independently but they contribute proportionally to their composition in the mixture (D'ippolito et al. 2007).

Some other researchers also claimed that the yield drastically increased when the temperature was changed from subcritical to supercritical state for transesterification with methanol or ethanol (Yin et al. 2008; Madras et al. 2004). This could be due to the absence of mass transfer interphase under these conditions to limit the reaction rate. Another positive effect of using supercritical conditions is that the alcohol behaves not only as

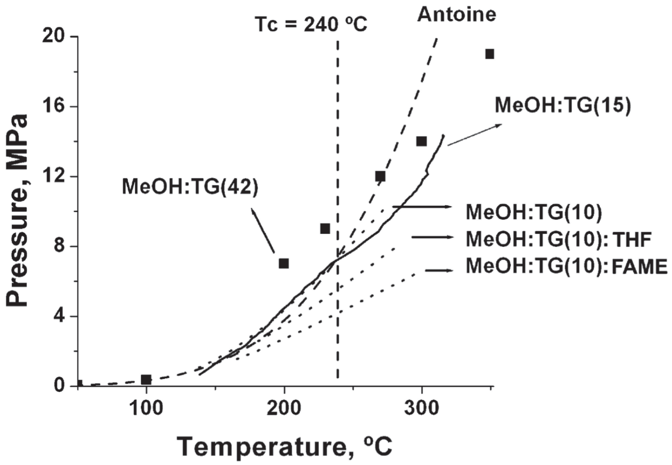


Fig. 3.5 The effect of pressure–temperature on co-solvent. The dashed line corresponds to Antoine's correlation for the vapor pressure of pure methanol (Adapted form D'ippolito et al. 2007)

a reactant but also as an acid catalyst (Kusdiana et al. 2004a). Moreover, the three types of reactions (transesterification, hydrolysis of triglycerides, and alkyl esterification of fatty acids) might be taking place simultaneously at high temperature when water and FFAs are present in the feed (Suwannakarn et al. 2009).

Other studies have also reported a lower yield of FAME when the temperature was increased above the critical temperature of reactant/product mixture (Gui et al. 2009). The lower activity was explained by the decomposition associated with the reactant/product mixture above the critical temperature. The influence of different alcohols on supercritical transesterification has also been investigated (Saka et al. 2001; Kusdiana et al. 2001; Gui et al. 2009). For instance, in methanol, the conversion increased from 78 percent to 96 percent with the increase in temperature. A similar trend was observed for conversions in ethanol but the conversions were higher. Higher conversions in ethanol may be attributed to the solubility of the oil in the system (Saka et al. 2001; Kusdiana et al. 2001). Because the solubility parameter of ethanol is lower than that of methanol and is closer to the solubility parameter of the oil, the conversions are higher in ethanol compared to the conversions obtained in methanol (Madras et al. 2004). Saka and Isayama (2009) developed an alternative new process

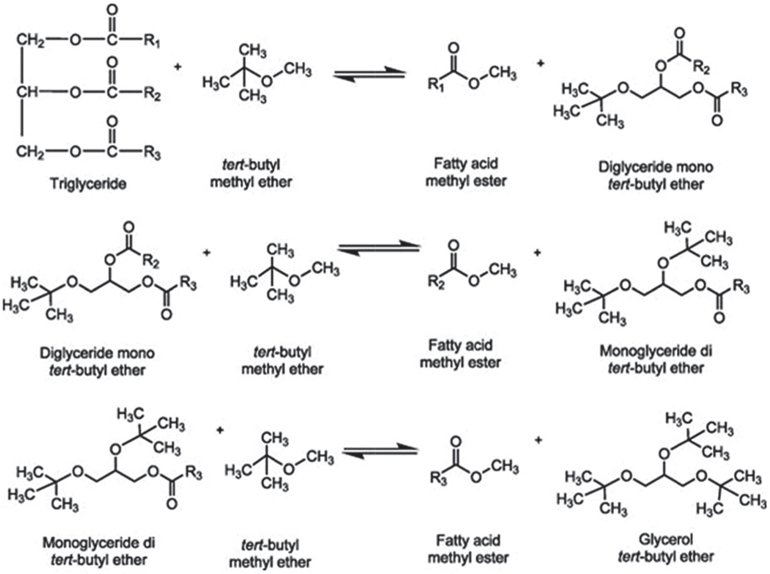


Fig. 3.6 Scheme of the reaction mechanism in transesterification of triglyceride in supercritical MTBE (Adapted from Farobie et al. 2014)

with other potential reactants such as methyl formate and methyl acetate of carboxylate esters to produce FAMEs (biodiesel) with triacin from oils and fats without producing glycerol. A FAME yield of 0.94 was obtained in a short reaction time of 12 minutes at 400 °C, with a molar ratio of MTBE-to-oil of 40:1, and under a pressure of 10 MPa. Recently, Farobie et al. (2014) reported a novel approach for biodiesel production from canola oil in supercritical tert-butyl methyl ether (MTBE) without the addition of a catalyst. The reaction characteristic of canola oil and MTBE has been proposed by Farobie et al. (2014), as shown in Fig. 3.6. The reaction mechanism of biodiesel production in supercritical MTBE proposed by Farobie et al. (2014) comprises three consecutive reversible reactions. First, the triglyceride reacts with MTBE to produce diglyceride mono tert-butyl ether (DGE), and then this intermediate moiety further reacts to generate monoglyceride di tert-butyl ether (MGE). Finally, MGE reacts with MTBE to yield FAME GTBE as by-products.

A potentially applicable to the biodiesel production using single step non-catalytic esterification method has been proposed by Cho et al. (2012) (Fig. 3.7). The recent progress in supercritical biodiesel (FAME)

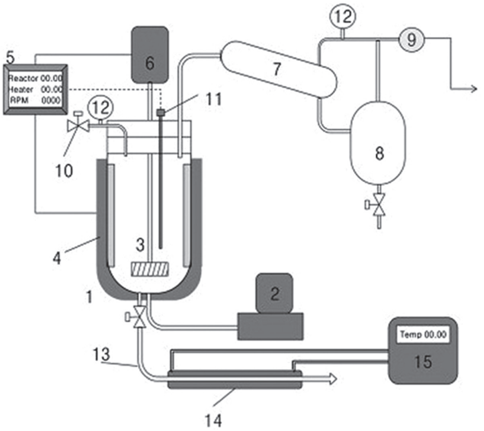


Fig. 3.7 Schematic diagram of the reaction system for non-catalytic esterification. 1. Reactor (internal volume: 2L); 2. Methanol feed pump; 3. Impeller; 4. Electrical heater jacket; 5. Temperature and RPM controller; 6. Motor; 7. Condenser; 8. Receiver; 9. Pressure regulator; 10. Nitrogen charging line; 11. Thermocouple; 12. Pressure gauge; 13. Sampling line, 14. Cooler (double jacketed); 15. Chiller

production is the two-step method. To improve the biodiesel quality, Kusdiana and Saka (2004a) and Minami and Saka (2006) proposed the continuous synthesis of biodiesel from canola oil in two reaction steps (Fig. 3.8), which consists primarily in the hydrolysis of triglycerides in pressurized water and subsequent esterification of fatty acids in supercritical methanol, with glycerol removed prior to FFA methyl esterification. This process is carried out under more moderate temperature and pressure compared to the process in one step. These new methods are highly tolerant against the presence of water in oils/fats, thus, being applicable for various oils/fats including their wastes for biodiesel production (Adapted from Kusdiana and Saka 2004a).

As reviewed by Pinnarat et al. (2008), transesterification under supercritical reaction condition has overcome the problems associated with acid- or base-catalyzed transesterification process. Many of the evidences have supported the technological and economic feasibility of biodiesel production under supercritical condition without catalysts. However, the decomposition of products at high reaction temperature is also supported by the recent finding by Imahara et al. (2008). It was reported that

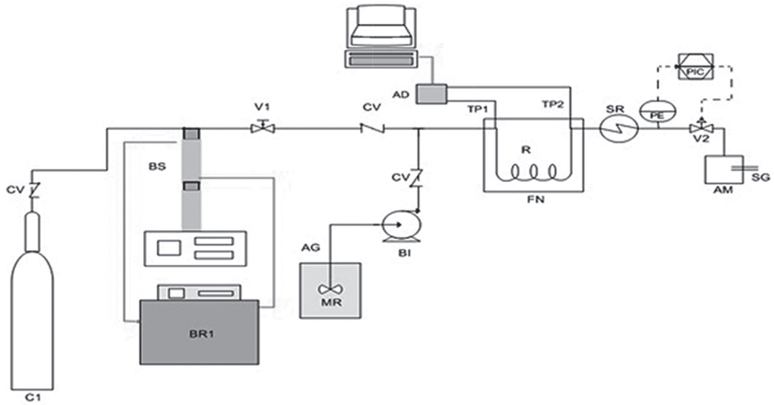


Fig. 3.8 Schematic diagram of the experimental apparatus. RM—reactional mixture; MS—mechanical stirring device; LP—high-pressure liquid pump; CV—check-valve; A—solvent reservoir; B—thermostatic baths; SP—syringe pump; F—furnace; R—reactor; T1—temperature indicator at the reactor inlet; T2—temperature indicator at the reactor outlet; DA—data acquisition system; CS—cooling system; V1—feed valve; PI—pressure indicator; PIC—controller; V2—pressure control valve; S—glass collector; G—gas output (Adapted from Silva et al. 2010)

unsaturated FAMEs were unstable and started to decompose at temperatures above 300 °C. At high temperatures, unsaturated fatty acids such as oleic acid and linoleic acid tend to decompose via isomerization of the double bond functional group from cis-type carbon bonding (C=C) into trans-type carbon bonding (C=C), which is naturally unstable fatty acids (Imahara et al. 2008). Thus, the decomposition nature of the glycerol at high temperature could be exploited.

3.2 Microwave Assistant Biodiesel Production

Microwave ovens were introduced into homes, and their popularity has continued to grow in 1954. Microwave irradiation is a form of energy that resides fairly low in the electromagnetic spectrum. It is slightly higher in frequency than radio waves, but much lower than X-rays, ultraviolet light, and other chemical bond-breaking forms of energy (Stuerga 2006). As a result, bonds are neither formed nor broken by microwave irradiation—it simply acts as an energy source, rapidly transferring energy to the sample.

Although microwave technology is widely used in homes, it has many other uses outside of the home. In fact, in industrial applications, microwaves are used for product drying, moisture and fat analysis of food products, solvent extraction applications, and to irradiate coal to remove sulfur and other pollutants. Since the late 1960s microwave technology has promised to be the "next big thing" for industrial chemical processing for almost half a century. Processors recognize microwave's potential to limit their carbon footprint and cut operating costs by reducing energy. In the 1970s, many industries began to explore the use of the new microwave technology for industrial and chemical processing. However, the home models were not reliable or rugged enough to withstand the rigors of laboratory use. More importantly, they were unsafe for use with chemicals due to the possible build-up of flammable vapors. These issues were addressed in the late 1990s with the introduction of microwave equipment specifically designed for use in laboratories. The microwave energy quantum is given by the well-known equation (Eq. 3.1):

$$W = h\nu \tag{3.1}$$

where, h is Planck's constant and ν is the radiation frequency. Within the frequency domain of microwaves and hyper frequencies (300 MHz–300 GHz), the corresponding energies are $1.24 \times 10.6 - 1.24 \times 10.3$ eV, respectively. These energies are much lower than ionization energies of biological compounds (13.6 eV), of covalent bond energies such as OH^- (5 eV), hydrogen bonds (2 eV), van der Waals intermolecular interactions (lower than 2 eV), and even lower than the energy associated with Brownian motion at 37 °C ($2.7\ 10^{-3}$eV) (Metaxas and Meredith 1983; Peterson 1994; Chemat-Djenni et al. 2007). Microwave irradiation is the electromagnetic irradiation with frequency range of from 0.3 to 300 GHz (Kappe and Dallinger 2005). They lie in the electromagnetic spectrum between infrared waves and radio waves with wavelengths between 0.01 and 1 m. Telecommunication and microwave radar equipment occupy many of the band frequencies in this region. In order to avoid interference with these systems, the household and industrial microwave ovens operate at a fixed frequency of 2.45 GHz (Surati et al. 2012). Typical bands approved for industrial applications are 915 and 2,450 MHz. Most of the reported microwave chemistry experiments are conducted at 2,450 MHz, since this frequency is approved worldwide and used in currently available commercial microwave chemistry equipment (Mende et al. 2004). Microwave heating offers several advantages over conventional heating (Varma 2001; Refaat 2010; Clark and Sutton 1996) are given below:

Benefits

- Cost savings (time and energy, reduced floor space),
- Rapid heating of thermal insulators (most ceramics and polymers),
- Energy transfer instead of heat transfer (penetrative radiation),
- Precise and controlled heating (instantaneous odoff heating),
- Selective heating,
- Volumetric heating, fast start-up and stopping, and reverse thermal effect, i.e., heat starts from the interior of material body,
- Short processing times,
- Improved quality and properties,
- Synthesis of new materials,
- Processing not possible with conventional means,
- Reduction of hazardous emissions,
- Increased product yields,
- Environmentally friendly (clean and quiet),
- Self-limiting heating in some materials,
- Power supply can be remote,
- Clean power and process conditions,
- Microwaves, as an energy source, produce heat by their interaction with the materials at molecular level without altering the molecular structure.

Challenges:

- Heating low-loss poorly absorbing materials,
- Controlling accelerated heating (thermal runaway),
- Exploiting inverted temperature profiles,
- Eliminating arcing and controlling plasmas,
- Efficient transfer of microwave energy to work piece,
- Compatibility of the microwave process with the rest of the process line,

- Reluctance to abandon proven technologies,
- Timing,
- Economics.

In terms of biodiesel production, the resultant value could include more effective heating, fast heating of catalysts, reduced equipment size, faster response to process heating control, faster start-up, increased production, and elimination of process steps (Chemat-Djenni et al. 2007). Energy efficiency of the microwave energy is the ratio of the observed resultant temperature effect to the total energy supplied to the sample as in the following equations (Nüchter et al. 2004; Kuhnert 2002):

$$Q_{mw} = P_{mw}t \tag{3.2}$$

$$Q_{th} = mc_p\Delta T \tag{3.3}$$

$$\eta = \frac{Q_{th}}{Q_{mw}} \tag{3.4}$$

η is the efficiency factor, P_{mw} is the available microwave power, and Q_{th} is the energy required to reach a certain temperature. The energy efficiency of the microwave-assisted reactions depends on several factors such as the sample volume, nature of the medium (solvents), dissipation level of the microwave device, and the penetration depth of the microwaves required in the reaction sample volume (Nüchter et al. 2004; Strauss et al. 1995). Poor efficiencies can be observed when a high power microwave device is used for a very small sample volume (Rao et al. 1999). It is very important to consider the effective level of power dissipation in microwave-assisted chemical synthesis to eliminate the energy losses to the surroundings.

Methanol is a strong microwave absorption material and, in general, the presence of an OH group attached to a large molecule behaves as though it were anchored to an immobile raft and the more localized rotations result in localized superheating which assists the reaction to complete faster (Tierney and Lidstrom 2004). Microwave effect on the transesterification reaction can be two-fold: (1) enhancement of reaction by a thermal effect and (2) evaporation of methanol due to the strong microwave interaction of the material (Loupy et al. 1993; Yuan et al.

2009). The microwave interaction with the reaction compounds (triglycerides and methanol) results in large reduction of activation energy due to increased dipolar polarization phenomenon (Perreux and Loupy 2001). The amount, by which the activation energy is reduced, is essentially dependent on the medium and reaction mechanism (Perreux and Loupy 2001). For this reason, methanol is preferred over ethanol for microwave-assisted transesterification process (Yuan et al. 2009).

