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Advancement in Catalysts for Transesterification in the Production of Biodiesel: A Review

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Abstract

Biodiesel is mono alkyl ester of long chain fatty acids derived from transesterification of triacyl glycerol present in renewable feed stocks such as vegetable oils and animal fats. Transesterification is a reversible process and proceeds appreciably by the addition of a catalyst. The catalysts can be homogenous, heterogeneous or enzymatic catalysts. It is affected by molar ratio of oil to alcohol, type and amount of catalysts, reaction temperature, reaction time and free fatty acids and water content of oils or fats. The present review is an effort to give insight into the various catalysts used, their advantages and disadvantages in the context of biodiesel production.

Keywords: Transesterification, Catalyst, Enzyme, Nanoparticle catalyst

Introduction

Major share of the fuel consumed in today's world is for transportation and energy production. At present, fossil fuels meet this requirement to a large extent which is leading to their depletion at an alarming rate (Heinberg and D. Fridley 2010). The gap between their demand and supply is continuously increasing because of overgrowing population and Industrialization resulting in the increase in their price. Moreover, they are associated with emission of green house gases and other pollutants (Miao X and Wu 2006, Bruce 2008, Groom et al. 2008, Vasudevan and Briggs 2008). The need for clean and renewable energy source necessitated the emphasis on biodiesel as it is non toxic, biodegradable, has high flash point and low inflammability (Sérgio and Graciela 2006,Lìlian et al. 2008, Abdullah et al. 2009, Coronado et al. 2009, Cumali et al. 2011, Haseeb et al. 2011, Adewale et al. 2017, Singh et al. 2017). It has also gained much public attention because of need for energy security and concern over global warming. It provides an alternative to petroleum based fuels (Hill et al. 2006, Demirbas AH and Demirbas 2007, Demirbas 2007, Nizami et al. 2017).

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Biodiesel is fatty acid methyl ester (FAME) derived from transesterification of triglyceride (TAG) in vegetable oils (Sylvain et al. 2009, Ghanei et al. 2011, Mário et al. 2011, Avhad et al. 2015, Mardhiah et al. 2017, Knothe and Razon 2017) and animal fat (Kirubakaran and Selvan 2018) with methanol in the presence of methanol catalyst (Kudre et al. 2017). Biodiesel is also produced by esterification of free fatty acid (Tan et al. 2015, Lourinho and Brito 2015, Lee et al. 2014, Doyle et al. 2016). Various feedstock used for biodiesel production are oils like soybean oil, sunflower oil, rapeseed oil , palm kernel oil, coconut oil, waste cooking oil, Jatropha, palm oil (Sarin and Sharma 2007) , soybean oil (Yang and Xie 2007) , microalgal oil (Gaurav et al 2016).

Oils and fats basically contain monoglycerides, diglycerides, triglycerides, lipids and free fatty acids. Various groups have shown that triglycerides (TAGs) hold promise as alternative fuels. This has an advantage of being renewable and biodegradable with higher cetane number (Meher et al. 2006, Demirbas 2009). But vegetable oils are highly viscous (Al-Zuhair 2007) as a result they can cause poor fuel atomization, incomplete combustion, and carbon deposition on the injector. Therefore, direct use of TAGs is not practical since it causes engine choking and carbon deposition (Akoh et al. 2007). However this problem is eliminated by transesterification of oil to alkyl ester (Helwani et al. 2009). This review presents the transesterification of oil using different catalyst and their mechanism along with their advantages and disadvantages.

This review also gives insight on the microwave heating of reactions and traditional method of heating of reactions. Apart from this, the current status of enzyme based catalyst and nano-size catalyst is also discussed.

Transesterification

Transesterification, also known as alcoholysis (Busca 2009, Avhad et al. 2015), is a multistep reversible reaction in which triglycerides are converted to di-glycerides and then to mono-glycerides which finally gets converted to biodiesel (Moreira et al. 2010, Gao et al. 2011) and glycerol (by-product) as in Figure 1 This is a chemical process in which carboxylic acid ester is converted into different carboxylic acid esters. During the process, exchange of 'R' group of an ester with 'R' of an

alcohol takes place in presence of a catalyst resulting in an ester with larger alkoxy group (starting from methyl/ ethyl esters), Figure 2.

