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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 emission of greenhouse gases as it has biodegradability, good lubricity, non-toxicity and environmentally benign nature. Utilization of vegetable oil as feedstock for the production of biodiesel may disturb the food industry therefore waste seed oil are best for the biodiesel production. The transesterification reaction is one of the convenient methods for biodiesel production because 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 waste water. However, nowadays composite catalysts are novel trends in heterogenous catalysis. 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. KI/ γ Al_2O_3 gave highest yield of FAME upto 99.99% for 1st generation biodiesel production by using sunflower as feedstock while $Mg(NO_3)_2/Al_2O_3$ calcined at 450°C and $Ca(NO_3)_2/Al_2O_3$ calcined at 550°C provide poor yield of FAME from palm kernel oil. For the production of 2nd generation biodiesel $CaO\text{-}La_2O_3\text{-}Al_2O_3$ gave best yield of biodiesel approximately 96.77% from karanja oil and poor yield of FAME was provided by KI/Al_2O_3 only 31.8% by using rubber seed oil as feedstock. Although, no much work is reported in literature for the production of 3rd generation biodiesel by using alumina supported catalysts. However, both $CaO\text{-}MgO/Al_2O_3$ and $KOH/La\text{-}Ba\text{-}Al_2O_3$ provide good FAME yield upto 97%. Rate of conversion of oil into biodiesel depends on calcination time and reaction parameters such as methanol to oil ratio, catalyst loading, the, agitation speed, reaction temperature and the reaction time.

Keywords: Biodiesel, FAME, alumina, KI/ γ Al_2O_3, $Mg(NO_3)_2/Al_2O_3$, $Ca(NO_3)_2/Al_2O_3$, $CaO\text{-}La_2O_3\text{-}Al_2O_3$, KI/Al_2O_3, $CaO\text{-}MgO/Al_2O_3$, $KOH/La\text{-}Ba\text{-}Al_2O_3$

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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. Demand and prices of non-renewable fuels are increasing rapidly, and these resources will be vanished in few years if these resources use at the same rate [1]. 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 [2]. 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 [3-4]. It has been shown that 98% of carbon emission are resulted from the burning of the conventional fossil fuels [5].

The search for renewable fuel that contributes less to carbon cycle is ongoing [6]. The worldwide struggles to encourage the move from non-renewable fuels to the renewable and environment friendly biofuels, many studies have been conducted to develop an alternative property liquid fuel. As 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 CO_2, NO_x and SO_2 [7].

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 [8]. 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 use in internal combustion (IC) engines. Its higher cetane number enhance its ignition quality, even when blend with petroleum diesel [9]. 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 [10].

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 [11]. 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 Indian literature. There are many non-edible oil seed species such as Karanja, Jatropha, Neem, Mahua and Simarouba etc., which could be used for the production of biodiesel. 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 [1]. 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 [12].

Many experiments have been performed successfully by the blending of vegetable oil with non-renewable diesel fuel. Caterpiller 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 [13]. 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 [14].

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 [15]. 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) [16].

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 speed 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 [15]. Homogeneous-base catalyzed transesterification have many disadvantages due to difficulty in the purification of biodiesel. 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 utilized 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 [17].

Solid catalysts are the most promising for the production of the biodiesel that could decrease its cost, so that its price could compete with diesel oil. Heterogeneous catalysts have many advantages over a homogeneous catalysts, its separation from the reaction mixture is comparatively easy so it can be reused. Glycerol is produced with high purity (more than 98%), it does not form soap during transesterification and it does 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 [18].

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 heterogenous 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 [16]. 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 [19].

2. Biodiesel Production

Biodiesel can be divided as first, second and third generation biofuel on the basis of their feed stock and

production technologies. First generation biodiesels are generated from food oils such as soybean, corn and rapeseed so they are unsustainable. Although for second generation raw materials are non-edible 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; for example, about 80% of the total operating costs come on canola oil while mass production and industrial uses of the biodiesel are not greater in number. Due to the above mentioned issues the production mechanisms 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 and microalgae oil as biological feedstock in third generation could be the best alternative of conventional diesels as it is economically and environmentally benefits [20]. Biodiesel is often mixed with diesel fuel in 2, 5 and 20% ratios because of the more power output and economic benefits. Greater is the ratio of biodiesel to diesel, lesser will 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 [21].

