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ARTICLE TYPE

Esterification of glycerol over a solid acid biochar catalyst derived from waste biomass

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Karanja seed shells were subjected to pyrolysis in inert atmosphere at different temperatures to prepare biochar. The biochar was characterized by X-ray diffraction, FT-infra red, Laser Raman, thermo gravimetric analysis, CHNS-elemental analysis, BET surface area and temperature programmed desorption of ammonia. These biochar carbon catalysts were used as catalysts without any functionalization/treatment for the esterification of glycerol with acetic acid. Carbonization at 400 ^{o}C led to the formation of biochar with more number of strong acidic sites. High temperature carbonization amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion. The biochar obtained at 400 ^{o}C exhibited highest glycerol esterification activity. The catalytic activity of the biochar was explained based on its properties derived from different characterization methods. The biochar catalyst can be reusable with consistent activity.

Keywords: Karanja seed shells; pyrolysis; biochar; glycerol; esterification

1. Introduction

The Conversion of variety of biomass materials into useful products such as liquid, gas and char is important area of research due to their abundant availability and low cost.[1] Lignocellulosic biomass can be converted into useful chemicals by different thermo-chemical processes.[2] Gasification or pyrolysis of biomass has been widely used to gain the energy content of biomass.[3] Pyrolysis is the main process to recover energy from biomass by generating char, oil and gas as major products.[4] One of the products, biochar produced from the variety of biomass was found to be useful for the production of active carbon.[3] Biomass like rice husk,[5] sunflower shells,[2] pistachio nutshells,[5] peanut hulls,[6] almond shells[7-9] were effectively utilized for the production of active carbon. These carbons were utilized for different applications such as adsorbents,[10,11] catalysts and catalyst supports.[6] The nature of the carbon derived from biomass depends on the kind of biomass, treatment temperature and exposure time etc. These carbons generally contain high surface areas with different pore structure. The biochar produced from different biomass were used directly or after suitable modifications, as catalysts for different reactions.[12] The biochar obtained from low temperature slow pyrolysis would generate a highly cross-linked, multi ringed aromatic structure anchored to lignin. This biochar can be easily functionalized to make them as strong acid catalysts. Canola meal, a byproduct of canola based biodiesel industry was also explored for the production of biochar.[13] After suitable modifications the canola based acid activated biochar exhibited good activity.

The seed of Karanja (general name) or Pongamia pinnata (scientific name) are available abundantly in the world particularly in the tropical and temperate regions such as India, Japan, China, Malaysia, Australia and Pacific Islands. Karanja comes from the tree in the pea family, Fabaceae.[14,15] Karanja seed is being non-edible in nature; the oil extracted from the kernels has been identified as suitable oil for the production of biodiesel.[16,17] Karanja seed deshelling produces 60-65% of shells and 35-40% kernels. The shells of the seeds are major waste component discarded or used as domestic fuel after removing the oil bearing kernel from the seed. The shell being a major by-product of karanja seed processing industry and value addition to this material would certainly help the economics of karanja based biodiesel industry. In recent times lot of research has been focused on the utilization of biomass and other agricultural wastes to retrieve their energy content.

Glycerol is the main by-product in biodiesel synthesis by transesterification of oil with methanol or ethanol. Glycerol is a renewable feedstock which can be converted into valuable chemicals.[18,19] Glycerol, as it is a highly functional molecule can undergo oxidation, carbonylation,[20-22] hydrogenolysis,[23,24] esterification and etherification[25] etc. to yield useful commodity chemicals. Esterification of glycerol with acetic acid is one of the important reactions to synthesis glycerol acetin which are known for their fuel additive properties. Different acid based heterogeneous catalysts have been studied for the esterification of glycerol.[26-30] Glycerol acetylation has been carried out by using

different heterogeneous catalysts like amberlyst and niobic acid,[26] Heteropolyacids like dodecamolybdophospheric acid encaged in USY zeolite,[27] dodecatungstophospheric acid immobilized into a silica matrix and sulfated zirconia[28] etc. In above some catalysts are not applied for industrial scale because of HPAs are soluble in polar media[29] and some are too expensive.[30]

In present study Kanraja seed shells are subjected to pyrolysis in inert atmosphere at different temperatures to make catalytically useful biochar. The biochar was evaluated for its physico-chemical properties using different spectroscopic methods. The biochar is used directly as acid catalyst without any modifications for the esterification of glycerol with acetic acid.

