



Alumina supported catalytic materials for biodiesel production - A detailed review

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Abstract

Biodiesel has been recognized as good harmonious and possible alternative of non-renewable petro-diesels because of its similar characteristics to petroleum diesel. Use of biodiesel in the engines cause lesser emissions of greenhouse gases as it has biodegradability, good lubricity, non-toxicity, and environmentally benign nature. Utilization of vegetable oils as feedstock to produce biodiesel may disturb the food industry therefore waste seed oils are best for the biodiesel production. The transesterification reaction is one of the convenient methods for biodiesel production as it is cost effective and gives maximum biodiesel yield. Although, mostly homogeneous catalysts are used for transesterification for maximum oil to diesel conversion but recently heterogenous catalysts are of more interest because of their reusability and no production of wastewater. Composite catalysts are novel and popular trends in heterogenous catalysis, now-a-days. Alumina is the best support for loading of the catalyst due to its suitable pore size distribution, greater surface area and high thermal stability. When a catalyst is incorporated into/onto alumina, textural and structural properties of the catalyst are affected. The KI/ γ Al₂O₃ gave highest yield of FAME upto 99.99% for 1st generation biodiesel production by using sunflower as feedstock while Mg(NO₃)₂/Al₂O₃ calcined at 450°C and Ca(NO₃)₂/Al₂O₃ calcined at 550°C provided poor yields of FAME from palm kernel oil. To produce 2nd generation biodiesel CaO-La₂O₃-Al₂O₃ gave good yield of biodiesel (approximately 96.77%) from karanja oil and poor yield of FAME was provided by KI/Al₂O₃ only 31.8% by using rubber seed oil as feedstock. Although, not much work is reported in literature to produce 3rd generation biodiesel by using alumina supported catalysts. However, both CaO-MgO/Al₂O₃ and KOH/La-Ba-Al₂O₃ provided good FAME yield upto 97% in case of 3rd generation biofuels. Rate of conversion of oil into biodiesel depends on calcination time and reaction parameters such as methanol to oil ratio, catalyst loading, agitation speed, reaction temperature and the reaction time.

Keywords: Biodiesel, FAME, alumina, KI/ γ Al₂O₃, Mg(NO₃)₂/Al₂O₃, Ca(NO₃)₂/Al₂O₃, CaO-La₂O₃-Al₂O₃, KI/Al₂O₃, CaO-MgO/Al₂O₃, KOH/La-Ba-Al₂O₃

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1. Introduction

Presently the energy demands of the world are met through non-renewable energy resources such as petrochemicals, coal, and natural gas [1-6]. Demand and prices of non-renewable fuels are increasing rapidly, and these resources will be vanished in few years if these resources are used at the same rate [7]. Because of the non-renewable nature of the fossil raw materials, their continuous utilization over last few years causes limitation of the fossil fuel reserves [8]. Many necessary factors such as in peril dependence of the world economy on the fossil fuel, political concerns related to the oil producing countries, outpouring of greenhouse gases and the change in climate have moved the main focus of many governments to explore renewable energy resources [9-11]. It has been

shown that 98% of carbon emission are resulted from the burning of the conventional fossil fuels [12].

The search for renewable fuel that contributes less to carbon cycle is ongoing [13]. The worldwide struggles are continued to encourage the movement from non-renewable fuels to the renewable and environment friendly biofuels. Many studies have been conducted to develop an alternative property liquid fuel [14]. As per the result of these studies, biodiesel have been identified as a sustainable and cleaner alternative fuel that will help in decreasing the world's temperature by reduction in the discharge of the greenhouse gases like CO₂, NO_x and SO₂ [15].

Biodiesel is a substitute biogenic fuel that has various fatty acid esters and has been accepted worldwide due to the issues that are connected to the fuel derived from petroleum [16]. Biodiesel is a clean renewable fuel as it has

minimum amount of sulphur, aromatics and has 10% of oxygen, which helps it in combustion completely when used in internal combustion (IC) engines [17]. Its higher cetane number enhance its ignition quality, even when blend with petroleum diesel [18]. Climate and local soil conditions has a great influence on the feedstock of biodiesel, consequently different regions use different types of oil for the production of biodiesel [19].

Biodiesel feedstocks can be categorized as oil crops such as rapeseed, soybean and so on; oil trees like palm oil and Chinese pistachio; and others are animal fat and waste oil food [20]. Rapeseed oil in Europe, soybean oil in USA and palm oil in Malaysia (a region with tropical climate) are the significant oils of edible seeds that are being used for biodiesel production to run the compression ignition engines. The use of edible oils as engine fuel is not considered feasible in literature [2-21]. There are many non-edible oil seed species such as Karanja, Jatropha, Neem, Mahua and Simarouba etc., which could be used to produce biodiesel [2]. Among above mentioned sources of seed oil, an excessive oil seed producing tree is Karanja, which is not used as food thus considered as waste seed oil. Out of 200 million tons yield per year, only 6% is being used for the production of biodiesel [7]. The use of the waste and non-edible seed oils as feedstock for biodiesel production, is feasible in sense of their low prices, renewable nature and promptly high availability [22].

Many experiments have been performed successfully by the blending of vegetable oil with non-renewable diesel fuel. Caterpillar is a Brazil Company that in 1980, conducted an experiment on the pre-combustion chamber engines by mixing 10% of vegetable oil with 80% of diesel oil. It was concluded that the blended fuel maintain its total power without any change in the engine [23]. Subsequently in 1982, the mixture of 95% cooking oil and 5% of diesel was tested. After that it has been concluded that with some modifications, 100% vegetable oil can also be used in engine. The main problem associated with the use of blended fuel in compressed ignition engines is their high viscosity. This problem can be overcome by pyrolysis, micro-emulsification and transesterification [24].

