

Screening, optimization and kinetics of *Jatropha curcas* oil transesterification with heterogeneous catalysts

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ABSTRACT

This work investigates the production of fatty acid methyl esters (FAME) from *Jatropha curcas* oil using a variety of heterogeneous catalysts: resins, zeolites, clays, hydrotalcites, aluminas and niobium oxide. For this purpose, a catalyst screening was first conducted in a batch reactor at the following operating conditions: oil to methanol molar ratio of 1:9, 6 h of reaction, 5 wt% catalyst, at 333 and 393 K. From the screening step, KSF clay and Amberlyst 15 catalysts were selected to carry out a 2^3 full factorial central composite rotatable design so as to elucidate the effects of process variables on FAME yield. The optimum reaction conditions for both catalysts were found to be oil to methanol molar ratio of 1:12, 5 wt% of catalyst, 433 K and 6 h of reaction with a FAME yield of about 70 wt%. A kinetic study was then experimentally performed and a semi-empirical model was built to represent the experimental data. Finally, catalyst re-utilization in five successive batch experiments was evaluated at the optimized conditions.

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1. Introduction

Biodiesel has been produced from a variety of vegetable oils and its merits as an alternative, renewable energy source to mineral diesel is well documented in the literature [1–4]. Transesterification, either using alkaline or acid catalysts has been the most common way to produce biodiesel, but both methods are known to suffer from several drawbacks [5,6]. The use of enzyme-catalyzed transesterification methods, however, can overcome these problems, but at present, the high cost of enzyme production still remains the major obstacle to commercialization of enzyme-catalyzed processes [7,8].

In an attempt to overcome the drawbacks of chemical and enzyme-catalyzed processes, a free-catalyst technique for the transesterification of vegetable oils using an alcohol at supercritical conditions has been recently proposed, but the so-called supercritical method usually requires the use of high temperatures and pressures, which mean high operating costs associated and significant install investments [9–11].

Heterogeneous catalysts have been proposed in this context towards improving the transesterification process efficiency [12] as separation and re-utilization of catalyst may be feasible, formation

of microemulsions may be avoided with separation steps reduced, and also due to the possibility of using various types of low cost vegetable oils, even for fried and waste oils. Some works are available in the literature regarding the use of heterogeneous catalyst transesterification of vegetable oils, such as oxides applied to colza oil [13], NaX zeolites and metals [14], alkaline metals doped with zinc oxide [15] and calcium methoxide [16] employed for soybean oil, Nafion acid resins applied to olive oil [17], hydrotalcite Mg–Al impregnated with 1.5 wt% of K [18] and montmorillonite KSF [19] for FAME production from palm oil.

As mentioned by Helwani et al. [20] in a recent review paper, all questions related to planting and harvesting conditions, area of land, amount of fertilizers, may result in dramatic increase in the price of some food items due to food–biodiesel demand competition. In this context, the use of *Jatropha curcas* oil as raw material may be of great interest, as it comprises a non-edible oil, coming from a perennial plant, with high oil content in the seed, with good productivity per hectare [21,22]. Nevertheless, the use of heterogeneous catalysts for the transesterification of *J. curcas* oil has hardly been reported in the literature, except for the work of Vyas et al. [23] who utilized alumina impregnated with potassium nitrate.

The present report is part of a broader project aiming at building a platform to allow developing new processes for the production of biodiesel from vegetable oils [10,11,24–27]. Here, the main objective is to investigate the use of a variety of solid catalysts to produce

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FAME from *J. curcas* oil, performing a screening of potential catalysts, optimizing the reaction conversion for the selected one and then performing a kinetic study.

2. Materials and methods

2.1. Materials

The *J. curcas* oil used in this work was kindly donated by Biotins Energia S.A. company (Brazil) and was extracted by (cold) mechanical pressing and used as received. The commercial resins, montmorillonite KSF and K10 clays were purchased from Sigma Aldrich. The acid, basic and neutral commercial aluminas were purchased from Merck. The NaX zeolite was purchased from Baye, while zeolites NaY, Beta, Mordenite and ZSM-5 were kindly provided by the Technological Institute of Chemistry, University of Valencia (Valencia, Spain). The hydrotalcites were supplied by Sigma–Aldrich. The niobium pentoxide was provided by the Brazilian Company of Metallurgy and Mining (CBMM).