2. Experimental Section

2.1. Materials and Preparation of Karanja biochar

Karanja kernels were collected from local suppliers. Glycerol, acetic acid was obtained from SD Fine Chem., India. Karanja seeds were collected from local gardens and the shells were separated from the seeds manually. The shells were grounded to small pieces and subjected to oven drying at 100 °C for 12 h to remove moisture content in it. Biochar was prepared by pyrolysis of dried karanja seed shell powder under nitrogen atmosphere at 300, 400 and 500 ^{o}C for 4 h. These samples are denoted as KJ-300, KJ-400 and KJ-500 where the number represents the carbonization temperature. The main products of the glycerol esterification with acetic acid are mono (MA), di (DA) and tri acetin (TA).

2.2. Characterization of catalysts

BET surface areas of the catalysts were calculated from nitrogen adsorption-desorption data acquired on an Autosorb-1 instrument (Quanta chrome, USA) at liquid N_2 temperature.

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on RigikuMiniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered CuK_{α} radiation (λ=1.5406 A^{o}) with a scan speed 2^{o} min^{-1} and a scan range of 2-80^{o} at 30kV and 15mA.

FT-IR spectra of the samples were recorded on FT-IR DIGILAB (USA) IR spectrometer by using a KBr disc method. Confocal Micro-Raman spectra have been recorded in air at room temperature in the range of 50–4000 cm^{-1} using a Horiba Jobin-Yvon LabRam HR spectrometer with a 17mW internal He–Ne (Helium–Neon) laser source of excitation wavelength 632.8 nm. The catalyst samples in powder form (about 5-10 mg) were usually loosely spread onto a glass slide below the confocal microscope for Raman measurements

Thermal stability of biochar was examined using TA500 analyzer in the temperature range of 25 to 800 °C at a heating rate of 10 °C/min with a continuous flow of nitrogen gas at 20 mL/min. The samples were subjected to thermo gravimetric analysis (TGA) to determine the decomposition temperatures.

Temperature programmed desorption of ammonia was carried out on a laboratory built apparatus equipped with a gas chromatograph using thermal conductivity detector (TCD). In this TPD around 50mg of sample was placed in a quartz tube. Then catalyst sample was treated at 300 ^{o}C for 1 hour by passing pure helium (99.9%, 50ml min^{-1}). After pretreatment, the sample was saturated with anhydrous ammonia (10%NH_3) at 100 ^{o}C at a flow rate of 50 ml min^{-1} for 1 hour and subsequently flushed with helium at the same temperature to remove physisorbed ammonia. The TPD analysis was carried out from ambient temperature to 800 ^{o}C at a heating rate of 10 ^{o}C min$^{-1.}$ The amount of ammonia evolved was calculated from the peak area of the calibrated TCD signal. The NMR spectra were recorded on a Varian 500 MHz spectrometer and chemical shifts are reported in ppm. C, H, N and S were measured by the elemental analysis on a Vario Micro Cube elemental analyzer.

2.3. Reaction procedure

Esterification of glycerol was carried out in liquid phase at atmospheric pressure. In a typical experiment, 5g of glycerol and 9.78g of acetic acid were taken in a round bottom flask and 0.2g of catalyst was added. The reaction mixture was kept in oil bath maintained at reaction temperature at 120 ˚C. The course of the reaction and the products were monitored by gas chromatography (GC) equipped with flame ionization detector (FID) by separating them on Equity-5 column.

