Preparation, characterization, and modelling activity of potassium flouride modified hydrotalcite for microwave assisted biodiesel conversion

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ABSTRACT

In this paper, potassium fluoride (KF) modification of hydrotalcite (HT) and its activity as a solid base catalyst for microwave (MW) assisted biodiesel conversion was investigated. The catalyst was prepared simply and rapidly by the solid reaction of KF and HT, and characterization was performed using x-ray diffraction, surface profile analysis using gas sorption analyses, SEM, FTIR, and the determination solid basicity. The effect of KF content on the physicochemical character, yield, and turn over frequency (TOF) of the reaction is presented. A statistical optimization of the effects of the reaction parameters on yield using logit transformation regression showed that the reaction time and the KF content of the catalyst strongly affected the reaction's yield. The data shows the potency of the modified HT as a catalyst for biodiesel conversion. From the TOF data, it is suggested that the MW-irradiation method gives a better yield compared to the reflux method. It was also found that the catalysts are reusable.

1. Introduction

Biodiesel is still the most high potential energy resource substitute in developing countries. The main features of its potency are the renewable resources of plant oil and its simple production reaction procedure. Traditionally, biodiesel has been obtained from the transesterification of triglycerides using methanol over a basic catalyst of NaOH or KOH. However, further work is required for green and environmental efficiency reasons. Proposed schemes for creating a greener process is the use of a heterogeneous catalyst for the reaction so that the catalyst can be recycled and reused for more economical cost, and the use of other efficient energy sources for biodiesel production (Martins et al., 2013; Mittelbach, 2009). The use of NaOH as a homogeneous catalyst in the transesterification process has some advantageous, such as rapid reaction due to the miscibility of the reactant; however, NaOH being a non-recyclable catalyst is a disadvantage. Another problem faced by soluble, basic catalysts is the saponification reaction; plant oils contain high levels of free fatty acid. For these reasons, some solid base catalysts were simulated and applied (Rustamaji et al., 2011; Santos et al., 2009). Another captured technique for fast biodiesel production is the utilization of the microwave- (MW) irradiation method. The reaction can be conducted in a few minutes instead of hours for a targeted yield.

As catalyst alternatives, basic oxides of Ca, Mg, and Ba have been reported as active in biodiesel conversion as well as some zeolites, clays, and silica-alumina, and its modified forms (Atadashi et al., 2013; Helwani et al., 2009). Within the clay scheme of materials, hydrotalcite (HT) is a well-known base material. HT, or layered double hydroxide (LDH), is an anionic and basic clay with the general formula ($M^{2+}_{(1-x)}M^{3+}(OH)_2]^{b+}$ [$A_n b^-$] M H_2O), where M^{2+} is a divalent or monovalent cation and A_n is the interlayer anion. The basic properties of HT as a reusable catalyst in the transesterification of biodiesel production have been reported to be active and efficient. However, many attempts have been made to enhance the basicity and effectivity of HT as a catalyst; an increase in the basicity of the catalyst has been attributed to HT's increased intralayer electron density and pore volume by calcination and the surface modification of HT (Climent et al., 2004). Factors that determine the solid basicity, for the modification concept, include the Mg/Al mole ratio, the calcination temperature, and metal framework modification (Coriolano et al., 2017; Teng et al., 2010; Xie et al., 2006). Previous investigations have reported the effect of HT modification using potassium salts such as K_2CO_3, KI, and KF for the enhancement of biodiesel conversion (Guzmán-Vargas et al., 2015; Katekong et al., 2017; Teng et al., 2010). It was observed that impregnation with potassium generates basic surface sites and directly plays a role in increasing the catalytic activity in the transesterification mechanism. As a background for improving the effectivity and efficient production of biodiesel, this work aimed to study the effect of modified HT and the
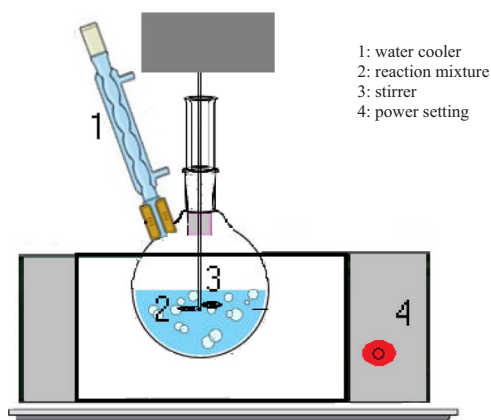

Fig. 1. Schematic representation of microwave reactor.

use of MW for biodiesel production. Although a similar studies to this have been reported, the effect of the KF content on the physicochemical character and catalytic activity in the modified HT has not been reported. Furthermore, it is also important to study catalyst reusability related to the catalyst's character.

2. Material and methods

HT (Sorbacite®) was obtained from Süd-Chemie Ltd., Munchen, Germany. Jatropha oil was obtained from PT. Cipta Kimia, Indonesia, and directly used without further purification. Chemicals used comprised methanol, KF, NH_4OH, citric acid, and n-hexane (Merck, Berlin, Germany).

