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Synthesis of Biodiesel by Transesterification Using Homogeneous and Heterogeneous Catalysts: A Review

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ABSTRACT: In the recent times the biodiesel has becomes one of the most notable alternative fuel for diesel engines because of owing to biodegradability, renewability and low toxicity. The biodiesel is produced by a variety of feedstocks such as edible oil, non-edible oil and waste cooking oil. Transesterification process is generally used for biodiesel production. In transesterification process catalysts are used for carrying out the reaction. In the reaction the catalyst performs a crucial role in the conversion of biodiesel of free acid or feed stocks to respective esters at faster rate and in minimum reaction temperature. The production of biodiesel by transesterification have been done by several researchers using methanol or ethanol along with catalysts of different kinds catalyst**.** The catalysts used for production of biodiesel are homogeneous and heterogeneous catalysts. Several researchers have worked on development of homogeneous and heterogeneous catalysts for transesterification process. This paper provides the review of the production of biodiesel from homogeneous and heterogeneous catalysts of the past 10 years.

KEYWORDS: Biodiesel, Transesterification, Homogeneous Catalysts, Heterogeneous Catalysts.

I. INTRODUCTION

The petro-diesel fuel is one of the primary source of energy. In the present time the energy demand increasing concurrently in the world. The petro-diesel fuel are fossils fuels, non-renewable nature in nature and limited reserves of petro-diesel fuels around the world has become a matter of great concern [5-7]. Moreover, the instability in the price of crude oil and the environmental problems such as global warming and release of harmful gases in the environment by petroleumbased energy sources have created serious have created a serious concern in worlds community. Such concerns about fossil fuels have led to the utilization of alternative energy sources. The primary source of energy in transportation industry is petro-diesel fuel. The fuel which will be alternated to petro-diesel fuel must be suitable and acceptable technically [23-26]. Biodiesel, as an alternative fuel, has many merits that make it preferable to the conventional petro-diesel diesel. The use of biodiesel has alternative fuel can become a propitious answer to meet the current energy demand. The concept of running the engine from vegetable oil is 100 years old. In 1900 at the world exhibition in Paris, Dr. Rudolf Diesel the inventor of the diesel engine successfully ran his diesel engine using peanut oil as fuel. Biodiesel fuels are biodegradable, environmental friendly, non-toxic, renewable, free of sulphur and aromatic compounds. [15, 21-22]. Biodiesel is commonly produced from a transesterification reaction of triglyceride with alcohol, with or without catalyst, to form fatty acid alkyl esters. In this process, triglyceride from vegetable oil or animal fat reacts with alcohol (usually methanol or ethanol) in the presence of a catalyst (acid or base) to generate fatty acid alkyl esters [8-11, 23-26]. Biodiesel can substitute petro-diesel fuel with little or no modification in engine because of its properties like kinematic viscosity, flash point, cetane number and heating value, which are comparable to that of petro-diesel fuel. Biodiesel can be blended with petro-diesel. In the case of mixture, the respective portion of biodiesel in petro-diesel should be indicated. B30 blend means a mixture of 30% biodiesel and 70% petroleum diesel. While the B100 is pure biodiesel [12-16].

II. BIODIESEL FUEL

Biodiesel is defined as a mono-alkyl ester of long chain fatty acids derived from vegetable oils, seeds or animal fats and it is produced by chemically reacting lipids by transesterification of vegetable oil or animal fat with methanol or ethanol in the presence of catalysts [6-8]. The transesterification process detaches the hydrocarbon chain to make biodiesel and glycerine [10]. The steps involved in biodiesel production is shown in Fig.1. The glycerine can be used to make soaps or fermented to make ethanol, which is reused to make biodiesel or it can be burned as heating fuel. Biodiesel can be produced from a variety of edible or non-edible oils such as palm, soybean, sunflower, non-edible oils derived from jatropha, karanja, mahua oil, biodiesel can also be produced from waste cooking oil [17-19]. The biggest difference between biodiesel and petro-diesel is oxygen content. Biodiesel have oxygen levels of 10 to 45% while petro-diesel has none, making the chemical properties of biodiesel very different from those of petro-diesel [16, 24]. Biodiesel have very low sulphur content and have a low nitrogen levels [1, 5]. In order for biodiesel to be used commercially as a fuel, the Finished biodiesel is analysed using sophisticated analytical Equipment to ensure it meets international standard. The European EN 14214 and the American Society for testing and materials (ASTM) D-6751 standards are the most commonly used [15, 19-20].

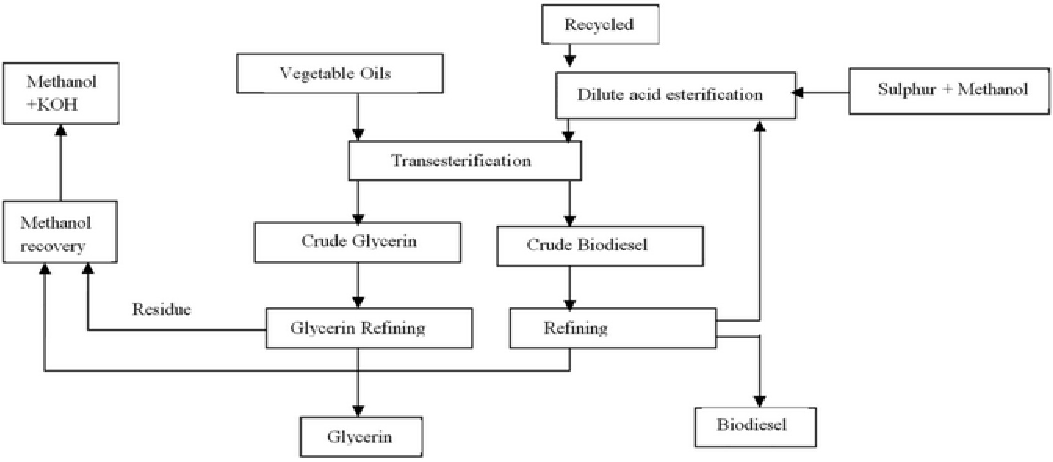

Fig. 1: Steps Involved in Biodiesel Production.

