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A mini – review on heterogeneous chemical catalysts in biofuel production

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ABSTRACT

Catalysts perform vital part 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 operation catalysts are more helpful to reduce the cost where heterogeneous nature of a catalyst is more useful and economic compare to homogeneous catalysts. In this paper, we review the role of various heterogeneous chemical catalytic system used in transesterification of oils in bio fuel manufacturing.

Introduction

Global essential energy demand is expected to grow 1.2% on yearly basis [1]. More over 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, economic competitive environmental friendly and fairly available at reasonable cost. In this condition vegetable oils, bio alcohols bio gas and bio fuels are considered as appropriate options [1], [2]. Among this bio fuels, bio diesel is perfect alternative fuel for diesel engines, bio diesel is formed from mono alkyl esters long chain fatty acids acquired from vegetable oils [3]. It is renewable non-toxic, bio degradable and environmental friendly. It is often utilized in compression – ignition engines with either little or no alterations due its accommodating physical and chemical properties. It is also has supportive combustion emission figure generating much fewer CO, SO_2 and unburned hydro carbons compared to petroleum based diesel fuels [3], [4]. One of the major issues present itself in the bio fuels production path is the use of a perfect catalyst in associated with the oil the functional efficiencies and by products during transesterification has become a major role for discussion and analysis. Bio fuels is 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 a raw materials for a bio fuels [5]. Prominent non-edible oils being deal with bio fuel 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 (*Balanitesa egyptiaca*) [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 speciosa*) [21] Sichuan pepper (*Zanthoxylum bungeanum*) [22], cotton (*Gossypium herbaceum*) [23] and *Euphorbia tirucalli* [24]. A few edible-

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oil basics, such as coconut (*Cocos nucifera*) [25], soybean (*Glycine max*) [26], palm (*Elaeis guinensis*) [27] and canola (*Brassica napus*) [28], have also been in use for bio fuel production due to their accessible opportunity and minor free fatty acid (FFA) content than non-edible oil.

There are lot of choices in making the triglycerides amenable, like coalesce 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 transpire as another additional product [30]. Transesterification consists of seriatim convertible strides. The process involved in is that the conversion of triglycerides to monoglycerides, the primary step is triglycerides converted in to diglycerides and then conversion of diglycerides to monoglycerides and glycerol, producing one methyl ester molecule in primary as well as 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]. The various methods of chemical catalytic transesterification nearly new to produce bio fuels are conferred in Fig.1

Chemical catalysts

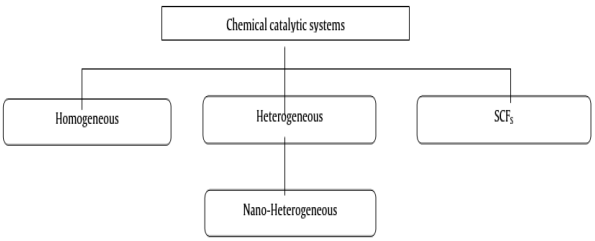

Fig.1. Different chemical catalytic systems for transesterification

Hetrogeneous Catalyst

Hetrogeneous catalysts are acknowledged to improve the transesterification process by waiving the additional processing cost involved in homogeneous catalysis along with reducing an engender of pollutants[33]. Hetrogeneous catalyst bolster quick recovery, transformable and a worthwhile green process[[34]. The above mentioned catalysts tolerate an immense amount of FFA and moisture content.Economic and an energetic heterogeneous catalysts support to curtail the overall cost of biofuel process [35]. Hetrogeneous catalyst are more capable in high temperature and pressure. The above said catalysts are effortless to recoup from the reaction compounds are efficient of withstanding aqueous treatment process and are susceptible for conversion to attain high activity, selectivity and protracted catalysts life career. Heterogeneous catalysts can be performed to emphasize propagate and enticement of the active compounds on the surface of or inner part of the pores of a solid support silica, alumina or ceria. Alkali earth metal oxides [36], transition metal oxides [37] blended metal oxides [38], ion exchange resins [39], [40] and alkali metal compounds supported on alumina or zeolite [41] are used in various chemical reactions such as isomerization, Aldo condensation, Knoevengal condensation, Michael condensation, oxidation and transesterification [34], [42]. Alkaline earth metal oxides are profitably utilized as a catalyst that have BeO, CaO, SrO, BaO and RaO. MgO and SrO. SrO (Strontium oxide) has long basicity and is not adrift in methanol due to solubility. It preserves its tolerance for up to 10 cycles [42]. Altered zeolites, anionic clays (hydro talacite), Calcium carbonate rock, EST-4 (Eni slurry Technology), Li/Cao,Mgo/KoH and Na/NaOH/ɤ-Al_2O_3 are efficient heterogeneous catalysts for transesterification reaction [41]. Solid acid catalysts assist one and the other transesterification and esterification together for biofuel manufacturing from oils among more FFA content [35].