2.2. Catalyst structural characterization

Catalyst samples were analyzed with respect to structure through nitrogen adsorption at 77 K (Autosorb-1 equipment, Quatachome, 2200e series). Before analysis, samples were treated under vacuum at 373 K for complete drying and then submitted to liquid N₂. Average specific superficial area was determined by the BET method while the average porous diameter was obtained using the BJH (Barret, Joyner, Halenda) technique.

2.3. Transesterification reactions

Reaction experiments were performed in a jacketed 50 mL reactor (Parr Instrument Company, model 4843, Moline, IL, USA), equipped with mechanical agitation (kept fixed throughout this work at 300 rpm), temperature control and pressure indicator. Amounts of the substrates (oil and methanol) and catalyst were weighed on a precision scale balance (Ohaus Analytical Standard with 0.0001 g accuracy) and loaded into the reaction vessel, which was immediately closed and the temperature control (accuracy of 0.5 °C) was turned on. The amount of reactants was chosen to almost completely fill the reaction vessel so as to minimize the vapor phase space and accordingly avoid partition of the lightest component. After a pre-established reaction time, the reactor was turned off, the catalyst was removed by vacuum filtration and the remaining mixture was centrifuged (3000 rpm) for the separation of glycerol. The mixture was then submitted to a gentle nitrogen flow up to constant weight and submitted to gas chromatography (GC) analysis. It may be important to emphasize that in the case of the kinetic study performed in this work, destructive experiments, without sampling, were carried out.

2.4. Screening of catalysts

Preliminary reaction runs were performed with the following catalysts: KSF, K10 and Natural Montmorillonite clays; zeolites NaX, NaY, ZSM-5, Beta and Mordenite, in its acidic and basic forms; neutral, acid and basic aluminas; Amberlyst 15 dry resins ($\leq 1.5\%$, $< 2\%$, 5%), Amberlyst wet (48%), Amberlite XAD 16; hydrotalcite 30, 63 and 70 (Al/Mg), in commercial forms and calcined; niobium pentoxide. The operating conditions employed in the experiments were as follows: oil/methanol molar ratio 1:9, 5 wt% of catalyst, 6 h of reaction time, at temperatures of 333 and 393 K.

2.5. Experimental design

On the basis of the results from the screening step previously mentioned, the influence of process variables on FAME yield was assessed through an experimental design. A central composite rotatable design (CCRD) was carried out using KSF and Amberlyst 15 as catalysts. The variables investigated were oil to methanol molar ratio (1:4–1:14), catalyst concentration (1–20 wt%) and temperature (353–453 K). The software Statistica® 7.0 (Statsoft Inc., Tulsa, USA) was used to assist the design and statistical analysis.

2.6. Analysis of fatty acid methyl esters, mono-, di-, and triglycerides

A detailed description of the sample analyses is provided in the work of Bertoldi et al. [27]. The following major compounds were found in the *J. curcas* oil (wt%): palmitic acid (C16:0 – 13.73), stearic acid (C18:0 – 5.79), oleic acid (C18:1 – 42.37), linoleic acid (C18:2 – 37.52), linolenic acid (C18:3 – 0.59), which are in agreement with the results presented by Berchmans and Hirata [28]. Additionally, the acid value (mg KOH/g) and water content (wt%, Karl Fischer titration method, DL 50, Mettler-Toledo) were determined to be approximately 12.3 and 0.33, respectively.

2.7. Kinetic modeling

In an attempt to represent the experimental kinetic data, a semi-empirical model based on balance equations was adopted. Modeling was then carried out by the estimation of rate constants for some possible reactions, hence making use of the sequential reactions taking place. The overall transesterification reaction is given by:



The overall reaction is assumed to occur in three consecutive steps: in the first step (Eq. (2)), the transfer of a fatty acid (FA) from triglycerides (TG) to methanol (MetOH) gives diglycerides (DG) and fatty acid ethyl esters (FAME). In the second step (Eq. (3)), monoglycerides (MG) and FAME are formed by transfer of a FA from DG to methanol. Finally, in the third step (Eq. (4)), FAME and glycerol (GLY) are formed by transfer of a FA from MG to methanol.