Numerous studies (Clark et al. 1996; Roy et al. 1999; Lin et al. 2013) have shown that microwave heating system has better performance when compared with conventional heating system, and offers a fast route of biodiesel production, which is also more energy-efficient and cost-effective (Fig. 3.9). Mazzocchia et al. (2004) conducted a series of transesterification reactions under microwave irradiation. The transesterification reactions were carried out on rapeseed oil with barium hydroxide as the catalyst and methanol as the alcohol. The tests were conducted with a rapeseed oil to methanol molar ratio of 1:9, 1:18, and 1:30 and with different catalyst concentrations. The best result obtained by the author was 99 percent conversion, with oil:alcohol molar ratio of 1:9, 1.5 percent catalyst loading, 3.5 bar and 376 K for 10 minutes. In another study by Lertsathapornsuk et al. (2008) a domestic microwave oven (Ecolux, 800 W, 2450 Hz) was modified and used as a continuous reactor in biodiesel synthesis from waste palm oil containing 4.5 percent FFA. The oil was treated with an alkaline alcoholic solution containing 3.0 percent NaOH in ethanol. Part of the added NaOH was used in the

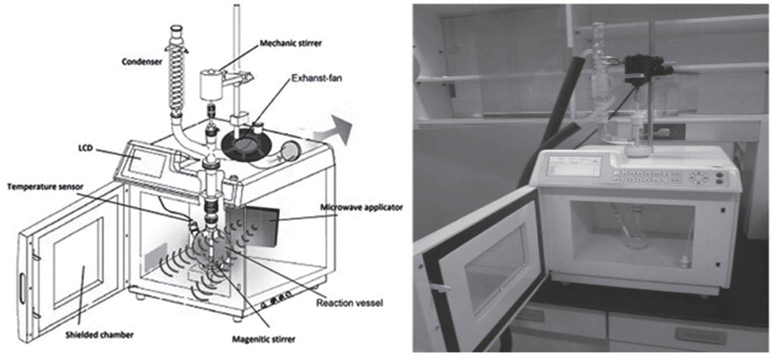


Fig. 3.9 Experimental setup of microwave assistant biodiesel production (Adapted from Lin et al. 2013)

neutralization of the FFA, and the rest served as a catalyst for the transesterification reaction. Initially, the authors used an oil:alcohol molar ratio of 1:6 and 3.0 percent NaOH for 30 seconds, which led to a conversion of only 30 percent of the residual oil. When the oil:alcohol molar ratio was increased to 1:9 and all other conditions were kept constant, the conversion of residual oil increased to 82 percent. In the same way, a third test was performed with an oil:alcohol molar ratio of 1:12 and the conversion reached over 97 percent.

Majewski et al. (2009) showed that 20 minutes is the optimal microwave reaction time since decreasing the hold time reduces the yields of biodiesel from corn and soybean oil. Microwave reaction times of 10 and 15 minutes have generally been proven to be inadequate, with 17.5 minutes being the threshold for an appreciable yield of biodiesel (>80 percent). El Sherbiny et al. (2010) indicated that the application of radiofrequency microwave energy enhances the reaction rate for the conversion of Jatropha oil to biodiesel. A high biodiesel yield (97.4 percent) was obtained. Venkatesh Kamath et al. (2011) found that an optimal combination of a 150-s irradiation time, a 33.4 wt% methanol–oil ratio, and a 1.33 wt% KOH (potassium hydroxide) concentration yielded 89.9 percent biodiesel from crude karanja oil. Hsiao et al. (2011) indicated that nanopowder calcium oxide was very efficient in converting soybean oil to biodiesel, and that microwave irradiation is more efficient than the conventional bath for biodiesel production. A 96.6 percent conversion rate was obtained with a methanol/oil molar ratio of 7:1, 3.0 wt% catalyst, a reaction temperature of 65 °C, and a reaction time of 60 minutes. Energy consumption studies show that the continuous-flow preparation of biodiesel (Fig. 3.10) using microwave heating proves to be more energy efficient than the conventional (non-microwave) synthesis of biodiesel in large tank reactors (Motasemi and Ani 2012; Lertsathapornsuk et al. 2008). Barnard et al. (2007) evaluated the energy consumption of batch and continuous microwave irradiation for biodiesel production (Table 3.2). It was reported that the continuous system is more energy efficient that conventional heating and batch microwave system.

Recently, the esterification of high FFA oil with catalytic membranes under microwave condition has been reported by Azcan and Yilmaz (2013) as a promising technique for biodiesel production in a

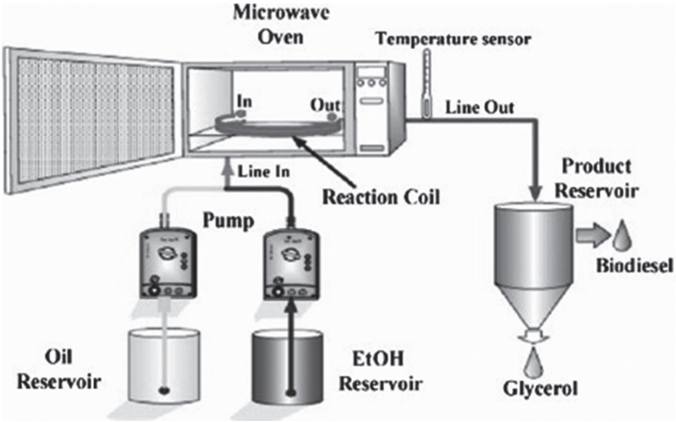


Fig. 3.10 Schematic diagram of a continuous microwave biodiesel production process (Adapted from Lertsathapornsuk et al. 2008)

Table 3.2 Comparison between energy consumption by conventional and microwave processes (Adapted from Barnard et al. 2007)

Method	Energy requirement (kJ/L)[a]
Conventional heating[b]	94.3
Microwave continuous flow (7.2 L/minutes feedstock flow)	26
Microwave continuous flow (2 L/minutes feedstock flow)[c]	60.3 (92.3)[d]
Microwave heating (4.6 L batch reaction)[e]	90.1

[a] Normalized for energy consumed per liter of biodiesel prepared.

[b] On the basis of values from the joint U.S. Department of Agriculture and U.S. Department of Energy 1998 study into life cycle inventory of biodiesel and petroleum diesel for use in an urban bus.

[c] Assuming a power consumption of 1700 W and a microwave input of 1045 W.

[d] Assuming a power consumption of 2600 W and a microwave input of 1600 W.

[e] Assuming a power consumption of 1300 E, a microwave input of 800 W, a time to reach 50 °C of 3.5 minutes, and a hold time at 50 °C of 1 minutes.

short reaction time with high product yield (Fig. 3.11). The highest biodiesel conversion (98.87 percent) was obtained using 1 wt% $NaOCH_3$, 1:6 WCO:methanol at 60 °C and 5 minutes reaction time. Further, low methyl ester content of biodiesel was enriched from 90.04 percent to 97.66 percent by molecular distillation, applying optimum molecular distillation conditions of 60 °C feed temperature, 170 °C evaporator temperature, 10 mbar pressure, 175 minutes −1 rotor velocity, and

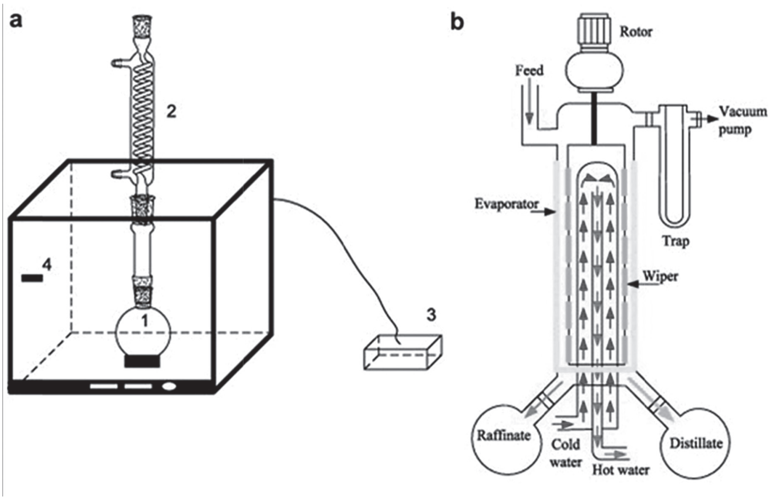


Fig. 3.11 (a) Microwave synthesis unit; (b) Molecular distillation unit. 1-glass reactor; 2-condenser; 3-control unit; 4-infrared temperature sensor (Adapted from Azcan and Yilmaz 2013)

0.24 mL/minutes feed flow rate. Thus, this technique could potential for biodiesel production.

Since waste and virgin oils are common feedstocks, restaurants could convert fryer oil into biodiesel on site for use as heating oil. Microwave irradiation is revolutionizing many different industrial applications, and biodiesel production is merely the latest field to see the impact of this technology. Implementing multiple microwave units could have a major impact on land, energy, and time savings compared with a single large reactor tank process. While microwave energy is still a relatively young technology in the biodiesel arena, it is a technology whose time has come.

3.3 Ultrasonic-Assistant Biodiesel Production

Many researchers have tried to solve the mass-transfer limitation problem in biodiesel synthesis using ultrasonic cavitation and hydrodynamic cavitation. It is well-known that as the ultrasonic power increases, the size of the cavitation bubbles increase leading to more intense collapse of bubble, which causes better emulsion formation of oil and methanol resulting into higher interfacial surface area for mass transfer and hence

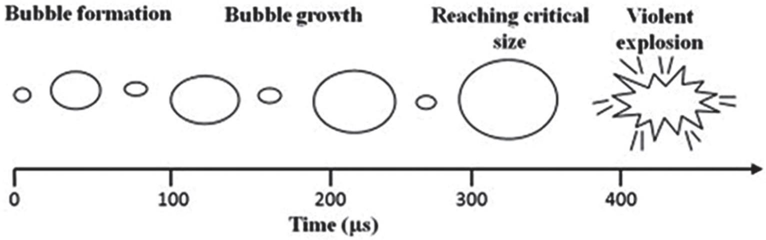


Fig. 3.12 Formation, growth, and collapse of a cavitation bubble (Adapted from Ji et al. 2006)

the higher biodiesel yield (Mahamuni and Adewuyi 2009). Ji et al. (2006) have reported that the bubbles are formed at zero time and undergoes breakdown after an approximate period of 400 μs (Fig. 3.12). These phenomena result in severe mixing between the two immiscible liquids close to the phase boundary and force the liquids to inspire micro jets which can reach to a speed up to 200 m/s. The cause for the micro jets generation is the asymmetric breakdown of the cavitation bubbles (Ji et al. 2006; Leighton 1995).

Radial motion of cavitation bubbles generates intense convection in the medium through two phenomena, viz. micro-convection, shock, or acoustic waves. Magnitudes of these entities can be determined using numerical result of bubble dynamics model as following equations:

Micro-convection (Shah et al. 1999; Parkar et al. 2012):

$$A_{\mathrm{turb}}(r,t) = \frac{R^2}{r^2}\frac{dR}{dt} \tag{3.5}$$

Shock waves (or acoustic waves) (Grossmann et al. 1997; Moholkar and Warmoeskerken 2003):

$$P_{AW}(r,t) = \frac{\rho}{4\pi r}\frac{d^2V_b}{dt^2} = \rho L\frac{R}{r}\left[2\left(\frac{dR}{dt}\right)^2 + R\frac{d^2R}{dt^2}\right] \tag{3.6}$$

where, V_b is the volume of the bubble. A representative value of r is taken as 1 mm.

The numerical solution of bubble dynamics model can give the temperature and pressure reached in the cavitation bubble at transient collapse, and also the number of gas and solvent molecules inside the bubble. Further it has been shown by other workers (Choudhury et al.

2014a) that the collapse of these bubbles lead to local transient high temperatures and pressures, resulting in the generation of highly reactive species. Due to extreme conditions reached in the bubble, the solvent as well as gas molecules undergo dissociation to form numerous chemical species, which also react among themselves. Due to very high temperature as well as concentration (due to extremely small volume of the bubble), the kinetics of the reactions among these species is several orders of magnitude higher than the time scale of bubble dynamics (Muley and Boldor 2013). The chemical effect attribute to the manifestation of the dissociation of alcohol to RO^- and H^+ on basic sites of catalyst surface (Fig. 3.13) while the physical effect depends on the intensity of mixing in the reaction system (Chorkendorff and Niemantsverdrie 2006). It was reported (Choudhury et al. 2014) that the physical mechanisms only responsible for the beneficial action of ultrasound was the formation of fine emulsion between oil and methanol. Due to this, the interfacial area between the reactants increases enormously, assisting to enhance the transesterification reaction. Thus, ultrasonic-assisted transesterification method presents advantages such as shorter reaction time and less energy consumption than the conventional mechanical stirring method, efficient molar ratio of methanol to TG, and simplicity (Ji et al. 2006; Siatis et al. 2006).

A high methyl ester yield can be achieved by ultrasound-assistant process at a lower reaction temperature, alcohol to oil molar ratio and reaction time than those achieved by conventional biodiesel production (Veljković et al. 2012; Yaakob et al. 2013). Gryglewicz (1999) found that in the methanolysis of rapeseed oil using calcium methoxide catalyst, reaction time reduced from 150 to 45 minutes for 93 percent FAME yield when ultrasonic bath (25 kHz, 300 W) without temperature control

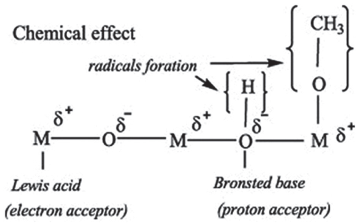


Fig. 3.13 Chemical effect of ultrasound on biodiesel production (Adapted from Islam et al. 2014)

was used compared to the conventional reaction under refluxing condition. Georgogianni et al. (2009b) studied the ultrasonic transesterification (24 kHz, 200 W) of rapeseed oil using Mg/MCM-41, MgAl hydrotalcite, and K/ZrO_2 catalysts. At 60 °C and 10 percent catalyst loading, and very high methanol/oil mole ratio of 285:1, biodiesel yields of 89 percent, 96 percent, and 83 percent were obtained after 300 minutes using Mg/MCM-41, MgAl hydrotalcite, and K/ZrO_2 catalyst, respectively. Mootabadi et al. (2010) also studied the ultrasonic transesterification (20 kHz, 200 W) of palm oil and obtained improvement of 75 percent, 47 percent, and 30 percent over magnetically stirred system for CaO, SrO, and BaO catalysts, respectively. Kumar et al. (2010) studied the performance of an immobilized catalyst and prepared a supported Na/SiO_2 catalyst to investigate the effects of ultrasonication on the transesterification process. Under the optimum conditions and with the use of Jatropha curcus oil as feed stock, the biodiesel yield was achieved as 98.53 percent with 15 minutes of reaction time.

Deng et al. (2011) prepared nano-sized mixed Mg/Al Oxides. Due to of their strong basicity, the nano particles were further used as catalyst for biodiesel production from Jatropha oil after pretreatment. Experiments were conducted with the solid basic catalyst in an ultrasonic transesterification reaction under different conditions. At the optimized condition, biodiesel yield of 95.2 percent was achieved. Qian et al. (2010) have recently exposed the reaction mixture in the frequency range between 20 and 48 kHz. The biodiesel yield was found to be increased with increase in the ultrasonic intensity up to 1.01 W/cm^2. Ren et al. (2010) newly discussed that the highest biodiesel yield of 98.7 percent was obtained at 53.3 W/dm^3 in the range of ultrasonic sound energy varied from 26.7 to 66.7 W/dm^3.

Gude and Grant (2013) reported that the transesterification reaction can be completed in a very short reaction time as much as 1990s even without any temperature control settings via direct sonication. A similar method has been used by Shahraki et al. (2015) who attempted to study the biodiesel from soybean oil by KF/γ-Al_2O_3 as a nano-solid-base catalyst (Fig. 3.14). The premise for this approach lies in the fact that ultrasonics induce intense mixing due to continuous compression and rarefaction cycles which cause the cavitational bubbles to generate with super high local temperatures and pressures. This phenomenon automatically

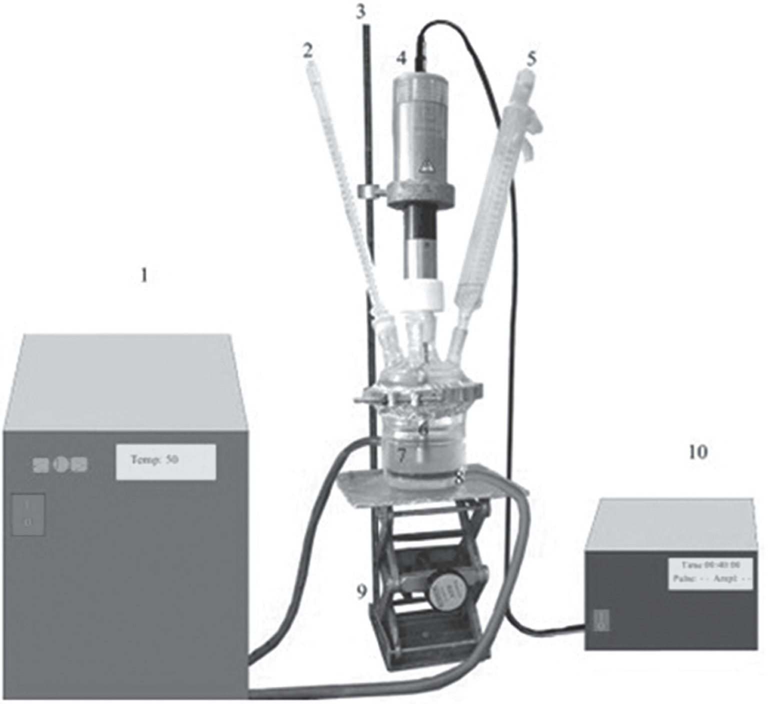


Fig. 3.14 Experimental setup used for the synthesis of biodiesel: (1) circulator, (2) thermometer, (3) laboratory stand, (4) transducer, (5) condenser, (6) horn, (7) biodiesel, (8) glycerol, (9) laboratory jack, and (10) ultrasonic generator (Adapted from Shahraki et al. 2015)

increases the temperature of the bulk of the sample medium with disruption of the microbubbles and promotes the desired chemical reactions (Shahraki et al. 2015).

