

RESEARCH ARTICLE

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Production of biodiesel from soybean and *Jatropha Curcas* oils with KSF and amberlyst 15 catalysts in the presence of co-solvents

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Abstract

Experimental conditions for the production of fatty acid methyl esters (FAME) from *Jatropha curcas* and soybean oils using two acid heterogeneous catalysts (Amberlyst15 and KSF) was optimized, in the presence of different co-solvents (THF, acetone, petroleum ether and n-hexane) in a batch reactor at fixed conditions: oil to methanol molar ratio (1:9), catalyst concentration (4.8 wt%), co-solvent mass ratio (1:1), 160°C and 6 hours. Results showed that the use of co-solvents led to a reduction in the FAME conversion. Higher conversions were obtained for *Jatropha curcas* compared to soybean oil. The Amberlyst15 presented an enhancement in the catalytic activity after regeneration, providing high biodiesel conversions compared to the fresh resin. The catalyst also presented stability after 5 cycles of reuse. Activity lost was observed for KSF after 2 successive batch experiments, probably due to a deactivation of acid sites.

Keywords: Biodiesel, *Jatropha curcas* oil, Soybean oil, Reuse, Heterogeneous catalysis

Background

The global interest in renewable combustibles has been intensified nowadays, mainly due to the environmental concerns related to the use of fossil fuels, reduction on petroleum reserves and adaptation to recent legislation that poses the need of reduction in vehicles emissions [1-4]. 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 [5-7].

Biodiesel is mainly produced by transesterification of oils and fats with a monohydric alcohol in the presence of homogeneous basic catalysts, like sodium and potassium hydroxide, carbonates and alcoxides [8]. However, the use of acid catalysts requires the neutralization and separation of the final reaction mixture, leading to environmental problems related to the use of high amounts of solvent and energy [9]. Therefore, this reaction system can result in soap production, especially when oils and fats with free fatty acids and moisture contents higher

than 0.5 wt% and 2% (v/v), respectively, are used as reactants [10].

To overcome these problems, several studies involving the use of heterogeneous catalysts have been presented in the literature, including zeolites [11,12], clays [13], mesoporous silica [14], heteropolyacids [15], resins [16] and inorganic oxides [17,18]. The advantages presented by these catalysts [19,20], in general, do not permit the industrial production of biodiesel, mainly due to the high temperatures (120-200°C), alcohol to oil molar ratio (12-30) and reaction time (3-8 hours) [21]). To accelerate the reaction rates, some works presented the possibility of including co-solvents in the reaction medium, towards enhancing the solubility and mass transfer between oil and methanol [22-25]. The use of co-solvent in a liquid phase can affect the activity of the catalyst by the modification of its surface characteristics [26], react with the reactants/products and also to promote an enhancement in the viscosity of the reaction medium [27], especially when high temperatures are used [28-30].

A previous study by our research group evaluated five different groups of heterogeneous catalysts for transesterification of *Jatropha curcas* oil [31]. A total of twenty-eight materials belonging to the class of resins, clays,

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alumina, zeolites and niobium pentoxide were screened for biodiesel production. The most promising catalysts were observed to be Amberlyst 15 and KSF, both solid heterogeneous acid catalysts. In that study, the experimental design technique was employed to establish the reaction parameters for high biodiesel conversion.

Based on the results obtained by Zanette et al. [31], the main objective of the present study was to investigate the behavior of the heterogeneous catalysts Amberlyst 15 and KSF in transesterification reactions of soybean and *Jatropha curcas* oils in the presence of different co-solvents and also to verify the possibility of reuse of these catalysts. Here it is opportune to mention that 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, as emphasized by Zanette et al. [31].

Results and discussion

Screening of co-solvents

Figure 1 presents the FAME yield obtained from the transesterification of soybean oil using KSF montmorillonite and Amberlyst 15 with and without co-solvents. From this figure it can be observed that better yields were obtained, for both catalysts, in reaction medium without the addition of co-solvents. A reduction in the yield of biodiesel was verified for all tested co-solvents, from 4.4 to 69.5% for petroleum ether using Amberlyst 15 and KSF as catalysts, respectively. The KSF clay presented high sensibility to the presence of co-solvents, leading to low conversions compared to the co-solvent-free system. The solvents acetone and THF presented the worst results for Amberlyst 15 resin. This fact can be attributed to the similar solubility parameter of these solvents and of the monomer constituent of the resin. As low the difference between the solubility parameter of the solvent and the resin, high is the adsorption of the solvent, leading to a polymer swelling. The

internal surface of the material, where most part of the acid sites are located, becomes unavailable to the reactant alcohol, here methanol. As can also be seen in Figure 1, for KSF clay, polar co-solvents showed lower interference on the reaction yield, however it was not evidenced any synergy in binary phase formed with methanol.