Assuming that Eqs. (2)–(4) are reversible, parameters k_{1-6} represent the rate constants for each step. In addition, it was assumed that the available acyl groups are randomly distributed among the TG, DG and MG moieties and that water is not participating in these reactions. By considering the reaction steps described in Eqs. (2)–(4), the following set of equations can be written:

$$\frac{1}{m_{\text{CAT}}} \frac{dC_{\text{TG}}}{dt} = -r_1 \quad (5)$$

$$\frac{1}{m_{\text{CAT}}} \frac{dC_{\text{DG}}}{dt} = r_1 - r_2 \quad (6)$$

$$\frac{1}{m_{\text{CAT}}} \frac{dC_{\text{MG}}}{dt} = r_2 - r_3 \quad (7)$$

$$\frac{1}{m_{\text{CAT}}} \frac{dC_{\text{FAME}}}{dt} = r_1 + r_2 + r_3 \quad (8)$$

$$\frac{1}{m_{\text{CAT}}} \frac{dC_{\text{MetOH}}}{dt} = -r_1 - r_2 - r_3 \quad (9)$$

where

$$r_1 = k_1 C_{\text{TG}} C_{\text{MetOH}} - k_2 C_{\text{DG}} C_{\text{FAME}} \quad (10)$$

$$r_2 = k_3 C_{\text{DG}} C_{\text{MetOH}} - k_4 C_{\text{MG}} C_{\text{FAME}} \quad (11)$$

$$r_3 = k_5 C_{\text{MG}} C_{\text{MetOH}} - k_6 C_{\text{FAME}} C_{\text{GLY}} \quad (12)$$

in which m_{CAT} represents the mass of catalyst used.

The parameters of the model (Eqs. (10)–(12)), k_i , were estimated from fitting the experimental data through minimization of the following objective function (F):

$$F = \sum_{j=1}^4 w_j \sum_{i=1}^n \left(\frac{x_{i,j}^{\text{exp}} - x_{i,j}^{\text{calc}}}{x_{i,j}^{\text{exp}}} \right)^2 \quad (13)$$

where $x_{i,j}^{\text{exp}}$ and $x_{i,j}^{\text{calc}}$ represent the experimental and calculated molar fraction of species j , respectively, w_j is the mass of species j and n is the number of experimental data points.

A Fortran code was developed and implemented for the parameter estimation, with the differential equations solved using the DASSL code (differential algebraic system solver) [29] and the Downhill Simplex [30] method employed for minimizing the objective function.

2.8. Catalyst recycle

To check the catalyst re-use, repeated reaction runs were performed at the optimum conditions found. The catalyst recovered from the reaction medium by filtration was washed with *n*-hexane to remove possible substrates and products adhered to the catalyst walls. Then, it was dried at ambient temperature ($\sim 25^\circ\text{C}$) and stored under nitrogen atmosphere and protected against light prior to re-use.

3. Results and discussion

3.1. Screening of catalysts

At a first step, a screening involving 28 catalysts was performed at 333 and 393 K, with results presented in Table 1. One can observe from this table that the best yields were obtained at the highest temperature (393 K), exception for the zeolites and XAD 16 resin, which led to a yield reduction with increasing temperature. A possible explanation could be based on the essential water removal from the catalyst, thus negatively affecting the catalyst performance. As preliminary tests with some solid catalysts revealed that the temperature of 333 K afforded very low reaction yields, this variable level was not used for hydrotalcites and basic zeolites. Moreover, further experiments were not considered at this temperature.

Results of the structural characterization of the solid catalysts are presented in Table 2. According to Gregg and Sing [31], porous diameter smaller than 20 Å are considered microporous, and hence all zeolites, HDL 63 calcined and niobium fall in the category of

Table 1

FAME yield (wt%) obtained from the transesterification of *Jatropha curcas* oil using solid catalysts. Experimental conditions: oil/methanol molar ratio 1:9, 5 wt% of catalyst, 6 h of reaction time.