Recently the two-step process with ultrasonic irradiation was shown to be effective and time-saving for biodiesel production (Thanh et al. 2010) and schematically shown in Fig. 3.15. In one-step processes biodiesel yield after 4 hours were 47.2 percent (with a saponification problem) while in the two-step process, the biodiesel yield of 96.4 percent was achieved in 1.5 hours (Deng et al. 2010). According to the process (Deng et al. 2010; Badday et al. 2012; Thanh et al. 2010), waste cooking oil and KOH dissolved in methanol were pumped at a desired ratio to the first reactor where ultrasonic irradiation was provided. The reaction mixture flow rates were kept between 0.5 and 2.5 L/minutes. After that,

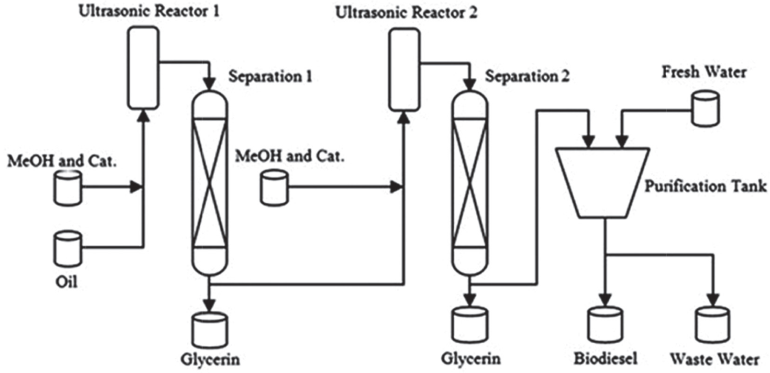


Fig. 3.15 Flow diagram of two-step continuous process for biodiesel production (Adapted from Thanh et al. 2010)

the mixture was fed into a separation unit where phase separation took place. The upper layer that contained FAME, triglyceride and amounts of diglyceride and monoglyceride were fed to the second reactor which was also provided with ultrasonication. As in the first stage, the second one was followed by phase separation unit to collect the final product of FAME. This final product was then sent to a purification unit to extract the remaining catalyst and the excess of methanol.

The formation of much smaller methanol droplets in ultrasonic mixing leads to improved methanol and catalyst utilization in biodiesel production, thereby lowering the usage of methanol and catalyst. Additionally, ultrasonic cavitation influences the reaction kinetics, leading to a faster reaction and more complete conversion. However, following considerations should be taken into account to improved ultrasound biodiesel production (Luo et al. 2014; Hsiao et al. 2012; Deshmane et al. 2008):

- Direct sonication could be improved the reaction kinetics.
- Addition of a second organic solvent or surfactant could be enhanced performance and efficiency of ultrasonic cavitation.
- Reactor design and optimization of parameter could reduce the consumption of energy.
- Analysis on the mechanism and kinetics levels with theoretical methods and simulation could be traced real challenge in high-intensity ultrasound application.

- The distribution of ultrasonic energy in the scaled reactor was seriously non-uniform.
- Single-celled morphology of microalgae is not easy to be degraded by ultrasound and may require for ultrasonic intensity higher than that in starch treatment.
- Micron-/nanosize of lignocellulosic particles in suspension, as well as high volume density of small microalgal cell clusters in the liquid reactant results in serious attenuation of ultrasonic energy.
- Integration of the ultrasonic treatment with other intensification methods, especially for processing high solid concentration of biomass feedstock in large scale could improve the ultrasound technology.
- Catalyst separation and reusable technique should be improved.
- The recycling and reuse of the catalysts and the prolonged catalyst lifetime should be improved.
- The added economic values of the by-products such as glycerol and the waste extracts should be promoted, possibly with ultrasound technologies.
- Optimization of reactor design and operating parameters could be improved ultrasound biodiesel production.

CHAPTER 4

Catalytic Advances in Third Generation Biodiesel from Microalgae

Biodiesel derived from oil crops is being recognized as a green, potential renewable, and carbon neutral alternative to petroleum fuels. This renewable diesel fuel has attracted vast interest from researches, governments and local and international traders. Currently, first generation biodiesel is usually produced from vegetable oils, i.e., soybean, rapeseed, sunflower, and palm oil are the major feedstock (Rathore et al. 2007; Islam et al. 2013a). Unfortunately, there was a lot of objective from public and non-government organizations regarding the issues of utilization of food-based oils as energy sources, which will increase the biodiesel cost production (Lam et al. 2009). To meet the demand of rapid growth of biodiesel production, non-edible second generation oils such as jatropha oil, sea mango oil, *Pongamia pinnata* oil, castor oil, and rubber seed oil emerged as an attractive feedstock for the biodiesel industry (Gui et al. 2008; Jibrail et al. 2009). Non-edible oils have similar properties compare with edible oils. Regrettably, some regular irrigation, heavy fertilization, and good management practices are still required ensuring high oil yield obtained from these sources. Apart from that, some researchers have been reported that biodiesel from oil crops (canola oil, palm oil, corn oil, and jatropha oil), waste cooking oil, and animal fat realistically not satisfy even a small fraction of the existing demand for transport fuels (Felizardo et al. 2006; Shajaratun Nur et al. 2014; Lam et al. 2010; Taufiq-Yap et al. 2014). Due to these limitations, much attention has been paid to the exploration of microbial oils for a more sustainable biodiesel feedstock in the future.

4.1 Potential Role of Microalgae in Biodiesel Production

In the 1970s, algae were first examined as a potential alternative fuel source for fossil fuels (Barkley et al. 1988). Consequently, the research developments are able to facilitate the commercial potential of microalgae to move from aquaculture, fine chemicals, and health food to biofuel production in the 1980s (Noue et al. 1988). Recently, microalgae have been recognized as a superior feedstock for producing biodiesel (fatty acid methyl ester [FAME]). Microalgae are defined as the oldest lifeforms (Song et al. 2008). Several microalgae strains are able to accumulate large quantity of lipid in which the lipid can be converted to biodiesel (Chisti 2007). Biodiesel production using microalgal cultivation offers the following advantages, i.e., (i) high growth rate (100 times faster than terrestrial plants) of microalgae that make it possible to be satisfy the high demand on biofuels, (ii) microalgae farming require less water demand than crop that resulted in more cost effective, and (iii) high efficiency CO_2 mitigation in photosynthesis process (Li et al. 2008). The lipid production ranges from 4.5 to 7.5 tonne/ha/year from microalgae (Tsukahara and Sawayama 2005), which is higher than the production of oil from jatropha (4.14 tonne/ha/year), palm (3.62 tonne/ha/year), rapeseed (0.68 tonne/ha/year), and soybean (0.4 tonne/ha/year) (Chisti 2007; Lam and Lee 2011). Hence, biodiesel production through culturing microalgae strain requires the least land area. Apart from that, critical survey of the literature suggests that microalgae oil has the potential to produce higher biodiesel yields with about 25 percent reductions in production costs (Yahaya et al. 2013).

4.2 Cultivation Microalgae for Oil Production

Microalgae can either be autotrophic or heterotrophic (Fig. 4.1) whereby the former requires CO_2 as carbon sources and sunlight as the energy for oil accumulation under some special conditions; whereas, the latter are non-photosynthetic for that reason it requires an external source of organic compounds such as carbohydrates as well as nutrients as an energy source (Tamarys et al. 2010). Moreover, some photosynthetic algae are

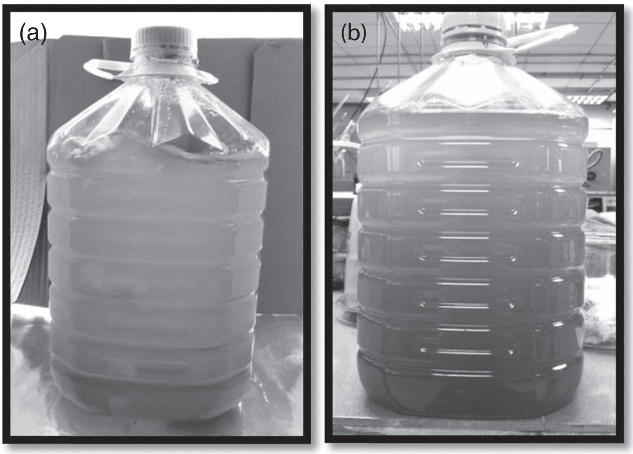


***Fig. 4.1** (a) Photoautotrophic and (b) heterotrophic cultivation of Nannochlopsis oculata (after 14 days) (Adapted from Teo et al. 2014a)*

mixotrophic, i.e., they have the ability to perform both photosynthesis and acquire exogenous organic nutrients (Tamarys et al. 2010). Cultivating microalgae at industrial scale for biodiesel production required additional cares in order to produce huge amount of oil with good quality for biodiesel production. Figs. 4.1a and 4.1b demonstrated cultivation volumetrically for a period of 14 days and then, the microalgae was harvested and dewatered through chemical flocculation method (Fig 4.2).

For this reason, the oil yield from the microalgae itself is always the key factor to achieve the suitability of a feedstock for biodiesel production. Species microalgae strains with higher oil yield are more preferable in the biodiesel industry because it can reduce the production cost. Generally the cost of raw materials accounts about 70 percent to 80 percent of the total production cost of biodiesel (Gui et al. 2008). Table 4.1 shows the related information about various microalgae species with different cultivation methods for oil production. Other possible cultivation parameters which have influence on oil production are light intensity, temperature, pH, salinity, nutrient, nitrogen, and phosphorus sources (Qiang et al. 2008).Tang et al. (2011) reported that the environmental parameters, i.e., red light-emitting diodes (LEDs), white LEDs, and fluorescent lights revealed effectively for *Dunaliella tertiolecta* microalgae growth. Moreover, the supplementation of the

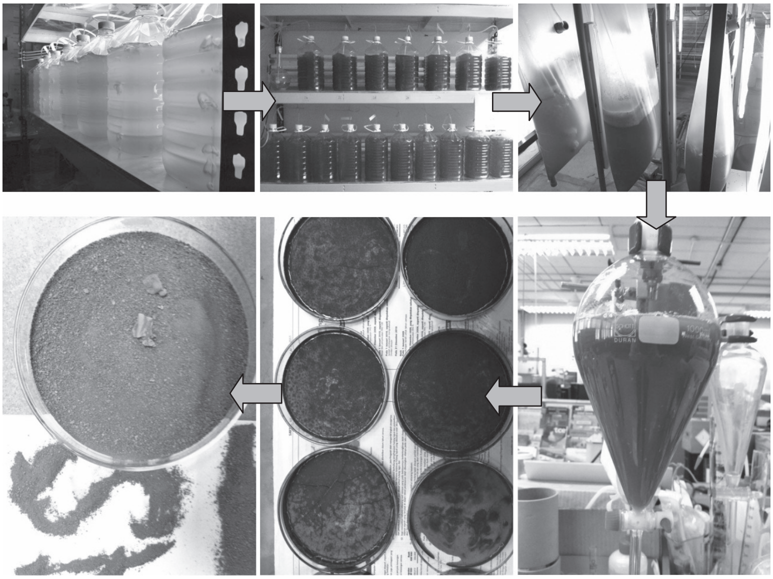


Fig. 4.2 ***Culturing, harvesting, and dewatering of oleaginous microalgae (Adapted from Teo et al. 2014a)***

inorganic culture medium included different carbon sources, concentration of trace metals, and stress and nitrogen deficiency are key factor for oil accumulation in microalgae (Ana et al. 2012; Solovchenko et al. 2008; Liu et al. 2007).

4.3 Oil Composition

One of the important criterion to establish the suitability of lipid as a source for the biodiesel production is the substitutions of the extracted oil. Many microalgae species, such as *Chlorella vulgaris*, *Nannochloropsis oculata*, *Botryococcus braunii*, *Neochloris oleoabundans*, *Phaeodactylum tricornutum*, *Tetraselmis sueica*, *Scenedsmus acutus*, *Crypthecodinium cohnii*, *Dunaliella primolecta*, *Monallanthus salina*, and *Navicula pelliculosa*, were reported to have the capacity of accumulating large quantities of oils in cells under favorable culture conditions (Liang et al. 2006; Liu et al. 2000; Prakash 2010). The composition of lipid presence in the oil will subsequently determine the properties of the biodiesel obtained from different algae species. The fatty acid (FA) compositions of various types of microalgae oils are shown in Table 4.2. It could be observed

Table 4.1 Various microalgae oil accumulation via autotrophic, heterotrophic, and mixotrophic

Species	Cultivation	Oil content*	Reference
Botryococcus braunii	Autotrophic	63	Prakash et al. (2010)
Botryococcus braunii	Heterotrophic	25–75	Chisti (2007)
Chlamydomonas reinhardtii	Mixotrophic	21	Becker (1994)
Chlorella vulgaris	Autotrophic	40	Illman et al. (2000)
Chlorella vulgaris	Mixotrophic	11.8–57.9	Chi et al. (2007)
Chlorella emersonii	Autotrophic	63	Illman et al. (2000)
Chlorella protothecoides	Autotrophic	23	Illman et al. (2000)
Chlorella sorokiniana	Autotrophic	22	Illman et al. (2000)
Chlorella minutissima	Autotrophic	57	Illman et al. (2000)
Chlorella vulgaris	Autotrophic	56.6	Liu et al. (2007)
Chlorella protothecoides	Heterotrophic	50.3	Xiong et al. (2008)
Chlorella protothecoides	Heterotrophic	55	Miao and Wu (2006)
Chlorella protothecoides	Heterotrophic	55.2	Xu et al. (2006)
Chlorella protothecoides	Heterotrophic	44	Chen et al. (2008)
Crypthecodinium cohnii	Heterotrophic	15–70	Borowitzka and Borowitzka, 1988
Dunaliella Salina	Mixotrophic	15–55	Weldy and Huesemann (2010)
Monodus subterraneus	Autotrophic	39.3	Khozin-Goldberg and Cohen (2006)
Monoraphidium	Autotrophic	26	Gabriel et al. (2014)
Nannochloropsis sp.	Autotrophic	60	Liliana et al. (2009)
Nannochloropsis sp.	Autotrophic	33.8–59.9	Jiang et al. (2011)
Neochloris oleaabundans	Autotrophic	54	Metting (1996)
Parietochloris incisa	Autotrophic	62	Solovchenko et al. (2008)
Phaeodactylum tricornutum	Autotrophic	9.4	Boris and Brian (2010)
Scenedesmus sp.	Autotrophic	16.6	Hanifa et al. (2014)
Spirogyra sp.	Autotrophic	42	Prakash et al. (2010)
Nitzschia laevis	Autotrophic	54	Chen et al. (2008)

*Percent dry cell weight.

