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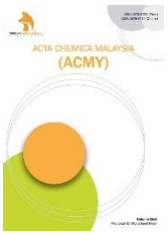

REVIEW ARTICLE

CHEMICALLY-BASED HETEROGENEOUS ACIDIC CATALYSTS FOR BIODIESEL PRODUCTION: A REVIEW

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ABSTRACT

Unless appropriately catalyzed, a transesterification reaction with/out esterification reaction cannot proceed towards the production of biodiesel. It is observed that chemically-based heterogeneous acidic catalysts for biodiesel production are several and gaining an attention due to their good catalytic activity, stability and reuse. Furthermore, among investigations reviewed, it has been found that such catalysts have been found to be tolerant with a high level of free fatty acids contained in the used oil as a feedstock for which an esterification reaction is required. On the other hand; however, chemically-based heterogeneous acidic catalysts usually require harsh reaction conditions and are associated with law mass transfer rates.

KEYWORDS

Heterogeneous, homogenous, esterification, transesterification, impregnation

1. INTRODUCTION

Worldwide, energy shortage as well as environmental issues have become well recognized. The former is due to depletion of classical fossil fuels while the latter is due to the atrocious pollutants generated out of combusting such fuels for different applications. This has urged the human chase to look for other widely available while cleaner resources as a supply for energy generation. Almost worldwide, biodiesel has been a successful candidate resource among such resources. Production of biodiesel relies on the use of an open list of feedstocks including edible/non-edible vegetable oils including but not limited to sunflower, soybean, cottonseed, rapeseed, peanut and palm oils as well as fats (animal source) that could be generated from domestic animals such as chickens, cows and sheep, etc. Due to economical and logistic circumstances, other feedstocks have been a necessity. Non-edible oils and used waste oils can constitute a long list of such other feedstocks. However, the content of free fatty acids of such oil wastes as well as animal fats is higher than that of fresh oils. This comes with a detrimental effect on the performance of the catalyst used in the transesterification reaction for biodiesel production. Microalgae, fungi and bacteria can also be a possible feedstock for biodiesel production.

Next to the discussion dedicated to homogeneous-acidic/basic catalysts in biodiesel production, chemically-based heterogeneous (solid)-acidic catalysts are now discussed (Shakorfow and Mohamed, 2020). Nevertheless, those emerging heterogeneous acidic catalysts synthesized from solid waste materials are not. Although acidic/basic homogenous catalysts are reasonably efficient in catalyzing transesterification reactions for biodiesel production relatively at mild conditions, their usage; however, is somewhat associated with severe contamination problems. In order to separate, purify and neutralize the product (biodiesel) from its accompanying contaminants, costly, multiple and complicated processes should be performed. Also, in order for homogenous catalysts to perform in a transesterification reaction, they have to be dissolved in the alcohol employed. Afterwards, they require washing with water which has to be separated out in a slow and tedious manner. This results in the generation of a nasty waste water. Moreover, such catalysts are non-reusable. Besides, acidic catalysts are greatly corrosive while basic ones promote saponification; particularly, when employed for the transesterification of cheap feedstocks rich in free fatty acids. Saponification is undesirable since it leads to the consumption of the used catalyst; thus, to the deterioration of its catalytic activity.

Accordingly, from the operability; hence, economical standpoint of view, homogeneous-acidic/basic catalysts might not be a viable means in biodiesel production. A robust heterogeneous (solid)-acidic/basic catalyst that reasonably offers a good activity, simplicity and continuity in biodiesel production cycle via transesterification with a reduced waste generation, with no need for water washing (minimal or no waste, a green process) and with an easy product separation and the likelihood of catalyst recycling with a reasonable catalytic stability can be; therefore, beneficial. Hence, produced biodiesel can be economical; thus, commercially competing with ordinary-petroleum diesel as well as with minimal environmental impacts (Hanna et al., 2005; Lotero et al., 2005; Xie et al., 2007; Refaat, 2010; Endalew et al., 2011; Wei et al., 2015). A heterogeneous acid/base-catalyzed transesterification reaction involves neither catalyst recovery nor aqueous treatment steps rendering product purification steps much more simplified via which very high yields of methyl esters (biodiesel), close to the theoretical value, can be obtained. Glycerin (a by-product of transesterification reaction) is directly produced with high purity levels (at least 98%) and is exempt from any salt contaminants (Bournay et al., 2005). Another practical feature of the application of heterogeneous catalysts in the area of biodiesel production is their regeneration for a subsequent use(s) with no or little catalyst deactivation with time of use. In general, such solid heterogeneous catalysts can withstand high temperatures required for a transesterification reaction since they are non-volatile (solids), although catalyst coking is a possibility (Wilson et al., 2000; Skoda-Foldes, 2014).

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Also, they are generally more tolerant to oils with high levels of free fatty acids and water resulting in no formation of soap. In effectively doing so, they can replace those strong nasty liquid catalysts, acidic ones in particular, and; thus, getting rid of their corrosive effect on the process equipment and the environment, etc. (Cao et al., 2008). Furthermore, with advances in catalysis research, acidic/basic heterogeneous catalysts are open to new designs that guarantee high reactivity, stability and selectivity as well as longer lifetime via their capability to entrap those concerned active molecules on their surface or inside their pores particularly if a solid support is integrated in their design, e.g., alumina, ceria or silica (Puna et al., 2010; Salamatinia et al., 2012). For the purpose of biodiesel production, silica; in particular, has been coupled with: heteropoly acids, ion exchange resins with sulphonic acid groups, sulphated/mixed oxides and metals having molecular sieves for the purpose of esterification and transesterification of several oil feedstocks as it would be discussed later.