Air- stable and water tolerant zirconocene perflurooctane sulphonate lewis acid catalyst was utilized in the unequivocal esterification of FFA and transesterification of triglycerides besides the above said catalyst performing as a reaction lured self-separating agent as during the course of reaction it modified from homogeneous to heterogeneous. Finally the catalyst precipitate a white solid as a byproduct that is supportive one for recycling. Solid base catalysts have more catalytic activity than solid acid catalysts. Various solid base catalysts used in transesterification consist of CaO, MgO, SrO, KNO_3/Al_2O_3, K_2CO_3/ Al_2O_3 [37,38]. KF/ Al_2O_3,Li/CaO, KF/ ZnO basic hydrotalcite of Mg/ Al, Li/ Al, anion exchange resins and base zeolites [39], [40]. Calcined Li/Al hydrotalacites are very effective with in the glycerolysis carboxylic acid with long chain hydrocarbons (FA) than Mg/Al material because of high Lewis basicity [41]. Different molar ratios of Mg/Al catalysis in the range of 1.5-5 have been utilized in biofuel process.

The high ratios of Mg/Al catalyst have demonstrated excellent characteristics despite a little area. The Mg/Al catalyst has strong delineated flake like crystals consists of strong basic sites with H-values greater than 11.The above said catalysts provides more than 92% yield of biofuel certain flawless reaction conditions [42]. An aspiration of permeating the varied metal oxides is to augment the base or acid strength, build up the surface area and bolster the stability more than that of an exclusive metal oxides [43]. Li intoxicated MgO catalyst at a 9% level gives a fatty acid methyl ester (FAME) product of 93.9% at 60°C in a 12:1 methanol/oil molar ratio. The above said catalyst reveals a strong base site formed by the addition of Li resulting in an increasing biofuel product output[44]. Li-intoxicated BaO has exhibited more activity than Na/BaO and K/Bao in a transesterifications [45]. Lithium doped Zincoxide

Catalysts (Li/Zno) shows good catalytic activities, but their achievement belongs to amount of Li loading and temperature[46]. The catalyst KF/ɤ-Al_2O_3 has a strong base site that speed up the transesterification process at a less temperature although the medium base strength requires more temperature [47]. Calcium Oxide a solid base catalyst is performed as an environmental friendly substance that develops long catalyst life, high activity and moderate reaction conditions [3]. Commonly calcium nitrate and calcium hydroxide are the base substances for the creation of CaO, besides many calcium rich waste materials are accessible in nature being chicken egg shells, mollusk shells and bone these can be used as a base materials for catalytic synthesis so that the problem of waste disposal are minimized more over producing highly cost effective catalysts [48]. A Calcium oxide/ Potassium fluoride, (KF/CaO) solid base catalyst is prepared by loading CaO on KF which exhibits high catalytic activity[48]. When CaO given high catalytic activity in transesterification this catalyst leached out the calcium(Ca^{2+}) ions that affects the nature of the output. The leaching of Ca^{2+} ions are considering the existence of moisture that hydrolyzes the calcium di glyceride (derived by the instability of CaO with the bye product glycerol). The arrangements of soluble Ca^{2+} also directly detaches CaO being reaction with methanol. The leached calcium ions react with FFA of oil that undergoes to saponification and disbands an impressive function of the catalyst so that utilize an appropriate aiding substances can avoid leaching of Ca active species [49-53].