Ngaosuwana et al. [25] presented similar results using THF as co-solvent for the heterogeneous transesterification of triglycerides, showing a reduction of 36% in the reaction yield compared to the system without co-solvent. When ethanol was used as co-solvent, the authors observed an enhancement of about 15% on the yield of the reaction. These differences might be associated to the interactions between the catalyst and the solvent. In our case, as THF and acetone (polar aprotic solvents) are more adsorbed on the polar surface of the heterogeneous catalyst, a competition by the acid sites can occur.

Results obtained here are also in accordance with works related to the supercritical production of biodiesel [32-35]. In these works, also the use of co-solvents (propane, n-hexane, CO₂ and n-heptane) led to reduction in biodiesel yield. Studies using lower amount of co-solvents than those used in the present work [23,36] also showed the same tendency on process conversion.

The experimental conditions (with and without acetone and KSF and with and without petroleum ether and Amberlyst 15) that led to the highest yields for soybean oil were also performed using *Jatropha curcas* oil as reactant. Figure 2 presents the results obtained in this step, where it can be concluded that high yields on biodiesel were achieved when this oil was used. This fact is relevant since the high content of free fatty acids and the presence of other lipid materials (phospholipids and gums) did not affect the reaction using the two catalysts tested here. Results obtained here corroborate those reported by Jacobson et al. [37], where solid acid catalysts did not lose activity in the presence of high

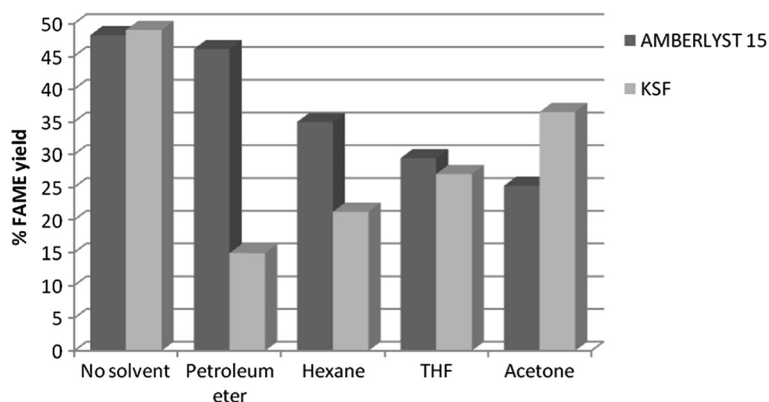


Figure 1 FAME yield from the transesterification of soybean oil using KSF montmorillonite and Amberlyst 15 with and without co-solvents.

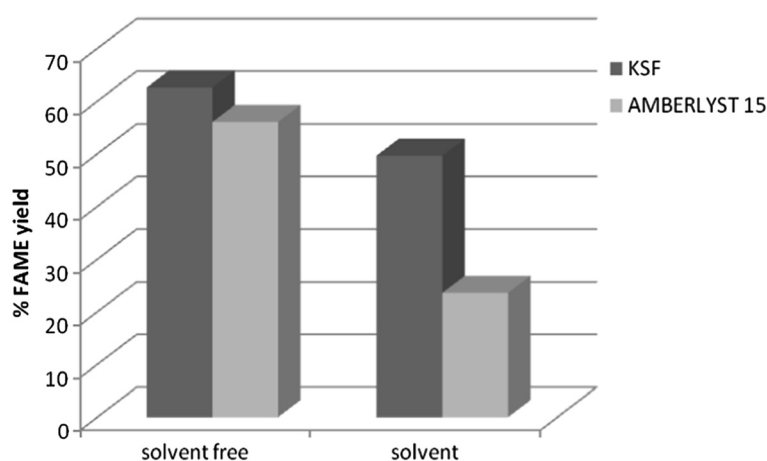


Figure 2 FAME yield from the transesterification of *Jatropha curcas* oil using KSF montmorillonite and Amberlyst 15 with and without co-solvent.

free fatty acids content. This conclusion shows the high potential of using these catalysts for transesterification of oils of low quality for biodiesel production.

