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Biodiesel Production from Jatropha Curcas Oil Using Li/Pumice as Catalyst in a Fixed-Bed Reactor

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Abstract. A packed-bed catalytic configuration reactor using pumice granules loaded with lithium (Li/Pumice) as a heterogeneous catalyst was developed for the continuous biodiesel production. For this purpose, *Jatropha curcas* oil was used as an alternative feedstock to edible oils and diethyl ether was used as a cosolvent to improve the mass transfer between the phases present in the transesterification reaction. The solid catalyst was characterized, and its catalytic activity was evaluated for the biodiesel production. Fatty acid methyl esters (FAME) yield of 100% was achieved under the conditions of 1.4 mL min^{-1}, 20.0 methanol/oil molar ratio, 0.57:1 cosolvent/methanol molar ratio and 40ºC. Moreover, Li/Pumice catalyst shows high stability for the continuous biodiesel production.

Key words. Biodiesel, heterogeneous catalyst, packed bed, pumice, cosolvent.

1. Introduction

Biodiesel is a processed fuel derived from the esterification and transesterification of free fatty acids (FFA) and triglycerides respectively that are naturally produced from renewable biological sources such as vegetable oils and animal fats. The production of biodiesel involves a chemical reaction between the vegetable oil or animal fat and methanol to create a fatty acid methyl ester (FAME) and glycerol mixture product [1]-[4].

Biodiesel synthesis occurs by either batch or continuous processing. In the batch method, the main purpose of investigating the parameters' influences on the FAME yield is to optimize the reactions conditions. However, for continuous biodiesel production, parameters effects on the FAME yield are investigated with the aim of scaling up the process [5]. Different continuous reactors are used to produce biodiesel, such as fixed beds, packed beds and rotary fixed bed type reactors.

Currently, on the industrial scale biodiesel production, slurry batch reactors are generally employed to carry out the transesterification reaction because homogeneous catalysts are used. Batch processes are characterized by low productiveness and high operating costs.

The productivity of a process can be greatly increased with the implementation of continuous operations; in this case, the use of heterogeneous catalysts for transesterification reaction may allow the design of a continuous and efficient biodiesel production process that will improve its economy [6]. The use of a packed-bed catalytic reactor system shows clearly advantages compared with a slurry batch reactor system from a products separation and simple operation point of view; specifically, because the catalyst stays confined in the reactor bed, reaction products can be easily separated and the mechanical stability of the catalyst particles can be achieved [7]. However, methanol and vegetable oil are immiscible, this causes less mass transfer since mass transition just happens in the interface of the two phases. A solution to improve the mutual solubility of methanol and oil is using a cosolvent [8]-[11].

Cosolvents have polar and nonpolar sites, causing a decrease in the surface tension between the methanol and triglyceride phases; then, a single phase is created during transesterification and the reaction can occur in a mild condition with less reaction temperature and less reaction time [12],[13]. It has been suggested that the addition of cosolvents such as tetrahydrofuran (THF), diethyl ether (DEE), or 1,4-dioxane into the reaction mixture can increase the dissolution of methanol into the oil, creating a homogeneous reaction system. The reaction can thus be accelerated through molecule–molecule reaction and can be completed in a shorter reaction time, with an increased FAME yield [14],[15].

In this work, a study on continuous biodiesel production using a heterogeneous catalyst in a packed-bed reactor assisted with diethyl ether as cosolvent was carried out. For this purpose, a catalytic packed-bed reactor with inner diameter of 1 cm and height of 20 cm and pumice granules loaded with lithium (Li/Pumice) as catalyst was employed.

2. Experimental

A. Materials

Jatropha curcas oil was extracted from its seeds by soxhlet-extraction with n-hexane as solvent and the obtained oil was subjected to the esterification reaction to reduce the free fatty acids content. Both processes are described in a previous work [16]. The physical properties of Jatropha curcas oil are: $\mu_{40^{\circ}C}=17.5$ cSt, $\rho_{15^{\circ}C}=931.4$ kg m^{-3} and acid value=0.1 mg KOH g^{-1}. Methanol (99.8% purity) and diethyl ether (DEE) (99.7% purity) were supplied by Sigma-Aldrich (Germany). Lithium nitrate anhydrous (≥ 98%) was acquired from Fisher Scientific (Belgium) and pumice particles were purchased from Panreac (Spain). Methyl heptadecanoate (99.9% purity), used as internal standard for gas chromatography, was purchased from Fluka Analytical (Germany).

