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*Research article*

## Magnetic fraction from phosphate mining tailings as heterogeneous catalyst for biodiesel production through transesterification reaction of triacylglycerols in bio-oil

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**Abstract:** Biodiesel is an interesting alternative fuel for complementing or even completely replacing the mineral diesel. It is industrially obtained through the transesterification reaction of triacylglycerol in bio-oils with alcohol of short molecular chain, to produce the corresponding mixture of esters of fatty acids (biodiesel). Mineral rejects from mining usually constitute a major environmental and economic problem. Herein, it is described the study devoted to evaluate the chemical efficiency of the transesterification reaction of triacylglycerols in soybean oil with methanol, catalyzed by a material based on the magnetic fraction from rejects of a phosphate ore being commercially exploited in Tapira, Minas Gerais, Brazil. The magnetite-containing material from those mining tailings was used to form a new heterogeneous catalyst, by first mixing it with a commercial synthetic calcium oxide. The mixture was then heated at 200 °C for 4 h. The magnetic, crystallographic and <sup>57</sup>Fe hyperfine structures of the resulting catalyst were assessed by VSM magnetometer, X-ray diffraction and <sup>57</sup>Fe Mössbauer spectroscopy, respectively. The transesterification reaction was performed at 65 °C, at a molar ratio methanol:oil 30:1. The chemical yields in esters for this heterogeneously catalyzed transesterification was 99 ± 1 mass%, through a

reaction completed in  $135 \pm 30$  min. The reaction catalyzed by the sole magnetic fraction, without CaO, did not produce any esters even after 24 h reaction; the pure CaO catalyst yielded  $84 \pm 10$  mass% esters, after reaction completion, which took  $128 \pm 16$  min. The magnetic fraction with CaO was found to act synergically on the transesterification reaction. From the technological, economic and environmental points of view, these results strongly evidence the real viability of using this magnetic fraction-CaO catalyst, to produce biodiesel.

**Keywords:** biodiesel; transesterification; heterogeneous catalysis; magnetite; mining reject

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## 1. Introduction

Chemically, biodiesel is a relatively complex mixture containing fatty acid esters, usually obtained through the transesterification reaction of triacylglycerols in bio-oils, with alcohols of short molecular chains, almost uniquely methanol or ethanol. In the industrial process, the chemical reaction is homogeneously catalyzed with a strong alkaline base, as potassium hydroxide, in the liquid medium [1,2,3]. This is by far the most common chemical industrial process worldwide. However, any solid heterogeneous catalyst is conceptually thought to lead to cleaner processes, relative to the liquid homogeneous catalyst, on such transesterification reactions, as the solid material requires much less water to clean the produced biodiesel from impurities relatively to that from the homogeneous route and the catalyst can be removed and reused in subsequent reaction cycles. Some recently reported reviews [4–7] hardly mention the chemical role of iron oxide-based solid catalysts towards the transesterification reaction to produce fatty acid methyl or ethyl esters. Regarding the envisaged industrial process, it would be still more interesting if the solid is magnetic as it can be more easily removed from the reaction medium with a magnetic field from a permanent magnet or generated with an electric coil [8]. Magnetic materials [9] are thus conceptually strong candidates to be valuable components of solid catalysts, taking into account their potential chemical catalytic activity and the feasibility of being easily separated [8], with an applied magnetic field, from the liquid mass in the industrial line, whenever it is required.

From the economic and environmental points of view, mining rejects containing magnetic minerals may be largely available depending on the geology and on the ore matrix being processed. In most cases, the rejects represent a real threat to the surrounding natural environment, particularly in areas around the mine. Such a specific circumstance may be found in tailings from some phosphate ores containing a given proportion of magnetite.