III. TRANSESTERIFICATION REACTION

Transesterification is a common method for biodiesel production from vegetable oils and animal fats [7]. In transesterification or alcoholysis, oils or fats react with alcohol in presence of a catalyst to form alky esters and glycerol. In transesterification the displacement of alcohol from an ester by another alcohol [12-14]. The reaction in shown below in equation 1. The transesterification process reduces the viscosity of oils which is higher than petro-diesel. Selecting a suitable alcohol and catalyst is important for transesterification method. Various alcohols such as methanol, butanol, and amyl alcohol can be used for transesterification [9]. Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides into glycerol, yielding one ester molecule from each glyceride at each step [2, 5, 19-20]. Methanol is used widely because it is relatively cheaper than other alcohols and has chemical and physical advantages over other alcohols [3]. The transesterification reactions are performed using homogeneous base catalysts such as sodium hydroxide, potassium hydroxide or acid catalyst like sulfuric, sulfonic, phosphoric, or hydrochloric acid [6-7]. In recent times base catalysts such as metal hydroxides, metal alkoxides, alkaline-earth oxides, or hydrotalcites [25-28]. Base catalysts are usually preferred to acid catalysts because the higher reaction rates and the lower process temperatures are required as compared with acid catalyzed transesterification [11].

$$\text{Triglycerides} + \text{ROH} \rightleftarrows \text{Diglycerides} + \text{R}^1\text{COOR}$$

$$\text{Diglycerides} + \text{ROH} \rightleftarrows \text{Monoglycerides} + \text{R}^2\text{COOR}$$

$$\text{Monoglycerides} + \text{ROH} \rightleftarrows \text{Glycerol} + \text{R}^3\text{COOR} \qquad (1)$$

IV. HOMOGENEOUS CATALYSTS

The homogeneous catalyzed transesterification has been the commonest method used at laboratory, pilot and industrial scale levels [4]. Homogeneous catalysts function in the same phase (liquid, gaseous, etc.) as the reactants. Homogeneous catalysts are dissolved in a solvent with the substrates. Basically, in this transesterification process, there are two types of homogeneous catalyst which is acid catalyst (H_2SO_4 or HCl) and alkali catalyst (KOH or NaOH) [6-9]. The production cost of these catalysts is low and they show a very high performance when feedstocks (vegetable oils) with low free fatty acid are used [2-3]. The production cost of these catalysts is low and they show a very high performance when feedstocks (vegetable oils) with low free fatty acid are used [1]. Also, this reaction leads to high conversion of triglycerides to their corresponding methyl esters. However, this method also has its own shortcomings as it is energy intensive, recovery of glycerol is difficult, the catalyst has to be removed from the product [10-13].

V. PRODUCTION OF BIODIESEL FROM HOMOGENEOUS CATALYSTS

In important research work **Meher L.C. et al. [1]** investigated biodiesel production from karanja oil using rate of stirring (180–600 rev. per min), catalyst concentration (0.25–1.5% wt), temperature (37–65°C), and alcohol/oil molar ratio (6:1–24:1). The karanja oil for investigation was extracted by mechanical extraction method and the acidic value of extracted oil was 5.06 mg KOH/g. The transesterification was carried out in the presence of freshly prepared KOH-methanol solution. The result showed the biodiesel yield of 97% after 3 h of reaction time for a molar ratio of 6:1, while a similar yield was achieved in 30 min for a molar ratio of 24:1. The authors observed that a higher molar ratio of methanol to oil provided faster reaction rates while a lower methanol to oil molar ratio (6:1) requires longer reaction times to achieve equal conversion. In another research work **Encinar et al. [2]** studied the transesterification reaction of used frying oil by means of ethanol, using sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide as catalysts. The transesterification process was performed in a 1000 ml spherical reactor, provided with a mechanical stirring, sampling outlet, thermostat, and condensation systems. The operation variables used were ethanol/oil molar ratio (6:1–12:1), catalyst concentration (0.1–1.5 wt.%), temperature (35–78°C), and catalyst type. The researcher found that, with a 6:1 M ratio and after 2 h, the conversion to alkyl esters was close to 45 wt.%. The biodiesel with the highest yield of 72.5% was obtained using an ethanol/oil molar ratio of 12:1, potassium hydroxide as catalyst (1%), and 78 °C reaction temperature. However, a lower yield of 66.2% biodiesel yield was obtained, when the molar ratio was increased to 15:1. The effect of operating variable on biodiesel properties is shown in table 1. While **Ha Ho Sung et al. [3]** demonstrated the methanolysis of soybean oil catalyzed by lipase in 23 different ionic liquids. The highest yield of biodiesel obtained was 80% after 12 hours of reaction at 50°C with four equivalents of methanol in the ionic liquid was achieved in [Emim][TfO]. The production yield of 80% was eight times higher compared to the conventional solvent-free system. It was 15% higher than the FAMEs production system using tert-butanol as an additive. The optimum substrate molar ratio of methanol to soybean oil for FAMEs production in [Emim][TfO] was found to be 4:1. The Fig. 2 shows time courses for the alcoholysis of soybean oil with methanol by Novozym 435 in [Emim][TfO], [Omim][Tf_2N], [Emim][MS], tert-butanol and solvent free system.

Table 1: Influence of Operating Variables On Viscosity, Temperature Corresponding to A 50% Distillation, And Yield of Esters [2].

Run	1	2	3	4	5	6	7	8	9	10	11	Standard EN-14214 values
Ethanol/Oil	6:1	9:1	12:1	15:1	12:1	12:1	12:1	12:1	12:1	12:1	12:1	
T, °C	60	60	60	60	60	60	60	60	60	35	78	
Catalyst	KOH	KOH	KOH	KOH	NaOH	KCH_3O	$NaCH_3O$	KOH	KOH	KOH	KOH	
%Catalyst	1	1	1	1	1	1	1	0.5	1.5	1	1	
Viscosity, cSt												
10°C	21.56	11.57	10.47	11.02	12.76	12.65	14.01	12.69	10.53	11.29	10.83	
15°C	17.02	10.18	8.73	9.25	10.44	10.32	12.84	10.38	8.75	9.70	8.59	
20°C	14.75	8.10	6.98	7.52	9.28	9.19	11.68	8.65	7.02	8.11	6.06	
25°C	12.48	7.75	6.11	6.80	8.12	8.03	10.51	7.50	6.20	6.93	5.46	
30°C	11.35	6.36	5.24	5.80	6.96	6.75	9.34	5.77	5.26	6.05	5.08	
40°C	9.08	4.63	3.49	4.01	5.80	5.76	7.59	4.33	3.62	4.03	3.19	3.5–5.0
Temperature 50% distillation, °C	281	284	284	283	270	278	274	273	275	276	276	
Yield of esters, %	46.8	60.1	72.5	66.2	63.3	63.9	59.4	52.4	70.6	61.1	74.2	96.5

