CHAPTER I

Introduction
CHAPTER I

INTRODUCTION

I. INTRODUCTION

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through the interchange of the alkoxy moiety.\textsuperscript{1,2} Transesterification is one of the classic organic reactions that have enjoyed numerous applications in academic laboratories as well as in industries.\textsuperscript{3,4} It, also known as alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water (Scheme I.1). Since the reaction is an equilibrium process, the reaction occurs by essentially mixing the reactants. However, it gets accelerated in presence of a catalyst. It is a reversible reaction and alcohol has to be used in excess to achieve high yield of ester. Transesterification of esters with alcohols plays important role in the production of organic esters, especially for some important products and intermediates in the laboratory and industry.\textsuperscript{5}

\[
\begin{array}{ccc}
\text{RCOOR'} + \text{R''OH} & \underset{\text{Catalyst}}{\xrightarrow{\text{Ester}}} & \text{RCOOR''} + \text{R'OHH} \\
\text{Ester} & \text{Alcohol} & \text{Ester} & \text{Alcohol}
\end{array}
\]

Scheme I.1: General equation of transesterification

Transesterification is a crucial step in several industrial processes such as (i) intramolecular transesterifications leading to lactones and macrocycles, (ii) biodiesel from vegetable oils, and (iii) co-synthesis of dimethyl carbonate and ethylene glycol (in polyester manufacturing) (iv) polyethylene terephthalate (PET) from dimethyl terephthalate (DMT) and ethylene glycol (in
polyester manufacturing). With increasing public concern over environmental degradation and future fossil fuel resources, it is increasingly necessary to develop alternative clean and renewable energy sources. The necessity to find alternatives to petroleum products and energy sources with low cost and with a reduced environmental impact is a reality that has been considered for several years. Fatty acid alkyl ester (FAME), which is called biodiesel fuel, is a well-known biodegradable and renewable energy source produced by transesterification. This process has widest application in the production of biodiesel. Biodiesel is an oxygenated fuel that is produced by transesterification of triglycerides derived from animal fats and vegetable oils with alcohol in the presence of a homogeneous or heterogeneous catalyst. It has been used since mid-1800s. This method was originally used to distill out glycerin to make soap. The bye-products of this process are monoalkyl esters which are the constituents of biodiesel.

Biodiesel fuel or fatty acid methyl ester (FAME) from vegetable oil, which primarily contains triglycerides and free fatty acids, is considered to be the best substitute for diesel fuel. It can be used in diesel engines and is used in neat (100% biodiesel) or can be blended with petroleum diesel. It is an attractive and useful alternative to petroleum diesel fuel due to the following advantages:

(i) It is a renewable resource,

(ii) It is biodegradable,

(iii) It has a lower combustion emission profile (especially SOx),

(iv) Reduced greenhouse gas emissions because of the closed CO₂ cycle,

(v) It exhibits low toxicity,

(vi) It can be used without engine modifications.
Chapter I

Transesterification is more advantageous than the esterification reaction of carboxylic acid and alcohols. For instance, some carboxylic acids are sparingly soluble in organic solvents. Common synthetic routes to esters include condensation reactions of carboxylic acids with alcohols or acylating alcohols with highly reactive acylating reagents such as acyl halides and acid anhydrides.\textsuperscript{11} These reactions can be made spontaneous by using Dean-Stark apparatus or high temperature conditions.\textsuperscript{3} On the other hand esters are soluble in most organic solvents. Transesterification is useful when the parent carboxylic acids are labile and difficult to isolate.\textsuperscript{7} It is more advantageous than esterification due to handling ease and high stability of esters as well as their high solubility in most organic solvents.\textsuperscript{7,12}

Transesterification is an equilibrium reaction and it is difficult to attain high conversions. The following methods have been used to force the reaction toward the product side: (i) use of excess amounts of either of the reactants (ii) use of an enol ester as a reactant, accompanied by the formation of the corresponding aldehyde or ketone and (iii) removal of the resulting lower alcohol by molecular sieves or continuous distillation. The last approach is the most ideal method, and several catalytic transesterifications at high temperature using esters of lower alcohols were developed using this approach.\textsuperscript{11}

I.1 Biodiesel synthesis by transesterification

Transesterification of vegetable oil is a sequence of three consecutive and reversible reactions, in which di and monoglycerides are formed as intermediates leading to the product fatty acid alkyl ester. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of alcohol is used to increase the yields of the alkyl esters.\textsuperscript{1}
Scheme I.2: General equation for transesterification of a triglyceride

\[
\begin{array}{c}
\text{OCOR'} + \text{OCOR''} + 3\text{ROH} \rightarrow \text{OH} + \text{OH} + \text{OH} + \text{R'}\text{COOR} + \text{R''}\text{COOR} \\
\text{Triglyceride} & \text{Alcohol} & \text{Glycerol} & \text{Fatty acid alkyl ester}
\end{array}
\]

Generally, alcohols used in the transesterification are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are utilized most frequently, especially methanol because of its low cost and its physical and chemical advantages. This process has been widely used to reduce the high viscosity of triglycerides,\textsuperscript{13} thereby enhancing the physical properties of renewable fuels to improve engine performance.\textsuperscript{14} The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one alkyl ester molecule per mole of glyceride at each step (Scheme I.3).

\[
\begin{array}{c}
\text{Triglyceride} + \text{ROH} \rightarrow \text{Diglyceride} + \text{R'}\text{COOR} \\
\text{Diglyceride} + \text{ROH} \rightarrow \text{Monoglyceride} + \text{R''}\text{COOR} \\
\text{Monoglyceride} + \text{ROH} \rightarrow \text{Glycerol} + \text{R''}\text{COOR}
\end{array}
\]

Scheme I.3: The transesterification reactions of vegetable oil with alcohol to esters and glycerol

I.2 Catalysts used in transesterification

Transesterification reactions are catalyzed by acids, bases and biocatalysts. Classification of the catalysts are given in the flow chart.
All the three types of catalysts have been attempted and reported. Acid catalyzed reactions are slower than the base catalyzed reaction.\textsuperscript{15} According to an acid catalyzed mechanism for esterification, carboxylic acid can be readily formed by hydrolysis of the carbocation intermediate formed upon protonation of the ester. This suggests that acid catalyzed transesterification should be carried out in the absence of the water to avoid the competitive formation of carboxylic acids and concomitant reduction in the yields of alkyl ester.\textsuperscript{16} The most common solid base catalysts are more effective than acid catalysts and enzyme catalyst. The solid base catalyst system eliminates the corrosion problems and unwanted waste product formation. Heterogeneous catalysts are always advantageous over homogeneous ones. Homogeneous catalysts act in the same liquid phase as the reaction mixture, whereas heterogeneous catalysts act in a different phase from the reaction mixture, usually as a solid. Heterogeneous catalysts can be easily separated from the reaction mixture and thus they can be recovered and reused. Due to their long life span, they are economic too. In general, the heterogeneous catalyzed transesterification processes have less number of unit operations, with simple product separation and purification steps and no neutralization process is required.\textsuperscript{17} It decreases the cost of separation of the catalyst. The effectiveness of the heterogeneous catalytic conversion depends on the activity of the solid catalyst used. Homogeneous catalyzed transesterification downstream processing disadvantages have motivated intense research on heterogeneous catalyzed transesterification methods.
Chapter I

There are several techniques investigated for the transesterification - transesterification via radio frequency microwave, alcohol reflux temperature, alcohol supercritical temperature and ultrasonication.\textsuperscript{17}