Catalyst preparation was conducted by the solid reaction method. A mixture of KF and HT was ground for 20 min followed by heating to 200 °C for 2 h. KF content varied from 5, 10, 20, and 30 wt% and the results obtained were designated KF5/HT, KF10/HT, KF20/HT, and KF30/HT, indicating the KF percentage, respectively. Characterization of the prepared catalysts was performed using x-ray diffraction (XRD), gas sorption analyses, pyridine FTIR, and solid basicity measured by the titration method. XRD (X6000; Philips) with Ni-filtered Cu-Kα radiation was utilized with a step size of 0.4°. For surface profile analysis, a NOVA 1200e instrument was used, and FTIR analyses were conducted using a Perkin Elmer ATR instrument with $4\,cm^{-1}$ resolution over a scanning range of 400–4000 cm^{-1}.

Solid basicity was determined by the potentiometric titration method. The sample was mixed with citric acid under stirring for 24 h, and unreacted citric acid was measured by titration with NH_4OH. Solid basicity was defined as the total citric acid adsorbed by the surface of the catalyst (mg/g).

The biodiesel conversion reactions were performed using the reflux method and the MW-irradiation method. For the MW-irradiation technique, a modified, commercial MW oven was utilized as shown in the schematic presented in Fig. 1. The machine worked at a frequency of 2.45 GHz and the power output was from 0 to 900 W. The reaction parameters, the catalyst, the methanol to oil molar ratio, and the reaction time, and the reaction method uses were studied. From each experiment, the reaction result was separated using a separating funnel and the biodiesel fractions were analyzed with a gas chromatography mass spectrometer (GCMS) (Shimadzu) equipped with a capillary column (TG-5MS). The condition of GCMS analysis is as follow: column oven temperature of 80.0 °C, injection temperature of 300.00 °C, column flow of 1.24 mL/min, and the split ratio of 59.1.

Testing of the catalysts' activities was conducted by identifying the influencing parameters such as the methanol to oil molar ratio, catalyst loading, irradiation time, and the identification of the applied recycled catalyst.

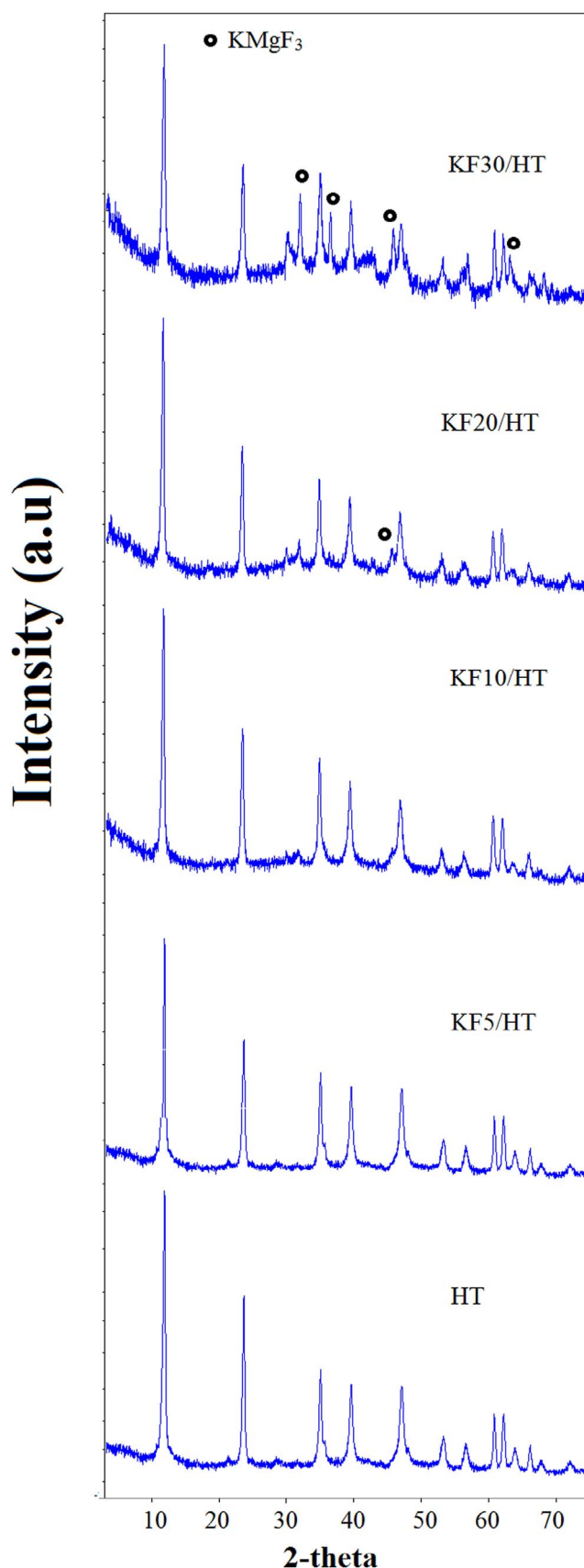Eqs. (1) and (2) were used to calculate the yield (%) and the turn
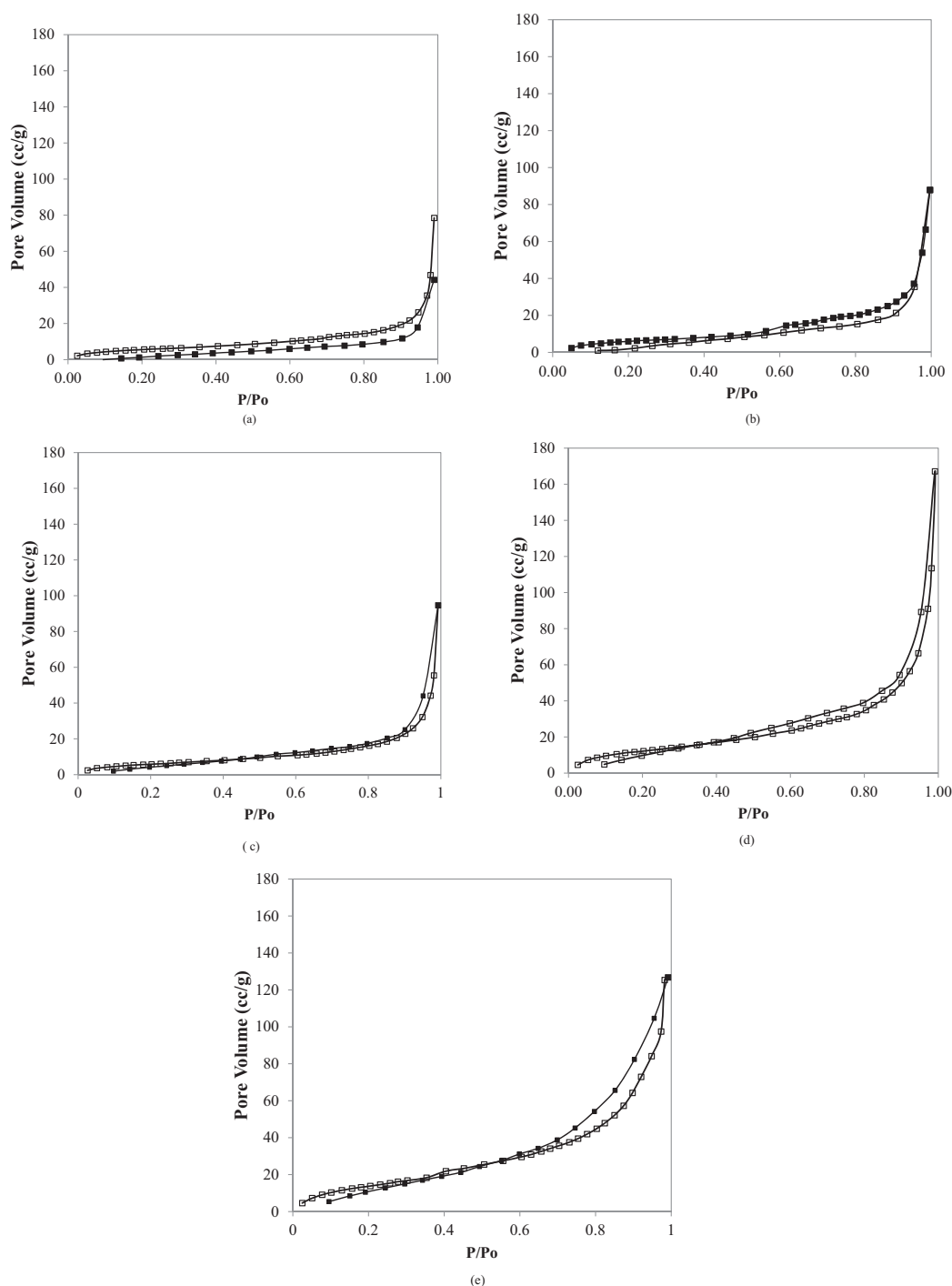