Esterification and transesterification are the two chemical reactions that are used for production of biodiesel. But transesterification is the commonly used reaction as it is only a single step reaction between oil and methanol [25]. Transesterification of oils or fats with short chain alcohols such as methanol or ethanol is practiced at commercial scale to get the fatty acid alkyl esters (biodiesel) and glycerol. The transesterification of triglycerides consists of three successive and reversible steps. Triglycerides react with methanol to form diglycerides, monoglycerides, and finally glycerol and fatty acid methyl ester (FAME) [26].

Transesterification reaction can be carried out in the presence or absence of a catalyst and acid, base or enzyme can be used as catalyst. Catalyst reduces the

reaction time by speeding up the transesterification. Acid catalyzed transesterification is a slow reaction, therefore is not favorable. On the other hand, enzymes are too costly. The cost of enzyme-catalyzed production of biodiesel is about twice than that of the alkali-catalyzed process. Base catalysts can be in the form of a homogeneous catalyst which is soluble in the reaction medium or heterogeneous catalyst which are insoluble [25]. Homogeneous-base catalyzed transesterification has many disadvantages due to difficulty in the purification of biodiesel. The presence of large amount of free fatty acids in vegetable oils increases the chances of the soap formation during transesterification that can cause severe problems. Because of the soap formation, some amount of catalyst is lost and therefore reduces the catalytic efficiency. Moreover, during the biodiesel purification or washing, large amount of wastewater is produced to remove catalyst. Therefore, used catalysts cannot be recovered and cannot be used again for transesterification [27].

Solid catalysts are the most promising to produce the biodiesel that could decrease its cost, so that its price could compete with diesel oil. Heterogeneous catalysts have many advantages over a homogeneous catalyst: its separation from the reaction mixture is comparatively easy so it can be reused. Glycerol is produced with high purity (more than 98%), it do not form soap during transesterification and it do not need to wash with water so waste liquid is not produced. Therefore, transesterification by a solid catalyst is commonly recognized as a green and clean process [28].

As compared to homogeneous catalysts, separation of heterogeneous catalysts is simple and does not generate wastewater. Use of heterogeneous catalysts could be proved as an efficient, continuous process and improve the economy of biodiesel production. Because of the three-phase system (oil-methanol-solid catalyst) and diffusion of the reactants to the active sites of solid catalyst, the rate of heterogeneous catalytic transesterification process is generally lower than that of the homogeneous catalytic transesterification. Active species of all the heterogeneous base catalysts leach out into the reaction medium and cause soap formation if vegetable oil has free fatty acids (FFAs). Dissolving of solid-base catalysts decreases the chances of their reuse in consecutive batches or cannot use in continuous process. The most important thing about the solid-base catalysts is that they are mainly active in the transesterification at the temperatures around boiling point of methanol [26]. Therefore, heterogeneous solid catalysts such as metal oxides, hydrotalcites, zeolites and γ -alumina have been used now-a-days to overcome the cost of the purification process, as these catalysts can be easily separated out from reaction medium and can be reused [29].

2. Biodiesel production

Biodiesel can be divided as first, second and third generation biofuel based on their feed stock and production technologies. First generation biodiesels are generated from food oils such as soybean, corn, and rapeseed and thus are unsustainable. Although for second generation biodiesel raw materials are non-edible, but these (such as jatropha and karanja etc.) require cultivated and fertile land and heavy irrigation. Raw materials for first and second generation are difficult to collect and are expensive. Due to the above-mentioned issues, the production mechanism of first- and second-generation biodiesel is not considered sustainable. Studies on biofuel production are continuously being developed to improve the sustainability and reliability of the biofuels as a green energy resource. Biodiesel cost is directly associated with feedstock source. Microalgae oil as biological feedstock in third generation could be the best alternative of conventional diesels because of its economic and environmental benefits [30]. Biodiesel is often mixed with diesel fuel in 2, 5 and 20% ratios to obtain more power output and economic benefits. Greater is the ratio of biodiesel to diesel, lesser will be the emission of the carbon dioxide. Using a mixture of 20% biodiesel decreases net emissions of carbon dioxide by 15.66% while the use of 100% biodiesel makes the net emission of carbon dioxide zero [31].

2.1. Direct use and blending

Direct use of vegetable oils in diesel engine is not feasible, as it causes many problems and many inherent failings. Although vegetable oils have similar properties to biodiesel fuel, but it needs some chemical changes before use in engine. Although pure vegetable oil can be used in some diesel engines, but many problems are prone in turbocharged direct injection engine such as trucks. The use of pure vegetable oils was found to have similar energy consumption to petroleum-based fuel. For short time, the use of ratio of 1:10 to 2:10 oil to diesel has been found to be effective [32].

2.2. Microemulsion process

In micro-emulsion process, alcohols are used to overcome the high viscosity issues of vegetable oil as fuel. Micro-emulsion is a colloidal equilibrium dispersion of optically isotropic fluid. The dimensions of microstructures in liquids are in the range of 1-150 nm. Vegetable oil and alcohol are immiscible and one of them must be ionic or non-ionic amphiphiles. It helps to improve the spray features during explosive vaporization of components in micelles [18].

2.3. Thermal cracking (pyrolysis)

Cracking is defined as the catalytic break down of a longer molecule into smaller one in the absence of air. Pyrolysis of the fatty acid methyl esters, animal fats, *Yaqoob et al., 2019*

vegetable oils and natural fatty acids can be done. Pyrolysis of fats had been done 100 years ago when there was a lack of petroleum reserves [33].

