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Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel

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Abstract: Solid acid (heterogeneous) catalysts have a unique advantage in esterification and transesterification reactions which enhances the use of high acid value oil to be used as feedstock for synthesis of biodiesel. Various solid acid catalysts such as resins, tungstated and sulfated zirconia, polyaniline sulfate, heteropolyacid, metal complexes, sulfated tin oxide, zeolite, acidic ionic liquid, and others have been explored as potential heterogeneous catalysts. The activity of the catalyst differs slightly resulting in moderate to high conversion and yield. The reuse of the solid catalyst is governed by their deactivation, poisoning, and the extent of leaching in the reaction medium. The applicability of these catalysts for synthesis of biodiesel along with their reusability aspect is discussed in this review. © 2010 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: solid acid catalysts; calcinations; activity; leaching; reuse; biofuels

Introduction

Development of heterogeneous catalysts has been a relatively recent area of research in the synthesis of biodiesel. The need for development of heterogeneous catalysts has arisen from the fact that homogeneous catalysts used for biodiesel development pose a few drawbacks. These drawbacks include washing of biodiesel with water to remove the catalyst present which results in wastewater generation and loss of biodiesel as a result of water washing.

Heterogeneous catalysts have the benefit of easy separation from the product formed without requirement of washing. Reusability of the catalyst is another advantage of the heterogeneous catalyst.

Heterogeneous catalysts are categorized as solid acid and solid base. Solid base catalysts include a wide group of compounds in the category of alkaline earth metal hydroxides, hydrotalcites/layered double hydroxides, alumina loaded with various compounds, zeolites, and various other compounds showing high basicity coupled with active basic

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sites, pore size, and other parameters. Solid base catalysts have been quite successful with high conversion and yield of biodiesel obtained. However, they are sensitive to the presence of free fatty acids and thus solid acids have a preference over solid base catalysts. Excellent review papers on solid catalysts are available.[1–6] This review focuses exclusively on solid acid catalysts as potential heterogeneous catalysts for biodiesel synthesis applied in recent publications. Solid acid catalysts have been used in various industrial applications. The solid acid catalysts differ in acidity, surface area, mechanical resistance, thermal and hydrothermal stability, and cost of production. Hence, a catalyst may be chosen on the requirements needed for synthesis of a compound. Nevertheless, they indeed are good alternates to the homogeneous catalysts such as H_2SO_4 and HF.[5] Heterogeneous solid acid catalysts can simultaneously catalyze esterification and transesterification reactions.[6] Thus, the application of such catalysts, which are efficient in both of these reactions, is preferable as most non-edible oil and waste cooking oil possesses high acid value that cannot undergo alkaline transesterification without reduction in acid value. In such feedstock with high acid value, biodiesel synthesis becomes a two-step process with acid esterification reaction followed by alkaline transesterification. In addition to their easy removal and reusability, solid acid catalysts do not cause corrosion as found with common acid homogeneous catalysts, such as sulfuric acid. As the heterogeneous catalysts are insoluble in the oil and methanol phase, they require high temperature for an optimum yield of biodiesel. The application of heterogeneous catalysts for production of biodiesel in the industrial perspective warrants for minimal energy requirement. This can be achieved if the heterogeneous catalysts are prepared easily and need moderate reaction conditions. The leaching aspect is another important criterion that governs the suitability of a particular catalyst. Hence, there is a need for development of heterogeneous catalysts that can produce biodiesel at conditions (e.g. temperature and pressure) comparable to that used in homogeneous catalysis.[7] This review deals with the recent publications dealing with catalyst preparation, operating reaction conditions, reusability, and feasibility of the catalyst.

Solid base catalysts have higher catalytic performance for transesterification than solid acid. However, the latter is preferred over the former because of simultaneous esterification and transesterification for feedstock possessing high acid value.[8]

Solid acid catalyst

In general, a catalyst that is to be used for synthesis of biodiesel should be selective, specific, and result in esterification/transesterification with high conversion and yield of biodiesel. A solid acid catalyst should posses high stability, numerous strong acid sites, large pores, a hydrophobic surface providing a favorable condition for reaction, and should also be economically viable.

Resins and membranes

Ion-exchange resins are composed of copolymers of divinylbenzene, styrene, and sulfonic acid groups grafted on benzene. Their catalytic activity depends strongly on swelling properties as swelling capacity controls the reactant's accessibility to the acid sites and hence their overall reactivity. Ion-exchange resins have often been used for esterification as well as transesterification reactions. These ion-exchange resins have a cross-linked polymeric matrix on which the active sites for the esterification reaction are due to protons bonded to sulfonic groups.[9] The surface area and pore size distribution of the resin is characterized by the content of the cross-linking component. Lower cross-linking is known to cause higher swelling of ion-exchange resins. Swelling capacity, in turn, controls the reactant's accessibility to the acid sites and thereby their total reactivity. Even with a low swelling capacity, the ion-exchange resin has higher pore diameter which can let the entrance of free fatty acids (FFAs) to the inner surface of the catalyst leading to a better esterification reaction.

Cation exchange resins (NKC-9, 001 × 7 and D61) were tried by Feng *et al.*[10] and found to be effective in esterification of high acid value (13.7 mg KOH/g) feedstock of waste cooking oil (WCO) origin. NKC-9 had high water-adsorbing capacity favoring its role in effective esterification. A high average pore diameter of NKC-9 was helpful for reactants to access the active sites of the resin resulting in greater than 90% conversion. The reaction conditions were 6:1 (alcohol to oil) molar ratio, 24 wt% of the catalyst at 64°C for 4 h of reaction time. The catalyst NKC-9 further reused up to

10 runs. The activity of the catalyst in subsequent reuse did not deteriorate, but rather it was enhanced. This has been attributed to the breakdown of the resin particles by mechanical agitation, which increased the surface area of the resin. After 10 runs, there was loss of the catalyst during separation which ultimately decreased the free fatty acid (FFA) conversion, so new resin was added. Kitakawa et al.[11] tried anion-exchange and cation-exchange resins as heterogeneous catalysts for batch and continuous transesterification reaction of triolein in an expanded bed reactor and found anion-exchange resin to perform better than the cation-exchange resin. The reason attributed to better performance of anion-exchange resin was the higher adsorption affinity of alcohol on resin rather than triolein. The lower cross-linking density and smaller particle size played more significant roles in enhancing the reaction rate than porosity and caused high reaction and high conversion rates. A high conversion of 98.8% was achieved with the optimized reaction conditions. The catalytic activity decreased in the subsequent run due to leaking of hydroxyl ions from the resin. A three-step regeneration method was adopted for the reuse of the catalyst, and for four runs similar activity of the catalyst was achieved. Ozbay et al.[12] observed high average pore diameter with high BET (Brunauer, Emmett, and Teller) surface area to be more effective than high swelling (low cross-linking level) of ion-exchange resin (Amberlyst-15) in esterification reaction with waste cooking oil as feedstock. High pore diameter enabled the free fatty acid molecules to enter the inner surface of the catalyst and enhance the esterification rate. Although moderate conditions (60°C and 2% catalyst) were sufficient for the reaction, the conversion of FFA to biodiesel was low (45.7%). This low conversion is a limitation of the study and further enhancement of the reaction conditions is warranted for the feasibility of the catalyst for esterification reaction.

Gelular and microporous type ion-exchange resins (EBD 100, EBD 200, EBD 300) were studied by Russbueldt and Hoelderich[13] and found to be successful for conversion of high FFA oil to biodiesel. The catalysts used were EBD-100 (with gelular polymer matrix), EBD-200 and EBD-300 (microporous resins), and Amberlyst-15. The low cross-linking in EBD-100 caused high methanol uptake which increased the catalyst volume 4.8 times by swelling in

methanol. The other resins (EBD-200 and EBD-300) had lower methanol uptake than EBD-100. 100% conversion was obtained by EBD-100 and EBD-200 catalysts. With EBD-300, 81% conversion was obtained. The activity of the catalysts decreased in subsequent runs and to almost negligible in the fourth run. The possible reason for deactivation was attributed to the presence of salt contaminants in the sunflower oil which blocked the acid sites. Thus, desalting the feedstock has been suggested as precursor for the transesterification of the feedstock with ion-exchange resin catalysts. Addition of small amounts of water was found to have only little influence on the completion of the reaction as water was trapped in the methanol phase, and not on the methyl ester in the oil phase, which maintained high conversion of feedstock to biodiesel.[13] A cation-exchange resin (D002) has been shown to effectively catalyze rapeseed oil deodorizer distillate of high FFA value of 48.80 ± 1.46 wt% corresponding to acid value of 97.61 ± 1.87 mg KOH/g. A high yield of 96% was obtained by 18 wt% catalyst at 9:1 alcohol to oil (A:O) molar ratio at 60°C for 4 h in a column reactor. The catalyst was reused effectively for 10 cycles with a yield greater than 88%.[14]

