



# High performance heterogeneous catalyst for biodiesel production from vegetal and waste oil at low temperature

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## ABSTRACT

A natural porous silica, pumice, was studied as heterogeneous catalyst in the transesterification reaction of sunflower oil and frying oil with methanol for biodiesel production. This low cost natural porous material was subjected to ion exchange with a KOH aqueous solution in order to increase its activity. The dependence of the reaction variables such as temperature, reaction time, catalyst loading and methanol/oil molar ratio were studied using sunflower oil and waste oil as feedstock. Moreover, in order to save production costs, the reusability of the catalyst in the transesterification reaction was studied.

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## 1. Introduction

Nowadays, biodiesel is produced in great amount and its production continues growing. The main technology used in the biodiesel industrial production is based on the transesterification of refined oils using basic homogeneous catalysts. However, problems related with this technology (mainly in product purification and residues generation) have stimulated research in the field of heterogeneous catalysts for biodiesel production, making great efforts to find the right solid catalyst with high activity at low temperatures.

Several materials have been tested as heterogeneous catalysts in the transesterification of vegetable oils for biodiesel production, achieving good yields only when reaction takes place at high temperatures [1–4]. Some researchers have achieved high yields at low reaction temperatures [5–8] but using catalytic solids in powder form. The scaling of these catalytic processes to an industrial system with fixed bed reactors would be impossible due to the high pressure drop occurring along the reactor when a powder catalyst bed is used. Therefore, in order to develop a catalyst with practical industrial applications, it is necessary to search a porous heterogeneous catalyst (particulated or in a pellet form) with high activity for biodiesel production by vegetable oils transesterification reaction.

Pumice is an amorphous, porous volcanic rock that is composed for silica and alumina. Its porous structure was mainly formed by

dissolved gases included into precipitated materials during the volcanic lava cooling through the air [9–11]. Pumice material is used in many applications such as chemical, dental, cosmetic, abrasives, cement, concrete, ceramic and glass industries because of being an inexpensive and widespread geological raw material [12]. Various researchers have studied the use of natural and/or modified pumice as catalytic material in order to carry out industrial typical reactions [13–15].

In the present work, potassium loaded pumice was used as heterogeneous catalyst in the sunflower oil and frying or waste oil transesterification reaction with methanol for biodiesel production. Several parameters, such as: reaction time, methanol/oil molar ratio, catalyst loading and reaction temperature, effects were studied. Moreover, the possible catalyst reuse and regeneration was evaluated in order to perform a continuous biodiesel production process.

## 2. Experimental

### 2.1. Catalyst preparation

Pumice granules (1.40–3.0 mm) from Panreac were used as catalyst. In order to increase its basic sites, pumice material was exchanged with a KOH aqueous solution. Firstly, pumice was dried in an oven at 120 °C for 2 h to remove the absorbed water on the surface. Ionic exchange was carried out with different KOH solution concentrations (0.5–4 M) for 24 h. After ionic exchange, pumice granules were dried at 120 °C for 3 h obtaining the potassium loaded catalytic material (K-Pumice, *patent pending* P201001183).

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**Table 1**  
Properties of sunflower oil and frying oil.

Property	Sunflower oil	Frying oil
Density at 15 °C (g/cm <sup>3</sup> )	0.924	0.930
Kinematic viscosity at 40 °C (cSt)	29.4	37.8
Acid value (mg KOH/g)	0.17	2.02
Iodine index (g Iodine/100 g sample)	138.8	122.3
Turbidity (NTU)	2.24	9.99

Xie et al. have used a similar treatment to prepare modified NaX zeolite with different KOH loadings [16].

## 2.2. Catalysts characterization

Natural Pumice and potassium supported Pumice (K-Pumice) materials were examined by X-ray diffraction (XRD). X-ray diffraction measurements for structure determinations were recorded on a X'Pert Pro diffractometer of Panalytical, using X'Celerator detector and Cu K $\alpha$  radiation. In order to quantify the Si/Al ratio of the samples, atomic absorption (AA) measurements were made by a Thermo Electron Corporation spectrophotometer. The samples were previously digested by acid mixture (hydrofluoric, nitric and hydrochloric acids). Moreover, the concentration of potassium cations was measured. 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).

For catalytic sites evaluation both ammonia and carbon dioxide Temperature Programmed Desorption measurements were carried out on a Micromeritics TPR/TPD 2900 equipment. Before each TPD experiment, 100 mg of catalyst sample was introduced in a U-shape quartz tube and outgassed in a He flow of 50 mL/min at 110 °C for 15 min with a heating rate of 10 °C/min from room temperature. Then, the sample was cooled to the temperature at which the adsorption will be carried out.