According to Di Serio and co-workers, a good heterogeneous catalyst should be: capable to catalyze both simultaneous esterification and transesterification reactions usually required with waste oils due to their high content of free fatty acids, stable showing no deactivation indication by water, with a high selectivity and effective if the transesterification reaction is carried out at a low temperature. While it should not be prone to initiation of leaching (Di Serio et al., 2008). In fact, in the technology of biodiesel production, among the factors that positively contribute towards the reactivity of a good heterogeneous catalyst in general are: hydrophobicity of the surface of the used catalyst, availability of medium to high concentrations of strong acid sites, good interaction between the active phase of the reaction and the support of the catalyst and enough number of an interconnected large pores within the body of the catalyst, to achieve the necessary selectivity during organic reactions. The hydrophobicity of the surface of the used catalyst is crucial in terms of the selective adsorption of the triglycerides of the used oil. Meanwhile, the hydrophobicity of the surface of the used catalyst can help avoid the deactivation of active sites of catalyst via the adsorption of polar glycerol and water which inevitably develop through a transesterification reaction as by-products. A good comparison that highlights main differences among a homogeneously and heterogeneously catalyzed-transesterification reaction can be found elsewhere (Helwani et al., 2009).

In the area of biodiesel production through transesterification, although heterogeneous catalysts can be made out of a wide variety of materials of different chemical nature, broadly; however, they can be limitedly classified as acidic and basic. Acidic heterogeneous catalysts compared to basic ones are more stable although are characterized with a lower reactivity. To this end, acidic heterogeneous catalysts are generally used in the transesterification of waste oils that possess a high amount of free fatty acids where a high stability of the catalyst is an advantage against catalyst deactivation by such free fatty acids. In the presence of an acidic heterogeneous catalyst, further to the transesterification of the esters (triglycerides) of the parent waste feedstock oil via which a biodiesel is produced, esterification of free fatty acids originally contained in the used oil and etherification of glycerol developed through biodiesel production are usually required to reduce the level of such acids to an acceptable level to be compatible with the standards of biodiesel production in further processing steps as well as to improve the flow properties of a synthesized biodiesel, respectively. In this paper; however, only use of such chemically-based heterogeneous-acidic catalysts in the transesterification route is chiefly discussed.

2. Chemically-based Heterogeneous Acidic Catalysts for Biodiesel Production

An application of a heterogeneous-acidic catalyst is the transesterification of esters (triglycerides), which are the principal ingredient of the parent oil, with an alcohol, usually of a low molecular weight, to produce a biodiesel with a reduced viscosity than that of the original used feedstock oil by one order of magnitude. The viscosity of a biodiesel is an important indicative parameter of biodiesel combustion characteristics. Thus, transesterification of a vegetable oil is pivotal for the purpose of viscosity reduction of the used oil. Viscosity reduction of the produced biodiesel is pivotal to avoid deposits formation on the engine parts by which its efficiency may deteriorate requiring expensive substantial maintenance (Mata et al., 2014). Transesterification is a reversible reaction in which the used alcohol is typically added to the reaction media in an excess amount to aid rapid triglyceride conversion to guarantee a complete conversion as possible. Transesterification reaction involves a reaction between a triglyceride molecule and an alcohol. Out of a transesterification reaction, a mono-alkyl ester with glycerine as a by-product are formed. In a study carried out by Schuchardt and others, the mechanism of an acid-catalyzed transesterification reaction, the subject of this review, is well-explained for which the reader is directed to for further information (Schuchardt et al., 1998). To date, to the best of knowledge of the authors of this research paper, in spite of the broad availability of catalytic materials through which heterogeneous (solid)-acidic/basic catalysts can be prepared, there has not been much research work on the direct transesterification of lipid feedstocks into biodiesel over a heterogeneous/solid-acidic catalyst. This perhaps may be due to low reaction rates and emergence of undesired side reactions accompanying the use of such catalysts. In the next paragraphs, some research investigations on the transesterification of lipid feedstocks for the purpose of biodiesel production via some chemically-based heterogeneous (solid)-acidic catalysts are reviewed. This review shall help in choosing the suitable, that's the most efficient, chemically-based heterogeneous catalyst(s) along with the optimum conditions for the purpose of biodiesel production.