Fig. 2. XRD pattern of prepared catalysts.

Fig. 3. Adsorption-desorption profile of (a) HT (b) KF5/HT (c) KF10/HT (d) KF20/HT (e) KF30/HT.

over frequency (TOF).

$$yield(\%) = \frac{m_{biodiesel} \, x \, total \, weigh(\%) \, of \, FAME \, in \, sample}{weight \, of \, jatropa \, oil}, \tag{1}$$

where, $m_{biodiesel}$ is the mass of resulting biodiesel and *FAME* is the fatty acid methyl ester identified by GCM spectrometry.

$$TOF = \frac{mol}{m_{cat} \, x \, f_m \, x \, t}, \tag{2}$$

where, *mol* is the mole amount of biodiesel; *mcat* is the catalyst mass; *fm* is the surface amount of the basic sites, and *t* is the reaction time.
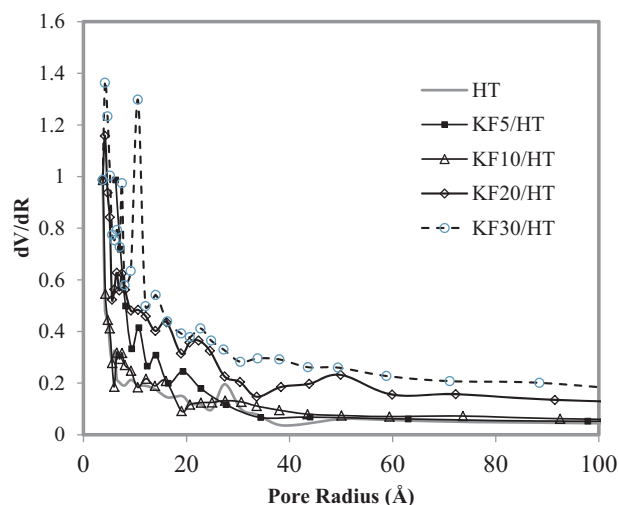
Table 1
Surface profile, surface basicity and KF content of materials.