2.4. Transesterification

Transesterification is the catalytic reaction of vegetable oil with alcohol and catalyst that improves reaction rate and yield of FAME. It is also named as alcoholysis. Methanol and ethanol are preferably used for transesterification reaction because of their low cost and unique physiochemical properties. Methanol and ethanol react rapidly with oil in the presence of catalyst. In transesterification process 3:1 oils to alcohol molar ratio is commonly used. Acid (H_2SO_4)/Base (NaOH or KOH)/Enzymes (Lipase) are used as the catalyst [24].

The physical methods like dilution and micro-emulsion do not require any chemical modification and can decrease the viscosity of the vegetable oil. Problems like carbon deposits and huge pollution limited the direct use of vegetable oil in diesel engines. Although, product that has low viscosity, high cetane number and enough amounts of sulfur, water and sediments contents can be produced by pyrolysis but the carbon residue, pour point and ash contents are unacceptable. Supercritical methanol needs high temperature and pressure conditions, high equipment cost and high energy input which significantly increase the biodiesel production cost. Because of its high conversion rate and comparatively low cost, transesterification has been widely used for industrialized biodiesel production [34].

3. Composite catalysts

Bifunctional heterogeneous catalysts show both acid and base property, therefore esterification of free fatty acids and transesterification of triglycerides can occur at the same time to develop the cleaner and economical process to produce biodiesel. A bifunctional heterogeneous catalyst can easily be chemically modified to develop the required physicochemical character so that the free fatty acids or water does not have any adverse effect on the reaction steps during the transesterification [35]. Therefore, the present review considers the possible development of composite heterogeneous catalysts [36].

3.1. Production of composite catalyst

Many methods for the preparation of potential composite catalysts (like precipitation, sol-gel method, and impregnation etc.) are extensively described in literature. Nevertheless, every technique has its own benefits and limitations [36].

3.1.1. Sol-gel method

Most applicable technique used for the preparation of the ultra-homogeneous structures is sol gel method and it has been extensively used for the preparation of ceramics, glasses and composites catalysts [37]. The rate of hydrolysis

and condensation, the shape of produced polymer particles and form of aggregation of particles is directly affected by the composition of the starting alkoxide solution, type of catalyst, the water content, the presence or absence of any additives and the reaction conditions. Thus, by changing various reaction conditions, properties of the produced sols and gels could be easily altered. Among different coating methods, sol-gel method has shown good results due to its lower prices, simple control of the operating conditions, and tendency to form a uniform coating of physically and chemically large and complex geometric shapes. This method has ability to modify the physiochemical properties of the products because of the nano crystalline features of the coatings [38].

3.1.2. Impregnation method

Impregnation is like ion-exchange or adsorption process, and the interaction with support is the most dominant in it. A lot of researchers used this method to synthesize supported heterogeneous catalysts to produce biodiesel. Lithium (Li) was impregnated on CaO for the catalytic transesterification of high FFA content oil and its activity was not much altered by the vegetable oil having more than 3 wt.% FFA. Impregnated ZnO with an aqueous solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, after pretreatment and calcination steps, CaO-ZnO was generated and used for transesterification. For the dispersion of the active phase over the required support, impregnation technique is a simple and commonly used method. Moreover, it allows high metal loading by rapid deposition. Nonuniform deposition of active phase at the pores of the support is the main drawback of this technique [36].

3.1.3. Co-precipitation method

The use of the precipitating agent to obtain a solid material in a porous form is the basic mechanism of precipitation technique. Co-precipitation method is used for the preparation of CaO-ZnO catalyst. Na_2CO_3 is used as a precipitant to speed up the rate of transesterification between palm oil and methanol. Ammonia solution was also used as a precipitant to synthesize CaO-ZrO₂ catalyst using co-precipitation technique. A mixture of Na_2CO_3 and NaOH was used as precipitants to prepare nanometer magnetic solid base catalysts by dispersing CaO on Fe₃O₄. The use of the multi precipitants is more effective as compared to the single precipitant. Researchers proposed triple precipitants that are ammonia solution, carbon dioxide, and ethanol which are base precipitant, acid precipitant, and neutral precipitant, respectively. This novel method was applied by researchers to prepare CaO-La₂O₃ and compared with those prepared by impregnation, physical mixing, and co-precipitation techniques. The authors observed that there was an interaction among the precipitants which provided a better specific BET surface area and a high catalytic activity during biodiesel production [36].

3.2. Alumina supported composite catalyst

Efficiency of a large number of catalysts like alkaline earth metals oxides and hydroxides, alkali metals (Na and K) hydroxides or salts supported on alumina, zeolites, hydrotalcites and also some acid solids have been tested at various reaction conditions and have shown variable degree of success. However, it is generally concluded that their efficiency is lower than that of the homogenous basic catalysts [29]. Utilization of heterogeneous catalysts becomes popular as they can be reused and can save the cost of production. These catalysts are in the form of metal oxides like alkaline earth metal oxides, TiO and MnO. Although these catalysts can be reused, but experimental studies have revealed that their reusability is limiting when they are subjected to leachate where some of the solid goes into the reaction medium. One method to deal with this problem is to bind the catalyst to a solid support. Alumina is extensively used as a support to bind the catalyst [25].

Due to the feasible catalytic properties of alumina, it is used extensively as a catalyst [39]. Greater surface area and sufficient pore size distribution of γ -alumina catalyst, make it an important catalyst for the binding of organic compounds [40]. Specific surface area, pore diameter and distribution of active sites on the surface of the catalyst affect the catalytic activity of the solid catalyst. Larger number of active sites can be achieved at per cubic centimeter of the catalyst by different methods. Active surface area of the catalyst can be increased by catalyst support or carrier. Mass transfer limitation of the three-phase reaction could be improved using alumina or silica supports without any modification. As compared to silica, alumina has been a good support for the loading of the catalyst, because it has high thermal stability and porosity [28].