B. Catalyst preparation and characterization

Li/Pumice (5 wt% of Li) was employed as heterogeneous catalyst for the transesterification reaction. Pumice catalyst particles (1.4–3.0 mm) were subjected to impregnation with lithium nitrate anhydrous ($LiNO_3$). Lithium impregnated pumice catalyst was prepared by a wet impregnation method. In a typical catalyst preparation procedure, Li precursor was fully dissolved in deionized water, and the precursor solution was added to 10 g of pumice support previously weighed. Then, the impregnated pumice particles were dried overnight at 100 ºC and finally calcined at 650ºC for 5 h under air flow in a muffle furnace.

The surface morphology of pumice and lithium supported pumice (Li/Pumice) was monitored using a scanning electron microscope (SEM) (Jeol LTD, mod. JSM-6300, Tokio, Japan). Due to the non-conductive nature of the pumitic materials, all samples were coated with a thin layer of sputtered silver.

BET surface area and physical properties of samples were evaluated by nitrogen adsorption–desorption isotherms recorded on a surface pore size analyzer (Gemini V, Micromeritics) and a mercury porosimetry (Autopore IV mercury porosimeter, Micromeritics). From these results, the pore size distributions of the materials were obtained.

PANalytical X'Pert diffractometer, equipped with a primary monochromator and X'Celerator detector, was used for recording the X-ray diffraction patterns (XRD) of the pumitic materials. The patterns were recorded in 4-80º 2θ range using Cu $K_{\alpha1,2}$ radiation (45 kV and 40 mA) as the X-ray source.

Pumice and Li/Pumice materials were examined by Fourier transform infrared spectrometry (FTIR) using an Agilent Cary 630 spectrometer with the attenuated total reflectance (ATR) accessory (ZnSe). FTIR spectra were recorded in the wavenumber range of 4000-400 cm^{-1}, with a resolution of 2 cm^{-1}. ATR unit was controlled by the Cary 630 MicroLab software and Resolutions Pro program was used for data processing.

C. Continuous transesterification in packed-bed reactor

The continuous biodiesel production was carried out in a packed-bed catalytic reactor configuration with Li/Pumice as heterogeneous catalyst. The schematic diagram of the packed-bed catalytic reactor is illustrated in Fig. 1.

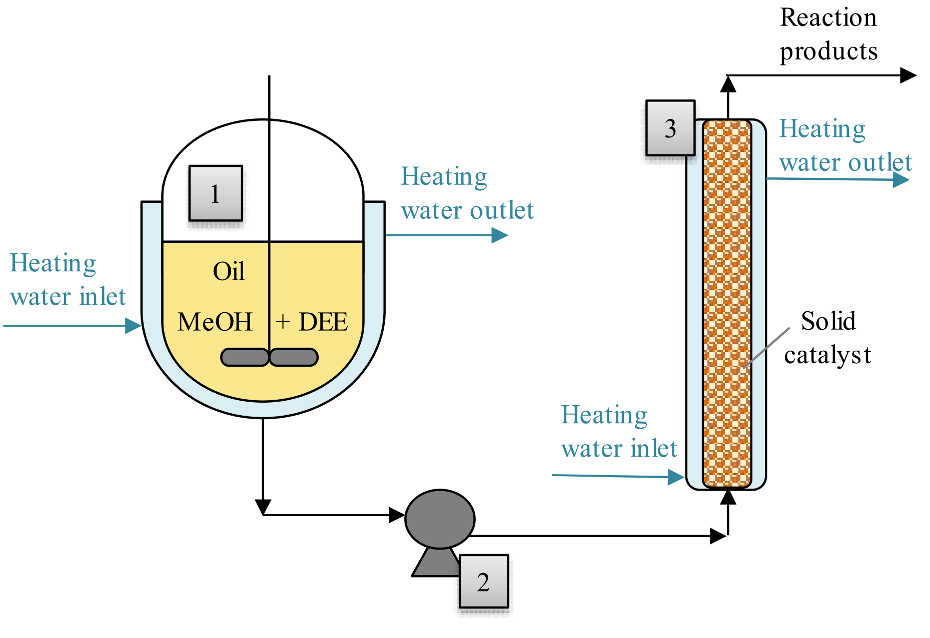

Fig. 1. Schematic diagram of the reaction system for continuous biodiesel production: 1) mixing tank, 2) peristaltic pump, 3) packed-bed reactor.