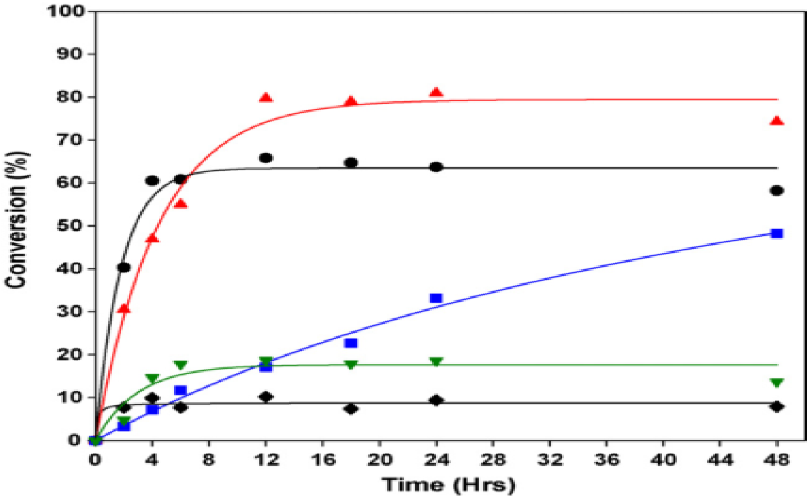

Fig. 2: Time Courses for The Alcoholysis of Soybean Oil with Methanol by Novozym 435 in [Emim][TfO] (▲), [Omim][Tf_2N] (■), [Emim][MS] (▼), Tert-butanol (●) and Solvent Free System (♦) [3].

In further research work **Lapis A. M. Alexandre et al. [4]** performed the immobilization of traditional acidic and alkaline catalysts H_2SO_4 and K_2CO_3 in ionic liquids. The ionic liquids tested were [BMI][NTf_2], [BMI][BF_4] and [BMI][PF_6] by transesterification of soybean oil. The best result was obtained when the organic salt [BMI][NTf_2] used, 98% of yield was obtained by transesterification of soybean oil and high purity of the biodiesel produced. The process employed simple purification steps to recover the catalyst and glycerol and the catalytic system can be used at least six times without loss of efficiency. Afterwards, **Fan Xiaohu et al. [5]** investigated the biodiesel production from recycled canola oil with a two-step acid and alkali catalyzed reaction. In the first step, they considered some variables for acid catalyzed esterification such as molar ratio of alcohol to oil (4.5:1–18:1), catalyst concentration, reaction temperature, and reaction time. The optimum condition was 40:1 molar ratio of methanol to oil and 5% sulfuric acid. The FFA level was reduced from 11% to 0.41% around 96.3% reductions at 550°C temperature for 1.5 h. After esterification, transesterification was carried out at 6:1 molar ratio of methanol to oil with 1% potassium hydroxide. The gas chromatography of the produced biodiesel done by the researcher is shown in Fig. 3. The team of researcher **Hossain A.B.M.S. and Al-Saif A.M. et al. [6]** produced biodiesel from pure soybean cooking oil (PSCO) and waste soybean cooking oil (WSCO) by alkaline transesterification process in combination with methanol, ethanol and 1-butanol using conventional catalyst KOH. The optimal condition for biodiesel production were the 1:6 volumetric oil-to-methanol weight ratio, 1% KOH catalyst at 40°C reaction temperature and 320 rpm stirring speed. The result of the study showed that the biodiesel yield increased in the order of 1-butanol < ethanol <methanol. In another research work **Aransiola Funmilayo Elizabeth et al. [7]** studied the transesterification of refined soybean oil using alkali catalyst NaOH and methanol as alcohol. In the experimental test the methanol-to-oil molar ratio was maintained at 6:1 while the catalyst loading and reaction temperature was varied. The reaction temperature and the catalyst loading were varied at 30, 40, 50, 60 and 70°C; and at 0.5 and 1.0% weight of oil, respectively. The result of the study revealed that the optimum methyl esters conversion of 97.89% was achieved at 60°C for 3 h with 1% (w/w) catalyst. The viscosity (at 40°C), density, cloud point, pour point, flash point and acid number were 3.40 cSt, 0.86 g/ml, -1°C, -7°C, 175°C and 0.19 respectively. The optimum methyl esters conversion obtained met ASTM standard of D-6751. The table 2 shows the effect of temperature with time on kinematic viscosity of soybean biodiesel observed by the researcher.

Table 2: Effect of Varying Temperature with Time On Kinematic Viscosity of Soybean Based Biodiesel [7].

Time (h)	**Kinematic Viscosity (cSt)**				
	30^0C	**40^0C**	**50^0C**	**60^0C**	**70^0C**
0.25	3.75± 0.005	3.73± 0.000	3.65± 0.002	3.61± 0.001	3.62± 0.000
0.5	3.76± 0.028	3.62± 0.001	3.60± 0.000	3.55± 0.001	3.58± 0.000
1	3.74± 0.000	3.60± 0.004	3.57± 0.002	3.44± 0.000	3.44± 0.001
2	3.68± 0.007	3.57± 0.000	3.56± 0.001	3.40± 0.000	3.41± 0.001
3	3.62± 0.000	3.67±0.007	3.56± 0.001	3.40± 0.000	3.39± 0.001

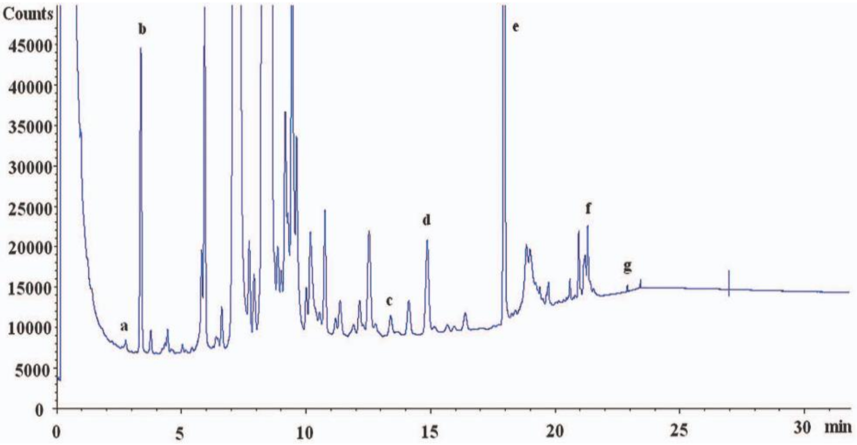

Fig. 3: Gas Chromatography of Biodiesel from Recycled Canola Oil. Lower Case Letters Represent: a: Free Glycerol, b: Butanetriol, c: Monopalmitin, d: Monoglyceride, e: Tricaprin, f: Diglycerides, g: Triglycerides [5].

