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Kinetics of transesterification of *Madhuca Indica* oil over modified zeolites: biodiesel synthesis

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Abstract

In this article production of biodiesel from Madhuca indica oil (MI-oil) containing high % of free fatty acids (FFA) by transesterification process with methanol over basic zeolites such as NaY loaded with 5-25% KOH is presented. The zeolites were characterized by PXRD, BET and CO_2-TPD methods prior to their catalytic activity studies. Optimization of reaction conditions for transesterification was conducted in order to get highest possible yield of biodiesel. 1HNMR and FTIR analysis confirms the conversion of MI-oil to biodiesel. The physico-chemical properties of MI-biodiesel were found to be comparable with that of the standard biodiesel. The NaY and KOH/NaY zeolites were found to be efficient and reusable catalysts without much loss of their catalytic activity when used for several times in biodiesel production.

Keywords: Biodiesel; *Madhuca indica*; Transesterification; KOH/NaY; Kinetics

Introduction

Biodiesel is a renewable, non-polluting, biodegradable as well as nontoxic fuel having a high potentiality towards replacement of conventional fuels (Ma and Hanna, 1999; Sharma *et al.*, 2008). In Indian scenario, biodiesel is obtained from oil extractions of non-edible feedstock, as the edible oil is scarce and a significant quantity of edible oil is imported (Fukuda *et al.,* 2001).

Madhuca Indica oil (MI-oil) is one of the less expensive and abundantly available non-edible oil in most of the states of India including Karnataka. The MI trees start bearing seeds from seventh year of planting and seed contain 30-40 percent of fatty oil commonly called Mahua oil (i.e., MI-oil). In Indian context, an estimated annual production of MI-oil is about 181,000 tones (Godignur and Murthy, *et al.,* 2009). As these trees grow mainly in jungle area, uncultivated and waste land, its cultivation has no impact on food production. Since MI-oil is less expensive compared to other vegetable oils, MI-oil was selected for the present study which makes production of biodiesel more economical.

Nowadays, commercial biodiesel is produced from transesterification reaction of vegetable oils using homogenous base catalysts such as NaOH or KOH, as base catalysts catalyze transesterification reaction of oils faster than acidic catalysts (Freedman *et al.,* 1986). But these homogeneous catalysts have disadvantages such as equipment corrosion, saponification and hydrolysis, disabling recovery and reuse of catalysts, purification of products thereby increasing the biodiesel production expensive (Jitputti and Kitiyanan, 2006; Kim *et al.,* 2004). These problems can be prevented by adopting basic heterogeneous catalysts, which offer many advantages such as easy separation, prevention of side reactions and reusability. Various heterogeneous catalysts have been developed so far to catalyze the transesterification of vegetable oils to produce biodiesel. For instance, anionic clays (Kim *et al.,* 2004), calcium carbonate rock (Leclercq *et al.,* 2001), EST-10 (Suppes *et al.,* 2001), Li/Cao and Na/NaOH/-Al_2O_3 (Watkins *et al.,* 2004), etc. But these type of catalytic materials are complicated to prepare, expensive and reaction rate is relatively slow which restricts their industrial applications. Therefore, it is highly indeed to find inexpensive as well as more efficient catalytic material for the production of biodiesel for commercial applications. Now a days, there is a drastic change in the growth of heterogeneous catalytic materials like potassium catalysts supported on alumina (Xie *et al.,* 2006) and zeolites (Suppes