Yee and co-workers have employed sulfated zirconia, loaded on alumina catalyst as a catalyst in the transesterification of jatropha curcas L. oil with methanol for the purpose of production of biodiesel. They obtained a relatively high yield of alkyl ester of more than 90%, provided that the transesterification reaction should last for four hrs, methanol to oil molar ratio is 9.88, reaction temperature is 150 °C and that catalyst amount is 7.61 wt.% (Yee et al., 2010). Transesterification of neem oil, that is rich with free fatty acids, using sulfated zirconia was also investigated by Muthu and co-workers. Suitability of the used catalyst with such a high level of free fatty acids contained in the oil was reported. They were able to reduce the level of free fatty acids down to nearly 8% following esterification with zirconia with methanol. Transesterification of the esterified-product was carried out with a homogeneous catalyst, 1% KOH, and produced a biodiesel with a yield of 95% and has properties comparable to those of petroleum diesel and was within ASTM standards (Muthu et al., 2010). Sulfated zirconia for esterification of croton gratissimus oil followed by transesterification with KOH were employed by Jiyane and others to produce biodiesel. Running the reactions at optimal conditions, produced a biodiesel with 84.51% yield and 90.66% purity (Jiyane et al., 2021). In addition to the sulfated zirconia, sulfated tin oxide and sulfated titanium oxide have also been considered in catalyzing simultaneous esterification and transesterification reactions. In general, such catalysts possess a superb acidity, good catalytic activities and good stability (Furuta et al., 2004; Jitputti et al., 2006; Kiss et al., 2006). Kim, et al., have examined the ability of a new class of an assortment of zirconia supported on various metal oxides to convert a bio-oil with a high level of free fatty acids into biodiesel, with a yield higher than 90%, using methanol as an alcohol (Kim et al., 2012). Furthermore, Lopez and co-workers have extensively compared the performance of several modified zirconias (WZ, SZ, and TiZ) under the same reaction conditions as catalysts for both the transesterification of triglycerides and the esterification of carboxylic acids (free fatty acids) with ethanol. In addition, the catalyzed rate of hydrolysis/esterification+transesterification of triglycerides has been quantified and compared to that of the rate of simultaneous esterification of free fatty acids present in the same reaction mixture. Tricaprylin and caprylic acids were used as representative compounds for the comparison of the catalyst for transesterification and esterification since they give reaction rates related to those of larger triglycerides and free fatty acids typically present in vegetable oils and animal fats. For the measurement of the kinetics for the simultaneous reaction of a triglycerides-free fatty acids mixture, the reaction of tricaprylin and oleic acid with ethanol was studied using the most promising Zr-based catalysts, WZ. Reaction was carried out in a well-mixed batch reactor under mild conditions (75–120°C). TiZ, while more active than WZ for transesterification, had by far the lowest activity for esterification. SZ, while the most active catalyst (on a weight basis) for both transesterification and esterification reactions, exhibited significant sulfur loss, which greatly reduced its long term activity. As expected, esterification occurred at a much faster rate than transesterification. However, under simultaneous reaction conditions, by virtue of water being produced in esterification and hydrolysis of the triglycerides, the conversion of the triglycerides to ester products was greatly increased. The resulting caprylic acid from hydrolysis did not accumulate in the reaction mixture due to its rapid esterification to ethyl caprylate (Lopez et al., 2008). Also, biodiesel was produced when zirconia catalyst prepared from zirconia sand was used to assist simultaneous esterification and transesterification reactions of a waste cooking oil at 60 C (Nisa et al., 2020). Moreover, Shi and co-workers have also used a mixed organic and inorganic hybrid membrane as a heterogeneous acid catalyst, they have previously prepared using a sulfonated poly (vinyl alcohol), SPVA, and zirconium sulfate (Zr(SO4)2), as a means to produce biodiesel from an acidified oil through transesterification with methanol. Out of their work, three hybrid catalytic membranes were prepared, namely: PVA, Zr(SO4)2 and Zr(SO4)2/SPVA. The performance of Zr(SO4)2/SPVA catalytic

membrane was the highest in the esterification of free fatty acids contained in the esterified acidified oil due to a strong interaction between Zr(SO4)2 particles and SPVA matrix. Also, due to its superior stability as a catalytic membrane, it was further employed in the transesterification reaction at an amount of 4 wt.%. Transesterification reaction lasted for two hrs and was performed at a temperature of 65 °C while varying the methanol to oil ratio between 1:1 to 12:1 through 3:1, 6:1 and 9:1. It was found that increasing the molar ratio results in increasing the conversion of free fatty acids into methyl esters (biodiesel). Among the molar ratios used, the obtained conversions were: 60.2%, 80.3%, 94.5%, 95.0% and 95.1%, respectively (Shi et al., 2009). In 2006, esterification of acetic acid by isoamylic alcohol using SPVA as a catalyst and transesterification of soybean oil with methanol were reported by Castanheiro, et al., and Guerreiro, et al.; respectively. In both works, catalyst activity and reusability were assured. Moreover, Guerreiro, et al. have observed that use of SPVA contained no additional cross-linking agent leads to the leaching of sulfonic acid groups (Castanheiro et al., 2006; Guerreiro et al., 2006). In addition, for the purpose of biodiesel production, Kulkarni, et al., have employed a solid heterogeneous acid catalyst, namely 12-Tungstophosphoric acid (TPA), impregnated on four different supports such as hydrous zirconia, silica, alumina and activated carbon for a simultaneous esterification of free fatty acids and transesterification of triglycerides of a low quality canola oil containing up to 20 wt% free fatty acids. Impregnation is usually sought in order to increase the surface area, enhance acidity/basicity strength and to toughen the stability of the catalyst (Chang et al., 2014). Kulkarni, et al., have found that hydrous zirconia supported TPA was found to be the most promising catalyst exhibiting the highest ester yield of nearly 77%. It was shown that Lewis acid sites generated by the strong interaction of TPA and surface hydroxyl groups of zirconia are responsible for their high activity. Optimum reaction parameters were: 9 oil to alcohol molar ratio and 3 wt% catalysts loading at a temperature of 200 °C. According to such optimum reaction parameters, a maximum ester yield of 90 wt% could be obtained. Due to negligible loss in the activity of the employed catalysts, they were recycled and reused (Kulkarni et al., 2006).