I.2.1 Acid catalyzed transesterification

Generally employed acid catalysts for transesterification are HCl, H\textsubscript{2}SO\textsubscript{4}, BF\textsubscript{3} and sulfonic acids.\textsuperscript{7,15,18} Transesterification by acid catalysis is much slower than that by alkali catalysis, requiring typically high temperature above 100 °C.\textsuperscript{1} Transesterification of soybean oil, in the presence of 1 mol% of H\textsubscript{2}SO\textsubscript{4}, with a methanol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%). On the other hand, butanolysis (at 117 °C) and ethanolysis (at 78 °C), in presence of same quantities of catalyst and alcohol, take 3 and 18 h, respectively. Homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction. However, acid-catalyzed transesterifications are advantageous than the base catalyzed ones: the performance of the acid catalyst is not strongly affected by the presence of free fatty acids (FFAs) in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification. Thus, a great-advantage with acid catalysts is that they can directly produce biodiesel from low-cost lipid feedstocks, generally associated with high FFA concentrations.\textsuperscript{19}

Jinhui Yang \textit{et al.}\textsuperscript{20} have demonstrated an efficient protocol for the transesterification of β-ketoesters with inhomogeneous alcohols using BF\textsubscript{3}.OEt\textsubscript{2} as a novel catalyst. This method offers significant advantages such as mild reaction conditions, faster reaction rates, good yields, ready availability of the catalyst, and cleaner reaction profiles, which is an attractive and superior method for synthetically useful transesterification. The transesterification reaction performed well in the presence of commercially available boron trifluoride diethyl etherate BF\textsubscript{3}.OEt\textsubscript{2} in toluene under
reflux (110–115 °C). The desired product was obtained with a complete conversion and an excellent isolated yield. A notable feature of this protocol is that allyl alcohols underwent transesterification efficiently with methyl acetoacetate to provide the corresponding β-ketoesters.

Recently, the use of molecular iodine as a catalyst has become popular because it is an inexpensive, nontoxic and readily available catalyst for various organic transformations that afford the corresponding products in excellent yields with high selectivity. The mild Lewis acidic character associated with iodine enhances its use in organic synthesis for several organic transformations and has been explored as an efficient catalyst for esterification and transesterification. Yiming Ren et al.\textsuperscript{5} have reported an efficient method for the transesterification reaction of β-ketoesters with alcohols using a catalytic amount of iodine in polyethylene glycol (PEG) ionic liquid (IL 1000) to afford the corresponding esters in good yields. By simple separation of the ionic-liquid phase containing the iodine, it can be reused several times.

Fathallaah Bazi et al.\textsuperscript{21} have successfully carried out the transesterification of methyl benzoate with various alcohols catalyzed by the available natural phosphate ore. This catalyst is reusable and can be used with or without solvent without loss in its activity. High conversions were observed with primary alcohol whereas the conversion can occur with cyclohexanol in solvent free condition.

\[
\begin{align*}
\text{O} & \quad \text{O}_\text{Me} \quad + \quad \text{R-OH} \quad \xrightarrow{\text{NP}} \quad \text{O} & \quad \text{O}_\text{R} \quad + \quad \text{CH}_3\text{OH}
\end{align*}
\]

Scheme I.4: Transesterification of methyl benzoate with various alcohols by natural phosphate (NP)\textsuperscript{21}
Transesterification of soybean oil with methanol was also studied using different solid super acids such as tungstated zirconia-alumina (WZA), sulfated tin oxide (STO), and sulfated zirconia-alumina (SZA)\textsuperscript{16,22} of which the WZA catalyst was the most effective, achieving conversions $>90\%$ at temperatures above 250 °C after 20 h.

M. Sasidharan \textit{et al.}\textsuperscript{23} have reported the transesterification catalyzed by aluminosilicates simply by refluxing in toluene under liquid-phase conditions. The reaction proceeds smoothly with primary alcohols than the tertiary, cyclic, and allylic alcohols. The large-pore zeolites such as Y, mordenite, and $\beta$ show higher activity than the medium-pore ZSM-5 and the partial removal of framework aluminum from the large-pore zeolites by dealumination increases their activity. The aluminum containing mesoporous MCM-41 shows poor activity.

Titanosilicate molecular sieves (TS-1, Ti-MCM-41 and amorphous TiO$_2$–SiO$_2$) exhibit excellent catalytic activity in transesterification reactions as demonstrated by D. Srinivas \textit{et al.}\textsuperscript{6} The activity increases with the acidity of the catalysts in the order: TS-1 < Ti-MCM-41 < amorphous TiO$_2$–SiO$_2$. Activity of the catalyst is also influenced by the structure and dimensions of the ester. High activities have been observed for the transesterifications of ethyl acetooacetate and diethyl malonate but TS-1 catalysts are inactive in the transesterification of propylene carbonate. Amorphous TiO$_2$–SiO$_2$ exhibits superior activity in the latter reaction. The catalyst could be recycled without loss in activity.

Shah \textit{et al.}\textsuperscript{24} investigated catalytic activity of Sn-SBA-15 samples in transesterification reaction. SBA-15 itself shows some activity in transesterification of diethyl malonate with various alcohols but Sn-SBA-15 samples are found to possess enhanced catalytic activity for the same. Incorporation of Sn does not affect the original mesopore structure of the parent SBA-15 even at high Sn loading.
Mirela Ines de Sairre et al.\textsuperscript{25} have demonstrated that niobium(V) oxide serves as an efficient catalyst for the transesterification of β-keto esters with a series of different alcohols, leading to good conversion and moderate to good isolated product yields. Among the various solid acid catalysts currently in use, niobium(V) oxide has drawn much attention for transesterification reactions, since it presents high acid strength associated with both Lewis and Bronsted acid sites. This compound is not affected by water vapor, which makes it an effective catalyst for reactions where water molecules participate or are released.

A series of carboxylic esters were converted into their corresponding esters using the Pd/C catalyzed hydrogenation conditions in the presence of catalytic bromobenzene in alcohols. Good to excellent yields were obtained for different aromatic starting materials with different alcohols. The success of this reaction relies on the \textit{in situ} generation of hydrobromic acid (HBr) from bromobenzene which provides a mild and acidic reaction environment. The palladium catalyst exhibits a remarkable activity and is reusable for up to three consecutive cycles.\textsuperscript{26}

The transesterification of methyl salicylate and phenol was studied by Shamshuddin et al.\textsuperscript{27} over ZrO\textsubscript{2}, SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} and Mo (VI)/ZrO\textsubscript{2}. Sulfate and Mo(VI) modified zirconia were found to be good catalysts. Mo(VI) modified zirconia was 100\% selective towards the formation of salol (excluding the primary by-product methanol). But over SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2}, selectivity of salol is slightly decreased. All the catalysts used in their study have considerable reusability; however, SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} showed a gradual decrease in the catalytic activity.