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and Dasari, *et al.,* 2004). Zeolites are representative support materials having a number of micro pores on the surface with a large specific area suitable for impregnation of basic metals (Rashtizadeh and Farzaneh, 2010; Noiroj *et al.,* 2009). The zeolite NaY is extensively used in industry mainly due to its high surface area as well as its large pore openings. Zeolite support and its stability mainly depend on Si/Al ratio and its structure (Xu *et al.,* 2006). Also, the stability of the crystal lattice structure of zeolites increases with increase in Si/Al ratio which clearly indicates that the zeolite NaY has higher crystal stability than that of NaX. KOH supported on NaY zeolite can prevent deactivation of the catalytic material and can act as heterogeneous-like system (Noiroj *et al.,* 2009; Xu *et al.,* 2006 and Ramos *et al.,* 2008). It is also known that the basicity or average oxygen charge increases with increase in Al content of zeolite as well as ionic radius of alkali cation (Barthomeuf *et al.,* 1991). Moreover, the influence of K ions on NaY zeolite has been rarely reported, under operating reaction temperatures <343 K at lesser reaction time. It is the prime reason behind selecting KOH/NaY catalytic system for the synthesis of biodiesel for the present work. Further, to the best of our knowledge no literature on the kinetic studies for the synthesis of biodiesel using MI-oil over KOH/NaY is reported. It is estimated that transesterification reaction takes place more than 4000 times faster in the presence of basic catalyst compared to acidic (Formo *et al.,* 1954). Hence, transesterification reaction in presence of basic catalysts was adopted for the present study. In order to obtain highest possible yield of biodiesel, the transesterification reactions were optimized by varying reaction temperature, weight of zeolite, molar ratio and reaction time of the catalysts. A kinetic study was conducted for transesterification reaction by utilizing the data obtained under optimized reaction conditions. Reusability of zeolite catalysts in the biodiesel synthesis was also taken-up.

Material and methods

Chemicals

MI oil containing high FFA (7-8%) was procured from local markets of Tumkur, Karnataka, India. Zeolites in their sodium forms were supplied by Sud-Chemie India Pvt. Limited, Baroda. Other chemicals such as potassium hydroxide and methanol were obtained from LOBA Chemie India Ltd.

Preparation of basic zeolites

The KOH/NaY zeolite was prepared by using the method as reported by Noiroj, *et al* (Noiroj *et al.,* 2011). The zeolite NaY was first dried in an hot air oven at 383 K for 2 h to remove any water content absorbed on its surface. Thus obtained zeolite NaY was impregnated with aqueous KOH with different % KOH loadings (5, 10, 15, 20 and 25). Finally all the impregnated zeolite samples were dried at 383 K for 24 h in a hot air oven.

Characterization of zeolites

The BET (surface area) of basic zeolites was calculated by adsorbing nitrogen using automated adsorption instrument (Micrometrics ASAP 2010 model). All the catalysts were characterized for their surface basicity by CO_2-TPD methods (Mayura Analyticals). The PXRD patterns were recorded on Philips X'pert X-ray powder diffractometer using CuKα radiation (λ = 1.5418 A^o) and graphite crystal monochromator.

Catalytic activity studies in biodiesel synthesis

Process: Base catalyzed transesterification of MI-oil over basic zeolites *(to synthesize biodiesel)*

Transesterification of MI-oil was carried in a 100 ml RB flask fitted with a water-cooled condenser and a thermometer. Known weights of MI-oil, basic zeolite and methanol were heated on a magnetic stirrer cum heater at a reaction temperature of 328-348 K using oil-bath with continuous stirring in a time period ranging from 20-100 min. After the completion of stipulated reaction time, the catalyst was recovered by the process of filtration, washed with acetone and dried for further use. The filtrate consisting of two liquid phases namely, glycerol-rich phase and biodiesel (methyl ester phase) were obtained. The two phases were separated by using a decantation funnel. Then, biodiesel phase consisting of methyl esters, un-reacted oil, methanol and other impurities were washed with de-ionized hot water for refinement. If any traces of catalyst present in the biodiesel was removed by centrifuge method. Thus obtained biodiesel was analyzed by GC-MS (Hewlett Packard) fitted with a capillary column (HP-624, 30 m × 25 μm × 0.25 μm), H^1NMR spectroscopy (Bruker NMR spectrometer, 400 MHz), FTIR analysis (Shimadzu, Spectrophotometer in the range of 800-3750cm^{-1}) and elemental analysis (Thermo scientific organic elemental analyzer).

