Chapter 4

Applications in Biodiesel production

(a) Esterification of free fatty acids (palmitic acid & oleic acid)

(b) Transesterification of triglycerides (Jatropha oil & Waste cooking oil)

- **Papers Published**

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Biodiesel Production by Esterification of Free Fatty Acids over 12-Tungstophosphoric Acid Anchored to MCM-41

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ABSTRACT: Heterogeneous acid catalyst comprising 12-tungstophosphoric acid (30%) and MCM-41 was synthesized and characterized by X-ray diffraction (XRD), surface area measurement (BET method), and solid state ^{29}Si NMR. The use of synthesized catalyst was explored for biodiesel production by esterification of free fatty acid, palmitic acid with methanol. The effect of various reaction parameters such as catalyst concentration, acid/alcohol molar ratio, and temperature were studied to optimize the conditions for maximum conversion. The catalyst shows high activity in terms of 100% conversion toward palmitic acid and a high turnover number, 1992. The kinetic studies as well as the Koros Nowak test were also carried out, and it was found that esterification of palmitic acid follows first order kinetics and the rates are not mass transfer limited. The excellent catalytic performance is attributed to the large surface area and pore diameter of the mesoporous support, MCM-41 as well as the Bronsted acid strength of TPA, as active sites. The catalyst shows the potential of being used as a recyclable catalytic material after simple regeneration without significant loss in conversion. As an application, preliminary studies were carried out for biodiesel production from waste cooking oil, as feedstock without any pretreatment, and with methanol over the present catalyst. Studies also reveal that the catalyst can be used for biodiesel production from waste cooking oil.

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(a) Esterification of free fatty acid (Palmitic acid & Oleic acid)

Biodiesel is gaining much attention in recent years as a renewable fuel. It is non-petroleum based fuel that consists of alkyl esters derived from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with low molecular weight alcohols [1-4].

The conventional biodiesel production technology involves the use of alkaline homogeneous catalysts such as NaOH and KOH but sometimes $NaOCH_3$ or $KOCH_3$ are also employed mainly in large-scale production plants. These are not compatible for feedstocks with large amounts of free fatty acids (FFAs) and moisture due to the formation of soaps that strongly affect the feasibility of glycerol separation which is an important co-product of transesterification reaction.

The traditional liquid acids such as HCl and H_2SO_4 were found to be more efficient but they need very long reaction time and very high molar ratio of methanol to oil. Also corrosion of reaction vessels and problem of recycling are the key issues with traditional liquid acids. Therefore commercialization of biodiesel production is difficult due to the technological drawbacks such as separation and purification steps that increase the cost factor to maximum.

Considering heterogeneous solid acid catalysts, a literature survey shows that there are fewer reports than those on solid bases. Compared with solid base catalysts, solid acid catalysts have lower activity but higher stability, thus, they can be applied for feedstock with large amounts of free fatty acids without catalyst deactivation.

A literature survey shows that esterifications of free fatty acids to produce biodiesel involve use of different heterogeneous acid catalysts such as, clays[5], zeolite [6-8], ion exchange resin [8-10], carbon based material [8, 11],

metal oxides as well as sulfated metal oxides [8, 12, 13], WO_3/ZrO_2 [14, 15], propylsulfonic acid functionalized mesoporous silica [16, 17], heteropolyacids [18-19] and heteropolyacids supported on to different supports such as zirconia[20], activated carbon, silica [21,22] and tantalum pentoxide [23]. Thus enormous literature is available for biodiesel production over variety of heterogeneous acid catalysts [24-26] and it would be quite difficult to summarise all the literature. Hence in the present thesis, we would like to restrict ourselves to biodiesel production over heteropolyacids catalysts.

J.E. Castanheiro have reported heteropolyacid supported on silica (SiO_2) for esterification of free fatty acids such as palmitic acid, oleic and stearic acid with methanol for biodiesel production [27]. M. J da Silva and co- workers have reported a detailed investigation on the biodiesel production by esterification of fatty acids Catalyzed by the $H_3PW_{12}O_{40}$ heteropolyacid [28, 29]. Jose´ A. Dias and co-workers have reported biodiesel production by esterification of fatty acid, oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia [30]. A study on recyclability indicated that a treatment of the spent catalyst involving a sequence of washing with n-hexane, drying at 100 °C and calcination at 300 °C for 4 h, recovered conversion values as high as 70%.

Srilatha et al. have reported the catalytic activity 12-tungstophosphoric acid (TPA) impregnated on niobium oxide [31] for esterification of palmitic acid and transesterification of sunflower oil, they also reported that temperatures higher than 400°C for calcination led to degradation of TPA to metal oxides, thus decreasing the catalytic activity.

A literature survey shows that biodiesel production by esterification of free fatty acids has been carried out over heteropolyacids supported on to different supports such as silica, zirconia, niobia and clays. At the same time

reports on the use of heteropolyacids anchored to mesoporous materials for biodiesel production are scanty. Recently Castanheiro et al reported esterification of free fatty acids for biodiesel production over 12-tungstophosphoric acid immobilized on SBA-15 [32]. They studied esterification of palmitic acid in detail.

Therefore it was thought of interest to carry out biodiesel production by esterification of free fatty acid over TPA/TSA anchored to MCM-41.

The present chapter deals with applications of TPA/MCM-41 and TSA/MCM-41, catalysts in biodiesel production by esterification of free fatty acids. Esterification of palmitic acid and oleic acid with methanol was studied. The effect of various reaction parameters such as catalyst concentration, acid/alcohol molar ratio and temperature were studied to optimize the conditions for maximum conversion. Also the catalyst was regenerated and reused. A detailed kinetic study was carried out for the same. The rate constants as well as the activation energy for the reaction were determined. Koros Nowak test for heat and mass transfer limitations was also carried out. Based on the catalytic and kinetic data the best catalyst was also proposed.

Experimental

Materials

All chemicals used were of A. R. grade. Palmitic acid, oleic acid methanol, propyl alcohol, iso-propyl alcohol, butyl alcohol and *sec*-butyl alcohol, were obtained from Merck and used as received.

Catalytic reaction

The esterification of palmitic acid and oleic acid with methanol was carried out in a 100ml batch reactor provided with a double walled air condenser, Dean-Stark apparatus, magnetic stirrer and a guard tube. Dean-Stark apparatus was attached to a round bottom flask to separate the water formed during the reaction. The reaction mixture was refluxed at 60°C for 6hrs. The obtained products were analyzed on a Gas Chromatograph (Nucon-5700) using BP1 capillary column. Products were identified by comparison with the authentic samples and finally by Gas Chromatography-Mass Spectroscopy (GC-MS). TON and TOFs were calculated similarly as mentioned earlier.

RESULTS AND DISCUSSION

The esterification of free fatty acids is an equilibrium-limited reaction. In order to overcome the equilibrium limitation, generally esterification of free fatty acids is carried out by taking alcohol in excess in order to favor the forward reaction. The esterification of fatty acid, oleic acid with alcohol is shown in figure 60.

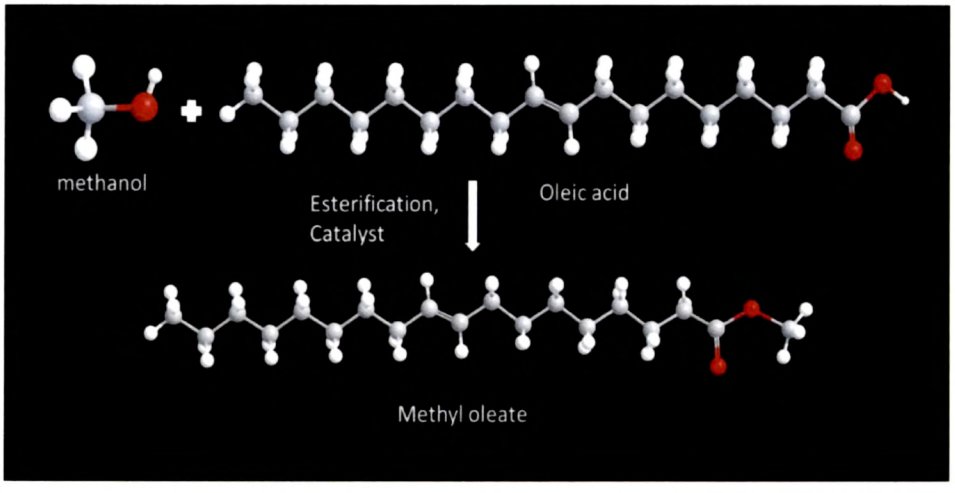

Figure 60. Esterification of oleic acid with methanol

The effect of various reaction parameters such as % loading of heteropolyacids, acid/ alcohol molar ratio, amount of catalyst, reaction time and temperature were studied to optimize the conditions for maximum conversion.

Effect of % loading of TPA/TSA

To study the effect of % loading esterification reaction was carried out with 10, 20, 30 and 40 % TPA/TSA loadings. The obtained results are shown in figure 61. It was observed that with increase in the % loading of TPA/TSA, % conversion also increases. For 10% and 20% loading of TPA, conversions for palmitic acid and oleic acid are considerably low even though the surface area is higher, this may be due to their less acidity. For 30 and 40% loadings, the difference in % conversion is not that much appreciable. Hence the catalyst containing 30% loading of TPA/TSA i.e. TPA_3/MCM-41and TSA_3/MCM-41 was used for the detail study.

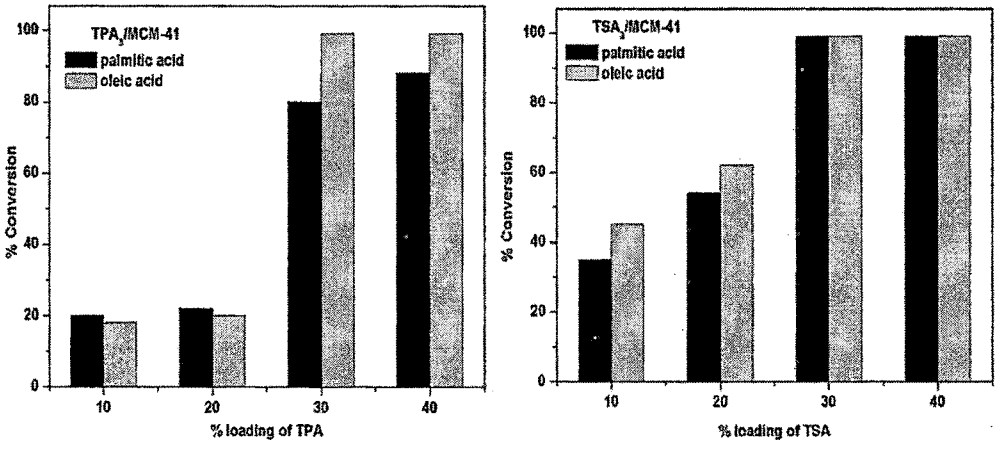

Figure 61. Effect of % loading of TPA/TSA ;Reaction conditions: mole ratio of acid to alcohol 1:40,amount of catalyst 0.1g, reaction temperature 60 °C, reaction time 6 and 8h for palmitic acid and oleic acid over TPA_3/MCM-41; 7 and 10 h for palmitic acid and oleic acid over TSA_3/MCM-41respectively.

Effect of mole ratio of acid to alcohol

To see the effect of mole ratio, esterification reaction was carried out by varying mole ratio of palmitic acid/oleic acid to methanol, with 0.1g of the catalyst for 4h at 60 ^{0}C. It can be observed from figure 62. The palmitic acid/oleic acid conversion increases with increase in the acid to methanol ratio and reaches to maximum conversion with the mole ratio of 1:40. With

further increase in molar ratio there is only a small increase in conversion. Hence molar ratio of 1:40 is optimum for obtaining high conversion products.