Catalytic reactivity of polyaniline protonated with organo-sulfonic acids, namely methanosulfonic (MSA-Pani), camphorosulfonic (CSA-Pani) and lignosulfonic (LG-Pani) acids was explored for the transesterification of triglycerides (triacetin, castor oil). In all experiments studied, MSA- and CSA-doped polyanilines exhibited the highest initial activity referred to the
acid site capacity. However, too weak acid sites in these catalysts resulted in their partial blockage during transesterification reaction, which requires stronger acid sites. Among all studied samples, the LG-Pani (commercial reagent) and MSA-Pani catalysts seem to be the most promising owing to their high activity and good stability in reaction mixture, in particular during methanolysis of triglycerides.\textsuperscript{28}

Titanium dioxide (TiO\textsubscript{2}) is among transition metal oxides that have drawn much attention for biodiesel production due to their acidic properties. In addition, introduction of sulfuric group on the surface of TiO\textsubscript{2} will enhance the acid strength of the catalyst. However, very few studies have been reported in the literature describing the application of such catalyst for transesterification of vegetable oils. Catalytic activity of SO\textsubscript{4}\textsuperscript{2−}/TiO\textsubscript{2} and SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} for transesterification of cotton seed oil high in FFAs content to FAME is reported.\textsuperscript{29} It was interesting to find that the activity of this catalyst is proportional to its specific surface area. SO\textsubscript{4}\textsuperscript{2−}/TiO\textsubscript{2} with a specific surface area of 99.5 m\textsuperscript{2}/g could achieve a higher yield of 90\% as compared to SO\textsubscript{4}\textsuperscript{2−}/ZrO\textsubscript{2} with a specific surface area of 91.5 m\textsuperscript{2}/g, which could only achieve a yield of 85\%. However, this catalyst requires high reaction temperature (230 °C), a negative factor for industrial application.\textsuperscript{29}

Kulkarni and co-workers explored 12-tungstophosphoric acid (TPA) impregnated on four different supports such as hydrous zirconia, silica, alumina and activated carbon as solid acid catalysts for the transesterification of low quality canola oil containing up to 20 wt.% free fatty acids. The hydrous zirconia supported TPA was found to be the most effective catalyst exhibiting the highest ester yield (77\%).\textsuperscript{30}

A novel, active, and recyclable magnetic nano-size solid acid catalyst was developed by Zillilah and co-workers for the high-yielding transformation of waste grease to biodiesel (fatty acid methyl esters, FAMEs) via simultaneous esterification of free fatty acids (FFAs) and
transesterification of triglycerides with methanol in one pot. One-pot transformation of grease (21.3 wt.% FFAs) with methanol using HPW–PGMA–MNPs (4 wt.%) gave a 98% FAME yield after 24 h, with 96% conversion for the esterification and >98% conversion for the transesterification.

Yu et al.\textsuperscript{32} reported biochar based catalyst for the transesterification of canola oil. It’s a heterogeneous catalyst bearing sulfonic acid group prepared using biochar as the carbon support. The reaction yield was found to be dependent on both catalyst surface area and total acid density, suggesting that the maximum yield would be obtained for a catalyst prepared from char carbonized between 675 and 875 °C. Reusability of the catalyst was poor under high temperature/pressure conditions.

Shu et al.\textsuperscript{33} prepared carbon based acid catalyst and used for transesterification of cotton seed oil to obtain a maximum yield of 94.8 wt.% of methyl ester at 220 °C in 4.5 h reaction time in presence of 0.2 wt.% of catalyst. The high catalytic activity and stability of this catalyst was related to its high acid site density (–OH, Bronsted acid sites), hydrophobicity that prevented the hydration of –OH species, hydrophilic functional groups (–SO\textsubscript{3}H) that gave improved accessibility of methanol to the triglyceride and FFAs, and large pores that provided more acid sites for the reactants.

The transesterification of waste cooking palm oil (WCPO) with methanol into fatty acid methyl esters (FAMEs) was investigated using solid acidic mixed oxide catalysts by MnZr with supported alumina as a potential heterogeneous catalyst.\textsuperscript{34} The catalyst Mn\textsubscript{3.5x}Zr\textsubscript{0.5y}Al\textsubscript{x}O\textsubscript{3} (0.1 ≤ x ≤ 0.5, and 0.5 ≤ y ≤ 2.5) was prepared via coprecipitation. The catalyst achieved a FAME content of more than 93%, and the optimal reaction conditions are as follows: reaction temperature of 150 °C, reaction time of 5 h, molar methanol-to-WCPO ratio of 14:1, and catalyst loading of 2.5 wt.%.
The Mn\textsubscript{1.4}Zr\textsubscript{0.35}Al\textsubscript{0.6}O\textsubscript{3} catalyst exhibited better catalytic performance (more than 93% FAME content) than the Mn\textsubscript{1.4}Zr\textsubscript{0.35}O\textsubscript{3} catalyst (52.8% FAME content) because of its greater surface area and different acid site concentrations.

The catalytic activity of solid Fe–Zn double-metal cyanide complexes for the transesterification of carbonates has been evaluated by R. Srivastava \textit{et al.}\textsuperscript{35} Dimethyl carbonate (DMC), for example, was synthesized with 100% selectivity and an isolated yield of >86% was obtained over these catalysts. Various dialkyl carbonates could be synthesized by transesterification of propene carbonate (PC) with a mixture of alcohols (methanol-ethanol) alcohols. The Fe–Zn catalysts are reusable, with little loss in their activity. The accessible and Lewis-acidic Zn\textsuperscript{2+} cations are the possible active sites in transesterification reaction.

Tongshou Jin \textit{et al.}\textsuperscript{4} demonstrated Montmorillonite K-10 as an efficient reusable catalyst for the transesterification of ethyl/methyl β-ketoesters with various alcohols in good yields. The main advantages of the catalyst are easy operation in the workup and a more economical and environmentalfly benign procedure. Montmorillonite K-10 is a type of acidic stratified silicate mineral with a three-layer structure with an ideal chemical formula of (Al\textsubscript{2.5}Mg\textsubscript{0.5})Si\textsubscript{4}O\textsubscript{10}(OH)\textsubscript{2}nH\textsubscript{2}O. In montmorillonite clay one octahedral aluminate layer is sandwiched between two octahedral silicate layers. The interlayer cations are exchangeable, which allows alteration of the acidic nature of the material by a simple ion-exchange procedure. Both Bronsted and Lewis acidic catalytic sites are available, and its natural occurrence as well as its ion exchange properties make it a useful catalyst.

Bronsted solid acids have also been proposed for the transesterification. Among the catalysts used were Amberlyst-15,\textsuperscript{36} Envirocot EPZG,\textsuperscript{37} natural kaolinite clay,\textsuperscript{38} even though β-keto esters usually show a higher reactivity than simple esters for transesterification, under the
right reaction conditions, a catalyst active for the transesterification of β-ketoesters could be effective in the transesterification of other types of esters as well.\textsuperscript{39} The clay has been found to be an efficient catalyst in transesterifying long chain alcohols, unsaturated alcohols, and phenols to give their corresponding β-keto esters in high yields. For the first time, transthiol esterification of β-keto esters with a variety of thiols has been achieved under catalytic conditions. Clay also catalyzes selective transesterification of β-keto esters by primary alcohols in the presence of secondary and tertiary alcohols giving corresponding β-keto esters.