In advance research work **Silva F. Giovanilton et al. [8],** produced biodiesel from soybean oil by transesterification with ethanol. Optimum conditions for the production of ethyl esters were the following: mild temperature at 56.7°C, reaction time in 80 min, molar ratio at 9:1 and catalyst concentration of 1.3 M. For esterification reaction, HR_2RSOR_4R was added as a catalyst and for transesterification KOH was added as the catalyst with methanol. Later **Aliyu Auwal et al. [9]** converted refined African mahogany oil into biodiesel via NaOH as catalyst in transesterification process. A solution of 0.1648 g of sodium hydroxide pellets in 42 cm^3 of methanol was added to a 250 cm^3 of this mahogany oil and heated at 60°C. The stirring of the reaction mixture was done at temperature 60°C for 30 minutes and then cooled to room temperature. The formed mahogany biodiesel has been then separated from glycerine. The biodiesel was washed with deionised water and dried. The yield of 53% was obtained by transesterification of mahogany oil. The researcher **Li Yihuai et al. [10]** transesterified soybean oil using potassium hydroxide (KOH) as catalyst and dichloromethane as co-solvent. The use of co-solvent improved the yield of the biodiesel and a much lower reaction time was required. The optimal condition for biodiesel were reaction temperature of 45°C, methanol to oil ratio of 4.5:1, co-solvent dichloromethane of 4.0% with 1 wt. % potassium hydroxide, a 96% yield of methyl esters was obtained in 2 h at these conditions. The characterization of biodiesel was done by FT-IR and ICP–OES spectrography. The researcher further analysed the cetane number, flash point, cold filter plugging point, acid number, water content, ash content and total glycerol content of produced biodiesel the result of test were found within the limits of ASTMD 6751-03, EN 14214 and GB/T 20828-2007 standards. The FT-IR of biodiesel done by the researcher is shown in Fig. 4. In the next work **K.L. Konge and A.S. Sabnis [11]** demonstrated production of biodiesel from soybean oil by application of sonic and mechanical energy to assist transesterification of soybean oil. The transesterification reaction was carried out in the presence of conventional catalyst NaOH. The experimental results showed that the optimized reaction conditions for biodiesel production were oil to methanol molar ratio 1:6, sonication power 210 W, catalyst concentration 0.2 wt% of oil and mechanical agitation speed 200-300 rpm at 45°C. The soybean oil methyl ester (SOME) yield obtained was 94.92% in 60 min.

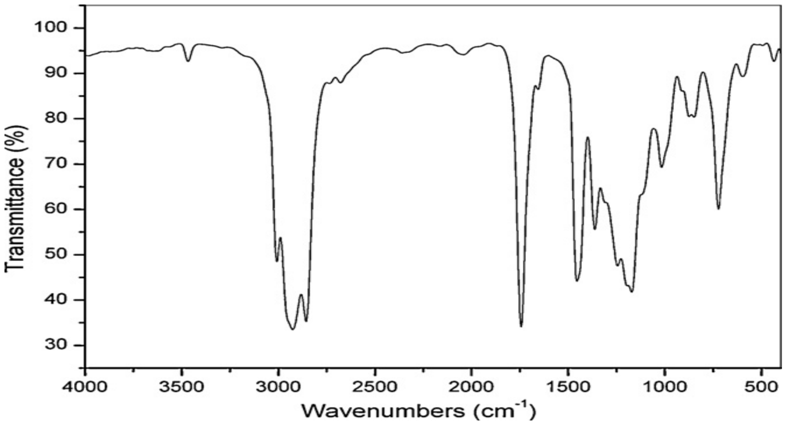

Fig.4: The FT-IR Spectrum of Biodiesel [11].

In the further research **Jahirul I. Mohammad et al. [12]** investigated transesterification process of beauty leaf oil to produce biodiesel. Due to the high FFA content of beauty leaf oil (12 wt%). The biodiesel production was done in two step pre-esterification of acid catalysed using sulphuric acid followed by transesterification of alkali catalyst by sodium methoxide. The result of the study disclosed that the optimal conditions for pre-esterification were 30:1 methanol to oil molar ratio, 10 wt% sulphuric acid catalysts and 75°C reaction temperature which reduced the FFA content to 1.8 wt%. While for transesterification the optimal condition was methanol to oil molar ratio, catalyst concentration and reaction temperature at 7.5:1, 1% and 55 °C respectively. Based on these condition 93% of FAME was achieved. On the other hand, **Ren Qinggong et al. [13],** synthesized morpholine alkaline basic ionic liquid (IL) 1-butyl-3-methyl morpholine hydroxide ([Hnmm]OH) catalyst. The characterization of catalyst was done by 1H NMR and FTIR. The study showed that the biodiesel yield was greatly increased from 61.2% to 96.6% with the increase of catalyst dosage from 1% to 4%. Moreover, the biodiesel yield was also affected by the molar ratio on increasing the molar ratio the yield increased and reached the maximum at molar ratio of 8:1. The reaction time increased with the increase in molar ratio. The optimum reaction conditions were found as [Hnmm]OH amount of 4% (mass fraction), the methanol to soybean oil molar ratio of 8:1, reaction temperature 70°C and reaction time 1.5 h the yield of biodiesel was 96.6%. The TG spectrum of the catalyst done by the author is shown below in Fig. 5. In the advance research work on catalyst **Benessere Vincenzo et al. [14]** prepared a homogeneous supported catalyst based on Zn(II) by anchoring complex $[Zn(OAc)_2(N,N`\text{-chelate})]$ on silica. The prepared catalyst was tested by transesterification of vegetable oil. The catalyst activity was tested in the esterification and transesterification of vegetable oils with different content of acidity. The reactions were conducted in methanol at 160°C temperature. The catalyst/oil ratio was 5.0% w/w. The transesterification of soybean oil along with two other substrates, lamp oil and residual olive oil. The study presented that increasing the quantity of methanol from 5 g to 20 g, the FAME yield increased in all cases and were higher than 90%. The highest yield of 94 ± 2 was obtained in transesterification of soybean oil. Further, the catalyst can be easily separated from the reaction mixture by simple decantation. In the most recent study **Tubino Matthieu et al. [15]** determined the rates of soybean oil methanolysis under NaOCH$_3$, KOCH$_3$, NaOH and KOH catalysis using a refractometric method for online monitoring of the reaction. The biodiesel synthesis experiments were performed in triplicate using soybean oil (150.0 g), methanol (30.0 g) and the catalyst (0.0157 mol). The reaction conditions included mechanical agitation at 400 rpm and temperatures of 30.0, 40.0, 50.0 and 60.0°C, which were controlled using a thermostatic bath. The study revealed that Potassium promotes faster reactions than sodium. The observed trend for the catalyst activities were as follows: KOCH$_3$> NaOCH$_3$> KOH > NaOH at temperatures higher than 34°C.