Due to strong Brønsted acidity which is higher than that of H_2SO_4, easier separation, reusability, higher proton mobility and higher selectivity, Chai and co-workers have used a solid acid, namely the heteropolyacid (HPA) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as a heterogeneous catalyst for the production of biodiesel from Eruca Sativa Gars, ESG, oils through transesterification with methanol. In order to attain a high yield of biodiesel, 99%, moderate conditions of transesterification reaction including: reaction time, temperature, oil to methanol molar ratio, amount of catalyst and usage times of the catalyst, were as high as necessary. At the optimum transesterification reaction conditions they considered, the authors compared the performance of the used heterogeneous acid catalyst, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, to that of a conventional homogeneous catalyst such as sodium hydroxide or sulfuric acid. They have found that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in addition to its ability to demonstrate a comparable reactivity to that of such conventional homogeneous catalyst such as sodium hydroxide or sulfuric acid, it is also featured with ease of separation from the product(s) and reuse. Furthermore, its reactivity does not deteriorate with a high content of free fatty acids or a high content of water in the parent vegetable oil used for biodiesel production, reflecting a great water/free fatty acids tolerance. Nevertheless, with water contents higher than 1%, the catalyst was with a nil activity. Also, when such a catalyst has been used, esterification reaction can take place at a lower temperature (room temperature) and that can be completed within a shorter time. Moreover, the authors have reported that their procedure is a clean, environmentally benign, facile and ecologically friendly procedure for the production of biodiesel. Besides, properties of ESG biodiesel as a fuel were found consistent with the US ASTM 6751 standards (Chai et al., 2007). In 2009, Li and co-workers carried out a replica work, using a replica catalyst and reported replica results and recommendations (Li et al., 2009). In an earlier study by Cao and co-workers, a similar procedure, results and recommendations were also reported although using a different heteropolyacid catalyst, $H_3PW_{12}O_{40}.6H_{20}$ known as (PW12) to transesterify a different oil, waste cooking oil.

Lewis, Bronsted, acids as catalysts have also been investigated for the purpose of converting vegetable oils into biodiesel in homogeneous and heterogeneous systems. Soriano and co-workers have investigated the use of two common Lewis acids, $AlCl_3$ and $ZnCl_2$, in biodiesel synthesis primarily to demonstrate an alternative catalyst for the simultaneous esterification of long chain fatty acid and transesterification of canola oil, which is a cheap vegetable oil and contains a high amount of free fatty acids, with methanol in the presence of terahydrofuran (THF) as a co-solvent to minimize the problems of limited mass transfer, via reducing the interfacial surface tension between the used alcohol and the oil, generally encountered in such heterogeneous systems so as to lead to an increased conversion (Ridwan et al., 2018). Being a stronger Lewis acid, $AlCl_3$ catalyzed the transesterification of canola oil far more effectively than $ZnCl_2$. Out of this work, a conversion of 98% was obtained provided that THF as co-solvent is used and that the molar ratio of methanol to canola oil is 24:1, reaction duration is eighteen hrs, reaction temperature is 100 °C and that the concentration of $AlCl_3$ is 5% (Soriano et al., 2009). A similar work was also carried out by (Deng et al., 2018).