Mesostructure materials such as silica have an exceptional potential to be utilized as heterogeneous acid catalyst in transesterification for biodiesel production. This mesoporous materials (silica) consist of large mesopores which can significantly minimize the diffusion problem for reactants to access into the active sites of the catalyst. Apart from that, the physical and chemical properties of these mesoporous materials can be manipulated by incorporating suitable organic or inorganic functional groups into the mesoporous silica matrix. In order to obtain a solid acid catalyst, organosulfonic groups can be incorporated onto the mesoporous silica material. The organosulfonic acid anchored on mesoporous silica acts as Bronsted acid (active sites) that is suitable to catalyze esterification and transesterification reactions. Mesostructure silica materials functionalized with propylsulfonic acid (SO\(_3\)H) groups have been reported to have good catalytic activity in esterification of refined and unrefined oil.\textsuperscript{29}

1.2.2 Base catalyzed transesterification

Alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides, and hydroxides, as well as sodium or potassium carbonates.\textsuperscript{1}
Chapter 1

There are several studies reported on base catalyzed transesterification. The most common basic catalysts are potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide (NaOCH₃), and sodium ethoxide (NaOCH₂CH₃).¹⁰

Sodium titanate prepared at low temperature is an effective catalyst for the transesterification reaction under mild reaction conditions, and achieved an ethyl acetate conversion around 30% as reported by Leticia L. et al.⁴⁰ The stability of the material was also studied in experiments involving consecutive catalytic cycles, which showed that the conversion rate remained almost constant for up to three runs. However, during the fourth cycle there was a sharp loss of activity, which then remained almost constant up to the eighth run.

Mg-Al-HT-like anionic clay catalyzed transesterification of α-haloesters with a series of alcohols have been studied by Bulbule et al.⁴¹ The corresponding esters were obtained from good to excellent yield. β-Ketoesters were also transesterified under similar conditions on reaction with alcohols with a wide variety of functional groups.

Alkaline earth metals such as Be, Mg, Ca, Sr, Ba and Ra, their oxides and derivatives are used by different researchers. MgO and SrO are widely used among the other alkaline earth metals, which have been reported as good heterogeneous catalyst.⁴²

SrO for the transesterification of soybean oil and reported 90% FAME yield in 30 min at a temperature 65 °C with alcohol/oil molar ratio of 12 and 3 wt.% catalyst loading. The reusability of the catalyst was reported to be 10 times. SrO had high basicity and insoluble in methanol.⁴²

Synthesis of biodiesel using supercritical or subcritical methanol with metal oxide catalysts was also investigated. The transesterification of rapeseed oil was carried out with the metal oxide catalysts (SrO, CaO, ZnO, TiO₂ and ZrO₂) to find out the most effective heterogeneous catalyst
with highest catalytic activity and minimum weight loss caused by dissolution. SrO and CaO dissolved in the biodiesel during the reaction because they were transformed to strontium methoxide and calcium methoxide, respectively. ZnO was the best catalyst for the transesterification of rapeseed oil owing to its high activity and minimum weight loss in supercritical methanol.\textsuperscript{42}

Rao et al.\textsuperscript{16} explored crystalline manganese carbonate as a versatile green, non-corrosive and environmental friendly catalyst for transesterification of vegetable oils. Crystalline manganese carbonate catalyzed transesterification of vegetable oils (palm, rapeseed, groundnut, coconut and caster oils) with methanol resulted in a conversion rate of 80\% - 95\% in the production of biodiesel. The advantage of this protocol is the use of an available low-cost catalyst, which is easy to manipulate and potentially less corrosive.

Very recently, MgO has shown to possess catalytic activity for synthesis of biodiesel with 92\% yield using 12:1 methanol to oil molar ratio with 5.0 wt.\% of the catalyst in 1 h.\textsuperscript{43}

Dossin et al.\textsuperscript{44} introduced the first heterogeneous catalytic transesterification pilot plant using MgO as catalyst with triolin and methanol as feedstock. Also, the use of MgO makes the process cost-effective.

Alkaline metal alkoxydes as CH$_3$ONa are the most active catalysts in transesterification. They give very high yields (> 98\%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol\%). However, they require the absence of water which makes them inappropriate for typical industrial processes.\textsuperscript{1,45} Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxydes, but less active. Nevertheless, they are a good alternative since they
can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%.

Metal oxides are the basic heterogeneous catalysts group most studied by the researchers. CaO is the most widely used solid basic catalyst with many advantages such as long catalyst life, high activity and requires only moderate reaction conditions. Beside, CaO has attracted much attention due to the fact that there are several natural calcium sources from wastes, such as egg shells or mollusk shells. The solid oxide catalysts derived from waste shells of egg, golden apple snail, and meretrix venus were employed to produce biodiesel from transesterification of palm olein oil. These shells are composed of calcium carbonates. The shell materials were calcined in air at 800 °C with optimum time of 2–4 h to transform calcium species in the shells into active CaO catalysts. All the catalysts are found to be efficient, whilst the eggshell derived catalyst showed comparable activity to the one derived from commercial CaCO₃. The transesterification of palm oil with methanol was studied using calcium oxide as catalyst. The catalyst was prepared by calcining eggshells of quail and chicken. Compared to chicken eggshell, the palisade layer of quail eggshell had more closely dispersed micron-sized pores. Following treatment with 0.005 M HCl solution for 2 h to remove its dense cuticle layer and subsequent calcination above 800 °C, the quail eggshell had a large amount of strong basic sites and showed high catalytic activity comparable to that of potassium methoxide in the transesterification.

Wen et al. prepared KF/CaO using impregnation method, as a catalyst for transesterification of Chinese tallow seed oil obtaining 96% FAME yield. Encimar et al. developed CaO impregnated with KNO₃, reaching 98.5% FAME yield from rape oil as feedstock when the transesterification reaction was carried out at 65 °C. The catalyst is highly efficient with a heterogeneous and highly basic character.
Chapter I

A series of Li-promoted CaO catalysts with Li loadings in the range 0.26–4.0 wt% have been prepared by Robert S. et al.\textsuperscript{51} which are effective in the transesterification of glyceryl tributyrate and methanol to methyl butanoate. A Li content of 1.23 wt.% provides the optimum activity towards methyl butanoate formation. Li doping increases the base strength of CaO, and XPS and DRIFTS measurements reveal that the optimum loading correlates with the formation of an electron deficient surface Li$^+$ species and associated –OH species at defect sites on the support.

Nanometer magnetic solid base catalysts were prepared by loading CaO on Fe$_3$O$_4$ by Liu C. et al.\textsuperscript{52} and the influence of the proportion of Ca$^{2+}$ to Fe$_3$O$_4$ on the catalytic performance was studied. The catalyst showed highest activity when the proportion Ca$^{2+}$ to Fe$_3$O$_4$ was 7:1; under the conditions of 15:1 methanol/oil molar ratio, 2 wt.% catalyst dosage at 70 °C reaction temperature, the transesterified product yield reached was 95% in 80 min. The catalytic activity of catalysts which are obtained by calcining Ca(OH)$_2$–Fe$_3$O$_4$ is better than that by calcining CaCO$_3$–Fe$_3$O$_4$. Furthermore, Ca$^{2+}$:Fe$_3$O$_4$ = 7 is the optimum proportion for catalytic activity. The conversion rate of transesterification reaction catalyzed by Ca(OH)$_2$7 (These catalysts are named with their precursors and the proportion of Ca$^{2+}$ to Fe$_3$O$_4$ for short. “Ca(OH)$_2$7” means that the precursor of the catalyst is Ca (OH)$_2$–Fe$_3$O$_4$ and the proportion of Ca$^{2+}$ to Fe$_3$O$_4$ is 7:1) can reach 95% in 80 min, and 99% in 4 h.