2.1 Direct Use and Blending

Direct use of vegetable oils in diesel engine is not feasible, as it cause 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 [22].

2.2 Microemulsion Process

In micro-emulsion process alcohols are used to overcome high viscosity issues of vegetable oil as fuel. Micro-emulsion is a colloidal equilibrium dispersion of optically isotropic fluid. The dimensions of the micro structures 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 [9].

2.3 Thermal Cracking (Pyrolysis)

Cracking is defined as catalytic brake down of a longer molecule into smaller one in the absence of air. Pyrolysis of the fatty acid methyl esters, animal fats, vegetable oils and natural fatty acids can be done. Pyrolysis of fats had been done since more than 100 years ago where there was a lack of petroleum reserves [23].

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. Low cost and unique physiochemical properties of methanol and ethanol, they are preferably used for transesterification. Methanol and ethanol react rapidly with oil in 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 [14].

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 lube pollution limited the direct use of vegetable oil in diesel engines. Although product that has, low viscosity, high cetane number and enough amount of sulfur, water and sediments contents can be produced by pyrolysis but the carbon residue, pour point and ash contents are unacceptable. While the supercritical methanol needs high temperature and pressure conditions, high equipment cost and high energy input which will increase the production cost. Because of its high conversion rate and comparatively low cost, transesterification has been widely used for industrialized biodiesel production [24].

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 cleaner and economical process for the production of biodiesel. A bifunctional heterogeneous catalyst can easily be chemically modified to develop required physicochemical character so that the free fatty acids or water does not have any adverse effect on the reaction steps during the transesterification [25]. Detailed experimental work on the catalytic action of two or more materials in a combined (composite) form to produce fatty acid methyl esters has not provided in previous research. This present study, therefore, considers the possible development of composite heterogeneous catalysts [26].

3.1 Production of Composite Catalyst

Many methods for the preparation of potential composite catalysts like precipitation, sol-gel method and impregnation are few among all that are extensively described in literature. Nevertheless, every technique has its own effectiveness and limitations [26].

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 [27]. 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 fewer 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 [28].

3.1.2 Impregnation Method

Impregnation is similar to ion-exchange or adsorption process, and the interaction with support is the most dominant. A lot of researchers used this method to synthesize supported heterogeneous catalysts for the production of 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 $Ca(NO_3)_2.4H_2O$, 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. Non uniform deposition of active phase at the pores of the support is the main drawback of this technique [26].

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 and 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 $CaO-ZrO_2$ 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 Fe_3O_4. The use of the multi precipitants is more effective as compared to 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 $CaO–La_2O_3$ and compare 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 [26].

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 checked at various reaction parameters and have different degree of success. However, it is generally concluded that their efficiency is lower than that of the homogenous basic catalysts [19]. Among researchers the utilization of heterogeneous catalysts is focused since they can reuse 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 [15].

Due to the feasible catalytic properties of alumina, it is used extensively as catalyst [29]. Greater surface area and sufficient pore size distribution of γ-alumina catalyst, make it an important catalyst for the binding of organic compounds [30]. 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 by the use of 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 [18].

Alumina (Al_2O_3) 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 tributyrate, model compounds by using alkali earth oxide and alumina supported alkali metal; however, for the biodiesel production using real feedstock such as vegetable oil from these catalysts has not been reported so far. Catalytic activity of the heterogenous base catalyst for the transesterification of a real feedstock (vegetable oil) is very important [31].

3.2.1 Production of 1st Generation Biodiesel

Maximum yield of fatty acid methyl esters have been obtained from palm oil via catalytic transesterification by using CaO/Al_2O_3, a solid base heterogenous 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, TPD CO_2, master sizer and 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. Almost colorless glycerol was obtained at some reaction conditions [15].

Experiments have been done to check the efficiency of a number of alumina supported NaOH 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/-Al_2O_3 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, XRD and BJH method to check the activity and efficiency of the catalyst during the process [19].

