RESEARCH ARTICLE   **OPEN ACCESS**

SILICA-RICH GEOMATERIALS AND THEIR USE AS HETEROGENEOUS CATALYSTS IN THE TRANSESTERIFICATION REACTION TO PRODUCE BIODIESEL

Alice Lopes Macedo[1], Edneia Lordeiro Macedo[2], Edivaldo dos Santos Filho[2], Eliane Cristina Costa[1], Franciele Martins de Queiroz[1], Rafael Mendes Coelho[2], Wanessa Lima Oliveira[2], Bárbara Gonçalves Rocha[1], Luis Carlos Duarte Cavalcante[3] and José Domingos Fabris[4,5]

[1]Federal University of the Jequitinhonha and Mucuri Valleys (UFVJM), 39100-000 Diamantina, Minas Gerais, Brazil
[2]Institute of Science and Technology, UFVJM, 39100-000 Diamantina, Minas Gerais, Brazil
[3]Center of Natural Sciences, Federal University of Piauí (UFPI), 64049-550 Teresina, Piauí, Brazil
[4]Department of Chemistry, Federal University of Minas Gerais (UFMG), Campus Pampulha, 31270-901 Belo Horizonte, Minas Gerais, Brazil
[5]Institute of Chemistry, Federal University of Uberlândia (UFU), Campus Santa Mônica, 38408-000 Uberlândia, Minas Gerais, Brazil

ARTICLE INFO

ABSTRACT

A silica-rich geomaterial of a mining tail was prepared and tested as a heterogeneous catalyst in the transesterification reaction in soybean oil to produce the corresponding fatty acid methyl esters (biodiesel). The dry raw geomaterial was characterized by powder X-ray diffractometry, scanning electron microscopy, energy dispersive X-ray (EDX) and ^{57}Fe-Mössbauer spectroscopy. The raw mineral sample was then dispersed in aqueous solution containing 35 g KI 100 mL^{-1} to form the chemically active solid catalyst. The EDX data showed that the silica-rich material contained mainly silicon (87.3 mass%), iron (8.4 mass%) and aluminum (3.5 mass%). From the 298 K-Mössbauer spectrum, two sextets were attributed to hematite (αFe_2O_3) and goethite ($\alpha FeOOH$). Meaning fully, although the silica-rich material, before being impregnated with KI, showed no chemical efficiency on the production of esters (biodiesel), the KI-impregnation made it an efficient catalyst: the biodiesel was produced after 7 h by the transesterification reaction using 5 mass% catalyst with respect to the oil mass; the reaction was performed with a methanol: soybean oil molar ratio 100:1, yielding 95 ± 2 mass% esters. These results encourage further essays focused not only on optimizing these reaction conditions but also on seeking for other formulations containing any silica-rich geomaterial as heterogeneous catalysts in transesterification.

INTRODUCTION

Mainly as a result of the global efforts to preserve the natural environment on Earth, the search for alternative cleaner and renewable energy sources to replace those of fossil origin, which include mainly oil, natural gas and coal and are being amply used in the global scale, has been gaining dramatic importance, especially over the last few decades (Liew *et al.*, 2014).

*Corresponding author: Alice Lopes Macedo,
Federal University of the Jequitinhonha and Mucuri Valleys (UFVJM), 39100-000 Diamantina, Minas Gerais, Brazil

Liquid fuels produced from biomass, such as bioethanol and biodiesel, are among the viable environmentally cleaner fuels with a perspective of reaching the whole global scale (Ji and Long 2016). In response to the enormous and increasing energy demands, the industrial production of biodiesel faces some technological challenges, particularly those related to the chemical efficiency and economical gain on converting triacylglycerols or free fatty acids in bio-oil with short-chain alcohols into esters (biodiesel) (Anuar and Abdullah, 2016). The main chemical route in the biodiesel industry involves the transesterification of triacylglycerols in bio-oils, usually with methanol, via the homogeneously catalyzed reaction with a strong alkali. The process leads to large volumes of liquid

effluent that is harmful to the natural environment and needs to be suitably treated, to be safely disposed. Also, the catalyst is rarely recovered to be reused in subsequent reaction cycles (Meher *et al.*, 2006; Garcia *et al.*, 2008). As an alternative procedure, the heterogeneous catalysis conceptually allows the catalyst to be reused and leads to much lower volumes of harmful effluents. The critical characteristics of a heterogeneously catalyzed transesterification reaction is, in general, the lower chemical efficiency compared with the homogeneous system; the time necessary for the heterogeneous reaction tends to be longer, and sometimes the chemical yields are lower (Janaun and Ellis, 2010). These are some of the main challenges for the technological development of new heterogeneous catalysts: (i) lowering the cost of preparing the multi-phase catalysts, which may require the natural availability of at least some of it components, such as from mining rejects or industrial or urban waste; (ii) chemical efficiency, meaning relatively rapid reactions and high chemical yields; (iii) reusability; (iv) environmental effects of the recovered catalyst itself or of any of the corresponding reaction by-products; and (v) facility to remove the catalyst (and, eventually, recover and reuse it) from the post-reaction medium or from the final industrial effluent (Garcia *et al.*, 2008).The development research work focused on preparing new inorganic multi-component catalytic materials based mainly on silica-rich mining tailings containing residual iron oxides is reported. Silica-rich materials are often found in deposits of rejects surrounding many mining areas; these materials may also contain significant amounts of iron oxides. A silica-rich sample from an ore-mining reject was collected, prepared and used as a heterogeneous catalyst in the transesterification reaction of the triacylglycerols in soybean oil with methanol to produce biodiesel.