A solid acid catalyst, poly vinyl alcohol (PVA) cross-linked with sulfosuccinic acid possessing sulfonic acid groups for transesterification of soybean oil, was found to be efficient and superior to commercial resins such as Nafion membranes and Dowex resins. Higher content of sulfonic groups led to better performance by the PVA polymer cross-linked with sulfosuccinic acid. Better catalytic activity of PVA has also been attributed to high swelling capability of PVA in oil and less in methanol. Due to this, oil concentration was found to be more with PVA than with Nafion, resulting in higher catalytic activity with PVA as catalyst. The reverse happened with Nafion membrane as catalyst, where swelling was observed in methanol but not in soybean oil. Swelling of Nafion membrane in methanol made the catalyst lipophobic, resulting in a low reaction rate.[15] Dowex monosphere 550 resin has been effective for esterification and transesterification of oils with higher FFA content. A conversion of 80% was obtained at approximately 6:1 A:O molar ratio, 2 wt% catalyst, 45°C, and 200 rpm stirring. Regeneration of the catalysts after each experiment was desired because the conversion was reduced to 25% after the first run. However, a leaching study of the

catalyst wasn't conducted, which could have provided an insight into the heterogeneity of the catalyst.[16]

The effect of water on the esterification of FFA by solid acid catalyst has been studied by Park *et al.*[17] Amberlyst-15 was found to be poisoned by the presence of water in the reaction medium and its activity was substantially reduced in comparison to the homogeneous sulfuric acid catalyst. The presence of water resulted in poor accessibility of reactants to the acid sites. This was overcome by a two-step esterification process (addition of fresh methanol and catalyst to the reactants in the second step), which increased the reaction rate and reduced the reaction time. In the case of H_2SO_4, presence of water up to 5 wt% was found to be tolerable when the methanol to oil ratio was 6:1.

The synthesis of biodiesel from silica functionalized with 4-ethyl-benzene sulfonic acid catalyst was carried out by Aiba-Rubio *et al.*[18] Leaching was found to be predominant in the first run and slowed down in subsequent runs. A high temperature of 150°C deterred regeneration of the catalyst for reuse as the organosulfonic acid sites were found to be combusted. A significant difference in the activity of the catalyst was observed between the first and second runs, whereas the reaction rate was found to be similar for the second, third, and fourth runs, which suggested that deactivation of the catalyst occurred in the first run. All of the products and reactants in general, and glycerol in particular, were responsible for leaching of the catalyst. This leaching was dominant in the first run which has been attributed either to the loss of active acid sites or activity of acid sites in formation of deactivating organic species. Thus, regeneration of the catalyst isn't possible because the organosulfonic group will be combusted. Ion-exchange resins have also found their applicability in purification of biodiesel when a homogeneous catalyst, sodium methoxide, was used. Although the ion-exchange resin wasn't so efficient in removal of methanol, it brought the glycerol level to the EN 14214 specification.[19] Table 1 depicts the reaction conditions of resins and membranes used as heterogeneous catalysts.

Superacid catalysts (Tungstated and sulfated zirconia)

Acids that are stronger than $H_o = -12$ corresponding to the acid strength of 100% H_2SO_4 are called 'super acids'.

Common super acids include HF (a Brønsted acid) and BF_3 (a Lewis acid).[20] Zirconia has shown catalytic activity, and also a good support for catalysts, owing to its high thermal stability, stability under oxidizing and reducing conditions, and the amphoteric character of its surface hydroxyl groups. Sulfated zirconia and tungstated zirconia are examples of solid super acids and exhibited high catalytic activities because of active acid sites.[21] Tungstated zirconia–alumina (WZA), sulfated tin oxide (SO_4/SnO_2; STO), and sulfated zirconia–alumina (SZA) were tried as solid super acid catalysts for transesterification of soybean oil and esterification of n-octanoic acid. More than 90% conversion during transesterification was obtained at a temperature of 250°C with WZA, with soybean oil as feedstock. During esterification of n-octanoic acid, the catalysts WZA, SZA and STO showed 94, 99, and 100% conversion at 175°C. Conversion of WZA and SZA catalyst further increased to 100% at 200°C.[22] Various solid acid catalysts such as Amberlyst-15, Nafion-50, supported phosphoric acid, sulfated zirconia (SZ), tungstated zirconia (WZ), zeolite Hβ, and ETS-10 H, along with solid base catalysts, were compared with that of conventional homogeneous acid and base catalysts for transesterification of triacetin by Lopez *et al.*[23] To obtain 50% conversion with the solid acid catalysts, a large variance in time was recorded. While only 10 min was needed for 50% conversion of triacetin, the times needed by the solid acid catalysts were 150, 330, 538, and 2047 min for Amberlyst-15, SZ, Nafion-50, and WZ, respectively. The catalysts showed decrease in triacetin conversion (40–67%) after five reaction cycles of 2 h each. The concentration of the species related to active sites showed 80–95% of the original values and hence the cause of deactivation was attributed to site blockage by adsorption of intermediates and/or products formed that are more polar than the original reactants.

Esterification of acetic acid and transesterification of triacetin by tungstated zirconia (WZ) were performed by Lopez *et al.*[24] The effect of calcination temperature on the experiments and the nature of active sites for esterification and transesterification reaction were observed. When calcined at 400°C, the X-ray diffractogram showed the catalyst to possess amorphous structure and small crystallites of tetragonal zirconia. At high calcination temperature (500–800°C), the catalyst was comprised primarily of tetragonal

phase of zirconia. At ≥800°C calcination temperature, crystalline WO_3 particles were formed. Increase in calcination temperature resulted in loss of total surface area of the catalyst which was due to loss of surface area of ZrO_2 structure. This resulted in transformation of tungsten oxide from monomeric to polymeric species. Calcination temperature was found to strongly influence activity of the catalyst for both the esterification and transesterification reactions, with the optimum at 800°C. Loss of catalytic activity occurred due to disappearance of heteropolyoxotungstate clusters, suggesting it to be the catalyst active site.

Calcination temperature plays an important role in the activation of the solid acid catalyst. A pioneering work on this aspect has been done by Kiss et al.[25] where calcination temperature of 600–700°C has been found to be optimum for sulfated zirconia catalyst for esterification of fatty acids. Modified zirconias, namely titania zirconia (TiZ), SZ, and WZ, have been used as heterogeneous catalysts for simultaneous esterification and transesterification by López et al.[26] The optimum calcination temperature was found to be different for the three modified zirconias. The optimum calcination temperature was found to be 500°C for SZ and 400–500°C for TiZ. Temperature higher than this results in sulfur loss, which decreases the catalyst's surface area and ultimately loss of its activity. Presence of sulfate ions stabilizes the zirconia structure and increases the surface area. Of the three catalysts, WZ showed better activity over SZ because of the easy generation of the former in the fixed bed reactor. Also, SZ will have to be re-impregnated with H_2SO_4 for its regeneration which could lead to leaching of sulfur and may be a hindrance in the production of biodiesel. TiZ, although suitable for transesterification, was not found to be suitable for esterification because of poisoning of its active basic sites by carboxylic acids and hence has been reported to be unsuitable for higher acid value feedstocks.

Zirconia-supported isopoly tungstate (WO_3/ZrO_2) was prepared by impregnation of ammonium metatungstate, and was used for transesterification of sunflower oil. Another catalyst, zirconia-supported heteropoly tungstate was prepared by the impregnation of silicotungstic acid and phosphotungstic acid on zirconium oxyhydroxide. The activity of zirconia-supported isopoly tungstate was better than zirconia-supported heteropoly tungstate. WO_3/ZrO_2 catalyst

calcined at 750°C gave 97% conversion of the feedstock to biodiesel at 200°C with 15:1 methanol to oil molar ratio. The catalyst was reused successfully after separating and calcined at 500°C for 3 h in air. The catalyst was also used to convert sesame and mustard oil to biodiesel, where conversion of 93% and 95%, respectively, were obtained. After removal from the solution of methanol, the catalyst showed minor conversion of 7% and displayed potential prospect as a heterogeneous catalyst.[27]

WO_3/ZrO_2 was pelletized and used in packed-bed continuous reactor by Park et al.[28] for conversion of high FFA feedstock. Hexane and biodiesel were found to be good solvents to enhance the miscibility of the oil and methanol, resulting in yield of 65% in 1 h but took substantial time (20 h) to rise to 85%. However, the conversion decreased thereafter to 65% when the reaction time was increased to 140 h. The reason attributed to this decreased yield with reaction time is the deposition of soybean oil on the particles of the catalyst and reduction of WO_3 by the feedstock oleic acid. The catalytic activity was restored by calcination in air. Pelletized catalyst resulted in less FFA conversion compared to that from the powdered catalyst due to reduced BET surface area and pore size distribution. The conversion of 65% was maintained for 140 h. Although Park et al.[28] advocate packed-bed reactor for large scale production of biodiesel using pelletized catalyst, a low yield in comparison to powdered form deems further justification. Leaching of SZ and impact of alcohol on its deactivation at higher temperature was carried out to see its potential as a heterogeneous catalyst by Suwannakarn et al.[29] It was found that at 100°C almost 70% of the sulfate ion in the form of sulfuric acid was leached from the solution, exhibiting homogeneous nature of the catalyst. The ability of the sulfate to leach from sulfated zirconia was attributed to the presence of –OH groups in the alcohol. Sulfuric acid reacted with alcohol to form monoalkyl hydrogen sulfate and dialkyl sulfate.