3. Results and discussion

3.1. Catalyst characterization

The surface area values of the biochar samples are shown in Table 1. The overall surface areas of the biochar materials were low. The surface area and pore volume of the samples were increased marginally with increase in the carbonization temperature. The increase in pore volume might be due to the formation of loosely bound carbonaceous material that led to the creation of channels in graphitic regions.[31]

Table 1.Physico-chemical properties of karanja catalyst

Catalyst Names	Surface area (m^2/g)	Pore volume (cm^3/g)	Acidity (mmol/g)		
			Moderate acidity	Strong acidity	Total acidity
KJ-300	13	0.015	6.863	1.100	7.963
KJ-400	14	0.021	4.263	2.065	6.328
KJ-500	16	0.027	2.062	1.815	3.877

The percentage of carbon, hydrogen, nitrogen, sulfur and oxygen present in biochar were measured by CHNS analysis and the results are shown in Table 2.

Table 2. CHNS-elemental analysis in Karanja catalysts

Catalyst	Elemental composition (%)			
	C	H	N	O
KJ-300	56.90	6.57	1.61	34.91
KJ-400	63.37	4.30	0.82	31.51
KJ-500	76.25	3.52	0.46	19.77

KJ-300 sample showed less carbon percentage compared to KJ-400 and KJ-500 catalysts. The low carbon content in case of KJ-300 is mainly due the incomplete carbonization of Karanja seed shell. As the carbonization temperature increases the percentage of carbon is increased and at the same time the content of hydrogen, nitrogen and oxygen are decreased.

The acid sites present on surface of biochar together with total acidity were measured by TPD of NH_3 and the results are shown in Table 1. and Fig. 1. The acidity of the catalysts are due to the presence of –OH and –COOH groups on the surface. The biochar samples showed two desorption peaks in their TPD profiles. These are moderate (lower temperature between 300 to 600 °C) and strong acidic sites (higher temperature between 600 to 750 °C) present in the biochar samples. KJ-400 exhibited strong acidity than KJ-300 and KJ-500. This is due to that upon calcination aliphatic groups are converted into orderly form of graphitic layers. The decrease in total acidity for the KJ-500 is mainly related to the loss of acidic groups as it is treated at higher calcination temperatures.

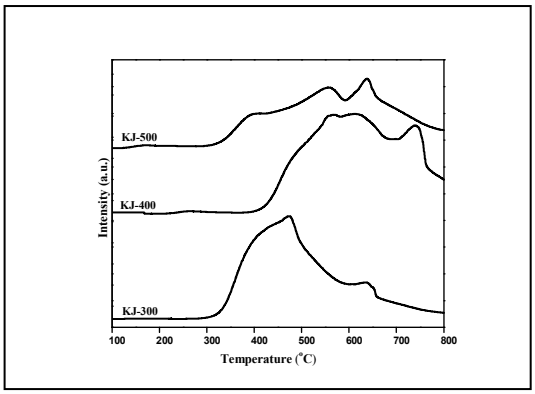


Fig. 1 NH_3-TPD of biochar catalysts

XRD patterns of biochar obtained from Karanja seed shells are shown in Fig. 2. The XRD pattern exhibits broad diffraction peak attributed at 2θ=10-30° and peaks at 35-40° due to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion.[32]

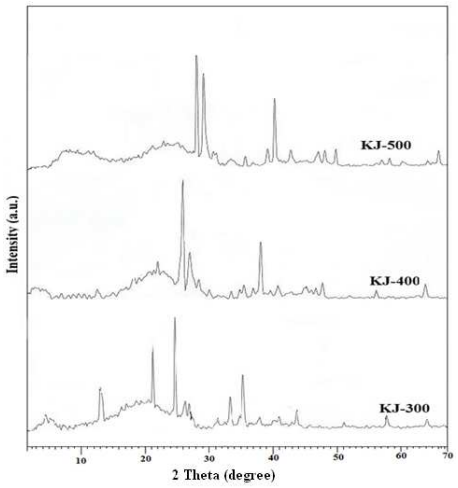


Fig. 2. X-ray diffraction patterns of biochar samples.

Fig.3. shows the FT-IR spectra of the samples for the detection of functional groups on the catalysts. The bands at 756 and 873 cm^{-1} were related to out of plane bending modes of C-H bonds of aromatic and heteroaromatic compounds.[33,34] The bands at 1581 and 1585 cm^{-1} corresponds to aromatic ring modes[35-36] and the band at 1140cm^{-1} related to C-O-C asymmetric stretching. The bands at 1043 and 1083 cm^{-1} corresponding to in plane C-H bending mode and the band at 1698 cm^{-1} related to C=O stretching modes of carboxylic groups.[35] The band at 1215 cm^{-1} was related to Ar-OH stretching or aromatic acidic groups.[36] The bands in the range of 3000-3400 cm^{-1} were related to O-H stretching of aromatic phenols and O-H of carboxylic acids.