Results and discussion

Characterization of zeolites

The surface area and basicity values of basic zeolites (NaY & 5-25% KOH/NaY) are presented in Table I. The surface area of pure NaY was found to be higher than the surface area of KOH/NaY. When the % KOH on NaY was increased from 5% to 25% the surface area was found to decrease gradually. This decrease in the surface area of NaY zeolite upon

Table I. Surface area, basicity and yield (%) of biodiesel over different zeolites used in the present study

Zeolite	BET Surface area (m^2/g)	Basicity by CO_2 -TPD (mmols/g).	Yield (%) of Biodiesel ***
NaY	570.5	1.50	20 .0
5% KOH/NaY	522.2	2.42	78 .0
10 % KOH/NaY	501.2	2.61	86 .0
15 % KOH/NaY	480.9	2.80	98.9
20 % KOH/NaY	370.2	2.49	88 .0
25 % KOH/NaY	210.6	2.36	83 .0

***[Reaction conditions: Molar ratio of methanol: MI-oil = 9:1; amount of catalyst = 0.3 g; reaction time = 60 min; reaction temperature = 338 K].

incorporation of KOH from 5 to 25% can be attributed to the formation of KOH agglomerates on the surface of NaY zeolites (Noiroj, *et al.,* 2009).

It was observed that the basicity of pure NaY was lesser than the basicity of KOH/NaY. When the % of KOH was increased from 5% to 15% the basicity of KOH/NaY was found to increase. This increase may be attributed to an effective dispersion of basic KOH molecules on the surface of NaY zeolite. But, when the percentage of KOH on NaY was increased beyond 15%, a decrease in the basicity of KOH/ NaY was observed which can be due to the formation of multilayers of KOH on KOH/NaY zeolite.

PXRD analysis

The PXRD patterns of KOH/NaY zeolite with different weight (%) of KOH loadings are presented in Fig. 1. The morphology of KOH/NaY is almost similar to that of pure NaY zeolite. Moreover, the intensity of XRD peaks decreases with an increase in the loading amount of KOH from 5 to 25%, indicated by peaks at 6°, 10°, 12°, 13°, 14°, 16°, 17°, 18°, 20°, 21°, 23°, 24°, 25°, 26°, 27°, 28°, 29°,30°, 31°, 32°, 33°, 34°, 35°, 36°, 38°, 40°, 41°, 42°, 43°, 44°, 45° and 46°. This shows that the loading of KOH on NaY has least significant effect on its crystalline structure. It is also reported (Xie *et al.,* 2007) that the loading of KOH maintains pore structure of NaY which is essential for its catalytic activity.

Catalytic activity studies of basic zeolites (in the synthesis of biodiesel via transesterification)

Transesterification of MI-oil was carried out with methanol (MeOH) over basic zeolite catalysts (NaY, 5-25% KOH/NaY) by varying the molar ratio, weight of the catalyst, reaction time & temperature in order to obtain optimized reaction conditions.

Prior to optimization and kinetic studies, transesterification of MI-oil was carried out in the absence of any catalyst and a negligible yield (%) of biodiesel (~6%) was obtained.

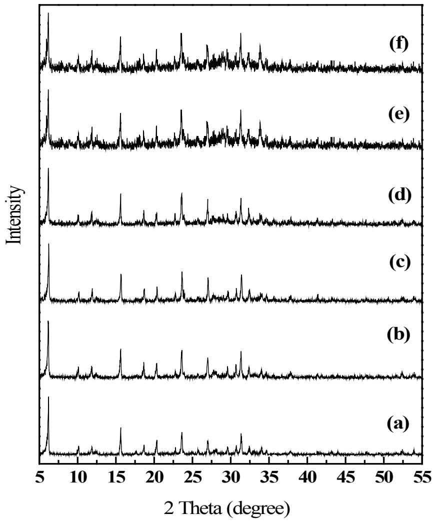

Fig. 1. PXRD patterns of: (a) NaY (b) 5% K/NaY (c) 10% K/NaY (d) 15% K/NaY (e) 20% K/NaY (f) 25% K/NaY.

Effect of KOH loading in KOH/NaY on the yield (%) of biodiesel

Effect of wt (%) of KOH loading in KOH/NaY on the yield (%) of biodiesel was studied and the results are represented in Fig. 2.