Alumina (Al₂O₃) supported alkali metal salt is an efficient solid base catalyst for transesterification process. A large amount of water also does not have any adverse effect on the efficiency of this catalyst. Alumina supported alkali metal salt has been reported for the transesterification of triolein with methanol. The transesterification reaction is only reported for triolein and tributyrates using alkali earth oxides and alumina supported alkali metals. However, the biodiesel production using real feedstocks such as vegetable oils from these catalysts has not been reported so far. Catalytic activity of the heterogeneous base catalyst for the transesterification of a real feedstock (vegetable oil) is very important [41].

3.2.1. Production of 1st generation biodiesel

Maximum yield of fatty acid methyl esters has been obtained from palm oil via catalytic transesterification by using CaO/Al₂O₃ (a solid base heterogeneous catalyst). Response Surface Methodology and central composite design was used to optimize the reaction conditions.

Methanol to oil ratio, catalyst amount and reaction temperature were taken as variables and biodiesel yields were checked against these variables. Experiment was performed in batch laboratory scale reactor for 5 h; with alcohol to oil molar ratio of 12:1 and 6 wt. % of catalyst amount at 65°C. Characterization of the catalyst was done by BET (Brunauer–Emmett–Teller), TPD (Temperature programmed desorption) CO₂, master sizer and inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS results showed that very small amount of CaO active species were leached into the reaction solution and the catalyst could be used successfully in two consecutive cycles. Under these reaction conditions, colourless glycerol was produced as a by-product [25].

Experiments have been done to check the efficiency of several alumina supported catalysts during the transesterification of sunflower oil with methanol. The activity of the supported NaOH catalysts was compared to that of homogeneous NaOH. The effect of methanol to oil ratio and catalyst to methanol ratios and NaOH loading on the supported catalysts was also considered during transesterification. It was concluded that catalyst to methanol ratio greatly affect the rate of transesterification and selectivity of reaction was determined by the methanol to oil ratio. Their activity was negatively affected by using calcined NaOH/-Al₂O₃ catalysts. Performance of the alumina supported NaOH catalysts that were dried at 393K was not much different from that of homogeneous NaOH catalyst. It was also observed that leaching of sodium during transesterification reactions cause some chemical instability of alumina supported NaOH catalyst at given reaction conditions. Characterization of the catalyst was done by BET (Brunauer–Emmett–Teller), XRD (X-ray Diffraction) and BJH (Barrett-Joyner-Halenda) method to check the activity and efficiency of the catalyst during the process [29].

Several alkali metals (Li, Na and K) supported on alkali earth oxides (CaO, BaO and MgO) and alumina (Al₂O₃) supported K₂CO₃ were synthesized and used for catalytic conversion of canola oil into biodiesel. Alumina loaded K₂CO₃ and alkali metal (Li, Na and K) loaded on BaO were effective for the transesterification of the oil and yield of methyl ester was about 85 wt%. It was shown by ICP-MS analysis that barium leaching in ester phase was remarkably high (*1,000 ppm) using BaO based catalysts. For further transesterification of canola oil, barium based catalyst were not used because they are highly toxic. BET, TPD CO₂ and ICP-MS techniques were used for the characterization of the catalysts. For maximum yield of fatty acid methyl ester from canola oil by using K₂CO₃/Al₂O₃, optimize reaction condition suggested by response surface methodology for this process included 11.48:1 alcohol to oil ratio at 60°C temperature, and catalyst amount 3.16 wt % at optimum reaction parameters [41].

The efficiency of CaO/Al₂O₃ catalyst was studied by taking loading amount of calcium oxide onto alumina, methanol to oil ratio and the amount of catalyst used as variable for the conversion of sunflower oil into FAME (Fatty Acid Methyl Ester) at 50°C. BET, XRD and BJH methods were used to check the reaction mode, activity, and efficiency of the catalyst. For the better understanding of the interaction between basicity and catalytic activity, turnover frequency (TOF) of the catalysts was measured. From volcano curve that was obtained for TOF verses basic strength, it was concluded that 60% of CaO/Al₂O₃ had the highest turnover frequency that was 0.028 s at 50°C and methanol to oil molar ratio of 9, whereas TOF obtained on 85% CaO/Al₂O₃ was 0.012 s⁻¹ and it gave the highest ester yield of 96.6%. It was observed that 60% CaO catalyst had enough basicity to obtain the highest TOF [42].

Cottonseed oil was converted into fatty acid methyl ester by using CaO-MgO/Al₂O₃ catalyst by transesterification with ethanol. The influence of loading of Al₂O₃ with CaO–MgO catalysts, reaction temperature and alcohol to cottonseed oil ratio were investigated on the yield of biodiesel. Co-precipitation method, a conventional method for the preparation of the composite catalyst, was used for the preparation of the alumina supported CaO-MgO catalyst. Characterization of the catalysts was done by X-ray diffraction, scanning electron microscopy and temperature-programmed desorption of CO₂. Reaction parameters of the FAME yield from cottonseed oil were studied using Design of Experiment. For 97.62% conversion of oil the predicted optimized conditions by Box–Behnken design were 12.24 ethanol to cottonseed oil ratio and 14.4 wt. % loading of CaO–MgO on Al₂O₃ at the approximate temperature of about 95.638°C. The expected results were in agreement with experimental results with 92.45% conversion (12.5 wt % loading of CaO–MgO on Al₂O₃, molar ratio of ethanol to cottonseed oil was 8.5 and reaction temperature of 95.8°C) [43].