In the presence of co-solvents, a significant difference occurred only for the resin Amberlyst 15 using petroleum ether, showing a reduction of 48 to 23% for soybean and *Jatropha curcas* oils, respectively. Probably, the free fatty acids were responsible for this reduction, since these polar compounds presents low miscibility in petroleum ether (apolar). The mixture petroleum ether and methanol produces a binary compound of apolar characteristics, due to the low proportion of methanol, not favoring the esterification of free fatty acids.

Reuse of catalysts

Catalyst reuse was investigated adopting the optimized reaction conditions for each catalyst tested in this work. Results related to this study are presented in Figure 3 (a and b) for Amberlyst 15 and KSF, respectively. The KSF clay presented higher activity lost after one cycle of use. The washing by ethylmethylketone followed by calcination at 400°C was not efficient for the regeneration of the catalyst. Most of acid sites of the clay seem to be deactivated in the first batch, leading to the activity lost. Similar results were obtained by Yang and Xie [23], which supposed deposition of reactants and products on the active sites of the catalyst and/or transformation of acid sites and their interactions during the reaction. In our particular case, due to the washing of catalyst by ethylmethylketone and posterior calcination, probably the second hypothesis could be occurred.

From Figure 3a, using Amberlyst 15 resin as catalyst, it can be see that the regenerative treatment proposed promoted an appropriate removal of impurities, leading

to an increase in the catalytic activity compared to the non-used resin. The material did not suffer color or morphological alterations after treatment. The literature [24,38] points out that most exchange ion resins, like Amberlyst 15, have low thermal stability, becoming unstable at temperatures high than 140°C, limiting its application in reactions that require high temperatures. However, in the present study, one could verify that the resin was stable to high temperatures, making possible its acid reactivation and posterior reuse for five successive cycles.

Conclusions

This work reported new experimental data on the transesterification of soybean and *Jatropha curcas* oils 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 use of several co-solvents at the molar ratio co-solvent/reactants of 1:1 led to a reduction in biodiesel yield for both tested catalysts. A slight increment in biodiesel production was observed for *Jatropha curcas* oil, making possible the use of Amberlyst 15 and KSF as catalysts for oils of low quality and/or cost. The reuse of catalysts demonstrated the possibility of using Amberlyst 15 as catalyst for several batches after acid activation, leading to an enhancement in biodiesel yield by an increase of catalytic activity. These results can be considered relevant since the feasibility of a continuous heterogeneous-catalyzed 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.

