Synthesis of biodiesel from non-edible *Jatropha curcas* oil using potassium hydrogen sulphate-graphene oxide based composite (KHS-GO*cat*) catalyst

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A composite (KHS-GO*cat*) catalyst has been demonstrated for the synthesis of biodiesel using non-edible *Jatropha curcas* oil (NEJC*oil*) as feedstock. Reaction variables are optimized, and maximum biodiesel yield 55 ± 5% obtained under optimum [e.g. KHS-GO*cat* = 20%, temperature = 70°C, time = 5 h and Methanol/NEJC*oil* = 9:1] reaction conditions. Synthesis of biodiesel has been confirmed by FT-IR, NMR and GC-MS. The essential fuel properties of the resulting biodiesel are found to be within the limits of ASTM specifications. This work opens new research areas on the development of composite catalysts to maximise the biodiesel production.

Biodiesel, have gained significant importance as a biodegradable non-toxic renewable alternative fuel for diesel engines due to the depletion of the world's limited non-renewable petroleum reserves and the increasing environmental concerns. Biodiesel is produced by the transesterification of oil under various suitable conditions in the presence of catalysts. In general, 1mol of triglyceride reacts with 3 mol of methanol in transesterification reaction in the presence of suitable acidic and/or alkaline catalysts, which mainly produced biodiesel in the form of fatty acid methyl ester (FAME) and by-product glycerol. The transesterification reaction required an excess amount of methanol, which can be isolated by distillation and reused for the next experiment[1,2]. The conventional methods of biodiesel use the homogeneous catalysts such as sodium hydroxide. Such catalysts required acid for neutralization and generates acid/base waste becomes an environmental problem. Furthermore, free fatty acid (FFA) must be removed before transesterification if oil contains high FFA content (>4%)[3]. Direct addition of NaOH as a catalyst is also consumed by thesaponification[4]. Use of an acid catalyst mostly complete transesterification in one-step and may solve the problem of FFA[5-7]. Esterification of free fatty acids to free fatty acid esters is faster by an acid catalyst compared to the transesterification. Therefore, development of a suitable acid catalyst is the need for fast transesterification[8]. The carbon-based acidic catalyst has been reported in the literature[9,10].

The preparation of carbon supported composite acidic catalyst (KHS-GO*cat*) using KHSO$_4$ and graphene oxide (GO), and tested for biodiesel production has been demonstrated. In addition, used graphene oxide (GO) as carbon support is oleophilic, which helps to adsorbed more oil on the catalyst surface as compared to hydrophilic KHSO$_4$. As a result, the rate of transesterification can be enhanced on the developed catalyst in this study. In this study essential reaction parameters namely reaction temperature & time, molar ratio and catalyst dosage are optimized to obtain the maximum conversion yields. Resulting biodiesel was characterised using FTIR, NMR and GCMS analysis.

Experimental Section

Materials and methods

Non-edible *Jatropha* crude oil (NEJC*oil*) with high-acid value (17 mg KOH/g) as expelled in our institute (CSIR-CSMCRI) used in all experiments without further purifiction[11]. Required chemicals namely methanol, hexane, potassium permanganate (KMnO$_4$), potassium hydrogen sulphate (KHS) and powdered graphite (CAS no. 7782-42-5) with the average particle size 400 nm were purchased from SRL,

Mumbai, India. In the present work, graphene oxide (GO) was synthesized from commercially available powdered graphite using previously reported Hummers method in the literature[12,13]. Other chemicals such as sodium nitrate ($NaNO_3$) (Qualigens), H_2O_2(TCI), HCl, KOH and H_2SO_4 (Fisher Scientific) were purchased. All chemicals were used as received.