Sample	Specific surface area (m²/g)	Pore Volume $\times 10^{-2}$ (cc/g)	Pore Diameter (Å)	Basicity (mmol/g)	KF (%)
H	18.98	6.78	69.39	0.404	n.d
KF5/H	19.02	6.78	47.12	0.413	4.89
KF10/H	21.09	8.11	43.15	0.422	9.94
KF20/H	22.98	6.74	43.46	0.524	19.67
KF30/H	24.55	7.26	30.75	0.538	27.80

Fig. 4. Pore distribution of materials.

(a)

(b)
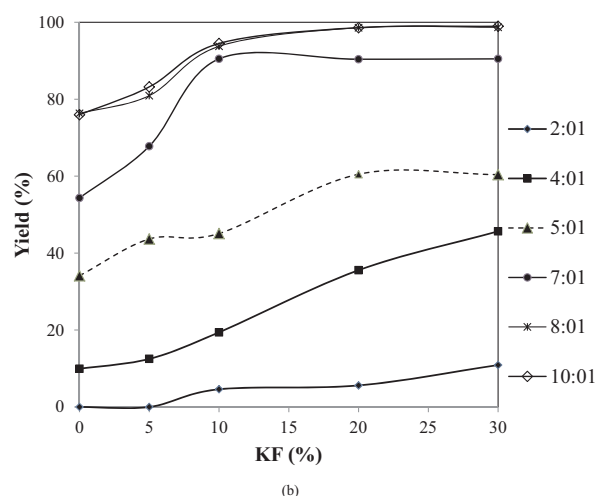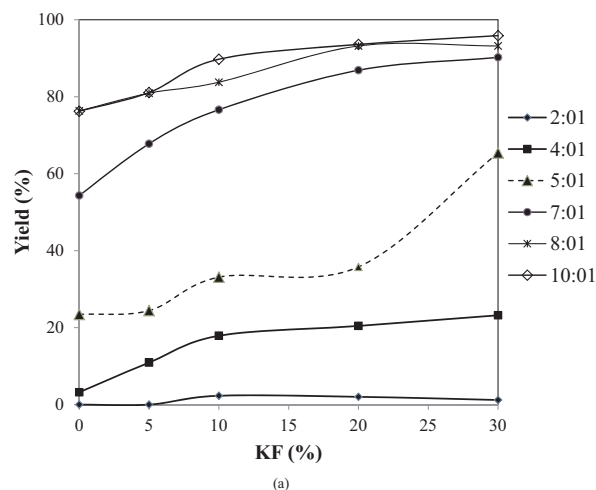
Fig. 6. Effect of KF content to reaction yield over (a) MW method (b) reflux method.

Fig. 5. FTIR spectra of (a) HT (b) KF5/HT (c) KF10/HT (d) KF20/HT (e) KF30/HT.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the catalysts are presented in Fig. 2. The presence of HT is identified from specific at $2\theta = 11.889°$ (003), 23.697° (006), and 35.015° (110). In general, there was no significant effect from KF modification because the characteristic peaks of the HT structure remained intact. It is noted that for KF20/HT and KF30/HT only, there are new signals, which were attributed to the reaction results of KF and HT, as identified by new crystalline phases of $KMgF_3$ (JCPDS 01–086-2480): $2\theta = 32.027°$, 45.93°, and 68.15°. These data suggested that the KF molecules were probably entrapped in the HT structure. Similar results of stable HT structure after KF modification have also been reported (Chen et al., 2014; Gao et al., 2010).

The effect of the modification of the surface profile of the materials was analyzed by the gas sorption analyzer, and the adsorption-desorption evolution is presented in Fig. 3. Calculated specific surface area, pore radius, pore volume, KF content, and solid basicity are listed in Table 1. KF modification increased the specific surface area and solid basicity of the HT but there is no linear correlation between the pore volume and the pore diameter. The increasing basicity theoretically came from the insertion of KF in the HT's surface as well as fluoride anions being important basic sites (Jia et al., 2015; Silva et al., 2014).

