2.1 Biodiesel

American society for testing and materials (ASTM) defines biodiesel as "the monoalkyl esters of long chain fatty acids derived from the renewable liquid feedstock, such as vegetable oils and animal fats, for use in compression ignition (CI) engines" [Knothe, 2011]. It is a clean burning, high energy returns (~90%), oxygenated (~10%) and sulfur-free fuel which results into reduction in the exhalation of carbon monoxide, sulfur dioxide, nitrogen oxide, and carbon dioxide over the petroleum diesel [Syazwani et al., 2015; Liaquat et al. 2010]. Biodiesel is a potential substitute to petroleum diesel fuel in terms of viscosity, lubricity, flash point, cetane number and can be applied in existing internal combustion and ignition diesel engines without any modification for low blend of 5-30% with petroleum diesel [Silitonga et al., 2013; Dupont et al., 2009].

2.2 Techniques for biodiesel production

The higher level of unsaturated fatty acids in triglycerides molecules is responsible for high viscosity and density of vegetable oils and animal fats. The problems such as carbon deposit, chocking, and contamination of lubricating oils are associated with the use of these oils and fats as fuel directly in engines. Therefore, some chemical treatment is required to reduce the viscosity of these feedstocks to be compatible with the existing engine. In literature, four methodologies for biodiesel production such as direct use or blending, microemulsion, pyrolysis and transesterification have been studied [Abbaszaadeh et al., 2012].

2.2.1 Direct use or blending

The direct use of vegetable oils and animal fats as diesel fuel were investigated because of their liquid nature, high energy content (80% of diesel fuel), readily availability and renewability. Rudolf Diesel (1858–1913), the inventor of the diesel engine had ran the 1st diesel engine with peanut oil in 1893 and presented an optimistic approach for biofuels for future. But the use of oils and fats as fuel was insignificant due to high viscosity, low volatility and corrosion by acid composition [Lin et al., 2011]. The viscosity of vegetable oils is 10–20 times higher than that of diesel fuel. After that blends of vegetable oil and diesel fuel, solvent or ethanol was used successfully for short-term experiments. The long term use (after 90 hours run) of the direct and blends of the oils were considered impractical for diesel engines causing gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening [Ma and Hanna, 1999].

2.2.2 Microemulsion

To reduce the viscosity of vegetable oil and fats, microemulsion approach is a potential solution to produce biodiesel. IUPAC defines the microemulsion as ''*dispersion made of water, oil, and surfactant(s) that is isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm.*'' Biodiesel microemulsion contains three components in suitable proportions; oil phase, aqueous phase and surfactant. Short chain alcohols such as methanol, ethanol and propanol as well as esters are used as viscosity lowering additives; higher alcohols butanol, hexanol and octanol are used as effective surfactants [Balat and Balat, 2010]. Alkyl nitrates are used as cetane improvers. Microemulsion method improves the spray characters and cetane

number of biodiesel but prolongs usage leads to issues like incomplete combustion, injector needle sticking, and carbon deposit formation [Zhang et al., 2003].

2.2.3 Pyrolysis or thermal cracking

Pyrolysis is the chemical conversion in which complex organic substrates are converted into simple compounds by application of heat in absence of air or oxygen. The triglycerides present in vegetable oils or animal fats are cracked into alkanes, alkenes, alkadienes, aromatics and carboxylic acids which are suitable for diesel engines in terms of viscosity. This technique improves the cetane number as well as flow characters of biodiesel by reducing viscosity. Disadvantages of this process include high equipment cost and needs for separate distillation equipment for separation of various fractions of pyrolyzed materials [Fukuda et al., 2001].