A number of alkali metal (Li, Na and K) supported on alkali earth oxides (CaO, BaO and MgO) and alumina (Al_2O_3) supported K_2CO_3 were synthesized and used for catalytic conversion of canola oil into biodiesel. Alumina loaded K_2CO_3 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 very high (*1,000 ppm) by the use of BaO based catalysts. For further transesterification of canola oil barium based catalyst were not used because they are highly toxic. BET, TPD CO_2 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 K_2CO_3/Al_2O_3, optimize reaction condition suggested by response surface methodology for this process included 11.48:1 alcohol to oil ratio at 60℃ temperature, and catalyst amount 3.16 wt% as optimum reaction parameters. In 2 h the predicted yield of ester was 96.3 wt%, which was in agreement with the experimental results within 1.28% [31].

The efficiency of CaO/Al_2O_3 catalyst was studied by taking loading amount of calcium oxide onto alumina, methanol to oil ratio and the amount of catalyst used as variables for the conversion of sunflower oil into FAME at 50℃. 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/Al_2O_3 had the highest turnover frequency that was 0.028 s at 50℃ and methanol to oil molar ratio of 9, whereas TOF obtained on 85% CaO/Al_2O_3 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 [32].

Cottonseed oil was converted into fatty acid methyl ester by using CaO-MgO/Al_2O_3 catalyst by transesterification with ethanol. The influence of loading of Al_2O_3 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 CO_2 was used get a sight into action mode of the catalyst during the process. 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 are 12.24 ethanol to cottonseed oil ratio and 14.4 wt. % loading of CaO–MgO on Al_2O_3 at the approximate temperature of about 95.638℃. The expected results were in agreement with experimental results with 92.45% conversion (12.5 wt% loading of CaO–MgO on Al_2O_3, molar ratio of ethanol to cottonseed oil was 8.5 and reaction temperature of 95.8℃) [33].

Fatty acid methyl ester was synthesized by catalytic transesterification of edible oil, rapeseed oil by using nano-solid-based K_2O/γ-Al_2O_3 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-Al_2O_3 to KNO_3, calcination time, catalyst amount, methanol to oil ratio, reaction time and reaction temperature were checked. The catalyst was prepared by calcinating KNO_3 and γ-Al_2O_3 mixture for 3 h at 600℃ 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℃ for 3 h, 94% FAME yield was achieved [34].

Transesterification of soybean oil was investigated by using potassium iodide supported onto alumina. Approximately, 35wt. % of potassium iodide loaded on alumina was calcined for 3 h 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. Besides, the relationship between catalytic activity and catalyst basicity was also studied [35].

Alkaline catalysts supported on γ-Al_2O_3 were used for the Catalytic transesterification of canola oil with methanol. Incipient-wetness impregnation of an aqueous solution of alkaline compounds on γ-Al_2O_3 support was used for the catalyst preparation. Characterization of the catalyst was done by Hammet 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-Al_2O_3 catalyst had the highest basicity and the best catalytic activity for transesterification and highest ester yield was 89.40% [36].

The γ-Al_2O_3 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 develop by the impregnation of Al_2O_3 with KI. Surface characters of the catalyst had great influence on its catalytic activity. KI/Al_2O_3 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 [37].

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, $LiNO_3/Al_2O_3$, $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3, with active metal oxides calcined at 450–550℃, gave a very high FAME yield, upto 93%. $Ca(NO_3)_2/Al_2O_3$ calcined at 450℃ yielded methyl ester contents upto 94% with very small loss of active oxides from the catalyst while calcined $Mg(NO_3)_2/Al_2O_3$ catalyst had an inactive magnesium-aluminate phase, it gave very low yield of methyl ester. Alkali metal aluminates ($NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3) that were soluble in water were catalytically active, the aluminate compounds ($LiNO_3/Al_2O_3$ and $Ca(NO_3)_2/Al_2O_3$) 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 $Ca(NO_3)_2/Al_2O_3$ were 6:5 methanol/oil ratio at 60℃ in 3h with 10 (for palm kernel) and 15–20% (w/w)(for coconut oil) [38].