The trend of increased surface area after KF modification differed from other clay modifications reported by previous investigations (Jia
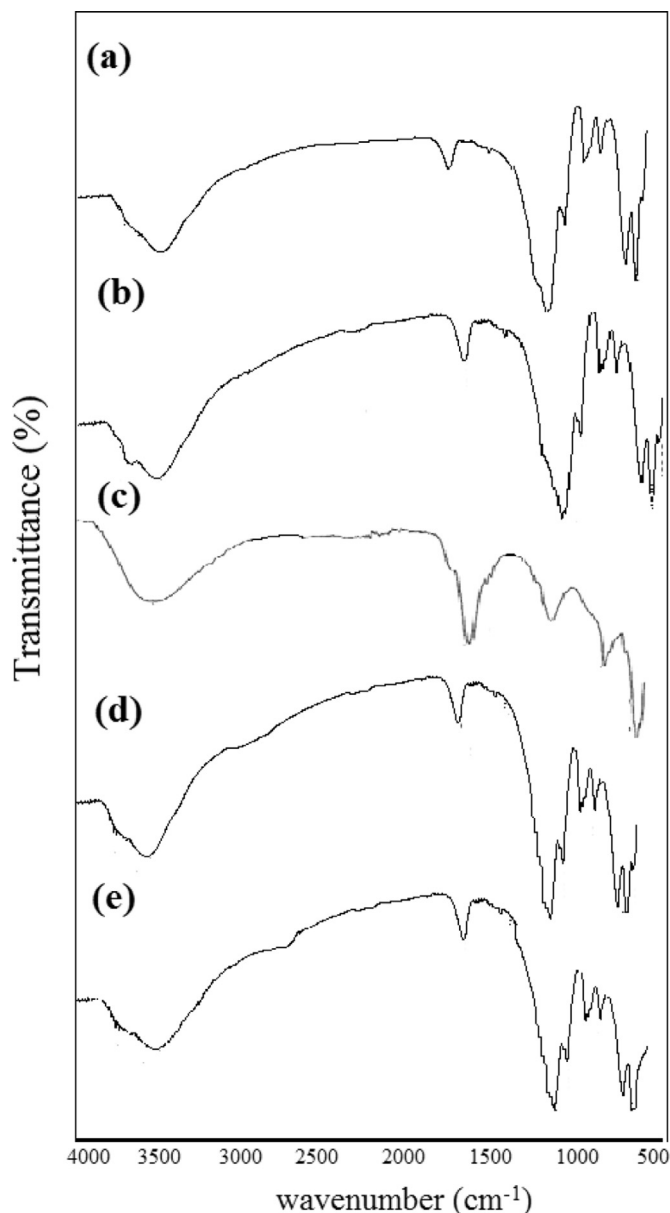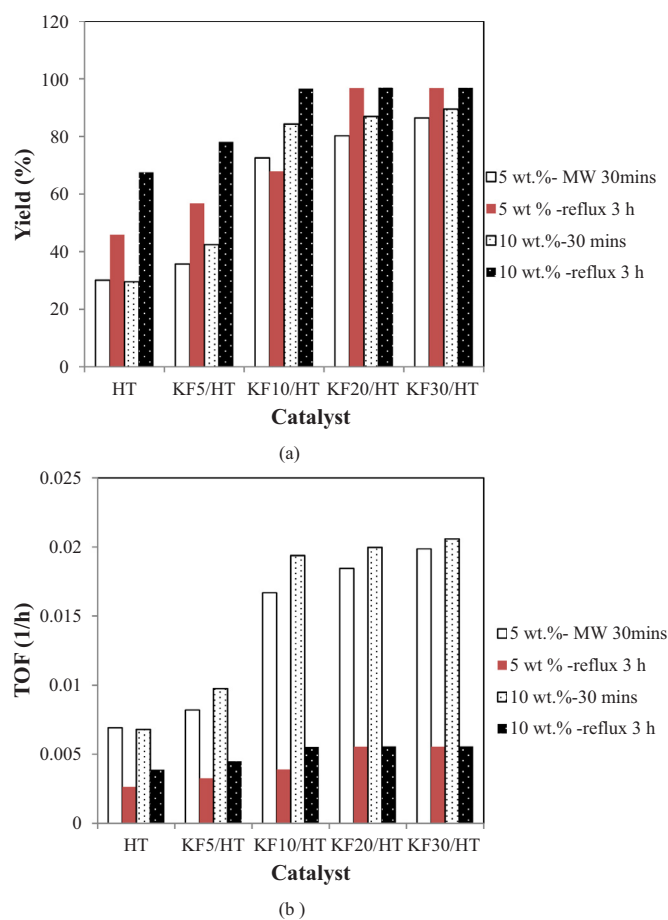
(a)

(b)

Fig. 7. Yield of biodiesel conversion at varied time of reaction (MW system, methanol:oil = 8:1; Catalyst:Oil ratio= 1:30).

Table 2
Yield of biodiesel conversion at varied methanol:oil ratio.

Catalyst/Time (min)	Yield (%)				
	2	5	10	20	30
Catalyst amount (3.33 wt%)					
HT	15.89	17.86	25.45	27.89	30.11
KF5/HT	17.65	28.98	30.67	44.9	55.09
KF10/HT	20.56	38.99	38.56	72.09	72.56
KF20/HT	34.7	66.56	70.32	80.32	80.23
KF30/HT	45.34	70.56	75.55	85.6	86.4
Catalyst (5.00 wt%)					
HT	39.1	39.1	42.1	40.8	42.44
KF5/HT	40.23	49.32	45.45	47.09	54.32
KF10/HT	45.6	40.34	47.56	68.5	76.89
KF20/HT	60.3	64.43	65.45	82.3	80.23
KF30/HT	67.56	75.56	76.6	86.03	86.6
Catalyst (10.00 wt%)					
HT	15.79	19.76	25.39	27.89	50.23
KF5/HT	16.79	21.99	45.90	45.89	55.99
KF10/HT	26.41	34.57	69.94	69.35	73.30
KF20/HT	64.22	65.57	78.39	79.98	86.99
KF30/HT	91.86	95.86	97.00	96.57	96.70

et al., 2015; Simonetti et al., 2014). This increasing parameter is probably related to the change in the surface structure along with the formation of other phases resulting from the interaction between KF and HT. This assumption is related to the change in the pore distribution of the materials depicted in Fig. 4. Higher KF content promoted the formation of increased homogeneous pore distribution that may have contributed to the increasing adsorption capacity of the surface.