Sulfated zirconia catalysts were prepared using different methods (such as solvent-free precipitation) by Garcia et al.[30] to examine their activity as heterogeneous catalysts. Only SZ prepared by solvent-free method gave an efficient conversion (98.6% in methanol and 92% in ethanol) of soybean oil to biodiesel in 1 h reaction time at 120°C. This has been attributed to the high quantity of acid sites. Low conversion with

Table 1. Resins and membranes as heterogeneous catalysts.

Catalyst	Feedstock, Acid value	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Reaction conditions			Conversion (C)/Yield (Y) (%)	References
					Molar ratio (alcohol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)		
Zeolite, Ion-exchange resin, Metal oxides (sulfated zirconia)	Dodecanoic acid	Sulfated zirconia catalyst: 50 g $ZrOCl_2.8H_2O$ was dissolved in 500 ml water followed by precipitation of zirconium hydroxide at pH = 9 using ammonia solution. $Zr(OH)_4$ was washed with water to remove Cl^- ions. $Zr(OH)_4$ was dried 16 h at 120°C and impregnated with 1 N H_2SO_4 and calcined in air	Sulfated zirconia catalyst: Surface area = 118 $m^2\,g^{-1}$ Specific pore volume = 0.099 $cm^3\,g^{-1}$ Average pore size = 3.0 nm	650, 3	3:1	1, 140–180	3.0	C = 96	4
Amberlyst 15, 16; Relite CFS	Soybean Waste fatty acids (Oleins), 50% Acidity	Resins were dried in a ventilated oven for 24 h at100°C	Not done	Not done	8:1	30 min, 120	5 g	C = 95	9
Cation-exchange resin (NKC-9, 001 × 7, and D61)	Waste fried oil, 13.7 mg KOH/g	NKC-9 was washed with deionized water and transformed with 1 M HCl.	Surface area = 77 m^2/g Average pore diameter = 56 nm	Not done	6:1	4, 64	20	C = 90	10
Anion/cation-exchange resin	Triolein (63% purity); Rest part (37% was impurity & unreactive)	Anionic exchange resin in chloride form was mixed with 1 M NaOH to displace chloride ions with hydroxyl ions.	Not reported	Not done	10:1	4, 50	40 (i.e. 4 g)	C = 98.8	11
Acidic ion-exchange resin (Amberlyst & Dowex)	Waste cooking oil Acidity = 0.41–0.47 wt%)	Amberlyst & Dowex resins were dried in an oven for 12 h after methanol washing.	Amberlyst (A-15) Surface area = 53 m^2/g Average pore diameter = 30 nm Porosity = 33%	Not done	20 vol%	100 min, 60	2.0	C = 45.7	12
Resin i) Gelular EBD 100 ii) Macroporous (EBD 200 EBD 300) iii) Amberlyst-15	Sunflower 0.6% FFA Rapeseed 0.6% FFA Used frying oils 15.7% FFA	Resin was dried by washing thrice with with 100 ml methanol for 1 h before use.	Micropore size = 1 nm Macropore size = 100 nm Inner surface area = 40 m^2/g Spherical particle of size 0.5 mm diameter	Not done	Not mentioned	24, 120	1.0	C = 100	13

Table 1. Continued

Catalyst	Feedstock, Acid value	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Molar ratio (alcohol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
						Reaction conditions			
Cation-exchange resin (D002, 002CR, 732)	Rapeseed oil deodorizer distillate, 48.80 ± 1.46 wt% FFA	The experimental resin was immersed in 5% HCl-ethanol mixture solvent for 30 min. and eluted with ethanol until neutral pH and dried in an oven at 70°C for 2 h	D002 Particle size = 0.05 mm, Cross linking density = 32% 002CR Particle size = 1.25 mm, Cross linking density = 38% 732 Particle size = 1.02 mm, Cross linking density = 35 ± 1%	Not done	9:1	4, 60	18.0	Y = 96	14
PVA5, PVA20, PVASS 20: cross linked with sulfosuccinic acid	Soybean oil	PVASS 20 membrane was prepared by esterification of 5-sulfosalicilicacid on the remaining hydroxyl group of a cross-linked PVA matrix	PVASS 20 Thickness = 0.14 mm Swelling (%) in methanol = 18.9	Not done	Not mentioned	–, 60	Not mentioned	Not mentioned	15
Dowex monosphere 550 A	Ideal frying oil (10% Oleic acid) FFA = 10.684% Soybean oil	Not done	Not done	Not done	6.128:1	2, 45	2.267 wt%	C = 80	16
Silica functionalized with 4-ethyl-benzene sulfonic groups	Sunflower	Commercial grade	Particle size = 40–63 μm	Not done	6:1	5, 150	1.5 wt%	Y = 60	18

ethanol has been attributed to the presence of 0.44% water in ethanol compared to 0.08% in methanol. Conversion with ethanol further increased to 96% when reaction was carried out for 6.5 h. However, the limitation observed with SZ was leaching of sulfate ions which resulted in significant deactivation of the catalyst when reused. No conversion was obtained with conventional zirconia, whereas standard sulfated zirconia prepared by precipitation and impregnation method gave a poor conversion of only 8.5 ± 3.8% under the same conditions.

Lou et al.[31] reported on sulfated zirconia and niobic acid ($Nb_2O_5.nH_2O$) used as catalysts for esterification and transesterification of waste cooking oils with high (27.8 wt%) FFA content to give a low yield of 44 and 16%, respectively, in 14 h reaction time. WO_3/ZrO_2, SO_4^{2-}/ZrO_2, and Amberlyst 15 were used as heterogeneous catalysts by Park et al.,[32] with all catalysts giving 93% conversion of FFA-bearing used cooking oil. However, SO_4^{2-} was leached in the reaction medium using SO_4^{2-}/ZrO_2 as catalyst, lessening its application as a catalyst. Among the three catalysts, 20 wt% WO_3/ZrO_2 showed high catalytic activity and structural stability. WO_x/ZrO_2 in nanoparticle size supported on MCM-41 silica exhibited acidic properties and was found to be suitable for esterification of oleic acid. 100% conversion was obtained with WO_3 loading of 15–20 wt% after activation at 700°C. The catalyst was found to be stable even after being operated at 200°C and was reusable for four cycles without leaching of tungsten. However, the reaction conditions were a problem. A high molar ratio of 67:1 A:O for 24 h reaction time and 18.7 wt% of catalyst at 65°C was needed for completion of the reaction. High amount of methanol and high reaction time increases the overall production cost of biodiesel.[33] A similar loading of WO_3 on ZrO_2 (i.e. 20 wt%) was observed to be optimum for 96% FFA conversion from waste acid oil by Park et al.[34] under optimized reaction conditions, which included 9:1 A:O molar ratio, 0.4 g of catalyst/ml of oil, at 150°C for 2 h. Although tungsten leached in the reaction, the catalytic activity was unaffected.

The catalytic activity and stability of sulfated zirconia and sulfated titanium oxide were improved by addition of lanthanum.[35] SO_4^{2-}/ZrO_2–TiO_2/La^{3+} prepared by precipitation and impregnation method for synthesis of biodiesel showed 95% conversion efficiency and decreased to only 5% even

after five runs. Loading lanthanum on the surface of ZrO_2–TiO_2 changed the chemical state of exterior atom and also strengthened the interaction of SO_4^{2-} with ZrO_2–TiO_2. The catalyst was observed to be stable for the purpose of its reuse and its activity was found to be better than SO_4^{2-}/ZrO_2–TiO_2 catalyst. Li et al.[36–37] observed the same SO_4^{2-}/ZrO_2–TiO_2/La^{3+} to work effectively for soapstock as feedstock. The conversion efficiency of esterification and transesterification was found to be 98.02 and 97.25% respectively, under moderate reaction conditions. The catalyst SO_4^{2-}/ZrO_2–TiO_2/La^{3+} was also observed to be effective for simultaneous esterification and transesterification of oil containing 60 wt% FFAs. The catalyst developed was reused for five times without any treatment and the yield observed after five cycles was 90.20 wt%, which is near the 92.8% yield obtained after the first cycle. Kansedo et al.[38] prepared biodiesel from Cerbera odollam using sulfated zirconia catalyst. Although optimization of variables affecting the reaction was not taken in account, a high yield of 83.8% was obtained.

A carbon-based solid acid catalyst was prepared by Shu et al.[39] by carbonizing vegetable oil asphalt and petroleum asphalt. The high catalytic activity observed owing to its high density and stability of acid sites, loose irregular network, and the hydrophobic property of its carbon sheets that prevented the hydration of –OH groups in the presence of water. The low surface area of 7.48 $m^2 g^{-1}$ was an indication that –SO_3H groups were in the interior of the catalyst. The large pores size of 43.90 nm was helpful for the reactants to diffuse into the interior of the catalyst. Increased catalytic activity was observed for the second run and decreased subsequently in the third run. Increase in catalytic activity has been attributed to swelling of the catalyst in the presence of swelling agent. The leaching of –SO_3H groups was the cause of decreased catalytic activity in the third run. Leaching of sulfate has also been reported by Petchmala et al.,[40] where conversion of feedstock to methyl esters decreased from 90.1% to 35.0% in the next run. Although the catalytic activity of the catalyst can be restored by re-impregnation with sulfuric acid and re-calcination, the leached sulfate in the product may cause biodiesel to get off-specification. Table 2 depicts the reaction conditions of tungstated and sulfated zirconia used as heterogeneous catalyst.

