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A comprehensive review on heterogeneous - nano chemical catalysts in biofuels production

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ABSTRACT

Catalysts play a vital role in transesterification of both edible and non-edible vegetable oils. At present here chemical catalysts are being investigated with their benefits and loss of points. In extensive operations catalysts are more helpful to reduce the cost in this heterogeneous nature of a catalyst is more useful and economical compare to homogenous catalysts. At present nanocatalysts are used for better results in this article reviews the role of the various chemical catalytic system used in the transesterification of oils in biofuel manufacturing.

Introduction

Global essential energy demand is expected to grow 1.2% on yearly basis[1].Moreover, fossil fuel resources such as crude oil 35% coal 29% and natural gas 24% whereas renewable energy resources account for 7% and 5% of world energy consumption respectively[2], therefore the single largest energy origin that is fossil fuels are representing 88% total world energy consumption. A substitute fuel for fossil fuel must be technically feasible, economically competitive, eco-friendly, and fairly available at a reasonable cost. In this condition vegetable oils, bio alcohols biogas, and biofuels are considered as appropriate options[1], [2]. Among these biofuel, biodiesel is the perfect alternative fuel for diesel engines, biodiesel is formed from mono alkyl esters long-chain fatty acids acquired from vegetable oils[3]. It is a renewable non-toxic, biodegradable, and eco- friendly one. It is often utilized in compression–ignition engines with either little or no alterations due to its accommodating physical and chemical properties. It also has a supportive combustion emission generating much fewer CO, SO2, and unburned hydrocarbons compared to petroleum-based diesel fuels[3], [4]. One of the major issues that present itself in the biofuels production path is the use of a perfect catalyst is associated with the oil the functional efficiencies and by products during transesterification has become a major role for discussion and analysis. Biofuels are now receiving attention as a fluid fuel developed as a modified oil hence the main target has shifted to the utilization of non-edible oil as raw materials for biofuels [5]. Prominent non-edible oils being deal with biofuel blossoming from Seemaikattamankku (*Jatropha curcas*)[5], Karanja (*Pongamia pinnata*) [6], Candlenut (*Aleurites moluccana*) [7], French peanut (*Pachira glabra*)[8], Alexandrian laurel ball tree (*Calophyllum inophyllum*)[9], rubber seed (*Hevea brasiliensis*) [10], desert date (*Balanites aegyptiaca*) [11], sea mango (*Cerbera odollam*)[12], Kenya croton(*Croton megalocarpus*)[13], Bedda nut (*Terminalia belerica*)[14], Neem (*Azadirachta indica*)[15], Mahua (*Madhuca indica* and *Madhuca longifolia*)[16], Tobacco seed (*Nicotiana tabacum* L.)[17], Chinese tallow (*Sapium sebiferum* L.)[18], Silk cotton (*Ceiba pentandra*) [19], Jojoba (*Simmondsia chinensis*)[20] Babassu (*Attalea*

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speciosa)[21], Sichuan pepper (*Zanthoxy lumbungeanum*) [22], Cotton(*Gossypium herbaceum*) [23]and *Euphorbia tirucalli* [24]. A few edible-oil basics, such as Coconut (*Cocos nucifera*) [25], Soybean (*Glycine max*)[26], Palm (*Elaeis guineensis*)[27], and Canola (*Brassica napus*)[28], have also been in use for biofuel production due to their accessible opportunity and minor free fatty acid (FFA) content than non-edible oil.

There are several choices in making the triglycerides amenable, like coalescing the oil with conventional diesel, micro-emulsion, thermal cracking, or catalytic cracking and transesterification. Among these, transesterification has become desired one[29]. In transesterification, triglycerides are formed to behave with dominant alcohol being with a catalyst supply fatty acid alkyl esters. During this process, glycerol transpires as another additional product[30]. Transesterification consists of seriatim convertible strides. The process involved is that the conversion of triglycerides to mono-glycerides, the primary step is triglycerides converted into di-glycerides, and the conversion of di-glycerides to mono-glycerides and glycerol, producing one methyl ester molecule in primary as well as a secondary step. The whole transesterification reaction is supported by an external catalytic system.

