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

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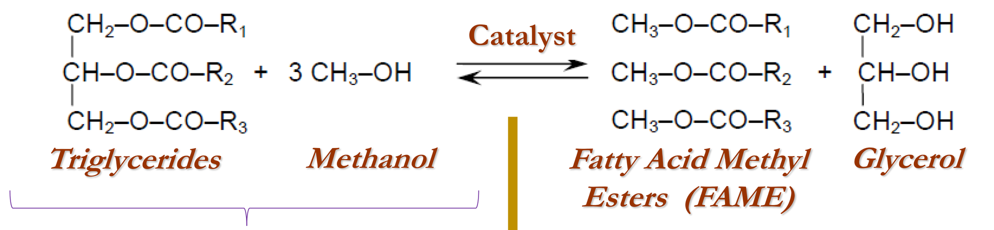
Introduction

BIODIESEL

Potential substitute of fossil fuels (mono-alkyl esters of long chain fatty acids derived from renewable sources, such as vegetable oils and animal fats).

TRANSESTERIFICATION REACTION



Methanol and oil are immiscible → **co-solvent** improves the mutual solubility.

CATALYST

Homogeneous	Heterogeneous
• Can not be recovered from reaction products. • Waste water stream from biodiesel washing.	• Can be easily separated from reaction products. • Continuous process.

BATCH PROCESS
Low productiveness and high operating costs.

CONTINUOUS PROCESS
Design of a continuous and efficient biodiesel production process that will improve its economy [1].

Packed-bed catalytic reactor system shows 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.

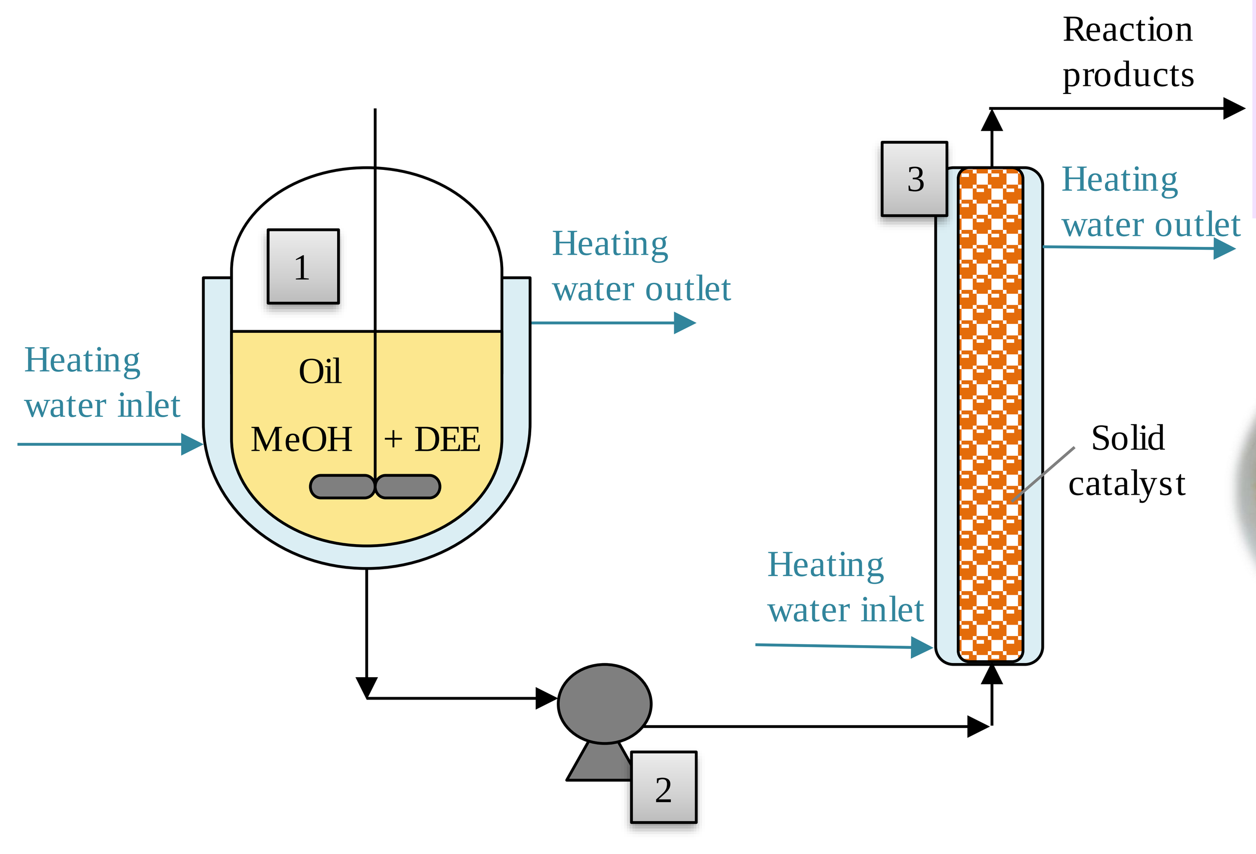
Objective

- In this work, a study on continuous biodiesel production using a heterogeneous catalyst in a packed-bed reactor assisted with diethyl ether as co-solvent 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.