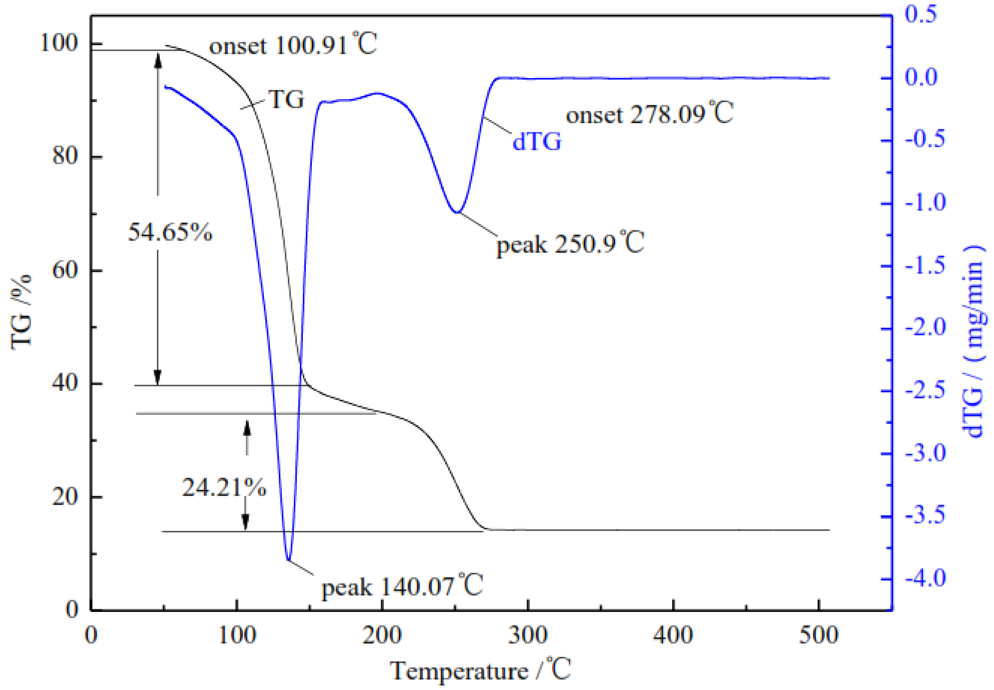

Fig. 5: TG Analysis of Various Ionic Liquids [Hnmm]OH [13].

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VI. HETEROGENEOUS CATALYSTS

Heterogeneous catalysis occurs in a different phase than the reactants. Heterogeneous catalysts are more economical, ecologically friendly, non-corrosive, easily separable from the liquid products, higher activity and longer catalyst life time [17-19]. Because of these advantages, research on chemical reaction using solid bases as catalysts has increased over the past decade. The use of heterogeneous catalysts does not produce soap through free fatty acid neutralization and triglyceride saponification [22, 25]. The additional benefit of the heterogeneous catalyst use is the possibility of their easy regeneration and reuse that make the biodiesel synthesis cost effective [27]. The most commonly studies for heterogeneous basic catalysts are alkaline metals carbonate (Na_2CO_3, K_2CO_3), alkaline earth metal oxides such as SrO, BaO, MgO and CaO, alkaline earth metal oxides ($CaCO_3$) and other oxides as ZnO [20-21, 28-30].

VII. PRODUCTION OF BIODIESEL FROM HETEROGENEOUS CATALYSTS

The researcher **Huaping Zhu et al. [16]** used CaO as a heterogeneous catalyst for biodiesel synthesis from Jatropha curcas oil. The base strength of calcium oxide was more than 26.5 after dipping in an ammonium carbonate solution followed by calcination. Under the optimal conditions of catalyst calcination temperature of 900°C, reaction temperature of 70°C, reaction time of 2.5 h, catalyst dosage of 1.5%, and methanol/oil molar ratio of 9:1, the oil conversion was 93%. The remaining calcium from the synthesized biodiesel was removed by decalcification method. The citric acid was used as decalcifying agents. The physio-chemical properties of synthesized biodiesel were found to in accordance to domestic and foreign standards. Further, **Granados López M. et al. [17]** used the activated calcium oxide as a solid base catalyst in the methanolysis of sun flower oil to avoid reduction of CaO catalytic activity. The catalyst was thermally treated at 700°C to chemically desorb CO_2 prior to being used in the reaction. After a 100 min. reaction time, 94% conversion was obtained at 60°C with alcohol/oil molar ratio of 13:1 and catalyst content of 3 wt.% based on the weight of the oil. Afterwards the group of researchers **Kouzu Masato et al. [18]** presented work on transesterification of soybean oil with refluxing methanol in the presence of calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$). The yield of fatty acid methyl ester found in research work was 93% for CaO, 12% for $Ca(OH)_2$, and 0% for $CaCO_3$ at 1 h of reaction time. CaO was used for further tests in transesterification of waste cooking oil with acid value of 5.1 mg KOH/g. The yield of FAME was above 99% at 2 h of reaction time, but a portion of catalyst changed into calcium soap by reacting with free fatty acids present in waste cooking oil at initial stage of transesterification. On the other hand, **Samart C et al. [19]** demonstrated that KI supported on mesoporous silica can be used to catalyze transesterification of soybean oil using methanol for biodiesel production with the conversion close to the conventional methods. The optimum condition was the reaction temperature at 70°C, 15 wt.% of KI, a reaction time of 8 h., and a catalyst amount of 5% by weight of the oil which yielded 90% conversion. The result shows that KI/mesoporous silica is a challenging heterogeneous catalyst for biodiesel production. The comparison of biodiesel conversion from fresh and regenerated catalyst is shown below in Fig. 6.