Other calcium-based mixed oxides catalysts (CaMgO and CaZnO) have been studied by Taufiq-Yap et al.\textsuperscript{53} for the Jatropha curcas oil transesterification reaction with methanol. Their catalytic activities were compared with CaO. Catalytic activities of both CaMgO and CaZnO catalysts are at par with CaO and they were easily separated from the product. However, CaMgO was found to be more active than CaZnO under the suitable transesterification conditions at 60 °C 4 wt.% catalyst amount (based on weight of oil), methanol to oil molar ratio 15:1 and 6 h reaction
time, achieving a conversion higher than 80%. Efficiency of the catalyst CaO decreased significantly after being reused for fourth run, whereas using CaMgO and CaZnO as catalyst the conversion slightly decreased after sixth run.

Ngamcharussrivichai et al.\textsuperscript{54} demonstrated the transesterification reaction of palm kernel oil with methanol over dolomite mainly consisting of CaCO\textsubscript{3} and MgCO\textsubscript{3}. It is a good heterogeneous base catalyst. The calcination of dolomite at 800 °C resulted in a Ca and Mg mixed oxide that presented activity for the methyl esters formation reaction at 60 °C reaction temperature.

Tamura et al.\textsuperscript{55} demonstrated that CeO\textsubscript{2} acted as an efficient and reusable heterogeneous catalyst for transesterification of esters with alcohols under the solvent-free conditions at 160 °C. CeO\textsubscript{2} is an attractive catalyst with its high catalytic efficiency, reusability and leaching resistivity. Various esters, including a sterically-hindered ester (tertiary-butyl ester) (Scheme I.5), and various alcohols (primary and secondary) (Scheme I.6) were transformed into corresponding esters, including the pharmacologically valuable esters such as heteroaromatic esters and benzyl benzoates.

\[
\begin{align*}
\text{R}^1\text{O} - \text{O}\text{R}^2 & \quad + \quad \text{R}^3\text{OH} \quad \xrightarrow{\text{CeO}_2, 160 \degree C} \quad \text{R}^1\text{O} - \text{O}\text{R}^3 \quad + \quad \text{R}^2\text{OH} \\
\end{align*}
\]

Scheme I.5: Transesterification of various esters by CeO\textsubscript{2}\textsuperscript{55}

\[
\begin{align*}
\text{Ph} - \text{O}\text{Me} & \quad + \quad \text{R-OH} \quad \xrightarrow{\text{CeO}_2, 160 \degree C} \quad \text{Ph} - \text{O}\text{R} \quad + \quad \text{CH}_3\text{OH} \\
\end{align*}
\]

Scheme I.6: Transesterification of methyl benzoate with various alcohols by CeO\textsubscript{2}\textsuperscript{55}
Transesterification of vegetable oil with subcritical methanol over newly developed heterogeneous Mn catalyst for the production of biodiesel fuel is reported by Tomoharu Oku et al.\textsuperscript{56} The catalyst has high activity and a long lifetime.

Babu et al.\textsuperscript{57} demonstrated Mg/La with a 3:1 (wt./wt. %) ratio as an efficient catalyst for the room-temperature transesterification of triglycerides of both edible and nonedible oils. The catalyst shows exceptional activity toward the transesterification of oils within a short reaction time and also showed good transesterification activity of oils even in presence of water and FFA at room temperature.

Saravananmurugan et al.\textsuperscript{58} reported transesterification reactions of diethyl malonate over morphology controlled amino-functionalized SBA-15 catalysts (NH\textsubscript{2}-SBA-15). They synthesized NH\textsubscript{2}-SBA-15-D, amino-functionalized materials (NH\textsubscript{2}-SBA-15-Pre) under strong acidic conditions and (NH\textsubscript{2}-SBA-15-PS) by post synthetic grafting method. The mono and diesters of \textit{n}-butanol, 2-butanol and \textit{n}-heptanol can be easily diffused out from the internal pores of highly dispersed short channeled NH\textsubscript{2}-SBA-15-D rather than NH\textsubscript{2}-SBA-15-Pre and NH\textsubscript{2}-SBA-15-PS catalysts was proven in these catalytic transesterification reactions. In the case of 2-ethyl-1-hexanol, post synthetic and prehydrolysed NH\textsubscript{2}-SBA-15 showed enhanced catalytic activity than direct functionalized NH\textsubscript{2}-SBA-15-D and confirming the presence of higher amount of amino groups nearby the pore mouth.

Sodium ethoxide-catalyzed transesterification to arrive at a variety of esters of \(\gamma\)-\((\text{diethylamino})\)-\(\alpha\)-phenylbutyric acid starting from the methyl ester has also been reported.\textsuperscript{59}

Anion-exchange resin have been investigated for transesterification of peptide alkyl esters by Pereira et al.\textsuperscript{60} Benzyl esters of L-amino acids or LL dipeptide derivatives were stirred with
anion exchange resin in presence of methanol at room temperature for 30-80 min. The methyl esters were obtained in 80-90% yields. Conversions from ethyl esters to methyl esters and from methyl esters to ethyl esters proceeded analogously but methyl esters were converted to benzyl esters in less than 50% yields.

Metal complexes of the type M (3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$, where M = Sn, Zn, Pb, and Hg, have been utilised for the methanolation of soybean oil under homogeneous conditions. Sn and Zn complexes showed great activities for this reaction, achieving yields of up to 90% and 40%, respectively, in 3 h, using a molar ratio of 400:100:1 (methanol:oil:catalyst), without emulsion formation. All complexes are active in this reaction, with the following decreasing activities

$$Sn^{2+} \gg Zn^{2+} > Pb^{2+} \approx Hg^{2+}$$

Liquid amine-based catalysts have been reported as successful catalyst for transesterification of refined vegetable and frying oil. Four amines diethylamine (DEA), dimethylethanol amine (DMAE), tetramethyldiaminoethane (TEMED), and tertramethylammonium hydroxide (TMAH) (as 25% in methanol) were used. 98% conversion was achieved with TMAH as a catalyst at 65 ºC in 90 min. In these cases, a large amount (13%) of liquid amine catalysts is required for the transesterification which also act as a solvent for both reactants and product.

Hydrated lime (HL) and CaO were evaluated as solid base catalysts in the transesterification of castor oil with methanol. 100% conversion of the raw materials into biodiesel (BD) was observed with both HL and CaO, the influence of the catalyst amount, methanol:oil ratio, reaction time, and reaction temperature was studied employing HL due to the economic and
process advantages of HL over CaO. From the results it was found that the catalyst’s active phase after the first use was Ca(OH)$_2$. However, when the catalyst was reused, calcium diglyceroxide was identified by X-ray analysis as the main crystalline phase and it remained up to the third reuse. The catalyst stability was determined and the results revealed that although a conversion decrease was observed after the first reuse, the catalyst increased its activity in the second reuse maintaining a conversion up to 84% after the third one. At room-temperature, 98% conversion was achieved in 14 h of reaction.$^{62}$

Winlei Xie et al.$^{63}$ developed an efficient and stable solid base catalyst tetraalkylammonium hydroxide-functionalized SBA-15 materials (SBA-15-pr-NR$_3$OH). It can be prepared by anchoring dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium hydroxide onto the surface of mesoporous SBA-15 silica. Catalytic activity was tested in the transesterification of soybean oil with methanol. By using this catalyst, an eco-friendly more benign process for the transesterification of soybean oil in a heterogeneous manner is developed. Under the suitable transesterification conditions (methanol/oil molar ratio 12:1, catalyst loading 2.5 wt.%, reaction time 30 min, and at reflux of methanol), a good yield to methyl esters of 99.4% could be achieved over the solid catalyst. The obtained SBA-15-pr-NR$_3$OH catalyst could be recovered and reused for several recycle runs with a negligible loss of activity.