Catalyst class	Catalyst		FAME yield (wt%)	
			333 K	393 K
Zeolites	NaX	Acid	13.6	6.8
		Basic	—	5.6
	NaY	Acid	13.9	7.8
		Basic	—	6.7
	ZSM-5	Acid	13.3	6.0
		Basic	—	8.8
	Beta	Acid	12.4	7.3
		Basic	—	5.8
	Mordenite	Acid	13.0	8.1
		Basic	—	6.4
Resins	Amberlyst 15 dry (5%)		17.5	40.7
	Amberlyst 15 dry ($\leq 1.5\%$)		14.4	33.0
	Amberlyst 15 dry ($< 2\%$)		16.3	37.1
	Amberlyst 15 wet (48%)		14.4	14.7
	Amberlite XAD 16		11.9	5.9
Clays	KSF		2.8	35.3
	K10		1.2	8.7
	Natural montmorillonite		2.9	6.7
Aluminas	Acid		0.9	9.6
	Basic		0.9	5.9
	Neutral		1.1	6.7
Hydrotalcites	HDL 30		—	12.2
	HDL 30 calcined		—	9.8
	HDL 63		—	8.2
	HDL 63 calcined		—	9.5
	HDL 70		—	10.0
	HDL 70 calcined		—	9.7
Niobium	Niobium pentoxide		1.6	7.7

microporous catalysts, while all other catalysts are characterized as mesoporous (porous diameter in the range of 20 and 500 Å). The greatest value of specific surface area was observed for Amberlite XAD 16, followed by zeolites.

One should notice that some of the catalysts tested present small average porous diameter, which may be the reason for the poor reaction yields obtained. Of course, small porous diameters may hinder or even avoid the access of reactants to the internal structure of the catalyst, making difficult the diffusion, thus limiting

Table 2

Results of structural characterization of solid catalysts.

Catalyst class	Catalyst	Specific surface area (m^2/g)	Average diameter (Å)
Zeolites	NaX	476.9	10.9
	NaY-CBV100	717.1	10.9
	Beta CP806	568.3	17.7
	Mordenite CBV10A	351.8	12.0
	ZSM-5 CBV3020	334.3	13.5
Aluminas	Acid	152.1	30.9
	Basic	141.3	33.2
Clays	KSF	224.5	26.6
	K-10	12.4	30.9
Amberlyst resins	Natural montmorillonite	58.0	24.1
	15 (5%)	44.0	53.7
	15 ($\leq 1.5\%$)	42.3	37.9
	15 (48%)	48.9	48.9
	XAD 16	796.9	30.4
Hydrotalcite	30	186.0	32.6
	30 calcined	206.8	36.9
	63	27.9	33.3
	63 calcined	180.0	18.9
	70	19.6	53.1
Niobium	70 calcined	166.0	22.2
	Niobium pentoxide	177.7	16.7

mass transfer process and accordingly decreasing the reaction yield. In fact, it is interesting to note that though the zeolites exhibit high specific surface area, they possess, comparatively, one of the smaller porous diameter and as a consequence they afforded one of the worst results in terms of reaction yield. Thus, this structural parameter may be of relevance in the present context considering the chain length, molar mass and viscosity of the raw material in use.

Conversely, it is known that the hydrotalcites present lamellar structure then not posing accessibility restrictions of vegetable oil molecules to catalyst sites. Perhaps, the low yields obtained in this case may be attributed to the chemical composition of the catalysts active sites. Alumina samples and niobium are oxide-based solid catalyst, which exhibit significant specific surface, but are not porous materials.

In a general sense, one can notice from Table 1 that the best yields were obtained for KSF clay and for the resins Amberlyst 15 dry (5%), Amberlyst 15 dry ($\leq 1.5\%$) and Amberlyst dry ($< 2\%$); based on such results KSF clay and Amberlyst 15 (5%) were selected to proceed with the investigation.

3.2. Experimental design

Table 3 presents the matrix of the CCRD (coded and real values) and the responses in terms of ester yield using KSF and Amberlyst 15 as catalysts for 6 h of reaction. The upper and lower limit values of the variables were chosen considering the ranges commonly employed in the works of literature [19,20,32], namely, temperature in the range of 353–453 K, oil to methanol molar ratio from 1:4 to 1:14 and catalyst concentration ranging from 1 to 20 wt% (by weight of substrates, oil + methanol).