First, the catalytic reactor (jacketed glass reactor) was loaded and packed with 10 g of Li/Pumice. Secondly, esterified *Jatropha curcas* oil was placed in a 1000 mL heated tank, equipped with a reflux condenser and a mechanical stirrer. When the selected reaction temperature (40ºC) was reached, methanol (MeOH) and DEE (pre-mixed in desired amounts) was added to the tank with continuous stirring (400 rpm). 20:1 MeOH/oil molar ratio and 0.57:1 DEE/MeOH molar ratio was used. The mixture was heated up to the reaction temperature and then fed into the packed-bed catalytic reactor using a peristaltic pump at a constant flow rate (1.4 ml/min). The feed solution was supplied to the bottom of the cylindrical reactor (20 cm length and 1 cm inner diameter) packed with Li/Pumice catalyst particles. The reaction products were collected at the outlet of the reactor and evaporated for removing excess methanol and DEE. Then, the liquid product was settled in a funnel by separating the biodiesel from glycerol. The biodiesel product obtained (upper phase) was analyzed by gas chromatography (GC) to estimate the FAME content in biodiesel product obtained in each run.

D. Analytical methods

FAME content analyzes were performed in accordance with UNE-EN 14103 [17], using a 3900 Varian gas chromatograph (GC-FID), equipped with an autosampler and the data acquisition software Star Workstation 6.0. Separations were accomplished using a 50 m long CP-SIL 88 capillary column (0.25 mm I.D. and 0.25 µm film thicknesses) at a constant hydrogen flow rate of 30 mL min^{-1}. The injector and FID detector temperatures were set a 250ºC. The oven was initiated at 160ºC for 5 min, then, it was elevated to 180ºC at 4ºC min^{-1} and held for 2 min, elevated to 225ºC at 15ºC min^{-1} and maintained for 5 min, finally elevated to 240 ºC at 15ºC min-1 and held for 1 min. Helium was applied as a carrier gas (1.0 mL min^{-1}) and nitrogen as make-up gas (30 mL min^{-1}). Samples (0.5 µL) were injected with a split ratio of 20:1.

3. Results and discussion

The surface topography of pumice (Fig. 2 a, b, and c) and pumice impregnated with lithium (Fig. 2 d, e, and f) was analyzed using scanning electron microscopy (SEM). SEM images show the high porosity of both pumitic materials. The porous structure of support material varied after the impregnation process; when pumice was impregnated with the lithium precursor, the porosity of the raw material seems to decrease. The decrease in porosity is confirmed by the results obtained by mercury porosimetry shown in Table I. Porosity decreased from 44.43% (pumice) to 37.10% (Li/pumice) after the impregnation process.

The main characteristics of the pumice and Li/Pumice are presented in Table I.

Table I. - Textural properties of catalytic solid.

Material	N_2 adsorption		Mercury porosimetry			
	S_{BET} ($m^2\ g^{-1}$)	D (nm)	A ($m^2\ g^{-1}$)	ε (%)	D (V) (nm)	D (4V/A) (nm)
Pumice	0.71	4.19	16.30	44.43	1534.1	91.9
Li/Pumice	0.39	3.71	6.90	37.10	1782.4	118.3

BET specific surface area (S_{BET}) and average micropore width (D) are shown for both materials. As can be seen there is a decrease of the S_{BET} and the average micropore width, when support material (pumice) is impregnated with lithium precursor due to pores blocking. The average pore diameter of the materials is between 2-50 nm, so it can be considered that none of the materials are microporous. The physical properties of the pumitic materials obtained by mercury porosimetry are also shown in Table I. The values of specific surface (A), porosity (ε) and average pore diameter (D) are shown. The specific area also decreased after the impregnation process and the average pore diameter, in the range of meso-macropores, increased.