2.2.4 Transesterification reaction

Transesterification reaction is the reaction of triglyceride molecules present in vegetable oils or fats with shorter chain alcohols in presence of the catalyst to produce fatty acid alkyl esters (FAAEs) and glycerol moiety (Figure 2.1). It is an accepted and best method to minimize the viscosity of oils and fats by producing fatty acid monoalkyl esters. Stoichiometrically, three moles of alcohol and one mole of oil are required, since transesterification reaction is reversible in nature, thus excess supply of alcohol is required to shift the equilibrium in alkyl ester formation direction [Leung et al., 2010]. The transesterification involves three consecutive reactions; triglycerides are stepwise converted into diglycerides followed by monoglycerides and then to glycerol, producing one alkyl ester molecule from each step (Figure 2.2).
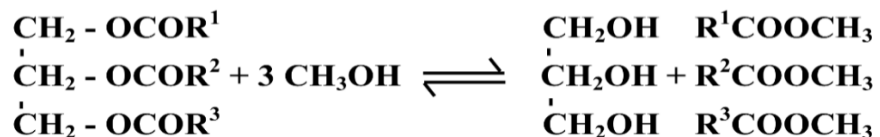
$$
\begin{array}{l}
\text{CH}_2 - \text{OCOR}^1 \\
\text{CH}_2 - \text{OCOR}^2 + 3\ \text{CH}_3\text{OH} \rightleftharpoons \\
\text{CH}_2 - \text{OCOR}^3
\end{array}
\qquad
\begin{array}{l}
\text{CH}_2\text{OH} \quad \text{R}^1\text{COOCH}_3 \\
\text{CH}_2\text{OH} + \text{R}^2\text{COOCH}_3 \\
\text{CH}_2\text{OH} \quad \text{R}^3\text{COOCH}_3
\end{array}
$$

Figure 2.1 Transesterification of triglycerides

$$
\textbf{Triglyceride} + \textbf{R}^1\textbf{OH} \rightleftharpoons \textbf{Diglyceride} + \textbf{RCOOR}^1
$$
$$
\textbf{Diglyceride} + \textbf{R}^1\textbf{OH} \rightleftharpoons \textbf{Monoglyceride} + \textbf{RCOOR}^1
$$
$$
\textbf{Monoglyceride} + \textbf{R}^1\textbf{OH} \rightleftharpoons \textbf{Glycerol} + \textbf{RCOOR}^1
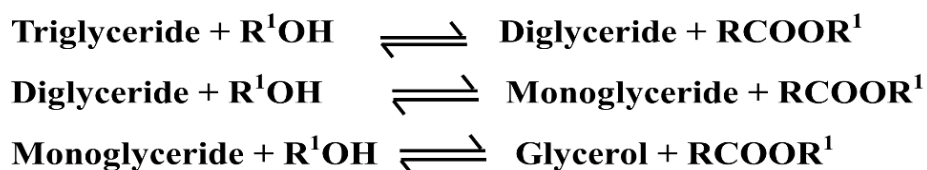$$

Figure 2.2 General equation of transesterification of triglycerides

Biodiesel production via transesterification is more advantageous than other methods in terms of improved fuel characteristics such as density, viscosity, lubricity, fire point etc. and glycerol produced as by-product can be used for medicinal and industrial purpose. Biodiesel produced by this method is miscible in any proportion with diesel fuel or can be used alone [Ma and Hanna, 1999; Lin et al., 2011].

2.3 Raw materials for biodiesel production

2.3.1 Alcohol

Alcohols are important feedstock in biodiesel production via transesterification reaction. These acts as acyl acceptor, particularly methanol and ethanol in the transesterification reaction. Other alcohols such as propanol, butanol, isopropanol, *tert*-butanol, branched alcohols and octanol can also be used but their cost is high. To minimize the steric effect, short chain alcohols, methanol and ethanol are commonly used but methanol is preferred because of its low price and chemical and physical advantages like it is polar and shortest

chain alcohol. Methanol can react with triglycerides readily and gets easily dissolve the alkali catalyst [Sanli and Canakci, 2008].

2.3.2 Lipid feedstocks

From the literature survey, copious lipid feedstocks are reported for the production of biodiesel which can be categorized as first generation, second generation and third generation feedstocks on the basis of type of processing technology, type of feedstock or their level of development.