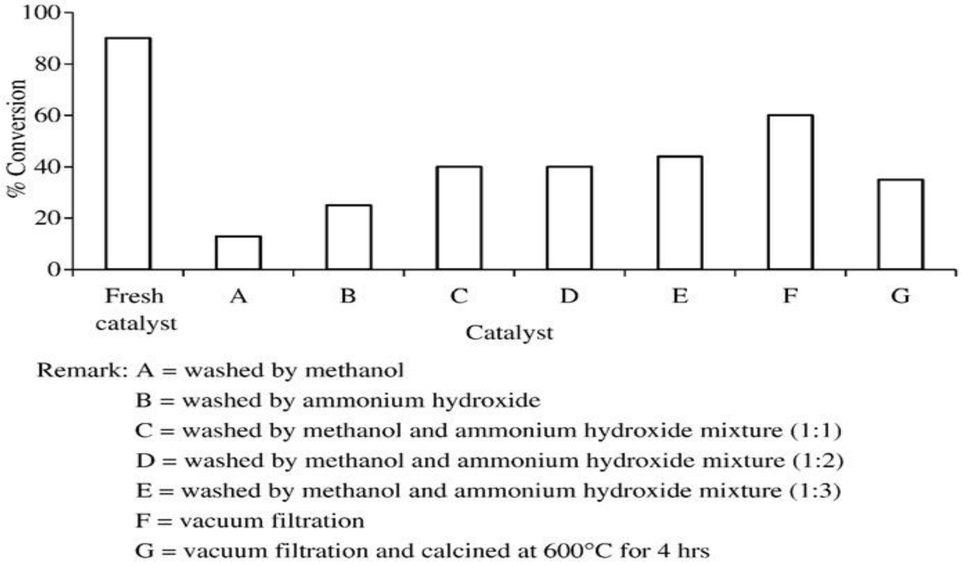

Fig. 6: Comparison of Transesterification of Soybean Oil and Methanol Between Fresh Catalyst and Different Regenerated Catalysts [19].

In the major study **Mootabadi Hamed et al. [20],** worked on ultrasonic assisted biodiesel production process from palm oil using alkaline earth metal oxides (CaO, SrO and BaO) as the heterogeneous catalysts. The SEM images of catalysts is shown in Fig. 7. The transesterification reaction process was done in a 500 ml three-neck glass batch reactor equipped with an ultrasonic transducer and probe, condenser, stirrer and thermocouple thermometer. The reaction time was kept between 10 min to 60 min and excess methanol was distilled off and the mixture was then centrifuged in an eppendorf centrifuge for 20 min at 2500 rpm. The biodiesel layer was then collected. The chemical stability of the heterogeneous catalysts was investigated by analysing the presence of free Ca, Sr or Ba in the biodiesel product. The activity of the heterogeneous catalysts correlated well with their basic strengths. In another important work **Chen Lie et al. [21]** synthesized a solid catalyst copper vanadium phosphate (CuVOP) and investigation showed that the catalyst is very active in the transesterification reaction for biodiesel production from soybean oil. The maximum conversion of 65.5% is obtained at loading of 1.5 wt.%, methanol to oil molar ratio of 6.75 at 65°C and reaction time of 5 h. A year later **Wang-Xun Jian et al. [22],** in their work synthesized biodiesel from soybean oil using transesterification over a lithium orthosilicate (Li_4SiO_4) solid base catalyst. Under the optimal reaction condition of a methanol/oil molar ratio of 18:1, a 6% (wt/wt oil) catalyst amount, and a reaction at 65°C for 2 h, the conversion to biodiesel could achieve 98.1%. The study reported the solid base catalyst was highly active, air in- sensitive and can be reused for at least ten cycles without loss of activity. In the next study **Guo Feng et al. [23]** examined transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. The researchers found that solid calcined sodium silicate can be used to produce biodiesel from vegetable oil. Calcined sodium silicate was demonstrated to be an excellent catalyst for the transesterification of oil with methanol, and it was a water resistant catalyst. At the beginning of the transesterification, ion-exchange proceeded after methanol absorbed on the surface of catalyst where the catalytic active species (CH_3O) were produced, and the mechanistic route of the transesterification was elucidated.