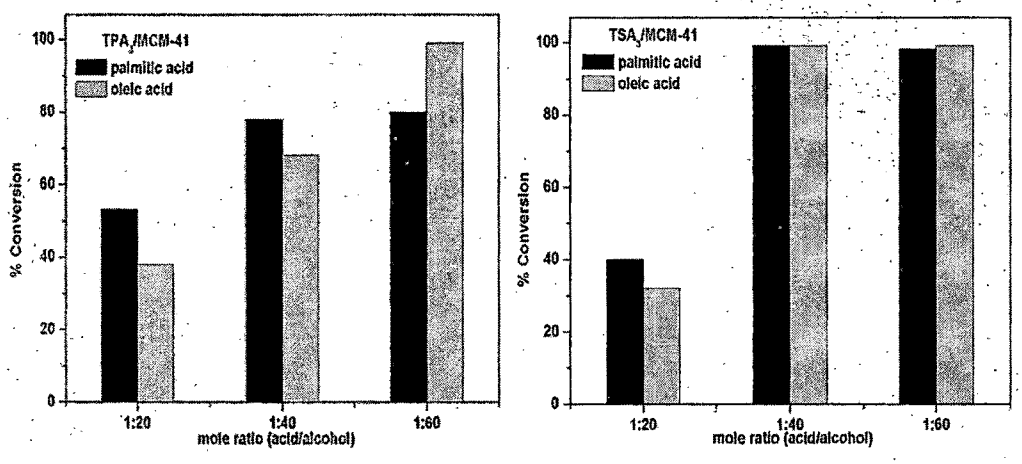

Figure 62. Effect of mole ratio oil/alcohol; Reaction conditions: amount of catalyst 0.1g, reaction temperature 60°C, reaction time 6 and 8h for palmitic acid and oleic acid over TPA_3/MCM-41; 7 and 10h for palmitic acid and oleic acid over TSA_3/MCM-41 respectively.

Effect of amount of catalyst

Effect of amount of catalyst on palmitic acid conversion was investigated. The catalyst amount was varied in the range of 0.025-0.125g. As shown in figure 63, the conversion increased with the increase in catalytic amount of TPA_3/MCM-41 and reaches to a maximum conversion with 0.1 g of catalyst. But with further increase in amount of catalyst the palmitic acid/oleic acid conversion remains constant. Hence 0.1g of catalyst amount was optimized.

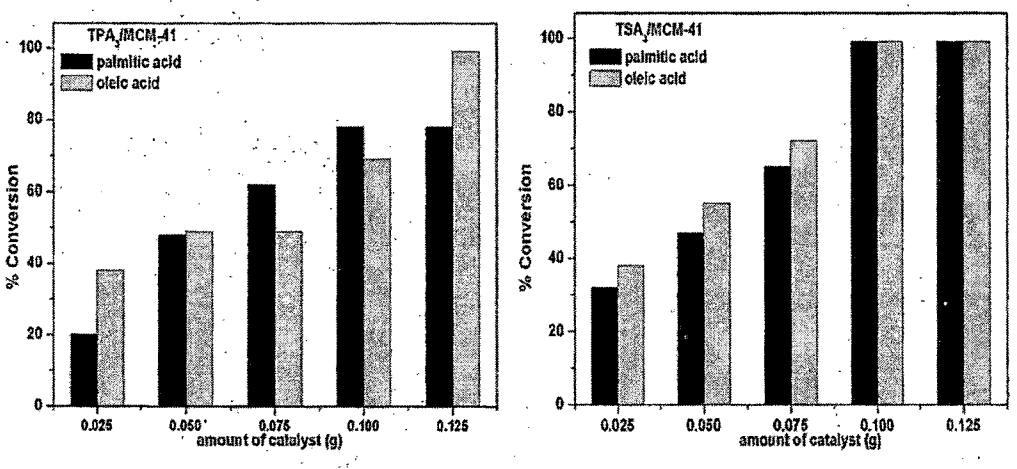

Figure 63. Effect of amount of catalyst; Reaction conditions: mole ratio of acid to alcohol 1:40, reaction temperature 60°C, reaction time 6 and 8h for palmitic acid and oleic acid over TPA_3/MCM-41; 7 and 10h for palmitic acid and oleic acid over TSA_3/MCM-41 respectively.

Effect of raection time

Effect of reaction time on conversion of fatty acids was investigated. It was observed (figure 64) that the palmitic acid/oleic acid conversion increases with increase in reaction time. The palmitic acid conversion was 100% palmitic acid in six hours, whereas oleic acid conversion was 99% in eight hours over TPA_3/MCM-41. However for TSA_3/MCM-41, 99% palmitic acid conversion was achieved in seven hours, whereas for oleic acid 99% in ten hours.

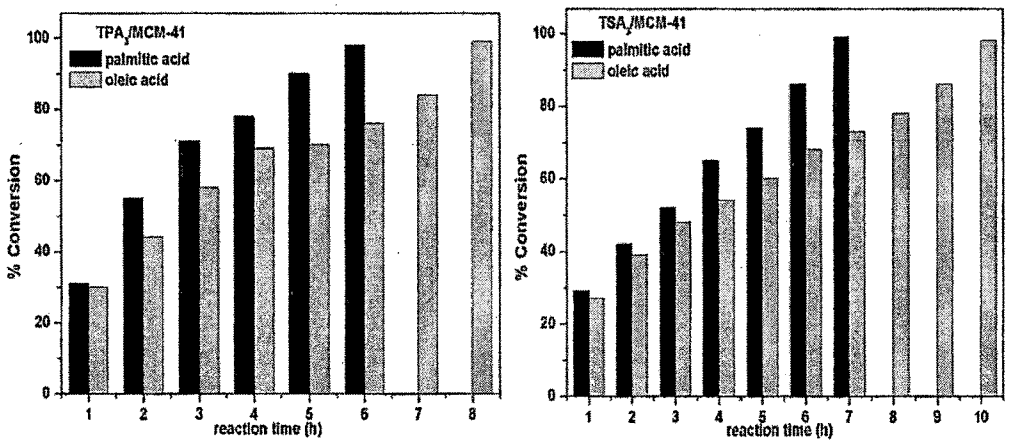

Figure 64. Effect of reaction time; Reaction conditions: mole ratio of acid to alcohol 1:40, amount of catalyst 0.1g, reaction temperature 60 °C.

Effect of reaction temperature

Effect of reaction temperature on palmitic acid/oleic acid conversion was studied and it was found that with increase in reaction temperature % conversion increases (figure 65). At temperatures higher than 60°C, higher conversions were achieved in short reaction time. However, the lower temperature i.e. 60°C was selected. Therefore all the reactions were studied at lower temperature i.e. 60°C.

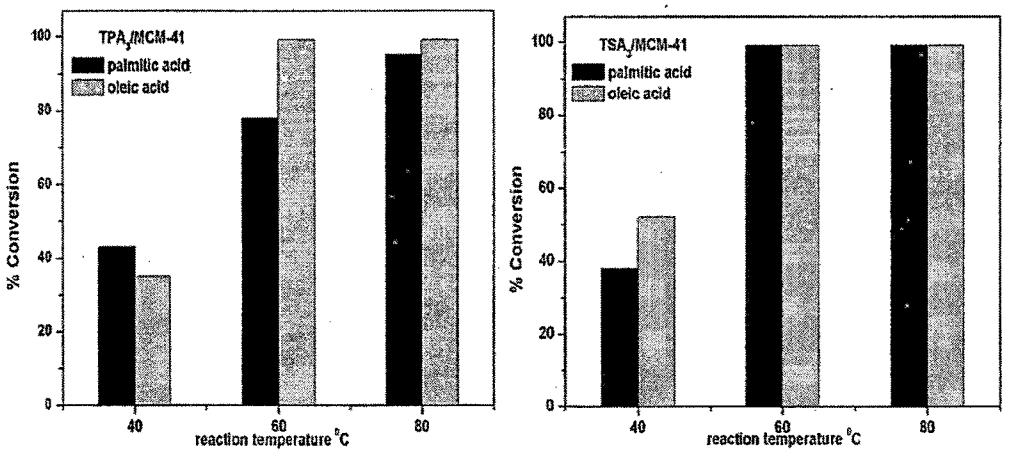

Figure 65.Effect of reaction temperature; Reaction conditions: mole ratio of acid to alcohol 1:40, amount of catalyst 0.1g, reaction time 6 and 8h for palmitic acid and oleic acid over TPA_3/MCM-41; 7 and 10h for palmitic acid and oleic acid over TSA_3/MCM-41 respectively.

The optimized conditions for esterification of palmitic acid are: Mole ratio of acid to alcohol 1:40; Amount of catalyst 0.1g; Reaction Temperature 60^{0}C and Reaction Time 6h (TPA_3/MCM-41) and 7 h (TSA_3/MCM-41).

The optimized conditions for esterification of oleic acid are: Mole ratio of acid to alcohol 1:40; Amount of catalyst 0.1g; Reaction Temperature 60^{0}C and Reaction Time 8h (TPA_3/MCM-41) and 10h (TSA_3/MCM-41).

Control experiments for esterfication of free fatty acids

The control experiments with MCM-41 and TPA/TSA were also carried out under optimized conditions.

Table 25. Control experiments for esterification of palmitic acid/oleic acid

[a]Materials	% Conversion	
	Palmitic acid	Oleic acid
[b]TPA	96	92
[b]TSA	94	90
MCM-41	<2	<2
TPA_3/MCM-41	100	98
TSA_3/MCM-41	99	90

[a]Reaction conditions: mole ratio of acid to alcohol 1:40,amount of catalyst 0.1g, reaction temperature 60°C, reaction time 6 and 8h for palmitic acid and oleic acid over TPA_3/MCM-41; 7 and 10h for palmitic acid and oleic acid over TSA_3/MCM-41respectively; [b]amount of catalyst for TPA/TSA : 23mg

It can be seen from table 25 that MCM-41 is not much active towards the esterification of oleic acid indicating the catalytic activity is mainly due to TPA/TSA. The same reaction was carried out by taking the active amount of TPA (23 mg) and the results obtained are shown in table 25. Almost the same activity was obtained for TPA_3/MCM-41 and TSA_3/MCM-41catalyst indicates that TPA/TSA is the real active species. Thus, we were successful in anchoring HPAs to MCM-41 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Esterification of free fatty acids with different alcohols

The esterification of palmitic acid with different alcohols was also carried out under optimized conditions and the conversions of palmitic acid for corresponding esters are shown in the Table 26. The order of catalytic activity is methyl palmitate< ethyl palmitate < propyl palmitate < butyl palmitate< iso-butyl palmitate< iso-propyl palmitate. The activities of alcohols were decreased as the carbon chain of the alcohols grew longer. This could be explained due to the alcohol reactivity, that was strongly affected by bulky hindrance on the hydroxyl group. Probably with the increase of hindrance on secondary hydroxyl, the attack onto fatty acid, palmitic acid carbonyl became more difficult, lowering the formation of esters. Similar trend was observed for oleic acid and the results are presented in table 27.

Table 26. Effect of alcohol chain length on fatty acid conversion over $TPA_3/MCM-41$

Alcohol	%conversion of palmitic acid	TOF(min^{-1})	%conversion of oleic acid	TOF(min^{-1})
Methanol	100	8.3	99	5.1
Ethanol	58	6.0	78	4.0
n-propanol	42	4.3	54	2.8
Iso-propanol	19	1.9	28	1.5
Butanol	32	3.32	45	2.3
Iso-butanol	30	3.29	36	1.9

Reaction conditions; mole ratio 1:40, amount of catalyst 0.1gm, reaction temperature 60 °C, reaction time 6h for palmitic acid, 8h for oleic acid.

Table 27. Effect of alcohol chain length on fatty acid conversion over TSA_3/MCM-41

Alcohol	% conversion of palmitic acid	TOF(min^{-1})	% conversion of oleic acid	TOF(min^{-1})
Methanol	99	6.0	99	4.0
Ethanol	75	4.4	73	3.0
n-propanol	55	3.2	52	2.1
Iso-propanol	27	1.6	25	1.0
Butanol	48	2.8	42	1.7
Iso-butanol	37	1.3	35	1.5

Reaction conditions; mole ratio 1:40, amount of catalyst 0.1gm, reaction temperature 60°C, reaction time 7h for plamitic acid, 10h for oleic acid.

Regeneration and Recycling of the catalyst

Characterization of Regenerated catalysts

The regenerated catalysts were characterized for DRS, elemental analysis (EDS) and leaching as well as heterogeneity test in order to confirm the retention of the catalyst structure, after the completion of the reaction as discussed earlier. The results are same and hence are not included.