The $CaO–La_2O_3–Al_2O_3$ mixed oxide composite catalyst was used to synthesize fatty acid methyl ester from crude palm oil, a high acid content feedstock. Different reaction conditions were studied by using a batch reactor was used to study different reaction conditions 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 $CaO–La_2O_3–Al_2O_3$ mixed-oxide catalyst is suitable for vegetable oil with high acid content [39].

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. Rate of conversion of Jatropha oil depended on calcination and on the reaction condition, including methanol to oil ratio, catalyst loading, agitation speed, reaction temperature and the reaction time. The conversion was over 84% at 70℃ with methanol to oil ratio of 12:1 for the reaction time of 6 h with agitation speed of 600 rpm and catalyst amount of 6 wt.%. This catalyst could be used atleast for three times without any pretreatment [40].

Conversion of Kesambi oil into biodiesel was done by the use of alumina supported zinc oxide catalyst. Zinc oxide catalyst loaded onto the alumina was synthesized by the precipitation and gel method and the prepared catalyst was calcined at 500℃. 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 6 h at reaction temperature of 65℃ [18].

Transesterification of the waste cooking oil was done with methanol by using CaO/KI/Al_2O_3 as heterogenous catalyst. Catalyst was prepared by impregnation and precipitation method. Waste cooking oil was treated that 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 [41].

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, 1–5 h 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 2h 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 [26].

Nano-alumina-zirconia composite catalyst was prepared by using $AlCl_3.6H_2O$ 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. Results of X-ray diffraction revealed that γ-Al_2O_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 varies from 8nm to 12nm. 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 γ-Al_2O_3/ZrO_2 composite catalyst have a good tendency to be used for the production of biodiesel [29].

Alumina supported potassium iodide (KI/Al_2O_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 calcined at 773K showed better catalytic activity with maximum yield of 31.8% at molar ratio of methanol to oil 15:1, amount of catalyst is 2 g at temperature 60°C in 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 [42].

Transesterification of rubber seed oil with methanol was carried out by three different alumina-supported catalysts for biodiesel production. Al_2O_3-CaO, Al_2O_3-KI and Al_2O_3-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 catalyst and fatty acid methyl ester yield with Al_2O_3-CaO-KI, Al_2O_3-KI and Al_2O_3-CaO composite catalyst was 91.6%, 90.7% and 63.5% respectively. Highest biodiesel yields were obtained by catalyst Al_2O_3-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 reaction temperature but Al_2O_3-CaO-KI catalyst gave the highest yield at all temperatures. Therefore, the study showed that among these three catalysts the most productive was Al_2O_3-CaO-KI [15].

An experiment was conducted over CaO–La_2O_3–Al_2O_3 mixed-oxide catalyst to produce fatty acid methyl esters (FAME) from karanja oil that is low acid content feedstock. Different reaction conditions were studied by using a batch reactor to find out best reaction condition 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, CaO–La_2O_3–Al_2O_3 mixed-oxide catalyst is suitable [39].

The tendency of the crude Jatropha for the production of fatty acid methyl ester by using aluminium modified heterogeneous basic oxides catalyst was investigated. The physicochemical properties of crude Jatropha prove it a suitable substitute for the available feedstocks of 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 6 h were the optimum reaction conditions for 92% yield of FAME. The employed catalyst provides a good yield in a single-stage process being selective to methyl esters from high percentage of FFA feedstock and easy separation of the catalyst from the reaction medium. Above all, crude Jatropha oil was proved an auspicious non-edible feedstock for FAME production which could appear to be a best alternative of conventional diesel fuel [43].

Edible oils were converted into biodiesel by taking different magnesium slag (derived from heterogeneous solid catalyst MgO–CaO/Al_2O_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 12 h. 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 brighten the efficiency of MgO–CaO/Al_2O_3 catalyst. Experimental data revealed that for the transesterification process temperature played an important role, lead to a FAME yield of 98–99% in 1 min when temperature varies 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 [44].

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, CaO/Al_2O_3 catalyst gave good yield. Basic site density and basic strength both are important for the high conversion rate of lipids to biodiesel. FAME yield was increased from 23% to 97.5% by taking 80 wt.% of CaO/Al_2O_3 catalyst loading and methanol to lipid ratio of 30 [32].