Fatty acid methyl ester was synthesized by catalytic transesterification of edible oil, rapeseed oil by using nano-solid-based K₂O/γ-Al₂O₃ catalyst. Diameter of the catalyst particle was measured by transmission electron microscopy and was about 50 nm. During transesterification, the reaction parameters that affect the biodiesel yield included calcination temperature, mass ratio of γ-Al₂O₃ to KNO₃, calcination time, catalyst amount, methanol to oil ratio, reaction time and reaction temperature were checked. The catalyst was prepared by calcinating KNO₃ and γ-Al₂O₃ mixture for 3h at 600°C and it showed highest catalytic efficiency in reaction medium. Rapeseed oil was converted into FAME by methanol to oil ratio of 12:1 with 3% catalyst loading at 70°C for 3h to achieve 94% FAME yield [44].

Transesterification of soybean oil was investigated by using potassium iodide supported onto alumina. Approximately, 35 wt.% of potassium iodide loaded on alumina was calcined for 3h at 773K, the catalyst showed

best catalytic activity for the transesterification as it has high basicity. Characterization of the catalyst was done by means of XRD, IR, SEM, and the Hammett indicator method. Rate of conversion of soybean oil into biodiesel depended on the reaction variables (catalyst loading, methanol to oil ratio and reaction time). At optimum reaction conditions 96% yield of biodiesel was reported [45].

Alkaline catalysts supported on γ -Al₂O₃ were used for the catalytic transesterification of canola oil with methanol. Incipient-wetness impregnation of an aqueous solution of alkaline compounds on γ -Al₂O₃ support was used for the catalyst preparation. Characterization of the catalyst was done by Hammett indicator, BET and XRD. The effects of alkaline compound, molar ratio, catalyst amount, reaction temperature, methanol/canola oil and reaction time for biodiesel production were investigated. The KOH/ γ -Al₂O₃ catalyst had the highest basicity and the best catalytic activity for transesterification and highest ester yield was 89.40% [46].

The γ -Al₂O₃ supported potassium iodide, prepared by sol-gel method was used to convert edible sunflower oil into biodiesel. Effect of various reaction conditions on conversion of sunflower oil to methyl esters was studied. It was concluded from results that basic strength of the catalyst was increased, and this positively affected the activity of the catalyst during transesterification of the sunflower oil. More basic catalytically active sites were developed by the impregnation of Al₂O₃ with KI. Surface characters of the catalyst had great influence on its catalytic activity. KI/Al₂O₃ catalyst gave 99.99% fatty acids methyl esters yield at mild reaction conditions in short period of time and catalyst could be used for two times. After separation of the catalyst, it was rinsed with methanol for short time and no other treatment was required [47].

Various alumina supported alkali and alkaline earth metal oxides were prepared by an impregnation method and used for transesterification of palm kernel oil and coconut oil. The supported metal catalysts, LiNO₃/Al₂O₃, NaNO₃/Al₂O₃ and KNO₃/Al₂O₃, with active metal oxides calcined at 450–550°C gave a remarkably high FAME yield, upto 93%. Ca(NO₃)₂/Al₂O₃ calcined at 450°C yielded methyl ester contents upto 94% with very small loss of active oxides from the catalyst while calcined Mg(NO₃)₂/Al₂O₃ catalyst had an inactive magnesium-aluminate phase, it gave very low yield of methyl ester. Alkali metal aluminates (NaNO₃/Al₂O₃ and KNO₃/Al₂O₃) that were soluble in water were catalytically active, the aluminate compounds (LiNO₃/Al₂O₃ and Ca(NO₃)₂/Al₂O₃) were sparingly soluble giving very low yield of methyl ester content. Suitable conditions for the conversion of palm kernel oil and coconut oil into biodiesel with Ca(NO₃)₂/Al₂O₃ were 6:5 methanol/oil ratio at 60°C in 3h [48].

The CaO–La₂O₃–Al₂O₃ mixed oxide composite catalyst was used to synthesize fatty acid methyl ester from

crude palm oil having high acid contents. Different reaction conditions were studied by using a batch reactor to reach at the best reaction condition that could provide the highest FAME yield from oil. Approximately, 97.81% biodiesel yield was obtained by transesterification of crude palm oil at 170°C with 15:1 methanol to oil molar ratio for 180 min and 10 wt.% catalysts loading. Experimental data has proved that CaO–La₂O₃–Al₂O₃ mixed-oxide catalyst is suitable for vegetable oil with high acid contents [49].

3.2.2. Production of 2nd generation biodiesel

Transesterification of Jatropha oil with methanol was carried out by alumina supported potassium nitrate for biodiesel production. The rate of conversion of Jatropha oil depended on calcination and on the reaction conditions including methanol to oil ratio, catalyst loading, agitation speed, reaction temperature and the reaction time. The conversion was over 84% at 70°C with methanol to oil ratio of 12:1 for the reaction time of 6h with agitation speed of 600 rpm and catalyst amount of 6 wt.%. This catalyst could be used at least for three times without any pretreatment [50].

Conversion of Kesambi oil into biodiesel was done using alumina supported zinc oxide catalyst. Zinc oxide catalyst loaded on the alumina was synthesized by the precipitation and gel method and the prepared catalyst was calcined at 500°C. Breneuer-Emmet-Teller and X-ray fluorescence methods were used for the characterization of the catalyst. Influence of different reaction parameters such as catalyst amount, oil to methanol and reaction time were checked on the yield of biodiesel and experimental results of entire study revealed that the yield of biodiesel was greatly affected by above mentioned variables. Maximum yield of biodiesel was 92.29% by a catalyst loading of 4 wt.%, and oil to methanol of 1:12 for the reaction time of 6h at reaction temperature of 65°C [28].