Catalytic activity of regenerated catalysts

The catalyst was recycled in order to test its activity as well as stability. The catalyst was separated from the reaction mixture only by simple filtration, first washing was given with methanol to remove unreacted palmitic acid and then the subsequent washings were done by conductivity water and then driying at 100 °C and the recovered catalyst was charged for the further run. There is no appreciable change in the % conversion of palmitic acid using regenerated catalyst up to four cycles (figure 66).

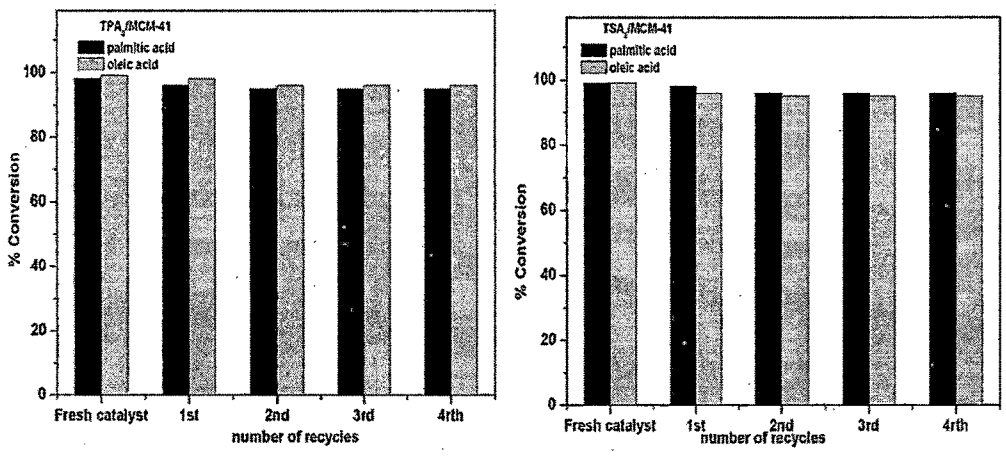

Figure 66. Recycling of the catalyst; Reaction conditions: mole ratio of acid to alcohol 1:40, amount of catalyst 0.1g, reaction temperature 60°C, reaction time 6 and 8h for palmitic acid and oleic acid over TPA_3/MCM-41; 7 and 10h for palmitic acid and oleic acid over TSA_3/MCM-41respectively.

Comparison of palmitic acid conversion with reported catalysts

The superiority of the present catalyst lies in obtaining higher conversion of palmitic acid under mild reaction conditions. It is observed from the table 28 that 100% conversion was obtained with PW-Silica catalyst [27], but the reaction time is very long 30hrs as well as high molar ratio of reactants which ultimately requires excess of methanol. With the TPA supported onto niobia catalysts [31], very high mole ratio of reactants was used and also there was no data about catalyst regeneration.

The alunmina incorporated MCM-41 catalyst [33] shows considerable activity at high reaction temperature. In the case of methane sulphonic acid sulphuric acid [34], 95% conversion was achieved at the cost of very high temperatures and corrosive nature of catalyst. Further, all the reported sulfated zirconia catalysts [35,36] exhibit sulfur leaching. For sulfonic acid modified SBA-15 [37] and sulfated zirconia on SBA-15 [38] catalysts systems, there is no data about catalyst deactivation behavior and regeneration of catalysts.

The present catalyst exhibits high palmitic acid conversions under mild reaction conditions. Further it is also interesting to note that the present catalyst gives very high TOF.

Table 28. Comparison of conversion of palmitic acid with reported catalyst

Reference	Catalyst	[a]Reaction conditions	%Conversion	Comments
Present work	**TPA_3/MCM-41**	**0.1g:40:60:6**	**100**	**Mild reaction condition, No deacticvation and easy regeneration**
Present work	**TSA_3/MCM-41**	**0.1g:40:60:7**	**99**	**Mild reaction condition, No deacticvation and easy regeneration**
[27]	PW-Silica	0.2g:4:60:30	100	Long Reaction time
[31]	TPA/Nb_2O_5	10:300:65:4	97.5	Very high mole ratio, No data about catalyst regeneration
[33]	Al-MCM-41	0.6:60:130:2	79	High temp
[34]	Methanesulphonic acid Sulphuric acid	0.01:3:130:1	95	High temp, Homogeneous catalyst
[35]	Tungstated zirconia1.0meq H+ g-1	75:200:60:6	>95	Tetragonal ZrO_2 And amorphous WO_3 is required
[36]	Sulfated zirconia 0.6 meq H+ g-1	40:30:60: 0.42	90	Sulfur leaching – deactivation
[37]	Sulfonic acid modified SBA15	0.05g:30:60:6	55	Low PA conversion
[38]	Sulfated zirconia on SBA-15 1.3 meq H+ g-1	2:80:68:6	89.2	No data about deactivation behavior

a: reaction conditions: amount of catalyst (%w/w, in some cases unit is g):mole ratio of methanol/palmitic acid: reaction temperature: reaction time(h)

Comparison of oleic acid conversion with the reported catalyst

The superiority of the present catalysts lies in obtaining higher conversion of oleic acid under mild reaction conditions. It is observed from the table 29 that 90% conversion was obtained under ultrasonic irradiations using sulphuric acid catalyst [39], although molar ratio and reaction time has been minimized but drawbacks of homogeneous sulphuric acid catalyst are well known.

Unsupported 12-tungstophosphoric acid [28] shows considerably high conversions but very large molar ration of reactants was used. Also the catalyst recovery requires use of organic solvent, hexane.

In case of TPA supported onto zirconia [30] the catalyst regeneration requires calcinations at high temperature; i.e. 300°C for 4h. For tungstated zirconia [40] catalysts systems, there is no data about catalyst deactivation behaviour and regeneration of catalysts. While zirconium doped MCM-41 silica supported WO_3 catalyst requires higher molar ratio of oleic acid/methanol and prolonged reaction time [41].

In case of Amazon flint kaolin and WO_3/USY solid acid catalysts, esterification reactions were carried out at very high reaction temperature [42, 43]. While cation-exchange resin, suffer from loss of resin catalysts which affects the reusability [44].

The present catalysts exhibit high oleic acid conversions under mild reaction conditions.

Table 29. Comparison of oleic acid conversion with reported catalyst

Reference	Catalyst	[a]Reaction conditions	%Conversion	Comments
* **Present work**	**TPA**	**0.023g%:40:40:4**	**92**	**Mild reaction conditions**
Present work	**TPA_3/MCM-41**	**0.1g/0.8wt%:40:40:8**	**99**	**Mild reaction condition, No deactivation and easy regeneration**
Present work	**TSA_3/MCM-41**	**0.1g/0.8wt%:40:60:10**	**99**	
*[28]	$H_3PW_{12}O_{40}$	0.0192mmole:164:25:4	92	Very higher molar ratio, catalyst recovery requires use of organic solvent, hexane.
[39]	H_2SO_4(under ultrasonic irradiation)	5:3:60:2	90	Use of corrosive homogeneous catalyst
[30]	20%H_3PW/ZrO_2	1:6:100:4	88	Catalyst was regenerated after calcinations at 300C for 4h, high reaction temperature
[40]	Tungstated zirconia. Uknown acid loading	4:20:75:1	65	No data about catalyst regeneration
[41]	WO_3/Zr-MCM-41	18.7:67:65:24	97	Higher molar ratio, long reaction time
[42]	Amazon flint kaolin	5:60:160:4	98.9	Very high reaction temperature
[43]	WO_3 /USY	1:6:200:2	74	Very high reaction temperature
[44]	Cation-exchange resin	18:3:66:3	90	Loss of resin catalyst which affects the reusability

[a]Reaction conditions: amount of catalyst wt%; mole ration oleic acid to alcohol; reaction temperature °C; reaction time h; * homogenous unsupported TPA catalysts

Kinetics

A detailed study on the kinetic behavior was carried out for esterification of palmitic acid/oleic acid over TPA_3/MCM-41 and TSA_3/MCM-41. In all the experiments, reaction mixtures were analyzed at fixed interval of time using gas chromatography. The esterification of palmitic acid/oleic acid methanol with was carried out with 1:40 molar ratio, since methanol was taken in large excess, the rate law is expected to follow first order dependence.

The plot of ln C/C_o *vs* time (figure 67) shows a linear relationship of palmitic acid/oleic acid consumption with respect to time. With increase in reaction time there is a gradual and linear decrease in the acid concentration over both the catalysts. These observations indicate the esterification of palmitic acid/oleic acid follows first order dependence with respect to time.

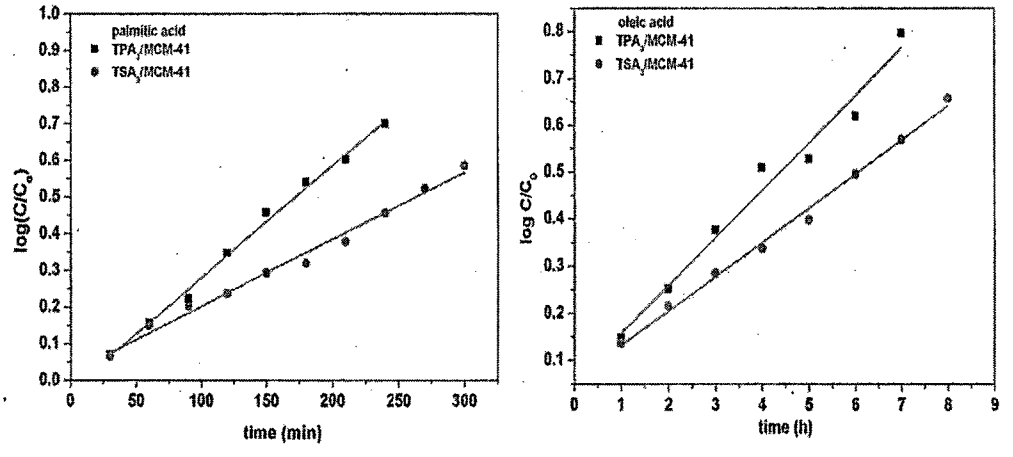

Figure 67. First order plot for esterification of palmitic acid and oleic acid

The catalyst concentration was varied form 2 x 10^{-3} to 10 x 10^{-3} mmol at fixed substrate concentration of 10 mmol and at temperature 60 °C. It can be observed from the figure 68 that rate of reaction increases with increase in the catalyst concentration. The plot of reaction rate *vs* catalyst concentration (figure 68) also shows a linear relationship with respect to catalyst concentration.

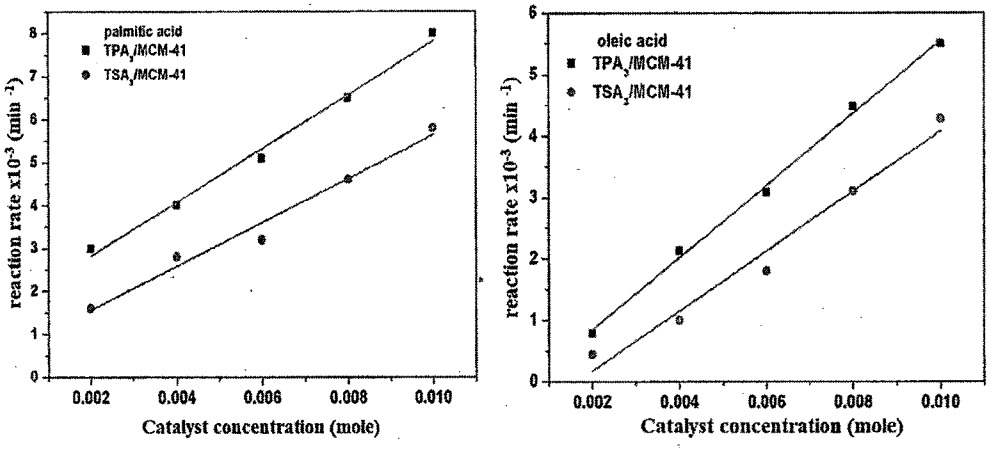

Figure 68. Plot of reaction rate vs catalyst concentrations

Estimation of activation energy

The graph of ln k vs. 1/T was plotted (Figure 69) and the value of activation energy (E_a) was determined from the plot. The value of activation energy (E_a), the pre-exponential factor (A) was determined using Arrhenius Equation.