Preparation graphene oxide (GO)

In this work, commercially available graphite in the powdered form is used to syntheses graphene oxide (GO) using a reported method in the literature[12,13]. In brief, 0.5 g powdered graphite was loaded in the round bottom flask (RBF). Then add 25 mL of 98% H_2SO_4. RBF was fixed in an ice bath at~4 °C and added 0.5 g of sodium nitrate 0.3 g of potassium permanganate ($KMnO_4$) was then added slowly under constant stirring. Then the reaction mixture transferred to the water bath at 35°C under stirring conditions followed by addition of 40 mL Milli-Q water slowly and kept at 90°C for 30 min. After that, 100 mL Milli-Q water was added in this mixture. 3.0 mL of H_2O_2 (30% *v/v*) was slowly added to the reaction mixture. During this reaction colour of solution changed from dark brown to yellowish indicates formation of GO. The solid GO was obtained by centrifugation at 10000 rpm for 10 min. Solid residue obtained was washed with 5% HCl, 0.3% H_2O_2 and finally with water to remove all the impurities from the oxidized graphite, and was freeze-dried to obtain GO.

Preparation of KHS-GO$_{cat}$

A simple blending method is used to prepare KHS-GO$_{cat}$ based catalyst, as shown in Scheme 1. In a typical experiment add 5g KHS in 100 mL glass beaker containing 25 mL water under stirring followed by addition of 0.05-0.2 g GO (Step-I, Scheme 1). Mixture was stirred for 30 min followed by sonication (Step-II, Scheme 1) at room temperature for 1 h. The final mixture was then lyophilised to obtain solid KHS-GO$_{cat}$ (Step-III, Scheme 1) and used for biodiesel synthesis.

Synthesis of biodiesel

To synthesise biodiesel from NEJC$_{oil}$ fixed the reactor (RBF) with thermostat, condenser, and mechanical stirred in a fume hood. Then pre planned quantity of NEJC$_{oil}$, methanol and catalysts were charged into the RBF reactor. The stoichiometry for the reactions are 3: 1, 6:1, 9:1and 12: 1 ratios of methanol to non-edible *Jatropha curcus* oil (MeOH/NEJC$_{oil}$). These reactants (e.g. methanol and NEJC$_{oil}$) were charged into the reactor in the above-mentioned molar ratios. Then add the known weight of KHS-GO$_{cat}$ from 1.0 to 3.04 g to optimise the catalyst dosages in the transesterification reaction. The reaction was carried out at different reaction temperatures from 60 to 80°C for 3 to 7 h to optimise the transesterification reaction parameters based on the maximum conversion of NEJC$_{oil}$ into biodiesel. The maximum ($55 \pm 5\%$) biodiesel yield was obtained under optimum reaction conditions (e.g. MeOH/NEJC$_{oil}$ ratio = 9: 1; temperature = 70°C; time = 5 h; and KHS-GO$_{cat}$= 2.0 g). The individual pure $KHSO_4$ or GO tested for transesterification reaction under identical conditions.

The reaction mixture was cooled to room temperature and transferred into separating funnel. Within 10 min the reaction mixtures become biphasic. The top layer is biodiesel while the lower layer contains mixture of glycerol, methanol and catalyst. The biodiesel layer was collected by decantation method and washed with distilled water to remove impurities. Then air was purged to remove the remaining water content from biodiesel. $KHSO_4$ is recovered by evaporates water on the hot plate. The bottom layers contained GO recovered by centrifugation (10000 rpm) and washed it by hexane.

Characterization of biodiesel

Spectral analysis

The formation of biodiesel was confirmed by FT-IR spectra [recorded on a Perkin-Elmer FT-IR machine (Spectrum GX, USA)] and ^{1}HNMR spectra [recorded on a Bruker Avance-II 500 (Ultra shield) spectrometer, Switzerland], while methyl esters of
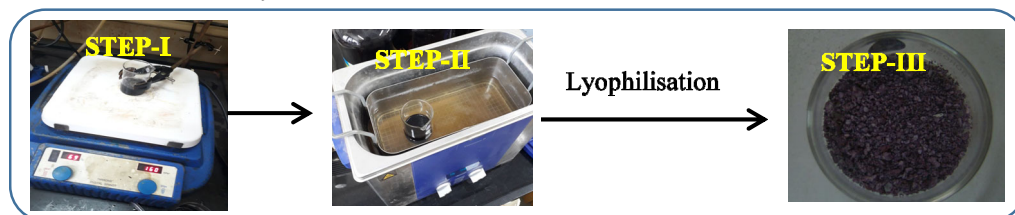
Scheme 1 — Schematic representation of the preparation of solid KHS-GO catalyst (KHS-GO$_{cat}$).