Table 4.2 Fatty acid profiles of microalgae based methyl esters

	Saturated Fatty Acids				Unsaturated Fatty Acids						
Species	Myristic acid (C14:0)	Palmitic acid (C16:0)	Stearic acid (C18:0)	Arachidic acid (C20:0)	Palmitoleic acid (C16:1)	Oleic acid (C18:1)	Linoleic acid (C18:2)	Linolenic acid (C18:3)	Arachidonic acid (C20:4)	Others	References
Chaetoceros calcitrans	21.48	9.32	2.13	n.d.	16.69	n.d.	n.d.	n.d.	n.d.	43.44	Sergio et al. (2013)
Chlorella sp. *NJ-18*	0.89	27.82	1.74	0.03	1.55	15.09	36.79	15.56	0.04	0.52	Zhou et al. (2013)
Chlorella vulgaris	n.d.	25.00	5.00	n.d.	n.d.	16.00	44.60	6.30	n.d.	3.10	Lam and Lee (2013)
Chlorella pyrenoidosa	0.68	10.48	3.20	0.24	0.31	70.18	14.53	n.d.	n.d.	–	Li et al. (2011)
Dinoflagellate sp.	6.01	16.65	n.d.	n.d.	3.35	2.10	n.d.	n.d.	n.d.	71.89	Chen et al. (2012)
Dunaliella tertiolecta	n.d.	26.60	0.57	n.d.	0.1	15.00	11.43	44.07	n.d.	–	Tang et al. (2011)
Nannochloropsis gaditana	6.40	33.20	2.10	n.d.	28.00	6.00	n.d.	n.d.	n.d.	24.50	Carrero et al. (2011)
Nannochloropsis oculata	7.69	35.43	2.50	n.d.	27.54	8.62	5.22	n.d.	2.47	10.53	Teo et al. (2014a)
Nannochloropsis salina	2.72	37.83	5.63	n.d.	31.34	11.31	n.d.	n.d.	2.24	6.35	Reddy et al. (2014)
Nannochloropsis oleoabundans	n.d.	31.10	2.20	n.d.	2.80	12.90	27.60	23.60	n.d.	–	Santos et al. (2012)
Phaeodactylum tricornutum	2.38	10.71	4.09	n.d.	30.27	4.22	1.27	n.d.	n.d.	47.08	Sergio et al. (2013)
Scenedesmus sp.	n.d.	18.42	3.43	n.d.	2.31	49.64	11.30	8.26	n.d.	6.64	Chen et al. (2012)
Spirulina	n.d.	49.31	n.d.	n.d.	2.36	8.81	26.46	n.d.	n.d.	13.06	Xu and Mi (2011)
Tribonema minus	6.85	28.35	1.02	n.d.	50.65	2.96	0.71	n.d.	3.02	6.44	Wang et al. (2013)

Others: eicosapentaenoic acid and docosahexenoic acid.
n.d.: not detected.

that the FA compositions in microalgae oils mainly consisted of myristic acid (C14:0), palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), arachidic acid (C20:0), arachidonic acid (C20:4), EPA (20:5), and DHA (20:6), respectively. From the table, C16:0, C16:1, C18:1, C18:2, and C18:3 represent the major portion of FAMEs compositions. These FAs are naturally found in oil-bearing crops, such as sunflower, palm and soybean oil (Shajaratun Nur et al. 2014; Lam et al. 2013), in which the FAs are suitable for biodiesel production. The FAs in microalgae oils are further classified into saturated and unsaturated FAs (Fig. 4.3 and Table 4.2). Apart from that, unsaturated FAs (C16:1, C18:1, C18:2, C18:3, C20:4, C20:5, and C20:6) were predominant in the FA profiles, accounted for total of above 85 percent. Generally, algae produce a lot of polyunsaturates, which have much lower melting points than monosaturates or saturates. Besides, it is also important to note that higher compositions of unsaturated FAs can reduce the pour point to biodiesel and making it significantly good properties than many others biodiesel (Teo et al. 2014a; Lam and Lee 2012; Abdelmalik et al. 2011). Other saturated FAs except palmatic acid, such as myristic acid, stearic acid, and arachidic acid, were also identified. Nevertheless, the compositions were very less and they accounted for only below 6 percent of the overall lipid contents. Apart from the lipid content in microalgae, microalgae produce different ratios of carbohydrates and proteins. The high contain of protein in microalgae cells, which contain all the essential amino acids necessary for human growth and can sustain health at all stages of development (Xu and Mi 2011; Tran et al. 2010). In addition, they are also rich source of valuable polynutrients, i.e., beta-carotene, alphacarotene, vitamin-E, lycopene, tocotrienols, and other carotenoids (Xu and Mi 2011; Li et al. 2011; Teresa et al. 2010; Kitada et al. 2009). Furthermore, *Chlorella vulgaris*,*Chlorella sp. NJ-18*,*Nannochloropsis oleoabundans, Spirulina*, *Chlorella pyrenoidosa*,and *Dunaliella tertiolecta* have high content of linoleic acid, with 45 percent, 37 percent, 28 percent, 27 percent, 15 percent, and 11 percent, respectively. Linoleic acid is also known as polyunsaturated FA whereby it is a compound of the essential FA group namely omega-6 FA. This compound is an essential dietary compound needed for all mammals.

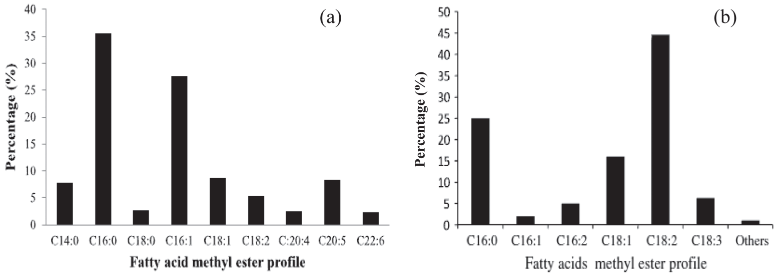


Fig. 4.3 Fatty acid methyl ester profile of (a) Nannochloropsis oculata *and (b)* Chlorella vulgaris *(Adapted from Teo et al., 2014a; Lam and Lee, 2012)*

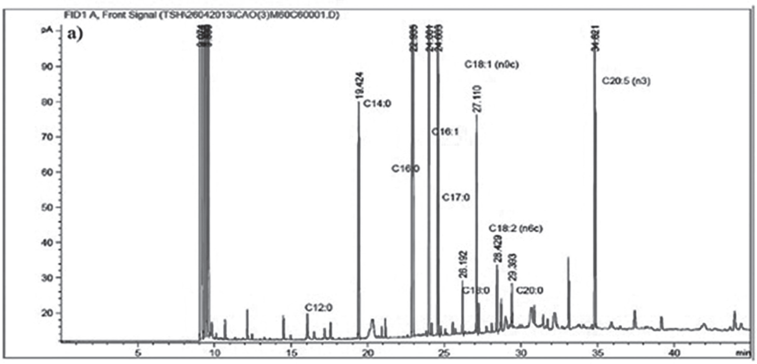


Fig. 4.4 Gas chromatography of N. oculata *microalgae derived biodiesel (Adapted form Teo et al., 2014a)*

This type of fat is a healthy fat and very useful, which can lower down the risk of heart disease (Gui et al. 2008).

On the other hand, it has been reported that such microalgae oils can be used as oil feedstocks for producing biodiesel in the presence of catalysis either by homogeneous or by heterogeneous catalytic systems (Teo et al. 2014b; Lee and Lee 2012; Miao and Wu 2006).

Fig. 4.4 showed the gas chromatography of the biodiesel product in which the FAME content was determined in agreement with the European regulated procedure EN 14103 (Adapted from Timonthy and Timon 2012). The effect of catalytic on production and properties of the biodiesel will be discussed extensively in the subsequent section.

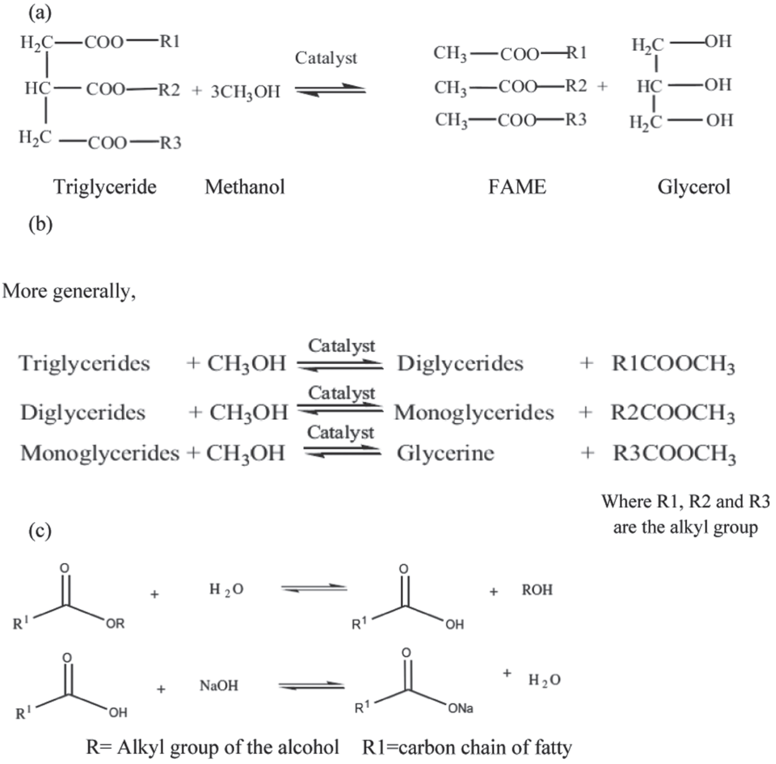


Fig. 4.5 Transesterification reactions of glycerides with methanol. (a) Overall reaction; (b) Stepwise consecutive and reversible reactions; (c) Esterification reaction of fatty acids (Adapted form Islam et al. 2013a; 2014)

4.4 Catalytic Microalgae-Biodiesel Production

FAME or biodiesel is mostly produced from vegetable oils or animal fats. Transesterification or esterification is the chemical conversion of FAs into methyl esters with lower alcohols in the presence of catalyst (Freedman and Pryde 1984), as shown in Fig. 4.5.

Up to now, studies reveal that a number of conventional catalysts in the petroleum industry comprising transition metals, zeolites, acid and base catalysts can be used with variable effect (Tran et al. 2010). Apart for biodiesel production, these have been employed for cracking, hydrocracking, liquefaction, and pyrolysis processes to produce diesel, jet fuel, and petrol (gasoline) (Chen et al. 2012; Peng et al. 2012; Fan et al. 2012). Traditionally, homogeneous (KOH, NaOH, and H_2SO_4) catalysis received wide acceptability because of its fast reaction rates than heterogeneous catalysis system (Piyushi et al. 2014; Patil et al. 2013; Hossain et al. 2008; Serio et al. 2008). Nevertheless, there is a considerable incentive for the substitution of liquid bases by solid bases due to following reasons, i.e., energy intensive product/catalyst separation, corrosiveness, and the costs associated with the disposal of spent or neutralized caustics (Zhang et al. 2003). The oil extracted from microalgae contains high free FAs (0.5 percent) which require pretreatment if conventional homogeneous catalysts are employed (Bahadar and Khan 2013). Furthermore, the moisture contain hydrolyze the TGs of feedstock into FFAs and diglycerides. The formation of stable emulsion will dissolve into glycerol phase during the separation stage. This reduces the biodiesel yield as it gets trapped in the soap phase during the downstream process (Guan et al. 2009b).

Transesterification or esterification reactions catalyzed by heterogeneous catalysts such as acid, base, and enzymes catalysts have been demanding for biodiesel production, especially biodiesel produced from microalgae biomass (Teo et al. 2014b; Yahaya et al. 2013; Shavon and Nirupama 2009). Table 4.3 demonstrates some of the species such as *Chlorella protothecoides* (Miao and Wu 2006), *Karlodinium veneficum* (Claudio et al. 2006), *Scenedesmus obliquus* (Shovon and Nirypama 2009), *Dunaliella tertiolecta* (Krohn et al. 2011), *Monoraphidium contortum* (Reyes et al. 2012), and *Nannochloropsis* species (Li et al. 2011; Teo et al. 2014c, Teo et al. 2014b; Umda et al. 2009) have also been reported to be the potential source for biodiesel production on the basis of FA composition.

Nannochlopsis oculata was transesterified in the presence of $Ca(OCH_3)_2$ (calcium methoxide) catalyst at 60 °C to give an FAME yield of 92 percent (Teo et al. 2014a). The $Ca(OCH_3)_2$ catalyst seem to be a flower-like cluster structure (Fig. 4.6a) which provides a large number of pores (Fig. 4.6b) that are visible on the surface of the catalyst and these pores together with thin plate-like morphology contributed to the high surface area (30.5 m^2/g) of $Ca(OCH_3)_2$ catalyst. Furthermore, the flower-like cluster provided rapid mass transfer into the interstices of the catalyst and lead reactants to reaction sites during transesterification reaction (Teo et al. 2014a; Kouzu et al. 2008).

Table 4.3 Transesterification process with homogneous and heterogeneous acid/alkaline catalysts for biodiesel production from microalgae

		^{a}Performance					
Catalyst	**Species**	**T (°C)**	**Me (%)**	**t (min)**	**P**	**^{b}Performance**	**Reference**
Homogeneous							
H_2SO_4	*Chlorella protothecoides*	30	56:1	240	n.r.	y>95.0	Miao and Wu (2006)
B_{F_3}	*Karlodinium veneficum*	90	–	60	n.r.	n.d.	Claudio et al. (2009)
H_2SO_4	*Scenedesmus obliquus*	–	60:1	–	n.r.	n.d.	Shovon and Nirypama (2009)
KOH	*Spirulina*	50	1 ml	30	n.r.	y = 76.0	Xu and Mi (2011)
Heterogeneous							
CaO/Al_2O_3	*Nannochloropsis oculata*	50	30:1	n.r.	1 atm	y = 97.5	Umda et al. (2009)
$Ca(OCH_3)_2$	*Nannochloropsis oculata*	60	60:1	180	1 atm	y = 92.0	Teo et al. (2014a)
CaMgO	*Nannochloropsis oculata*	60	60:1	180	1 atm	y = 75.2	Teo et al. (2014b)
$CaMgO/Al_2O_3$	*Nannochloropsis oculata*	60	60:1	180	1 atm	y = 85.3	Teo et al. (2014b)
Mg/Zr	*Nannochloropsis* sp.	65	10:1	240	1 atm	y = 22.0	Li et al. (2011)
SrO	*Eustigmatophyte Nannochloropsis* sp.	n.r.	n.r.	n.r.	1 atm	y = 18.0 &37.0	Koberg et al. (2011)
Zr, Ti, Al	Algae oil	>350	n.r.	n.r.	17.23 MPa	c > 90.0	McNeff et al. (2008)
Titatia	*Dunaliella tertiolecta*	360	32:1	n.r.	2295 psi	y = 20.9	Krohn et al. (2011)
Li_4SiO_4	Algae oil	68	18:1	240	1 atm	c = 76.2	Dai et al. (2014)
NbO_2 (HY-340)	*Monoraphidium contortum*	200	n.r.	n.r.	20684 kPa	c = 94.27	Reyes et al. (2012)

[a] Reaction condition: T= reaction temperature (°C); Me = methanol/oil molar ratio (%); t = reaction time (min); P = reaction pressure (atm, Mpa, psi and kPa).

[b] y = yield; c = conversion.

n.r. = not reported

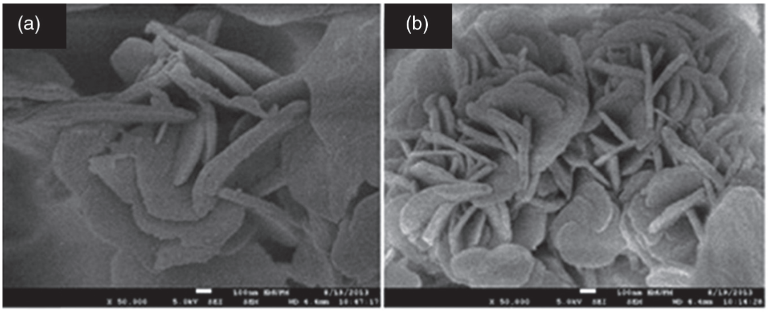


Fig. 4.6 FESEM micrograph of $Ca(OCH_3)_2$ (a & b) catalyst (Adapted from Teo et al. 2014a)

At optimization condition, CaMgO mixed oxide catalyst showed 75.2 percent of biodiesel yield with catalyst loading of 20 wt% at 3 hours. Meanwhile, the supported CaMgO mixed oxide catalyst gave a higher FAME yield of 85.3 percent with catalyst loading of 10 wt% at same conditions (Teo et al. 2014b). From Fig. (4.7), the reusability study of catalyst was performed to investigate the stability and durability of supported/unsupported catalysts. The high content of Ca^{2+} and Mg^{2+} precipitated on Al_2O_3 supported CaMgO mixed oxide catalyst tend to increase the total basicity and provide more active sites for transesterification reaction. Additionally, better moisture resistant on the Al_2O_3 supported CaMgO mixed oxide catalyst compared with CaMgO mixed oxide catalyst, which is favorable for transesterification reaction on high water content microalgae oil (Umdu et al. 2009; Jiang et al. 2011; Teo et al. 2014b).