The statistical analysis of the experimental data using both catalysts permitted the validation of empirical models for esters yield as a function of temperature, methanol:oil molar ratio and catalyst concentration. Eqs. (11) and (12) present the coded optimized models that was validated by variance analysis (ANOVA) with correlation coefficient (0.95 and 0.98, respectively) and *F*-test (calculated value 2.31 and 5.94 higher than the tabled one, respectively), making the model valid at 95% of confidence.

Table 3
CCRD results of FAME yield from the transesterification of *J. curcas* oil using KSF clay and Amberlyst 15 for 6 h reaction.

Run	<i>T</i> (K)	<i>R</i> ^a	[C] (wt%) ^b	FAME yield (wt%)	
				KSF	Amberlyst 15
1	373	1:6	4.8	22.0	24.6
2	433	1:6	4.8	45.9	51.6
3	373	1:12	4.8	10.1	28.2
4	433	1:12	4.8	67.9	58.9
5	373	1:6	16.1	8.9	42.6
6	433	1:6	16.1	23.1	37.9
7	373	1:12	16.1	8.47	47.8
8	433	1:12	16.1	46.5	54.9
9	353	1:9	10.5	6.3	13.1
10	453	1:9	10.5	42.0	43.3
11	403	1:4	10.5	8.6	41.8
13	403	1:14	10.5	58.2	54.6
14	403	1:9	1.0	39.2	36.7
15	403	1:9	20.0	24.0	53.7
CP1 ^c	403	1:9	10.5	27.0	51.3
CP2	403	1:9	10.5	30.0	52.2
CP3	403	1:9	10.5	32.8	52.3
CP4	403	1:9	10.5	29.8	49.6

^a *R*, oil to methanol molar ratio.

^b [C], catalyst content (wt%).

^c CP, central point.

$$\begin{aligned} \text{FAME yield(KSF, wt\%)} = & 29.95 + 14.21 \cdot T + 8.53 \cdot R - 6.19 \cdot C \\ & + 7.24 \cdot TR \end{aligned} \quad (14)$$

$$\begin{aligned} \text{FAME yield(Amberlyst, wt\%)} = & 50.79 + 8.11 \cdot T - 7.32 \cdot T^2 \\ & + 3.98 \cdot R + 3.53 \cdot C - 6.96 \cdot TC \end{aligned} \quad (15)$$

where *T* denotes the coded reaction temperature, *R* is the coded oil to methanol molar ratio and *C* represents the coded catalyst concentration.

Analyzing the obtained model using KSF as catalyst one can see that the effects of temperature and oil to methanol molar ratio are significantly positive, showing that higher FAME yields are obtained at higher levels of these independent variables. The catalyst concentration presents a negative effect, showing that at lower concentrations, higher FAME yields are obtained, corroborating the study carried out by Kansedo et al. [19] that optimized the catalyst concentration at 3 wt%. However, Benjapornkulaphong et al. [33] evaluated the effect of concentration of some heterogeneous catalysts on FAME production and verified that higher conversions were achieved for 15 wt% of catalyst.

In terms of the validated model using the Amberlyst as catalyst, one can observe that the main effects of all studied variables (reaction temperature, oil to methanol molar ratio and catalyst concentration) are statistically significant. It is important to mention that the interaction effect between temperature and catalyst concentration was significantly negative, showing that an increase in the levels of these variables results in a lower FAME yield. Finally, one should also notice from Table 3 the good reproducibility of the experimental FAME content at the central point of the design thus assuring the reliability of the experimental reaction data.

3.3. Transesterification kinetic results

Taking into account the FAME yields obtained from the execution of the experimental design, a kinetic destructive study was then performed for the selected catalysts at 433 K, oil to methanol molar ratio of 1:12 and catalyst concentration of 5 wt%. Results of experimental and calculated FAME yield values are presented in Figs. 1 and 2, for KSF and Amberlyst 15, respectively, where one can see that the semi-empirical kinetic model satisfactorily represented the experimental findings, and more importantly, the balance equations seem to be able to capture the essential trends of the complex transesterification reaction mechanism.