2.3.2 (a) First generation feedstocks

At present time, food-based virgin oils are utilized for more than 95% biodiesel production worldwide. The edible oils such as rapeseed oil, sunflower oil, palm oil, soybean oil, peanut oil and corn oil etc. are considered as first generation feedstocks [Celikten et al., 2010; Siler-marinkovic et al., 1998]. The first generation feedstocks are readily available as crops and relatively simple conversion processes are required for the biodiesel production. Contrarily, consumption of edible oils for commercial production of biodiesel contributes 'food versus fuel crisis', dramatically raising the prices of vegetable oil and environmental problems such as demolition of vital land resources, deforestation, and ample usage of available arable land [Sumathi et al., 2008].

2.3.2 (b) Second generation feedstocks

To overcome the tremendous setbacks of first-generation feedstocks, the meticulous variety of non-edible oils such as jatropha, karanja, mahua, cotton seed, kusum, jojoba, bahera, neem, moringa etc. and some waste products such as animal fats and waste cooking oil were

explored by researchers [Pramanik, 2003]. These feedstocks are termed as second-generation feedstocks. These are non-food materials and reduce the food vs. fuel competition. Non-edibles plant oils can be easily cultivated in marginal as well as wastelands which require less maintenance, low cost, less soil fertility etc. [Canakci, 2007]. They support the agricultural and rural development and do not affect the food supply with additional benefits of green belt on wastelands [Canoira et al., 2006; Singh and Singh, 2010].

2.3.2 (c) Third generation feedstocks

Oils derived from algae and microalgae biomass have attracted the attention as third generation feedstocks for biodiesel production. Currently, algal oil is an interesting alternative as the future feedstock for biodiesel because of high lipid content and rapid biomass production. Microalgae are fast-growing, photosynthetic eukaryotes with a simple cellular structure ranging from unicellular to multicellular forms [Mata et al., 2010]. These are very efficient solar converters that convert solar energy into chemical energy by photosynthesis in form of a variety of metabolites such as oils, carbohydrates, and proteins. Microalgae can be grown in fresh, saline, or brackish water habitat and produce algal biomass in presence of sunlight, carbon dioxide and water [Chisti, 2007]. The details of these feedstocks have been presented in Table 2.1.

2.3.3 Selection of feedstocks

Selection of feedstock plays an important role in deciding the cost of biodiesel production at commercial scale. The economics of biodiesel production is highly feedstock dependent and it comprises a very substantial portion of overall production cost. Various feedstocks such as edible oils, non-edible oils, animal fats, and waste cooking oil etc. have been reported in the

literature as a feedstock material. Table 2.2 presents the world's biggest biodiesel producing countries according to their production volume along with their major feedstocks. Cost of raw materials makes up to 70–95% of the total production cost of biodiesel and its cost might be decreased 60-70% by utilizing non-edible oils as a feedstock. The nature of feedstock used is reliant on the geographical position and climate conditions of the place. For instance, Europe employs sunflower and rapeseed oils; palm oil predominates in tropical countries, soybean in the United States and canola oil in Canada etc. The cost of feedstocks falls as FFAs content rises. For industrial biodiesel production, there is a need for low-cost (high FFAs) feedstocks such as waste cooking oils, and non-edible oils which improve the economic viability of biodiesel.

Since biodiesel synthesized from refined oils are costly as compared to petrodiesel fuel [Sahoo and Das, 2009]. Besides, the application of such feedstocks in biodiesel production could minimize competition between the demand for edible vegetable oils and cost of biodiesel. For the purpose, in the present study, used vegetable oil (UVO) and kusum oil (KO) were selected as feedstocks materials.

2.3.3 (a) Used vegetable oil

Used vegetable oil defined as ''vegetable oil which has been used in food production and which is no longer viable for its intended use''. Alves et al. (2013) and Farooq et al. (2013) deliberated that the cost of feedstock and catalyst contributes approximately 70–95% of the total biodiesel production cost. By giving higher priority to used vegetable oils (UVO) as feedstock, this cost can be adequately cut down to 60–70%. Used vegetable oil is waste material of deep frying of food at household, restaurants, hostel-kitchen, food manufacturing

industry and catering industries which are usually disposed of like water and soil pollutant with water drainage system [Gude et al., 2013]. Thus, incorporation of these problematic waste oils into the economic production of biodiesel gives additional benefits in terms of minimizing environmental impacts. Investigation of performance, emission and combustion characteristics of engine running by UVO-biodiesel as fuel have shown comparable results at lower blend with diesel fuel [Farooq et al., 2013].