The FTIR spectra of the materials (Fig. 5) demonstrated the vibrations of the samples, which can be classified into molecular vibration groups: the hydroxyl groups, the lattice vibrations of the octahedral layers, and the vibrations of the interlayer species. All the samples show rather similar spectra but subtle differences are noted. All the spectra showed very intense bands around $3450\ cm^{-1}$, which were assigned to the stretching mode of the hydroxyl groups in the layered structures. This band is also involved in the stretching mode of the interlayer water molecules, as well as modes corresponding to a vibration around $1640\ cm^{-1}$. Octahedral layers of the materials are identified from vibrations in the range of $1111–1130\ cm^{-1}$, which refer to the stretching mode of Si-O, and the bands at $1030\ cm^{-1}$ corresponded to the stretching vibration of Si-O-Si. The band observed at $538\ cm^{-1}$ is due to the vibration of Al-O-Si. The vibration of the inner surface hydroxyl group at $912\ cm^{-1}$ and Si-O-Si at $470\ cm^{-1}$ confirmed the existence of corresponding groups (Guzmán-Vargas et al., 2015; Silva et al., 2014). There is no appreciable shift or spectra change identified as the presence of KF over the FTIR spectra.

3.2. Catalysts assay

3.2.1. Effect of KF loading and the methanol:oil molar ratio

Fig. 6 shows the influence of the different loading amounts of KF catalyst and the methanol:oil molar ratio on the biodiesel yield and the TOFs for the MW-irradiation method compared to the reflux method; biodiesel conversion occurred by refluxing a mixture of Jatropha oil with the catalyst for 3 h, while for the MW-irradiation method, the reaction was conducted for 30 min. The biodiesel yield exhibited increasing value along with increasing KF content in the catalyst. The data are in confirmation with the basicity data, in that, the basicity of the surface plays an important role in the transfer mechanism of transesterification. It is also concluded that the MW-irradiation method gave insignificant yield compared to the conventional method except for the KF30/HT catalyst. Furthermore, by comparing TOF values, it is found that, in general, the MW-irradiation method is the more effective process since the conventional method required 3 h for a similar yield, while the MW-irradiation method only needed 30 min.

From the trends, it is concluded that both KF content and the methanol:oil molar ratio are the important and significant reaction parameters. A higher ratio produced a higher yield for both the reflux and the MW-irradiation methods due to the basic condition of the transesterification reaction being an equilibrium reaction. Higher molar ratios of methanol in the reaction system force the equilibrium toward the formation of the result (Helwani et al., 2009).

The stoichiometric molar ratio of methanol to Jatropha oil for the transesterification reaction was 3:1. As the methanol:oil molar ratio increased, the equilibrium was shifted in a forward direction and made the reaction easier. The data fitted this theory and it was confirmed by the significant increase in yield obtained from a ratio higher than 7:1. A similar trend is obtained for the effect of reaction time, in that, a higher yield as produced with increasing reaction time as the result of the same chemical equilibrium concept. By comparing the reflux and the MW-irradiation methods, it is also noted that a relatively similar yield was produced using reflux (for 3 h) and MW irradiation (for 30 min) for KF30/HT, meaning that both conditions were in equilibrium and achieved in the high basic condition (Gao et al., 2010).

3.2.1.1. Comparison of the microwave-irradiation and the reflux method.
The effectivity of the MW-irradiation method compared to the reflux method was evaluated by determining the TOF values (Fig. 7).

TOFs provide a comprehensive method for making catalyst comparisons on a per-site basis. The similar yields for both of the catalyst loadings, 5 wt% and 10 wt%, demonstrated that the reflux method gave slightly higher values compared to the MW-irradiation method. However, the TOF values demonstrated that the MW method is a more
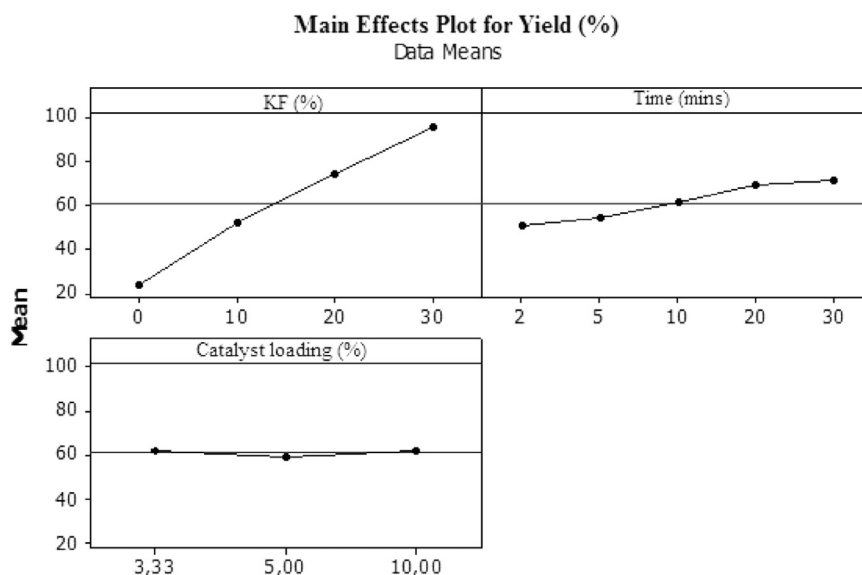
Main Effects Plot for Yield (%)
Data Means

Fig. 8. Main effect plot of parameters for yield (%).

effective procedure. The different mechanism between MW-assisted and conventional heating is on the maximum heat adsorption of MW by all material in the reaction system. MW forces dipoles to align with the oscillating electric field. MW force dipoles to align with the oscillating electric field. Meanwhile, with conventional heating, the wall of the container is heated before the material is heated through conduction or convection loss. Any material subjected to MW irradiation has a higher temperature at its center, as opposed to the outer surface in conventional heating. Consequently, MW irradiation activates all sites of a catalyst and also the reactants in a system (Coriolano et al., 2017; Nomanbhay and Ong, 2017).