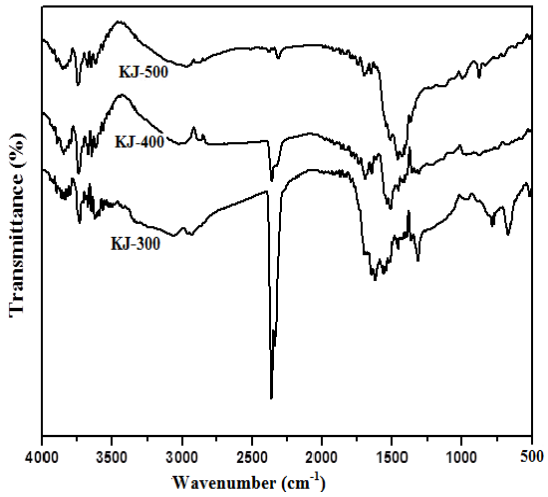


Fig. 3. FT-IR spectra of biochar samples.

Raman spectra of Karanja biochar samples are shown in Fig.4. The Raman spectra showed the main bands at 1370 and 1600 cm^{-1}. The band centered at 1370 cm^{-1} is related to the stretching vibrations of amorphous carbon and the band at 1600 cm^{-1} corresponds to stretching vibrations of graphite C=C bonds.[37,38] The increase in pyrolysis temperature led to increase in the intensity of 1600 cm^{-1} band. This suggests the formation of uniform carbonaceous graphite structure.

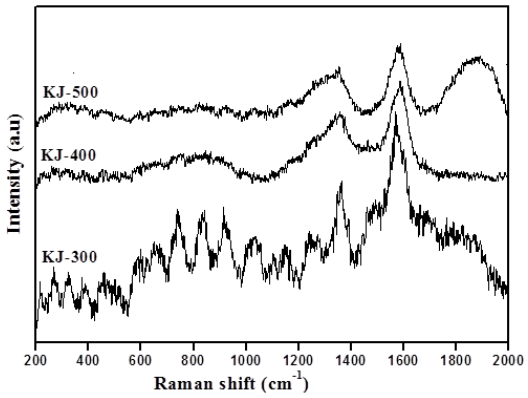


Fig.4. Laser Raman spectra of biochar sample.

The thermal stability of the Karanja seed shell and biochar catalysts were studied by thermo gravimetric analysis under nitrogen flow and the results are shown in Fig.5. Karanja seed shell has lot of moisture content and removed at 100 °C. A maximum weight loss was noticed in between 200-450 °C. In this

temperature range most of the biomass was carbonized. The overall weight loss in case of Karanja seed shell was about 66%. The weight loss for the biochar samples is varied depending on their carbonization temperature. The KJ-300 sample showed maximum loss up to 38% weight compared to KJ-500 which cshowed only 11% loss in weight. The maximum loss in weight for the biochar obtained at 300 ^{o}C might be related to the decomposition oxygen containing functional groups. The decrease in weight loss with increase in carbonization temperature supports the loss of surface functional groups.

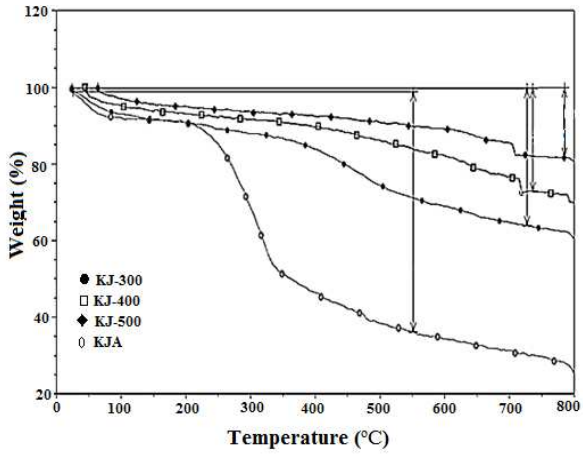


Fig. 5. Thermo gravimetric analysis of biochar samples.