Metal oxides like MgO, CeO$_2$, La$_2$O$_3$, and as well as alkali doped MgO (Li/MgO and Na/MgO) have been used as solid base catalysts for the transesterification of methyl stearate with glycerol in solvent free condition.$^{64}$

Suppes et al.$^{65}$ investigated calcium carbonate as a catalyst for the transesterification of soybean oil. Conversions above 95% are achieved at 260 °C for ethyl esters, using flow reactors
with residence times of approximately 18 min. No loss in the activity of calcium carbonate was observed after weeks of utilization, but these catalytic systems need high energy requirements.

The catalytic activity of crystalline mixed oxides of $\text{AB}_2\text{O}_4$ composition, where $\text{A} = \text{Co, Ni, Cu and Zn}$ and $\text{B} = \text{Al, Fe and Co}$, was investigated in the transesterification of sunflower oil with methanol to produce fatty acid mono esters (FAME; biodiesel). The transesterification activity was found to depend on element A, the order of activity being: $\text{Zn} > \text{Cu} > \text{Ni} > \text{Co}$. The Zn containing spinels were found to be more active than the others. Further investigation on $\text{ZnFe}_2\text{O}_4$ revealed it to be a suitable solid catalyst for the transesterification of used cooking oil and Jatropha oil. The catalyst was reusable many times. The order of activity of the different spinel type materials (on weight basis) is: $\text{ZnAl}_2\text{O}_4$ ~ $\text{ZnFe}_2\text{O}_4$ ~ $\text{ZnCo}_2\text{O}_4$ ~ $\text{CuAl}_2\text{O}_4$ ~ $\text{NiAl}_2\text{O}_4$ ~ $\text{NiFe}_2\text{O}_4$ ~ $\text{CoAl}_2\text{O}_4$, Zn-containing spinels being more active than the others.

Maurizio Selva et al. studied the use of carbonate, acetate and phenolate phosphonium salts as catalysts in transesterification reactions for the synthesis of non-symmetric dialkyl carbonates. This salt was a convenient source to synthesize different ionic liquids where the methyl triocetylphosphonium cation was coupled to weakly basic anions such as bicarbonate, acetate, and phenolate. At 90–220 °C, all these compounds $[\text{P}_{8881}]^+\text{X}^-$; $\text{X} = \text{MeOCO}_2; \text{HO}_2\text{CO}; \text{AcO}; \text{PhO}$ were excellent organocatalysts for the transesterification of dimethyl and diethyl carbonate with primary and secondary alcohols, including benzyl alcohol, cyclopentanol, cyclohexanol, and the rather sterically hindered menthol (Scheme 1.7). Conditions were optimized to operate with very low catalyst loadings up to 1 mol% and to obtain non-symmetric dialkyl carbonates ($\text{ROCO}_2\text{R}'$; $\text{R}' = \text{Me, Et}$) with selectivity up to 99% and isolated yields >90%.


Scheme I.7: Transesterification of dimethyl and diethyl carbonate with primary and secondary alcohols\textsuperscript{67}

Xie \textit{et al.}\textsuperscript{68} investigated transesterification by alumina loaded with different potassium precursor catalysts. However, when potassium compounds were loaded on alumina and activated at high temperatures, the supported catalysts except KCl/Al\textsubscript{2}O\textsubscript{3} showed catalytic activities. Thus, it is essential to support potassium compounds on alumina to generate the catalytic activities for the transesterification reaction. Among the catalysts tested, alumina loaded with KI, KF or KOH exhibited comparatively high activities, giving conversions higher than 80\%. The conversion to methyl esters over the catalysts is in the following order: KI/Al\textsubscript{2}O\textsubscript{3} > KF/Al\textsubscript{2}O\textsubscript{3} > KOH/Al\textsubscript{2}O\textsubscript{3} > K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} > KBr/Al\textsubscript{2}O\textsubscript{3}. After loading KI of 35 wt.\% on alumina followed by calcination at 773 K for 3 h, the catalyst gave the highest basicity and the best catalytic activity for this reaction.

E. Leclercq \textit{et al.}\textsuperscript{69} studied the transesterification of rapeseed oil with cesium-exchanged NaX faujasites, mixed magnesium–aluminum oxides, magnesium oxide, and barium hydroxide for different methanol:oil ratios. Barium hydroxide was found to be catalytically active and gave a very high yield of esters. On the other hand, cesium-exchanged NaX faujasites and mixed magnesium–aluminum oxides required a long reaction time (3 h) and a high methanol:oil molar ratio to achieve high yields in methyl esters.
The transesterification of soybean oil with methanol was also investigated in the presence of a series NaX faujasite zeolite, ETS-10 zeolite and metal catalysts. The stock zeolites were exchanged with potassium and cesium; NaX containing occluded sodium oxide (NaOx/NaX) and occluded sodium azide (NaOx/NaX*, * indicates sodium azide loaded samples). The catalysts were calcined at 500 °C prior to use in order to increase its efficiency. The ETS-10 catalysts provided higher conversions than the zeolite-X type catalysts. The increased conversions were due to the higher basicity of ETS-10 zeolites and larger pore structures that improved intra-particle diffusion. Methyl ester yield increased with an increase in temperature from 60 to 150 °C. The metal catalysts increased conversion by one to over two orders of magnitude over the homogeneous reaction with several of the zeolite catalysts performing better than the metal catalysts. The catalyst can be reused without loss in its activity. A preliminary design assessment shows that these catalysts are sufficiently active to be commercially viable contingent upon the costs of the catalysts achieving conversions in excess of 90% at temperatures below 125 °C.70

Insoluble salts of amino acids have also been utilized as catalysts for the methanolysis of triglycerides.71 Some metal salts of amino acids such as those of copper, zinc, cadmium, nickel, lanthanum, cobalt, calcium, magnesium, and iron were studied. Zinc arginate catalysts are also applied for the methanolysis of palm oil with a methanol to oil ratio of 6:1 and deliver 67 wt.% of methyl ester. However, reasonable reaction rates could only be achieved at temperatures above 130 °C.

A mild protocol for transesterification of simple esters is described by Castillo et al.72 The method is based on the use of t-BuNH₂/ROH (R = Me, Et, i-Pr, t-Bu) with or without LiBr. A variety of aliphatic and aromatic compounds have been subjected to transesterification using different types of alcohols (Scheme I.8 and Scheme I.9). The reactions are, in general, very clean
and give very high yields. Besides, the simplicity of this approach and the low cost of the reagents enhance its attractiveness. The method is well applicable when going from higher to lower hindered esters but for the reversal of the process harsh reaction conditions are needed.

![Scheme I.8: t-BuNH₂ transesterification with methanol]

Scheme I.9: t-BuNH₂ transesterification with EtOH, i-PrOH, t-BuOH

Anand et al. investigated the basic catalytic performance of the mesoporous carbon nitride (MCN) for the transesterification of ethyl acetoacetate with various alcohols such as 1-butanol, 1-octanol, cyclohexanol, benzyl alcohol and furfuryl alcohol without any solvents. The catalyst showed high activity, affording a high conversion of long and short chain primary alcohols, cyclic and aromatic alcohols. The desired product was obtained in good to excellent yield.