Apart of the surface area and pore volume properties of catalyst, there is strong evidence that new nano-scale materials containing a high number of active sites and high surface areas may offer more potential. Li et al. (2011) reported Mg/Zr solid base catalyst is suitable for biodiesel production from *Nannochloropsis* sp. microalgae with a yield of 22 percent. From XRD profile (Fig. 4.8a), Mg/Zr solid base catalyst consisting of MgO and magnesium–zirconium composite oxide (cubic $Mg_2Zr_5O_{12}$) was observed in the catalyst, whose crystalline sizes calculated by Sherrer formula were 24.8 and 19.0 nm, respectively. In addition, the super basic site (Fig. 4.8b) might be generated by the strong interaction between MgO and ZrO whereby the former three basic sites

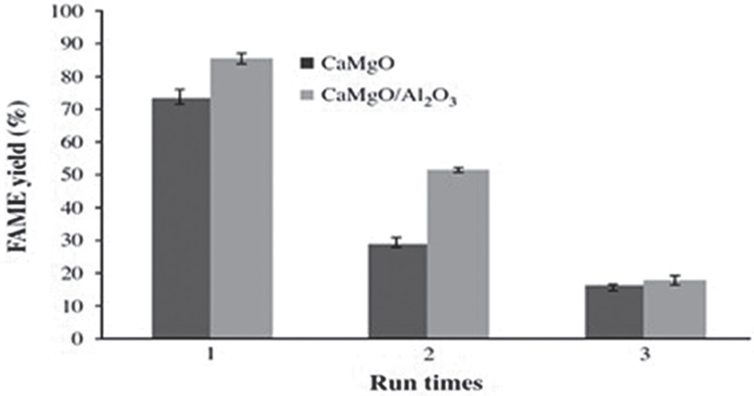
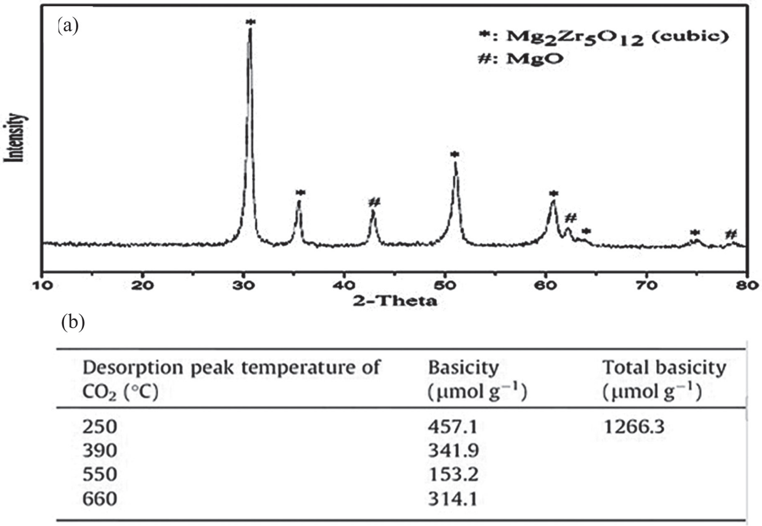


Fig. 4.7 Stability and reusability test (Adapted from Teo et al. 2014b)



Desorption peak temperature of CO_2 (°C)	Basicity (μmol g^{-1})	Total basicity (μmol g^{-1})
250	457.1	1266.3
390	341.9	
550	153.2	
660	314.1	

Fig. 4.8 (a) X-ray powder diffraction pattern and (b) total basicity of Mg-Zr catalyst (Adapted from Li et al. 2011)

were assigned to OH groups, metal O^{2-} pairs and isolated O^{2-}, respectively (Di Cosimo et al. 1998; Take et al. 1971).

Furthermore, transesterification of *Eustigmatophyte Nannochloropsis* sp. biomass using microwave and ultrasonic radiation with the aid of SrO catalyst resulted in 18 percent and 37 percent biodiesel yield, respectively (Koberg et al. 2011). In another experiment, algae were transesterified in the presence of Zr, Ti, and Al catalysts at 350 °C to 400 °C and 2500 psi (17.23 MPa), giving an oil conversion of >90.2 percent (McNeff et al. 2008). Krohn et al. (2011) demonstrated the production of algal biodiesel from *Dunaliella tertiolecta*, *Nannochloropsis oculata*, wild freshwater microalgae derived lipids using a highly efficient continuous catalytic process. The heterogeneous catalytic process uses supercritical methanol and porous titania microspheres in a fixed bed reactor to catalyze the simultaneous transesterification and esterification of triacylglycerides and FFAs, respectively, to biodiesel. Next, Dai et al. (2014) extracted microalgae lipid (30 wt%) using microwave assistant and, then transesterified lipid to produce FAME. The results indicated that the Li_4SIO_4 catalyst was more active (76.2 percent) than CaO and Li_2SiO_3 catalysts in production of biodiesel from microalgae oil. Nevertheless, the catalytic activity of the catalyst was not directly related to the surface area, but rather the basic strength generated during solid-state synthesis as shown in (Figs. 4.9 and 4.10).

Currently, in order to achieve commercial productionthat will sustainably meet the global biodiesel demands, the production process must be efficient and affordable. Zeolites are known as microporous crystalline solids whereby it contains silicon (Si), aluminum (Al) and oxygen in their framework. This inorganic solid catalyst was applied for the production of organic compound such as ester (Balaji and Chanda 1998). This is due to the behavior of zeolite that can be customized to fulfill its function.

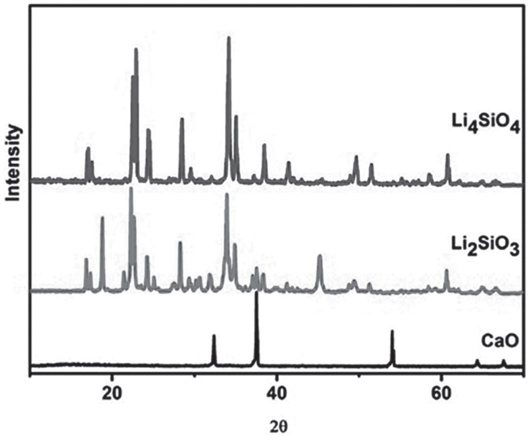
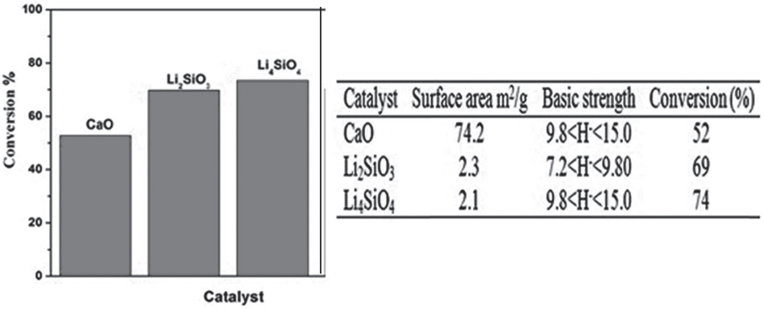


Fig. 4.9 XRD pattern of Li_4SiO_4, Li_2SiO_3, and CaO catalysts (Adapted from Dai et al. 2014)



Catalyst	Surface area m^2/g	Basic strength	Conversion (%)
CaO	74.2	$9.8<H_-<15.0$	52
Li_2SiO_3	2.3	$7.2<H_-<9.80$	69
Li_4SiO_4	2.1	$9.8<H_-<15.0$	74

Fig. 4.10 The conversion of Li_4SiO_4, Li_2SiO_3, and CaO catalysts correlation with physic-chemical properties of the catalysts (Adapted from Dai et al. 2014)

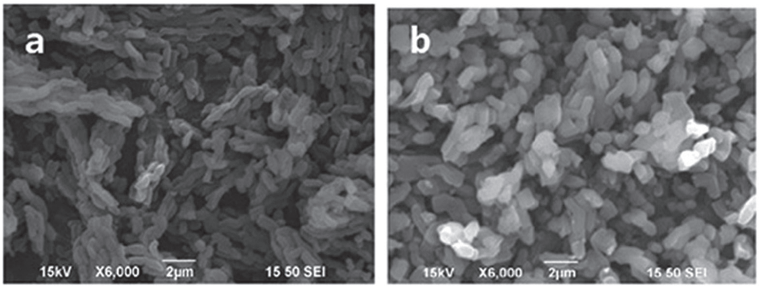


Fig. 4.11 (a) SEM images of SBA-15, (b) SBA-15-pr-NR_3OH catalysts (Adapted from Xie and Fan 2014)

To these purposes, the tetraalkylammonium hydroxide-functionalized SBA-15 materials (SBA-15- pr-NR3OH) have been prepared by anchoring dimethyloctadecyl[3(trimethoxysilyl)propyl]ammonium hydroxides onto the surface of mesoporous SBA-15 silica, and then the catalytic activity was tested in the transesterification of soybean oil with methanol. Typically SEM (Fig. 4.11) and TEM (Fig. 4.12) images of parent SBA-15 silica and functionalized SBA-15 catalysts exhibited a unique morphology feature that favorable for esterification reaction (Xie and Fan 2014).

The parent SBA-15 (Fig. 4.11a) catalyst was composed of well-defined wheat-like macrostructures. Apart from that, the particles were aggregated with rope-shaped domains with relatively similar particle sizes of 1 μm (Kalita and Kumar 2011; Citak et al. 2012).

Interestingly, the SBA-15-pr-NR_3OH catalyst demonstrated similar SEM images to the parent SBA-15 catalyst as after the incorporation of

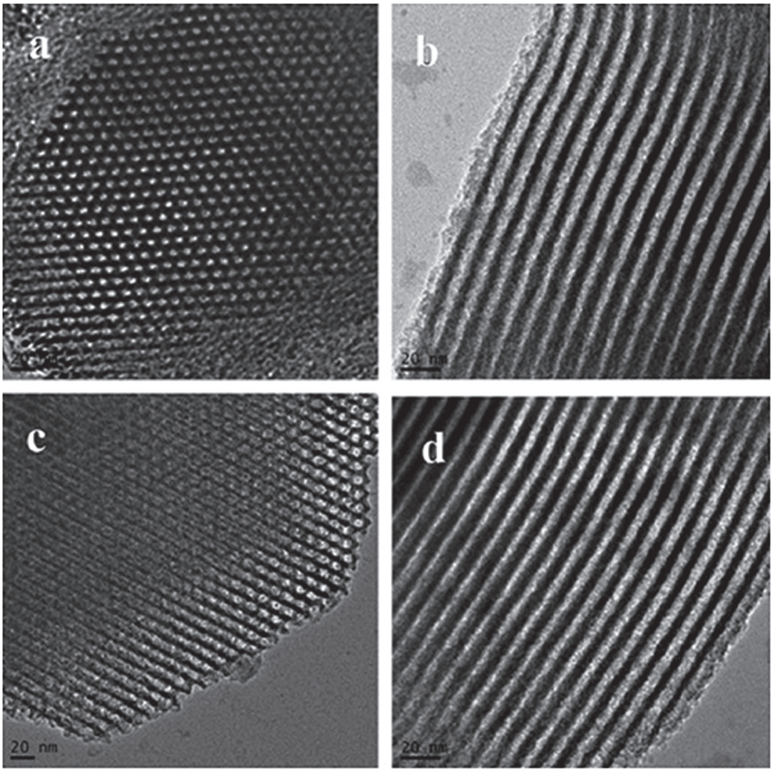


Fig. 4.12 (a) TEM images of SBA-15 in top view, (b) SBA-15 in side view, (c) SBA-15-pr-NR3OH in top view, and (d) SBA-15-pr-NR3OH in side view (Adapted from Xie and Fan 2014)

functional groups (Fig. 4.11b). It was observed that the organic moieties are well-dispersed on the SBA-15 particles, and the rope-like domains with average sizes of 1 µm are still largely remained after the functionalization reaction (Lam et al. 2010; Teo et al. 2014c). Thus, the mesoporous structures of SBA-15 materials are largely preserved during the organofunctionalization reaction (Xie and Fan 2014). The TEM images of SBA-15 silica and SBA-15-pr-NR_3OH (Fig. 4.12) catalysts revealed the existence of well-ordered hexagonal arrays of one-dimensional channels with a mean diameter of about 6 nm and a wall thickness of around 3 nm (Citak et al. 2012). Furthermore, the 2D hexagonal symmetry types of pores was observed from the top view and the straight channels, and was open without obstacles from the side view. For that reason, the highly ordered periodic hexagonal mesostructure of SBA-15 catalyst is reserved as the organic moieties which are incorporated into the SBA-15 silica.

The catalytic activity of zeolite in transesterification reactions is relative low mainly due to diffusion limitation of bulky reactants, i.e., triglycerides into the microporous structure (Kiss et al. 2006). The average molecular size of triglycerides is approximately 2 nm, which undergo mass transfer resistance in the zeolite's micropore (1 to 2 nm) during the reaction. As a result, it is assumed that transesterification reaction will take place only on the surface of zeolite crystal (Yahaya et al. 2013; Carrero et al. 2011). In order to overcome this drawback, Okuhara (2002) suggested that the pore size and structure of zeolite can be adjusted with varying the Si/Al ratio. Higher Si/Al ratio resulted in larger pore size for better diffusion, but the reaction rate is still rather slow due to weak acidity strength (Chung et al. 2008; Okuhara 2002). Apart of the zeolites mentioned above, different zeolite Y was also reported to have poor performance in transesterification reaction even when the reaction was carried out at high reaction temperature of 460 °C (Brito et al. 2007a; Brito et al. 2007b; Shu et al. 2007; Kiss et al. 2006; Okuhara 2002).

In the same line, Carrero et al. (2011) currently produced biodiesel from oleaginous *Nannochlopsis gadinata* using another types of zeolite such as ZSM-5, hierarchiral ZSM-5 (h-ZSM-5), Beta and hierarchiral Beta (h-Beta) zeolites (Figs. 4.13a and 4.13b). The author found that higher catalytic activity was observed from h-Beta compared to h-ZSM-5. The lower activity of h-ZSM-5 on biodiesel conversion was due to the narrow pore structures which hindered diffusion of the microalgae oil to the active sites of the catalyst (Fig. 4.14). In additional, seed silanization treatment increased BET surface area on h-Beta zeolite. This phenomenon was due to the enhancement of the secondary porosity in micro-mesopores ranges on h-Beta zeolite. Therefore, the h-Beta catalyst retained most of its acid strength and acid site population (Rathore and Madras 2007). Similarly, earlier investigation by Giannakopouloua et al. (2010) revealed that the selectivity and activity of h-ZSM-5 and h-Betadepend on the method of preparation. Consequently, their reportshowed that h-ZSM-5 had better activity than the h-Beta zeolite.