Other related studies on transesterification can also be reported. Madje, et al. used B_2O_3/ZrO_2 and Bandgar, et al. used Envirocat EPZG and natural kaolinite clay, for the transesterification of β-ketoester, Chavan, et al. used Amberlyst-15, Ponde, et al. used natural kaolinite clay, Chavan, et al. used sulphated SnO_2 and Sasidharan, M. and Kumar, R. used zeolites, for the transesterification of ketoester (Madje et al., 2004; Bandgar et al., 2001; Chavan et al., 2001; Ponde et al., 1998; Chavan et al., 1996; Sasidharan and Kumar, 2004). Out of such studies, it can be concluded that a catalyst that can be suitable for the transesterification of β-ketoester can also be a suitable catalyst for the transesterification of other kinds of esters provided that the reaction conditions are right. Transesterification of soybean oil with methanol was carried out at 60, 120, and 150 °C in the presence of a series NaX faujasite zeolite, ETS-10 zeolite and metal catalysts. The stock zeolites were exchanged with potassium and cesium; NaX containing occluded sodium oxide (NaOx/NaX) and occluded sodium azide (NaOx/NaX). The catalysts were calcined at 500 °C prior to use in order to increase their activity. The ETS-10 catalysts provided higher conversions than the Zeolite-X type catalysts. The increased conversions were attributed to the higher basicity of ETS-10 zeolites and larger pore structures that improved intra-particle diffusion. Methyl ester yield increased with an increase in temperature from 60 to 150 °C. The metal catalysts increased conversion by one to over two order of magnitude over the homogeneous reaction with several zeolite catalysts performing better than the metal catalysts. The catalyst was reused without observed loss of activity. A preliminary design assessment showed that these catalysts are sufficiently active to be commercially viable contingent upon the costs of the catalysts achieving conversions in excess of 90% at temperatures below 125 °C (Suppes et al., 2004). Use of natural zeolite as a heterogenous catalyst for biodiesel production via transesterification of a waste kapok seed oil was examined by Sutrisno, et al. Out of this work, biodiesel with a yield of 84% was produced using 10% as a catalyst amount (Sutrisno et al., 2021). A related work in which natural zeolite is used again is reported elsewhere (Hartono et al., 2018). In another work, Du and co-workers, at optimal reaction conditions, have used NaY zeolite-supported La_2O_3 catalyst to transesterify castor oil and obtained a yield for biodiesel of 84.6% (Du et al., 2018). Alos, zeolites have extensively been used in transesterification reactions. Zeolites can be used as a catalyst in transesterification reactions for their generous surface area, high thermal stability and unique porosity (Albuquerque et al., 2008; Leon et al., 2010; Zheng et al., 2011; Chen et al., 2012; Wu et al., 2014; Chang et al., 2015; Soltani et al., 2017). They can also be prepared with a great control of their acidic/basic character tailored to the content of free fatty acids of the oil to be transesterified. Their acidic level can be boosted via protonation in which cations of the alumino-silicate cage, which are of a positive charge, are exchanged with protons. Also, elimination of water generated during hydration can induce their hydrophobicity promoting their activity (Sivasamy et al., 2009). Koh and Chung have used several proton-exchanged zeolites with different acidity and pore structure, such as: H+ ion exchanged MOR, MFI, FAU and BEA, with silica-lite which has no strong acid sites in the production of biodiesel by transesterification of waste frying oil. They found that H+ ion exchanged MOR(10) zeolite, which has more acid sites and stronger acidity strength than other used zeolites, exhibited the highest methyl esters yield as 95%. They also found that de-alumination to the HMOR zeolite induced decreasing of acid amount and acidity strength. The yield increased linearly with enhancing the acidity strength and increasing the amount of strong acid sites. Also, it was shown that the yield obtained out of the used catalysts was independent on pore structure of the zeolites (Koh and Chung, 2008). Also, transesterification of a waste oil with methanol in the presence of several Y-type zeolites with different Al_2O_3 contents was carried out by Brito et al. Viscosity of the product was lowered to that of biodiesel, although reaction temperature was too high, 476 °C (Brito et al., 2007). Zeolite HY catalyst activated by sodium ions, on its surface via an ion-exchange procedure, was used for the transesterification of triolein with methanol at 65 °C. A high biodiesel conversion of 97.3% and catalyst durability were reported for more than three cycles (Wang et al., 2013).

Seeking a high activity of heterogeneous (solid)-acidic catalysts, Kaita, et al. prepared a catalyst made out of aluminum phosphate for the purpose of transesterification of kernel oil using methanol as an alcohol. In their preparation, several metal-to-phosphoric acid ratios were selected, namely (1:3-1:0.01). Prepared catalysts were durable and thermally stable. In terms of reactivity and selectivity, prepared catalysts

demonstrated a sound reactivity and selectivity to methyl esters. Nonetheless, effective use of such catalysts may encounter some obstacles. One obstacle is that they employ quite high temperatures (200 °C). They also consume high amounts of alcohol, e.g., a methanol-to-oil molar ratio of 60:1 (Kaita, 2002). Production of biodiesel from mixed waste vegetable oils, with high contents of free fatty acids, using an aluminum hydrogen sulphate $Al(HSO_4)_3$ as a heterogeneous acid catalyst and methanol as an alcohol, was investigated by Ramachandran and co-workers. The maximum conversion of triglyceride was achieved as 81 wt.% with 50 min reaction time at 220 °C, 16:1 molar ratio of methanol to oil and 0.5 wt.% of catalyst. The high catalytic activity and stability of this catalyst was related to its high acid site density, hydrophobicity that prevent the hydration of –OH group and hydrophilic functional groups (–SO3H) that give improved accessibility of methanol to the triglyceride. The fuel properties of methyl esters (biodiesel) were found to be observed within the limits of ASTM D6751 (Ramachandran et al., 2011). Also, Jiang and co-workers have used sodium phosphate (Na_3PO4) as a solid heterogeneous catalyst for biodiesel preparation from rapeseed oil through transesterification with methanol. They investigated the effects of mass ratio of catalyst to oil, molar ratio of methanol to rapeseed oil, reaction temperature and rotation speed on biodiesel yield. The highest yield attained was 95% using a mass ratio of catalyst to oil of 3%, a molar ratio of methanol to oil of 9:1, a reaction temperature of 70 °C and a rotation speed of 600 rpm. During transesterification reaction for 8 runs, sodium phosphate (Na_3PO4) as a catalyst exhibited a superb reactivity and stability (Jiang et al., 2010). Stern and co-workers patented the production of linear mono-carboxylic acid esters with 6 to 26 carbon atoms via the alcoholysis of vegetable oils or animal fats using mono-alcohols, that have from 1 to 5 carbon atoms and a low molecular weight, in the presence of a catalyst with a spinel type structure and is selected from among zinc oxide, mixtures of zinc oxide and aluminum oxide and the zinc aluminates that correspond to the formula:

ZnAl.sub.2 O.sub.4, x ZnO, y Al.sub.2 O.sub.3

In the formula, x and y are each being in the range of 0-2. In one or more stages, the authors were able to directly produce an ester of multiple applications such as a fuel, combustible or pure glycerine (Stern et al., 1999). In another patent, a degummed/soapstock soybean oil, a turkey fat, a yellow grease as well as mixtures of partial acylglycerols oil, were methanolyzed using a catalyst of a mixture of calcium and barium acetates (Basu et al., 1996). In another recent work, Ferrero and co-workers used a glycerol-enriched heterogeneous catalyst, CaO, for biodiesel production from two triglyceride sources, soybean oil and waste frying oil. They evaluated the catalyst performance at different glycerol concentrations and reaction conditions (under ambient atmosphere). The used catalyst was most active when its mass ratio, during preparation, relative to the mass ratio of glycerol and methanol, was 1:1.6:13.4, respectively. They also prepared the catalyst using ethanol instead of methanol, although <4% differences in biodiesel conversion as a product were observed. The authors have found that a good quality biodiesel could be obtained from both tested triglyceride sources, soybean oil and waste frying oil, via a transesterification reaction at a temperature of 60 °C, a molar ratio of methanol to oil of 7:1 and a catalyst dose of 0.4 wt.%. Also, the authors have suggested that the glycerol by-product, for being rich in calcium soaps, can be used for the enrichment of animal diets. It was also observed that the catalyst could be reused for four cycles (Ferrero et al., 2015). Kafuku, et al. have used the sulphated tin oxide with silica ($SO4\ 2-/SnO2$ –$SiO2$) to catalyze the transesterification of croton megalocarpus oil with no need for a pretreatment. Out of this work, 95% biodiesel was obtained (Kafuku et al., 2010).

Also, Jacobson, et al. have employed a solid acidic catalyst, zinc stearate immobilized on silica gel, ZS/Si, for a simultaneous esterification of free fatty acids and transesterification of triglycerides of a low quality oil such as waste cooking oil containing 15 wt% free fatty acids. They used a molar ratio of alcohol to oil of 18:1, an amount of catalyst of 3 wt.%. A higher maximum ester yield than that obtained by the work of Kulkarni, et al., was obtained, 98 wt.%. However, to do so in both works, high temperatures of 200 °C had to be used although the used catalysts were recycled and reused with no loss in activity (Jacobson et al., 2008). Another heterogeneous catalyst of silica-supported niobia was employed for biodiesel production from a waste oil that, as previously mentioned, usually requires simultaneous esterification and transesterification reactions. Owing to the acidity of niobia, the used catalyst was successful in both reactions maintaining its reactivity for more than hundred hrs of use (Tesser et al., 2015).

Due to high surface areas as well as bespoke, that is uniform and large, pore sizes of surfactant-templated with metal oxides mesoporous heterogeneous catalysts and outstanding reusability as well as resistance against leaching of the supporting material, their use in biodiesel production has also been reported. Furthermore, physical and chemical properties of such catalysts can be altered via attaching certain functionalized organic groups to their surfaces or during their synthesis via condensation (Zhao et al., 1998; Stein et al., 2000; Xie and Zhao, 2014). In a study by 100, another synthesized catalysts, ZnO/SBA(Santa Barbara Amorphous)-15 and MgO/SBA-15 were used for the esterification of lauric acid. Due to the higher basicity of the latter catalyst than that of the former one, better conversions out of the use of the latter one were reported (Barros et al., 2013). Catalyzing the transesterification of palm oil using SBA-15 impregnated with a KOH solution, as a catalyst with a pore volume of 0.63 cm^3/g and a high surface area of 539 m^2/g, with methanol as an alcohol was tested by Abdullah and co-workers. They also performed the optimization process using the response surface methodology, RSM. The optimum conditions were found to be 70 °C for the reaction temperature, 11: 6 mol/mol for methanol to oil ratio, 3.91 wt.% for the catalyst loading and 5 h for the reaction time to achieve 93% of biodiesel yield. High catalytic activity was attributed to high surface area of the catalyst and the relatively easy diffusion of reactants in the mesopores. The effect of catalyst loading and reaction time was relatively more dominant in affecting the biodiesel yield. High potential of SBA-15 as a catalyst for biodiesel production was demonstrated (Abdullah et al., 2009). Also, catalyzing the transesterification of canola oil in a pressurized batch stirred reactor using a functionalized order mesoporous silicate, SBA-15 impregnated with cesium species ($CsNO_3$), as a catalyst with a pore volume of 0.837 cm^3/g and a high surface area of 628.15 m^2/g, with methanol as an alcohol was tested by Kazemian and co-workers. The aim of the authors was to test the effect of, two methanol: oil molar ratios of 20:1 and 40:1, catalyst concentration between 100 and 200 mg, reaction duration between three and twenty four hrs, as well as reaction temperature between 65 and 135 °C, on reaction's conversion. By allowing the reaction for five hrs, the authors found that the highest biodiesel yield, which was not any higher than 25.35%, was achieved with using the higher methanol: oil molar ratio, the highest reaction temperature and the lowest catalyst concentration, they have examined (Kazemian et al., 2013). Albuquerque and co-workers tested the catalytic activity of SBA-15 impregnated with several ratios of calcium acetate (CaO) in the transesterification of ethyl butyrate with methanol. To do so, they added several catalyst concentrations between 0.4 and 1.6 wt.% mg to the reaction. At an average concentration of 1 wt.%, the conversion was the highest, indicating that SBA-15 impregnated with several ratios of calcium acetate (CaO) is a highly catalytic catalyst for such a reaction (Albuquerque et al., 2008). In a separate investigation, a mesoporous catalyst, MgO, of a surface area of 32.9 m^2/g and of a good transportation structure in the presence of a template-MgO with a surface area of 79.6 m^2/g was used in the transesterification of a canola oil in methanol using a batch reactor. A conversion of 96.5% was obtained when: the methanol: oil molar ratio was 20:3, reaction temperature was 190 °C, catalyst concentration was 3 % and the reaction duration was for two hrs (Jeon et al., 2013).