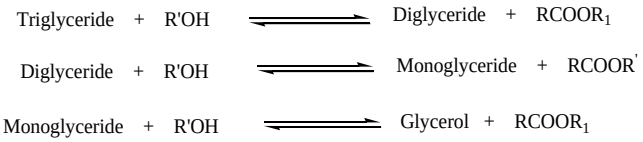

Figure 1: General equation for transesterification of triglyceride

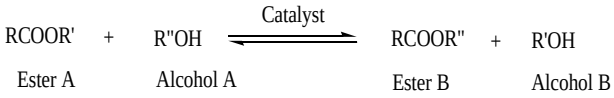

Figure 2: General equation for transesterification reaction

The two reagents involved here are oil/fat and a short chain alcohol, in presence of a catalyst. Theoretically, 1 mol of triglyceride requires 3 mols of alcohol, Figure 3, but generally higher amounts of alcohol are used to obtain high ester outputs, dependent on the type of oil used as feedstock, type and amount of catalyst, temperature, etc (Sharma and Singh 2009, Jose et al. 2011, Rashid et al. 2016) . Alcohols that can be used are methanol (methanolysis, most preferred due to its low cost, polar structure, most available and being the shortest chain alcohol) and ethanol (renewable source as it is produced from the fermentation of glucose) due to low cost. However propanol, butanol and octanol can also be used but their cost is higher as compared to methanol and ethanol (Shahid and Jamal 2011, Balat and Balat 2010, Demirbas and Demirbas 2007).

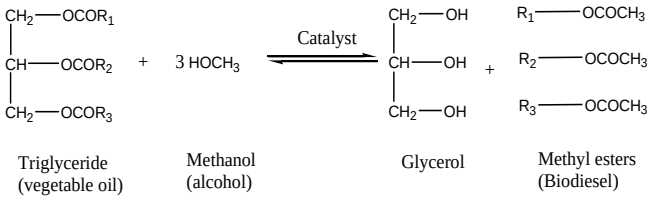

Figure 3: Transesterification of a triglyceride

Non catalytic transesterification reaction is too slow and energetically unfavored, so the reaction generally takes place in presence of catalyst which can be acidic (sulfuric acid, hydrochloric acid) or basic (sodium hydroxide, potassium hydroxide). As alcohol is scarcely soluble in oil, so catalyst increases the solubility, thus accelerates the reaction (Atabani et al. 2012). Commercially base catalyzed transesterification is often preferred since it is faster than acid catalyzed transesterification. The transesterification process removes the glycerin, so viscosity decreases but heating value and cetane number does not change (Awolu and Layokum 2013).

Kinetics of transesterification reaction

Although, mechanism of acid or base catalyzed transesterification is well known (Mu'azu K et al. 2015, Aransiola et al. 2013, Birla et al.2012) but various parameters governing the kinetics of transesterification are not known much. They can provide operational advantage and contribute to the commercial performance of the overall process (Vujicic et al. 2010). As discussed already, biodiesel is mainly produced from vegetable oil (more unsaturated) and animal fat (more saturated). Their main constituent is triglyceride (TAG) which is a complex molecule that plants and animals use for storing food energy. Transesterification of triglyceride in presence of base catalysts follow SN2 mechanism (Lee et al. 2009).TAGs are formed by covalent bonding of carboxylic acid with alcohol. In this context, TAG is an ester formed by combining of three molecules of fatty acids covalently bonded with glycerol molecule (Gaurav et al. 2010).

The economy of process mainly depends on type and quantity of catalyst used. Overall yield and reaction rate is affected by various physical and chemical factors such as temperature of the reaction, type and amount of catalyst used, mixing intensity, quality of TAG, starting material and water content. Reaction rates are needed in proper designing of reactor to produce biodiesel and theses are in different form in presence of catalyst (Davison et al. 2013). In presence of homogenous catalyst, they follow either first order or second order kinetic model (Krishnan 2012). Liu et al (Liu et al. 2016) reported second-order mechanism during transesterfication of corn oil using trace sulphuric acid. In case of heterogeneous-catalyzed transesterfication, reaction rate are different like adsorption of reactant (Dossin et al. 2016), desorption of product. Eley-Rideal and Langmuir-Hinshelwood-Hougen-Watson are proposed kinetic models heterogeneously catalyzed transesterification. Al-Sakkari et al. (Al-Sakkari et al. 2017) suggested Eley-Rideal and Langmuir-Hinshelwood models for transesterfication of soybean oil in presence of cement kiln dust. Various groups studied the reaction as a two phase system in the beginning (oil and methanol constitute two immiscible liquids and a solid catalyst) followed by a single phase system (when sufficient methyl ester is formed which acts as a mutual solvent) and then again as a two phase system (when glycerol is formed). Generally, transesterification is a three step process (scheme earlier) with three equilibrium constants. The comparison of values of rate and equilibrium constants for the three different reaction steps was done by Sivaswamy and group (Sivasamy et al. 2009). Second-order kinetics has been observed at 6:1 methanol/oil molar ratio in most cases. Depending on the systems, second-order, pseudo-second-order or, at higher excess of MeOH, pseudo-first-order kinetics was observed (Li et al. 2018). In some studies, mixing was found to be critical for the reaction to proceed according to the kinetics. Single –phase system (when methyl ester formed acts as a mutual solvent) is found to be kinetically controlled and favored (Karmee et al. 2009).