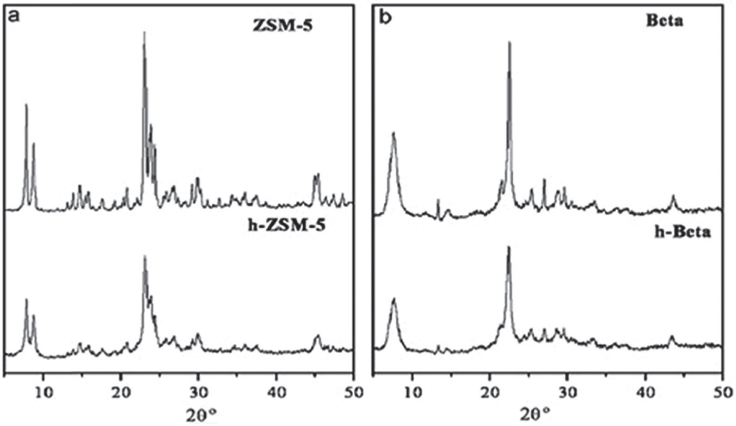


Fig. 4.13 XRD profiles of (a) ZSM-5 and (b) Bete zeolites (Adapted from Carrero et al.2011)

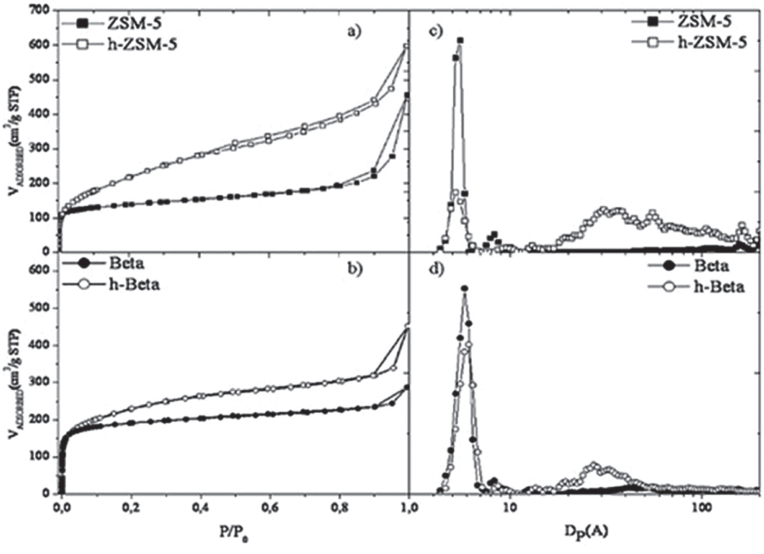


Fig. 4.14 Adsorption/desorption isotherm and pore size distribution of ZSM-5 and h-ZSM-5 (a & c) and Beta and h-Beta (b & d) catalysts (Adapted from Carrero et al. 2011)

4.5 Conclusion

Sustainable energy development has become one of the key challenges in this century. Less availability of fossil fuel and emissions of greenhouse gases are the main driving force to search for alternative and renewable energy options. Due to these reasons, the need for renewable fuel such as biodiesel has come to caught global attention. Biodiesel fuel is made from renewable sources, alternative fuel to petroleum diesel, and as such it is non-toxic, biodegradable and does not contribute net carbon emission to the atmosphere. Biodiesel has been envisaged as a future fuel in the transport sector. However, the major constraint in the commercialization of biodiesel in the global market is its high cost and making it no longer economically feasible as compared to mineral diesel which is contributed primarily by the feedstock. Furthermore, the plant-based oil is an essential commodity in food supply chain, thus its conversion to biodiesel in a long-term may not be sustainable. As an alternative, microalgae have been attracting increasing interests as feedstock for biodiesel production due to compelling evidence of its significant potential in reducing particulate emission and solving the energy problem.

At present, algae oil from microalgae have been projected as potential feedstock for biodiesel production because of its high growth rate (100 times faster than terrestrial plants) of microalgae that make it possible to be satisfy the high demand on biofuels; microalgae farming requires less water demand than crop that resulted in more cost effective; high efficiency CO_2 mitigation in photosynthesis process and the conversion of algae oil does not compete with good in human food supply chain. Interestingly, about 25 percent reductions in cost of biodiesel production from microalgal oil have been predicted. The progress in research work accounted states that though the microalgae can be utilized as a potential feedstock for the synthesis of biodiesel, certain aspects have to be dealt scrupulously to make the process more sustainable, green, and economical. As the lipid profile of microalgae is different from the plant oil, the conversion of the former to biodiesel has been found to vary considerably among the microalgal species. The FA constituent also bears a significant effect on the fuel properties of biodiesel. Therefore, there is still a long way to go for the microalgal oil to cater the fulfillment of enormous amount of fuel demand with affordable price and reduced environmental impacts. Several effort are recently toward the reduction of biodiesel cost by different culturing microalgae to reach high lipid contents, which qualify to produce biodiesel of desired quality so as to meet the national/ international specifications.

In order to accomplish the mission, catalytic (homogeneous/heterogeneous systems) reactions to produce microalgae-biodiesel is thus on its way to becoming the ideal process for the future. Transesterification reaction can be performed by using homogeneous catalysts However, homogeneous catalysts were found not suitable for the transesterification of algae oil due to its high FFA and moisture contents, respectively. Furthermore, homogeneous acid (H_2SO_4) catalyst needed longer reaction time and could potentially cause corrosive on equipment. In term of sustainable and green process, it is very obvious to declare that research on heterogeneous catalyst, i.e., acid or base type, should be carried out extensively to develop a suitable catalyst to convert algae oils from different species to biodiesel with special emphasis on catalytic performance, durability, stability, and degree of lixiviation. Hence, there are a few aspects should be taken in consideration in order tolower the production cost, shorter reaction time and greater production capacity. The recovery of high quality glycerol could be another way to lower production cost.

CHAPTER 5

Recent Practice in Biodiesel Production

The depletion of the reserves and the uncertain political situation in some oil-producing countries are leading to a rapid increase in the cost of crude oil. Understanding the barriers to acquiring an adequate supply of multiple feedstocks is a challenge because of the simultaneous and ongoing interactions between energy markets and feedstock production on the one hand and feedstock, food/fiber, and wood product sectors on the other. Energy prices that are high enough, relative to the cost of producing biofuels, could induce a level of biofuel production and, thus, feedstock demand that exceeds the levels implied by mandates. Although the biodiesel industry has experienced tremendous growth, raw material supplies have served as a natural brake and created a strain on margins for biodiesel producers. The price of crude oil is still lower than that of refined vegetable oil, as shown in Fig. 5.1, primarily due to the link between crude petroleum oil, vegetable oil refining process, and speculation (Lin et al. 2011; Santori et al. 2012; Srinivasan 2009).

Commercial biodiesel production is currently a base-catalyzed process with homogeneous catalyst. Biodiesel is currently produced via transesterification of triglycerides with alcohol such as methanol. Methanol is commonly used in industrial biodiesel production as a result of its relatively low cost and easy availability. The most common homogenous catalysts used in the biodiesel production are sulfuric acid during esterification and sodium methylate during transesterification (Vicente et al. 2004; Dunford 2007). The alkaline catalysts are used in industrial

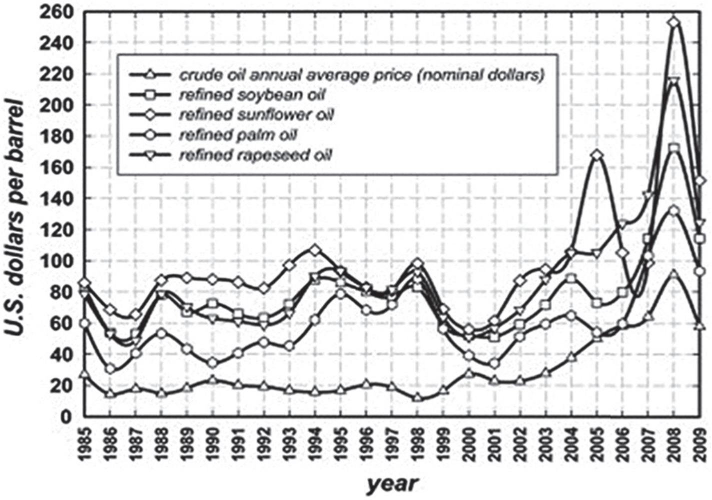


Fig. 5.1 Prices of some refined vegetable oil varieties (Adapted from Santori et al. 2012)

biodiesel processes due to the following reasons (Santori et al. 2012; Demirbas 2007b; Meher et al. 2006a):

- low costs,
- a high yield,
- high reaction rate,
- a low temperature,
- a low corrosive power of intermediate products,
- a quite fast reaction.

In most cases, the alkaline catalyst are varied at concentration from 0.1 percent to 1.5 percent of vegetable oil mass, and the alcohol involved is in a molar ratio alcohol:vegetable oil of 6:1 (Santori et al. 2012; Sivasamy et al. 2009). In most cases, second-order kinetics has been observed at 6:1 methanol/oil molar ratio (Vicente et al. 2005).

$$\frac{d[TG]}{dt} = -k_1[TG][MeOH] + k_2[FAME][DG] \tag{5.1}$$

$$\frac{d[TG]}{dt} = k_1[TG][MeOH] - k_2[FAME][DG] - k_3[DG][MeOH] + k_4[FAME][MG] \tag{5.2}$$

$$\frac{d[MG]}{dt} = -k_3[DG][MeOH] - k_4[FAME][MG] - k_5[MG][MeOH] + k_6[FAME][G] \tag{5.3}$$

$$\frac{d[G]}{dt} = -k_5[MG][MeOH] - k_6[FAME][G] \tag{5.4}$$

$$\frac{d[FAME]}{dt} = k_1[TG][MeOH] - k_2[FAME][DG] + k_3[DG][MeOH] - k_4[FAME][MG] + k_5[MG][MeOH] - k_6[FAME][G] \tag{5.5}$$

$$\frac{d[MeOH]}{dt} = -k_1[TG][MeOH] + k_2[FAME][DG] - k_3[DG][MeOH] + k_4[FAME][MG] - k_5[MG][MeOH] - k_6[FAME][G] \tag{5.6}$$

where TG, DG, MG, MeOH, FAME, and G, are triacylglycerol, diacylglycerol, methanol, fatty acid methyl esters, and glycerol, respectively.

The use oils such as yellow or brown grease are thermally or chemically degraded waste oils that primarily contain grease collected from restaurant or industrial grease traps. Most of this is spent cooking oil from restaurants that has been thermally degraded by high temperatures (Canakci and Van Gerpen 2001). It further degrades when in contact with water in the grease trap through a process known as hydrolysis. This degradation produces molecules known as free fatty acids (FFAs). The high percentage of FFAs in the feedstock is the main challenge to biodiesel production due to the following reasons (Lam et al. 2010; Lou et al. 2008; Atadashi et al. 2012):

- The FFAs react with the base-catalyzed biodiesel reactions to form soap.
- The catalyst is consumed resulting in either an increased catalyst requirement and therefore higher chemical costs—or an incomplete or failed reaction.
- The reaction between the fatty acid molecule and catalyst creates soaps which manifest themselves as impurities in the biodiesel and must be washed out.

- This reduces the level of free catalyst and thus reduces the speed of the transesterification reaction.
- Soap formation tends to inhibit the separation of the ester from the glycerin and slow down the reaction.

However, this problem can be overcome by using pretreatment process to reduce the FFAs of the oil or grease. Thus, the vegetable oils for biodiesel production must be suitably pretreated before entering the transesterification process (Fig. 5.2), whenever feedstock quality and refinement cannot otherwise be adequately guaranteed. Pretreatment solutions should always be considered an integrated component of a plant, and one that is designed to make plant operations more efficient and economical.

A wide variety of feedstock pretreatment materials and technologies are readily available. From steam stripping, to acid esterification, glycerolysis, enzyme pretreatment, or even adsorbents, biodiesel producers have a number of options to consider and vet for possible implementation at their facilities (Canakci and Van Gerpen 2001; Gerpen 2005; Kumar Tiwari et al. 2007; Felizardo et al. 2011; Samukawa et al. 2000; Abrams et al. 2009). Each method clearly has its relative advantages and drawbacks when compared to other technologies and materials available to the industry. Not all pretreatment methods are appropriate for a given plant. In most cases, economic considerations coupled with feedstock characteristics and plant design will be driving forces in the final selection of a pretreatment solution. The most prevalent pretreatment method has traditionally been acid esterification, since it can be done at relatively low

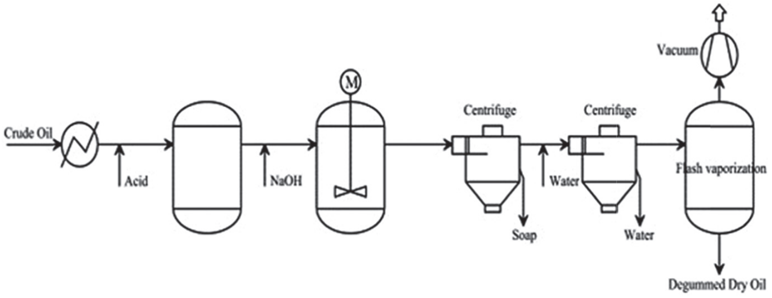


Fig. 5.2 Vegetable oils neutralization process for biodiesel production (Adapted from Santori et al. 2012)

process temperatures. During acid esterification, each mole of fatty acid converted to methyl esters produces one mole of water.

$$\mathrm{RCOOH + R'OH \longleftrightarrow R'COOR' + H_2O} \tag{5.7}$$

Industrially, both esterification and transesterification are employed in a two-step process to first convert the FFA into alkyl esters and then to convert the remaining triglycerides into methyl esters (Minami and Saka 2006; Wang et al. 2007b). The high-FFA oil is elevated in temperature, and then methanol (MeOH) and sulfuric acid (H_2SO_4) are added in appropriate quantity. The reaction is allowed to progress for several hours until the FFA concentration is reduced to an acceptable level for base-catalyzed transesterification. The methanol is decanted which carries the majority of the sulfuric acid and water with it. The methanol is either neutralized after decanting or neutralization is done prior to decanting with a base such as sodium hydroxide or potassium hydroxide. This converts the sulfuric acid into non-corrosive salts. The esterified oil is then transferred to another reactor where additional methanol and a base catalyst are added to transesterify the remaining triglyceride. Washing and other post-processing steps are done to prepare the resulting methyl esters for sale as biodiesel fuel.

The pretreatment of feedstocks with high FFAs *transesterification* using acid-catalyzed and *followed* by *base-catalyzed* reaction has been proposed by several authors (Naik et al. 2008; Wang et al. 2007; Wang et al. 2006) as an effective process for the appropriate quality of biodiesel as per ASTM specification. The process can lower a high-FFA feedstock to ≤0.5 percent quickly and effectively. However, depending on the amount of FFA in the oils or fats, one-step pretreatment may sometimes not reduce the FFA efficiently because of the high content of water produced during the reaction (Ghadge and Raheman 2005). In this case, a mixture of alcohol and sulfuric acid can be added into the oils or fats three times (three-step pre-esterification) and the water must be removed before transesterification (Leung et al. 2010). Gerpen (2005) suggested the use of high molar ratios of alcohol to oil as high as 40:1 to dilute the water formed during pretreatment, yet this will require more energy to recover the excess alcohol used. The water formed during the pretreatment phase requires removal and the use of corrosive nature or catalysts commonly

H_2SO_4 which requires high capital intensive reactors, has limited the application of the process.

The primary alcohols used for biodiesel production in both transesterification and esterification reactions are of the lower types, namely methanol and ethanol (Mittelbach and Remschmidt 2004). Each has distinct advantages and disadvantages. Methanol is by far the most popular alcohol used in industrial biodiesel production. The primary reasons for this are its low price and high reactivity. The advantages include the fact that methanol has less of an affinity to atmospheric moisture absorption and retention and can be obtained in anhydrous form (Christie 1993). Ethanol also has an additional carbon atom which has been shown to increase the heat and cetane values of ethyl esters (Fillières et al. 1995). Other disadvantages of ethanol are difficulty separating of the ester and glycerol phases, higher reaction temperatures, reaction sensitivity to trace moisture, and lower conversion than methanol (Mittelbach and Remschmidt 2004).