Ammonia was adsorbed by exposing the outgassed sample to a stream containing 5% NH<sub>3</sub> in He for 15 min at 30 °C and then purged with He at above temperature for 15 min to remove physisorbed ammonia. Desorption of ammonia was carried out in He flow by increasing the temperature to 850 °C at rate of 10 °C/min with a flow rate of 50 mL/min while monitoring the evolved NH<sub>3</sub> using a thermal conductivity detector.

Carbon dioxide was adsorbed by exposing the outgassed sample to a stream containing 90% CO<sub>2</sub>/He at 80 °C for 60 min and then purged with helium up to room temperature, and keeping at this temperature during 15 min. The desorption of CO<sub>2</sub> was carried out in He flow by increasing the temperature to 850 °C at a rate of 10 °C/min with a flow rate of 50 mL/min while monitoring the evolved CO<sub>2</sub> using a thermal conductivity detector.

Signals were integrated in order to obtain amounts of carbon dioxide or ammonia desorbed, after calibrating the device with known pulses of above gases.

## 2.3. Transesterification reaction

Transesterification reactions were performed in a 250 mL jacketed glass reactor equipped with a reflux condenser and a mechanical stirring. Two types of oils were used as feedstock in transesterification reactions: commercial edible-grade sunflower oil purchased from the market (used without further purification) and waste oil from frying in a canteen (filtered to remove suspended solids). The properties of these oils are shown in Table 1.

The reaction system was heated to selected temperature in the range 50–60 °C and 100 g of oil was added. When the oil reached

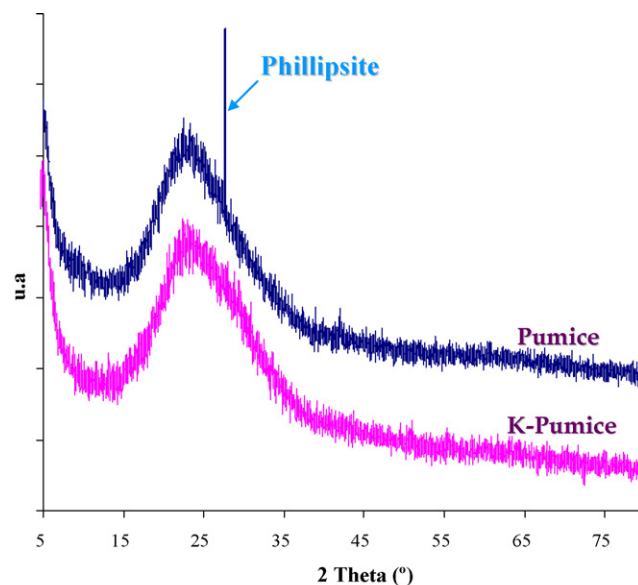


Fig. 1. XRD pattern of natural pumice and K-supported pumice.

selected temperature, methanol (methanol/oil molar ratio in the range 6:1–24:1) and the catalyst amount (between 4 and 20 wt% related to oil weight) were added with continuous stirring. After completion of the reaction or stipulated reaction time (1–4 h), the catalytic solid was separated from the reaction mixture by filtration. The liquid product obtained was rotary evaporated to remove methanol in excess, and then settled in a separating funnel. The upper phase consisted of fatty acid methyl esters (biodiesel product, FAME) and the lower phase contained the glycerol by-product. Viscosity and density of the obtained biodiesel product was measured using a rotational viscometer VISCO STAR Plus L and a pycnometer, respectively. Moreover, the biodiesel product obtained was analyzed by <sup>1</sup>H Nuclear Magnetic Resonance (NMR) spectrometry to estimate the fatty acid methyl ester yield using the Gelbard et al. method [17].

In order to examine the potential reutilization of the heterogeneous catalyst, used catalyst particles were washed with ethanol to remove all remaining organic compounds (triglycerides and esters tracks), dried and calcined at 560 °C for 10 h. Moreover, a new ionic exchange was carried out with a potassium hydroxide (1 M) solution when solid catalyst was regenerated.

Finally, a comparison of the K-Pumice catalytic performance with conventional KOH homogeneous basic catalyst was performed.

## 3. Results and discussion

### 3.1. Catalyst characterization

XRD pattern of pumice (Fig. 1) presents amorphous silica and also a peak at  $2\theta = 27.5^\circ$  corresponding to phillipsite, which is a kind of natural zeolite [18]. XRD pattern of modified pumice in Fig. 1 shows a loss of crystallinity, disappearing the peak corresponding to phillipsite.

Table 2  
Potassium concentration and Si/Al molar ratio of the catalytic materials.

Catalyst	K (mg/l)	K (% peso)	Si/Al
Pumice	56.6	5.7	7.7
K-Pumice	74.4	7.4	9.9

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