biodiesel was characterised by GC-MS analysis (Shimadzu GCMS QP 2010, Japan, using RTX5 column with dimensions 30m X 0.25mm X 0.25 u).

Other characterisations

Free fatty acid of the crude oil was determined by titrating it against potassium hydroxide (KOH), and phenolphthalein use as an indicator[14]. In brief, 2 g oil was dissolved in 50 mL methanol followed by addition of 3-5 drops of indicator. This mixture was then titrated against 0.1 N KOH with constant stirring until a pink colour was obtained. The determination of total glycerol in biodiesel sample was done by reported procedure (ASTM D7637, 2010).Density of biodiesel was measured using density bottle as reported in the literature[14]. In brief, take dry bottle (25 mL) and weighed (w_0) it then filled the oil. The filled bottle was reweighed with stopper to give (w_1). Similarly oil was substituted with water and weighed to give (w_2) as given below[14,15].

$$\text{Specific gravity} = w_{1-w_0} / w_{2} - w_0$$

Viscosity of *Jatropha* oil and biodiesel samples was measured on a Brookfield viscometer (DV-II +Pro), using SC4-18 spindle at 60 rpm at 40 °C. Moisture content (MC) was measured with an automatic Karl-Fisher method (Radiometer TIM 880 Titration Manager, France)[14,15].

Result and Discussion

Physicochemical properties of biodiesel

Here we demonstrated the transesterification efficiency of KHS and GO based composite catalyst (KHS-GO$_{cat}$) using non-edible *Jatrophacurcus* oil (NEJC$_{oil}$) as shown in Fig. 1. In this study KHS-GO$_{cat}$ used as catalyst for synthesis of biodiesel from NEJC$_{oil}$. Result of this study shows that essential (e.g. density, viscosity, glycerine, water content, FFA, etc.) properties of biodiesel were comparable with the German standard (DIN V 51606, 1997; Table 1), and also in good agreement with those reported in the literature from *Jatropha curcus* oil[14,15]. The clogging engine components mainly depend on the fuel viscosity and high viscosity value enhanced the tendency of clogging. KHS-GO$_{cat}$ produced biodiesel with medium viscosity (3.96cP) and found within the range as mentioned by ASTM (1.9-6.0cP)[14]. Resulting biodiesel shows 0.18% free fatty acid and a moisture content of 190 mg/kg, while the density was 0.86. These parameters are also in the range of the standard biodiesel sample (Table 1)[14]. In addition the values of
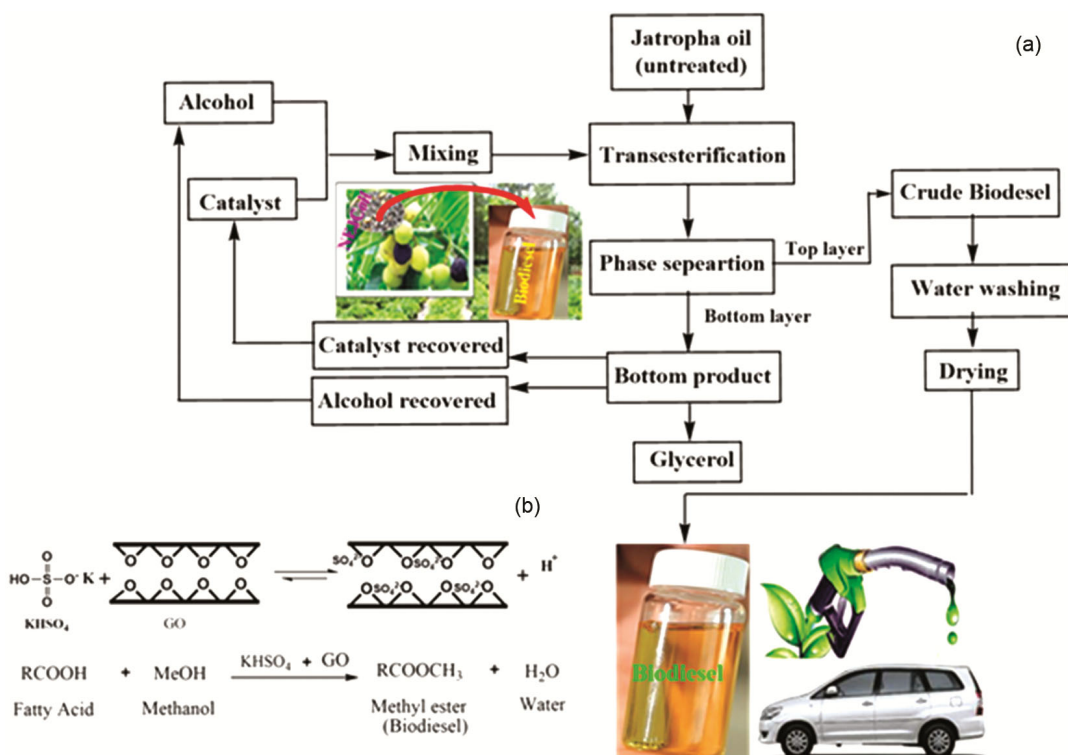