In Figure 3 pore size distributions from N_2 adsorption isotherms and mercury porosimetry are compared for the studied materials, showing an irregular pore structure of both materials, in the micro-mesopore range (Fig. 3 a) and in the meso-macropore range (Fig. 3 b). The greater intrusion volume of mercury versus nitrogen, indicates that the materials are mainly meso-macroporous; which is an advantage because the average pore diameter is greater than the diameter of the triglyceride molecule (5 nm), therefore, it is expected that the triglyceride molecules will diffuse easily through the pores of the catalyst and, consequently, there will be an efficient contact between the reactants and the active sites present on the surface of the catalyst, which are necessary for the reaction transesterification occurs[18].

Diffraction patterns of pumitic materials are shown in Fig. 4. Crystalline phases do not appear in the XRD pattern of pumice, a broad and diffuse peak is observed in the range of 2θ = 20-30º, typical of amorphous aluminosilicates; specifically, it reflects the amorphous structure of silica (SiO_2), since it is the majority oxide present in pumitic materials [19]-[20].

However, after the impregnation process, XRD pattern of Li/Pumice presents crystalline phases, which can be attributed to the formation of the phases $LiAl(Si_2O_6)$, $Li(AlSi_4O_{10})$ and $LiAl(SiO_3)_2$ obtained through the QualX software, using the POW_COD_2007 database (Fig. 4).