Transesterification process reactions of catalysis

Catalysts are dynamic in leading the tactic completeness, although the reaction demands high energy and a complicated purification process to urge a purified outcome [31,32].

Heterogeneous nano catalysts

A nanocatalysts performs as a binding between homogeneous and heterogeneous catalyst towards the prudent uniqueness of the two systems. An investigation on nanocatalysts to generate a catalyst with excessively elevated activity, selectivity, and towering stability with a towering output is achieved by an alter in surface functionality, elemental composition, or the number of atoms in the particle[33], [34], [35]. The above-said components are empowering Nano heterogeneous catalytic systems to come out reaction rates comprised to a homogeneous system[33].

Nanosphere catalysts provide a low ratio of methanol/oil, separation, and revamp the megoporous silica Nanosphere by providing high catalytic loading to reform transesterification productivity. The nanoscale metal-oxides have well-being catalytic activity for methanol analysis of oils over a large number of active sites parked at the fringe of the crystals[36], Nanocrystalline CaO brings a transformation capability of 100% in a reaction duration around six hours at 35°C utilizing methanol on vegetable oil and poultry fat[37]. Nano sized calcium oxide is an efficient catalyst for transesterification of jatropha oil by double stage process and has been realized to raise biofuel product to 98% catalysts readopting is about nine cycles providing stable activity up to six cycles with an output of ~ 96%[38]. Nano structured CaO borrowed from calcium nitrate (CaO/CaN) and Snail shells (CaO/snail shells) have been assessed for their catalytic activity in transesterification the biofuel output was 93 & 96% individually [39].Li-doped calcium oxide nanocatalysts delivered of biofuel at methanol oil, the molar ratio of 12:1 at 65°C within two hours duration using 5 wt% catalysts [40].Nano structured mixed-metal oxides of CaO–MgO produced a yield of 98.95% biodiesel as the mixed-metal oxides catalyst demonstrated better activity than nano CaO alone[41].KF/CaO prepared by the penetration method the Chinese tallow oil output product was around 96%[18]. Another CaO-based nanocatalysts of Ca/Fe_3O_4 @ SiO_2 has become suitable for the biofuel process. A catalyst backed on magnetic material can be comfortably detached by an extraneous magnetic field due to Fe_3O_4 and managed its catalytic activity in quite a lot of cycles[42]. Cadmium oxide (CdO) and tin oxide (SnO) nanocatalysts backed by magnetic substances have been utilized in esterification, transesterification, and hydrolysis reaction. The above-said catalysts are more vigorous in esterification than transesterification and hydrolysis reactions[43].Guanidine- functionalized Fe_3O_4 and Fe_3O_4 @ SiO_2 magnetic nanoparticles(MNP_s) have been utilized as an elemental recyclable catalysts for biofuel process Fe_3O_4-TBD(1,5,7-tri-azabicyclo[4,4,0]dec-5-ene) also exhibited more catalytic conduct in the first cycle and attained 96% biofuel conversion[44].A nano- solid base catalyst, K_2O/ɣ-Al_2O_3 reached 94% change over in rapeseeds oil[45]KOH pervaded with Al_2O_3& $CaAl_2O_4$ has also been utilized in the transesterification process[46]. The solid base nanocatalysts of zirconium-loaded $KC_4H_5O_6$ (potassium bitartrate) was also utilized in the biofuel process[47].

Transesterification was accomplished in microwave, auto-clave, or ultrasound using nano-structured MgO. An utmost conversion was gleaned in the microwave than in autoclave or under ultra sound[48]. Transesterification of *Madhuca indica* oil was carried out by heteropoly acid (HPW)-coated ZnO catalyst and the FAME resumption was superior to 95% in five hours[49].Fe^{2+}-doped ZnO nanocatalysts contributed a changeover of 91% from castor oil[50]. Ni-doped ZnO nano composite brings out 92% biofuel[51]. Mn-doped ZnO nanocatalysts attained 97% biofuel from mahua oil[52].$Zn_{1.2}H_{0.6}PW_{12}O_{40}$ (Nanotubes with double acid sites) Nanotubes are familiar to perform higher catalytic movements together for esterification and transesterification of palmitic acid than parent acid catalysts of $H_3PW_{12}O_{40}$ (HPW) [53].The solid acid of an aluminium dode Catungs to phosphate($Al_{0.9}H_{0.3}PW_{12}O_{40}$,ALPW) nanotubes catalyst be evidence for superior catalytic activity and stability apropos biofuel process beneath delicate reaction positions than other catalyst resembling AIPW salt with nanotubes formation $Cs_{2.5}H_{0.5}PW_{12}O_{40}$(CsPW) and HPW.