Fig. 1—(a) Schematic representation of the synthesis of biodiesel from *J oil* using KHS-GO$_{cat}$, and (b) possible reaction mechanism of transesterification.

Table 1 — Comparative properties of *Jatropha* biodiesel obtained in this study.

Properties	Unit	DIN (V 51606, 1997) value	Value of the Reference Biodiesel Sample (Ref.22)]	Result / value of the present study
Density	g/ml	----	-----	0.86
Viscosity at 40°C	mm²/s	3.5-5.0	4.34	3.96
Water content	mg/kg	<500	450	190
Free glycerin	% mass	<0.2	<0.02	0.014
Total glycerin	% mass	<0.25	0.04	0.14
FFA	% *wt*	----	----	0.18

free glycerin (0.014%) and total glycerin (0.14%) are also in the range of reported values for biodiesel[14]. Results of this study revealed that biodiesel prepared in the present study might be useful for fuel in the existing diesel engine with no modification.

FTIR and NMR analysis

Biodiesel formation in this work was first confirmed using FTIR analysis (Figs 2a-d). Figure 2a shows the IR spectrum of crude non-edible *Jatropha curcus* oil (NEJC$_{oil}$), which does not show characteristic IR peaks of biodiesel. FTIR spectrum of the resulting biodiesel with KHS-GO$_{cat}$ shows two characteristics IR bands at 1440 cm^{-1} (ester carbonyl stretch, (CO)-O-CH$_3$) and 1744 cm^{-1} (C=O,ester), which confirmed the conversion of NEJC$_{oil}$ in to fatty acid methyl esters (FAMEs) through transesterification reaction in presence of KHS-GO$_{cat}$ (Fig. 2b).The results confirmed that almost no transesterification of *Jatropha curcus* oil was observed with individual KHSO$_4$ and/or graphene oxide (Figure 2c). Biodiesel obtained by conventional method (US 7,666,234 B2)[14,15] also exhibited two identical IR bands (Fig. 2d), confirmed that KHS-GO$_{cat}$ could use as a catalyst for transesterification of NEJC$_{oil}$.