Catalyst by the Loading of lanthanum and barium onto aluminum were prepared by peptization. Impregnation method was used to prepare modified alumina supported catalysts with different KOH loadings. N_2 adsorption-desorption, X-ray diffraction, scanning electron microscopy, and Fourier transform infrared absorption spectroscopy were used to examine the properties of the catalysts. The GC-MS and GC was 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 [45].

Table 1 A comparison of the main technologies for Biodiesel production [24]

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	Transetrification	❖ 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	Preparation of Catalyst	Feedstock	Yield	Reaction Conditions				References
				Reaction Temperature (℃)	Methanol to Oil Ratio	Catalyst Amount (wt.%)	Reaction Time (h)	
CaO/Al_2O_3	Impregnation and Precipitation	Palm Oil	98.64%	65	12:1	6	5	[15]
$NaOH/Al_2O_3$	Impregnation	Sunflower	88%	50	12:1	0.4	24	[19]
$CaO/KI/Al_2O_3$	Impregnation and Precipitation	Palm Oil	95%	290	24:1	3	1	[2]
K_2CO_3/Al_2O_3	Wet Impregnation Method	Canola Oil	84. 6%	50	6:1	2	4	[31]
CaO/Al_2O_3	Sol-Gel Method	Sunflower Oil	96.6%	50	9:1	6	4	[32]
$CaO-MgO/Al_2O_3$	Co-Precipitation Method	Cottonseed	92.45%	95.8	8:5	12.5	3	[33]

$K_2O/\gamma Al_2O_3$	Grinding Calcining Method with Some Modification	Rapeseed Oil	94%	70	12:1	3	3	[34]
KF/Al_2O_3	Impregnation Method	Soybean Oil	85.8%	Methanol Reflux Temperature	15:1	2	6	[35]
KCl/Al_2O_3	Impregnation Method	Soybean Oil	No Reaction	Methanol Reflux Temperature	15:1	2	6	[35]
KBr/Al_2O_3	Impregnation Method	Soybean Oil	16.7%	Methanol Reflux Temperature	15:1	2	6	[35]
KI/Al_2O_3	Impregnation Method	Soybean Oil	87.4%	Methanol Reflux Temperature	15:1	2	6	[35]
K_2CO_3/Al_2O_3	Impregnation Method	Soybean Oil	48%	Methanol Reflux Temperature	15:1	2	6	[35]
KNO_3/Al_2O_3	Impregnation Method	Soybean Oil	67.4%	Methanol Reflux Temperature	15:1	2	6	[35]
KOH/Al_2O_3	Impregnation Method	Soybean Oil	80.2%	Methanol Reflux Temperature	15:1	2	6	[35]
$KOH/\gamma\text{-}Al_2O_3$	Incipient-Wetness Impregnation	Canola Oil	89.40%	60	12:1	3	9	[36]
$LiNO_3/Al_2O_3$	Impregnation Method	Palm Kernel Oil	91.6%	60	6:5	10	3	[38]
$KI/\ \gamma\ Al_2O_3$	Sol Gel Method	Sunflower Oil	99.99%	Reflux Temperature	12:1	2.5	3	[37]
$NaNO_3/Al_2O_3$	Impregnation method	Palm Kernel Oil	95.1%	60	6:5	10	3	[38]
KNO_3/Al_2O_3	Impregnation Method	Palm Kernel Oil	94.7%	60	6:5	10	3	[38]
$Ca(NO_3)_2/Al_2O_3$	Impregnation Method	Palm Kernel Oil	94.3%	60	6:5	10	3	[38]
$CaO\text{-}La_2O_3\text{-}Al_2O_3$	Co Precipitation	Crude Palm Oil	97.81%	170	9:1	5	3	[39]
$Mg(NO_3)_2/Al_2$	Impregnation	Palm	10.4%	60	6:5	10	3	[38]