Transesterification of the waste cooking oil was done with methanol by using CaO/KI/Al₂O₃ as heterogenous catalyst. Catalyst was prepared by impregnation and precipitation method. Waste cooking oil was collected from fast food restaurant. Maximum yield of biodiesel was about 83.08% at optimum reaction conditions. It was concluded from results that heterogeneous alumina supported base catalyst are very promising for the transesterification of the waste cooking oil [51].

Conversion of waste frying oil to biodiesel by using a novel composite heterogeneous anthill-eggshell Ni-Co mixed oxides was also practiced. Co-precipitation method was used for the preparation of catalyst and Brunauer-Emmett-Teller surface area analysis, fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffraction and X-ray fluorescence techniques were used for characterization of the catalyst. Influence of different reaction conditions that effect the rate of transesterification of oil including 40–80°C temperature,

1–5h reaction time, 1–9 wt.% catalyst loading, and 3:1–15:1 methanol to oil ratio were checked. Maximum FAME yield was 90.23% with 12:1 methanol to oil ratio at 70°C temperature in 2 h with 3 wt.% of catalyst loading. Stability of the used catalyst was also checked during process and it was seen that the catalyst could be reused without any treatment maximum for four cycles [36].

Nano-alumina-zirconia composite catalyst was prepared by using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and ZrCl_4 as precursors by aqueous sol-gel method. Thermal decomposition of the reactants and synthesis of alumina supported t-Zr were checked by thermal analysis. The results of X-ray diffraction revealed that $\gamma\text{-Al}_2\text{O}_3$ and t- ZrO_2 phases were prepared at 700°C. TEM analysis of the calcined powder showed that diameter of the catalyst particles was varied from 8 nm to 12 nm. The particles of the nano alumina zirconia composite catalyst were mesoporous and equally distributed in the crystalline phase. Continuous packed column reactor was used for the esterification of the oil. Heterogeneous catalytic esterification of free fatty acid (FFA) with ethanol was performed in a reactor. It has been shown by the experimental results that $\gamma\text{-Al}_2\text{O}_3/\text{ZrO}_2$ composite catalyst have a good tendency to be used for the production of biodiesel [39].

Alumina supported potassium iodide ($\text{KI}/\text{Al}_2\text{O}_3$) was used as catalyst and rubber seed oil as a sample to produce biodiesel by transesterification. The experimental result showed that the transesterification of rubber seed oil by the heterogenous catalyst that was calcined at 773 K showed better catalytic activity with maximum yield of 31.8% at molar ratio of methanol to oil 15:1, amount of catalyst was 2g at temperature 60°C for reaction time of 8 hours. GC-MS analysis of fatty acid methyl esters (FAME) in the sample ratio 15:1 confirmed the presence of stearic acid and palmitic acid [52].

Transesterification of rubber seed oil with methanol was carried out by three different alumina-supported catalysts for biodiesel production. $\text{Al}_2\text{O}_3\text{-CaO}$, $\text{Al}_2\text{O}_3\text{-KI}$ and $\text{Al}_2\text{O}_3\text{-CaO-KI}$ were alumina supported catalysts. The mixture of alumina and the corresponding salt was heated at 700°C in a furnace to synthesize the catalysts. Transesterification reaction was carried out by using the mixture of rubber seed oil and methanol with ratio of 1:9 by varying the catalyst loadings between 0 and 3.5% at 65°C. The optimum catalyst loading was 2.0% for all types of catalysts and fatty acid methyl esters yield with $\text{Al}_2\text{O}_3\text{-CaO-KI}$, $\text{Al}_2\text{O}_3\text{-KI}$ and $\text{Al}_2\text{O}_3\text{-CaO}$ composite catalyst was 91.6%, 90.7% and 63.5%, respectively. Highest biodiesel yields were obtained by catalyst $\text{Al}_2\text{O}_3\text{-CaO-KI}$ for a wider range of catalyst loadings as compared to the other two composite catalysts. Reactions were carried out at 25°C, 40°C and 65°C and it was observed that the yield increased sharply by increasing the reaction temperature. $\text{Al}_2\text{O}_3\text{-CaO-KI}$ catalyst gave the highest yield at all temperatures [25].

An experiment was conducted over $\text{CaO-L}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed-oxide catalyst to produce fatty acid methyl esters (FAME) from karanja oil having low acid contents. Different reaction conditions were studied by using a batch reactor to find out best reaction conditions that gives the highest FAME yield from the oil. The transesterification of karanja oil resulted in 96.77% biodiesel yield at 150°C reaction temperature, 9:1 methanol to oil molar ratio for reaction time of 180 min with 5 wt. % of catalyst loading. The above results showed that for low acid content vegetable oil, $\text{CaO-L}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed-oxide catalyst is more suitable [49].

The tendency of the crude *Jatropha* to produce fatty acid methyl ester by using aluminum modified heterogeneous basic oxides catalyst was investigated in a previous study. The physicochemical properties of crude *Jatropha* proved, it a suitable candidate for biodiesel production. On the basis of the FFAs contents and water in the oil, 11:1 molar ratio of methanol to oil, 3.32 wt. % of catalyst loading, reaction temperature was 182°C at the atmospheric pressure for reaction time of 6h were the optimum reaction conditions for 92% yield of FAME. The employed catalyst provided a good yield in a single-stage process [53].