The proton NMR (^{1}H NMR) spectrum of crude *Jatropha* oil (NEJC$_{oil}$) shows some distinct peaks from the resulting biodiesel spectrum (Fig. 3a). The NMR peaks at 4.13-4.31 ppm represent the protons of -CH$_2$ (C1 & C3) of glyceride moiety, which disappeared in the biodiesel (Fig. 3b). Figure3b shows the ^{1}H NMR spectrum of the prepared biodiesel from NEJC$_{oil}$. The NMR spectrum of biodiesel shows two characteristic intense peaks of methoxy protons at 3.66 ppm and of α-CH$_2$ protons at 2.30 ppm. These NMR peaks are the distinct peaks for confirmation of
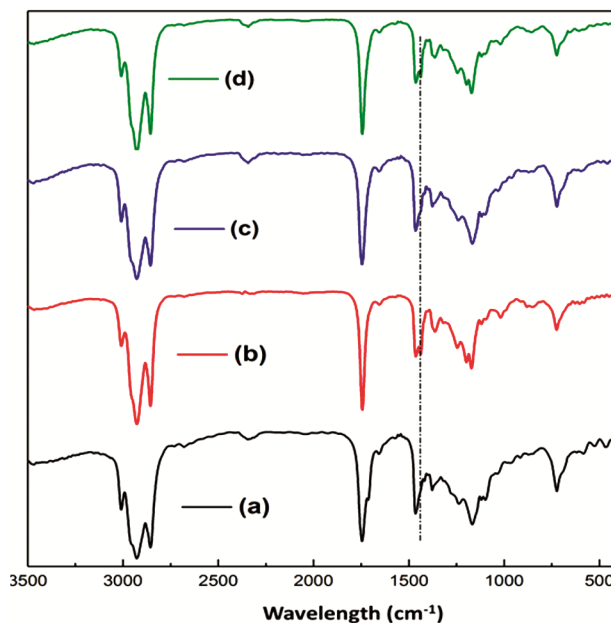

Fig. 2 — FTIR spectra of (a) crude *Jatropha curcus* oil, (b) *Jatropha* biodiesel with KHS-GO$_{cat}$, (c) *Jatropha* biodiesel with KHSO4, and (d) *Jatropha* biodiesel of the conventional method.

methyl esters present in the resulting biodiesel of this study. The peak obtained at 0.88 ppm represented the terminal methyl protons and intense peaks at 1.26-1.30 ppm assigned to methylene protons, while a peak at 5.34 ppm represented olefinic (-CH=CH) hydrogens[16,17]. The NMR spectrum of the reference biodiesel sample is comparable to biodiesel obtained in the present study (Figure 3c). In addition no proper transesterification reaction of *Jatropha oil* was obtained with pure KHSO$_4$ (KHS) or pure GO. Results of this study confirm that individual pure KHSO$_4$ or GO not suitable for transesterification reaction. Furthermore IR and NMR analysis result shows the formation of biodiesel in the presence of composite (KHS-GO$_{cat}$) catalyst.