3.2.2. Catalyst loading and Time Optimization

In order to optimize the conditions for MW-assisted biodiesel conversion, the effects of catalyst weight, irradiation time, and KF content of the KF/HT catalysts was studied. The effect of catalyst loading and irradiation time on the yield (%) is presented in Table 2. The important finding obtained from the data was that both catalyst loading and irradiation time played important roles in the conversion reaction. The higher KF content tended to give higher conversion rates, as well as the effect of catalyst loading. The higher the percentage of catalyst in the reaction system, the greater the surface area and basicity to accelerate the formation of methyl ester (Jia et al., 2015; Diamantopoulos, 2015).

The main effect of each parameter is presented in Fig. 8, and from this plot, it was concluded that the reaction time and KF content strongly affected the yield but the catalyst amount was not significantly affected.

Two-way analysis of variance (ANOVA) was applied to evaluate the effect of the parameters by eliminating the catalyst weight; it was determined that the KF content and the time they interacted with each other followed the linear regression equation:

$$\text{Yield}(\%) = 7.33 + 2.62 \ KF + 2.01 \ t - 0.0199 \ KF.t - 0.0299 \ t^2, \quad (3)$$

where, KF is the KF content in the catalyst and t is the reaction time. The feasibility of the linear model is presented by the following statistical parameters:

a. In the partial test, if each regression coefficient had *p*-values less than $\alpha = 0.05$, this meant that all the variables were significant variables in the model.
b. The determination value, $R^2 = 93.5\%$ meant that all the variables determined the good correlation between the observed values and the prediction.
c. The Durbin-Watson statistic was equal to 2.35205, which meant that there was no serial correlation

However, the model has a limitation in that it has neither maximum nor minimum values and the regression equation is not appropriate for all time and KF content variables. In order to overcome this, a logit transformation was applied. The equation is as follows:

$$Y' = ln\frac{Yield}{(1-Yield)} = f(x) \quad (4)$$

or, it can otherwise be represented as:

$$Yield = \frac{\exp(f(x))}{1 + \exp(f(x))} \quad (5)$$

However, the best model is:

$$Y' = -1.86 + 0.137.KF + 0.0415.t \quad (6)$$

The effect of time and KF content is graphically depicted in Fig. 9. The trends of the effect of a parameter to the probability are presented. The model suggested that the optimum yield was achieved at an irradiation time of 30 min and KF content in the catalyst of around 60%.

3.2.3. Catalyst reusability

From the green chemistry point of view, catalyst reusability was examined. The used catalyst was separated from the reaction mixture by simple centrifugation or filtration followed by washing with n-hexane and drying at 120 °C. The comparison of yield to fresh and recycled catalyst is shown in Fig. 10.

From the data, it is found that HT catalyst does not show reusability properties because no yield was obtained from recycled catalyst from
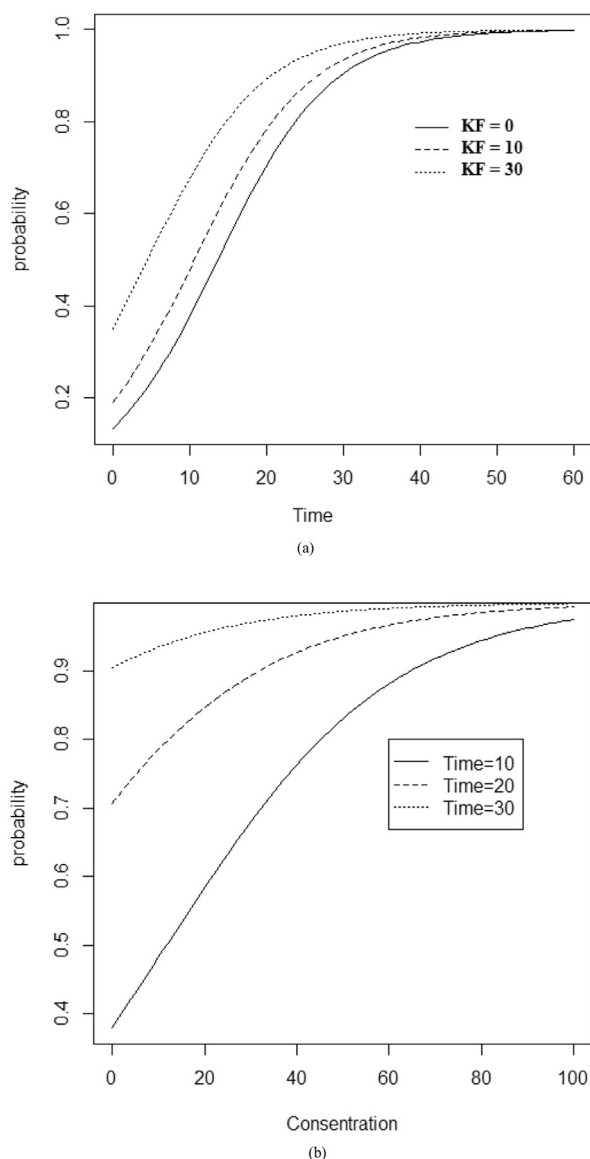
(a)

(b)