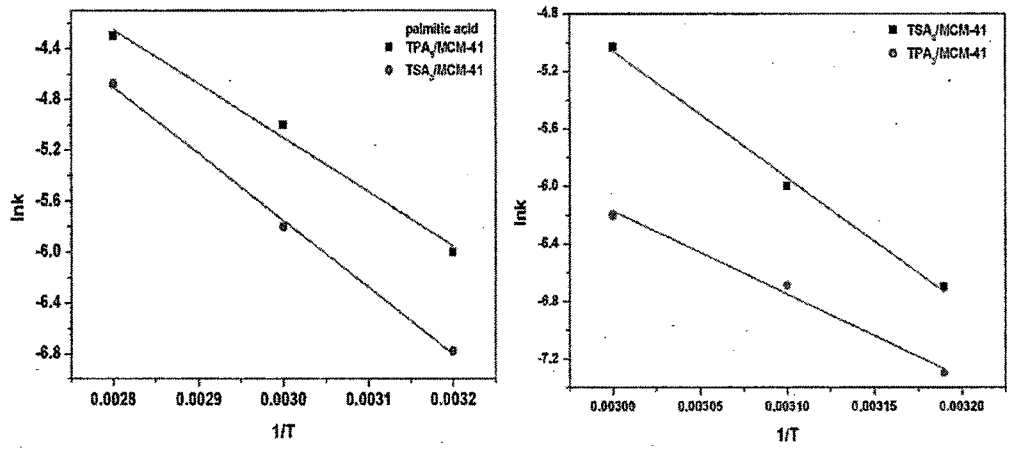

Figure 69. Arrhenius Plots for determination of activation energy

The kintetic parameters such as rate constant (k) , pre- exponential factor (A) and activation energy (Ea) for esterification reaction of palmitic and oleic acid are presented in Table 30.

Table 30. Esterification of free fatty acid with methanol

Catalyst	Free fatty acid	% Conversion	Kinetic parameters		
			Rate of reaction (min^{-1})	Arrehenius constant (A) (min^{-1})	Activation energy ($kJmol^{-1}$)
$TPA_3/MCM-41$	Palmitic acid	100	$6.4x10^{-3}$	9	38 .0
	Oleic acid	98	$2.33x10^{-3}$	12.8	52.4
$TSA_3/MCM-41$	Palmitic acid	98	$4.0x10^{-3}$	10	44.6
	Oleic acid	99	$1.8x10^{-3}$	21	72

It is important to recognize that the whether the reaction rate is diffusion limited/mass transfer limited or it is truly governed by the chemical step where the catalyst is being used to its maximum capacity. It is reported that the activation energy for diffusion limited reactions is as low as 10-15 $kJmol^{-1}$ and for reactions whose rate is governed by a truly chemical step usually show activation energy excess of 25 kJ mol^{-1} [45]. In the present case the observed values activation energy were higher than 25 kJ mol^{-1} and hence the rate is truly governed by chemical step.

Koros Nowak test

Koros and Nowak proposed an elegant experimental test to identify heat or mass transfer limitations in measurements of catalytic rates [46, 47]. If the observed TOF's are the same, it can be concluded that, under tested conditions, rates are not subjected to heat or mass transfer limitations.

Table 31. Koros Nowak Test for heat and mass transfer limitations

[a]Catalyst (%TPA anchored to MCM-41)	Concentration of active species TPA (mg)	Reaction rate ($x10^{-6}$ min^{-1})	TOF (min^{-1})
TPA_1/MCM-41	9.1	1.7	11.1
TPA_2/MCM-41	16.7	4.0	11.1
TPA_3/MCM-41	23.1	5.1	11.1
TPA_4/MCM-41	28.6	6.7	11.1

[a]Reaction conditions: mole ratio palmitic acid(0.01moles)/ alcohol(0.4 moles) : 1/40, amount of catalyst ;0.1 gm, reaction temperature; 60^0C, reaction time ; time at which the same palmitic acid conversion was observed.

In the present case, rate measurements were carried on the catalyst with similar dispersion but different active species loading (in the present case TPA). The comparison was done at the same conversion of palmitic acid. As shown in the Table 31 the observed TOF's are the same at different TPA loadings and hence the rates are not heat and mass transfer limited. The same trend is expected in case of oleic acid esterification over TPA_3/MCM-41. Similar trend was also expected in case of TSA_3/MCM-41 catalyst in esterification of palmitic acid as well as oleic acid.

Comparison of activation energy with the reported Catalysts for esterification of palmitic acid

Comparison of activation energies obtained for esterification of palmitic acid for the reported catalysts with the present catalyst is shown in Table 32.

Table 32. Comparison of activation energy with the reported Catalysts

Reference	Catalyst	Free fatty acid	Activation energy (kcal mol^{-1})
Present work	**TPA_3/MCM-41**	**Palmitic acid**	**9.2**
Present work	TSA_3/MCM-41	Palmitic acid	11.2
[48]	Sulphuric acid	Palmitic acid	13.34
[34]	Sulphuric acid	Palmitic acid	15.1
	Methanesulfonic acid		10.1
[31]	TPA/Nb_2O_5	Palmitic acid	13.7

The observed activation energy value (9.2 kcal mol^{-1}) for esterification of palmitic acid with methanol over TPA_3/MCM-41 is much less than the activation energy obtained by using traditional homogeneous sulphuric acid catalyst [48, 34]. Further, by comparing with other reported solid acid catalysts [31] the present catalyst exhibits much lower activation energy for esterification of palmitic acid.

Comparison of activation energy with the reported Catalysts for esterification of oleic acid

Comparison of activation energies, obtained for esterification of Oleic acid for the reported catalysts with the present catalyst is shown in Table 33. The observed activation energy value (12 kcal mol^{-1}) for esterification of Oleic acid with methanol over TPA_3/MCM-41 is near to the activation energy obtained by using traditional homogeneous sulphuric acid catalyst [34]. Further, by comparing with other reported solid acid catalysts [49], the present catalyst exhibits comparable activation energy but looking at reaction condition the present catalyst operates at much lower temperature; i.e. 60°C while the reported one works at 80 °C.

Table 33. Comparison of activation energy with the reported catalyst

Reference	Catalyst	Free fatty acid	Activation energy (kcal mol^{-1})
Present work	TPA_3/MCM-41	Oleic acid	12
Present work	TSA_3/MCM-41	Oleic acid	16.6
[34]	Sulphuric acid	Oleic acid	9.66
[49]	mesoporous SnO_2/WO_3	Oleic acid	9.1

Proposed Mechanism

The reaction mechanism of esterification using Brønsted acid [26] is as shown in Figure 70. The esterification takes place between free fatty acids (RCOOH) and alcohol, in the present case palmitic/oleic acid and methanol (CH_3OH). The interaction of the carbonyl oxygen of free fatty acid acidic site of the catalyst forms carbocation. The nucleophilic attack of alcohol to the carbocation produces a tetrahedral intermediate (Figure 70). During esterification the tetrahedral intermediate eliminates water molecule to form the alkyl ester of fatty acid (Biodiesel).

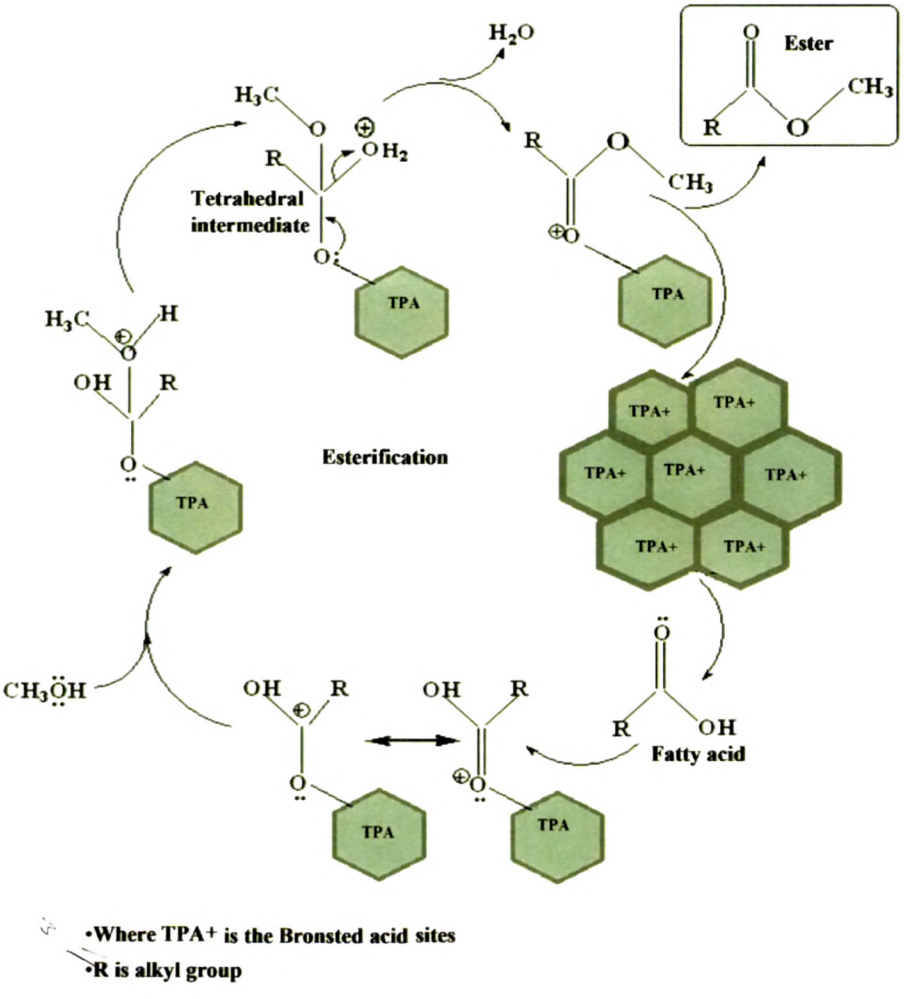

Figure 70. Mechanism of fatty acid esterification.

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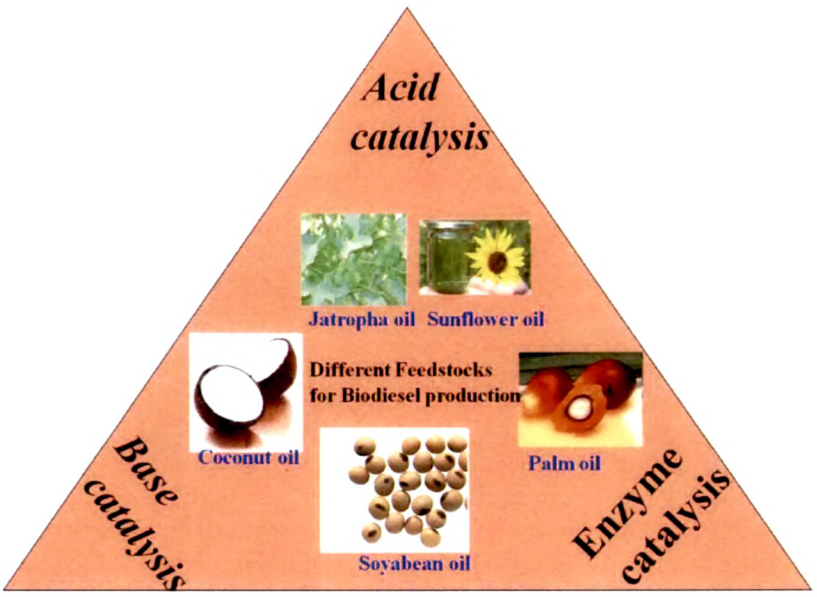
(b) Transesterification of triglycerides (Jatropha oil and Waste cooking oil)

In biodiesel production process, raw materials account for almost 75% of total biodiesel cost. The major obstacle to the commercialization of biodiesel, in comparison to petroleum-based diesel, is primarily the high raw material cost [1-4].