An addition to that the dominant drawback in using CaO is that it needs heat energy to nullify the absorbed CO_2 and moisture and it is mandatory either the reaction in a vacuum or N_2 gas atmosphere to avert carbonization [3]. The variant metal oxide catalysts have given an admirable resistance to FFA and water content of the crude oil in transesterification. Various metal oxide catalysts in addition to $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, CaZrO3 and CaO-CeO_2 are involved in a biofuel production, in this Calciumzirconicoxide and Calcium oxide-Ceriumdioxide catalysts have more stability and output [35, 54]. The Cao-MgO catalysts were assessed by transesterification of jatropha oil under specified process points and recovered a 75%-90% product output of FAME [53]. Acid- base epicene utilitarian mixed- metal oxide catalysts of $Mn_{.5}Ce_{.5}O_x$ were highly effective for biofuel synthesis reached almost (~)100% conversion under dominant functional situations. The above said catalysts were observed to have acid cites in that Manganese offered basic sites Potassium integrated in to the catalyst structure during the reaction strategy could complement the $MnCeO_x$ catalytic activity [54]. Different types of varied metal oxide catalysts like CaO-MgO, CaO-ZnO, CaO-La_2O_3 and MgO-ZnO are utilized in transesterifications synthesis with a catalyst amount of 3wt% an oil/methanol molar ratio 1:25, at 120°c and functioning span of below three hours. In that CaO-ZnO achieves maximum catalytic activity [56]. The varied metal oxides of CaO-MgO burdened on Al_2O_3 catalyst gave 97.6% product in transesterification of cotton seed oil [23]. Li permeated CaO-La_2O_3 varied metal oxides were used in transesterification with Li, Ca and $La_2(CO3)_3$ in the structure, this material showed that Li-doping improved the basic strength and the presence of La_2O_3 in the backing structure controlling the BET (Brunauer-Emmett-Teller) surface area and the stability of the catalyst alike later Li retention. The catalyst given the best result of 96% at 65°C in 2.5 to 3 hrs of reaction duration [57]. Mesostructured materials have been developed to improve the catalytic performance of the solid catalysts. Mesoporous materials offer versatile support to a variety of catalytically active functional groups. The sulphonic acid altered mesostructured catalyst is used in transesterification reaction reaches as high as 100% nonetheless the strong concentration of methanol has been created to be adverse the catalytic activity [58]. Mesoporous SBA-15 an extensively used in catalytic applications with metal oxides for its peculiarity high surface area, large uniform pore sizes resistance to leaching of supporting materials and intensity catalyst reusability [59], [60]. CaO-MoO_3-SBA-15 catalyst at a 6% level when used in transesterification of soybean oil /methanol at a 1:50 molar ratio given 83.2% biofuel output. The acid base interactions between the basic CaO and the acidic MoO_3 could promote a good, stable dispersion of catalytically active sites thus ultimately increasing the stability of a catalyst [61]. An active molecules in heterogeneous catalyst mostly not usable in a homogeneous system and in a final stage catalytic activity may be slacken also external-surface active sites of a porous solid support are actively participated in slacking the overall activity of the catalysts. In this sort of cases, it is essential to expand catalyst system that not only exhibits high catalytic activity and selectivity more over hold on to catalyst separation and regeneration. This may be attained by grafting through covalent binding and adsorption [36].

Conclusion and Future prospects

Transesterification is the enhanced option for biodiesel production judge against with 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, wherein 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. Nanotechnological 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. 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 confront at the planning level. Genetic evolution of high yielding assortments must be encouraged so as to enhance low-FFA oil accessibility. One notion worth consideration is the make use of CO_2 enclosed in stack emissions from industrial progression, thereby accomplished 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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