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Kiss *et al.*[4] have reported sulfated zirconia as the most promising among the various solid acid catalysts (others being zeolite, ion-exchange resin) tried for esterification of dodecanoic acid. The catalyst was observed to be stable towards thermal decomposition. The catalyst also did not get deactivated in the organic phase in presence of small amount of water. The activity of the catalyst dropped to 90% of the original value and remained constant thereafter. The activity was restored to the original value after re-calcination.

Polyaniline sulfate

Polyaniline sulfate deposited on carbon support has been used as solid acid catalyst by Zieba *et al.*[41] This catalyst has the potential to overcome the limitations of sulfated zirconia catalyst and has been chosen because of its easy preparation, handling, environmental and thermal stability, and its insolubility in most inorganic solvents. The catalyst also does not swell in methanol, methyl esters, and glycerol and possesses a low surface area. The catalyst was prepared by *in situ* polymerization of aniline on carbon support. Almost negligible leaching of the catalyst occurred as evidenced by low (2%) conversion obtained after filtering catalyst from methanol in 30 min. However, a high molar ratio of 29:1 A:O was needed to obtain high conversion. The catalytic activity dropped to 10–11% after reuse of the catalyst for five times. The acid capacity of the catalyst reduced to 80–95% of the initial activity of the catalyst after the experiments.

Heteropolyacid (HPA)

Heteropolyacids (HPAs) are very strong Brønsted acids and can be employed as either heterogeneous or homogeneous catalysts depending of their composition and the reaction medium. They are known to possess good thermal stability, high acidity, and high oxidizing ability. Among the heteropolyacids, 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) has been preferred over others because of its high activity. $H_3PW_{12}O_{40}$ displays a Keggin structure that is comprised of an oxygen tetrahedral-coordinated heteroatom (PO_4) surrounded by 12 edge-shared oxygen octahedraly-coordinated addenda atoms (WO_6).[42] Although in general, heteropolyacids work as homogeneous catalysts, they can be transformed to solid acid catalysts by combining them with monovalent cations such as NH_4^+, K^+, Cs^+, and Ag^+.[43]

The Keggin heteropolyacid as $H_3PW_{12}O_{40}$ is soluble in methanol and ethanol, while the ammonium salt is insoluble in alcohol. They have been used as solid catalysts for hydration of isobutylene and polymerization of tetrahydrofuran. Heteropolyacid is soluble in aqueous solution. However, its solubility decreases on addition of Cs.[44] Their major disadvantages, however, are low thermal stability and low surface area. Homogeneous heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_4SiMo_{12}O_{40}$) have been tried by Morin *et al.*[45] where biodiesel was developed from rapeseed oil using ethanol at moderate conditions. The catalytic activity was not affected by the acid strength of the various homogeneous heteropolyacids employed. Rather, the proton solvation with molecule was found to be responsible for the efficient transesterification reaction and found to be fast with ethanol as compared to methanol.

To enhance the thermal stability and surface area of heteropolyacids, Narasimharao *et al.*[46] used $Cs_xH_{3-x}PW_{12}O_{40}$, with x ranging from 0.9 to 3, for esterification as well as transesterification of palmitic acid and tributyrin. The insoluble nature of the catalyst in polar media makes it a good candidate as a heterogeneous catalyst. The most active catalyst was observed with Cs_x in the range x = 2.0–2.3, with 100% conversion with Cs = 2.3 in 6 h reaction time. Performance of the catalyst was far better than other solid acid catalysts such as SO_4/ZrO_2, Nafion, and H ZSM-5 for esterification reaction. The catalyst was also found to be suitable for simultaneous esterification and transesterification reaction with 100% conversion of palmitic acid and 52% conversion of tributyrin. The catalyst was then recycled 3 times with minor loss of activity. Esterification of palmitic acid by heteropolyacid catalysts has been performed by Caetano *et al.*[47] Tungstophosphoric acid (PW), molibdophosphoric acid (PMo), and tungstosilicic acid (SiW) immobilized on silica by sol–gel technique were tried as heterogeneous catalysts. PW was found to be the best catalyst among the three, so it was further studied with different loading concentrations on silica. PW-Silica2 (0.042 g_{PW}/g_{silica}) resulted in 100% conversion of palmitic acid. The heterogeneous nature of the catalyst was confirmed by centrifuging the catalyst dissolved in methanol for 72 h and then adding the methanol to palmitic acid. Negligible conversion of the reaction confirmed the heterogeneous nature of the catalyst. PW-Silica2

Table 2. Tungstated and sulfated zirconia as heterogeneous catalysts

Catalyst	Feedstock, Acid value	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Reaction conditions Molar ratio (methanol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
Tungstated zirconia-alumina (WO$_3$/ZrO$_2$)	Soybean oil, n-octanoic acid	Mixture of hydrated zirconia powder, hydrated alumina, aqueous ammonium metatungstate solution and deionized water was prepared and then kneaded for 25 min. to shape into pellets and dried at 130°C and calcined	Not done	800, 1	40:1	20, 300	4 g	C > 90	22
					4.5:1	20, 200	4 g	C = 100	
Sulfated zirconia and other Mixed metal oxides	Dodecanoic acid	First step: Hydroxylation of zirconium, titanium, and tin complexes Second step: Sulfonation with H$_2$SO$_4$ followed by calcination in air	ZrO$_2$/SO$_4^{2-}$ Surface area: 118 m^2/g, pore volume: 0.098 cm^3/g; Sulfur content: 2.3%	650, 4	3:1	1, 130–150	3.0	C = 90%	25
Zirconia supported isopoly and heteropoly tungstates (HPA)	Sunflower, Sesame, Mustard	Zirconium oxyhydroxide was prepared by hydrolysis of zirconyl chloride solution and dried at 120°C for 12 h, powered, and again dried for 12 h	Surface area = 70 m^2/g, Surface density = 6.4 W nm^2, Acidity = 2.60 NH$_3$ nm^2	750, 4	20:1	5, 200	3	C = 97	27
WO$_3$/ZrO$_2$ (pellet type)	Used Vegetable oil	ZrO$_2$ pellets were steamed at 190°C with ammonium metatungstate (aq). The mixture was stirrer for 2 h and after removing. excess water, it was calcined	BET Surface area = 40 m^2/g, Average pore size = 110 Å	800, 5	Not given	Not given	Not given	C = 70	28
S-ZrO$_2$	Soybean oil	ZrO$_2$Cl$_2$.8H$_2$O was mixed with (NH$_4$)SO$_4$ for 20 min. at 1:6 molar ratio in agate mortar	S-ZrO$_2$ was found to be amorphous; BET surface area = 126 m^2/g	600, 5	20:1	1, 120	5	98.6 (M) 92.0 (E)	30

Table 2. Continued

Catalyst	Feedstock, Acid value	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Reaction conditions Molar ratio (methanol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
WO_3/ZrO_2	Soybean oil (4 wt% oleic acid)	WO_3/ZrO_2 was prepared by impregnating $Zr(OH)_4$ with ammonium metatungstate solution	WO_3 and ZrO_2 were crystalline in nature. Surface area = 55.1 m²/g at 30 wt% WO_3 loading.	800, Not given	9:1	2, 75	0.29 g/ml of oil	C = 93	32
SO_4^{2-}/ZrO_2		SO_4^{2-}/ZrO_2 prepared by dehydration of H_2SO_4 and $Zr(OH)_4$							
Amberlyst 15		Amberlyst 15 was of commercial grade							
MCM-41 Silica supported WO_3	Oleic acid	Si/Zr molar ratio = 5:1, Zr-MCM-41 was steamed at 190°C for 4 h to generate surface OH groups. Tungsten was incorporated by impregnation technique using ammonium metatungstate aq. solution and then dried at 60°C	Mesoporous structure	700, 2	67:1	24, 65	18.7 wt%	C = 100	33
WO_3/ZrO_2	Waste acid oil (Dark oil) FFA = 54.9%	WO_3/ZrO_2 was prepared by impregnating $Zr(OH)_4$ with ammonium metatungstate solution	Surface area = 56.7 m²/g Pore size = 130.1 Å	800, 5	9:1	2, 150	0.40 g/ml of oil (20 wt%)	C = 96	34
SO_4^{2-}/ZrO_2-TiO_2/La^{3+}	Rapeseed oil feedstock FFA = 201. 1 mg KOH/g	$TiCl_4$ and $La(NO_3)_3$ were added to aq. solution of $ZrOCl_2\cdot8H_2O$. Conc. NH_4OH and the mixture were stirred vigorously to pH 9–10 and kept for 24 h. The precipitate was washed with deionized water until Cl^- in the filtrate was removed. The cake formed was dried at 110°C for 12 h. The powered complex oxide was then impregnated with 0.5 M H_2SO_4 for 24 h and filtered.		550, 3			5.0 wt%	C > 95	35