Edible oils were converted into biodiesel by taking different magnesium slag (derived from heterogeneous solid catalyst $\text{MgO-CaO}/\text{Al}_2\text{O}_3$) to methanol ratios in terms of fatty acid methyl ester yield. Optimum reaction conditions for transesterification by untreated magnesium slag were checked, and maximum FAME yield was 96% in 12h. Maximum FAME yield was determined for 15 to 20% untreated magnesium slag to oil ratio and 20% methanol to oil ratio. In 30 minutes, 98% FAME yield was achieved, and it was noted that presence of CO_2 brightens the efficiency of $\text{MgO-CaO}/\text{Al}_2\text{O}_3$ catalyst. Experimental data revealed the important role of temperature for the transesterification process. FAME yield of 98–99% in 1 min was achieved when temperature was varied from 350 to 500°C. In short, the use of the environmental friendly magnesium slag is an efficient alternative of homogeneous acid/base catalysts at commercial level [54].

3.2.3. Production of 3rd generation biodiesel

Transesterification of lipids of yellow green microalgae, *Nannochloropsis oculata*, was performed by Al_2O_3 supported CaO and MgO . This process was done at optimum reaction temperature of 50°C by taking different methanol amounts and catalysts loadings as variables. Pure catalysts were not active and among all the mixed oxide catalysts, $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst gave good yield. Basic site density and basic strength both were important for the high conversion rate of lipids into biodiesel. FAME yield was increased from 23% to 97.5% by taking 80 wt.% of $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst loading and methanol to lipid ratio of 30 [42].

Catalyst prepared by the loading of lanthanum and barium onto aluminum by peptization. Impregnation method was used to prepare modified alumina supported catalysts with different KOH loadings. N₂ adsorption-desorption, X-ray diffraction, scanning electron microscopy, and Fourier transforms infrared absorption spectroscopy were used to examine the properties of the catalysts. The GC-MS and GC were used to check catalytic conversion of microalgae oil to methyl ester by transesterification process. Furthermore,

BET results revealed that the support has suitable pore size, high specific surface area and suitable pore size distribution. Efficiency results cleared that 25 wt.% KOH loading showed best efficiency for microalgae oil conversion to methyl ester. XRD and SEM results indicated that for maximum oil conversion to fatty acid methyl ester, Al-O-K compound was the active phase. When amount of KOH was exceeded from 30 wt.%, agglomeration and changing of pore structure deactivated the catalyst [55].

Table 1: A comparison of the main technologies for biodiesel production [34]

Sr.No	Technologies	Advantages	Disadvantages
1	Direct Use	Simple Process No Chemical Treatment	High Viscosity High Energy Consumption
2	Microemulsion	Simple Process	High Viscosity Low Volatility Low Stability
3	Pyrolysis	Simple Non-Polluting	High Temperature Expensive Equipment Low Purity
4	Transesterification	Fuel Properties Close to Diesel High Efficiency Low Cost Suitable for Industrialized Production	Low FFA and Water Contents Pollutants Will be Produced Some Side Reactions Difficult Product Separation
5	Super critical Methanol	No Need of Catalyst Short Reaction Time High Efficiency Good Adaptability	High Temperature and Pressure Expensive Equipment High Energy Consumption

Table 2: Production of 1st generation biodiesel from different alumina supported composite catalysts

Catalyst	Catalyst preparation method	Feedstock	Yield	Reaction conditions				References
				Reaction temperature (°C)	Methanol to oil ratio	Catalyst amount (wt.%)	Reaction time (h)	
CaO/Al ₂ O ₃	Impregnation and Precipitation	Palm oil	98.64 %	65	12:1	6	5	[25]
NaOH/Al ₂ O ₃	Impregnation	Sunflower	88 %	50	12:1	0.4	24	[29]
CaO/KI/Al ₂ O ₃	Impregnation and Precipitation	Palm oil	95 %	290	24:1	3	1	[8]
K ₂ CO ₃ /Al ₂ O ₃	Wet Impregnation	Canola oil	84.6 %	50	6:1	2	4	[41]
CaO/Al ₂ O ₃	Sol-Gel	Sunflower oil	96.6 %	50	9:1	6	4	[42]
CaO-MgO/Al ₂ O ₃	Co-Precipitation	Cottonseed	92.45 %	95.8	8:5	12.5	3	[43]
K ₂ O/γAl ₂ O ₃	Grinding Calcining method with	Rapeseed oil	94%	70	12:1	3	3	[44]

	Some Modification							
KF/Al ₂ O ₃	Impregnation	Soybean oil	85.8%	Methanol reflux temperature	15:1	2	6	[45]
KCl/Al ₂ O ₃	Impregnation	Soybean oil	No Reaction	Methanol reflux temperature	15:1	2	6	[45]
KBr/Al ₂ O ₃	Impregnation	Soybean oil	16.7%	Methanol reflux temperature	15:1	2	6	[45]
KI/Al ₂ O ₃	Impregnation	Soybean oil	87.4%	Methanol reflux temperature	15:1	2	6	[45]
K ₂ CO ₃ /Al ₂ O ₃	Impregnation	Soybean oil	48%	Methanol reflux temperature	15:1	2	6	[45]
KNO ₃ /Al ₂ O ₃	Impregnation	Soybean oil	67.4%	Methanol reflux temperature	15:1	2	6	[45]
KOH/Al ₂ O ₃	Impregnation	Soybean oil	80.2%	Methanol reflux temperature	15:1	2	6	[45]
KOH/ γ -Al ₂ O ₃	Incipient-Wetness Impregnation	Canola oil	89.40%	60	12:1	3	9	[46]
LiNO ₃ /Al ₂ O ₃	Impregnation	Palm Kernel oil	91.6%	60	6:5	10	3	[48]
KI/ γ Al ₂ O ₃	Sol Gel	Sunflower oil	99.99%	Reflux temperature	12:1	2.5	3	[47]
NaNO ₃ /Al ₂ O ₃	Impregnation	Palm Kernel oil	95.1%	60	6:5	10	3	[48]
KNO ₃ /Al ₂ O ₃	Impregnation	Palm Kernel oil	94.7%	60	6:5	10	3	[48]
Ca(NO ₃) ₂ /Al ₂ O ₃	Impregnation	Palm Kernel oil	94.3%	60	6:5	10	3	[48]
CaO-La ₂ O ₃ -Al ₂ O ₃	Co-precipitation	Crude Palm oil	97.81%	170	9:1	5	3	[49]
Mg(NO ₃) ₂ /Al ₂ O ₃	Impregnation	Palm Kernel oil	10.4%	60	6:5	10	3	[48]