Base catalyzed transesterification

The transesterification using base catalyst involves four steps. In the first step, base reacts with alcohol to form a protonated catalyst and an alkoxide. This is followed by nucleophilic attack of alkoxide at the carbonyl group of TAG to give a tetrahedral intermediate. In the next step, formation of alkyl ester and corresponding anion of diglyceride takes place and finally deprotonating the catalyst takes place to regenerate the active species. Abdullah et al. (et al. 2017) studied esterification and transesterfication of palm oil sludge by alum and KOH respectively, with 93% of biodiesel yield.

Factors affecting base catalyzed transesterification

Effect of alcohol to oil molar ratio

The yield of methyl esters generally depends upon methanol to triglyceride molar ratio. Theoretically three moles of methanol

are required per mole of oil for transesterification. Prafulla and Deng 2009 studied the amount of alcohol required for transesterification of vegetable oil in terms of alcohol to oil molar ratio (Prafulla D and Deng 2009). Shazia sultana et al. studied transesterification on five different molar ratios in the range 2:1 to 10:1 and obtained maximum yield 92% with 6:1 methanol to oil molar ratio (Sultana et al. 2014). On further increase in methanol to oil molar ratio the ester yield decreases. Enciner J.M et al. , studied different ethanol to oil molar ratio between ranges 3:1 to 15:1 for the transesterification of vegetable oil and reported that reaction is incomplete when molar ratio is less than 6:1. The yield of ester increases as the molar ratio increased upto 12:1 and obtained optimum value at 9:1(Enciner et al. 2002). However many authors reported that with increase in methanol to oil molar ratio the yield decreases, for instance, working on different molar ratio ranges from 1:1 to 1:10 and reported that the maximum yield is obtained at 1:1 and this may be due to inhibitory effect of alcohol on lipase activity (Lu et al. 2010). Similarly, Li et al. gave same trend that with increase in molar ratio yield decreases, the achieved 95% yield in 12 hr at molar ratio 4:1 (Li et al. 2006).

Effect of catalyst concentration

The effect of NaOH concentration between the range of 0.1-0.9 wt% was studied and obtained that yield increases with increase in catalyst concentration from 0.1-0.5% which decreases with further increase in NaOH concentration and reduced to 50% with 1.5% NaOH concentration. This is because with increase in the concentration of catalyst, soap formation will take place and reduce the yield with increase in viscosity (Sultana et al. 2014).

Acid-Catalyzed transesterification

In Acid catalyzed transesterification, carbonyl group protonation leads to carbocation which forms tetrahedral intermediate after the nucleophilic attack of alcohol. The glycerol is separated and forms new ester. These reactions should be carried in the absence of water because carbocation reacts with water to form carboxylic acids (Gaurav et al. 2013).

Catalyst for transesterification process

Traditional biodiesel processing is comprised of two processes esterification and transesterification. The conventional esterification process uses methanol with a homogenous acid catalyst such as sulfuric acid to convert free fatty acids (FFAs) into esters. Conventional transesterification uses a homogenous base catalyst such as sodium/ potassium hyroxide or sodium/ potassium methoxide along with methanol to convert to the triglycerides into biodiesel and glycerol.

Thus, typically there are two kinds of catalysts which are used in any biodiesel process:

1. Homogeneous catalysts (Rashid et al. 2008, Qian et al. 2008, Hassan and Vinjamur 2014) which function in the same phase (liquid, gaseous, etc.) as the reactants. Typically, they are dissolved in a solvent with the substrates.
2. Heterogeneous catalysts (Ramos et al. 2008, Arzamendi et al. 2008, Kiss et al. 2008) occur in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. The total surface area of solid has an important affect on the reaction rate; the smaller the catalyst particle size, the larger the surface area for a given mass of particles.