Fig. 9. (a) Effect of time in yield probability (b) Effect of KF (wt%) in yield (%) probability.
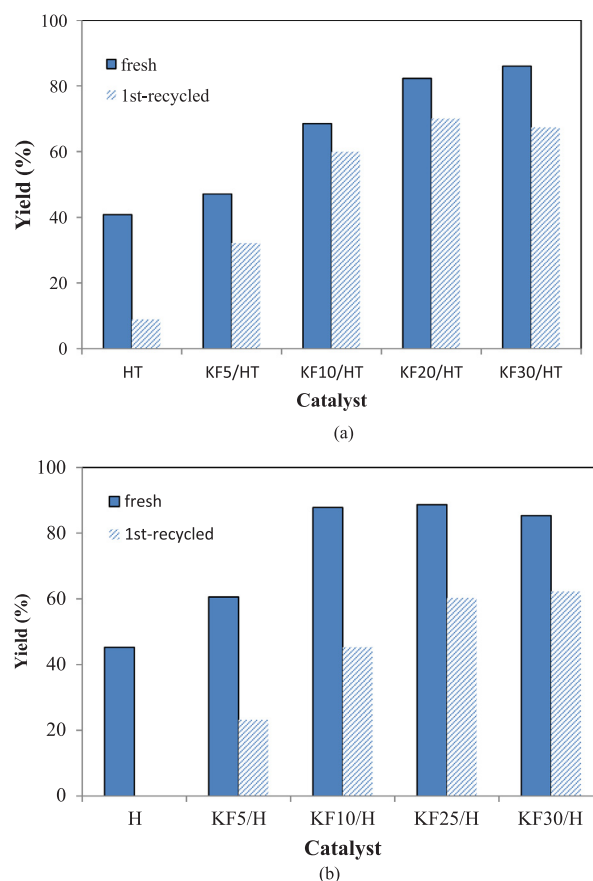

(a)

(b)

Fig. 10. Comparison of yield by fresh and recycled catalysts over (a) MW irradiation method (b) reflux method (methanol:oil = 8:1; Catalyst:Oil ratio = 1:30).

the reflux method and low yield was obtained from 1-recycled catalyst from the MW-irradiation method. The yields obtained from other 1st-recycled catalysts showed that the use of MW gave better yields for the recycled catalyst compared to that of the reflux method. The solid basicity and the specific surface area after utilization, including reaction time, are presented in Figs. 11 and 12, respectively.

The data demonstrated an insignificant evolution of values as the possible reason for the blockage of the catalyst's active sites due to previous usage.

4. Conclusions

In the current study, the modification of HT with KF demonstrated excellent catalytic activity for the catalyzation of Jatropha oil transesterification with methanol to produce biodiesel. The materials demonstrated better performance as a solid base catalyst and exhibited excellent catalytic activity in the MW assisted conversion system. The
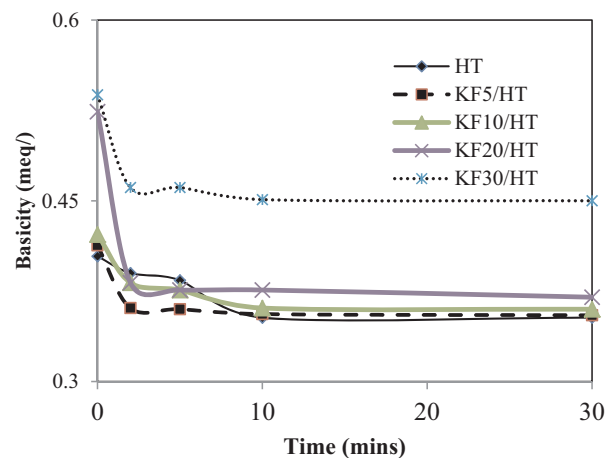

Fig. 11. Basicity of used catalyst as function of irradiation time in the reaction.

yields and TOFs of the conversions were closely related to solid basicity. It was also concluded that the catalysts are recyclable, and therefore, they have the potential to be developed for green biodiesel conversion. The yield of biodiesel obtained by MW irradiation was strongly affected by time and KF concentration in the catalyst, while the weight of catalyst was not significant.
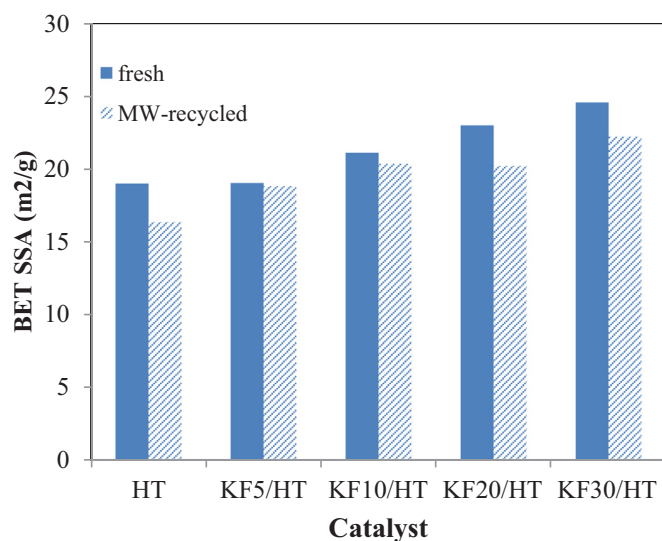
Fig. 12. The change in BET SSA of catalysts after reaction (MW irradiation: 30 min; methanol to oil ratio = 5:1, catalyst = 3.33wt%).

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