Table 2.1 First, second and third generation of feedstocks for biodiesel production

	First generation feedstocks	Second generation feedstocks	Third generation feedstocks
Examples	Palm oil, Soybean oil, Corn oil, Rapeseed oil, Sunflower oil	Jatropha oil, Kusum oil, Mahua oil, Waste cooking oil, animal fat, Yellow grease	Microalgae such as *Chlorella*, *Spirullina*, *Dunaliella*
Advantageous	o Simple production method	o Non-food materials o Inexpensive o Abundant availability o Virtually grow anywhere	o Non-food materials o Fast growing o Virtually grow anywhere
Disadvantageous	o Food vs. fuel debate o Expansive o Limited availability o Required land availability	o Difficult processing	o Advance processing o Very expansive and contamination

Table 2.2 Leading biodiesel producers worldwide in 2016, by country (in billion litres) and their major feedstock

Country	Annual biodiesel production (2017) in billion liters	Major feedstocks
U.S.	6	Soybean oil, waste oil, peanut oil
Brazil	4.3	Soybean oil, palm oil, castor oil
Germany	3.5	rapeseed oil
Indonesia	2.5	palm oil and its derivative
Argentina	3.3	Soybean oil
France	2.3	Rapeseed oil, sunflower oil
Thailand	1.4	palm oil and its derivative
India	0.14	Jatropha and palm oil

2.3.3 (b) Kusum oil

Kusum is a forest-based plant and its botanical name is *Schleichera oleosa.* It is also called Ceylon oak, Lac tree and Gumlacis and is abundantly found in India, China, Malaysia, Indonesia and Sri Lanka. In India, it is generally found in sub-Himalayan tracts in the north, central parts of eastern India, particularly in Orissa. *Schleichera oleosa* belongs to the Sapindaceae family and is the member of the family are rich in oil containing cyanogenic compounds to the extent of 0.03-0.05% as hydrogen cyanide (HCN) which makes the oil toxic, non-edible and bitter in taste [Banković et al., 2012; Kundu and Bandyopadhyay, 1969]. It is a large deciduous tree with a short fluted trunk and grows in rocky, gravelly and slightly acidic

well-drained soil. The fruits are available between the months of March-June. The seeds are covered in a succulent aril having acidic taste and contain 51-52% oil which is dark brown in appearances [Kumar and Sharma, 2011]. The oil contains 3.6–3.9% of glycerin and 5–11% of FFA (free fatty acids). The annual production of kusum oil in India is 25000 t/year which can be a potential feedstock for biodiesel production [Rathod and Lawankar, 2013]. The studies by Sharma and Singh (2010) showed the successful use of kusum for biodiesel synthesis with high yields and conversion via esterification followed by a transesterification reaction.

2.4 Catalyst selection

In transesterification reaction, acid, base and enzyme catalyst are used which enhance the rate of reaction and yield of biodiesel in considerable time [Rawat et al., 2011]. The selection of a suitable catalyst for biodiesel synthesis mainly depends on the fatty acid composition of the oil mainly free fatty acid (FFA) content. High free fatty acid containing oils feedstocks require acid catalyst for transesterification reaction. Usually, sulfuric acid, hydrochloric acid and sulfonic acid are used as acid catalyst which is corrosive in nature and reaction rate is slow. The base-catalyzed transesterification is superior over its acid counterpart as it displays less corrosive property, faster kinetics, high purity of the product and mild catalytic conditions, such as low temperature and atmospheric pressure, high yield in shorter time [Ma and Hanna, 1999]. However, high free fatty acid containing feedstocks need a pretreatment step esterification involving acid catalyst to avoid the saponification reaction (in between FFA and base catalyst) prior to base-catalyzed transesterification. Enzymes are naturally occurring bio-catalyst and can tolerate high free fatty acid contents but these are very

expensive and unstable at high reaction temperature and because of these fact enzyme catalysts are not commercialized yet [Ghaly et al., 2010].