Homogeneous alkaline catalysts such as sodium/ potassium hyroxide are most commonly used industrially for biodiesel production as compared to homogenous acid catalyst or heterogeneous (solid) catalysts. This is because of their ability to promote the reaction efficiently at relatively lower temperatures, their cost effectiveness and good performance. But there are certain issues related to these conventional homogenous catalysts such that higher acid number, yield loss, higher post cleaning cost, quality of glycerin, process and product consistency, their sensitivity to FFAs and water, corrosive nature, their reusability and the resulting saponification phenomenon etc. So these catalysts are associated with their own sets of drawbacks. Moreover, the formation of immiscible glycerol phase during the course of the reaction solubilizes the homogeneous base catalyst and, therefore, withdraws it from the reaction.

In order to overcome above difficulties, heterogeneous catalyst came as fairly newer development in the realm of biodiesel production where combination of solid acid and base catalysts was used. They have general advantage of being reusable, easy to separate from the reaction products, do not form soaps, almost 90% pure glycerol is obtained, more tolerant to water and FFAs content in the feedstock. Associated drawbacks are they require high temperature and pressure and possibility of leaching is always there which can contaminate the pure product.

Homogenous catalyst

Base catalyst

The most widely used catalysts for transesterification reaction are basic catalysts. Base-catalyzed transesterification proceeds faster and they are less corrosive but can be used only when free fatty acid content in TAG is less than 2% (Sharma and Singh 2007). Any strong base capable of deprotonating the alcohol will serve as a suitable catalyst such as NaOH, KOH, NaOMe etc. (Oguzhan 2011, Ruzaimah et al. 2011, Mi et al. 2011, Siddharth et al. 2011, Zahir et al. 2011). The presence of water causes undesirable hydrolysis of base so reaction must be carried out in dry atmosphere. Homogeneous base catalyst such as carbonates (Arzamendi et al. 2008), alkaline metal hydroxide (Rashid et al. 2008) and alkoxides are most commonly used. Alkoxide does not form soap from triglyceride saponification due to the presence of hydroxide ion which act as an impurity in alkoxide (Sivasamy et al. 2009). While using alkaline catalyst, the free fatty acid content should not increase 0.5% by wt. otherwise soap formation will takes place which hampers the production of biodiesel. Various authors reported that 90% yield is obtained by using potassium hydroxide and boiler ashes in the methanolysis and ethanolysis of coconut and palm oil (Ejikeme 2008). Alkaline catalyst NaOH was found to perform better than NaOMe. However to obtain higher yield the concentration of NaOMe is slightly higher as compared to NaOH. Singh et al. studied about alkaline catalyst (NaOH, KOH, KOMe and NaOMe) and found that better yield is obtained by potassium based catalyst as compared to sodium based catalyst. Whereas methoxide based catalyst produces higher yield compared to hydroxide based catalyst (Singh et al. 2006). Base catalyst are mostly used because reaction takes place at low temperature and pressure

that is 60^0C and 20 psi and obtain high yield about 98%. However there are some shortcomings it requires high energy, to separate the catalyst from the media after transesterification pro-reaction treatment is required, difficult to recover glycerol after the reaction moreover it forms soap with free fatty acids.

Acid catalyst

The acid catalyzed transesterification does not gain much popularity because of its very slow rate than the alkali catalyzed reactions (Sharma and Singh 2007). Its performance does not get affected by the presence of free fatty acids and it can catalyze simultaneously both esterification and trans-esterification. Acid catalyst can produce biodiesel from low cost feed stock having high free fatty acid (FFA). However acid catalyzed reactions have lower moisture sensitivity as well as non-appearance of soap formation. Acid catalysts are used where oil has higher FFAs (Sivasamy et al. 2009). Acid catalyzed reactions are two stage processes, in first stage esterification takes place in the presence of acid catalyst while in the second stage reaction takes place in the presence of base catalyst (Sivakumar et al. 2011, Ritesh et al. 2011 Romain et al. 2011). The acid catalysts mostly used are sulphuric acid, organic sulfonic acid, hydrochloric acid, and phoshphoric acid.. Zullaikah et al. uses sulphuric acid as catalyst for the transesterification of rice bran oil between temperature range of 60-80ºC (Zullaikah et al. 2005).