Also, inspection of Figs. 1 and 2 reveals that important initial reaction rates (calculated as the slope of the linear part of the curve) are observed with considerable conversions obtained up to 30 min of reaction, reaching around 55 wt% and 40 wt% of FAME yields, followed by a nearly asymptotic behavior at larger times, especially after 6 h, achieving about 70 wt% and 60 wt% of FAME yields, for KSF and Amberlyst 15, respectively. From a practical standpoint, therefore, the reaction might be interrupted to meet economic aspects – small gains after a certain time. Data scattering observed in this figure may be explained in terms of experimental errors associated, and the fact that destructive experiments were carried out without sampling, which may be viewed as an important internal consistence test of the results.

Though just few reports can be found in the literature regarding transesterification of *J. curcas* oil using heterogeneous catalysts, one may cite the work of Vyas et al. [23], who obtained 84 wt% FAME yield using alumina impregnated with potassium nitrate as

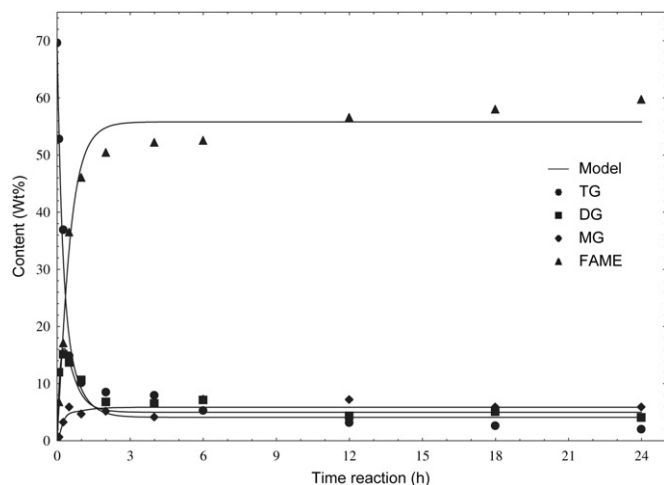


Fig. 1. Experimental kinetic data and modeling results of *Jatropha curcas* oil transesterification with KSF clay at 433 K oil to methanol molar of 1:12 and 5 wt% catalyst concentration.

catalyst, at 343 K, oil to alcohol molar ratio of 1:12, 6 wt% of catalyst concentration and 6 h of reaction. Xie and Li [32] reported a conversion to FAME as high as 96% using soybean oil and alumina-supported potassium iodide as catalyst at methanol reflux temperature, oil to methanol molar ratio of 1:15, 2.5 wt% of catalyst concentration and 8 h reaction.

3.4. Catalyst re-use

Catalyst re-use was investigated adopting the optimized reaction conditions for the catalyst at 18 h for KSF clay and 6 h for Amberlyst 15. Results related to this study are presented in Fig. 3, where one can see a decrease in FAME yield as the number of re-use increases. According to many works in the current literature, an important factor to be considered when dealing with heterogeneous-catalyzed biodiesel process is the gradual decline in catalyst activity as the number of re-uses increases. Then, from a practical point of view, operation in continuous mode with a set of packed-bed (columns) reactors (PBRs) may be employed, with stepwise addition of methanol before each column together with glycerol