5.1 Pretreatment of High Free Fatty Acids Oils

5.1.1 Pretreatment with Acid

Biodiesel production from oils and fats with high FFA was studied by Canakci 2001. It was reported that the acid-catalyzed pretreatment reaction decreased the acid value of the synthetic mixture to less than 2 mg KOH/g with a two-step process. Using the two-step acid-catalyzed pretreatment followed by an alkali-catalyzed final reaction, the transesterification reaction was completed in much less time than would be possible with acid-catalyzed transesterification alone. The researchers (Canakci 2001) concluded that increasing the acid catalyst amount is very effective in decreasing the acid value of the mixture. In the first pretreatment step, using a 10:1 molar ratio and 30 minutes of reaction time, the acid value of the simulated high-FFA feedstock was reduced from 41.33 mg KOH/g to 1.37 mg KOH/g using 15 percent acid catalyst. Chongkhong et al. (2007) studied the biodiesel production by esterification of palm fatty acid distillate. Batch esterifications of palm fatty acid distillate (PFAD) were carried out to study the influence of, including reaction temperatures of 70 °C to 100 °C, molar ratios of methanol to PFAD of 0.4:1 to 12:1, quantity of catalysts of 0 percent to 5.502 percent (wt of sulfuric acid/wt of PFAD) and reaction times of 15 to 240 minutes. The optimum condition for the continuous esterification process reported that the molar ratio of methanol to PFAD at 8:1 with 1.834 wt% of H2SO4 at 70 °C under its own pressure with a retention time of 60 minutes. The reduction of FFA from 93 wt% to less than 2 wt% at the end of the esterification process was reported by Chongkhong et al. (2007). Park et al. (2010) studied the feasibility of the production of biodiesel from trap grease containing 51.5 percent FFA. The esterification of FFA by an acid catalyst (H_2SO_4 or Amberlyst 15) followed the transesterification of the remaining triglycerides by an alkali catalyst (KOH). After the esterification of the trap grease using 0.5 wt% sulfuric acid and a molar ratio of methanol to oil of 9:1, the acid value decreased from 102.9 to 2.75 mg KOH/g (97.3 percent FFA conversion). The product with 2.75 mg KOH/g acid value was then transesterified using potassium hydroxide. With a molar ratio of methanol to oil of 6:1, 0.8 wt% of potassium hydroxide, 353 K and 0.5 hour, fatty acid methyl ester (FAME) content reached 92.4 percent. In the esterification test using 21 percent of Amberlyst 15, a molar ratio of methanol to oil of 8.37:1, 368 K, and 3 hours, the acid value decreased to 3.23 mg KOH/g. With the transesterification using 1.2 percent potassium hydroxide, a molar ratio of methanol to oil of 6:1, 353 K, and 0.5 hour, FAME content increased to 94.1 percent.

Microwave heating has proved to be very efficient for the conversion of fatty acids to esters in the biodiesel synthesis. High conversions were easily obtained, even with moderate reaction conditions such as a FFA:methanol molar ratio of 1:6, 2.5 percent of sulfuric acid catalyst, a reaction time of 15 minutes and temperature of 393 K (Fernandes et al. 2014). Moreover, no significant difference was observed in using methanol or ethanol in the esterification reactions. Esterification of palm fatty acids to produce biodiesel in a batch reactor was conducted by Aranda et al. (2008) using homogeneous acid catalysts, evaluating the effect of the alcohol used, presence of water, type and concentration of catalysts. It was reported that acid strength of the catalyst was responsible for the higher activity of sulfuric and methanesulfonic acids, releasing more H+ species to protonate the carboxylic moiety of the fatty acid (rate determinant step). It was reported by Fernandes et al. (2014) that the esterification reaction equilibrium was attained much faster under microwave heating. Using the standard test conditions, equilibrium was reached within 15 minutes under microwave heating, but only after 30 minutes with conventional heating. Optimal parameters used by Farag et al. (2011) to obtain conversion efficiency of nearly 96.6 percent with low production cost were methyl/oil molar ratio 6:1, temperature = 60 °C, catalyst mass concentration 2.5 percent and stirring speed 300 rpm for 60 minutes as shown in Fig. 5.3.

5.1.2 Pretreatment with Glycerol

While the acid pretreatment is effective in reducing FFAs, the acid can cause damage to metal tanks. Use tanks coated with Teflon or plastic or invest in super-alloy tanks. Another disadvantage of the acid pretreatment is that extra methanol is required because methanol is added with the acid and then removed with the water/acid layer. This methanol becomes contaminated with water. To recover and reuse the methanol, a distillation tower is required to separate the water from the methanol. To be economically viable and environmentally sustainable, this methanol must be recycled, which requires a distillation process to remove water (Kirk 2012). Glycerolysis reduces the amount of FFA in low-grade oils without use of acid or methanol, and enables them to be converted into final product, rather than removing them and reducing product yield. The resulting glycerides formed during glycerolysis are then converted directly to biodiesel via base-catalyzed transesterification. Moreover, glycerolysis is done at high enough temperatures to completely dry the feed oil before the transesterification process, thus avoiding the formation of excess soaps and the decanting problems that can result. Over the past decade, glycerolysis has continued to grow in popularity among those companies successful in the industry (Kirk 2012).

The glycerolysis process has the capability of converting FFA back to their respective glyceride molecule (Sonntag 1982). This technique involves adding glycerol to the high-FFA feedstock and heating it to temperature of about (200 °C). The glycerol reacts with the FFAs to form monoglycerides, diglycerides. and triglycerides as shown in Fig. 5.4 (Felizardo et al. 2011). It produces a low FFA feed that can be processed

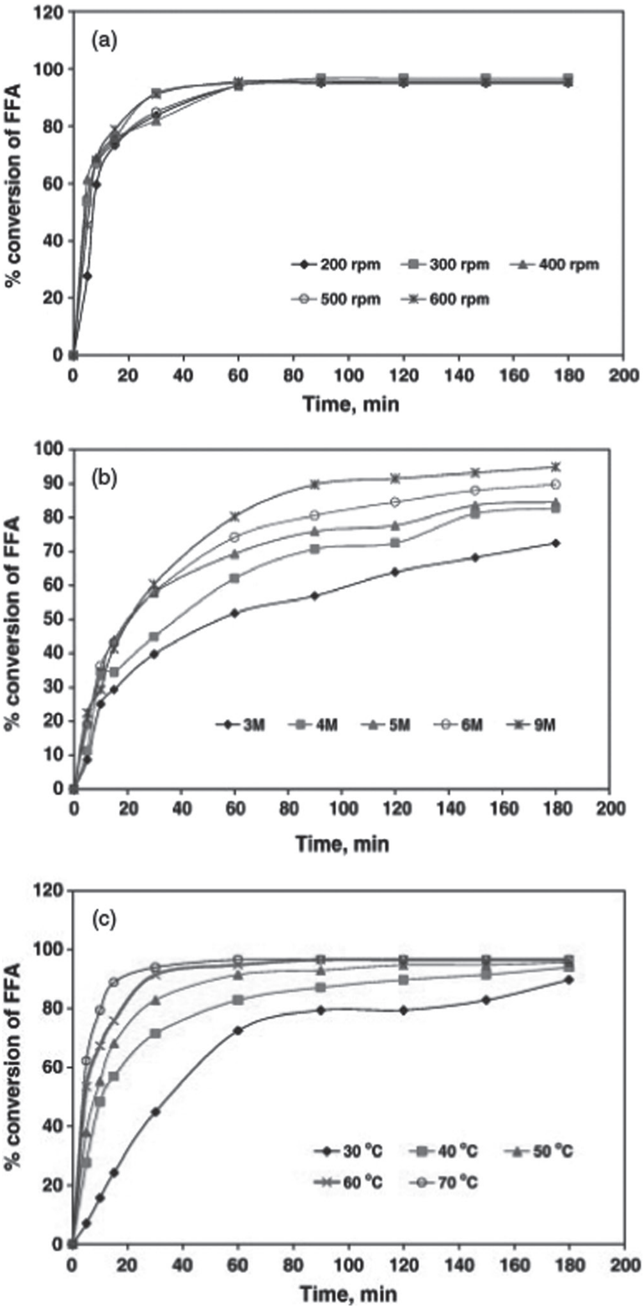


Fig. 5.3 Effect of reaction parameters on the conversion of FFAs: (a) Effect of stirring rate, (b) Effect of methanol/oil molar, (c) Effect of reaction temperature (Adapted from Farag et al. 2011)

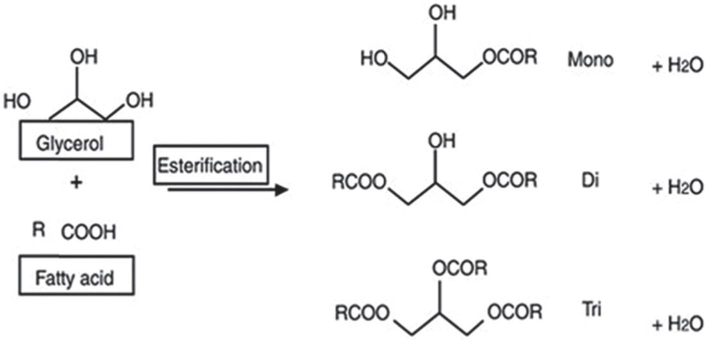


Fig. 5.4 Primary reactions for glycerolysis (Adapted from Felizardo et al. 2011)

to methylesters using traditional homogeneous base transesterification technique. An important aspect of this approach is that no alcohol is needed during the pretreatment and the water formed from the reaction can be immediately vaporized and vented from the reaction mixture (Anderson 2014). The process has also the potential of utilizing glycerol, a by-product from transesterification and thereby lowers the cost of biodiesel. The rate of the glycerolysis reaction is determined by two variables: the initial concentration of FFA and temperature.

Glycerolysis can occur at different temperatures, depending on the type of oil used. The FFA content of the acidulated soap stocks was reduced from 50 percent to 5 percent after 3 hours of reaction at 200 °C. Similar observations have been made by other researchers (Bhosle and Subramanian 2005; Bhattacharyya and Bhattacharyya 1987) in glycerolysis of high-FFA rice bran oil whereby the rate at which raw rice bran oil glycerolysis was maximum between 180 °C and 200 °C. De and Bhattacharyya (1987) showed that the reaction temperature of 210 °C was more effective than temperature below 200 °C in glycerolysis of rice bran oil containing high FFA (9.5 percent to 35.0 percent) with monoglycerides. The reaction temperature was also found to influence the rate of glycerolysis process by Ebewele et al. (2010) in chemical glycerolysis of high acidic rubber seed oil with 37.69 percent FFA. At low temperature of 150 °C, the FFA was lowered to about 7.03 percent in 6 hours. While at 200 °C, the FFA dropped to 1.5 percent over the same period. On increasing temperature further to 250 °C, the reduction in

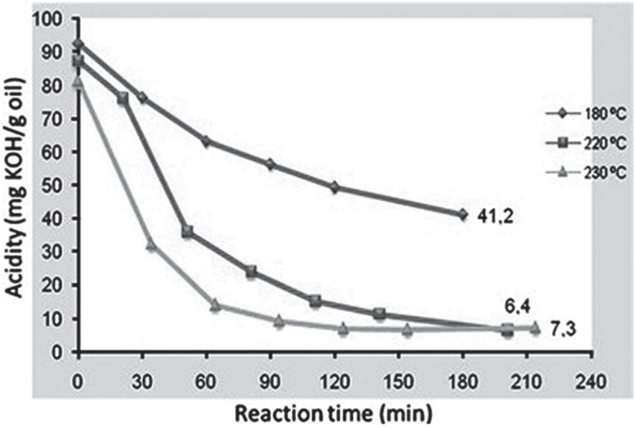


Fig. 5.5 Effect of reaction temperature on the glycerolysis reaction (Adapted from Felizardo et al. 2011)

FFA was fastest within the first 2 hours. However, the FFA dropped to 3.88 percent after 6 hours of the reaction time. It is supposed that there was a small degree of fat splitting at this elevated temperature after being held for 6 hours. The rate at which FFA re-esterifies was at its maximum between 200 °C and 250 °C. Variable temperatures of 180 °C, 220 °C, and 230 °C were used by Felizardo et al. (2011) in pretreating acidulated soap stock of 50 percent FFA. It was found that temperature increase favors the reaction kinetics considerably faster at 230 °C. However, more significant difference in FFA drop seems to occur when the temperature increases from 180 °C to 220 °C, as shown in Fig. 5.5.

The effect of amount glycerol on the glycerolysis reaction was studied by Felizardo et al. (2011). The experiments were performed at 220 °C with a glycerol excess of 4 percent, 11 percent, and 52 percent. The use of more than 10 percent (molar ratio glycerin/FFA = 1.10) excess glycerol did not show any improvements in the reaction kinetics at a temperature of 220 °C, as shown in Fig. 5.6. In their study, Ebewele et al. (2010), the stoichiometric amount of glycerol (4.3 %w/w of oil) in reesterifing rubber seed oil of 37.69 percent FFA was shown to be significant in FFA reduction as compared to when no glycerol was used in the reaction. However, using 5.6 %w/w of oil that is 30 percent excess of glycerol there was no significant improvement in FFA reduction as compared to the stoichiometric amount of glycerol. With 30 percent

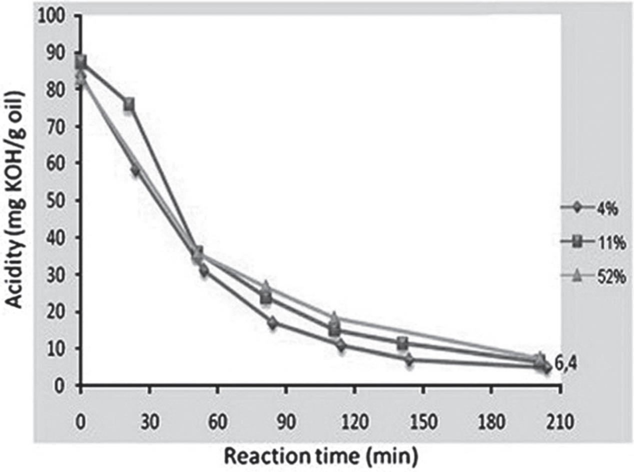


Fig. 5.6 Effect of glycerin excess on the glycerolysis reaction (Adapted from Ebewele et al. 2011)

excess of glycerol, the rate of FFA reduction was rapid during the initial 2 hours of reaction and thereafter decreases considerably. This could possibly due to high reesterification reaction occurring between the hydroxyl groups from the added glycerol and FFA at the initial stage which leads to an increase in triglycerides content. A reduction in FFA from 37.69 percent to 1.5 percent was achieved in a reaction time of 6 hours with 4.3 percent glycerol (stoichiometric amounts) at 200 °C while under the same reaction condition and time the FFA dropped from 37.69 percent to about 15 percent when no glycerol was used. In this case reduction in FFA content is thought to be the reaction between FFA and the free hydroxyl groups remaining in the oil (Bhosle and Subramanian 2005). De and Bhattacharyya (1999) studied the effect of the amount of glycerol on the extent of glycerolysis of raw rice bran oil. The addition of glycerol was shown to increase the rate of reaction. The excess theoretical amounts of glycerol used were 10 percent, 30 percent, and 50 percent. After 6 hours of reaction, the FFA was reduced from 15.3 percent to 4 percent by using 50 percent excess amount of glycerol while the drop in FFA was from 15.3 percent to 6 percent, 5.6 percent, and 4.8 percent for 10 percent, 20 percent, and 50 percent excess glycerol, respectively. Singh and Singh (2009) tried to use 50 percent, 70 percent, and 100 percent in excess of the theoretical amount of glycerol required in reesterification of

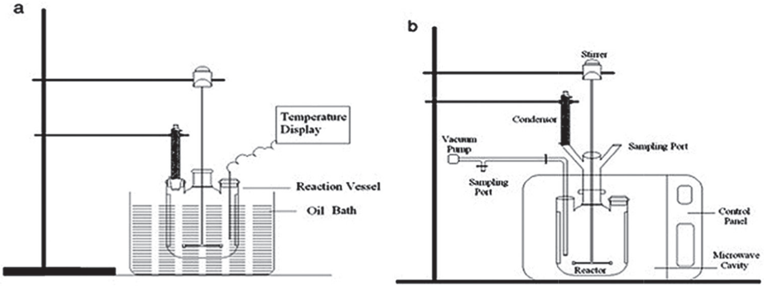
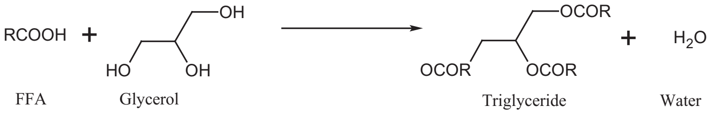


Fig. 5.7 Schematic representation of experimental setup (a) conventional and (b) microwave methods (Adapted from Gole et al. 2014)

rice bran oil with acid value of 24.3 mg KOH/g. When using 50 percent excess glycerol, the drop in acid value was about 19.3 percent at 200 °C for 6 hours. On increasing the excess glycerol up to 70 percent, the glycerolysis rate was faster and the maximum reduction in acid value was 20.2 percent at 200 °C within 4 hours. The use of 100 percent excess glycerol followed similar trend to that of 70 percent excess glycerol. However, the impact of increasing the amount of glycerol was not encouraging as the maximum drop in acid value was only 20 percent after 5 hours.

Recently, Gole et al. (2014) studied intensification of glycerolysis reaction of higher FFA containing sustainable feedstock using microwave irradiation (Fig. 5.7). The superiority of microwave-based synthesis approach with much lower energy requirement for microwave as compared to the conventional method was calculated based on the following equations.