Heterogeneous catalyst

It is difficult to separate homogeneous catalyst from the reaction mixture so heterogeneous catalysts are developed. They are advantageous because they does not form soap through saponification of triglyceride and eliminate corrosion problems and reaction requires high temperature and pressure (Arzamendi et al. 2008, Zhen et al. 2014, Guldhe et al. 2017, Al-Sakkari et al. 2017). However there are some limitations like, they have poor performance compared to homogeneous catalyst, and due to less surface contact catalyst does not participate effectively in reaction so catalyst must be in porous state (Kiss et al. 2008). The surface of heterogeneous catalyst must be hydrophobic in nature so that it adsorb triglyceride and to avoid adsorption of polar by products like water and glycerol on surface. Solid catalysts which are mostly used are alkaline earth alkoxides, solid organic bases, basic metal oxides (Arrieta et al. 2005), acid zeolites, basic zeolites (Shu et al. 2007, Chai et al. 2007), heteropolyacids (Cao et al. 2008), sulfated zirconia and mixed metal oxides, insoluble/ immobilized metal salts and hydroxides, basic metal oxide (Oguzhan 2011), ion exchange resins and immobilized sulfonic acids, hydrotalcite, double metal cyanide complexes (Lee et al. 2014).

Alkaline earth oxide and alkoxides

Ca and Mg are alkaline earth metals which are most widely used as heterogeneous base catalyst. Alkali earth metal oxides successfully catalyzed the transesterification reaction. Alkaline earth oxides are basic due to M^{2+} and O^{2-} ion pairs. Various authors reported the use of CaO as catalyst for the transesterification of sunflower, and rapeseed oil with methanol. Moreover, strontium oxide, CaO, MgO also investigated as catalyst for transesterification with high basicity, high catalytic activity, non toxicity, low price and low solubility in methanol (Verziu et al. 2011, MacLeod et al. 2008, Montero et al. 2007, Ghanei et al. 2016, Marinkovic´ et al. 2016, Nisar et al. 2017). The presence of atmospheric carbon dioxide and water, the active site of CaO is poisoned and catalyst shows their insensitivity and ineffective to the raw material whose free fatty acid (FFA) content greater than 2% (Soares et al. 2016). To overcome this problem CaO is loaded on carrier or support such as alumina, silica and other oxide and have better perspective i.e. greater availability of catalytically active site, better stability and resistance to poisoning than neat CaO (Marinkovic´ et al. 2016). Marinkovic´ et al. (Marinkovic´ et al. 2017) loaded CaO on γAl_2O_3 and tranesterfied sunflower oil and reported that the yield of biodiesel was 94.3% in a batch reactor. Alkali-doped CaO and MgO have also been investigated for TAG transesterification. Alkaline earth metal oxides incorporated into metal oxides to form composite oxides (Lee et al. 2014, Dai et al. 2017, Narula et al. 2017) which are also suitable as solid base catalysts for biodiesel production. They exhibit greater stability and are less susceptible to dissolution, facilitating separation from the reaction media. Martyanov and Sayari used calcium methoxide as catalyst for the transesterification of triglyceride and found that initially reaction is slower as compared to homogeneous sodium methoxide and magnesium methoxide, but at later stage, the rate of reaction is higher than magnesium methoxide (Martyanov and Sayari 2008). Alkaline earth metal oxides assimilate with metal oxide and form composite oxide which can be used as solid base catalyst for transesterification. Composite oxides are more stable and easy to separate from the reaction media (Woodford et al. 2014).

Acid/ Base Zeolite

Now-a-days, zeolites are widely used as heterogeneous catalyst in industrial applications as they are environmentally benign and offer high surface area and porosity [Hassani et al. 2014, Endalew et al. 2011). Zeolites are most widely used as solid acid catalyst for transesterification of oil and made hydrophobic by elimination of water of hydration. The acidic properties ofzeolites are usually improved by protonation (Sivasamy et al. 2009). La/Zeolite beta catalyst for the batch transesterification of soybean oil was carried out (Shu et al. 2007) and found that La/Zeolite base catalyst have higher conversion rate than zeolite beta heterogeneous acid catalyst used in biodiesel production are mostly mesoporous (Carrero et al. 2011, Xu et al. 2008).

Hetropolyacids

Hetropolyacids attains much attention due to its super acidic nature (PK H^+> 12) and porous structure. They are highly soluble in polar media in their native form which make their contribution in reaction as homogeneous catalyst . Heterogeneous catalyst ($C_{s2.5}$ H $_{0.5}$ $PW_{12}O_{40}$) was used for transesterification of oil and same result was obtained as by using sodium hydroxide or sulphuric acid with one advantage of easy separation of catalyst from media and its reuse (Chai et al. 2007). Cao et al. (Cao et al. 2008) uses the hetro polyacids ($H_3PW_{12}O_{40}$. $6H_2O$) catalyst for transesterification of waste cooking oil. In 10 hr, 87% yield is obtained using hexhydrate catalyst. The catalyst would be separated easily and was reused many times. In the presence of FFAs, $H_3PW_{12}O_{40}$/ Ta_2O_5 showed better activity for both esterifications and transesterification (Alsalme et al. 2008).