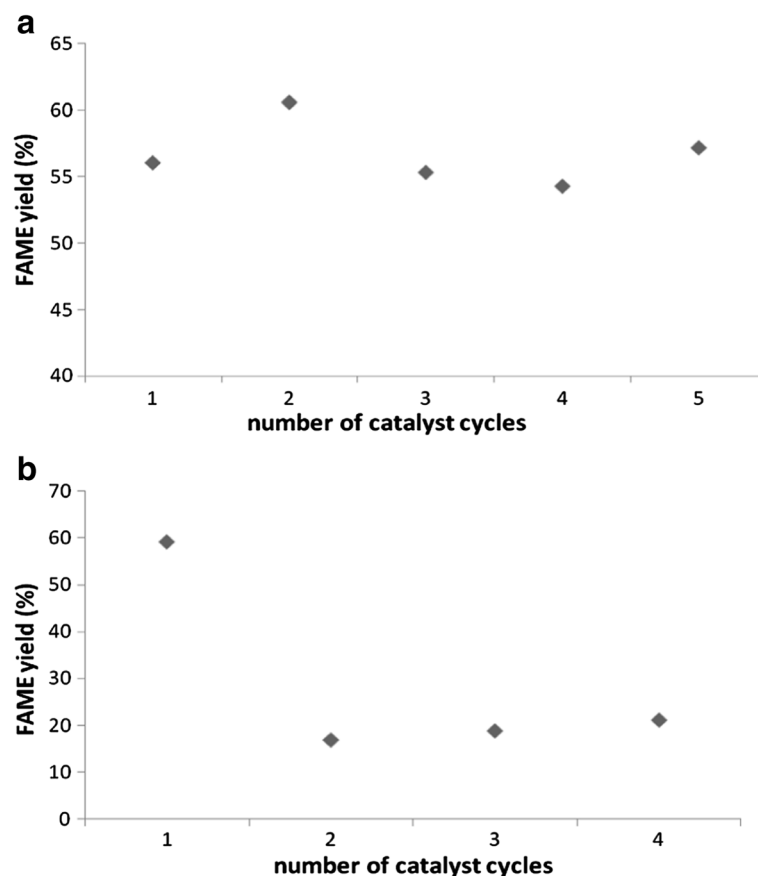


Figure 3 Influence of catalyst reuse in FAME yield after the transesterification of *Jatropha curcas* oil using Amberlyst 15 (a) and KSF (b).

Material and methods

Materials

The *Jatropha 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 soybean oil (Soya) was purchased from a local market. Both oils were used as received, without previous treatment. Methanol (Merck, 99.9% purity) was also used as reactant for biodiesel production. The catalysts Amberlyst 15 and KSF were purchased

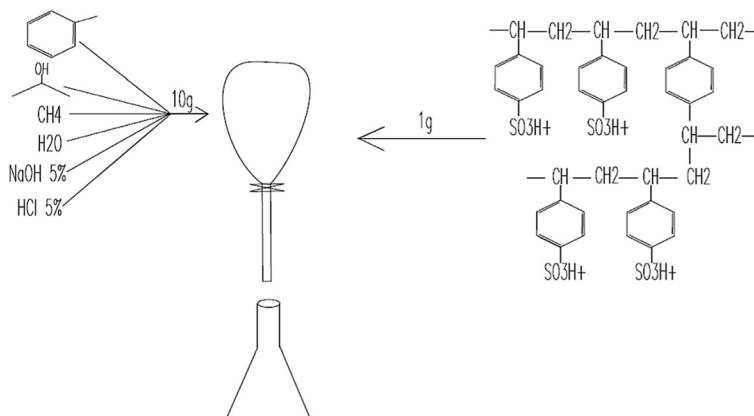


Figure 4 Schematic diagram used for the reactivation of Amberlyst 15 resin.

from Sigma-Aldrich. Tetrahydrofuran (THF), petroleum ether, n-hexane and acetone, all of analytical grade, were from Merck.

In the recuperation of the catalysts it was used toluene, iso-propanol and methyl-cetone, all of analytical grade and purchased from Sigma. Aqueous solutions of NaOH 5% and HCl 5% were also used in this step.

Apparatus and experimental procedure

Reaction experiments were performed in a jacketed 100 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.

Screening of co-solvents

All experiments using soybean oil as reactant were carried out in the presence at fixed mass ratio of co-solvent to reactants of 1:1, using acetone, petroleum ether, n-hexane and THF, and also in the absence of co-solvent for both catalysts, KSF and Amberlyst 15. The experimental conditions used were temperature of 160°C, oil to methanol molar ratio of 1:12, 4.8 wt% of catalyst and 6 hours of reaction, as defined previously by Zanette et al. [31]. The experimental condition that led to the highest FAME yield was then applied to *Jatropha curcas* oil as reactant.

Products quantification

A detailed description of the samples analyses is provided in the work of Bertoldi et al. [39]. The following major compounds were found in the *Jatropha 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 [40]. 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.

Reuse of catalysts

To check the possibility of catalyst reuse, repeated reaction runs were performed at the optimal conditions found. For Amberlyst 15, the stored material (8°C) was submitted to room temperature (25°C) to remove volatile compounds, up to constant weight. The procedure described by Malshe and Sujatha [41] was used with some modifications in terms of contact system between the catalyst and the solvent, as demonstrated in Figure 4. The total residence time of the resin in the system was 8100 s, 900 s in each experiment. In the acid activation, the catalyst was kept in dispersion for 3600 s. The resin was withdrawn by filtration and submitted to oven at 105°C overnight. Then, the catalyst was kept in desiccator until stabilization of temperature and then weighed.

The procedure described by Al-Zahrani and Daous [42] with some modifications (ratio of solvent to catalyst of 8) was used for the reactivation of KSF. The catalyst was weighted before and after the regenerative treatment to evaluate losses in the process.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

CC, SC carried out the FAME synthesis and chemical characterization, MAM assembled the experimental apparatus, DO, SP and JVO conceived the study, and participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

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