GC-MS analysis of FAMEs

As shown above, IR and NMR spectra of the resulting biodiesel sample confirmed the conversion of NEJC$_{oil}$ to fatty acid methyl esters (FAMEs). GC-MS analysis was further carried out to confirm the composition of FAMEs in the resulting biodiesel sample. GC analysis result of this study confirmed that the transesterification process developed in this study has successfully converted NEJC$_{oil}$ into FAMEs[14,15]. GC results confirmed that biodiesel of this study comprises seven FAMEs: (i) 9-Hexadecenoic acid, methyl ester, (Z)- (Palmitoleic acid, C16:1) = 1.12%; (ii) Hexadecanoic acid, methyl
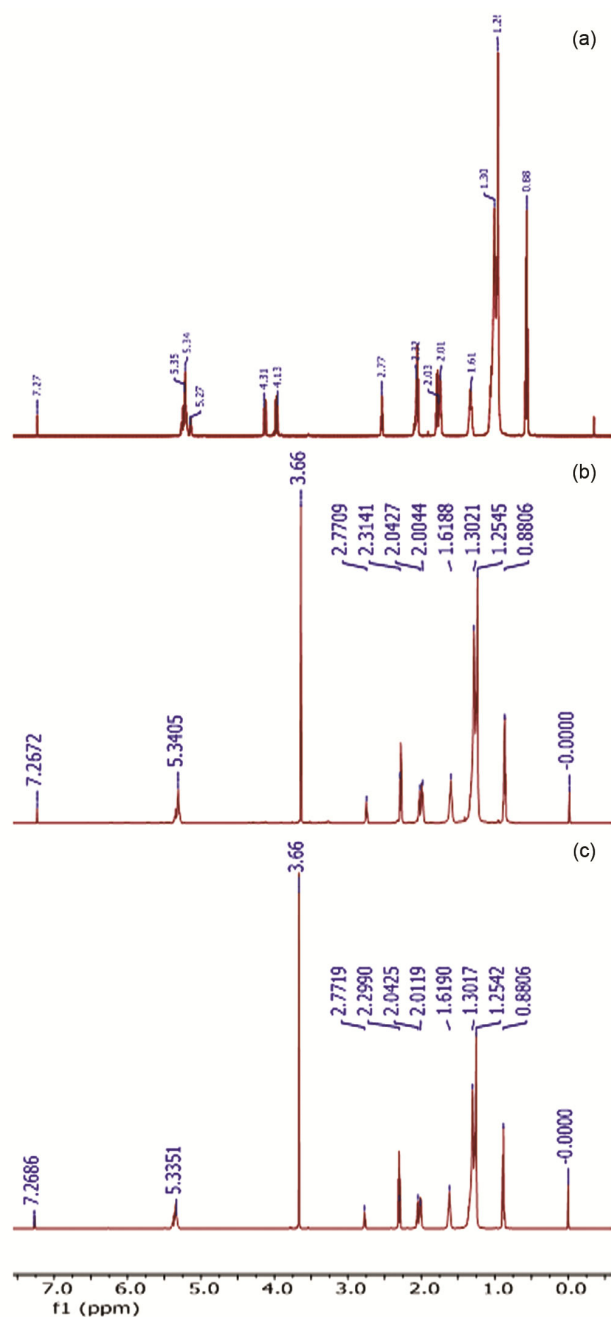
Fig. 3 — ¹H NMR of (a) NEJCoil, (b) biodiesel, and (c) Reference biodiesel obtained through the conventional method.

ester (palmitic acid (C16:0) = 23.04%; (iii) 9,12-Octadecadienoic acid (Z,Z)-, methyl ester (Linoleic acid, C19:2) =27.17%; (iv) 9-Octadecenoic acid, methyl ester, (E)- (Elaidic acid, C19:1) = 36.22%; (v) Heptadecanoic acid, 16-methyl-, methyl ester (Methyl isostearate, C19:0) = 11.79%; and (vi) 6-Octadecenoic acid, methyl ester, (Z)- (cis-6-Octadecenoic acid, C19:1) = 0.66% (Table 2).

Optimisation of reaction parameters

Effect of MeOH/NEJC$_{oil}$ ratio

As reported, transesterification of each mole of oil requires 3 moles of methanol[18,19]. In this study transesterification reactions were carried out varying MeOH/NEJC$_{oil}$ molar ratios from 3: 1 to 12:1*v/v*, also the effect of MeOH/NEJC$_{oil}$ molar ratios and the catalytic performance of KHS-GO$_{cat}$ is investigated. Figure 4a shows conversion efficiency of NEJC$_{oil}$ into biodiesel with various MeOH/NEJC$_{oil}$ molar ratios. Result shows that biodiesel yield was significantly higher 55± 5% with 9: 1 molar ratio of MeOH/NEJC$_{oil}$ and gradual decrease beyond this molar ratio (Fig. 4a). The conversation yield was increased when increasing the amount of methanol may be due to the better dispersion of catalyst and oil which can promote the catalytic activity or may be due to increase in solubility of KHSO$_4$ or may be decrease in viscosity of reaction mixture result in increase of effective collision of molecules. In this study 9: 1 molar ratio is optimum molar ratio of MeOH to NEJC$_{oil}$, which is significantly lower compared to 20:1 or 24:1 molar ratio reported for acid catalystsin the literature [20,21].