In order to improve the catalytic performance, mesostructured materials such as, but not limited to, Amberlyst-15 and Nafion have been developed for biodiesel production. Ttransesterification of sunflower oil in the presence of Amberlyst-15, acidic styrene divinylbenzene sulfonated ion-exchange resin, has been reported by Vicente and others. They have found that at a somewhat low temperature, 60 °C, oil conversion was quite poor, not more than 0.7%. Although this conversion is not satisfactory, it is; however, a mandatory option to evade from catalyst degradation (Vicente et al., 1998). Talukder and co-workers have used Amberlyst-15 for the purpose of transesterification of a waste oil of palm fatty acid distillate. A biodiesel yield of 97% was obtained with a multiple usages of Amberlyst-15 while no loss in its catalytic activity was reported (Rahman et al., 2009). Huang and co-workers have used Amberlyst-15 catalyst for the pretreatment of trap grease for the purpose of biodiesel production. Catalyst used was stable after 10 times of use and was capable to reduce the acid value from 100 to only 1.3 mg KOH/g in the produced biodiesel (Huang et al., 2011). In fact, biodiesels with a low acid value/number are better than those biodiesels that possess a higher acid value/number. A high acid value/number of a biodiesel is an indication of corrosive biodiesel, presence of water; thus, poor production and susceptibility to oxidative degradation (Bello et al., 2012). Boz, et al., have also investigated the production of biodiesel through a simultaneous esterification and transesterification reactions of another waste cooking oil. They have used Amberlyst-15 and a modified Amberlyst-15 as catalysts and methanol as an alcohol. Again, a biodiesel yield between 75 and 81% was obtained when the non-modified Amberlyst-15 was used (Boz et al., 2015). Simone, et al., have investigated the transesterification of several Brazilian vegetable oils such as babassu coconut, corn, palm, palm kernel and soybean with methanol at 60 C in the presence of several ion-exchange resins of different structures such as Amberlyst-15, Amberlyst-31,

Amberlyst-35 and Amberlyst-36. Transesterification was successfully achieved using these catalysts, with a maximum methyl ester (biodiesel) yield obtained via Amberlyst-15 from palm kernel oil, perhaps due to its high content of shorter- chain free fatty acids, in comparison to the other catalysts used and oils of babassu coconut and soybean, respectively. Such findings may reveal that the activity of the used resin depends on the composition of free fatty acids found in the used oil (Simone et al., 2005). In addition, the viability of Amberlyst-45 for the direct transesterification of a refined corn oil (Tegut) and used frying vegetable oil with a high acidity and a high water content to biodiesel using methanol and ethanol as alcohols was studied. With both alcohols for both oils, Amberlyst-45 catalyst was shown to be an efficient catalyst. It exhibited a great performance despite high acidity and high water concentration of oils examined. Also, it was recycled and reused for five cycles with no indication of loss in its catalytic activity. In order to be effective; however, Amberlyst-45 requires a high reaction temperature and is responsible on producing glycerol ether as a by-product that requires a separation procedure (Cabral et al., 2020). Recently, batch and continuous esterification of waste cooking oil using Amberlyst-15 coupled with poly-vinyl alcohol (PVA) membrane as a catalyst system with methanol as an alcohol was investigated. In this investigation, it was demonstrated that the catalyst system exhibited a high activity and reusability whether in batch as well as continuous mode of operation. Also, it was demonstrated that it is with a great potential in biodiesel production from a waste cooking oil since the produced biodiesel exhibited a good properties that are compatible with current diesel engines (Zhang et al., 2020). Production of biodiesel from soybean and jatropha curcas oils using Amberlyst-15 catalyst in the presence of co-solvents was reported in a study by Calgaroto, et al. Among the oils tested, jatropha curcas oil gave more biodiesel, around 70 wt% as a yield was achieved at mild conditions. Surprisingly; however, presence of co-solvents within the reaction environment was with a negative effect on biodiesel yield. Reusability of amberlyst-15 catalyst was not out of reach (Calgaroto et al., 2013). In another work by Ridwan and others; understandably, it was shown that use of THF as a co-solvent brought a positive influence on conversion of free fatty acids. Amberlyst-15 catalyst was also used for the purpose of transesterification of different oils in another works (Liu et al., 2008; Mbaraka and Shanks, 2005; Mbaraka and Shanks, 2006; Sim and Kim, 2011; Pappu et al., 2011; Ray and Ajay, 2016). In order to produce biodiesel, Guerreiro and co-workers have used solid acid catalysts, at 60° C and atmospheric pressure, including: Nafion membranes, ion-exchange resins and PVA membranes containing sulphonic groups, to transesterify soybean vegetable oil with methanol. They used Nafion and PVA membranes in the form of film in a membrane reactor. They were able to produce biodiesel with a higher activity of the catalyst PVA membrane modified with sulfossucinic acid. The obtained concentration profiles with the catalysts in the form of pellets exhibited an initial induction period, which disappeared when the reaction is performed in the membrane reactor. Peng and co-workers, following preparing and characterizing a solid acidic catalyst comprising $SO_4^{2-}/TiO_2–SiO_2$, have investigated its activity for the production of biodiesel from several low cost feedstocks with a high free fatty acids content using methanol as an alcohol. They found that such a catalyst can be recycled, easily removed, stable and can simultaneously catalyze esterification and transesterification. Optimum transesterification reaction conditions were: reaction temperature 200 °C, molar ratio of methanol to oil 9:1 and catalyst concentration 3 wt.%. A continuous process for biodiesel production from such cheap raw feedstocks was proposed, and a 10,000-tonnes/year biodiesel production demonstration plant has been built (Peng et al., 2008).