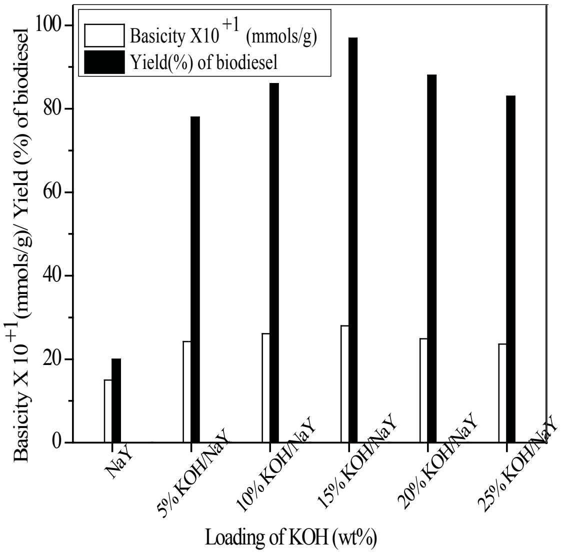

Fig. 2. Yield (%) biodiesel v/s basicity of 5-20% KOH/NaY

Among the basic zeolites pure NaY showed least activity in the transesterification reaction of MI-oil. A correlation between the catalytic activity and basicity of the basic zeolites was observed, i.e., 15% KOH/NaY which has highest basicity was found to be highly active in transesterification resulting in 98.9% yield of biodiesel.

Even though the surface area of 15% KOH/NaY is lower than the surface area of pure NaY, 15% KOH/NaY showed good activity in transesterification. This indicates that, it is not the surface area which is determining the catalytic activity of KOH/NaY but it is the number of active sites (basic sites) which play an important role in its catalytic activity. i.e., no correlation between the surface area and surface basicity of basic zeolite was observed. But rather a correlation between the basicity and the catalytic activity could be observed. For further optimization studies 15%KOH/NaY was selected as the catalytic material.

Effect of molar ratio of MeOH: MI-oil on the yield (%) of biodiesel

Effect of molar ratio of MeOH: MI-oil was studied over 15% KOH/NaY zeolite. The molar ratio was varied in the range MeOH: MI-oil = 6:1 to 15:1.

When the molar ratio (MeOH: oil) was increased, the yield (%) biodiesel was also increased and the highest yield (98.9%) was observed over 15% KOH/NaY at a molar ratio of MeOH: MI-oil of 9:1. Beyond the molar ratio of 9:1, i.e., when the amount of MeOH was taken in excess no impact on yield (%) of biodiesel was found.

Effect of weight of the zeolites on the yield (%) of biodiesel

Effect of weight of the zeolites catalyst on transesterification reaction of MI-oil was studied over 15% KOH/NaY basic zeolite by varying the weight from 0.1 to 0.5 g.

When the weight of catalyst was increased from 0.1 to 0.3 g, the yield (%) of biodiesel increased and a maximum yield (98.9%) was observed over 0.3 g of 15% KOH/NaY. The yield (%) of biodiesel was found to decrease when the amount of the zeolite was increased beyond 0.3 g. This may be due to improper mixing of reactants (MI-oil and MeOH) and catalysts (Kim *et al.,* 2004). Therefore, 0.3 g was found to be an optimum weight of the catalyst.

Effect of reaction temperature on the yield (%) of biodiesel

Transesterification reactions were conducted by varying the reaction temperature from 328 to 348 K over 15% KOH/NaY zeolites. When the transesterification was carried out at 328 K, the yield (%) of biodiesel was low because at low temperature, there was no sufficient energy to promote collisions extensively among the reactants. But, the yield (%) of biodiesel increased when the temperature was increased from 328 K to 338 K. A maximum yield of biodiesel (98.9%) was observed at 338 K over 15% KOH/NaY zeolite. But when the reaction was carried out above 338 K, it leads to a decrease in the biodiesel yield. Therefore, an optimum temperature was found to be 338 K.

Effect of reaction time on the yield (%) of biodiesel

Effect of reaction time on transesterification reaction of MI-oil was studied over basic zeolite (15% KOH/NaY) by varying the reaction time from 20-100 min.

The yield (%) of biodiesel increases when the reaction time was increased from 20 min to 60 min. However, beyond 60 min not much increase in the yield (%) biodiesel was observed. Besides, longer reaction time may lead to the reduction of biodiesel because of reversible transesterification reaction results in the loss of esters (Canakcin *et al.,* 2001). Therefore, reaction time of 60 min was found to be an optimum reaction time for the transesterification to obtain good yield (%) of biodiesel.