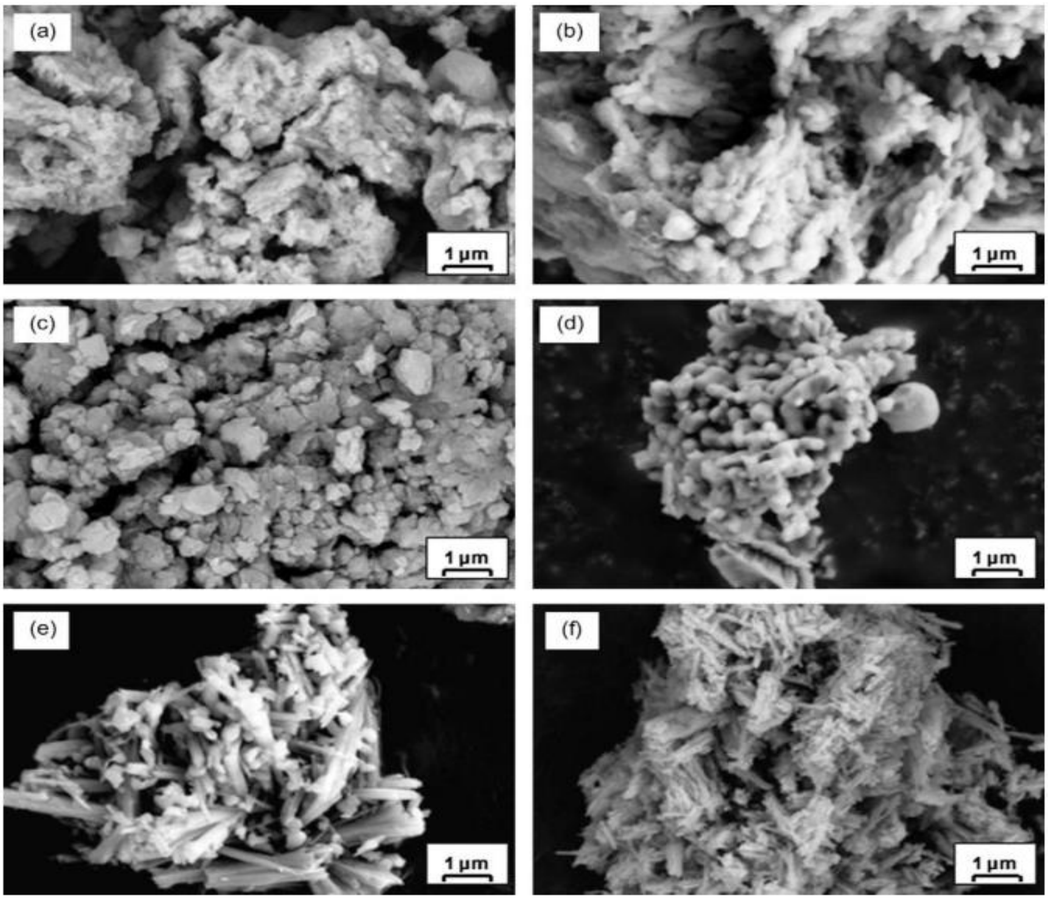

Fig. 7: Scanning Electron Micrographs (SEM) of (a) BaO Catalyst Before Reaction, (b) BaO Catalyst After Reaction, (c) CaO Catalyst Before Reaction, (d) CaO Catalyst After Reaction, (e) SrO Catalyst Before Reaction, and (f) SrO Catalyst After Reaction. (Conditions: catalyst/oil mass ratio 3%, methanol/oil molar ratio 9:1) [20].

In the further research work **Haitang Wu [24]** compared catalytic activity of pure CaO catalysts NaY, KL and NaZSM-5 zeolites supported CaO catalysts by transesterification of soybean oil. The preparation of the catalyst was done by microwave radiation followed by calcination at a high temperature in air. The catalyst was characterized by XRD and is shown in Fig. 8. In the research work it was found that the activity of CaO catalyst increased after supported on zeolites, and the CaO/NaY exhibited the best performance. The active component CaO was dispersed on the surfaces and pores of NaY zeolite, which caused the active basic sites of CaO increased and catalytic activity improved compared to pure CaO. Under the optimal conditions, i.e., a 9:1 molar ratio of methanol to oil, a catalyst amount of 3 wt.% and 65°C, the biodiesel yield exceeded 95% after 3 h of reaction with 30 wt.% CaO loading on NaY and microwave irradiation for 20 min**.** A year later the team of researchers, **Xie Wenlei and Zhao Liangliaang [25]** developed the heterogeneous CaO–MoO_3–SBA-15 catalysts by incipient impregnation method. The prepared catalyst was tested for the transesterification process of soybean oil to produce biodiesel. In transesterification reaction of soybean to biodiesel the solid catalyst, with the CaO–MoO_3 loading of 40% and calcined at 823 K, showed the best catalytic activity. The test presented that a fame yield of 83.2% is obtained at a 6 wt.% of catalyst with methanol/oil molar ratio of 50:1 at reflux of methanol and 50 h of reaction time. Moreover, the catalyst can be easily recovered and reused without significant loss of activity. The influence of catalyst on yield is shown in table 3. In the next work **Alves B. Melquizedequeet al. [26]** examined magnetic mixed iron/cadmium (ICdO) and iron/tin (ISnO) oxide nanocatalyst for production of biodiesel from soybean oil. The surface area of the ICdO catalyst was twice that of ISnO. Despite this difference in surface area no significant catalytic activity difference was observed in the esterification reaction. The result of the study revealed that highest catalytic activity in the esterification of soybean fatty acids was presented by the ISnO catalyst with 84% yield in FAME after 1 h reaction at 200ºC. Furthermore, ISnO catalyst did not present any significant change in the structure after the reactions and showed excellent potential for reuse. It was reused four times in recycling reactions without loss of catalytic activity.

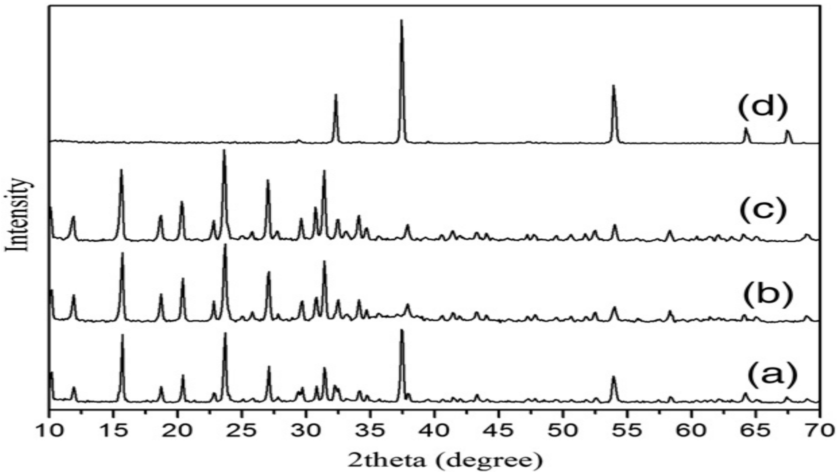

Fig. 8: XRD Patterns of CaO, NaY and CaO/NaY. (a) 30%CaO/NaY Before Radiated by Microwave, (b) 30% CaO/NaY After Radiated by Microwave (c) NaY zeolite (d)CaO [24].

Table 3: Influence of Preparation Conditions on the Catalytic Activity of the Solid Catalyst (Reaction Conditions: Molar Ratio 50:1, Catalyst Amount 6 wt.%, Reaction Temperature 338 K, Reaction Time 50 h) [25].

Entry	Calcination Temp. (K)	CaO–MoO_3 amount (%)	Conversion (%)
1	623	40	35.3
2	723	40	68.5
3	773	40	74.2
4	823	40	83.2
5	923	40	84.1
6	823	10	8.4
7	823	20	37.4
8	823	30	53.6
9	823	50	83.8