Basically all vegetable oils and animal fat can be used as feedstock for biodiesel production. Most of these oils and fats have a similar chemical composition; they consist of triglycerides with different amounts of individual fatty acids. The major fatty acids are those with a chain length of 16 and 18 carbons, whereas the chain could be saturated or unsaturated. Methyl esters produced from these fatty acids have very similar combustion characteristics in a diesel engine, because the major components in fossil diesel fuel are also straight chain hydrocarbons with a chain length of about 16 carbons (hexadecane, 'cetane'). The major feedstocks for the biodiesel production today are rape seed oil (Canola), soybean oil, coconut oil, sunflower oil and palm oil [5-9].



Different Feedstocks in biodiesel production

Especially in Asian countries like India and China the use of non-edible seed oils for biofuel production is very popular; in that case there would be no competition with the food production, especially when these oil plants are grown on marginal areas not suitable for food production. Especially *Jatropha curcas L.* has attracted enormous attention in last few years, especially in India, Indonesia and in the Philippines. As there would be no competition with the food production and also with the traditional agricultural areas, Jatropha could fill the gap between actual vegetable oil production and demand for biofuels [10-11].

An interesting alternative for low cost biodiesel production is the utilization of low quality raw materials as feedstocks such as waste cooking oil obtained from canteens restaurants and from houses which are rich in free fatty acids [12-16].

A literature survey shows that transesterifications of triglycerides to produce biodiesel involve use of different heterogeneous acid catalysts such as ion exchange resins[17], superacids such as tungstated and sulphated zirconia [18] polyaniline sulphate[19], metal oxides[20, 21], zeolites [22,23], acidic ionic liquids[24] and supported heteropolyacids[25]. The present thesis focuses, biodiesel production by transesterification of triglycerides over heteropolyacids catalysts.

Z. Su and co workers have reported $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, as a heterogeneous catalyst for the production of biodiesel from *Eruca sativa Gars.* oils (ESG oil) with methanol. The fuel properties of ESG biodiesel were found to be in agreement with the ASTM standard [26].

K. Wilson and co workers have reported structure activity relations in Cs-doped heteropolyacid catalysts for biodiesel production. Optimum performance occurs for Cs loadings of x = 2.0–2.3, correlating with the accessible surface acid site density. These catalysts were recoverable without any leaching [27].

X. Wang et al have reported transesterification of waste cooking oil with high acid value and high water contents using heteropolyacid $H_3PW_{12}O_{40}$ $6H_2O$ (PW_{12}) as catalyst was investigated. The hexahydrate form of PW_{12} was found to be the most promising catalyst which exhibited highest ester yield 87% for transesterification of waste cooking oil and ester yield 97% for esterification of long chain palmitic acid, respectively [28]. The same group has also reported a zirconiumdodecatungstophosphate $Zr_{0.7}H_{0.2}$ $PW_{12}O_{40}$ with nanotube structure. This nanotube catalyst shows high activity in biodiesel production by simultaneous esterification and transesterification [29]. They have also reported $Zn_{1.2}H_{0.6}PW_{12}O_{40}$ annotates with double acid sites as heterogeneous catalysts for the production of Biodiesel from waste cooking oil [30].

B. Hamad et at have reported supported 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 [31].

Y. Guo et al have reported transesterification of soybean oil to biodiesel catalyzed by mesostructured Ta_2O_5 -based hybrid catalysts functionalized by both alkyl-bridged organosilica moieties and Keggin-type heteropoly acid. The enhanced acid-catalytic reactivity after the introduction of both acidic and hydrophobic functionalities within the Ta_2O_5 matrix was discussed. Finally,

the reusability of the hybrid materials was evaluated through three catalytic runs [32-35].

Yu-Jie Fu et al have reported microwave-assisted transesterification technique to prepare biodiesel from yellow horn (*Xanthoceras sorbifolia Bunge.*) oil with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. A study for optimizing the reaction conditions such as reaction temperature, time, molar ratio of methanol/oil, catalyst amount, and recycle number of catalyst has been performed [16].

N. Lingaiah et al have reported cesium-exchanged 12-tungstophosphoric acids biodiesel synthesis from rice bran fatty acids [36]. They have reported a pseudo-first order kinetic model to analyze the experimental data and the apparent activation energy was 37.09 kJ/mol. P.S. Sai Prasad's group has reported biodiesel production from used cooking oil by two-step heterogeneous catalyzed process. The free fatty acids were first esterified with methanol using a 25wt%TPA/Nb_2O_5 catalyst followed by transesterification of the oil with methanol over ZnO/Na-Y zeolite catalyst [37]. Srilatha et al. have reported the catalytic activity 12-tungstophosphoric acid (TPA) impregnated on niobium oxide [38] for esterification of palmitic acid and transesterification of sunflower oil, they also reported that temperatures higher than 400 °C for calcination led to degradation of TPA to metal oxides, thus decreasing the catalytic activity.

G. D. Yadav and co-workers have reported the use of 12-tungstophosphoric acid supported on K-10 montmorillonite clay for transesterification of edible and non-edible oil at very high temperatures and pressure [39]. The activity decreases significantly during the fourth recycle and any post treatment cannot be given to regenerate the catalysts due to the alteration in clay pore structure, because of a collapse resulting in a severe reduction in surface area·

A. K. Dalai and co-workers have reported the use of 12-tungstophosphoric acid impregnated on four different supports such as hydrous zirconia, silica, alumina and activated carbon was used for the biodiesel production from low quality canola oil. They have reported 12-Tungstophosphoric acid supported on ZrO_2 showed best activity, but the reaction temperature was high affecting the cost factor in biodiesel production [40]. The same group has also reported 12-Tungstophosphoric acid supported on niobia, Nb_2O_5 catalyst for esterification and transesterification of used cooking oil. The catalyst was recycled and reused with negligible loss in activity. The kinetic studies suggested that the reaction follows the first-order kinetics [32].

A literature survey shows that development of biodiesel production process by transesterification of low triglycerol feedstocks over heterogeneous acid catalysts is still in a challenging stage. Keeping in mind the importance of biodiesel as a green fuel, as well as supported heteropolyacids as a green catalyst, in the present thesis we have made an attempt to develop an efficient reusable heterogeneous acid catalyst for biodiesel production via transesterification of waste cooking oil and jatropha oil.

The present chapter deals with applications of TPA/MCM-41 and TSA/MCM-41, catalysts in biodiesel production by transesterification of triglyceride feedstocks. Trasesterification of triglyceride feedstocks, jatropha oil and waste cooking oil with methanol was studied. The effect of various reaction parameters such as catalyst concentration, acid/ alcohol molar ratio and temperature were studied to optimize the conditions for maximum conversion. Also the catalyst was regenerated and reused. The obtained biodiesel, methyl esters were characterized for FT-IR and NMR. Also the properties of biodiesel were studied. Based on the catalytic activity data the best catalyst was also proposed.

Experimental

Materials

All chemicals used were of A. R. grade. Methanol and KOH were obtained from Merck and used as received.

Transesterification reaction

The properties of waste cooking oil and jatropha oil are as follows: acid value of waste cooking oil and jatropha oil was 49 and 37 mg KOH/g respectively. Free fatty acid content of waste cooking oil and jatropha oil was 24.5 and 18.5 respectively. The typical reaction of transesterification was carried out in a 100 ml batch reactor, provided with thermometer, mechanical stirring and condenser. Waste cooking oil and methanol were added in 1:8 wt/wt ratios and followed by catalyst addition, and then reaction mixture was held at 65 ^{0}C for 8h with stirring in order to keep system uniform in temperature and suspension. After the reaction is completed, the mixture was rotary evaporated at 50 ^{0}C to separate the methyl esters. The conversion of FFA in the WCO to biodiesel was calculated by means of the acid value (AV) of the oil layer with the following equation [41].

$$\text{Conversion (\%)} = \left(1 - \frac{AV_{OL}}{AV_{WCO}} \right)$$

Where OL and WCO refer to oil layer and waste cooking oil respectively.

RESULTS AND DISCUSSION

Transesterification of triglycerides: Waste cooking oil and Jatropha oil

Transesterification of triglycerides (TGs) with low molecular weight alcohols (figure 71) produces biodiesel. Jatropha oil (JO) is non-edible and does not compromise the edible oil, which are mainly used for food consumption. Non-edible oils are not suitable for human consumption because of the presence of toxic components. Further, Jatropha seed has a high content of oil and the biodiesel produced has similar properties to that of petroleum-based diesel. An interesting alternative for low cost biodiesel production is the utilization of low quality raw materials as feedstocks such as waste cooking oil (WCO) obtained from canteens restaurants and from houses which are rich in free fatty acids. Waste cooking oil used was a vegetable oil, obtained as waste from household activities.

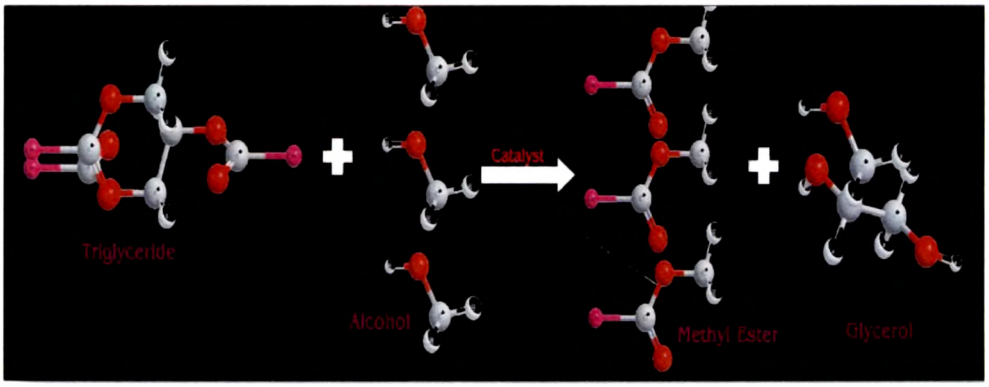


Figure 71. Transesterification of triglycerides with methanol

The effect of various reaction parameters such as % loading of TSA, acid/ alcohol molar ratio, amount of catalyst, reaction time and temperature were studied to optimize the conditions for maximum conversion.

Effect of % loading of TPA/TSA

To study the effect of % loading of TPA/TSA transesterification reaction was carried out with 10, 20, 30 and 40%laoded catalysts. The obtained results are shown in Figure 72. It is observed from the figure that with increase in the % loading of TPA/TSA, % conversion also increases. For 30 and 40% loadings, the difference in % conversion is not that much appreciable. Hence TPA_3/MCM-41 and TSA_3/MCM-41 was selected for carrying out detailed study.

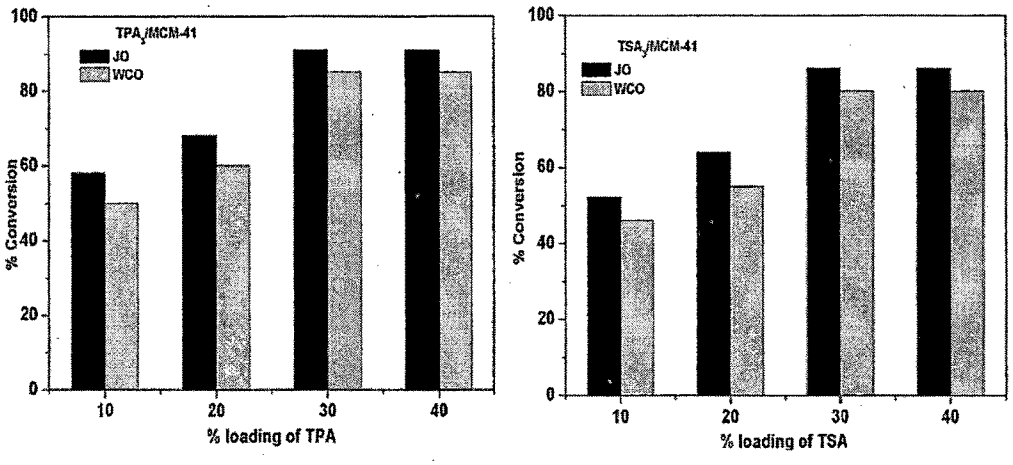


Figure 72. Effect of % loading of TPA/TSA; Reaction conditions: mole ratio oil to alcohol 1:8, amount of catalyst 0.3g,reaction temperature 65 °C, reaction time 16 and 20 h for TPA_3/MCM-41 and TSA_3/MCM-41

Effect of molar ratio of oil to alcohol

An important variable which can effect on the yield of methyl ester is the molar ratio of oil to alcohol. The reaction stoichiometry requires three moles of alcohol per mole of triglyceride to yield three moles of fatty esters and one mole of glycerin. But in practice a higher alcohol/oil ratio is employed in order to obtain a higher yield of ester production. We selected molars ratio of oil to methanol (wt/wt) between 1:2 and 1:8 (Figure 73).