Effect of Reaction temperature& time

Trasesterification reaction was planned at different temperatures ranging between 50 to 90°C to optimise the reaction temperature. Figure 4b shows that the biodiesel yield was gradually increased with increasing temperature up to 70°C and beyond this temperature yield was declined. As shown in Figure 4b minimum 20 ± 2% biodiesel yield was obtained at

Table 2 — Fatty Acid Methyl ester composition by GC-MS analysis.

Peak Report TIC

| Peak	R. Time	Area	Area %	Height	Height %	Name
1	21.011	2314667	1.12	1164496	1.28	9-Hexadecenoic acid, methyl ester, (Z)-
2	21.208	47064886	22.78	24372407	26.85	Hexadecanoic acid, methyl ester
3	22.954	56135495	27.17	23630657	26.03	9,12-Octadecadienoic acid (Z,Z)-, methyl ester
4	23.028	74834228	36.22	28376274	31.26	9-Octadecenoic acid, methyl aster, (E)-
5	23.250	24359870	11.79	12604861	13.89	Heptadecanoic acid, 16-methyl-, methyl ester
6	24.774	1359863	0.66	199718	0.22	6-Octadecenoic acid, methyl ester, (Z)
7	24.967	530232	0.26	418051	0.46	Hexadecanoic acid, methyl ester
		206599241	100.00	90766464	100.00	
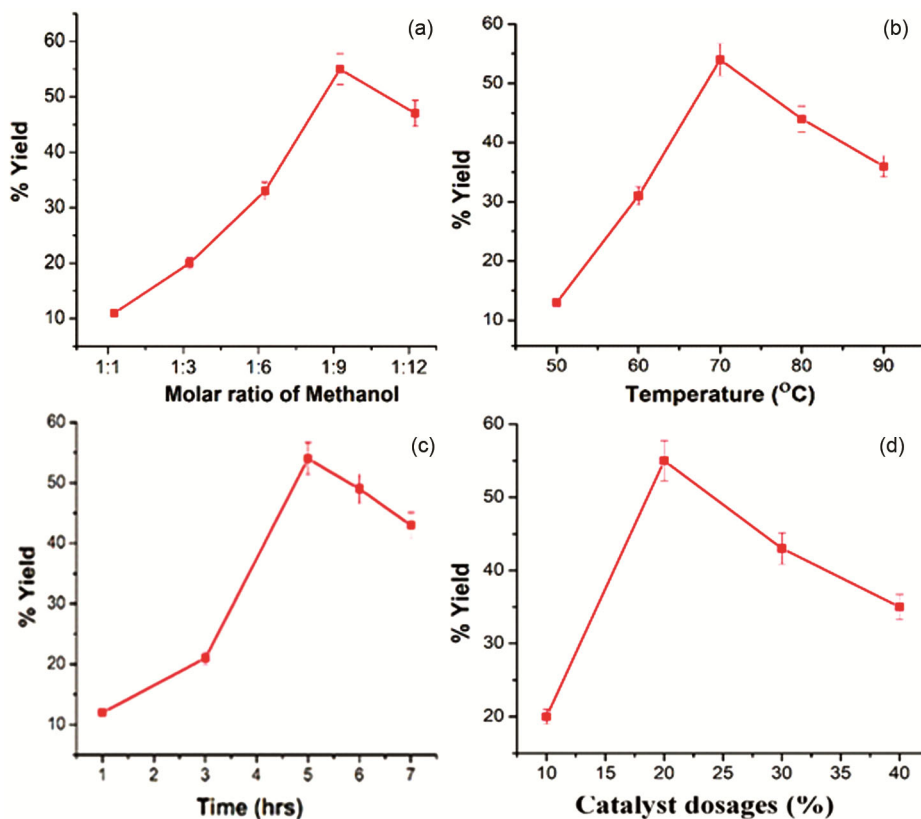
Fig. 4 — Influence of (a) methanol/NEJC*oil*/molar ratio, (b) reaction time, (c) reaction temperature, (d) catalyst KHSO-GO$_{cat}$ dosages on the conversion yield of biodiesel (Optimum reaction parameters: Temperature = 70°C; Catalyst (KHSO$_4$: GO) 20:0020 wt%, Reaction duration = 7 h).