Hydrotalcites

Another class of solid base catalyst of the general molecular formula $[(Mx^{2+})^-(My^{3+})(OH)_2(x+y)]A^{y/n}{}_{n-}.mH_2O$ where M^{2+} and M^{3+} represent divalent and trivalent metal ions, respectively, and An_ is an intercalated anion. It attracted attention because of their high activity and robustness in the

presence of water (Xie et al. 2006, Georgogianni et al. 2009). Magnesium -aluminum hydrotalcites catalyst was synthesized by coprecipitation method with Mg/Al molar of 1.5-5 for transesterification of sunflower oil with biodiesel yield of 51-75% but yield was increased up to 96 % with methanol / oil ratio 48(Navajas et al. 2018).

Ion Exchange resins immobilized sulfonic acids

Transesterfication of triglycerides is not possible if free fatty acid content (FFA) more than 3%, to reduce the FFA content less than 1%, esterification is required, for this strong acid such as hydrochloric acid or sulphuric acid is used and they act as homogeneous catalyst. However, there are number of drawbacks in using homogeneous acid catalyst such as equipment corrosion, side reaction, difficulty in separation of catalyst and not environment friendly. To overcome this problem, enzymatic catalyst and supercritical methanol (Zeng et al. 2017) have been investigated but they are unsuitable due to cost and high temperature and pressure is required for supercritical method. Cation exchange-resin, act as solid acid and serve as heterogeneous catalysts for transesterfication (Grob and Hasse 2006, Wang et al. 2017) have several advantages over enzyme and supercritical methods. Ion-exchange resin has several advantages over homogenous catalysts such as better electivity and efficiency, reusability and easy removal from the reaction medium. Solid-acid catalyst (ion-exchange resin) composed of copolymers if divinyl benzene, styrene and sulfonic acid on benzene. Catalytic performances of various ion exchange resins depends on swelling capacity (Lotero et al. 2006) and studied by various groups (Lou et al. 2008, Kitakawa et al. 2007, Mbaraka et al. 2006, Feng et al. 2010). Suresh et al. (Suresh et al. 2017) synthesized partially sulfonated polystyrene from expanded polystyrene waste and used as esterification of non-edible oil such as simulated acid oil and rubber seed oil. They reported that the acid value of simulated acid oil reduces form 17 to 3.2 mg KOH/g while acid value of rubber seed oil 28.8 to 4.8 mg KOH/g and these non-edible oil can be used for biodiesel production. Anion exchange resin was found to be better than cation exchange resin (Shibasaki-Kitakawa et al. 2007). So far, Amberlyst-15 was found to be best among the commercial resins.

Insoluble/ immobilized metal salts and hydroxides

The transesterification of tiolein could be achieved using alumina loaded with alkali metal salts as a solid base catalyst. These catalysts were found to be insensitive to the presence of water (Ebiura et al. 2005).

Nanoparticles as heterogeneous catalysts

One way to maximize the activity of heterogeneous catalysts is by increasing the concentration of the active surface (Gardy et al. 2017). The surface area of the catalyst can be increased by reducing the particle size. In order to achieve this aim, synthesis of nanoparticle size catalyst was carried out. Highest methyl esters can be produced by catalyst with high surface area (Yan et al. 2009). Many authors investigated that Nano sized catalyst have large contact area. For instance, Wang et al (Wang et al. 2009) produced biodiesel from waste cooking oil in the presence of nano-sized catalyst (Aluminum dodecatungstate to phosphate AIPW) and observed that ≈ 96% conversion was achieved at 55ºC due to large surface area of nanoparticle. CaO catalyst has been studied extensively for transesterification reactions due to its high catalytic activity even when very small amount is used, easy availability, higher activity, reusability, low cost and mild reaction condition (Jookjantraa and Wongwuttanasatian 2017, Priti and Fulekar 2017). Pretreatment temperature range between 700-1000K is used to remove water and CO_2 which is adsorbed on the surface of CaO. Other oxides or alkaline earth metal hydroxides are known to cause difficulty in separation of the catalyst from reaction products (Abdullah et al. 2009). Combination of CaO and ZnO (CaOZnO) catalyst is an effort in this direction which resulted in 90% conversion of transesterification of sunflower oil (Granados et al. 2007). In a separate study, ZnO nanoparticle catalysts were prepared and utilized as catalysts (Yan et al. 2010).