This report describes a work devoted to the use of the magnetic fraction of the mining reject of the Tapira Mining Complex, in the state of Minas Gerais, Brazil. The magnetic fraction from the rejected material from extracting the mainly exploited ore is ordinarily separated during the mining industrial process. A sample of that magnetic fraction was further magnetically enriched with a hand magnet and tested in the laboratory as a component of a heterogeneous catalyst, either straightly or mixed with calcium oxide, on the transesterification reaction of triacylglycerols in the soybean oil with methanol, to produce biodiesel. The chemical performance of the heterogeneous catalyst based on this magnetic fraction mixed with CaO was evaluated by comparing with that of the pure magnetic fraction and with that of the sole CaO.

## 2. Materials and Methods

The magnetic fraction was separated from tailings of an ore mine for phosphate in the municipality of Tapira, state of Minas Gerais, Brazil.

The industrial magnetic fraction was still further magnetically enriched in the laboratory by separating magnetic particles with a hand-held permanent magnet and this fraction was mixed with calcium oxide PA (Aldrich) at a mass ratio 1:1, in a porcelain crucible. This solid mixture was heated in a muffle at 200 °C for 4 h. The so-prepared catalyst was stored in a desiccator until being used in the transesterification reaction. The used raw source of triacylglycerols was a commercial soybean oil destined to domestic use, purchased in a supermarket.

A primary mineralogical characterization of the mineral catalyst sample was performed by powder X-ray diffraction (XRD) in a Rigaku diffractometer model Ultima IV set to a current of 30 mA and a voltage of 40 kV, with the  $\text{CuK}\alpha$  ( $\lambda = 1.541838 \text{ \AA}$ ) radiation, at a scan rate of  $1^\circ 2\theta \text{ min}^{-1}$ , from  $4$  to  $80^\circ 2\theta$ . Silicon was used as an external standard.

The chemical states of iron were assessed by Mössbauer spectroscopy, making it also possible to infer about the proportions of the iron minerals (more specifically magnetite, hematite or ilmenite) in the sample. The Mössbauer spectrum was collected at room temperature ( $\sim 298 \text{ K}$ ) in the constant acceleration transmission mode with a  $\sim 20 \text{ m Ci } ^{57}\text{Co/Rh}$  gamma-ray source. Data were stored in a 512-channel MCS memory unit, with Doppler velocities ranging between approximately  $\pm 12.1 \text{ mm s}^{-1}$ . Mössbauer isomer shift values are quoted relative to an  $\alpha\text{-Fe}$  foil at room temperature. The experimental data were least square-fitted to Lorentzian-shape resonance lines, with the WinNormos™ for Igor™ Pro computer program.

The magnetization measurement of the sample was performed with a vibrating sample magnetometer (VSM LakeShore 7404) with a noise base of  $5 \times 10^{-5} \text{ emu}$ , a time constant of 100 ms, at room temperature, and a maximum magnetic field of 2 T.

The X-ray fluorescence analysis of the sample was made with a Shimadzu EDX-720 energy dispersive X-ray fluorescence spectrometer, with a rhodium tube and silicon-lithium detector. Data were collected without vacuum, with a collimator of 10 mm.