The maximum activity is accredited to the joined outcome of Lewis acid sites. Bronsted acid sites and the nanotube format[54]. The acid-base biutilitarian HPA nanocatalyst $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$ (abbreviated as ly_2HPW)was maximum productive in the esterification of FFA and transesterification of triglycerides[55]. The catalytic performance of Cs-MgO and nano MgO-500 criterion was determined successively against transesterification of tricaprylin(C_8),trilaurin (C_{12}), and olive oil at 60°C, Cs-MgO has the longest catalytic activity to nano MgO-500 for all trifatoils[56]. The spinal-structured catalyst of urea designated MgO/$MgAl_2O_4$ obtained 95% transformation and the activity was observed to have been possessed after six reaction cycles[57]. Ionic liquids (Ils) have fascinated momentous as green elements substitute reaction tools and bright catalysts. Poly ionic fluids are ionic polymers having a polymeric backing and IL units that can perform both polymer and IL with maximum heat stability and corrosion resistance. Magnetically reproducible acidic polymeric ILs decorated with hydrophobic regulators have been utilized as a catalyst for biofuel production. The above-said catalysts had maximum activity and reproducibility in the process of biofuel via acid transesterification processes the catalysts gained a product output of 95% under delicate reaction conditions (1:17 oil/methanol molar ratio 4% catalyst dosage at 75°C in 3Hrs.)In that 92% yield was gleaned via concurrent esterification and transesterification in crude *Euphorbia lathyris* seed oil[58]. The magnetically reproducible catalyst of MgO- supported $MgFe_2O_4$ was utilized as a heterogeneous nanocatalyst in transesterifications of sunflower oil. The spinel ferrite catalyst of $MgFe_2O_4$ has particular and tunable magnetic, electronic and formational properties the catalyst given a biofuel output of 91% and managed its catalytic activity up to five cycles with a stable transformation[59].$Ni_{0.5}Zn_{0.5}$ Fe_2O_4 was an effectual nanocatalyst in methyl and ethyl esterification with 99.5% recovery[102]. In-Situ decorated TiO_2 on lessened graphene oxide nanocomposite via the hydrothermal route on transesterification of waste cooking oil offered a product of 98%[60]. Tungsten-infused TiO_2/SiO_2 nanocatalyst has been comfortable in the transesterification of vegetable oils. The aperture size of $W/Ti/SiO_2$ was bigger than the apertures of assist material as tungstate ions ducked the apertures of assist material (TiO2 /SiO_2) consequently the surface area and an aperture volume are linked to tungsten insemination. The catalyst generated above 98% biofuel[61]. Sulphonic acid-carried graphene catalysts are capable of getting rid of the problems of robustness and extensive leaching in the aqueous phase fitting to their partial limited solubility in methanol. Sulphonated graphene catalysts comprise highly accessible active acidic sites firmly tied up to a stable, insoluble platform that would aggregate **s**tructured plan of action and have attained superior to 98% biofuel output with an excessive purity[27].

Supercritical fluids (SCF)