Comparison of physico-chemical properties of MI-biodiesel with conventional diesel

Fuel properties of MI-biodiesel are tested as per ASTM standards and compared with standard commercial biodiesel and presented in Table III. It is observed from the table that the values are comparable. An important property of

Table II. Reaction rate constant and energy of activation of basic zeolites (5 to 20% KOH/NaY) for the synthesis of biodiesel via transesterification of MI-oil with methanol

Basic zeolite catalyst	Rate constant × 10^{-3} min^{-1}		Energy of activation (Ea) for the formation of biodiesel (kJ mol^{-1})
	333 K	338 K	
5% KOH/NaY	1.38	2.5	111.2
10% KOH/NaY	2.04	3.0	72.62
15% KOH/NaY	1.52	2.38	39.51
20% KOH/NaY	2.04	2.72	53.8

Table III. Comparision of physico-chemical properties of MI-Biodiesel, commercial biodiesel and standard biodiesel

Parameter	MI -Biodiesel	Commercial biodiesel	Stanadard biodiesel
Density at 15 °C (g/cc)	0.85	0.844	0.872
Kinematic viscosity at 100 °C (cSt)	3.5	-	1.9 to 6.0
Pour point (°C)	1	-10	-15 to 10
Flash point (°C)	121	70	100 to 170
Acid Value (mg KOH/g)	0.01	0.34	>0.80
Water content (%)	Nil	0.0 2	0.05
Ash content (%)	0.01	-	Nil
Cetane number	50	52	51
Carbon residue (%wt)	0.33	-	0.80
Heating value (MJ/Kg)	39.01	40.9	40.13
Calorific value (kcal/kg)	9268	10665	10020

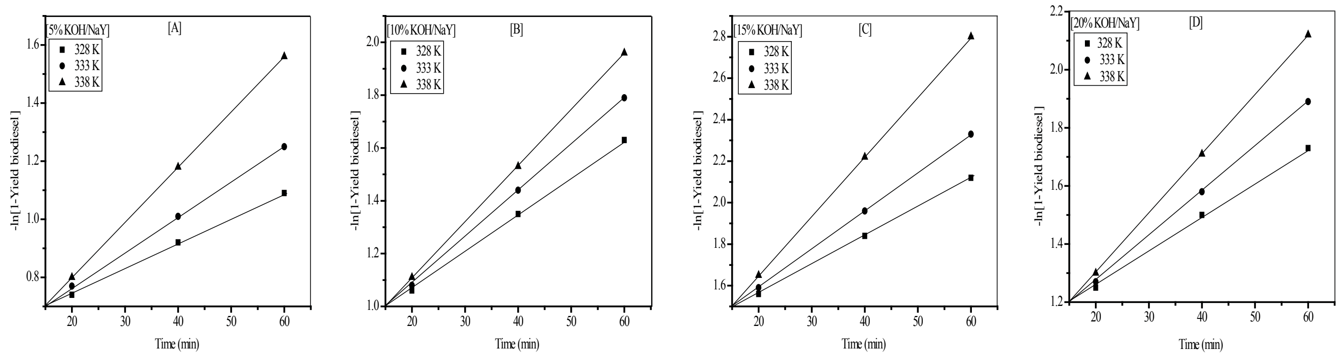

Fig. 3. Plot of first-order rate constants for transesterification reaction of MI-oil over zeolites: (A) 5% K/NaY (B) 10% K/NaY (C) 15% K/NaY and (D) 20% K/NaY at 328 K, 333 K and 338 K