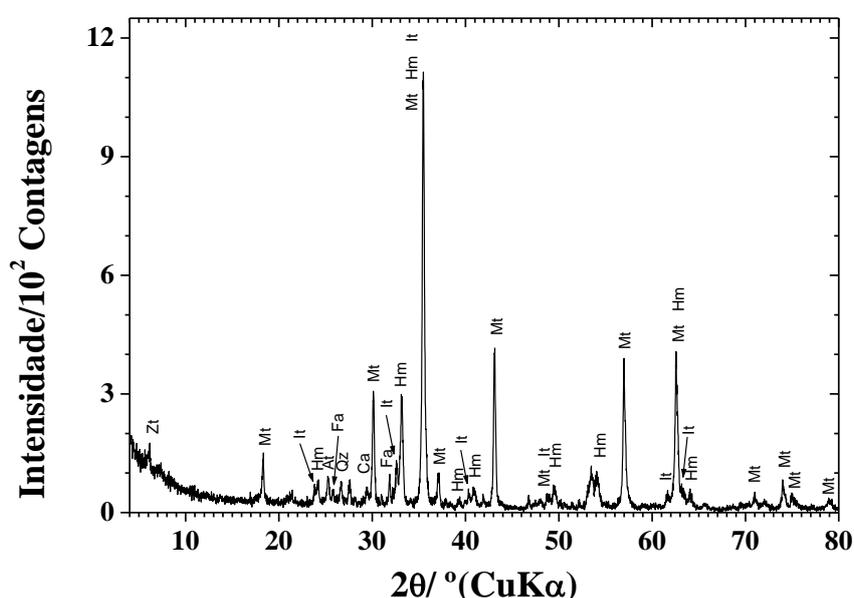
The triacylglycerol conversion to fatty acid methyl esters was obtained by using a molar ratio methanol:oil 30:1. The catalyst corresponded to 8 mass% of the oil mass. The reaction was monitored with thin layer chromatography (TLC) by using hexane:ethyl acetate at the ratio 9:1 as an eluent and iodine as developer. The reacting liquid was rotaevaporated and the methanol was recovered. The fraction containing glycerin and biodiesel was placed in a separation funnel. The glycerol was then removed; the volume of the biodiesel was measured and subsequently washed with distilled water.

Samples from the produced biodiesel were analyzed according to the European Standard, by gas chromatography. Analyses were performed on a gas chromatograph model HP7820A equipped with flame ionization detector. The column was the BP20 (SGE)  $12 \text{ m} \times 0.25 \text{ mm} \times 0.2 \text{ }\mu\text{m}$  in a temperature gradient of  $10^\circ \text{C min}^{-1}$ , from  $120^\circ \text{C}$  to  $220^\circ \text{C}$ ; gun (split of 1/50) to  $250^\circ \text{C}$  and detector to  $260^\circ \text{C}$ . The gas carrier was hydrogen ( $3 \text{ mL min}^{-1}$ ). Data acquisition software: EZChrom Elite Compact (Agilent).

### 3. Results and Discussion

#### 3.1. Powder X-ray diffraction

The powder X-ray diffraction pattern (Figure 1) revealed the occurrence of magnetite ( $\text{Fe}_3\text{O}_4$ ; according to the JCPDS card #19-629 [10]), hematite ( $\alpha\text{Fe}_2\text{O}_3$ ; JCPDS card #33-664), ilmenite ( $\text{FeTiO}_3$ ; JCPDS card #29-733), fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ; JCPDS card #15-876), anatase ( $\text{TiO}_2$ ; JCPDS card #21-1272), calcite ( $\text{CaCO}_3$ ; JCPDS card #5-586), zeolite ( $\text{K}_{69.8}\text{Al}_{69.8}\text{Si}_{122.2}\text{O}_{384}$ ; JCPDS card #26-893) and quartz ( $\text{SiO}_2$ ; JCPDS card #46-1045). The cubic unit cell edge dimension for this magnetite was found to be  $a = 8.394(3) \text{ \AA}$ , as estimated with the UnitCell computer program [11], based on the  $\text{K}\alpha_1$  reflection peaks corresponding to the planes (220), (311), (400) and (511).



**Figure 1.** XRD pattern for the magnetic fraction from phosphate mining tailings. Mt = magnetite ( $\text{Fe}_3\text{O}_4$ ), Hm = hematite ( $\alpha\text{Fe}_2\text{O}_3$ ), It = ilmenite ( $\text{FeTiO}_3$ ), Fa = fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), At = anatase ( $\text{TiO}_2$ ), Ca = calcite ( $\text{CaCO}_3$ ), Zt = zeolite ( $\text{K}_{69.8}\text{Al}_{69.8}\text{Si}_{122.2}\text{O}_{384}$ ) and Qz = quartz ( $\text{SiO}_2$ ).

#### 3.2. X-ray fluorescence analysis

The X-ray fluorescence data reveal that the magnetic material is relatively rich in iron, titanium, silicon, calcium and phosphorus (Table 1).