Table 2. Continued

Catalyst	Feedstock, Acid value	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Reaction conditions Molar ratio (methanol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
SO_4^{2-}/ ZrO_2– TiO_2/ La^{3+}	Soapstock	Not given	Not given	Not done	15:1	4, 60	5.0 wt%	C > 95	36
SO_4^{2-}/ ZrO_2– TiO_2/ La^{3+}	Acid oil FFA = 60 wt% (119.58 mg KOH/g)	$TiCl_4$ and $La(NO_3)_3$ were added to aq. solution of $ZrOCl_2 \cdot 8H_2O$. The mixture and NH_4OH (conc.) solution was prepared by vigorously stirring at pH 9-10 and kept for 24 h. The precipitate was then washed with deionized water and filtered until Cl- in the filtrate was removed. The cake obtained after filtration was then dried at 110°C for 12 h. The powdered complex oxide was then impregnated with sulfuric acid of 0.5 M for 24 h and filtered. The sample was then dried and calcined to prepare SO_4^{2-}/ ZrO_2– TiO_2/ La^{3+}	Not given	550, 3	15:1	2, 200	5.0 wt%	Y = 90; C = 96.24	37
Sulfated zirconia alumina	*Cerbera. Odollam* (Sea Mango)	Not given	Not given	400, 2.5	8:1	, 180	5.0 wt%	Y = 83.8%	38
Carbonized and sulfonated vegetable oil asphalt (V-C-600-S-210) Petroleum asphalt catalyst (P-C-750-S-210 and P-C-950-S-210)	Waste oil	Carbon-based solid acid catalysts were prepared from carbonized vegetable oil asphalt and petroleum asphalt.	Surface area = 7.48 m^2g^{-1} Average pore diameter = 43.90 nm	Not done	18.2:1	2.5, 260	1.0 wt%	C = 89.93	39

Table 2. Continued

Catalyst	Feedstock, Acid value	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Reaction conditions Molar ratio (methanol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
SO₄/ZrO₂	Purified palm oil Palm fatty acid	H_2SO_4 was impregnated over zirconium oxide to prepare SO_4/ZrO_2	Total acid sites (at 1.8% sulfur loading) = 495 μmol/g	500	25:1 6:1	10 min, 250 1 min, 250	0.5 wt%	C = 90 C = 75	40
Polyaniline sulfate	Triacetin, Castor oil (Transesterification) Ricinoleic acid (Esterification)	Aniline sulfate (0.1 M) was oxidized with ammonium peroxydisulfate in 50 vol (%) ethanol water mixture. Approx. 2 g of PANI sulfate (s) was formed from 100 cm³ of reaction mixture. Solid formed was collected on filter, rinsed with H_2SO_4 (0.1 M), acetone and dried	Specific surface area = 25.9 m²/g; Porosity = 0.054 cm³/g	Not done	35:1	-, 50	7.9 g/dm³ (5.0 wt%)	C = 70–80 C = 95–98	41

M = with methanol.
E = with ethanol.

was found to esterify oleic acid and stearic acid as well. Tungsten HPA catalysts are active for esterification as well as transesterification reactions. The activity of the catalyst was tried in homogeneous as well as heterogeneous media. Among the homogeneous catalysts were HPA hydrates, $H_3PW_{12}O_{40}.25H_2O$, and $H_4SW_{12}O_{40}.25H_2O$. The heterogeneous catalyst used was $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Sulfuric acid had better activity than HPA in homogeneous medium, whereas Amberlyst-15 performed better than HPA in heterogeneous medium. In heterogeneous medium, the HPA catalysts were leached. This can be avoided by severe pre-treatment of the catalyst, but the resultant activity of the catalyst will be affected.[48] Heterogenized HPAs such as $H_3PW_{12}O_{40}$/SiO_2, $Cs_2HPW_{12}O_{40}$, and $H_3PW_{12}O_{40}$/SiO_2 were studied as catalysts for transesterification of rapeseed oil. These catalysts possessed Brønsted acidity of high strength and catalytic activity, better than H_2SO_4 and H_3PO_4, but the acid strength didn't necessarily correlate with catalytic activity. The catalyst was prepared by precipitation steps using precursor solutions. The precipitate was recovered by centrifugation and then water washed. Based on the method of preparation, $Cs_2HPW_{12}O_{40}$ offered good resistance to leaching of active phase present in the catalyst.[49]

The sol-gel hydrothermal method was used to prepare mesoporous polyoxometalate tantalum pentoxide composite solid acid catalyst ($H_3PW_{12}O_{40}$/Ta_2O_5) and tried for esterification reaction of lauric acid, which resulted in 99.9% yield with 7:1 alcohol to oil molar ratio at 78 ± 2°C for 3 h reaction time. ICP-AES analysis of the reaction solution after removal of catalyst confirmed that the catalyst was not leached. Upon regeneration of the catalyst by boiling ethanol and washing with hexane overnight, 95.6–94.8% ester yields were obtained after successive runs, and its reusability was confirmed.[50] A heteropoly solid acid catalyst ($H_4PNbW_{11}O_{40}$/WO_3-Nb_2O_5) has been shown by Katada et al.[51] to have high catalytic activity when used for transesterification of triolein and methanol/ethanol. Calcination at 500°C gave the best results. The high activity of the catalyst has been attributed to strong Brønsted acidity, bearing ester yield of 81%. The catalyst also worked in the presence of water in 95% ethanol. Thus, crude alcohol can be used in the reaction, resulting in lower production costs for biodiesel. The dissolution of the catalyst was undetectable for niobium and low (<0.5%)

for tungsten. A fixed-bed continuous flow reaction has been proposed for large-scale production of biodiesel using the catalyst, with easy separation.

Niobium oxide has been used to impregnate heteropoly tungstate by Srilatha et al.[52] 12-tungstophosphoric acid (TPA) was impregnated on niobium oxide for this purpose. Acid strength was found to increase with TPA content and was optimum with 25 wt% loading on Nb_2O_5. A high conversion of methyl esters (99.1 and 97.3%) were observed with palmitic acid and sunflower oil, respectively with 4 h reaction time at 65°C. Moderate calcination temperature of 400°C was adequate for the performance of the catalyst. Temperatures higher than 400°C for calcination led to degradation of TPA to metal oxides, thus decreasing the catalytic activity.

Zhang et al.[53] used microwave-assisted transesterification reaction to produce biodiesel by heteropolyacid catalyst ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) from *Xanthoceras sorbifolia* oil. The method resulted in a high yield (>96%) in only 10 min of reaction time with 1.0 wt% of oil, 12:1 methanol to oil molar ratio, at 60°C of optimized reaction conditions. The presence of four exchangeable protons and the distribution of alkali cation in the Keggin network prompted Pesaresi et al.[54] to try low amount of Cs loading on heteropoly acid ($H_4SiW_{12}O_{40}$) and found that Cs loading >0.8 per Keggin resulted in heterogeneous activity of the catalyst. A high yield of 99% was obtained using heteropoly acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) tried by Li et al.[55] for transesterification of *Eruca Sativa* oil possessing FFA of 3.5%. Although a longer reaction time was taken for completion of the reaction, the other variables were moderate such as methanol to oil molar ratio of 6:1, 85×10^{-3}:1 (catalyst to oil) weight ratio, at 65°C.

Ta_2O_5 has been incorporated on Keggin-type heteropoly acid by sol-gel co-condensation method by Xu et al.[56] as a hybrid catalyst for preparation of biodiesel. The incorporation of Ta_2O_5 on the heteropoly acid resulted in enhanced activity of the catalyst. The hydrophobic nature of the catalyst has been enhanced by hydrophobic alkyl group such as methyl or phenyl. The Keggin structure was found to disperse homogeneously throughout the hybrid catalyst. The catalyst was reused for subsequent runs and wasn't leached in the reaction medium and was easily desorbed from the glycerol.

Pure hydropoly (H_3PW) follows the homogeneous catalytic pathway because of its solubility in ethanol. To make the catalyst heterogeneous, the heteropoly acid was supported with zirconia (ZrO_2) by Oliveira et al.[42] for conversion of oleic acid to methyl esters taking ethanol as solvent. The heteropoly acid was found to be well dispersed over the support, and only the monoclinic phase of ZrO_2 was detected. 20 wt% of H_3PW loaded on ZrO_2 provided 88% conversion of oleic acid with 10 wt% of catalyst in with 6:1 A:O molar ratio in 4 h. Some amount of the catalyst (8 wt%) was leached in the solution. The catalyst when reused after washing with n-hexane, drying, and calcination at 300°C for 4 h resulted in 70% conversion. Silver has been doped over heteropoly acid to form $Ag_xH_{3-x}PW_{12}O_{40}$, with Ag content varying from 0.5 to 3 by Zieba et al.[43] The FTIR analysis indicated no change in structure of Keggin anions of the heteropoly acid when the protons were replaced by the silver cations. With silver content x > 1, only one phase of silver salt with good crystallinity was observed. With silver content x = 0.5, a two-phase mixture of silver salt and crystalline hydropoly acid was observed. The catalyst loading up to x = 1 showed leaching of the catalyst silver loaded heteropolyacid leading to the homogeneous pathway reaction. Loading x > 1 resulted in lowering of homogeneous nature and occurrence of heterogeneous pathway. The homogeneous catalytic activity resulted in gel-type material which had to be immobilized on a support to make the catalyst. Heteropoly acid has been used for simultaneous esterification and transesterification reaction by Baig et al.[57] for synthesis of biodiesel. Although a high temperature of 200°C and a high molar ratio was adopted, the biodiesel obtained fulfilled the specifications of ASTM. The reaction condition of heteropolyacids as heterogeneous catalysts is given in Table 3.