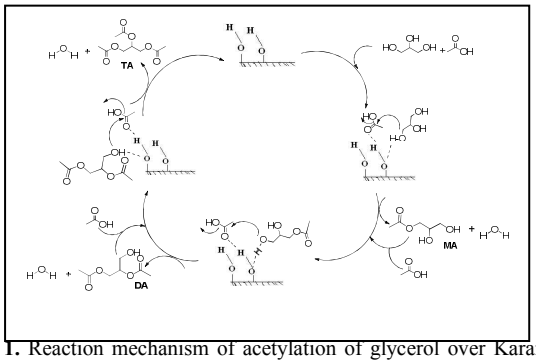
3.2. Acetylation of glycerol activity of the biochar catalysts

Acetylation of glycerol with acetic acid was carried over biochar catalysts and the results are shown in Table 3. Acetylation of glycerol over the biochar resulted in the formation of MA, DA and TA. The biochar derived from Karanja seed shells showed reasonable activity towards glycerol acetylation within 1 h of reaction time. A experiment was carried without using any catalysts and it was observed about 8% conversion. The acetylation activity of the biochar increased with increase in the carbonization temperature from 300 to 400 ^{o}C. The sample carbonized at 400 ^{o}C showed highest activity compared to other samples. The variation in activity with carbonization temperature related to their physico-chemical properties. The high glycerol acetylation activity for KJ-400 sample is due to the presence of intense strong acidic sites as observed from TPD of ammonia results. The low activity of the KJ-300 is related to the presence of different functional groups as the carbonization carried at low temperature. On the other hand the decrease in activity for KJ-500 is because the loss of acidic groups (–COOH) due to high carbonization temperature. Based on the activity profiles over these catalysts a plausible reaction mechanism was proposed and shown in Scheme 1. The acidic site of the catalyst activates acetic acid followed by the participation of glycerol hydroxyl group leading to the mono acetylation of glycerol to yield MA. This MA other hydroxyl group participate again to yield DA. Similarly formation of TA takes place as shown in scheme 1.

Table 3. Glycerol acetylation activity over different biochar catalysts.

Karanja catalysts	Conversion (%)	Selectivity (%)		
		MA	DA	TA
KJ-300	84.5	62.4	30.5	1.8
KJ-400	88.5	56.0	40.0	4.0
KJ-500	83.0	59.0	38.3	2.7

Reaction conditions: Temperature: 120 ˚C, Glycerol: Acetic acid: 1:5, Catalyst weight: 0.2g.



Scheme 1. Reaction mechanism of acetylation of glycerol over Karanja catalysts

3.3. Effect of reaction time and temperature

The KJ-400 catalyst showed excellent activity for esterification of glycerol and this catalyst was selected as a system catalyst to evaluate the reaction parameters for the acetylation of glycerol. The influence of reaction time and temperature on the acetylation of glycerol was studied and the results are presented in Fig. 6 (A) and (B) respectively.