3. Summary

According to the literature cited; however, in biodiesel production, use of chemically-based acidic heterogeneous (solid) catalysts in the transesterification of triglycerides of an oil or a fat is initially associated with the formation of three phases, oil, solid catalyst and alcohol, due to mutual immiscibility by which a good contact between these reacting materials can be hindered; thus, lowering the rate of transesterification reaction (Kulkarni et al., 2006; Lotero et al., 2006). Thus, reaction conditions, in comparison to homogenous catalysts, are usually intensified; reaction temperature is elevated between 60 and higher than 450 °C, catalyst amount is increased between 3 and 10 wt.% as well as a higher alcohol to oil molar ratios between 10:1 and 25:1 are used. This, unfortunately, renders use of such acidic heterogeneous catalysts an energy intensive costly process. With the use of such heterogeneous catalysts, low mass transfer is also observed due to their small surface area with which a low contact between such catalysts and the reactants is caused. Hence, reaction duration is prolonged while the yield of biodiesel is reduced. To avoid this and to enhance mass transfer among reactants, a compromise between the rate of diffusion by the formation of two phases of fluid and shifting of the reaction towards biodiesel production should be made. To do so, the initial concentration of the used alcohol should be well-determined (Encinar et al., 2010). Equally useful is to use some co-solvents that could improve the miscibility of oil, to be transesterified, and the used alcohol so as to the rate of transesterification reaction could be improved. Such co-solvents include ethanol and n-hexane, THF or di-methyl sulfoxide (DMSO) (Zabeti et al., 2009). However, in case a co-solvent is used, bigger and particular while leak proof-reacting vessels are required. A facility to completely remove the used co-solvent from the produced biodiesel is also required (Sani et al., 2012). Deterioration of catalytic reactivity of such heterogeneous catalysts with time via catalyst poisoning, sintering, coking and leaching is another hurdle that may limit their application in the transesterification reactions of used oils, in particular (Lam et al., 2010). Also, use of heterogeneous acidic catalysts in transesterification reactions for the purpose of production of biodiesel suffers from the high cost of the catalyst and from a difficulty in the separation of small catalyst particles via filtration. Moreover, use of such catalysts with a narrow pore size distribution for biodiesel production may suffer from lower penetration of large particles of free fatty acids of the oil. Such catalysts also suffer from matrix-bound acidic sites and high molecular weight/active-site ratios.

An alternative of such ordinary heterogeneous catalysts is heterogeneous nano-catalysts that rely on altering the elemental composition, surface functionality and/or number of atoms within the structure of the particle(s) of the heterogeneous catalyst. It has been reported that a heterogeneous nano-catalyst could deliver a higher activity and a higher selectivity while showing a higher stability (Thangaraj et al., 2016; Uddin and Chowdury, 2007; Thangaraj et al., 2015). It is beyond the scope of this paper to further discuss heterogeneous nano-catalysts.

4. Conclusion

Transesterification reaction alone or with esterification reaction carried out simultaneously catalyzed by several acidic heterogeneous catalysts has been effective for biodiesel production although the nature of the feedstock oil, in terms of the content of free fatty acids; in particular, employed is a pivotal factor. Also, it has been observed that progress of such two reactions is severely dependent on conditions maintained. Despite the successfulness of heterogeneous catalysts in catalyzing both reactions, use of such catalysts is inevitably associated with high reaction temperatures, law mass transfer rates and prolonged reaction times, etc. Having said this; however, heterogeneous catalysts are advantageous as they could be recycled and reused with a negligible loss in their activity. Compatibility of the produced biodiesel via such catalysts to ASTM standards should be ensured. Anyway, it seems that such hurdles could be partially overcome by replacing heterogeneous catalysts by heterogeneous nano-catalysts.

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