Jian-Xun et al. investigated recycling of cement as a catalyst in the production of biodiesel by transesterification of soybean oil with methanol. Concrete is a composite construction material composed of cement, aggregate, water, and chemical admixtures. In these composite, Portland cement was supposed to be an efficacious catalyst for biodiesel production by transesterification. Finally, the waste concrete catalyst was successfully used in the transesterification reaction of soybean oil with more than 98% FAME conversion.
Yadav et al.\textsuperscript{75} investigated the synergism between microwave irradiation and solid base catalysis for a highly selective mono-transesterification of diethyl malonate with cyclohexanol using Mg–Al calcined hydrotalcite as catalyst (Scheme I.10).

![Scheme I.10: Transesterification of diethyl malonate with cyclohexanol\textsuperscript{75}](Image)

Microwave irradiation showed threefold increase in cyclohexanol conversion than that in conventional heating where only the mono-transesterified product was obtained. Hydrotalcite with Mg:Al composition as 3:1 gave the best results. Under optimised reaction conditions, 69% conversion with 98% selectivity for cyclohexyl ethyl malonate was obtained at 100 °C in 2 h. The catalyst showed excellent reusability.

The amino-grafted multiwalled carbon nanotubes (N-MWCNTs) were used as an effective base catalyst in transesterification of triglycerides (glyceryl tributyrate). Their studies revealed that, all the amino grafted nanotubes are basic in nature (pH >7). The nanotubes grafted with 3° amines (Et\textsubscript{3}N-CNTs) 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. The higher activity was due to the higher basicity of 3° compared to the 2° and 1° amines.\textsuperscript{76}

Guo et al.\textsuperscript{77} investigated the use of calcined sodium silicate as a solid base catalyst for transesterification of soybean oil with methanol at 60 °C, achieving high activity. The calcined silicate can tolerate with 4.0 wt.% water or 2.5 wt.% FFA contained in soybean oil. Loss in catalytic activity of the catalyst was observed when the catalyst was recycled for more than five
times. Sodium silicate is a low-cost solid base catalyst that can be used in the transesterification of crude oil containing a certain amount of water and FFA.

Transesterification of soybean oil, using solid base catalyst such as sodium hydroxide loaded γ-alumina, was also studied.\textsuperscript{78}

The catalytic efficiency of non-ionic bases for the transesterification of vegetable oils was also investigated. In a first series of studies, the catalytic activity of some guanidines was compared to that observed using other bases such as the amidines DBU and DBN, and the triamino(imino)phosphoranes BEMP and Me\textsubscript{T}P. TBD was found to be highly efficient and it produces more than 90\% of methyl esters after 1 h even if applied at only 1 mol\%. Under the same experimental conditions, with the other bases the yields were not more than 66\%. The order of the catalytic activity is not directly related to the relative basicity of these compounds, since BEMP and Me\textsubscript{T}P should be the more efficient catalysts, followed by TBD. However, the guanidines are more active catalysts and the activity follows their relative basicity. Other bases such as DMAP, pyridine and triethylamine were also studied. However, even at 5 mol\%, these amines did not give satisfactory yields. DMAP was the most active within this series, producing only 20\% of methyl esters after 1 h.\textsuperscript{1}

The catalytic synthesis of biodiesel from soybean oil by transesterification over basic ionic liquid catalysts had been studied by Mingming Fan \textit{et al.}\textsuperscript{79} at atmospheric pressure. Choline hydroxide (ChOH) catalyst exhibited better catalytic activity compared with other basic ionic liquid catalysts, and methanol is the best alcohol for biodiesel synthesis. This catalyst is reusable and possessed better basicity in methanol solution.
Deka et al.\textsuperscript{80} introduced a novel catalyst derived from the trunk of \textit{Musa balbisiana} (one variety of banana plant) into biodiesel industry and showed that 96 wt.% of the \textit{Thevetia peruviana} seed oil was converted to biodiesel at 32 °C in 3 h using the catalyst (20 wt.% of oil). The catalyst is heterogeneous and easily prepared from the waste of post-harvest banana plants. Deka et al.\textsuperscript{81} also studied the catalytic efficacy of the trunk of \textit{Musa balbisiana} for the transesterification of dimethyl malonate with a variety of higher alcohols. Dimethyl malonate underwent transesterification with moderate to low yield in presence of the catalyst.

\textbf{I.2.3 Enzyme catalyzed transesterification}

Enzyme catalysis is another growing area of research in the field of catalytic transesterification. Enzymes are well-known as nature’s catalyst, performing various biological processes about which we can just wonder and that are difficult to study in laboratory. However, in past few decades, numerous efforts have been made to mimic various biochemical reactions, such as hydrolysis, esterification, transesterification, amidation, oxidation-reduction reaction, methyl like group transfer reaction, in the laboratory using enzymes as a biocatalyst for synthesis of industrially important compounds.\textsuperscript{82}

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc.) in order to establish suitable characteristics for an industrial application.
Ultrasound assisted enzyme catalyzed transesterification of waste cooking oil with dimethyl carbonate in solvent free system by immobilized enzyme (Novozym 435) was demonstrated by Gharat et al.\textsuperscript{83} As compared with the conventional stirring method, where FAME conversion was 38.69\% at 4 h, the Ultrasonic Irradiation without stirring significantly increases the conversion of enzymatic transesterification to 57.68\% in the same reaction time. However the reaction rate was further increased under the condition of ultrasonication coupled with stirring and resulted into higher conversion of 86.61\% for the same reaction time.

Lipase-catalyzed transesterification of vinyl esters having aromatic ring in acyl moiety with 2-phenyl-1-propanol has been studied and investigated by Masashi Kawasaki and his co-workers.\textsuperscript{84}

The use of biocatalysts in transesterification provides an opportunity for carrying out reactions under milder conditions leading to better quality products suitable in fragrance and flavor industry. Yadav et al.\textsuperscript{85} studied transesterification of vinyl acetate with \textit{n}-octanol at 30 °C as a model reaction in presence of different lipases as catalysts such as \textit{Pseudomonas} species lipase immobilized on diatomite, free \textit{Candida rugosa} lipase, Novozym 435 (lipase B from \textit{Candida antarctica}; immobilized on macro-porous polyacrylic resin bead) and \textit{Lipozyme} IM 20 (\textit{Mucor miehei} lipase immobilized on anionic resin). \textit{Novozym} 435 was found to be the most active catalyst in heptane as a solvent. A conversion of 82\% with 100\% selectivity of \textit{n}-octyl acetate was obtained at 30 °C in 90 min using equimolar quantities of the reactants with 0.833 g L\textsuperscript{-1} of \textit{Novozym} 435. The order of transesterification reactivity of vinyl acetate with various alcohols in presence of \textit{Novozym} 435 under identical conditions at 30 °C was found to be as follows:

\textit{n}-octanol > \textit{n}-decanol > benzyl alcohol > cinnamyl alcohol > 2-ethyl-1-hexanol > 2-phenyl ethyl alcohol > 1-phenyl ethyl alcohol.
Cheng Li et al. synthesized valuable methionol-derived esters from the readily available natural material butter oil as the fatty acid source through Lipozyme TL IM-mediated transesterification. The long fatty acid methionyl esters with high odour thresholds can provide long-lasting flavouring in food products.