The supercritical fluid system could be utilized for the production of biofuel over transesterification of vegetable oils in the absenteeism of catalyst Saka and Kusdiana offered that biofuels could be drawn up from oil through non-catalytic transesterification with supercritical methanol[62].
Comparableness of the conservative catalytic activity the SCF approach gives several valuable advantages easy segregation of the outputs, rapid reaction, and the SCF approach was also credited with solving issues coupled with the two-phase nature of methanol and oil combination by forming a single phase as an effect of the dielectric invariable of methanol in the supercritical state. The above-said operation results in the utmost output of ester in the nonexistence of a catalyst at a towering reaction heat needed above 400°C[30]. The productive capability of transesterification can be improved by utilizing calcium oxide catalysts in the SCF system[30], [34], [63]. The consequence of putting H_2O on the output of biofuel in transesterification of triglycerides and methyl esterification of FFAs underneath supercritical methanol has been identified. The H_2O put on supercritical methanol attributes effortless segregation of outputs, because glycerol a co-output in transesterification is higher dissolved in water than methanol[64]. It is a unique process of biofuel production progressed by a non-catalytic supercritical method in that the output was 96% within 10 minutes[30]. An additional solvent-held supercritical methanol system can increase the output of biofuel.C_6H_{14}(Hexane) and supercritical CO_2 act as effortful solvents for oils[65].Transesterification of soybean oil in supercritical methanol has been accomplished in being there with propane and bringing out a FAME ability of 98% with flawless reaction situations like 280°C temperature, 24:1 methanol to oil molar ratio, 10 minutes interval, and130.5237 Kg/cm^2 reaction pressure. Supercritical CO_2 an enforced in enzymatic reactions due to that the enzyme can be isolated effortlessly by decreasing the pressure. As the enzyme and the product cannot be soluble in CO_2 at 1.03323 Kg/cm^2 conditions they can be easily reproducible. The output of biofuel is caught to raise as the temperature, methanol –to–oil molar ratio concentration with stirring rate is above 850 rpm[65], [66].Supercritical $C_3H_6O_3$ is utilized in biofuel production at 350°C at 203.943 Kg/cm^2[67].Wet-depleted coffee grounds a waste product of coffee seethe business have high interest in utilizing in biofuel. An inquiry indicated the destruction of both biomass infertile and catalyst usage by assimilating the extraction and conversion transforms to confer biofuel[68]. Methanol and ethanol which are being utilized in the supercritical process are hygroscopic and corrosive; the above said issue can be weather by embroiling high-carbon alcohol being 1-Proponal. It is influenced over ethanol as it is borrowed from glucose without CO_2 evolution while the biosynthetic track in ethanol synthesis has CO_2 emission strides, as a result, the utilize of 1-Proponal as a reactant for biofuel generation attempts commitment. The reaction criteria of biofuel generation commit supercritical 1-proponal exhibited that compelling changeover of oil into biofuel can be gleaned at 350°C and 203.943 Kg/cm^2 after 30 minutes resistance time with an emanating biofuel output of 94%[69]. The above-said transform requires a lot of safety measures in consequence of superior temperature and pressure.

Conclusion and Future prospects

Transesterification is the enhanced option for biodiesel production judged against other existing methods. Transesterification reaction for the most part depends on catalytic systems. There are two kinds of major catalytic systems, chemical and biological. In the chemical-based catalytic system, homogeneous catalysts are effectual but the progression involves high energy spending as well as wastewater treatment due to untreated chemicals. In heterogeneous catalysts, external-surface active species of porous solid support only is concerned. In some catalysts, particularly CaO, leaching takes place that adversely influences the reaction. Nano technological synthetic protocols can help to design and modify the catalyst's surface to congregate the requirements of specific applications and solve the concerns of the homogeneous as well as heterogeneous catalysts. Nanocatalysts perform as a junction between homogeneous and heterogeneous catalysts, which can make potential solid-acid or solid-base catalysts. Conservative filtration and centrifuge are not adequate to get better the materials after synthesis due to the tiny particles. Magnetic nanoparticle-sustained catalysts could be recovered easily by a magnetic field. Growth of effective and reasonably priced catalysts with an environmentally gentle process is essential to overcome the present problems still if the biofuel-making system is just right the problem may not reach a tangible end because the oil-making charge per unit area of derelict land needs to be perked up. This will be a huge confrontation at the planning level. Genetic evolution of high-yielding assortments must be encouraged to enhance low-FFA oil accessibility. One notion worth consideration is the make use of CO2 enclosed in stack emissions from industrial progression, thereby accomplishing the benefit of greenhouse gas resource recovery. An appropriate catalyst, if identified for effective transesterification, will represent a milestone in the fuel sector.

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