**Table 1.** Chemical composition for the magnetic fraction from phosphate mining tailings, as determined by X-ray fluorescence spectroscopy.

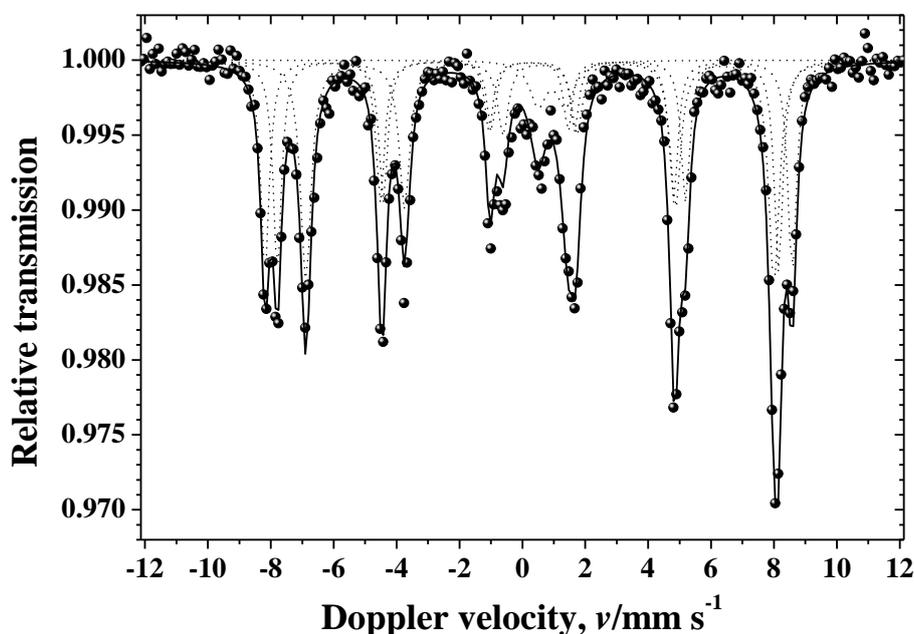
	Content/mass%		Content/mass%
Fe	81.1 (2)	V	0.21 (2)
Ti	6.19 (6)	Sr	0.104 (4)
Si	5.9 (3)	Zr	0.087 (3)
Ca	3.57 (4)	Nb	0.078 (4)
P	1.3 (2)	Cr	0.05 (1)
Mn	0.93 (2)	Zn	0.054 (7)
K	0.39 (3)	Th	0.03 (1)

The numbers in parentheses are uncertainties over the last significant digit, as provided by the spectrometer.

### 3.3. Mössbauer spectroscopy

Numerically fitting the 298 K-Mössbauer spectrum provided information on some chemical characteristics of the material: (i) Fe<sup>3+</sup>; (ii) mixed valence Fe<sup>3+/2+</sup> and (iii) a Fe<sup>2+</sup> doublet.

From the hyperfine parameters (Figure 2; the corresponding spectral parameters are presented in Table 2), the sample contains a magnetite (relative subspectral area,  $RA = 24.6 + 40.3 = 64.9\%$ ), with magnetic hyperfine field values for the tetrahedral  $[B_{hf}] = 49.42$  (3) tesla and octahedral  $\{B_{hf}\} = 46.17$  (2) tesla sites, along with a hematite sextet ( $RA = 25.4\%$ ),  $B_{hf} = 51.98$  (3) tesla, and an ilmenite doublet ( $RA = 9.7\%$ ) with quadrupole splitting  $\Delta = 0.88$  (2) mm s<sup>-1</sup> and isomer shift  $\delta/aFe = 1.04$  (1) mm s<sup>-1</sup>.



**Figure 2.** Mössbauer spectrum collected at room temperature (~298 K) for the magnetic fraction from phosphate mining tailings.