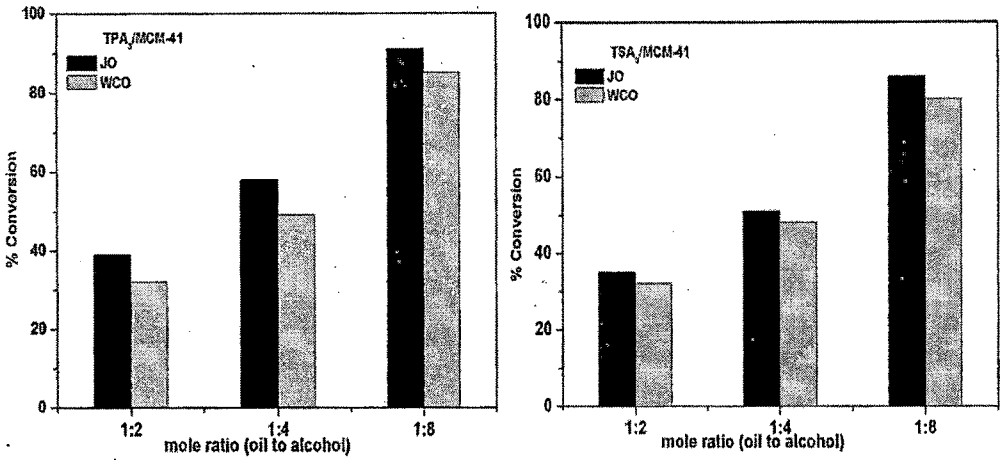


Figure 73. Effect of molar ratio; Reaction condition: amount of catalyst 0.3 g, reaction temperature 65 °C, reaction time 16 and 20 h for TPA_3/MCM-41 and TSA_3/MCM-41

The molar ratio 1:8 is suitable for obtaining high conversion of products as summarized in Figure 73. It was observed that oil conversion increased with the increases of the oil/methanol ratio and reached a maximum at 1:8, with a ratio of less than 1:8; the reaction was incomplete. When the oil/methanol ratio was higher than 1:8, the conversion decreased. So the molar ratio 1:8 is suitable for obtaining higher conversions.

Effect of amount of catalyst

The effect of the catalyst amount on the oil conversion is shown in Figure 74. Experiments were carried out by varying the amount of the catalyst between 0.1 to 0.5 g keeping the oil to methanol ratio at 1:8 at 65 °C. It was observed that an increase in the conversion of oil was noticed when the amount of the catalyst increased from 0.1g to 0.3 g and acid-catalyzed process attains a maximum conversion at 0.3 g of the catalyst. The increase in the oil conversion with an increase in the catalyst amount can be attributed to an increase in the availability and number of catalytically active sites. With further increasing the amount of catalyst from 0.3 to 0.5 g, decrease in the oil conversion was observed which may be due to the blocking of active sites.

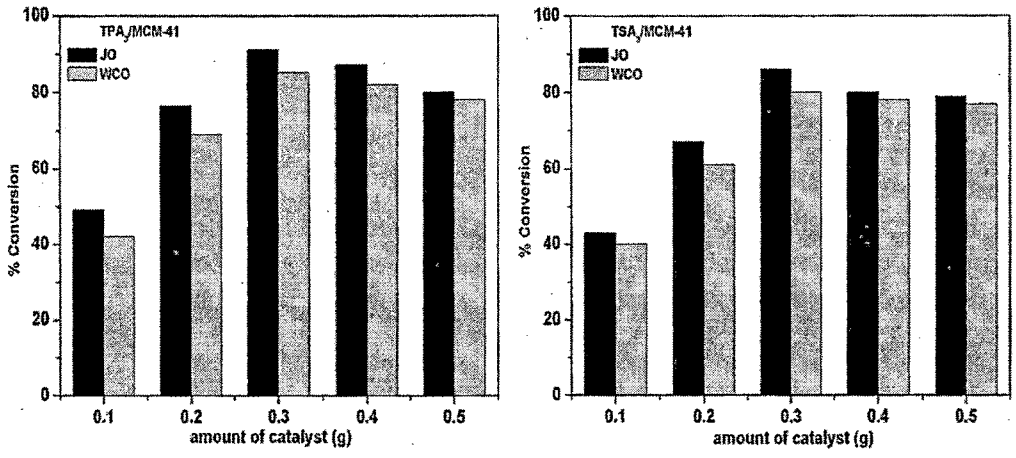


Figure 74. Effect of amount of catalyst; Reaction condition: mole ratio oil to alcohol 1:8, reaction temperature 65 °C, reaction time 16 and 20 h for TPA_3/MCM-41 and TSA_3/MCM-41

Effect of reaction time

Effect of reaction time on conversion of triglycerides was studied. It was observed (Figure 75) that the conversion increases with increase in reaction time. After 16 and 20 hours maximum conversion was achieved for jatropha oil and waste cooking oil over TPA_3/MCM-41 and TSA_3/MCM-41 respectively.

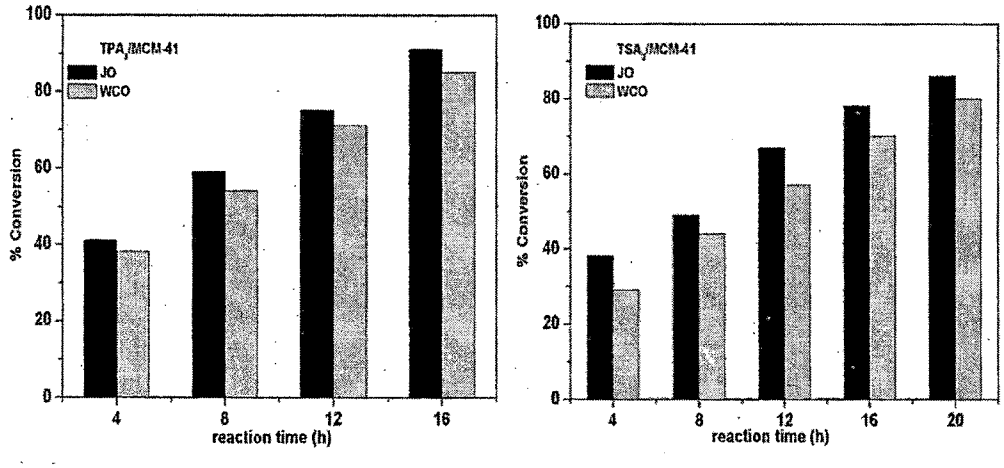


Figure 75. Effect of reaction time; Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g, reaction temperature 65 °C.

Effect of reaction temperature

Methanolysis of oils is normally performed near the boiling point of the alcohol. Effect of reaction temperature on conversion was studied and it was found that with as the reaction temperature increases conversion also increases (Figure 76). At 65 ^{0}C maximum 92% and 88% conversion was achieved for jatropha oil and waster cooking oil respectively. But with further increasing the temperature up to 70 ^{0}C, % conversion decreases. Usually the increase in reaction temperature, should lead to usual increase of reaction extent but also it could cause acceleration of secondary reactions which reduce the conversion towards desired product.

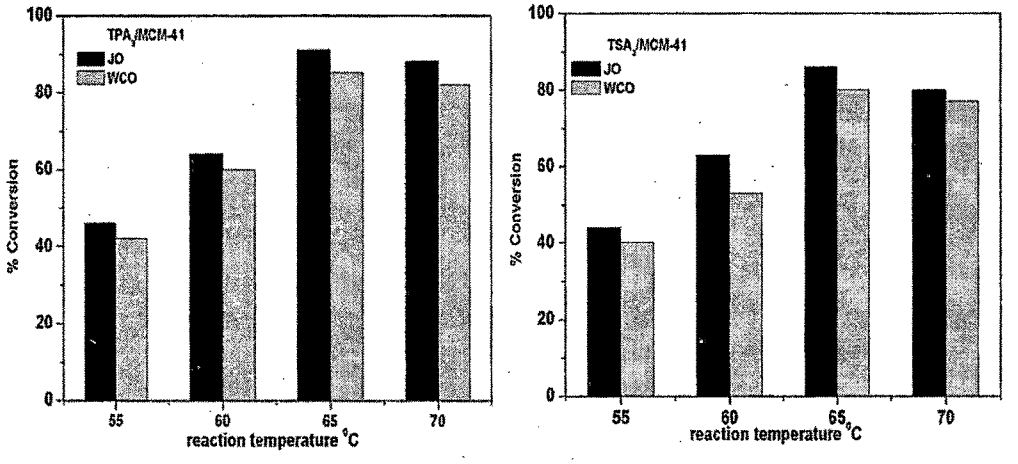


Figure 76. Effect of reaction temperature; Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g, reaction time 16 and 20 h for TPA_3/MCM-41 and TSA_3/MCM-41

The optimized conditions for transesterification of WCO and JO over TPA_3/MCM-41 are: Mole ratio of acid to alcohol 1:8; Amount of catalyst 0.3 g; Reaction Temperature 65 ^{o}C and Reaction time 16 h.

The optimized conditions for transesterification of WCO and JO over TSA_3/MCM-41 are: Mole ratio of acid to alcohol 1:8; Amount of catalyst 0.3 g; Reaction Temperature 65 ^{o}C and Reaction time 20 h.

The control experiments with MCM-41 and TPA/ TSA were also carried out under optimized conditions (Table 34).

Table 34. Control experiments for esterification and transestreification

[a]Catalyst	% conversion	
	Jatropha oil	Waste cooking oil
[b]TPA	88	84
[b]TSA	82	78
MCM-41	<2	<2
TPA_3/MCM-41	91	85
TSA_3/MCM-41	86	80

[a]Reaction condition; mole ratio oil to alcohol 1:8, amount of catalyst 0.3g,reaction temperature 65 °C, reaction time 16 and 20 h for TPA_3/MCM-41 and TSA_3/MCM-41; [b] amount of active species TPA/TSA 69 mg

It can be seen from Table 34 that MCM-41 is not much active towards the transesterification of triglycerides indicating the catalytic activity is mainly due to TSA. The same reaction was carried out by taking the active amount of TPA/TSA (69 mg) and the obtained results are shown in Table 34 .Almost the same activity was obtained for TPA_3/MCM-41 and TSA_3/MCM-14 catalyst indicates that TPA/TSA is the real active species. Thus, we were successful in anchoring HPAs to MCM-41 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Regeneration and Recycling of the catalyst

Characterization of Regenerated catalysts

The regenerated catalysts were characterized for DRS, elemental analysis (EDS) and leaching as well as heterogeneity test, in order to confirm the retention of the catalyst structure, after the completion of the reaction as discussed earlier. The results are same and hence are not included.

Catalytic activity of regenerated catalysts

The catalytic activity of the regenerated catalysts is shown in Figure 77. The catalyst was easily separated from the reaction mixture, because at the end of the reaction, the catalyst settled at the bottom of the reactor, and was used without any treatment. As the catalyst was able to settle from the mixture of fatty acid methyl ester and glycerin into the bottom of the reactor, the upper phase consists of fatty acid methyl ester did not contain any solid.