50°C while at maximum 55 ± 5 % yield was obtained at 70°C. At higher reaction temperature (above 70°C) biodiesel yield was decreased may be due to the quick evaporation of methanol (boiling point = 64.7°C). These experiments indicate that 70°C reaction temperature is suitable to obtained maximum biodiesel yield with KHS-GO$_{cat}$.

Figure 4c shows that the biodiesel yield increased steeply when increases the reaction time up to 5 h and declined beyond this reaction duration. The biodiesel yield was 10 ± 2% after 1 h transesterification reaction and increased up to maximum 55 ± 5% after 5 h transesterification reaction (Fig. 4c). Initial low biodiesel yield (10 ± 2%) due to the mixing and dispersion of methanol in NEJC*oil*[22], and increased with increasing the reaction time up to 5 h. Figure 4c shows that yield was declined after 5 h due to favouring of backward reaction of transesterification and also probably due to the intermediate soap formation[23]. Conclusively, 5 hours of reaction time could be the optimal reaction time for the transesterification reaction in the presence of KHS-GO$_{cat}$, which is significantly lesser compared to 18-24 h

reaction time reported for acid catalysed transesterification of *Jatropha curcas* oil in the literature[24].

Effect of Catalyst dosage

Figure 4d shows the effect of varying catalyst dosages on biodiesel yields. In this work we used KHS-GO$_{cat}$ from 1.0 g to 4.0 g. Result shows that yield of biodiesel increased when increase the KHS-GO$_{cat}$ dosage from 10 to 20% *w/w* (Fig. 4d) and declined beyond this catalyst dosage. Figure 4d shows that initial 20% conversion yield may be due to no enough reactive sites for the reaction with 10 wt% catalyst dosage. The biodiesel yield was 55 ± 5% with 20 wt% catalyst due to the enough active sites are available for reaction. In addition, biodiesel yield decreased to 35% with 30 wt% catalyst dosage. This could be explained on the basis of the formation of soap and reverse reaction in presence of high catalyst dosage. Thus 20 wt% catalyst dosage can be regarded as the optimal catalyst dosage for obtaining maximum biodiesel yield in this study. The transesterification

reaction was also carried out with 20% pure KHSO4 keeping all other parameters constant, and found that biodiesel yield was low (15%), while no transesterification reaction was observed with 20 mg pure GO. Hence the combination of both is suitable for transesterification of $NEJC_{oil}$.

Conclusion

In summary, in this paper we demonstrate potassium hydrogen sulphate (KHS) and graphene oxide (GO) based carbon supported composite (KHS-GO$_{cat}$) catalyst for transesterification reaction of *Jatropha curcus* oil. This study confirmed that pure $KHSO_4$ and/or pure GO do not yield the transesterification reaction of $NEJC_{oil}$, while composite KHS-GO$_{cat}$ catalyst offers the best catalytic activity with good biodiesel yield. At the end of use, mother liquor containing $KHSO_4$ can be converted into nitrogen, potassium, and sulphur rich liquid, which can be used as manure. Thus, the effect of the transesterification on the environment will be significantly reduced and the composite catalyst may be a suitable option to develop zero liquid discharge(ZLD) transesterification of *Jatropha* oil.

Acknowledgements

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