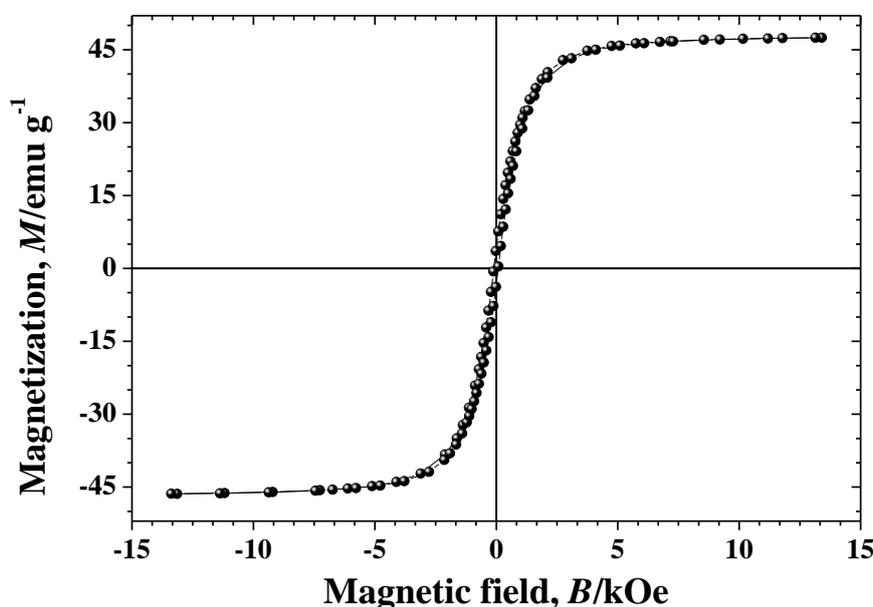
**Table 2.** Fitted Mössbauer parameters for the magnetic fraction from phosphate mining tailings.

<sup>57</sup> Fe site	$\delta/\text{mm s}^{-1}$	$\Gamma/\text{mm s}^{-1}$	$2\varepsilon, \Delta/\text{mm s}^{-1}$	$B_{\text{hf}}/\text{T}$	RA/%
$\alpha\text{Fe}_2\text{O}_3$	0.367 (3)	0.33 (1)	-0.137 (7)	51.98 (3)	25.4
Fe <sub>3</sub> O <sub>4</sub>	[Fe <sup>3+</sup> ]	0.287 (4)	0.33 (1)	-0.017 (8)	24.6
	{Fe <sup>3+/2+</sup> }	0.660 (3)	0.41 (1)	-0.003 (6)	40.3
FeTiO <sub>3</sub>	1.04 (1)	0.64 (4)	0.88 (2)		9.7

$\delta$  = isomer shift relative to the  $\alpha\text{Fe}$ ;  $\Gamma$  = resonance linewidth;  $2\varepsilon$  = quadrupole shift;  $\Delta$  = quadrupole splitting;  $B_{\text{hf}}$  = magnetic hyperfine field and RA = relative subspectral area. [ ] denotes tetrahedral and { } octahedral symmetries of the Fe-O coordination sites of the spinel structure. [Fe<sup>3+</sup>] and {Fe<sup>3+/2+</sup>} stand, respectively, for iron in tetrahedral and octahedral coordination sites of the spinel structure of the magnetite. Numbers in parentheses are standard deviation over the last significant digit of the value, as output by the computer fitting program, based on the least squares algorithm.

### 3.4. Magnetic measurement

From the room temperature magnetization curve (Figure 3), the saturation magnetization for this sample is  $M_s \sim 47 \text{ emu g}^{-1}$ . Iron represents 81.1 mass% of all determined chemical elements (normalized values) in the sample (Table 1). The relative Mössbauer spectral area due to magnetite is 64.9 % (Table 2). If no difference of the recoilless fractions corresponding to the various <sup>57</sup>Fe sites is taken into account, a rough estimation of the mass proportion of magnetite in the sample is  $\sim 52.6 \text{ mass\%}$ . If so, the saturation magnetization for this magnetite is  $M_s \sim 89 \text{ emu g}^{-1}$ . This value is reasonably close to the reported value for a pure bulk magnetite, or 92–100  $\text{emu g}^{-1}$  [12].