O_3	Method	Kernel Oil						

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

Catalyst	**Preparation of Catalyst**	**Feedstock**	**Yield**	**Reaction Conditions**				**References**
				Reaction Temperature (°C)	**Methanol to oil ratio**	**Catalyst Amount, wt.%**	**Reaction Time (h)**	
KNO_3/Al_2O_3	Impregnation Method	Jatropha Oil	84%	70	12:1	6	6	[40]
ZnO/Al_2O_3	Precipitation and Gel Method	Kesambi Oil	92.29%	65	12:1	4	6	[18]
$CaO/KI/Al_2O_3$	Impregnation and Precipitation Method	Waste Cooking Oil	83.08%	65	15:1	6	5	[41]
Anthill-eggshell-Ni-Co	Impregnation Method	Waste Frying Oil	90.23%	70	12:1	3	2	[26]
γ-Al_2O_3/ZrO2	Sol and gel Method	-	90%	250	3:5	-	-	[29]
KI/ γ Al_2O_3	-	Rubber Seed Oil	31.8%	60	15:1	2	8	[42]
$CaO/KI/Al_2O_3$	Heating a Mixture of Alumina and Salt	Rubber Seed Oil	91.6%	65	9:1	2	5	[15]
KI/Al_2O_3	Heating a Mixture of Alumina and Salt	Rubber Seed Oil	90.7%	65	9:1	2	5	[15]
CaO/Al_2O_3	Heating a Mixture of Alumina and Salt	Rubber Seed Oil	63.7%	65	9:1	2	5	[15]
CaO-La_2O_3-Al_2O_3	-	Karanja Oil	96.77%	170	9.1	5	3	[39]
Al_2O_3/Mg-Zn	Co-precipitation	Crude Jatropha	94%	182	11:11	8.68	6	[43]
MgO-CaO/Al_2O_3	-	Waste vegetable Oil	96%	350	10:2	15-20%	12	[44]

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

Catalyst	Preparation of Catalyst	Feedstock	Yield	Reaction Conditions				References
				Reaction Temperature (°C)	Methanol to Oil Ratio	Catalyst Amount, wt.%	Reaction Time	
CaO-MgO/Al_2O_3	Single Step Sol-Gel Method	Nannochloropsis Oculata Oil	97.5%	407	30	80	-	[32]
KOH/La-Ba-Al_2O_3	Impregnation Method	Microalga	97.7%	60	-	25	3h	[45]

4. Summary

It was concluded from the study of the 1st generation biodiesel that KI/γ Al_2O_3 catalyst has been a promising catalyst providing a surprising FAME yield upto 99.99% from sunflower oil in a very short reaction time of 3 hours. CaO/Al_2O_3 composite catalyst gave FAME yield of 98.64% in a comparatively longer reaction time that was 5 hours from edible seed oil of palm oil. Transesterification of crude palm oil with heterogenous CaO-La_2O_3-Al_2O_3 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 CaO/Al_2O_3, heterogenous composite catalyst in 3 hours. The $Mg(NO_3)_2$/Al_2O_3 catalyst that was calcined at 450°C gave drastically very low yield of biodiesel (10.4%). Temperature for calcination of the catalyst has also a great influence over rate of conversion of oil into biodiesel, when $Ca(NO_3)_2$/Al_2O_3 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/Al_2O_3 give a good yield of FAME from sunflower oil but the main problem with it is the very long reaction time that is 24 hours. The results of the literature review of 2nd generation biodiesel has shown that transesterification of karanja oil with CaO-La_2O_3-Al_2O_3 gave 96.77% yield of biodiesel in reaction time of 3 hours. Al_2O_3/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/Al_2O_3, a heterogenous catalyst in 6 hours. Heterogenous catalyst MgO-CaO/Al_2O_3 has not been proved promising for the conversion of waste cooking oil into biodiesel. Although FAME yield was 96% but main issues are the reaction time (12 h) and reaction temperature (350°C) so it is not economically feasible. KI/Al_2O_3 also did not give a good yield of biodiesel, it only provide 31.8% FAME yield from rubber seed oil in a longer reaction time of 8 hours. CaO/Al_2O_3 also gives biodiesel yield only upto 63.7% in a longer reaction time of 5 hours. There was no much work reported in literature for the production of 3rd generation biodiesel. However above discussion shows that transesterification of *Nannochloropsis Oculata* oil with CaO-MgO/Al_2O_3 and FAME yield of micro algae KOH/La-Ba-Al_2O_3 was very good high upto 98% and economically advantageous.

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