Catalysts used in the transesterification can be classified as homogeneous and heterogeneous catalysts on the basis of its physical appearance as presented in Table 2.3. Homogeneous catalysts are present in the same phase i.e. liquid phase as the reactants oil and methanol, whereas heterogeneous catalysts act in dissimilar phase from reactants, usually as solids [Chauhan and Sharma, 2011]. Currently, homogeneous catalysts are preferable for biodiesel production at industrial scale due to their simple use and mild reaction conditions are required for the completion of the reaction [Maleki et al., 2017]. Homogeneous catalysts can be base catalysts such as hydroxides and methoxide of sodium and potassium, or acid catalyst such as inorganic acids including sulfuric, sulfonic, phosphoric, and hydrochloric acids. Homogeneous base catalysts are preferred over acid catalysts because of higher catalytic efficiency (about 4000 times faster), lower cost and lower reaction temperature and pressure [Lee et al., 2014; Talebian et al., 2013]. However, base catalysts are highly sensitive to water and free fatty acid content in feedstocks and saponification reaction may occur. Saponification causes the reduction in yield, formation of the emulsion and difficult separation of glycerol. The main disadvantage of the homogeneous catalyst is; it generates large amounts of wastewater leading to loss of biodiesel yield; production of copious amounts of wastewater; equipment corrosion; high energy accumulation, and high operation costs [Baskar et al., 2017; Sano et al., 2017; Noiroj et al., 2009; Marinković et al., 2016]. On the contrary, heterogeneous catalysts can provide a green and recyclable catalytic activity for large scale biodiesel production. Thus, currently, the development of highly active, cheaper, environmentally safe heterogeneous

catalyst is the fascinating area for researchers [Zhang et al., 2016; Hernández et al., 2015].

As consequences, numerous heterogeneous catalyst such as Nafion-NR50, sulfated zirconia and tungstated zirconia as acid catalyst and alkali earth metal oxides CaO, SrO, MgO, etc, alkali-doped metal oxides CaO/Al$_2$O$_3$, MgO/Al$_2$O$_3$, Li/CaO, etc., mixed metal oxides Ca/Zn, Ca/Mg, etc., Al$_2$O$_3$-supported alkali metal oxide catalysts Na/NaOH/c-Al$_2$O$_3$, K$_2$CO$_3$/Al$_2$O$_3$, and KF/c-Al$_2$O$_3$, hydrotalcites, Ca/Al/Fe$_3$O$_4$ magnetic composites, zeolites and silica supported alkali metal oxides, as well as ion resins as base catalysts, have been synthesized and tested in literature for biodiesel production exhibiting good to high biodiesel yield as presented in Table 2.4 [Madhuvilakku and Piraman, 2013; Wang et al., 2017; Zhang et al., 2016]. However, most of the catalysts show low to high catalytic activity but some disadvantages such as poor reusability, high cost, high reaction temperature and long reaction time, low stability during storage, leaching of the catalytically active species in the reaction medium need to be addressed. Hence, development of new catalytic systems which are effective, reusable, easier to synthesize for biodiesel synthesis exhibit growing interested [Dehkordi and Ghasemi, 2012; Madhuvilakku and Piraman, 2013].

2.5 Special reference to alumina-based catalysts

Alkaline earth oxide (MgO, CaO, SrO and BaO) and alkali metal oxides () are most extensively studied heterogeneous base catalyst in biodiesel production. They all catalyst possess strong basic sites originated by the presence of M2+−O2- ion pairs. The basic strength order in alkaline earth oxides is BaO > SrO > CaO > MgO and K$_2$O > Na$_2$O > Li$_2$O in alkali metal oxides. The feature of these catalyst is high ability to abstract the H$^+$ from alcohol used in the transesterification reaction. These metal oxide catalysts are very sensitive

to H_2O and CO_2 molecules and lost the catalytic activity by blockage of the active sites. The leaching of the active sites in reaction media results poor reusability and contamination of reaction media. The dispersion of these active metal oxides catalyst on support such as Al_2O_3, TiO_2, SiO_2, MgO, ZrO_2, zeolites etc. ameliorate its catalytic activity, high surface area and stability. These mixed metal oxide catalyst consist active phase where the reaction occurs and support carries and stabilize the active phase.