Pyrone complexes with metals

A group of pyrone complexes were used as catalyst by Abreu et al.[58]. Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$, Pb(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$, Zn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$ were develop a homogeneous catalyst for transesterification using various oils. Among the three pyrone complexes, tin complex showed a comparatively high yield of 35.6 and 37.1% with babassu and soybean oil respectively. The maximum yield with lead and

Table 3. Heteropolyacids as heterogeneous catalysts.

Catalyst	Feedstock	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Reaction conditions			Conversion (C)/Yield (Y) (%)	References
					Molar ratio (methanol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)		
$H_3PW_{12}O_{40}$ (HPA)	Rapeseed oil	$Cs_xH_{3-x}PW_{12}O_{40}$ (x = 1–3) was prepared from 0.02 mol dm^{-3} CsCl (aq.)-ethanol solution (50:50) volume ratio to 0.08 mol dm^{-3} ethanol solution of HPA. The solution was then dried in a vacuum oven to evaporate ethanol and water. Fine white powders were obtained and dried in air at 100°C	Crystalline size = 8.0 nm, Specific surface area = 97.6, Average pore diameter = 5.1 nm at Cs loading 2.3	Not done	Not given	6, Not given	Not given	C = 100	46
$H_3PW_{12}O_{40}/$ SiO_2, $Cs_2HPW_{12}O_{40}$	Rapeseed oil	$H_3PW_{12}O_4.24H_2O$ was recrystallized from deionized water for reuse. 2 mol% $H_3PW_{12}O_4$ was dispersed over SiO_2	BET surface area = 168 m^2 g^{-1} BET surface area = 70 m^2 g^{-1}	Not given	Not given	Not given	Not given	Not given	50
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Yellow horn (*Xanthoceras sorbifolia*)	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was purchased from Guangfu fine chemicals research institute, China	Not given	Not done	12:1	10 min., 60	1 wt%	Y = 96.22	53
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Eruca Sativa Gars vegetable oil	$Cs_{2.5}PW$ was prepared from $H_3PW_{12}O_{40}$ and Cs_2CO_3	Surface area = 130 m^2 g^{-1}	300, 3	6:1	12, 65	1.85 × 10^{-3}:1 (catalyst to oil)	Y = 99	55
$H_3PW_{12}O_{40}/ZrO_2$	Oleic acid	$H_3PW_{12}O_{40}$ was dissolved in HCl and then zirconia was added. The slurry of $H_3PW_{12}O_{40}$ and zirconia was kept at 80°C until evaporation. The solid obtained was then pulverized and dried at 120°C for 12 h. The product was then calcined at 200°C for 4 h in a muffle furnace in static air	Monoclinic phase of zirconia was observed. Specific surface area (BET) = 4.3 m²/g Average pore size = 7.0 nm	200, 4	6:1	4, 100	10 wt%	C = 88%	42

zinc complex obtained were 17.0 and 26.2% respectively with babassu oil. Though the yield obtained with pyrone complexed with metals were low, this paved a way for their modification for a high yield and conversion of biodiesel. $Sn(3\text{-hydroxy-2-methyl-4-pyrone})_2(H_2O)_2$ was hence tried to be used as heterogeneous catalyst by immobilization. However, leaching of the catalyst in the ionic phase could not be prevented and the catalyst could not be reused.[59]

Metal oxides

Tin oxide as a solid acid catalyst has shown a heterogeneous pathway with yield of 92.6% in 3 h and was recycled for reuse up to three runs without loss in catalytic activity.[59] Guo et al.[60] incorporated aluminum on SO_4^{2-}/SnO_2, a solid super acid, and was found to possess catalytic activity and acidity better than zirconia- and titanium-based super acids. The incorporation of aluminum on $SO_4^{2-}/SnO_2\text{-}Al_2O_3$ via co-condensation method at Sn/Al ratio of 9:1 and calcined at 500°C, gave the highest activity. FT-IR results showed that active sites were due to Sn, which was chelated with sulfuric acid. Thermogravimetric analysis showed that, by introducing aluminum, the number and intensity of the sulfuric groups attached on the surface increased, strengthening the catalyst's activity. Lam et al.[61] observed a yield of 92.3% with $SO_4^{2-}/SnO_2\text{-}SiO_2$ with a weight ratio of 3:1 at 150°C, 3 wt% of catalyst, and 15:1 methanol to oil molar ratio in 3 h. The calcination temperature was found to affect catalytic activity immensely. At low calcination temperature (i.e. 200°C), the catalyst was not crystallized and remained in gel form, whereas, at high calcination temperature (i.e. 500°C), the catalyst collapsed due to loss of sulfate group. The optimum calcination temperature was found to be 300°C. The sulfate content in biodiesel was determined and found to be less than 0.1 mg/kg which isn't significantly different from the norm of 10 mg/kg.

Acidic and basic solids such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite, and KNO_3/ZrO_2 were used for the transesterification of palm oil and coconut oil. While carrying out the experiments without catalyst at higher reaction temperature (200°C) for 4 h reaction time, the purity and yield of esters were very low (i.e. 0.3 wt%). The transesterification of palm oil by SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2 showed maximum yield of 90.3 wt%, with methyl ester content of 95.4 and 95.8%, respectively. ZnO catalyst

showed the maximum conversion of 98.9 wt% with a yield of 86.1%. However, when the same set of catalysts were used in the transesterification of coconut oil, the conversion and yield of the methyl esters were reduced significantly. The yields obtained with SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2 as catalysts were 80.6 and 86.3%, respectively. Conversion obtained with these catalysts was reduced to 88.3 and 93.0%, respectively. Conversion with ZnO was only 83.2% with 77.5% yield. Based on better performance of the catalyst SO_4^{2-}/ZrO_2, it was reused after regeneration for transesterification of palm oil and the same activity of the catalyst was achieved.[62] Table 4 depicts the optimum conditions for sulfated tin oxide as heterogeneous catalysts.

Kiss et al.[63] have reported use of oxides of Zr, Ti, Sn, and Nb as catalysts for synthesis of biodiesel adopting reactive distillation in which reaction and separation steps were merged in a single step. A short reaction time was needed for high productivity of biodiesel with all the catalysts. With application of reactive distillation, the cost of biodiesel production was also lowered. However, a catalyst with high activity has been recommended for the purpose of reactive distillation. Thus, a hydrophobic surface of catalyst is preferred to avoid being covered by water. Reaction pockets will be created in the hydrophobic environment and will allow the fatty acid molecules to get absorbed and react to form biodiesel. The energy requirement of the process was found to be near to 150 kcal/kg of fatty ester. The reaction time was only 10 min for the reactants to be placed in the column. The production of fatty acid ester reached 21.4 kg ester.kg of catalyst^{-1}.h^{-1}.

Zeolite

Zeolites are microporous crystalline solids with well-defined structures containing silicon, aluminum, and oxygen in their framework and cations. La/zeolite beta catalyst has been developed and used as an alternate to homogeneous catalysts. La/zeolite beta catalyst possessed higher quantity of external Brønsted acid sites obtained by lanthanum ion exchange on zeolite beta. A comparatively lower conversion (48.9 wt%) of methyl esters was obtained at 60°C in 4 h reaction time with 14.5:1 alcohol to oil molar ratio. The catalyst was easily separable from the product and free from corrosion-causing agents.[64] Benson et al.[65] used a variety of zeolites as catalysts for catalytic cracking of mono-, di-, and

triolein. A high product yield comprising of C_2-C_5 paraffins and olefins, aromatics, CO, and CO_2 were formed.

Zeolite (H-ZSM5) catalyst has been applied by Danuthai et al.[66] to convert methyl esters (methyl octanoate) to hydrocarbons. The deoxygenation of methyl octanoate resulted in formation of high molecular weight ketone and octanoic acid, which on cracking results in formation of hydrocarbons (C1–C7) and aromatic compounds. Addition of water was found to have a favorable effect on conversion of methyl octanoate to hydrocarbons. The conversion took place through condensation and hydrolysis process. H^+ ion exchanged ZSM-5 (HMFI) Zeolite and Mordenite (HMOR) Zeolite catalyst used by Chung and Park[67] resulted in 80% conversion of oleic acid to biodiesel when the acid amount was above 0.06 mmol/g. The desorption peaks were observed at 350–550°C which were characteristic of strong acid sites. A linear relationship was observed between the acidity and conversion of the feedstock and a high catalytic activity was observed with increased acidity. The two zeolites (H-ZSM-5 and H-Beta) synthesized by Giannakopouloua et al.[68] in a batch reactor showed varying catalytic activity depending on vapor grading. H-ZSM-5 was found to have better catalytic activity than the H-Beta catalyst when vapor upgrading was not done as less residue and more gas products were formed. When vapor upgrading was followed, H-ZSM-5 showed better catalytic activity. H-ZSM-5 Zeolites are known to possess high acidity due to the presence of a large number of Brønsted and Lewis acid sites and was found to be more stable than H-Beta catalyst. Zeolite H-ZSM-5 shows high catalytic activity owing to both Brønsted and Lewis acid sites. It also shows high selectivity due to a network of internal canals and well-defined diameters.[69] H-β Zeolite and Amberlyst have also been used for etherification of glycerol showing 85–97% selectivity to mono-and di-octyl ethers.[70] Kiss et al.[25], however reported zeolites to possess small pores and have diffusion limitations for the large fatty acid molecules thus restricting its catalytic activity. Optimum reaction conditions with zeolites used as heterogeneous catalyst is discussed in Table 5.