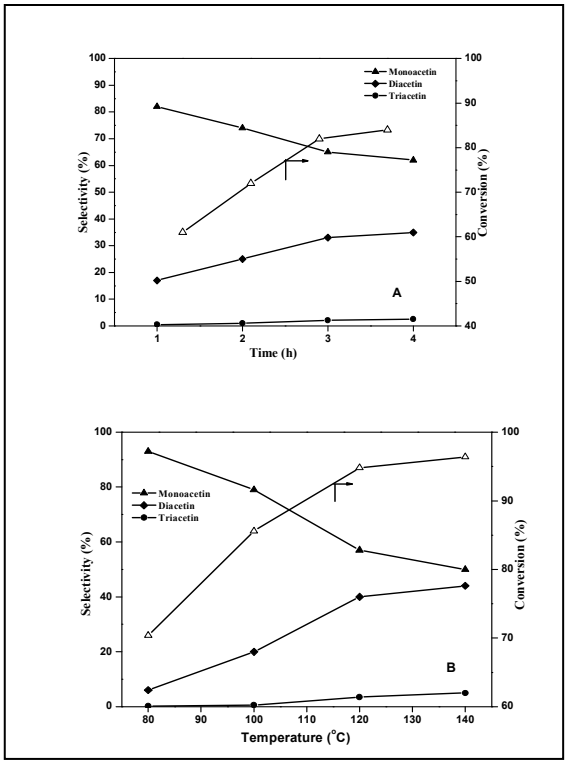


Fig. 6. Effect of (A) reaction time and (B) reaction temperature during glycerol acetylation over KJ-400 sample.

The conversion of glycerol increased gradually with time and attained maximum at a reaction time of 4 h. The increase in reaction time resulted in the variation of selectivity. The selectivity towards DA and TA was increased with reaction time. The increase in the DA and TA is expected with time because the acetylation of MA takes place as the availability of glycerol is less.

The conversion of glycerol increased from 25 to 85% with increase in reaction temperature from 80 to 120 °C as shown in Fig 6 (B). Further increase in temperature to 140 °C there was no appreciable enhancement in glycerol conversion. The selectivity is also varied with reaction temperature. The selectivity towards DA and TA increased continuously with increase in reaction temperature. The selectivity to MA is very high at lower reaction temperature and further decreased with reaction temperature. The variation in selectivity is mainly related to the increased activity of catalysts with reaction temperature.

3.4. Effect of glycerol to acetic acid mole ratio and Catalyst weight

The conversion of glycerol not only depends on the nature of the catalyst but also on mole ratios of glycerol to acetic acid as shown in Fig. 7 (A).

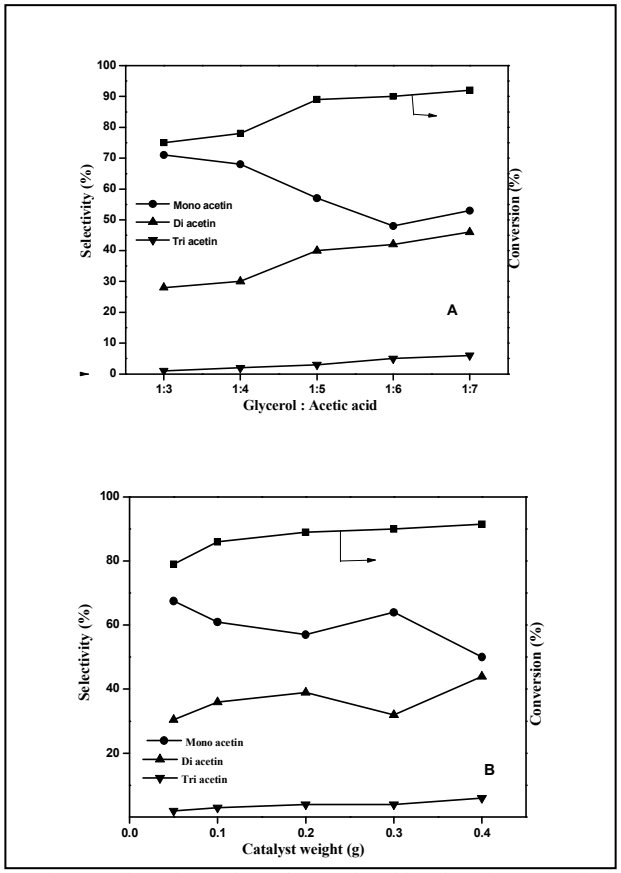


Fig. 7. Effect of (A) Glycerol to acetic acid mole ratio (B) Catalyst weight

The mole ratios of glycerol to acetic acid varied from 1:3 to 1:7. About 75% glycerol conversion was obtained at a glycerol to acetic acid mole ratio of 1:3 and reached up to 89% for 1:5. Further increase in mole ratio there was no considerable variation in glycerol conversion. Most of the reputed solid acid catalysts showed high activity at a glycerol to acetic acid molar ratio of 1:9.[39] The interesting observation is that the selectivity of DA and TA increased up to 60% with increase in glycerol to acetic acid mole ratio. The increase in selectivity towards DA and TA was mainly due to more availability of acetic acid.