A exact year later, **Jia Lihua et al. [27]** synthesized KF- and CaO- supported montmorillonite (KCa/MMT) heterogeneous base catalyst by facile impregnation method. The synthesized heterogeneous base catalyst used for producing biodiesel in transesterification of commercial soybean oil with methanol. The result of the study showed that the biodiesel yields exhibit a volcano-type behaviour with different loading amounts of KF; the highest yield of biodiesel (98 %) was obtained with a catalyst with 30 wt% KF loading at Methanol to oil molar ratio 12:1, catalyst amount 3 wt%, reaction temperature 65°C, reaction time 1.5 h. The effect of reaction condition and KF loading on the yield of biodiesel is shown below in Fig. 9. In another study **Istadi I. et al. [28]** determined the performance of active solid catalyst of sulphated zinc oxide (SO_4^{2-}-ZnO and SO_4^{2-}/ZnO) by transesterification of soybean oil with methanol to produce biodiesel. The SO_4^{2-}-ZnO catalyst was prepared by co-precipitation method, while the SO_4^{2-}/ZnO prepared by wet impregnation. The SO_4^{2-}-ZnO showed better performance in transesterification reaction than SO_4^{2-}/ZnO. The trend of performance of both catalyst was due to effect of sulfonate incorporation into the zinc oxide structure to form active acid sites. The result of transesterification reaction of soybean oil with methanol shown that at reaction temperature of 65°C, methanol to oil mole ratio of 6 and 4 wt % catalyst loading and 4 h of reaction time fame yield of 80.19% is obtained by using SO_4^{2-}ZnO as catalyst. In the most recent study **Hashmi Sidra et al. [29],** investigated production of biodiesel from jatropha oil through transesterification process by using CaO-Al_2O_3 nanocatalyst, synthesized via top down technique. The synthesized nanoparticle was characterized by XRD and the average crystalline size found from XRD analysis was 29.9 nm. The fatty acid content of the oil and the biodiesel was analyzed using gas chromatography-mass spectroscopy (GC-MS). The study revealed that under optimized condition the transesterification of jatropha curcas oil catalyzed by CaO-Al_2O_3 nanoparticles showed maximum yield i.e. 82.3% at 5:1 methanol to oil molar ratio. Afterwards, **Patil Pramod and Pratap Amit [30]** prepared the zirconia supported cadmium oxide basic nanocatalyst by simple co-precipitation method using aq. ammonia as precipitating reagent for transesterification of soybean. The catalyst was characterised by XRD, scanning electron microscopy (SEM) and transmission electron microscopy technique (TEM). The prepared nanocatalyst was spherical in shape with a 58 nm average crystalline size. Trans-esterification of oil showed a pseudo first order reaction Kinetics with activation energy of 41.18 kJ/mole. In the research work 97% yield of biodiesel was observed using 7% catalyst loading (with respect of oil), 1:40 molar ratio of oil to methanol at 135℃.

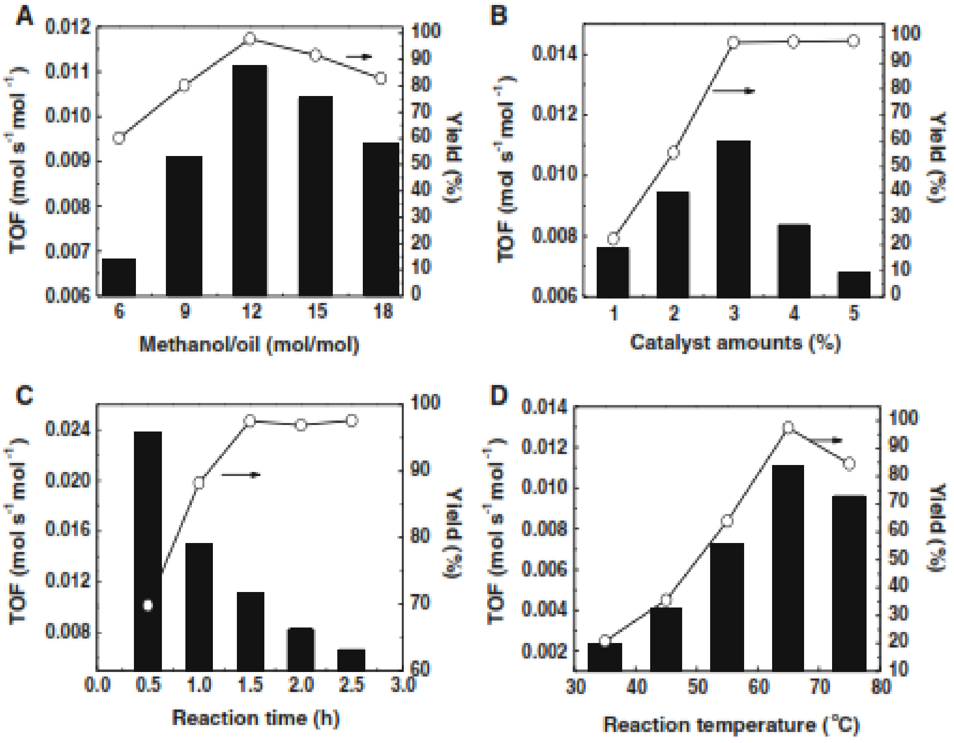

Fig. 9: Influence of Reaction Conditions on the Yield and TOF for KCa/MMT-30. (a) Temperature 65°C, Catalyst Amounts 3 wt%, Time 1.5 h; (b) Temperature 65°C, Methanol to Oil Molar Ratio 12:1, Time 1.5 h; (c)Temperature 65°C, Methanol to Oil Molar Ratio 12:1, Catalyst Amounts 3 wt%; (d) Methanol to Oil Molar Ratio 12:1, Catalyst Dosage 3 wt%, Time 1.5 h [27].

VIII. CONCLUSION

The present research work provides the comprehensive review of the previous researches done in past years on synthesis of biodiesel from different feedstocks using homogeneous or heterogeneous catalysts. An effort has been made to comprise all the important contributions and highlighting the most pertinent available literature for investigating the catalyst for synthesis of biodiesel. The conclusion from the current literature survey are as follows: -

1. Biodiesel has become the attractive alternative fuel to replace the petroleum fuel. Biodiesel renewable, non-toxic and biodegradable and has lower sulphur content [2-6].
2. The studies reported that biodiesel can economically produce from the vegetable oils. Currently, biodiesel is produced through transesterification reaction from vegetable oils such as rapeseed, soybean and palm oil [7-10].
3. Currently of the various processes available for synthesis of biodiesel, transesterification process is most commonly used for production of biodiesel from vegetable oils [11-14].
4. The methanol is widely used as alcohol because it is relatively lower cost and short-chain molar size than other alcohols available for carrying out transesterification reaction. Most of the researchers prefers the molar ratio between 3:1 to 12:1 for methanol [1-2, 17, 27].
5. The homogeneous catalysts require longer reaction time and could not be easily separated from biodiesel [17-19].
6. The use of heterogeneous alkaline earth metal oxides as catalyst is promising in the production of biodiesel as the heterogeneous catalyst are more effective than conventional homogenous catalyst [20-23].
7. Further, the use of heterogeneous catalyst in the form of nanoparticles provides higher performances at relatively lower temperatures, enhances the quality of biodiesel and increases the yield [29-30].

Acknowledgement

The review presented in this work is by no means complete but it gives a comprehensive review of homogeneous and heterogeneous catalysts used in production of biodiesel. The author wishes to apologize for the unintentional exclusions of missing references and would appreciate receiving comments and pointers to other relevant literature for a future update.

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