Acidic ionic liquid

To overcome the low activity and deactivation of solid acid catalysts, Zhang et al.[71] tried a Brønsted acidic ionic

Table 4. Metal oxides as heterogeneous catalysts.

Catalyst	Feedstock	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Molar ratio (alcohol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
SO_4^{2-}/ SnO_2-SiO_2	Waste cooking oil	SO_4^{2-}/SnO_2 was prepared by amorphous SnO_2 to H_2SO_4 solution and stirred. The precipitated solid was calcined after filtration. SO_4^{2-}/SnO_2-SiO_2 was prepared by adding amorphous SnO_2 and SiO_2 to H_2SO_4 solution and stirred	BET Surface area 13.9 m^2/g, average pore width, 13.7 nm, pore volume 0.04 cm^3/g	300, 2	15:1	3, 150	3.0 wt%	Y = 92.3	61
Niobic acid, Sulfated Zirconia, Sulfated Titania, Sulfated Tin oxide	Dodecanoic acid	First step: Hydroxylation of zirconium, titanium, and tin complexes Second step: Sulfonation with H_2SO_4 followed by calcination in air	ZrO_2/SO_4^{2-} Surface area:118 m^2/g, pore volume:0.098 cm^3/g; Sulfur content: 2.3%	650°C, 4	5:1	10 min, 130–150; (Pressure = 6–10 Bar)	3.0	C = 72%	63

Table 5. Zeolite as heterogeneous catalysts

Catalyst	Feedstock	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Molar ratio (alcohol to oil)	Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
H-ZSM5 Zeolite	Methyl octanoate	Tetrapropylammoniumbromide used as an organic template for synthesis of H-ZSM5 Zeolite. Organic template was then decomposed by calcination in air at 600°C for 5 h. Na^+ ions in the zeolite was exchanged by NH_4^+ ions from 1 M NH_4NO_3 solution. Zeolite was then separated by filtration and washing	Particle size = 3 μm; Si/Al ratio = 36; BET Surface area = 377 m²/g; Acidity density = 382 μmol/g_{cat}	500, 5	6:1	20 min, 500	–	Y = 73.1, C = 100	66
H+ ion exchanged ZSM-5 (HMFI)	Soybean oil added with oleic acid	ZSM-5 zeolite prepared by hydro-thermal treatment of colloidal silica, aluminum hydroxide, potassium hydroxide, and deionized water and kept for 72 h and then heated at 190°C for 48 h	Particle size = 0.2–2.0 μm	HMFI, 550, 6	Not given	1, 60	>0.06 mmol/g	C = 80%	67
Mordenite zeolite (HMOR)		Mordenite zeolite purchased and treated with acetic acid solution for 5 h		HMOR, 500, 12					

liquid, N-methyl-2-pyrrolidonium methyl sulfonate ([NMP] [CH_3SO_3]), as catalyst for synthesis of biodiesel with high FFA content. The catalyst showed high activity with 95.3% yield at 70°C and 8 h reaction. High conversion was achieved with oleic, stearic, myristic, and palmitic acid as well as a mixture of the acids with lower group alcohols (methanol, ethanol, propanol, and butanol). The liquid catalyst was later reused eight times after removing its water content and >90% conversion was obtained. Han et al.[72] found esterification of FFA to occur quicker than transesterification reaction using Brønsted acidic ionic liquid with alkaline sulfonic acid group. After crystallization, the ionic liquid loses H_2O and forms sulfonate, which gave a yield of 93.5% using waste oil as feedstock. Table 6 depicts the optimum reaction conditions for acidic ionic liquid.

Other catalysts

Sulfonated multi-walled carbon nanotubes and carbonized vegetable oil asphalt have been used by Shu et al.[73] for synthesis of biodiesel from cottonseed oil. The average pore size of sulfonated vegetable oil asphalt was found to be 43.90 nm, which is sufficient for diffusion of reactants onto the interior of the catalyst, providing more active sites with better activity. 89.9% conversion was achieved with asphalt-based catalyst. Amberlyst-15 and Amberlyst-BD20 were observed to be good solid catalysts for biodiesel conversion with high FFA oleic acid by Park et al.[74] Conversion of oleic acid with Amberlyst-15 decreased with high water content, whereas Amberlyst-BD20 was unaffected by water. This has been attributed to poisoning of the active acid sites by water molecules in Amberlyst-15. Contrary to Amberlyst-15, which possessed several pores, absence of pores in Amberlyst-BD20 provided no opportunity for water to adsorb on its surface and thus prohibited the entry of water molecules. Kiss et al.[25] also observed that the hydrophobicity of the catalyst surface and the density of the acid sites play an important role in the catalyst's activity and selectivity.

The hydrophobic nature of Amberlyst-15 has been studied by Kiss et al.[4] and was observed that a catalyst with high acidic and hydrophilic acid sites would adsorb water on its surface and will lose its activity. The water adsorbed on the surface will prevent the access of triacylglycerol to the catalyst surface and hence a reduced activity will be observed.

Zieba *et al.*[75] reported that moderate strength of acid sites and their hydrophobic microenvironment will lead to a stable and active solid acid catalyst for esterification of tria-cylglycerols. It is confirmed[25] that Amberlyst possessed low thermal stability which makes it unsuitable for reaction at high temperature.

There are vegetable oils that possess high levels of FFA which can be most effectively converted to fatty acid alkyl esters by esterification reaction. Similarly, waste cooking oils with high FFA can be subjected to solid acid catalysis for biodiesel synthesis. Alkyl esters were prepared from cerium trisdodecylsulfate ($Ce[OSO_3C_{12}H_{25}]_3.3H_2O$) as catalyst by solvent-free method for esterification and transesterifica-tion reaction. The catalyst was found to be successfully used for 3 runs without loss in its activity.[76] A hybrid catalytic membrane has been prepared by Shi *et al.*[77] from sulfonated poly (vinyl alcohol) loaded with a solid acid catalyst $Zr(SO_4)_2$ (ratio of 1:1) and 94.5% conversion was obtained. A zinc amino acid complex has been immobilized on a monolith support to make it act as heterogeneous catalyst. Although a low conversion of 54% was obtained, the catalyst was found to be active until 24 h of use.[78]

Recently, alum ($KAl(SO_4)_2.12H_2O$) derived from Kaolin has been tried for a potential heterogeneous catalyst by Aderemi and Hameed.[79] However, the conversion obtained (i.e. 92.5%) is lower than the recommended value of methyl ester by European Norms (96.5%). A byproduct of pyrolysis, biochar has been use for synthesis of biodiesel by Dehkhoda *et al.*[80] Although conversion of 92% was obtained, the yield obtained was very low (10%). Zinc acetate has been used in the catalysis of oleic acid in subcritical conditions. A high conversion of 95.0% was obtained at 220°C and 6.0 MPa at 4:1 methanol to oleic acid ratio and 1.0 wt% catalyst amount.[81] The carbohydrate-derived catalysts (D-glocose, sucrose, cellulose and starch) gave a high yield (80%) and showed 93% catalytic activity even after 50 successive runs of reuse. The findings on sulfated zirconia aren't as encour-aging as the catalyst is observed to leach in the reactant medium, although high yield and conversion have been observed in some of the cases. On the contrary, the carbo-hydrate-derived catalysts exhibited high stability which has been attributed to presence of polycyclic aromatic carbon sheets which are hydrophobic and do not allow a water layer

Table 6. Acidic ionic liquid as heterogeneous catalysts.

Catalyst	Feedstock	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Reaction conditions Molar ratio (alcohol to oil)	Reaction time (h); tempera-ture (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
[NMP] [CH₃SO₃]	Oleic acid	Benzene was mixed with N-methyl-2-pyrrolidone. Methane sulfonic acid was added slowly in water bath. Benzene was removed under reduced pressure and dried at 90°C for 1 h	–	Not done	2:1	8, 70	10	C = 96.5	71
SO₃-H functional Brønsted acidic ionic liquid	Waste oil	Pyridine stirred with1,4-butane sulfone at 40°C for 1 day in absence of a solvent. Zwitterion formed was washed with toluene. Stoichiometric amount of H₂SO₄ was added to zwitterion and stirred at 40°C for 2–3 days until liqui-fied. The ionic liquid was then washed with toluene and ether and dried in vacuum	Crystallization of ionic liquid containing 1% H₂O was observed when stored at 5°C for 24 h. Crystallization was not observed when stored at 5°C for more than a month with water content more than 15%	Not done	12:1	4, 170	0.06%	Y = 93.5	72

to form on its surface.[31] The optimum reaction conditions of the catalyst are discussed in Table 7.