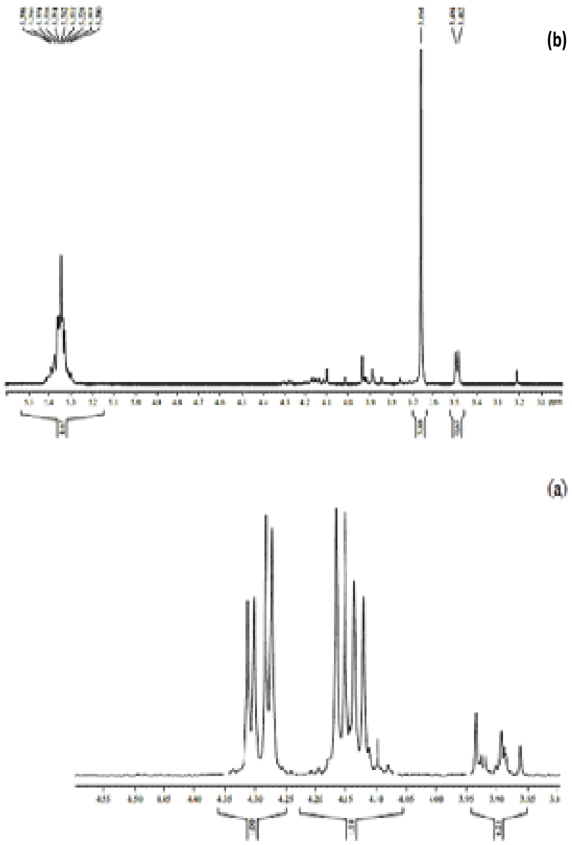

Fig. 4. H^1 NMR spectra of (A) MI-oil (B) MI-biodiesel

biodiesel is its water content. It has been found that the water content of MI-biodiesel is zero.

Kinetic studies for transesterification (synthesis of biodiesel)

Kinetic studies were conducted over basic zeolite catalysts (5-20% KOH/NaY). Prior to the kinetic studies, experiments were carried out to establish the effect of mass transfer limitations of transesterification reaction. According to Madon and Boudart (Madon *et al.,* 1982), a linear relationship between the rate of the reaction and weight of the catalyst indicates the absence of all transport limitations.

Plots of –ln [1-yield$_{\text{biodiesel}}$] v/s reaction time for the transesterification were conducted at different temperatures over basic zeolites (5, 10, 15, 20% KOH/NaY) are shown in Figure 3. (A-D) respectively. The plots are almost linear in all the cases, which indicate that the synthesis of biodiesel *via* transesterification reaction to be a first-order reaction.

The values of first-order rate constants obtained from the slopes of the plots and the energy of activation calculated from the Arrhenius equation (Eq. (1)) are presented in Table II. The values of energy of activation of the catalyst for the transesterification were found to be in the order:

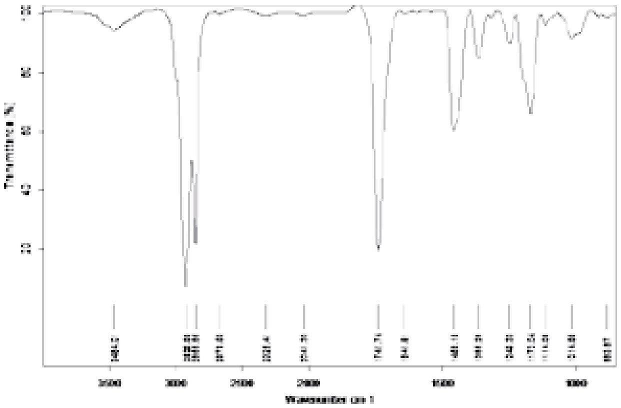

Fig. 5. FTIR spectra of MI-biodiesel

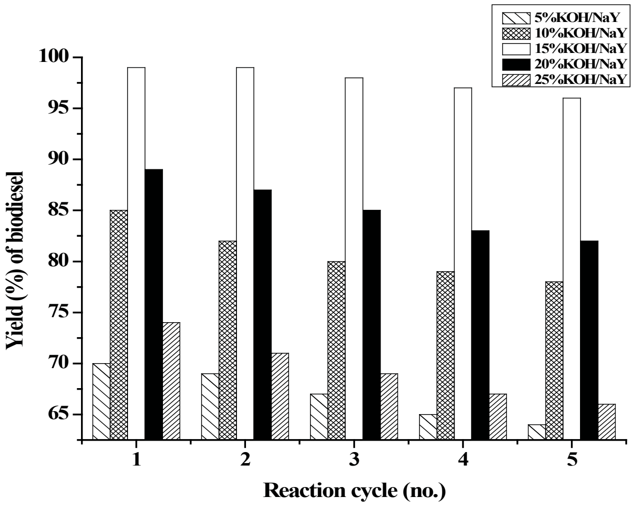

Fig. 6. Reusability of basic zeolites in transesterification of MI-oil

[Reaction conditions: amount of catalyst = 0.3 g; reaction temperature = 338 K; reaction time = 60 min; molar ratio of MeOH: MI-oil = 9:1].