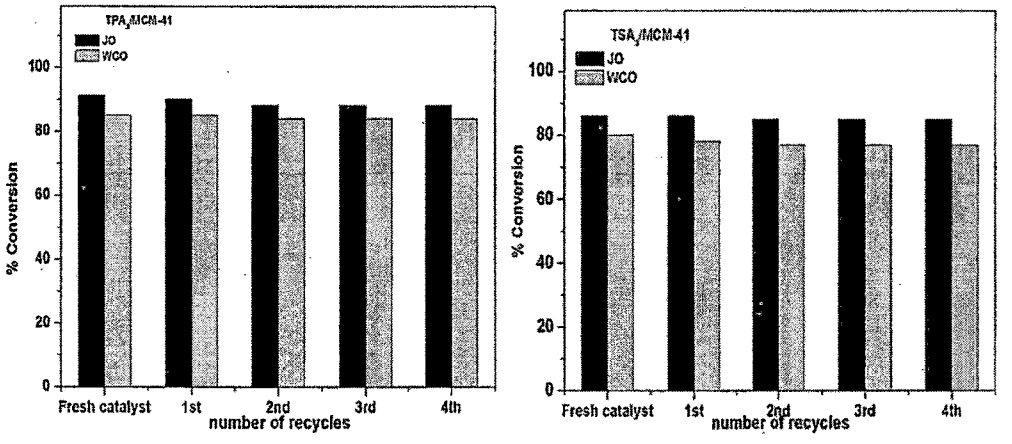


Figure 77. Recycling of the catalysts; Reaction condition: mole ratio oil to alcohol 1:8, amount of catalyst 0.3 g,reaction temperature 65 °C, reaction time 16 and 20 h for TPA_3/MCM-41 and TSA_3/MCM-41

This can be determined from the FT-IR spectra of the fatty acid methyl ester, in figure 78. The FT-IR spectra do not exhibit the characteristics stretching vibrational bands of 12-tungstophosphate ion, indicating that no TPA exists in the biodiesel. Hence, the product, i.e. biodiesel, did not need any washing treatment by base water, i.e., this process did not generate any waste water and is environmentally benign. The experiments were repeated four times by the same transesterification procedure and the conversions are given in Figure 77. This shows that there is no significant loss in activity of the catalysts even after four cycles.

Characterization of biodiesel derived from transesterification of jatropha oil and waste cooking oil.

The biodiesel samples from transesterification of jatropha oil and waste cooking oil were characterized by FT-IR and ^1H NMR spectra. The biodiesel i. e. fatty acid esters obtained by transesterification of jatropha oil and waste cooking oil were designated as BD1 and BD2 using TPA_3/MCM-41; and BD3 and BD4 using TSA_3/MCM-41 catalyst respectively.

FT-IR analysis for fatty acid methyl esters

The FT-IR spectra have been used to identify functional groups and the bands corresponding to various stretching and bending vibrations in the samples of biodiesel derived from jatropha oil and waste cooking oil (Figure 78). The position of carbonyl group in FT-IR is sensitive to substituent effects and to the structure of the molecule. The methoxy ester carbonyl group in BD1 and BD2 was appeared at 1741 cm^{-1} and 1743 cm^{-1} respectively. The band appeared at 3465 cm^{-1} showed the overtone of ester functional group. The C-O stretching vibration in BD1 and BD2 showed two asymmetric coupled vibrations at 1171 cm^{-1} and 1191 cm^{-1} due to C-C(=O)-O and 1017 cm^{-1} due to O-C-C respectively.

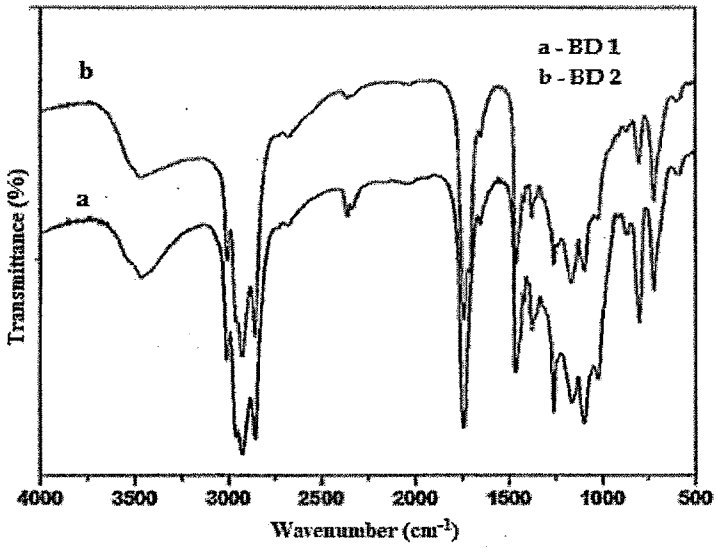


Figure 78. FT-IR spectra of biodiesel samples (a) BD1 (b) BD2

^{1}H NMR of biodiesel samples

Biodiesel samples BD1 and BD2 were characterized by ^{1}HNMR spectroscopy (figure 79) as summarized in Table 35. The characteristic peak of methoxy protons was observed as a singlet at 3.67 ppm and 3.669 ppm for BD1, and BD2 and a triplet of CH_2 protons at 2.28 ppm, and 2.8 ppm for BD1 and BD2 biodiesel samples. These two peaks are the distinct peaks for the confirmation of methyl esters present in biodiesel.

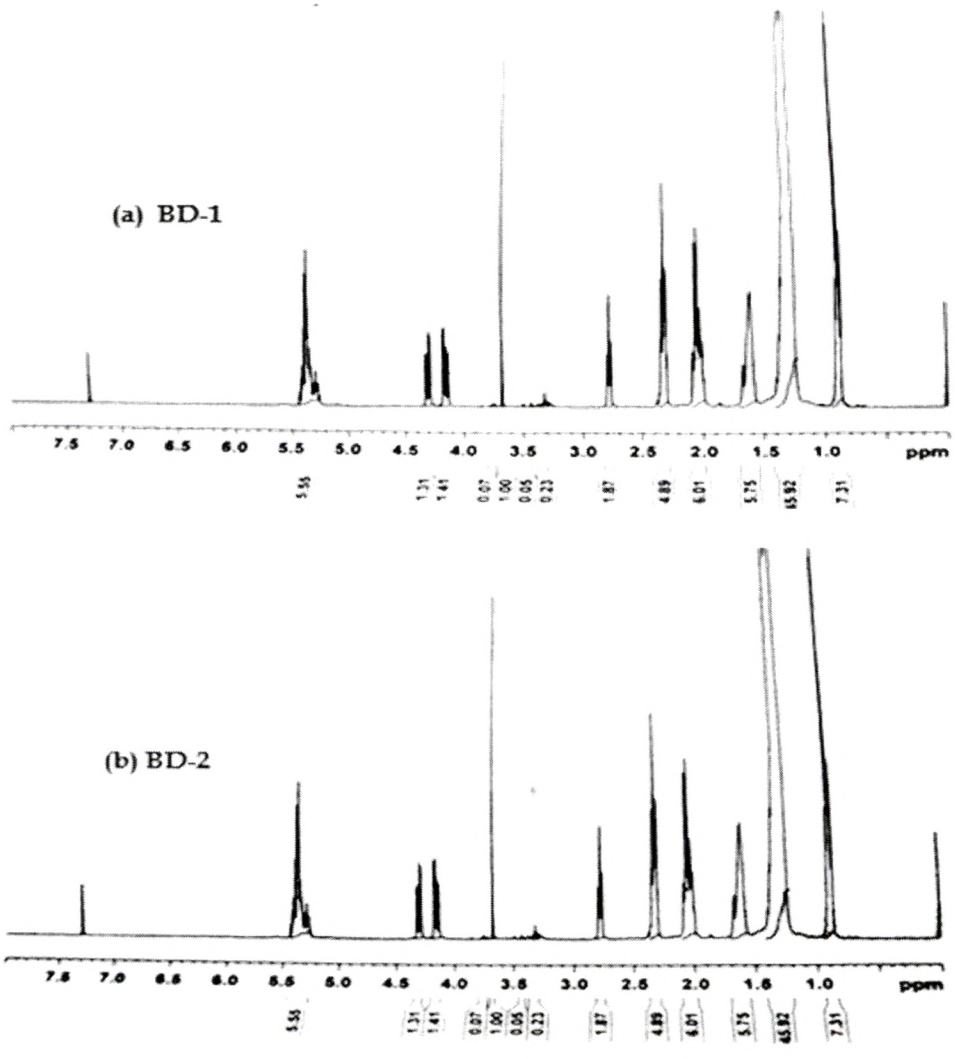


Figure 79. ^{1}H NMR of biodiesel samples (a) BD1 (b) BD2

Table 35. Chemical shifts assignments in ^1H NMR of BD1 and BD2

sample	OCH_3 -Methoxy proton (ppm)	α-CH_2 proton (ppm)	CH=CH unsaturation (ppm)
BD1	3.67	2.28	5.5-5.2
BD2	3.669	2.8	5.5-5.3

Properties of biodiesel produced

The physical and chemical properties of biodiesel from jatropha oil and waste cooking oil were studied [26, 42]. The biodiesel was prepared in the laboratory scale. The biodiesel samples BD1, BD2, BD3 and BD4 were analyzed for various properties. The properties measured were compared with the ASTM specifications and the results are presented in Table 36.

Table 36. Properties of biodiesel

Property	Testing procedure	ASTM D6751 Standard for Biodiesel	ASTM D 975 Standard for diesel fuel	BD1	BD2	BD3	BD4
Viscosity at 40°C	ASTM D446	1.9-6	1.3-4.1	4.8	5.0	4.9	5.2
Flash point(°C)	-	100-170	60-80	110	125	112	120
Pour point(°C)	ASTM D97	-15 to 10	(-35) -15	-2	-5	-1	-3
Cetane number	ASTM D613-95	48-65	40-55	50	52	48	49
Copper strip corrosion	ASTM D130	No. 3	-	No.1	No.1	No.1	No.1

The kinematic viscosity indicates that the flow capability of any fuel and it was found that for all the samples it was within the limits of ASTM standards. The flash point of biodiesel samples was within the limits of ASTM standard, biodiesel was safer than petro-diesel to handle and store because it has a little bit higher flash point than petro-diesel. The pour point of biodiesel samples BD1 and BD3 was -2 and -1, which may be due to the higher content of unsaturated fatty acid in raw jatropha oil. The result was found to be within the specified limit and biodiesel samples were suitable not only for the tropical region but also for moderate temperate region. The cetane index of biodiesel from jatropha oil with methanol was found to be within the ASTM specified limit. The higher cetane index of biodiesel compared to petrodiesel was indicated that it will be the high potential for engine performance. The copper strip corrosion test was also carried out and the results were within the ASTM specified limit for all the samples. The biodiesel samples were stored for about 11 months without any significant change. But further research and development on additional fuel properties and the effects of biodiesel on the engine are necessary.

Transesterification of triglyceride feedstocks with the different reported catalysts: A Comparison

The superiority of the present catalyst lies in obtaining higher conversion of triglycerides under mild reaction conditions. It is observed from the Table 37 that 12-tungstophosphoric acid supported on to Nb_2O_5, ZrO_2 and montmorillonite clay [38-40] exhibits higher conversions but the much higher temperature and pressure were required.

Ion- exchange resin based catalyst exhibited good activity much higher molar ratio of oil to alcohol [43] and prolonged reaction time [44] was required and there was no data about catalyst deactivation behaviour and regeneration of

catalysts. The tungstated zirconia catalyst and carbon based solid acid catalyst higher molar ratios and amount of catalyst [45] and reaction time [46] was required.