(5.8)

A typical second-order kinetic equation can be written as follows:

$$\frac{d[A]}{dt} = k[A]^{\alpha}[B]^{\beta} \tag{5.9}$$

From Eq. (5.2), 1 mol of FFA = 1 mol of glycerol and hence $\alpha = \beta = 1$, $[A] = [B]$

$$\frac{d[A]}{dt} = k[A]^2 \tag{5.10}$$

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \tag{5.11}$$

where

$[A]$ = concentration of FFA, moles/lit

$[A]_0$ = initial concentration of FFA, moles/lit

$[B]$ = concentration of glycerol, moles/lit

k second-order rate constant, lit/moles/minutes.

The superiority of microwave-based synthesis approach with much lower energy requirement for microwave as compared to the conventional method was calculated by Gole et al. (2014) as follows:

Energy Requirement for Conventional Method

Total energy requirement = energy for stirring + energy for heating

Energy for stirring = power required for stirring × time (second)

$= 120 \times 240 \times 60$

$= 1728 \times 10^3$ J

Energy for heating = $mC_p\Delta T$

$= 4.875 \times 4.18 \times 10^3 \times (200\text{–}30)$

$= 3464.2 \times 10^3$ J

where m is mass of solution (kg); C_p is specific heat (kJ/kg K), ΔT is the rise in the temperature (K).

Total energy = 5192.2×10^3 J

1mole ester formed = 1 moles of glycerin reacted

= initial moles of FFA × conversion × molecular weight of glycerin

$= 0.1 \times 0.935 \times 283$

$= 25.5$ g

$$\text{Energy required} = \frac{\text{Total energy requirement, J}}{\text{Mass of glycerin reacted, g}}$$

$$= \frac{5192.3 \times 10^3}{25.5}$$

$= 203.6$ kJ/g

Energy Requirement for Microwave-irradiation method

$$\begin{aligned}
\text{Total energy requirement} &= \text{energy for stirring} + \text{energy for equipment}\\
\text{Energy for stirring} &= \text{power required for stirring} \times \text{time (second)}\\
&= 120 \times 25 \times 60\\
&= 180 \times 10^3\ \text{J}\\
\text{Energy for stirring} &= \text{microwave power} \times \text{time (second)}\\
&= 480 \times 25 \times 60\\
&= 720 \times 10^3\ \text{J}\\
\text{Total energy} &= 900\ \text{kJ}
\end{aligned}$$

$$\begin{aligned}
\text{Energy required} &= \frac{\text{Total energy requirement, J}}{\text{Mass of glycerin reacted, g}}\\
&= \frac{900 \times 10^3}{25.5}\\
&= 35.3\ \text{kJ/g}
\end{aligned}$$

Energy consumption analysis also revealed the superiority of microwave-based synthesis approach with much lower energy requirement for microwave (35.3 kJ/g) as compared to the conventional method (203.6 kJ/g), as calculated from the above equations. Comparison based on kinetic analysis confirmed that the rate constant obtained for microwave-assisted glycerolysis was six times higher than that obtained in the conventional approach. Microwave effect results in the rapid molecular heating due to the dipolar rotation of molecules and the frequency of molecular level interaction, which is useful in intensifying the rate of glycerolysis on multifold basis as compared to the conventional approach (Gole et al. 2014). Another advantage offered by microwave-based approach is the significant reduction in the reaction time (240 to 25 minutes) and required reaction temperature (200°C to 105°C).

During the last decade, the rendering industry has successfully adapted to changing market conditions. From increased product safety and testing guidelines to entering new arenas like biodiesel, rendering has remained a vital process. However, these new developments are changing the way renderers look at their products. Technologies to upgrade low-quality oils such as brown grease are being researched in order to improve product specifications as well as expand into new industries such as renewable fuels. Whether glycerolysis is performed at either temperature, end products are essentially the same. Both contain high mole fractions of monoglycerides and diglycerides along with a significantly lowered FFA fraction, and some remaining triglycerides and free glycerin. Glycerolysis at the high temperature has the added benefit of lowering FFA concentrations significantly faster (Coteron et al. 1998). When scaled up to a continuous system, running glycerolysis at 237 °C instead of 175 °C will result in at least three times the amount of throughput, while producing a dry product.

Many biodiesel plants run their processes using steam heating systems and are limited to operating temperatures of 175 °C or less. Although glycerolysis can be run at these lower temperatures, reaction kinetics is vastly improved when run at temperatures at or above 237 °C. However, operating temperatures approaching 260 °C are not recommended due to possible glycerin decomposition, forming acrolein. Glycerolysis can be used with feedstocks containing more than 10 percent FFAs. This involves adding glycerin at 400 °F and letting it react with the FFAs to form monoglycerides, a glycerol molecule to which one FFA has been joined. These monoglycerides can then be processed using a standard alkaline catalyst transesterification process. On the other hand, glycerolysis can be expensive because of the high heat involved, which requires a high-pressure boiler and trained boiler operator. Also, vacuum must be applied while heating to remove water that is formed during the reaction. Another disadvantage is that the glycerin will also react with the triglycerides in the oil to convert some of them to monoglycerides. While this does not negatively impact the reaction, it means that more glycerin is required for the process, and therefore more glycerin must be removed at the end of the transesterification. However, the glycerolysis can be more easily implemented than acid esterification and thereby avoids the need for neutralization and alcohol removal steps.

Glycerolysis reduces the amount of FFA in low-grade oils without use of acid or methanol, and enables them to be converted into final product, rather than removing them and reducing product yield. The resulting glycerides formed during glycerolysis are then converted directly to biodiesel via base-catalyzed transesterification. Also, glycerolysis is done at high enough temperatures to completely dry the feed oil before the transesterification process, thus avoiding the formation of excess soaps and the decanting problems that can result. Over the past decade, glycerolysis has continued to grow in popularity among those companies successful in the industry. Some biodiesel producers have been using glycerolysis successfully for several years. Finally, the lack of use of this high-temperature process might be more a matter of inexperience by biodiesel producers. But the actual simplicity of the glycerolysis process could be its most appealing feature.

5.1.3 Pretreatment with Adsorbent

The pretreatment options specifically address acid, some specifically address soap, but with the adsorbents you can remove a broad range metal impurities present in biodiesel. In the last years there has been a great progress in adsorbent design and cyclic adsorption process developments, thus making adsorption an important separation tool (King 1980). Adsorption is usually performed in columns packed with adsorbent, but it can also be performed in stirred tanks with the adsorbent in suspension. The latter are usually known as bleachers since their most common application is the bleaching of edible oils with clays. The high separating power of the chromatographic effect, achieved in adsorbent-packed columns, is a unique advantage of adsorption as compared to other separation processes (Vera et al. 2011). The high separating power is caused by the continuous contact and equilibration between the fluid and sorbent phases. If no diffusion limitations are considered, each contact is equivalent to an equilibrium stage (theoretical plate) and several hundred or more of such equilibrium stages can be achieved within a short column. Adsorption is thus ideally suited for purification applications and difficult separations. The adsorptive separation is achieved by one of three mechanisms: adsorption equilibrium, steric effect, and kinetic effect. Most processes, especially those in solid-liquid phase, operate with the principle of adsorption equilibrium and hence they are called equilibrium separation processes (Vera et al. 2011).

It was reported that adsorbents can be very effective when dealing with low levels of FFA, generally up to 2 percent (Voegele 2012). The presence of sulfur is another area in which pretreatment solutions would be beneficial. The process would be much simpler if an adsorbent were available that could effectively reduce the sulfur level of a feedstock (Voegele 2012). Different adsorbents in that line are designed to remove a broad range of contaminants from oils, esters, and surfactants. The adsorbents can also be used to effectively remove phosphorus (Tian et al. 2009). In the case of the biodiesel feedstock and product, the low elution rates in the packed columns make the dynamic separation (kinetic effect) of no use for a practical separation. In the case of the steric effect this is expected to work fine for molecules differing widely in size and this could be the case for molecules of the organic and polar phases normally found at the outlet of the transesterification reactors. Triglycerides, diglycerides, monoglycerides, FFAs, and FAMEs have high molecular weights and long acyl chains, and they are the main components of the organic phase. On the other side glycerol, water, and methanol have small molecular sizes and could be retained in packed beds containing suitable adsorbents. Because of their relative high vapor pressure, water and methanol need a relatively few number of theoretical plates to be separated from the organic phase by distillation/evaporation (Zhang et al. 2003), and this is indeed the preferred method of water and methanol removal. However, some reports on the use of hygroscopic adsorbents for biodiesel drying can be found (Lastella 2005). Removal of glycerol from biodiesel using adsorbents has already been proved, but only equilibrium adsorption on open pore adsorbents has been tried (Yori et al. 2007). The use of the steric effect in the adsorption of water on zeolites has, however, been proposed for the drying of the methanol to be recycled to the biodiesel process (Voegele 2012). This leaves equilibrium adsorption as the main principle behind the adsorption refining of biodiesel and makes the adsorption isotherm as the main piece of information for the accurate design and scale-up of adsorption units.

The principal advantage of the use of adsorbers in biodiesel refining is that of reducing the amount of wastewater and sparing the cost of other more expensive operations such as water-washing and centrifugation. For big refiners that can afford the cost of setting up a water treatment plant the problem of the amount of wastewater might not be an issue, but this can be extremely important for small refiners. In the common industrial practice water-washing is used to remove the remaining amounts of glycerol and dissolved catalyst, and also the amphiphilic soaps, MGs, and DGs. If water-washing is used to remove glycerol and dissolved catalyst only, large amounts of water should not be required. However, in the presence of MGs and DGs, the addition of a small amount of water to the oil phase results in the formation of an emulsion upon stirring. Particularly when this operation is performed at a low temperature, separation of the aqueous phase from the emulsion becomes difficult. In order to prevent the formation of such an emulsion in the conventional water-washing practice a large amount of water must be used. Karaosmanoglu et al. (1996) concluded that a minimum of 3 to 5 grams of water per gram of biodiesel at 50 °C were needed to efficiently remove the impurities of the fuel (3000 to 5000 liters of water per ton of biodiesel). These numbers should be considered typical of once-through water-washing operations but are not representative of closed-loop water-washing schemes. It has been suggested that the methanol removal step needed for successful adsorption be performed before glycerol separation and under vacuum conditions (D'Ippolito et al. 2007). The best operation of dry refining is that with cyclic reversible adsorption of glycerol/glycerides in twin packed beds, as early suggested (D'Ippolito et al. 2007). Other advantages of adsorption are the low capital investment, the absence of moving parts, the simplicity, and robustness of operation. Possible drawbacks are the need for disposal and replacement of the spent adsorbent in the case of the use of bleaching tanks.

5.2 Solid Catalytic Commercial Biodiesel Production

The Esterfip-H process, marketed by Axens, was developed by IFP Energies nouvelles and Axens. This technology uses a heterogeneous catalyst composed of zinc oxide and alumina used in extrudate form in fixed-bed reactors (Singh et al. 2014). The Esterfip-H process is an improvement of the Esterfip process using heterogeneous catalysts for elimination of neutralization and washing steps compared to conventional operation. The main invention of the Esterfip-H process is two fixed-bed reactors with a catalyst of zinc and aluminum oxide. By the use of a heterogeneous

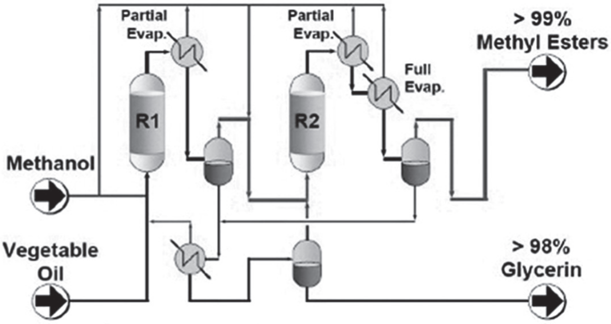


Fig. 5.8 The principal of the Esterfip-H process scheme (Adapted from Scharff et al. 2013)

catalyst problems related to formation of salt with catalyst, and thereby emulsion between the methyl ester and glycerol phase and the phase separation complexity will be reduced or removed (Islam et al. 2013a).

Fig. 5.8 shows a flow diagram of the designed process containing pumps, heat exchangers, reactors, decanters, and purification units. Pumps and heat exchangers are necessary to satisfy the required reactor conditions. There are two reactors in series with intermediate removal of methanol by pressure reduction and separation of glycerol and methyl phase. The pressure after reaction is released in two steps and methanol is flashed off. When the pressure is reduced the boiling temperature of the components will be reduced and due to the difference in boiling point between methanol and glycerol, methyl ester, triglyceride, diglyceride, and monoglyceride, methanol will be removed. The removed hot methanol is used for preheating of inlet streams to the reactors. The intermediate removal of glycerol is for driving the reaction in the desired direction and avoiding undesired reverse reaction in accordance with the principle of Le Chatelier (Oien 2013). When the phases have been separated the reaction could be pushed further in the desired direction after glycerol has been removed, new or recycled methanol is reintroduced in the methyl ester phase before compression and temperature increase back to reactor conditions. The two-step flash procedure is repeated after the second reactor and followed by vacuum distillation. Last purification of methyl ester phase after vacuum distillation is done in a decanter followed by a

Fig. 5.9 Diester Industrie Esterfip-H biodiesel facility in Sète, France (Adapted from Scharff et al. 2013)

coalescer for final removal of fine glycerol droplets (Oien 2013; Scharff et al. 2013).

The first industrial plant using Esterfip-H was set up in France producing 200 kt/year of biodiesel (Fig. 5.9). The design of the catalyst (geometry, chemistry, stability) allows it to operate at high throughput with a long lifetime which reduces the catalyst cost as compared to the homogeneous catalyst process. The somewhat lower activity of the catalyst is offset by operating conditions: temperature, pressure, and excess methanol. However, suppression of waste production of low value fatty acids leads to a very high yield of ester per ton of oil, near to stoichiometric value.

Conventional homogeneous catalyst transesterification process has several drawbacks: consumption of hazardous base and chemicals with associated operating cost and corrosion concern, low biodiesel yield with soap or low value fatty acid production, and production of low-grade glycerin containing high levels of salts and water. The use of a solid catalyst allows an almost water-free process, avoids these disadvantages and as such, has many advantages in terms of economics (high biodiesel yield, low catalyst cost, high quality glycerin), and environmental impact. However, the scientists are claiming that-

Splitting water with sunlight is the Holy Grail of a sustainable hydrogen economy.

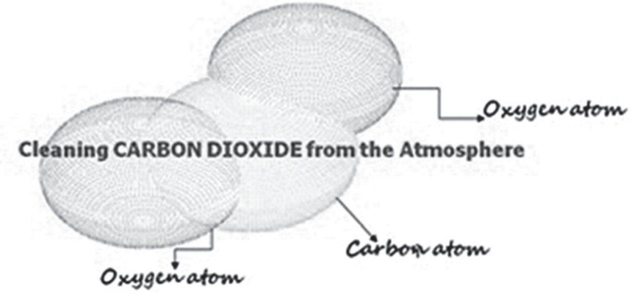


Fig. 5.10 Carbon-di-oxide molecule.

Thus, the successful process design, combined with any of the methods proposed for carbon dioxide disposal (Fig. 5.10), would be a major step toward solving the greenhouse gas problem and toward establishing a net zero carbon economy that would not have to abandon the vast fossil energy resources that could fuel economic prosperity for generations.

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Advanced Technologies in Biodiesel

New Advances in Designed and Optimized Catalysts

Aminul Islam • Yun Hin Taufiq-Yap • Siow Hwa Teo • Eng Seng Chan

The inadequacy of fossil fuel is the main driving force of the future sustainable energy around the world. Since heterogeneous catalysis is used in chemical industry for biodiesel production, achieving optimal catalytic performance is a significant issue for chemical engineers and chemists. Enormous attention has been placed in recent years on the selection of heterogeneous catalyst in biodiesel industry, where the catalyst could be facilitated highly selective toward desired products, easily handled, separated from the reaction medium, and subsequently reused.

This book stresses an overview on the contributions of tailored solid acid and base catalysts to catalytic biodiesel synthesis, and the influences of heterogeneous catalyst properties on biodiesel yield in order to develop a better understanding of catalyst design for the green production process as well as practical applications in the biodiesel industry.

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