15% KOH/NaY > 20% KOH/NaY > 10% KOH/NaY > 5% KOH/NaY

The energy of activation was calculated using Arrhenius equation (Atkins *et al.,* 1988):

$$E_a = 2.303R\log\left(\frac{k_2}{k_1}\right)\left[\frac{T_1XT_2}{T_2-T_1}\right] \qquad (1)$$

where, R, gas constant; k_2, rate constant at temperature T_2; k_1, rate constant at temperature T_1.

Over all the basic zeolite catalysts, 15% KOH/NaY showed lowest (Ea) value indicating that it could be a facile basic catalyst among other basic zeolites used in the present study for biodiesel synthesis.

Analysis of biodiesel

Using ^{1}HNMR technique

^{1}HNMR spetra of crude MI-oil and biodiesel are given in Figure 4. Appearance of a new peak at 3.66 ppm due to OCH_3 and disappearance of glyceride protons at 4.0 - 4.3 ppm in the NMR spectra of biodiesel favours the formation of biodiesel after transesterification of MI- oil.

The purity of biodiesel formed after transesterification can also explained using H^1NMR by the following methods reported literature (Knoothe *et al.,* 2001).

Biodiesel is a mixture of mono, di, triglycerides associated with glycerol as impurities. In the biodiesel sample, the presence of impurities must be less as specified by EN standards. The absence of peak in the range 3.9 - 4.5 ppm in ^{1}HNMR spectra of biodiesel after transesterification ruled out the presence of glycerol in the biodiesel sample (Serdarevich *et al.,* 1996).

Using FTIR technique

FTIR spectrum of MI-biodiesel (Figure 5) shows a carbonyl peak appears at1741.74 cm^{-1} (Sylvester et al., 2013). The most characteristic peak which represents typical biodiesel (methoxy group CH_3-O) appears at1456.18 cm^{-1} (Sylvester et al., 2013) and C=C double bond absorption appears at 1456.18-1509 cm^{-1}(Sylvester et al., 2013). Moreover, in the FTIR spectrum of MI-biodiesel, major peaks are observed at 1741.74 cm^{-1}, 2855.53 cm^{-1} and 2925.68 cm^{-1} respectively.

Elemental analysis of MI-biodiesel

Elemental analysis was done by using organic thermo scientific elemental analyzer (reactor temperature: 1173 K, Helium & Oxygen 250 k Pa each, Flash 2000) and the (%) elemental contents in biodiesel were found to be carbon (73.90), hydrogen (11.48), oxygen (14.62), nitrogen (0.0) and sulfur (0.0).

Reactivation of basic zeolite catalysts

Basic zeolite catalysts were recovered from the reaction mixture, washed with methanol and dried over 393 K for 2 h and calcined at 923 K for 1 h in a muffle furnace before their use in the next consecutive reaction cycle.

Reusability of reactivated basic zeolite catalysts in transesterification

The yield (%) of biodiesel v/s number of reaction cycles was studied over basic zeolites and the results are presented in the Figure 6. All the basic zeolites (KOH/NaY) used in the present work were found to be effectively reusable for transesterification to synthesize biodiesel at least for 5 reaction cycles.

Conclusion

In general, zeolites have been found to be effective and facile catalysts in the production of biodiesel from vegetable oils particularly for Madhuca Indica oil. In case of basic zeolites 15% KOH/NaY was found to be a better basic zeolite catalyst with lowest Ea (39.51 kJ/mol) for the synthesis of biodiesel from MI-oil via transesterification. Moreover, basicity of zeolites was found to be correlatable with their catalytic activity. But, no correlation between the surface area of zeolite and their catalytic activity was observed. The conversion of MI-oil to MI-biodiesel was confirmed by ^{1}HNMR spectrum and FTIR analysis. The fuel properties of MI-biodiesel were found to be comparable with standard biodiesel as well as commercial biodiesel samples. Furthermore, Elemental analysis shows the absence of sulfur and nitrogen which clearly indicates that the obtained MI-biodiesel is an environmentally benign and eco-friendly biodiesel.

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