The influence of catalyst weight on the esterification of glycerol was studied and the results are shown in Fig. 7 (B). A continuous increase in glycerol conversion with increase in catalyst weight was observed. The catalysts with minimum amount of 0.05 g showed about 79% glycerol conversion. A maximum conversion of 88% reached at a catalysts weight of 0.2 g. There was no much variation in conversion with further increase in catalyst amount. The selectivity toward DA and TA increased with increase in catalyst weight. These results are expected as the availability of more number of active sites led to high conversion of glycerol and simultaneous acetylation of MA and DA with progress of reaction.

3.6. Comparison with reported catalysts

The active KJ-400 catalyst was compared with the reported catalysts for the acetylation of glycerol and the data was tabulated in Table 4. The compiled data suggests that the reported catalysts like Amberlyst-36[40], heteropoly tungstate supported on active carbon (PW2_AC)[41] and silica matrix (PW-in-S2)[42] ,dodecamolybdophosphoric acid encaged in Na USY zeolite (PMo3_NaUSY)[27] and mesoporous silicate-niobium silicate type of SAB-15 (MP(5)/NbSBA-15-32)[43] require long reaction times or high glycerol to acetic acid molar ratio to give reasonable activity. Sulfated zirconia catalyst (SZ-1)[28] took long reaction time (24h) and gave mainly MA as major product. Morover, these catalysts require series of steps in their preparation. Compared to these catalysts KJ-400 showed better activity within reasonable reaction time and reactant molar ratios.

Table 4. Comparison of KJ-400 catalyst with other reported catalysts

Catalyst	Conditions			Conversion (%)	Selectivity (%)			Ref
	Time (h)	Temp (˚C)	Mole ratio (Gly:acid)		MA	DA	TA	
Amberlyst-36	12	105	1:8	95.6	70.3	4.5	-	[40]
PW2_AC	3	120	1:16	86.0	25	63	11	[41]
PW-in-S2	7	120	1:16	87.0	36	59	4	[42]
MP(5)/NbSBA-15-32	4	150	1:9	94.0	11	51	38	[43]
PMo3_NaUSY	3	120	1:18	68.0	37	59	2	[27]
SZ-1	24	55	8.2:1	54.0	98.9	1.2	-	[28]
KJ-400	4	120	1:5	88.5	56	40	4	Present work

3.8. Catalyst reusability

The catalyst reusability was tested and the results are shown in Fig. 8. The used catalyst was recovered after reaction by centrifuge and washed with methanol followed by drying at 100 °C in hot air oven and reused without any treatment. This procedure was continued up to five cycles. The activity of the catalyst was almost consistent. A marginal variation in the selectivity towards MA was probably due to the blocking of some active acidic sites on the surface.[44] It is noteworthy to mention that the biochar catalyst was reusable without any treatment with consistent activity.

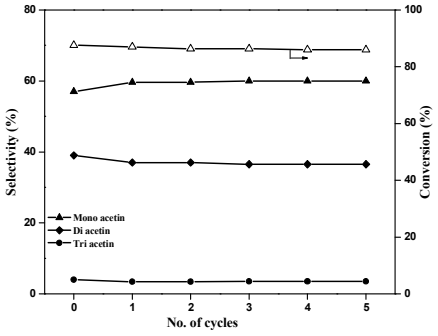


Fig.8. Reusability of KJ-400 catalyst in acetylation of glycerol.

4. Conclusions

Catalytically active biochar is prepared by simple pyrolysis of Karanja seed shells at different temperatures without any treatment before or after carbonization. The acidity of the biochar depended on the carbonization temperature. The biochar obtained at 400 °C exhibited moderate to strong acidic sites. These catalysts showed excellent activity for esterification of glycerol under mild reaction conditions and the catalyst carbonized at 400 °C showed high activity among all the catalysts. The conversion and selectivity in glycerol acetylation was also depended on reaction parameters. The catalyst is stable, easy to recover and reusable with consistent activity.

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Graphical abstract:

Esterification of bio-glycerol over solid acid biochar catalyst derived from waste biomass

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