Hydroxypropyl methyl cellulose (HPMC) and polyvinyl alcohol (PVA) film immobilized Rhizopus oryzae lipase was effectively applied by Dhake et al. to various alcohols for synthesis of industrially important acetates providing good to excellent yields of desired products (Scheme 11). Catalytic activity of immobilized lipase is found to be 4-fold greater than that of free lipase for transesterification reaction. The immobilized biocatalyst was effectively recycled for four consecutive cycles and exhibited remarkable stability for a period 90 days.

\[
\begin{align*}
R-OH + \text{Immobilized } R. \text{ oryzae} \xrightarrow{n\text{-hexane, } 45^\circ C} R-O \text{ester}
\end{align*}
\]

\(R = \text{Alkyl, aryl}\)

Scheme I.11: Immobilized Rhizopus oryzae lipase catalyzed transesterification

Hsu et al. studied the optimization of alkyl ester production from grease using a phyllosilicate sol–gel immobilized lipase. According to the studies, it was concluded that the immobilized lipase was active from 40 to 70 °C. Ester contents of 60–97% were highest when using a ratio of reactants of 2 mmol grease to 8 mmol alcohol and the biocatalyst was 10% (w/w) in the presence of a molecular sieve.

Watanabe et al. studied the enzymatic transesterification of waste edible oil in a fixed-bed bioreactor. Three-step methanolysis and one step methanolysis of waste oil were conducted using Candida antarctica lipase. 90% conversion was achieved in both the cases. The immobilized
biocatalyst could be used for 100 d in the two reaction systems without significant decrease in its activity.

Shimada et al.\textsuperscript{89} found that Candida antarctica lipase can be deactivated by shaking it in a mixture containing more than 1.5 M eq. of methanol to oil. Above this concentration, methanol is partially present as small droplets in the oil phase. These droplets are believed to cause enzyme deactivation. Therefore, methanol was added stepwise; after the addition of the third methanol equivalent, conversion to methyl esters was almost complete. The enzyme could be reused 50 times without loss of activity and its catalytic activity is not affected by the occurrence of free fatty acids.

Lipase from Pseudomonas cepacia was used as a catalyst for converting the oil from Madhuca indica into ethyl esters by Kumari et al.\textsuperscript{90} The lipase immobilized on accurel gave 96% conversion in 6 h. The best results were obtained using modified biocatalyst formulations, which are called cross-linked enzyme aggregates (CLEAs) and protein-coated microcrystals (PCMCs). While free enzyme powder after process optimization gave 98% conversion in 6 h using 50 mg of lipase, CLEAs gave 92% conversion in 2.5 h (using an equivalent of 50 mg of enzyme) and PCMCs gave 99% conversion in 2.5 h using the same amount of enzyme.

Nelson et al.\textsuperscript{91} also screened the potential of Lipases for their ability to transesterify triglycerides with short-chain alcohols to alkyl esters. The lipase from Mucor miehei was most efficient for converting triglycerides to their alkyl esters with primary alcohols, whereas the lipase from Candida antarctica was most efficient for transesterifying triglycerides with secondary alcohols to give branched alkyl esters. However, the efficiency of the P. cepacia (PS 30) enzyme in catalyzing the transesterification reaction was low, even when solvent was introduced into the reaction mixture. Biodiesel yield obtained was merely 13.9–28.8% for primary alcohols (methanol,
ethanol and isobutanol) and 44.1% for secondary alcohol (isopropanol). The reaction conditions reported are; reaction temperature at 45 °C, stirring speed of 200 rpm, 5 h reaction time, 0.34 molar of triglyceride in hexane, methanol to oil molar ratio of 3:1 and 12.5–25% enzyme by weight of tallow.²⁹,⁹¹ Screening reactions for transesterification of tallow with secondary alcohols showed a completely different trend, in which the lipases from *C. antarctica* and *P. cepacia* gave higher ester conversions than *Lipozyme* IM 60.

Chen *et al.*⁹² investigated the enzymatic conversion of waste cooking oil using immobilized *R. oryzae* lipase. A three-step batch transesterification reactor was used and stepwise process was introduced in the reactor to reduce the poisoning of enzyme by methanol. The optimum reaction condition was reported at 40 °C, methanol to oil molar ratio of 4, immobilized lipase to oils weight ratio of 30%, pressure of 1 atm and reaction time of 30 h. Biodiesel yield in the range of 88–90% can be obtained under these conditions.

Ying *et al.*⁹³ was the first group of researchers that used *Bacillus subtilis* for transesterification of waste cooking oil to biodiesel. *B. subtilis* was initially encapsulated within the net of hydrophobic carrier with magnetic particles (Fe₃O₄), and then the secreted lipase can be conjugated with carboxyl at the magnetic polymicrosphere surface. This magnetic cell biocatalyst (MCB) was claimed to have better dispersion during transesterification and can easily be separated from the reaction mixture by subjecting to an external magnetic field. From the study, it was found that biodiesel yield could reach up to 90% at reaction temperature 40 °C, pH 6.5, loading of 3.0% MCB, adding methanol in two stepwise and 72 h reaction time. Furthermore, MCB can be easily regenerated without losing its enzymatic activity.
I.3 Mechanism of transesterification

I.3.1 Mechanism of acid catalyzed transesterification

Acid catalyzed transesterification involves the protonation of the carbonyl group of the ester leading to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates alcohol to form the new ester IV, and to regenerate the catalyst $H^+$. 

![Scheme I.12 Mechanism of acid catalyzed transesterification](image)

(1) protonation of the carbonyl group by the acid catalyst;

(2) nucleophilic attack of the alcohol, forming a tetrahedral intermediate;

(3) proton migration and breakdown of the intermediate.
I.3.2 Mechanism of base catalyzed transesterification

The first step (Scheme I.13) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the ester generates a tetrahedral intermediate from which the alkyl ester and the corresponding anion of the ester is formed. The latter deprotonates the catalyst, thus regenerating the catalyst.

\[ R^2\text{OH} + B \leftrightarrow R^2\text{O}^- + BH^+ \]

\[ R - O^+ + OR^2 \leftrightarrow R - C - OR^2 + R^1O^- \]

\[ R^1O^- + BH^+ \leftrightarrow R^1\text{OH} + B \]

Scheme I.13: Mechanism of base catalyzed transesterification

(1) production of the active species, \( R^2\text{O}^- \);

(2) nucleophilic attack of \( R^2\text{O}^- \) to carbonyl group of ester,

forming of tetrahedral intermediate;

(3) intermediate breakdown;

(4) regeneration of the catalyst.
1.4 Conclusion

From the survey of literatures, we have come to know about different types of catalysts for transesterification. Most of the catalysts reported till now are efficient and some of them are reusable. Some of the catalysts need a support material to enhance their catalytic activity. Many of them are homogeneous that can’t be recovered thereby increasing the cost of purification. Most of the catalysts are toxic. A number of catalysts have been explored for transesterification in biodiesel synthesis. Catalysts from natural sources with high efficiency have also been reported but non-toxic, natural and low cost catalysts for the transesterification of aromatic and aliphatic esters are few in numbers. Search for a biodegradable, heterogeneous and reusable catalyst with high efficiency still remains as a central point of many research works.

1.5 Objective

The objective of our investigation is to look for an environmentally benign, non-toxic, heterogeneous and reusable catalyst for transesterification reaction.

A number of efficient catalysts for transesterification have been reported in the literature. But many of them are toxic and costly. Efforts are needed to explore an eco-friendly and efficient catalyst for transesterification. Developing a cheap, safe to handle and store, reusable and typically solid catalyst from banana plant is the central component of this investigation.

1.6 References