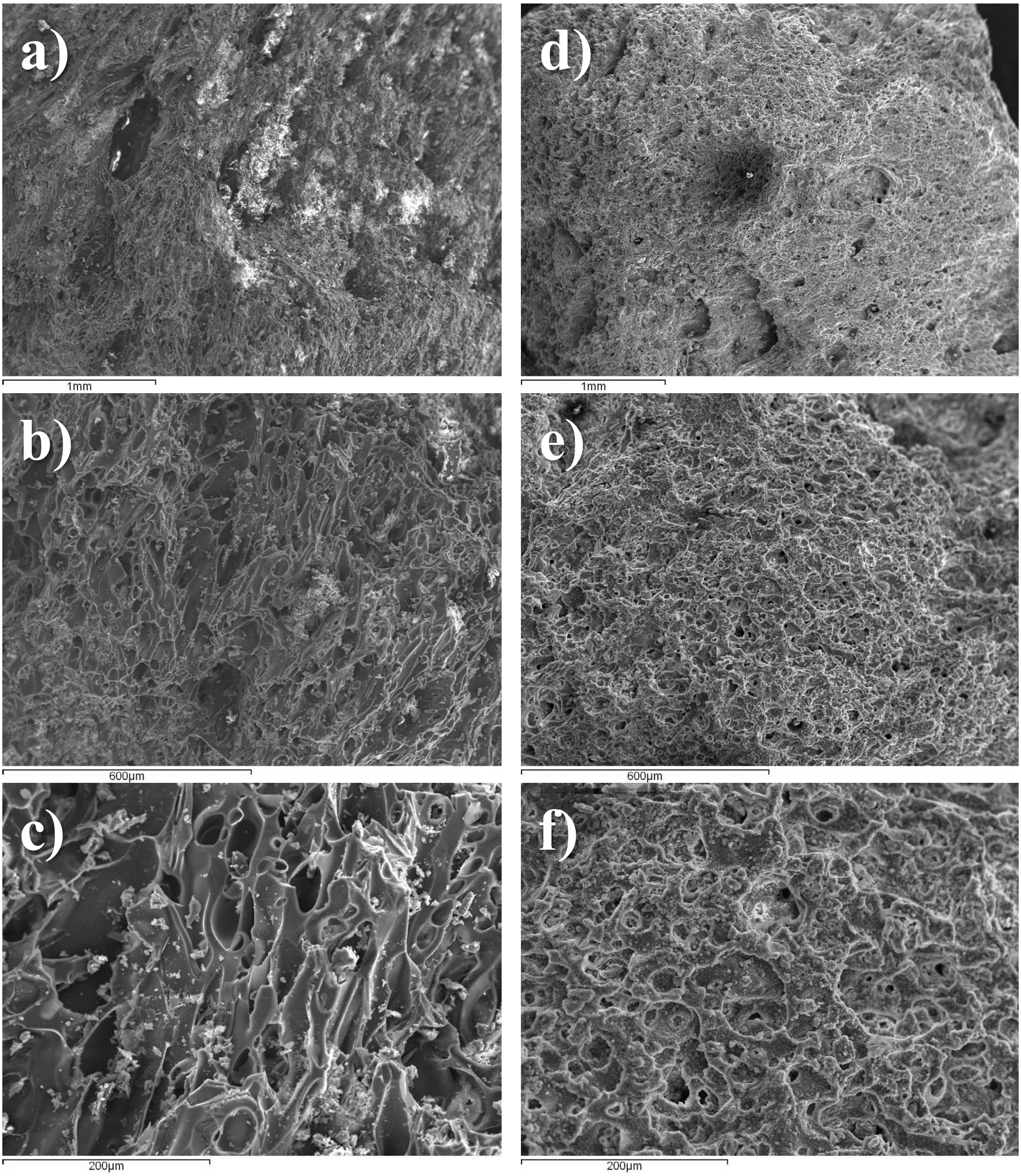

Fig. 2. SEM images for Pumice (a, b and c) and Li/Pumice (d, e and f).

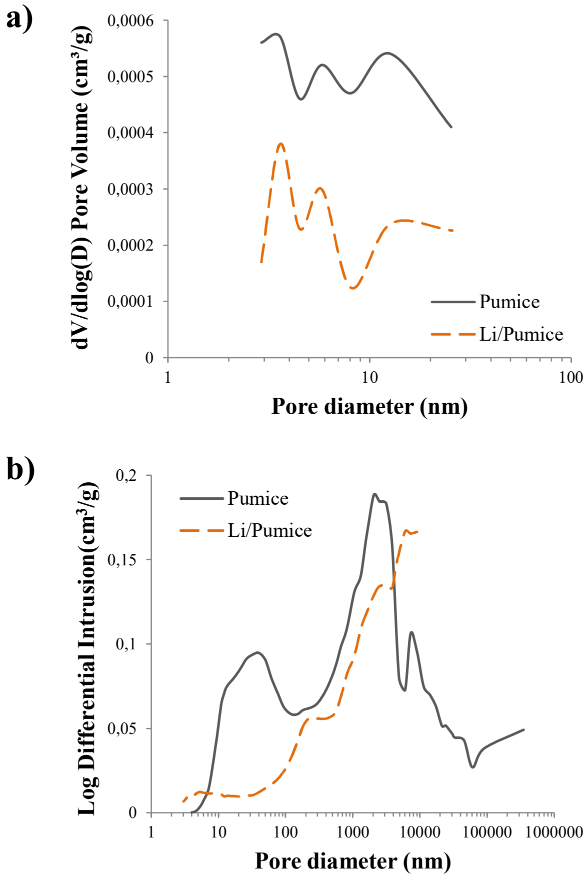

Fig. 3. Pore size distribution from (a) N_2 adsorption and (b) mercury porosimetry of the pumitic materials.

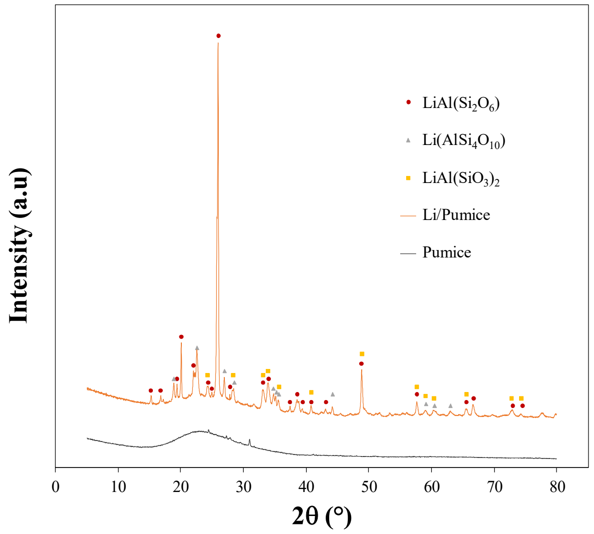

Fig. 4. XRD patterns of the of the Pumice and Li/Pumice.