Experimental

- *Materials: Jatropha curcas* oil (acid value=0.1 mg KOH g^{-1}), methanol (MeOH) and diethyl ether (DEE) as co-solvent.
- Heterogeneous catalyst: Li/Pumice (5 wt% of Li). Pumice particles (1.4–3.0 mm) were subjected to impregnation with lithium nitrate anhydrous ($LiNO_3$) [2]→ Catalyst characterization.
- Reaction conditions: 40ºC, 20:1 MeOH/oil molar ratio, 0.57:1 DEE/MeOH molar ratio, 1.4 ml/min.
- The reusability of Li/Pumice catalyst was examined for 8 h reaction. The solid catalyst was used directly for 8 h without any type of treatment.

The biodiesel product obtained was analyzed by gas chromatography in accordance with UNE-EN 14103 [3].



Li/Pumice

Figure 1. *Reaction system : 1) mixing tank, 2) peristaltic pump, 3) packed-bed reactor (20 cm length and 1 cm inner diameter).*

Results

Table 1. *Textural properties of catalytic solid.*

Material	N_2 adsorption		Mercury porosimetry			
	S_{BET}	D	A	ε	D (V)	D (4V/A)
	(m^2 g^{-1})	(nm)	(m^2 g^{-1})	(%)	(nm)	(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

- ✓ S_{BET} and the average micropore width decreased, when pumice was impregnated with lithium precursor due to pores blocking.
- ✓ The average pore diameter is between 2-50 nm → none of the materials are microporous.
- ✓ The specific area also decreased after the impregnation process and the average pore diameter, in the range of meso-macropores, increased.

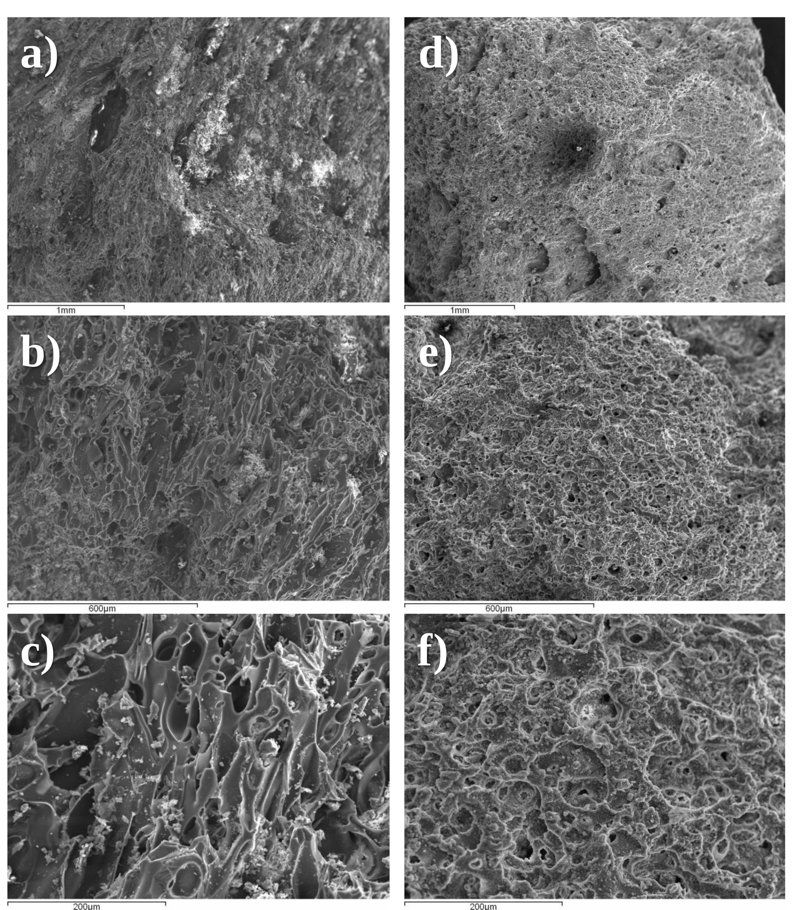


Figure 2. *SEM images for Pumice (a, b and c) and Li/Pumice (d, e and f).º*

- ✓ High porosity of both pumitic materials.
- ✓ When pumice was impregnated with the lithium precursor, the porosity of the raw material decreased.