In recent years, alumina-based mixed oxides are gaining considerable attention as the catalyst because of higher catalytic activity due to excellent textural properties such as high surface area, pore volume, and pore-size distribution and its surface chemical composition. Moreover, low toxicity, easiness in handling, non-corrosiveness, easy separation and reusability of the catalyst after completing the reaction make an attraction for alumina-based catalyst for both academic and industrial applications [Costa et al., 2016]. The surface chemical properties of alumina can be easily transformed into basic character using alkali and alkali earth metal oxides as promoters as well as acidic characters using sulphate or perchlorate as the promoter. The distinct interaction of promoters on the surface of alumina demonstrated excellent catalytic activity [Sulaiman et al., 2017]. Thus present study aims to synthesize the potassium-aluminum mixed metal oxide and barium-aluminum mixed metal oxide as efficient heterogeneous base catalyst for transesterification reaction.

Table 2.3 Advantages and disadvantages of catalysts used in the transesterification reaction

Catalyst		Advantages	Disadvantage
Homogeneous catalyst	Acid	• Insensitive to FFA and water content in water • Preferred with low-grade feedstocks • Simultaneous esterification and transesterification occur	• Slow reaction rate • Corrosion of reactor and equipment • Separation is problematic • Wastewater generation
	Alkali	• Faster reaction rate than acid catalyzed transesterification • Mild reaction conditions required so energy insensitive • Catalyst is cheap and widely available	• Sensitive to FFA and water content in the feedstock • Soap formation due to High FFA content • Wastewater generation
Heterogeneous catalyst	Acid	• Insensitive to FFA and water content in water • Preferred with low-grade feedstock • Simultaneous esterification and transesterification occur • Easy separation of catalyst from the product	• Complicated catalyst synthesis process • High reaction temperature required and time required • Leaching of catalyst active species • Contamination of product
	Alkali	• Relatively faster rate than acid catalyzed transesterification • Mild reaction conditions so energy insensitive • Easy separation of catalyst from product • High possibility to reuse and regenerate the catalyst • High biodiesel yield • Easy to synthesize	• Sensitive to high FFA content • Leaching of catalyst active species
Enzyme		• Insensitive to FFA and water content in oils • Simple purification step • Mild reaction conditions	• Slow reaction rate even slower than acid catalyst • High cost

Table 2.4 Various homogeneous, heterogeneous and enzyme catalyst for biodiesel production

Catalysts	Reaction conditions				Conversion (C) or yield (Y) %	References
	Oil: alcohol molar ratio	Catalyst Dose (wt%)	Reaction temperature (°C)	Reaction time (h)		
Homogeneous acid catalyst						
H_2SO_4	1:6	2.5	60	1	C= 96.6	[Farag et al., 2011]
HCl	1:6	2.5	60	2	C= 87.9	[Farag et al., 2011]
$AlCl_3$	1:6	2.5	60	2	C= 87.9	[Farag et al., 2011]
CH_3SO_3H	1:3	0.1	130	1	C= 91.0	[Aranda et al., 2007]
H_3PO_4	1:3	0.1	130	1	C= 50.0	[Aranda et al., 2007]
Homogeneous base catalyst						
NaOH	1:9	0.5	60	.75	C= 89.5	[Sharma and Singh, 2008]
KOH	1:6	1.0	60	1	C= 95.5	[Dias et al., 2008]
$NaOCH_3$	1:6	1.0	65	3	C= 83.6	[Chung et al.,2009]