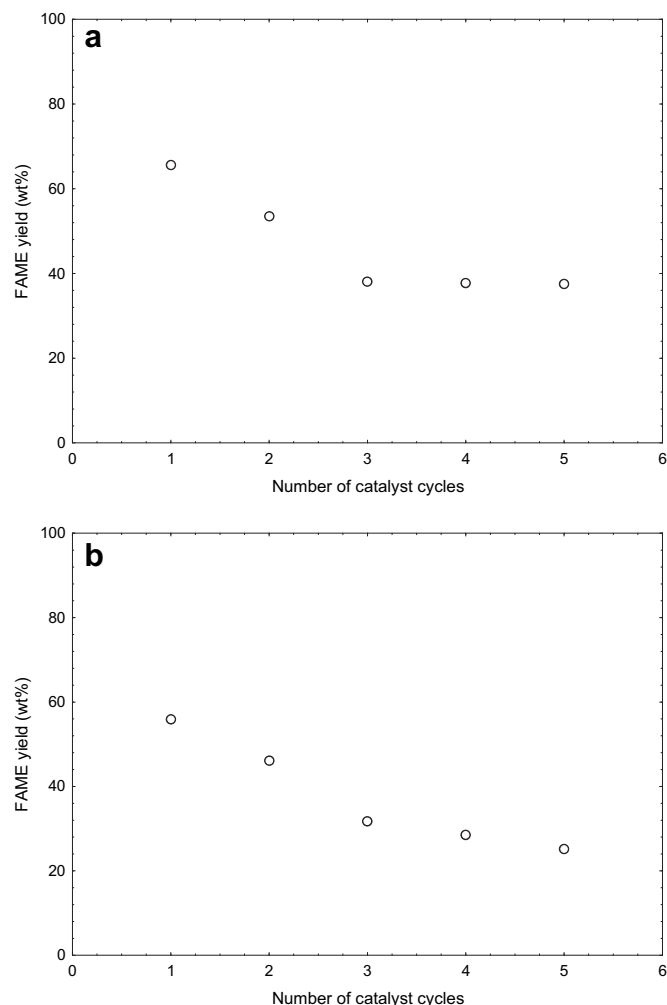


Fig. 3. Results of catalyst re-use for the transesterification of *J. curcas* oil: (a) KSF clay – 18 h of reaction, and (b) Amberlyst 15 – 6 h of reaction. Experimental conditions: 433 K, oil to methanol molar of 1:12 and 5 wt% catalyst concentration.

removal between the columns. Also, it is possible that higher ratio of alcohol to oil can help removing glycerol (a by-product, inhibitory substance) from the PBR, due to a higher superficial velocity of the substrates inside the reactor, promoting the dragging of glycerol from the catalyst bed and hence avoiding catalyst to be entrapped by glycerol [34,35]. Of course in a recent review paper, for the purpose of large-scale industrial processing, a full economic analysis should be performed taking into account several factors such as costs of oil and alcohol, cost of pre-processing steps, process yield, cost of water product handling, value of glycerol stream and cost of post-treatment stages [36].

4. Conclusions

This work reported new experimental data and kinetic modeling of transesterification of *J. curcas* oil using heterogeneous catalysts. Results show that the use of KSF clay and Amberlyst 15 as catalysts may be promising as around 70 wt% of FAME yield was obtained at relatively mild conditions and short reaction times. The re-use of catalysts demonstrated the occurrence of catalyst inactivation and hence large-scale production would require the establishment of an adequate strategy to conduct such transesterification reactions. Of course, feasibility of a continuous heterogeneous-catalyzed

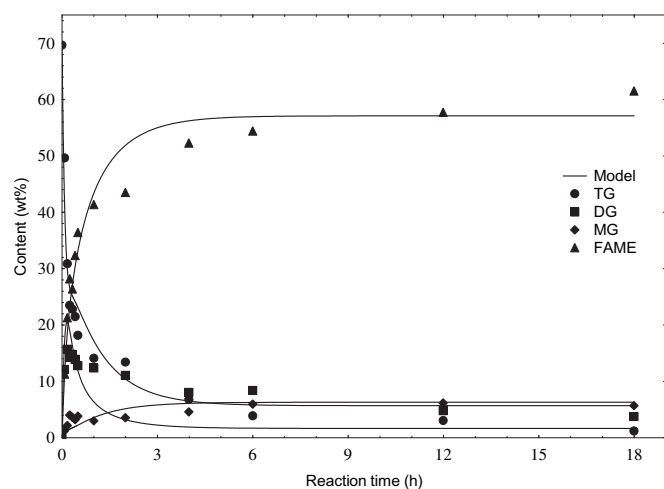


Fig. 2. Experimental kinetic data and modeling results of *J. curcas* oil transesterification with Amberlyst 15 at 433 K, oil to methanol molar of 1:12 and 5 wt% catalyst concentration.

transesterification process is of primary importance to assure a competitive cost to biodiesel fuel, since continuous method could be operated with higher reaction performance than batch reactors, in principle, with more consistent and reproducible product quality.

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