From a comparison of the FTIR spectra of the pumitic materials (Fig. 5), there is no significant difference in the interpretation and identification of the peaks; however, the most intense signal observed in the FTIR spectrum of pumice, located at 1009 cm^{-1}, undergoes a shift towards lower wavenumber values after impregnation of the material with the lithium precursor (976-994 cm^{-1}). The broad band located between 600-1200 cm^{-1} is characteristic of aluminosilicates and is attributed to the internal vibration of the TO_4 tetrahedrons (T = Al or Si). The wide range of this band is mainly attributed to the amorphous nature of the materials, as well as the short-range ordering of the Si and Al tetrahedrons [21].

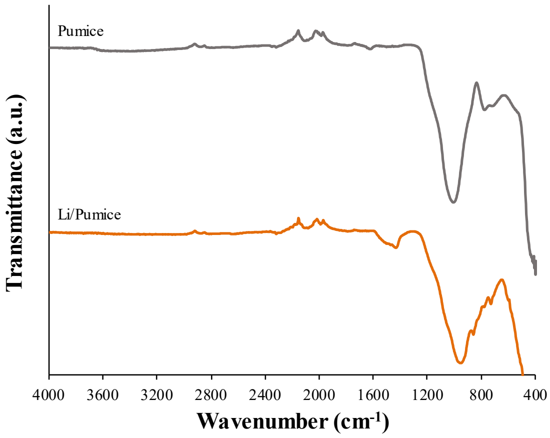

Fig. 5. FTIR spectra of the Pumice and Li/Pumice.

The Li/pumice catalyst showed a high catalytic activity in the transesterification reaction with *Jatropha curcas* oil, reaching a yield of 100% FAME, after 90 minutes. Therefore, the synthesized catalyst (Li/Pumice) is a suitable candidate to carry out continuous biodiesel production, solving the problems generated by homogeneous catalysts.

The ability to be recycled is one of the most significant features for the heterogeneous catalyst. The reusability of Li/Pumice catalyst in the transesterification of *Jatropha curcas* oil was examined for 8 h reaction and the results are shown in Fig.6. The solid catalyst was used directly for 8 h without any type of treatment.

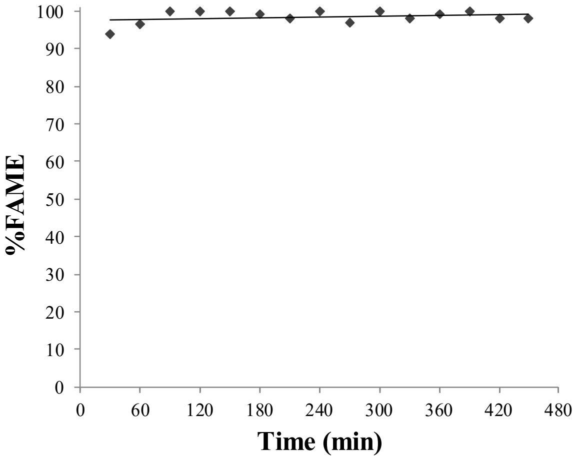

Fig. 6. Stability of the Li/Pumice catalyst.

These results show the high stability of the heterogeneous Li/Pumice catalyst for the continuous biodiesel production when compared to other heterogeneous catalysts found in the literature. Borah et al. [22] and Goli and Sahu [23] studied the reusability of Zn/CaO catalyst and eggshell waste derived CaO catalyst, respectively. In both studies, a high FAME yield was achieved in the first cycle, but a gradual drop-in catalytic activity was observed after each run. According to the authors, the cause of the decrease in the activity of the catalysts is due to the leaching of the active site to the reaction media (mainly alcoholic phase) or the blockage of catalysts active sites by products formed during the transesterification reaction.

In this work, the synthesis method appears to be appropriate since it appears that there is no leaching during the test time. However, for future research, longer production times can be investigated, analyzing how they affect the catalyst activity. Furthermore, a physical and chemical characterization of the catalyst used during long reaction times can be carried out to understand its behaviour.

4. Conclusion

In this work, a packed-bed catalytic configuration reactor using Li/Pumice as a heterogeneous catalyst was developed for the continuous biodiesel production.

The continuous transesterification of *Jatropha curcas* oil conducted in presence of DEE as a cosolvent, using a solid catalyst, allowed the production of biodiesel at low temperature (40ºC).

Li/Pumice and DEE, used as catalyst and cosolvent, respectively, is a useful and successful system to obtain biodiesel in continuous from renewable feedstock as *Jatropha curcas*.

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