Table 37. Transeterification of triglyceride feedstocks with the different reported catalysts

Reference	Catalyst	Feedstock	[a]Reaction conditions	Conversion
Present work	$TPA_3/MCM-41$	Waste cooking oil	1:8;0.3g;65;16	91
Present work	$TPA_3/MCM-41$	Jatropha oil	1:8;0.3g;65;16	85
Present work	$TSA_3/MCM-41$	Waste cooking oil	1:8;0.3g;65;20	86
Present work	$TSA_3/MCM-41$	Jatropha oil	1:8;0.3g;65;20	80
[38]	12-tungstophosphoric acid/Nb_2O_5	Rapseed oil	1:20:3wt%:200:20*	90
[39]	12-Tungstophosphoric acid/ Zirconia	Canola oil	1:9;3wt%:200:10*	77
[40]	12-tungstophosphoric acid supported on K-10 montmorillonite clay	Waste cooking oil	1:15;5wt%;170;8[b]	94
[43]	Acidic ion-exchange resin (amberlyst& Dovex)	Waste cooking oil	1:20;2wt%;60;100min	45.7
[44]	Amberlyst-15	Waste cooking oil	--;1wt%;120,24	100
[45]	WO_3/ZrO_2	Waste cooking oil	1:9;5wt%;60;5	96
[46]	Carbon based solid acid catalyst	Waste cooking oil	1:18;1wt%;260;2.5	89

[a]Reaction conditions: mole ratio of oil/alcohol; amount of catalyst; reaction temperature °C; reaction time (h)

* reaction was carried under pressure at 600psi ; [b] reaction was carried out under pressure at 17 atm/250psi

The present catalysts operates under mild conditions in transesterification of triglycerides and can be recycled and reused up to cycles without significant loss in activity.

Mechanism of transesterification

The reaction mechanism of transesterification using Brønsted acid [47] is as shown in Figure 80. The transesterification takes place between triglyceride and alcohol, in the present case oil and methanol (CH_3OH). The interaction of the carbonyl oxygen of free fatty acid acidic site of the catalyst forms carbocation. The nucleophilic attack of alcohol to the carbocation produces a tetrahedral intermediate (Figure 80). During transesterification the tetrahedral intermediate eliminates water molecule to form the alkyl ester of fatty acids (Biodiesel). The transesterification mechanism can be extended to tri- and di-glyceride. It is well known that transesterification is a stepwise reaction. In the reaction sequence, the triglyceride is converted stepwise to di- and monoglyceride and finally glycerol. The tetrahedral intermediate formed during reaction eliminates di-, monoglyceride and glycerol when tri-, di- and monoglyceride come in contact with the acidic sites, respectively, to give one mole of ester ($RCOOCH_3$) in each step.

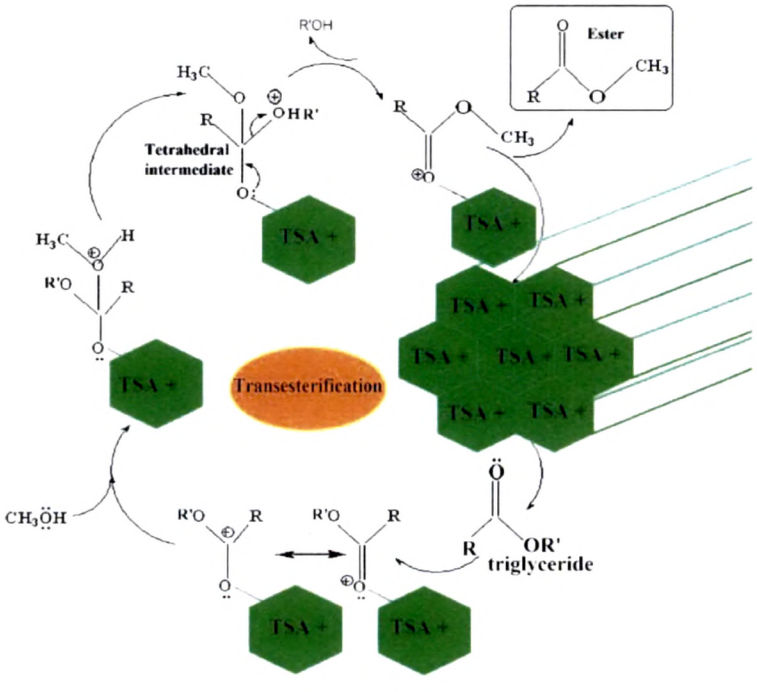


Figure 80. Mechanism of transesterification

Effect of heteropolyanion (Effect of heteroatom)

The catalytic activity of heteropoly acids TPA and TSA anchored to MCM-41 was compared in different reactions to see the effect of heteropolacid as shown in Table 38 and 39 respectively.

Table 38. Esterification of palmitic acid and oleic acid

Catalyst	Free fatty acid	Activation energy (kJ)	TOF (min^{-1})
TPA_3/MCM-41	Palmitic acid	38.0	8.3
TSA_3/MCM-41	Palmitic acid	44.6	6.0
TPA_3/MCM-41	Oleic acid	52.4	6.1
TSA_3/MCM-41	Oleic acid	72	4.0

Table 39. Transesterification of triglycerides

[a]Catalyst	Feedstock	%Conversion
TPA_3/MCM-41	Waste cooking oil	91
TPA_3/MCM-41	Jatropha oil	85
TSA_3/MCM-41	Waste cooking oil	70
TSA_3/MCM-41	Jatropha oil	78

[a]Reaction conditions: mole ratio of oil/alcohol 1:8; amount of catalyst 0.3 g; reaction temperature 65 °C; reaction time 16 h

It can be observed from Table 38 and 39 that the value of activation energy for TPA_3/MCM-41 is less than that of TSA_3/MCM-41 indicating the former is more active. This difference in catalytic activity is due to the nature of heteropoly acid. It is well known that TPA is more acidic as compared to that of TSA and hence the results are as expected. The high surface area, total acidity as well as higher TOF value observed for TPA_3/MCM-41 all adamantly reveal the superior activity of TPA_3/MCM-41 as compared to TSA_3/MCM-41.

The acid strength of heteropolyacids, follows the following order $H_3PW_{12}O_{40}$ > $H_4SiW_{12}O_{40}$. Hence the TPA_3/MCM-41 shows superior activity as compared to TSA_3/MCM-41, as expected.

Effect of Support pore diameter (Pore Expanded MCM-41)

The comparison of catalytic activity of TPA_3/MCM-41 and TPA_3/PE-MCM-41 in esterification of free fatty acids, palmitic acid and oleic acid as well as for transesterification of triglycerides such as jatropha oil and waste cooking oil as shown in Table 40 and 41 respectively.

Table 40. Esterification of free fatty acids

[a]Catalyst	Free fatty acid	% Conversion	TOF (min^{-1})
TPA_3/MCM-41	Palmitic acid	52	4
TPA_3/PE-MCM-41	Palmitic acid	98	14
TPA_3/MCM-41	Oleic acid	48	3
TPA_3/PE-MCM-41	Oleic acid	99	11

[a]Reaction conditions: mole ratio of acid to alcohol 1:40, amount of catalyst 0.1 g, reaction temperature 60 °C, reaction time 3 , 4 h for palmitic, oleic acid respectively

Table 41. Transesterification of triglycerides

[a]Catalyst	Feedstock	%Conversion
TPA_3/MCM-41	Waste cooking oil	55
TPA_3/PE-MCM-41	Waste cooking oil	89
TPA_3/MCM-41	Jatropha oil	60
TPA_3/PE-MCM-41	Jatropha oil	94

[a]Reaction conditions: mole ratio of oil/alcohol 1:8; amount of catalyst 0.3 g; reaction temperature 65 °C; reaction time 8 h.

First of all as the surface area of PE-MCM-41 is higher than that of MCM-41 and the same trend was observed for the catalysts. The higher value of surface area for TPA_3/PE-MCM-41 as compared to that of TPA_3/MCM-41 is responsible for higher catalytic activity.

In the present case, for PE-MCM-41 support, pore diameter is 5.0 nm and after anchoring TPA it decreases to 4.8 nm; still there is enough space available for reactants to enter. Whereas for MCM-41 support, pore diameter is 4.7 nm which decreases to 3.0 nm after anchoring TPA, hence the available space is much more suitable for small molecules rather than bigger molecules as reactants (Figure 81).

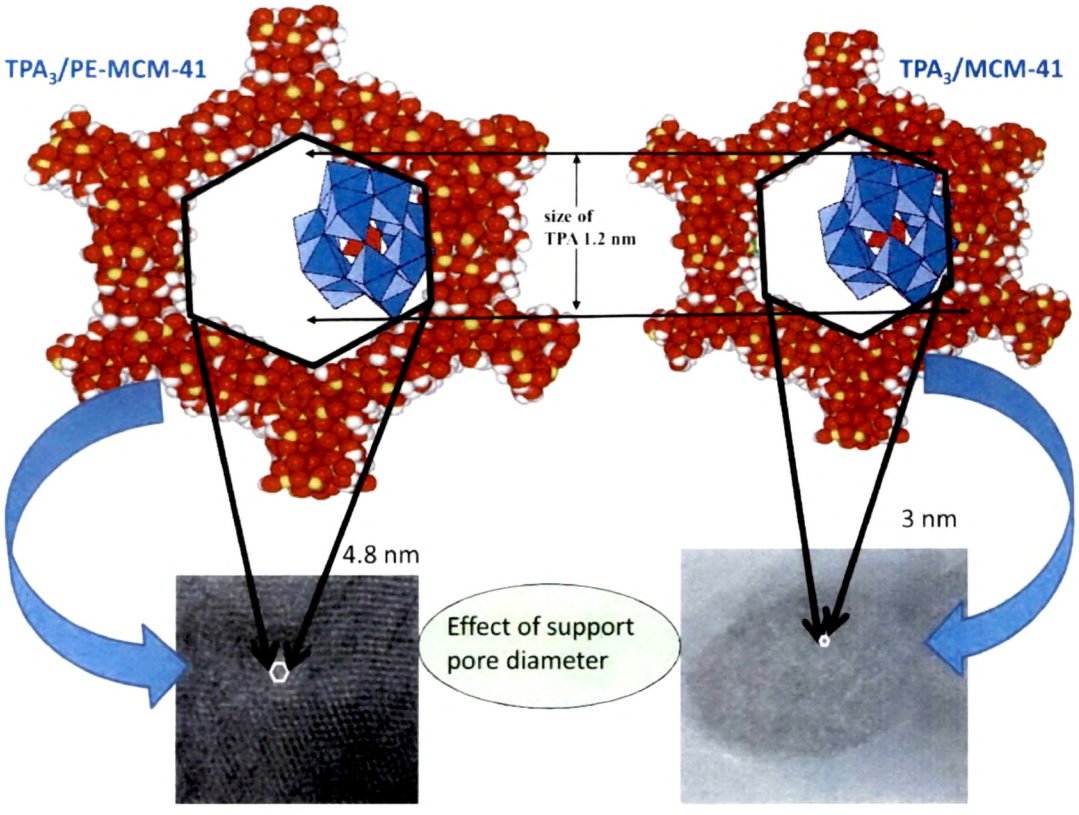


Figure 81. Effect of support pore diameter

Conclusion

- The present catalysts exhibit significant activity toward biodiesel production via esterification of free fatty acid, palmitic acid and oleic acid under relatively mild conditions.
- TPA_3/MCM-41 gives 98 and 99% conversion of palmitic acid and oleic acid in 6 and 8 h respectively.
- TSA_3/MCM-41 gives 99% conversion of palmitic acid and oleic acid in 7 and 10h respectively.
- Kinetic studies show that esterification of palmitic acid follows first order rate law. Also the activity of the present catalyst is much higher than the traditional sulphuric acid catalyst and the other solid acid catalysts.
- The present catalyst also exhibits excellent activity for the transesterification of triglyceride feedstocks, waste cooking oil and Jatropha oil with methanol under mild conditions.
- TPA_3/MCM-41 gives 91 and 85% conversion of jatropha oil and waste cooking oil respectively.
- TSA_3/MCM-41 gives 86 and 80% conversion of jatropha oil and waste cooking oil respectively.
- This excellent catalytic performance is mainly attributed to the large surface area and pore diameter of MCM-41 as well as the Bronsted acid strength of TPA/TSA, as active sites.
- EDS, DRS as well as acidity studies of reused catalysts shows no structural changes indicating catalytic systems are stable.
- The catalysts were regenerated and reused successfully up to four cycles.
- The TPA_3/MCM-41 shows superior catalytic activity as compared to TSA_3/MCM-41.
- TPA_3/PE-MCM-41 exhibits excellent catalytic activity compared to TPA_3/MCM-41 due higher pore diameter of former than the later.

- Also the catalytic results demonstrated that the size of the support channels plays a crucial role in catalyst performance
- We could successfully developed green catalysts for biodiesel production from waste cooking oil and jatropha oil

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