Heterogeneous acid catalyst

WO_3/ZrO_2	1:19.4	-	75	20	C (FFA)= 85.0	[Park et al., 2008]
Zeolite Y (Y756)	1:6	-	460	0.37	Y= 26.6	[Brito et al., 2007]
Carbon-based catalyst derived from starch	1:30	10	80	8	Y= 92.0	[Lou et al., 2008]
$H_3PW_{12}O_{40}.6H_2O$ (PW12)	1:70	3.7	65	14	Y= 87.0	[Cao et al., 2008]
$Zr_{0.7}H_{0.2}PW_{12}O_{40}$ (ZrHPW)	1:20	2.1	65	8	Y= 98.9	[Zhang et al., 2009]
Sulphated TiO_2-SiO_2	1:9	3.0	200	4	Y= 90.0	[Peng et al., 2008]
Sulphated SnO_2-SiO_2	1:15	3.0	150	3	Y= 92.3	[Lam et al., 2009]
Chlorosulphanic Zirconia	1:8	3.0	100	12	C= 100	[Zhang et al., 2014]

Heterogeneous base catalyst

CaO	1:26	1.0	60	3	C= 90.0	[Kawashima et al., 2009]

MgO	3:20	3.0	190	2	C= 82.8	[Jeon et al., 2013]
SrO	1:6	5.0	65	.25	C= 82.0	[Chen et al., 2012]
K_3PO_4	1:6	5.0	65	3	C= 78.0	[Viola et al., 2012]
Li/Cao	1:6	5.0	65	1	C= 99.0	[Kaur and ali, 2011]
Na/Al_2O_3	1:32	1.0	120	6	C= 97.1	[Tonetto and Marchetti, 2010]
Cs/SiO_2	1:40	-	135	5	C= 25.35	[Kazemian et al., 2013]
Mg Al Fe hydrotelcite	1:21	3.0	65	4	C= 81.0	[Wang et al., 2012]
Enzyme catalyst						
Pseudomonas cepacia (PS30)	1:6.6	13.7	38.4	2.47	C= 90.4	[Wu et al., 1999]
Candida Antarctica (Novozym 435)	1:3	4.0	30	50	C= 90.9	[Watanabe et al., 2001]
Novozym 435	1:4	4.0	40	12	C= 88.0	[Halim and Harum, 2008]

Bacillus subtilis encapsulated in magnetic particles (Magnetic cell biocatalyst)	1:1	3.0	40	72	C= 90.0	[Ying and Chen, 2007]
Rhizopus oryzae	1:4	30.0	40	30	C= 88-90	[Chen et al., 2006]
Immobilized *Penicillium expansum* on resin D4020	1:1	-	35	7	C= 92.8	[Li et al., 2009]

Table 2.5 Alumina based heterogeneous catalyst used in transesterification reaction

Catalyst	Reaction conditions			Conversion (C)	References
	Oil: alcohol molar ratio	Reaction time (h)	Catalyst amount (wt%)	Or yield (Y) %	
CaO–MgO/Al$_2$O$_3$	1: 12.24	3	14.4	C= 97.62	[Mahdavi and Monajemi, 2014]
KF/Al$_2$O$_3$	1:12	3	4	Y= 90.0	[Bo et al., 2007]
Alumina/silica supported K$_2$CO$_3$	1:15	2	2	C > 93	[Lukić et al., 2009]
Eu$_2$O$_3$/Al$_2$O$_3$	1:6	8	Not specified	C= 63.2	[Li et al., 2007]
K/KOH/ Al$_2$O$_3$	1:9	1	4	Y= 84.52	[Ma et al., 2008]
Ca$_2$Al$_2$O$_5$	1:6	0.41	1.2	C= 97.98	[Singh et al., 2017]
K$_2$CO$_3$/ γ-Al$_2$O$_3$	1:12	4	5	C= 97.0	[Junior et al., 2019]
Alumina-CaO-KI	1:9	2	Not specified	C= 95.0	[Razak et al., 2018]
SO$_4$/Fe-Al-TiO$_2$	1:10	2.5	3	C= 96.0	[Gardy et al., 2018]
Mg/Al hydrotalcites	1:48	2	1	C= 96.0	[Navajas et al., 2018]