Liu et al (Liu et al. 2008) obtained 95% yield at temperature 65ºC by using CaO catalyst. Hsiao et al. (Hsiao et al. 2011) used nano powder CaO as catalyst and obtained 96.6% yield at 1:6 oil to methanol ratio, reaction time 1 hr, 338 K temperature and 3 wt% catalyst. Due to easy preparation and low cost researcher focus attention on MgO and CaO catalyst. Huaping et al. (Huaping et al. 2006) obtained 93% yield using CaO as catalyst and 92% yield by using MgO as catalyst. Dossin et al. use MgO as catalyst in batch work reactor and found that satisfactorily at ambient condition. Magnesium oxide is identified as good homogeneous catalyst for transesterification of ethyl acetate with methanol (Dossin et al. 2006). Baskar et al (Baskar et al. 2017) use Ni doped ZnO nanocatalyst for transesterification of castor oil and reported that the biodiesel yield of 95.20% with catalyst loading 11% (w/w) , oil to methanol ratio 1:8 , reaction temperature of 55^0C and reaction time of 60 minutes. The combination of Cao and ZnO (CaOZnO) catalyst in palm kernel oil transesterification is studied. The mixture of CaO and ZnO has small particle size which result in large surface contact area as compared to individual oxides. Ngamcharussrivichai et al. (Ngamcharussrivichai et al. 2009) used CaOZnO catalyst with Ca/Zn ratio 0.25 for the transesterification of palm kernel oil and obtained greater than 94% yield at reaction temperature 60oC and reaction time 60 minute. CaOZnO catalyst is used for the transesterification of sun flower seed oil and 90% yield is obtained (Alba-Rubio et al. 2010). Mansir et al. (Mansir et al. 2018) synthesized calcium -base catalyst by wet-impregnation method for transesterfication of waste cooking palm oil and obtained 90.1% biodiesel yield. They have also reported that the reusability of catalyst for three cycle with more than 70% if yield. The CaO and ZnO are synthesized by Co-precipitation method or impregnation method. It was also found that the catalyst synthesized by the co precipitation method result in higher yield (94.2%) compared to impregnation method (90%) (Ngamcharussrivichai et al. 2009). The literature shows that the activity of reaction depends on Ca to Zn atomic ratio it is synthesized between ratio, from ¼ to 4. At atomic ratio of 0.25 the CaOZnO catalysts produce 93.5% of esters which is larger as compared to other atomic ratio.

Microwave irradiation effect on biodiesel production

Traditionally organic reactions are heated by various equipments such as sand bath, heating jackets and oil baths. These techniques are not effective because they are slower and temperature gradient took place. But now-a-days microwave dielectric heating is preferred. Alkali- catalyzed transesterification requires more than 60 minutes for efficient heat transfer but microwave irradiation-assisted alkali-catalyzed transesterification requires less time and also improve heat transfer efficiency (Nayebzadeh et al. 2017,

Singh and Sharma 2017, Milano et al. 2017). El Sherbiny et al. (El Sherbiny et al. 2010) compare the conventional and microwave irradiation-assisted transesterification of Jatropha oil and shown that the reaction time is significantly reduced from 150 minutes (in conventional) to 2 minutes (in microwave irradiation-assisted transesterification). Naor et al. (Naor et al. 2017), synthesized biodiesel from microalgal oil in presence of strontium oxide/ silicon oxide nanopowder using microwave irradiation-assisted transesterification and reported that the reaction was completed in 2 minutes. Xiang et al (Xiang et al. 2017) observed that microwave radiation improve the yield of biodiesel and also reported that the time required for microwave irradiation-assisted transesterification of waste cooking oil was 6 minutes. In microwave heating radiation passes the wall and only heats the solvent and reactants without heating the vessel. Ultrasonics/ microwave radiations lowers the cost of processing, speeds of transesterification, does not require high temperature and high grade of biodiesel is produced (Patil et al. 2011, Gupta et al 2015, Martinez-Guerra and Gude, 2016, Buasri and Loryuenyong 2017, Fatimah and Yudha 2017, Asif et al. 2017). Various groups used micro-algal oil to produce biodiesel by transesterification by heating with microwave radiation. Azcan and Yilmaz produced biodiesel by transesterification of micro-algal oil in the presence of KOH by conventional heating and microwave heating method and find that with conventional heating system reaction completes in 210 minute while with microwave heating reaction completes in 5 min, obtained 96.54% conversion using KOH 1% wt, 1:8 oil to methanol at 65ºC (Azcan and Yilmaz 2014).