In spite of development of biodiesel from various catalyst including solid acid and solid base catalysts, various parameters (viscosity, cloud point, flash point, cetane number, oxidation stability, etc.) have to be analyzed of make the biodiesel fuel fulfill the American Society for Testing and Materials (ASTM) D6751 specifications. A major disadvantage of biodiesel as fuel is its poor oxidation stability which makes the fuel off-specification during its storage. The reason is the presence of total number of *bis*-allylic sites i.e. methylene group allylic to the two double bonds.[82] As far as the feedstock is concerned, the majority of them taken for esterification/transesterification reaction are edible such as soybean, rapeseed, and sunflower oils. Though some of the researchers have tried waste cooking/frying oil, they comes from one source and still there is little awareness for their usage as biodiesel feedstock with no current plan by any industry to setup a plant based on this feedstock. Hence, it becomes pertinent for the usage of non-edible oils (e.g. *Pongamia pinnata*, *Jatropha curcas* etc. that are available in many parts of the world) and algae as feedstock for synthesis of biodiesel.

Crude oil is an exhaustible resource and its price is regulated by its scarcity issues.[83] Hence, even though the present mode of synthesis of a renewable fuel like biodiesel is costly, the advantages of biodiesel other than its renewability are many. The other advantages include its biodegradability; reduced emission of pollutants such as hydrocarbons, particulate matter, carbon-monoxide, and other toxic emissions; and being a good lubricant. Hence, even though a low-priced product i.e. biodiesel is developed through the application of various solid acid catalysts, the fuel synthesized is of a high significance in the development of the economy of any nation in addition to a clean, and sustainable environment.

Conclusion

Biodiesel is a renewable fuel and has been synthesized by various feedstocks and catalysts. The catalysts mainly belong to two categories: homogeneous and heterogeneous. While the former has been successfully tried for development of biodiesel, there are certain constraints and limitations in their application at production level. These constraints are the thorough washing of biodiesel by water and subsequent generation of excessive wastewater. Also, these catalysts cannot be reused. Hence, recent research on catalysts has focused on those that need minimal purification steps and those that are reusable, which enhances their easy application and reduces the overall cost of biodiesel production. Heterogeneous catalysts have these potentials where they can be reused and easily separated. They also ensure that no or minimal purification steps are involved in the process. Heterogeneous catalysts are further categorized in solid base and solid acid catalyst. Solid base catalysts have been used extensively for feedstock with low acid value and have resulted in high yield and conversion. Solid acid catalysts have the advantage of being used for high acid value feedstock and can lead to esterification and transesterification simultaneously. This becomes very important as the non-edible oils and waste cooking/frying oils commonly employed for synthesis of biodiesel have high acid value. Hence, instead of a two-step process where the acid value is reduced by the first step followed by conversion of oil to biodiesel in the second step, it is replaced by a single-step process when solid acid catalysts are adopted.

The present review deals with application of various types of solid acid catalysts for synthesis of biodiesel. The process adopted for their preparation, their textural properties, thermal treatment, reuse, and leaching aspect are discussed. The solid acid catalyst should be active, selective, and stable under the reaction conditions. Among the solid acid catalysts, resins have shown good catalytic activity. The low cross-linking density that corresponds to high swelling capacity, high average pore diameter, and high BET surface area are favorable for a better catalytic activity. Tungstated and sulfated zirconia belong to the super acid category and their potential as solid acid catalyst with a high yield and conversion of oil to biodiesel has also shown. Calcination temperature ranging from 500 to 850°C influences the activity of majority of the catalysts. Tungstated zirconia modified in pellet form was effective for continuous biodiesel production. However, SO_4^{2-} was leached in the reaction medium and this decreased the catalytic activity in subsequent runs. HPAs such as 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$), which are strong Brønsted acids, have shown high catalytic activity. High yield and conversion have been achieved with HPA in combination monovalent cations such as Cs^+. HPA loaded with niobia, tungstated zirconia, tantalum pentoxide, silver have shown

Table 7. Other catalyst as heterogeneous catalysts.

Catalyst	Feedstock	Method of preparation	Characterization	Calcination Temperature (°C), time (h)	Molar ratio (alcohol to oil)	Reaction conditions Reaction time (h); temperature (°C)	Catalyst amount (wt%)	Conversion (C)/Yield (Y) (%)	References
$Zr(SO_4)_2$/ sulfonated poly (vinyl alcohol)	Acidified oil, 16.0 mg KOH/g	30 g Poly (vinyl alcohol) was dispersed in 200 ml distilled water under stirring and dissolved by heating. 45 ml H_2SO_4 was dripped into PVA solution and continued to react at 65°C. SPVA was precipitated by addition of ethanol and pH was brought in range 6–7.3 g SPVA was dissolved in distilled water and heated and then appropriate amount of $Zr(SO_4)_2$ was added	The maximum weight loss appeared at 173°C	Not done	6:1	2, 65	4.0	C = 94.5	77
ZnL_2	Rapeseed	0.5 g ZnL_2 was dissolved in 200 ml water by heating and mixing the solution at 100°C for 30 min. A small section of monolith was dipped in the solution at and the excess liquid was drained out using a jet of air. The coated monolith was dried using hot air blower at 100°C. The dried sample was kept in furnace and heated at 200°C in continuous flow of nitrogen. The process was repeated 3–4 times to increase the catalyst loading on the support.	SEM study: Rod like external surface area	Not done	12:1	2, 195 (Pressure = 20 bar)	5	C = 54%	78
Alum $(KAl(SO_4)_2 \cdot 12H_2O)$	Palm	Kaolin was calcined to form metakaolin phase and dealuminated with Al. The dealuminated filtrate was crystallized by K_2SO_4 as a salting agent. Al and K sulfates were heated at 80°C for dissolution and then cooled for 6 h. The alum crystals were filtered and rinsed with ethanol to remove adsorbed H_2SO_4 and then dried and calcined	$KAl(SO_4)_2$ predominates at T < 600°C	200-550, Not reported	9:1	3, 170	7.09	C ≥ 72	79
Zinc acetate $Zn(CH_3COO)_2 \cdot 2H_2O)$	Oleic acid	$Zn(CH_3COO)_2.2H_2O)$ of purity >98.5% obtained from Fangzheng company.	Not done	Not done	4:1	1, 220 (Pressure = 6.0 MPa)	1.0	C = 95%	81

more resistance to leaching of the catalyst. Tin oxide loaded to ionic liquid, and sulfated tin oxide has also shown high catalytic activity. Zeolite owes Brønsted as well as Lewis acid sites and show enhanced catalytic activity in presence of water. Other potential catalyst are sulfonated and carbonized vegetable oil asphalt, cerium trisdodecylsulfate, sulfonated poly (vinyl alcohol) loaded on $Zr(SO_4)_2$, and alum.

Although these catalysts vary in their method of preparation, their catalytic activity is high with some leaching which limits the number of reuse runs. However, all of the catalysts were efficient for waste oils as feedstock with high FFA value.

Acknowledgement

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Dr Yogesh C. Sharma

Dr Yogesh C. Sharma holds a PhD in Applied Chemistry and a DSc in Chemistry. He has vast experience in Environmental research including his work on pollution of the Ganges, the Indian River. Dr Sharma started work on biofuels in 2006 and now leads one of the pioneer groups in India. He has been doing collaborative work with scientists in South Africa, USA, UK, Brazil, Mexico, Taiwan and China. Dr Sharma feels that biofuels are the 'future fuels' of the humanity. He intends to join people around the globe working on biofuels. He also realizes that the new 'crop' of young scientists needs to be 'cultivated' to take command of the future. A large number of qualified 'Fuel Scientists' is needed for the future. As the usual feedstock like edible and non-edible oils are available in limited quantity, more research on algal biofuels is needed. India, being a tropical country, can act as a hub for research on algal biofuels.

Bhaskar Singh

Bhaskar Singh has submitted his PhD thesis under the supervision of Dr YC Sharma and is presently working as senior research fellow in his research group on biodiesel development and related aspects. Bhaskar Singh holds an MPhil from Pondicherry University, India with a Gold medal (2006). His current interests lie in the application of algal biomass for biodiesel synthesis and development of heterogeneous catalysts.

John Korstad

John Korstad, PhD, is a Professor of Biology and Director of the Honors Program at Oral Roberts University in Tulsa, OK. His specialty is Limnology with specific expertise in nutrient – phytoplankton – zooplankton interactions. He has vast experience in aquaculture, including two sabbatical years doing research at the Foundation for Scientifc and Industrial Research (SINTEF) in Trondheim, Norway, resulting in three published and numerous technical publications. Dr Korstad's desire is to connect various industries like local oil refineries, electrical power plants, and cement factories that produce carbon dioxide waste and local industries like waste management landfills and the city's sewage treatment plants with high nutrient loads in their waste water, and to cultivate algae for biofuels. The algae would improve the air and water quality by taking up the waste CO_2 and nutrients, and then be of benefit by providing a feedstock for biodiesel. This would essentially be a win-win-win situation, and would hopefully develop into a vibrant industry that brings added jobs and revenue to the Tulsa area.