Table 3: Production of 2nd generation biodiesel from different alumina supported composite catalysts

Catalyst	Catalyst preparation method	Feedstock	Yield	Reaction conditions				References
				Reaction temperature (°C)	Methanol to oil ratio	Catalyst amount, wt.%	Reaction time (h)	
KNO ₃ /Al ₂ O ₃	Impregnation	Jatropha oil	84%	70	12:1	6	6	[50]
ZnO/Al ₂ O ₃	Precipitation and Gel	Kesambi oil	92.29%	65	12:1	4	6	[28]

CaO/KI/Al ₂ O ₃	Impregnation and Precipitation	Waste Cooking oil	83.08%	65	15:1	6	5	[51]
Anthill-eggshell-Ni-Co	Impregnation	Waste Frying oil	90.23%	70	12:1	3	2	[36]
γ -Al ₂ O ₃ /ZrO ₂	Sol and gel	-	90%	250	3:5	-	-	[39]
KI/ γ Al ₂ O ₃	-	Rubber seed oil	31.8%	60	15:1	2	8	[52]
CaO/KI/Al ₂ O ₃	Heating a mixture of alumina and salt	Rubber seed oil	91.6%	65	9:1	2	5	[25]
KI/Al ₂ O ₃	Heating a mixture of alumina and salt	Rubber seed oil	90.7%	65	9:1	2	5	[25]
CaO/Al ₂ O ₃	Heating a mixture of alumina and salt	Rubber seed oil	63.7%	65	9:1	2	5	[25]
CaO-La ₂ O ₃ -Al ₂ O ₃	-	Karanja oil	96.77%	170	9:1	5	3	[49]
Al ₂ O ₃ /Mg-Zn	Co-precipitation	Crude Jatropha	94%	182	11:11	8.68	6	[53]
MgO-CaO/Al ₂ O ₃	-	Waste vegetable oil	96%	350	10:2	15-20%	12	[54]

Table 4: Production of 3rd generation biodiesel from different alumina supported composite catalysts

Catalyst	Catalyst preparation method	Feedstock	Yield	Reaction conditions				References
				Reaction temperature (°C)	Methanol to oil ratio	Catalyst amount, wt. %	Reaction Time (h)	
CaO-MgO/Al ₂ O ₃	Single Step Sol-Gel	Nannochloropsis Oculata oil	97.5%	407	30	80	-	[42]
KOH/La-Ba-Al ₂ O ₃	Impregnation	Microalga oil	97.7%	60	-	25	3	[55]

4. Summary

It was concluded from the study of the 1st generation biodiesel that KI/ γ Al₂O₃ catalyst has been a promising catalyst providing a surprising FAME yield upto 99.99% from sunflower oil in a short reaction time of 3 hours. CaO/Al₂O₃ composite catalyst gave FAME yield of 98.64% in a comparatively longer reaction time of 5 hours from palm oil. Transesterification of crude palm oil with heterogenous CaO-La₂O₃-Al₂O₃ catalyst resulted in 97.81% yield of biodiesel in a reaction time of 3 hours. Sunflower oil has been converted into 96.6% of biodiesel by *Yaqoob et al., 2019*

CaO/Al₂O₃, heterogenous composite catalyst in 3 hours. The Mg(NO₃)₂/Al₂O₃ catalyst that was calcined at 450°C gave drastically low yield of biodiesel (10.4 %). Temperature for calcination of the catalyst has also a great influence on the rate of conversion of oil into biodiesel, when Ca(NO₃)₂/Al₂O₃ calcined at 450°C gave 94.3% yield of biodiesel from palm kernel oil and 21.7% biodiesel yield when catalyst was calcined at 550°C. Although, NaOH/Al₂O₃ give a good yield of FAME from sunflower oil but the main problem with it was the very long reaction time that was 24 hours. The results of the literature review of 2nd generation biodiesel has shown that transesterification of

karanja oil with CaO-La₂O₃-Al₂O₃ gave 96.77% yield of biodiesel in reaction time of 3 hours. Al₂O₃/Mg-Zn provided 94% yield of FAME from crude jatropha oil for a comparatively longer reaction time of 6 hours. According to an estimate, 92.29% FAME yield could be obtained from Kesambi oil by using ZnO/Al₂O₃, a heterogenous catalyst in 6 hours. Heterogenous catalyst MgO-CaO/Al₂O₃ has not proved promising for the conversion of waste cooking oil into biodiesel. Although FAME yield was 96% but main issues were the reaction time of 12h and reaction temperature of 350°C which make this process uneconomical. KI/Al₂O₃ also did not give a good yield of biodiesel. It only provided 31.8% FAME yield from rubber seed oil in a longer reaction time of 8 hours. CaO/Al₂O₃ also gave biodiesel yield only up to 63.7% in a longer reaction time of 5 hours. There was not much work reported in literature to produce 3rd generation biodiesel. Transesterification of *Nannochloropsis oculata* oil (for 3rd generation biodiesel production) with CaO-MgO/Al₂O₃ and micro algae with KOH/La-Ba-Al₂O₃ was remarkably high and economically advantageous.

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