**Figure 3.** The VSM magnetization curve for the magnetic fraction from phosphate mining tailings.

### 3.5. The transesterification reaction

According to these results, this magnetic material combined with CaO showed a significant chemical catalytic activity on the transesterification, yielding  $99 \pm 1$  mass% esters, once the reaction was complete, in a  $135 \pm 30$  min-process (Table 3). To compare, the sole magnetic material from the mining tailings has not produced any ester on transesterification, even after 24 h reaction. On the other hand, the reaction catalyzed with sole CaO yielded  $84 \pm 10$  mass% esters, after reaction completion, in  $128 \pm 16$  min (Table 3).

**Table 3.** Reaction time and proportion of esters yielded from the transesterification reaction of triacylglycerols in the soybean oil with methanol at a molar ratio methanol:oil 30:1, catalyzed either by the magnetic fraction from phosphate mining tailings mixed with CaO or by pure CaO, for both catalysts, heated at 200 °C during 4 h. Data for the transesterification reaction times and ester yields with the magnetic material + CaO were averaged over four experimental repetitions; those to the sole CaO were correspondently based on six repetitions. Uncertainties were taken as values of standard deviation over the mean.

Catalyst	Reaction time/min	Esters/mass%
Magnetic fraction + CaO	$135 \pm 30$	$99 \pm 1$
Pure CaO	$128 \pm 16$	$84 \pm 10$

The heterogeneous catalyst composed by the magnetic material mixed with CaO leads to high chemical yields in esters through the transesterification, and is readily recoverable to be reused, keeping its catalytic activity virtually unchanged for at least two subsequent reaction cycles, with chemical yields of 99.5 and 99.9 mass% esters for corresponding reaction times of 90 min each.

The chemical mechanisms involved the synergic action of the catalyst by this magnetite-rich mining reject mixed with calcium oxide are not fully understood, so far, and become an essential topic for further studies. From a comparable magnetic heterogeneous catalyst composed by SiO<sub>2</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and KI promoted the transesterification of triacylglycerols in soybean oil to yield 94.4 mass% esters [8].

## 4. Conclusion

The magnetically-enriched fraction (saturation magnetization,  $M_s \sim 47$  emu g<sup>-1</sup>) from tailings of the phosphate mining in Tapira, Minas Gerais, Brazil, was found to contain magnetite (Fe<sub>3</sub>O<sub>4</sub>, corresponding to  $M_s \sim 89$  emu g<sup>-1</sup>), hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), ilmenite (FeTiO<sub>3</sub>), fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F), anatase (TiO<sub>2</sub>), calcite (CaCO<sub>3</sub>), zeolite (K<sub>69.8</sub>Al<sub>69.8</sub>Si<sub>122.2</sub>O<sub>384</sub>) and quartz (SiO<sub>2</sub>). A sample of this fraction mixed with CaO at a mass ratio 1:1 and heated at 200 °C for 4 h was used as heterogeneous catalyst in the transesterification reaction of triacylglycerols in the soybean oil with methanol, to produce methyl esters of fatty acids (biodiesel). Results point to an effective synergic chemical catalytic effect of this mining tailing with CaO to produce biodiesel. The relatively short time of  $135 \pm 30$  min to complete the reaction and the expressive chemical yield of  $99 \pm 1$  mass% esters make this heterogeneous catalyst a strong candidate to be scaled up for industrial chemical processes on the production of biodiesel. The chemical mechanisms for the so catalyzed transesterification

reaction involve a synergic action of the catalyst by the magnetite-rich mining reject mixed with calcium oxide. This would represent, on one side, an enormous environmental meaning, as it tends to clean the tailings material from the mining area, and, on the other, an economic gain by a rational use of the disposable material towards a technologically advanced catalyst. Further developments on these magnetic materials are strongly envisaged and are currently in continuous progress by our research Group.

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## Conflict of Interest

All authors declare no conflicts of interest in this paper.

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