Enzyme catalyzed transesterification

The problem related to conventional catalytic process, like removal of catalyst, treat large amount of waste water and high energy requirement are solved by using enzymes. Enzyme do not form any soap like alkaline catalyst and without the need of washing they esterify both FFA and TAG in single step. These are biological catalyst and can catalyze different chemical reactions. They can be either used in free or immobilized form in transesterification that leads to the production of biodiesel (Haas et al. 2006, Guldhe et al. 2015, Guldhe et al. 2016 , Amini et al. 2017, Rafiei et al. 2018). A wide range of enzymes such as lipase has been used for esterification (Fjerbaek et al. 2009). Lipase from fungi and bacteria are mostly used for process and they belong to group of hydrolytic enzymes which is also known as hydrolases. Immobilization of lipase is the state of arrest of the enzyme in region (Jegannathan et al. 2008). Immobilization provides number of benefits such as enzyme reuse, easy separation of product from enzyme. Many other properties are also improved such as chemical, thermal and mechanical properties making them to use in harsher environmental condition (Awang et al. 2007, Bhushan et al. 2008). Compared with chemical methods using alkaline or acid catalysts, utilization of lipases for biodiesel production has the following advantages: more compatibility with variations in the quality of the row material and reusability; ability to produce biodiesel in a lower number of steps using less energy and with drastically reduced amount of wastewater; improving of product separation and glycerol quality. But the use of enzymes as catalysts presents also some drawbacks (Junmin et al. 2011, Shiva et al. 2011).

Transesterification in alternative solvents

Alternative solvents such as ionic liquids (IL) and supercritical fluids have received much attention in application to the transesterification of vegetable oils. They give almost complete conversion (95%) and the reaction time is very low only within 10 minutes. This is due to the fact that the oil and the supercritical alcohol form one phase, the solubility parameters of the two components becoming close in the given conditions. The conversion is even higher when supercritical ethanol is used, the solubility parameter of ethanol being closer to that of the oil, which makes their reciprocal solubility higher. ILs, green solvent, have negligible vapour pressure, high catalytic activity, easy separation of product, high chemical and thermal stability, low corrosivity, basicity and acidity can be designed and controlled. (Amarasekara 2016, Muhammad et al. 2015, Vafaeezadeh and Alinezhad 2016, Hu et al. 2017). Generally acidic nature of ILs is used for biodiesel production (Vafaeezadeh and Alinezhad 2016, Ishak et al. 2017). Conventionally, imidazole type Brønsted acid IL are used due to high catalytic activity but these ILs are expensive and not preferred for large scale production of biodiesel (Feng et al 2017). Feng et al. (Feng et al. 2017) synthesized quaternary ammonium based Brønsted acid ILs for transesterification of palm oil with 98.4% of biodiesel yield. These ILs are cheaper and eco-friendly as compared with imidazolium-based ILs. Li et al. (Li et al. 2018) synthesized novel triazolium-based ionic liquid for transesterification of palm oil with 99.75% of biodiesel yield and they have also reported that triazolium based IL have better catalytic activity than imidazolium-based ionic liquid. The advantages of such solvent are their density is comparable to liquids and diffusivity is comparable to gases. In some cases transesterification can also take place in absence of a catalyst (Marchetti et al. 2007, Cao et al. 2005, He et al. 2007, Bunyakiat et al. 2006).

Conclusion

This review includes the transesterification of oil using homogenous and heterogeneous catalyst. The effect of parameters such as, molar ratio, catalyst concentration and methanol to oil ratio are discussed. Homogeneous base catalysts are commonly used for industrial purposes whereas heterogeneous and homogeneous acid catalysts have lesser use. Homogeneous acid and base catalyst require excess alcohol. They are used for batch mode process, followed by catalyst separation. Moreover homogeneous alkali catalysts are sensitive to free fatty acids and H_2O, results in saponification. The feed stock having FFA require acid and base catalyst which is two stage process in which acid catalyst are firstly used and then removed before the use of alkaline catalyst. However the use of acid catalyst increases the corrosiveness. Now-a- days much more attention is focused on enzyme based catalyst instead of chemical catalyst because enzyme based catalytic reaction proceed at moderate conditions, require low alcohol to oil ratio, and easy product recovery. Use of nanoparticle catalyst and heating reactions with the help of microwave, and in supercritical fluids is discussed.

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