CATALYST CHARACTERIZATION

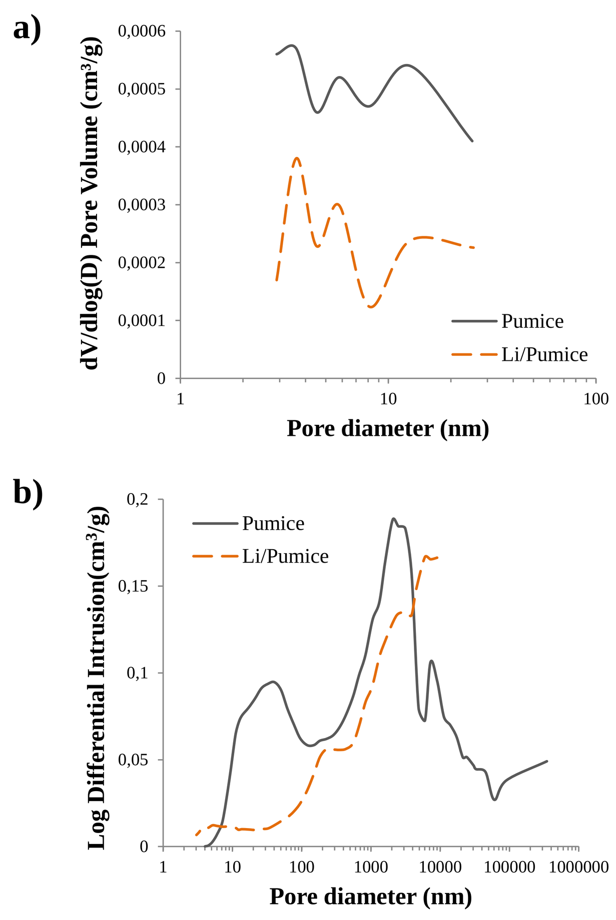


Figure 3. *Pore size distribution from (a) N_2 adsorption and (b) mercury porosimetry of the pumitic materials.*

- ✓ 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-macropours→ the average pore diameter> the size of the triglyceride molecule (5 nm)→ triglyceride molecules will diffuse easily through the pores of the catalyst→ there will be an efficient contact between the reactants and the active sites [4].

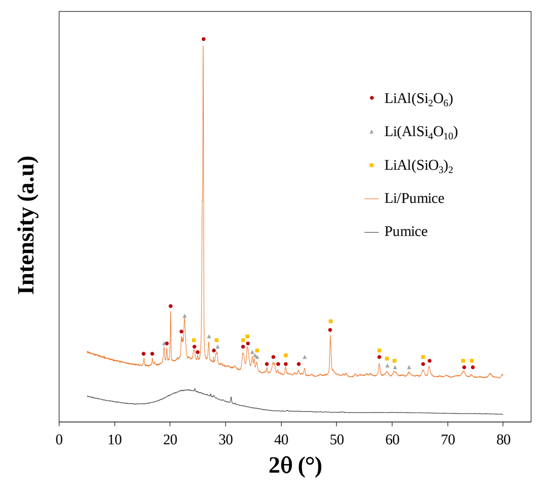


Figure 4. *XRD patterns of the of the Pumice and Li/Pumice.*

- ✓ 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→ it reflects the amorphous structure of silica (SiO_2).
- ✓ 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 $LiAl(SiO_3)_2$ identified through the QualX software, using the POW_COD_2007 database (Fig. 4).

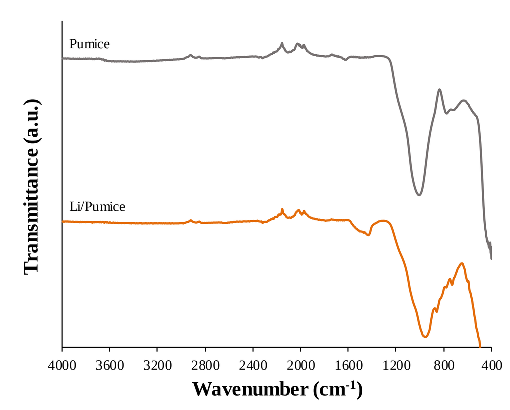


Figure 5. *FTIR spectra of the Pumice and Li/Pumice.*

- ✓ 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 [5].

TRANSESTERIFICATION REACTION

- ✓ 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.

- ✓ The ability to be recycled is one of the most significant features for the heterogeneous catalyst.
- ✓ These results show the high stability of the heterogeneous Li/Pumice catalyst for the continuous biodiesel production.
- ✓ The synthesis method appears to be appropriate since it appears that there is no leaching during the test time.

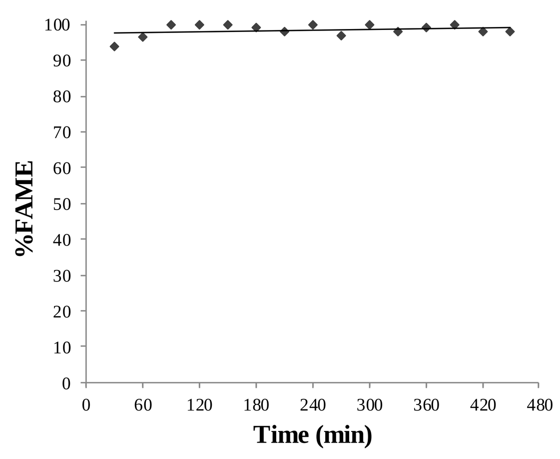


Figure 6. *Stability of the Li/Pumice catalyst.*

Conclusions

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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