Experimental

Samples: structural features of the silica-rich geomaterial: The silica-rich material from mining tailings was first dried at 150 °C for 2 h. The morphology of its particles was investigated by scanning electron microscopy (SEM) using a Hitachi TM-3000 microscope coupled to a SwiftED3000 (Oxford Instruments) energy dispersive X-ray spectrometer operated at 15 kV accelerating voltage for local chemical analysis. The main crystalline phases were identified by powder X-ray diffraction (XRD) data collected with a Shimadzu XRD 6000 diffractometer (CuKα radiation tube; λ = 1.541838 Å) equipped with a graphite monochromator; scans were performed between 10 and 80° 2θ with a scanning rate of 2° min^{-1}; silicon was used as an external standard. The transmission ^{57}Fe-Mössbauer spectrum for the prepared catalyst sample was collected under a constant acceleration regime of a ~25 mCi ^{57}Co/Rh gamma-ray source at 298 K. Doppler velocities ranged between approximately ± 12.4 mm s^{-1}. Mössbauer isomer shifts are quoted relative to an αFe foil at 298 K. The experimental data were least-squares-fitted with Lorentzian functions by using the WinNormos™ for Igor™ software.

The transesterification reaction to produce fatty-acid methyl esters (FAME): The heterogeneous catalyst was prepared from the silica-rich geomaterials to act as an acid carrier, which was impregnated with KI (to form catalytically active Lewis base sites). The sample was dispersed in 1 g ratio of the silica-rich material in 20 mL of a 35% aqueous solution of KI. The suspension was then sonicated for 25 min, filtered

and oven dried at 150 °C for 2 hours. Finally, the dry solid was calcined at 500 °C in air for 2 h, rendering the heterogeneous catalyst, which was stored in a desiccator until being used in the transesterification reaction. The chemical transesterification process to produce FAME was performed under reflux on a magnetic stirring heating mantle in a one-neck round bottom flask containing soybean oil and methanol, corresponding to a methanol:oil molar ratio of 100:1. Solid catalyst corresponded to 5% by weight relative to the amount of oil. The reactions were carried out at 60 °C for 7 h with the heterogeneous catalyst prepared and for 24 h with the pure, non-impregnated, silica-rich material. The reaction products were monitored by thin layer chromatography. After the reaction was complete, the solid catalyst was separated, and the liquid portion of the reaction medium was evaporated on a rotary evaporator to recover the methanol. The fraction containing the esters and the glycerol was transferred to a separator funnel. The glycerol was removed, and the ester mixture was washed with distilled water and kept in desiccator with magnesium sulfate as the desiccant. Analyzes to calculate the yields of biodiesel were carried out on an HP7820A gas chromatograph equipped with a flame ionization detector. A Supelcowax10 (Supelco) 15 m x 0.20 mm x 0.20 mm column was used with temperature gradient: 120 °C, 0 min, 10 °C/min to 240 °C; injector (split of 1/50) at 250 °C and detector at 260 °C. The drag gas used was hydrogen (4 mL min^{-1}). Data acquisition software was OPENLAB (Agilent).

RESULTS AND DISCUSSIONS

The SEM images of the silica-rich material are presented in Figure 1a. The EDX spectrum (Figure 1b), corresponding to the area delimited with the rectangle on Figure 1a, reveals signals due to silicon (87.3 mass%), iron (8.4 mass%) and aluminum (3.5 mass%); carbon is due to the sample preparation, for coating with graphite. The large amount of silica makes this sample suitable as a support for the prepared heterogeneous catalyst. The powder XRD pattern of the silica-rich geomaterial is presented in Figure 2. The corresponding XRD-pattern exhibits characteristic Bragg reflections corresponding to quartz (SiO$_2$; JCPDS card # 46-1045) and spikes indicating the occurrence of hematite (αFe$_2$O$_3$; JCPDS card # 33-664). The occurrence of hematite was confirmed from the Mössbauer data. The 298 K-Mössbauer spectrum was numerically fitted with three subspectra (Figure 3; corresponding spectral parameters in Table 1), two of them corresponding to sextets assignable to hematite (αFe$_2$O$_3$) and goethite (αFeOOH). The values of the parameters are reasonably close to those characteristically reported (e.g. Cornell and Schwertmann, 2003) for pure bulk hematite and goethite. The Fe^{3+} doublet may be assumed to be due to (super) paramagnetic species, either as iron (oxyhydr)oxides (likely including hematite or goethite) in very small particles or iron in the crystalline structure of aluminosilicates. The catalytic activity of this quartz-rich geomaterial containing iron oxides in the transesterification reaction was evaluated from the mass ratio of oil converted to methyl esters, starting from the fatty acids. The progress and completeness of the reaction were monitored by thin layer chromatography. No significant conversion was observed with the catalyst formed uniquely by the non-impregnated material, even after 24 h reaction. The reaction heterogeneously catalyzed with the catalyst prepared from the KI-impregnated quartz-rich geomaterial produced a rich conversion of triacylglycerol to metal esters after 7 h of reaction (Figure 4). The esters yield,

Table 1. Room temperature ^{57}Fe Mössbauer hyperfine parameters for the silica-rich material

| Fe site	δ/mm s^{-1}	2ε, Δ/mm s^{-1}	B_{hf}/T	RA/%
Hematite	0.367(2)	-0.207(4)	51.74(1)	58.3(5)
Goethite	0.38(3)	-0.24(5)	36.6(2)	33(1)
Fe^{3+}	0.45(7)	1.4(1)		8.7(5)

δ = isomer shift relative to αFe; 2ε = quadrupole shift; Δ = quadrupole splitting; B_{hf} = magnetic hyperfine field; RA = relative subspectral area.
The numbers in parentheses are uncertainties over the last significant digit, as a direct output from the least-squares fitting computer program.

Table 2. Comparison of fatty acid methyl esters (biodiesel) yields from heterogeneously catalyzed transesterification by KI supported on different matrices

Catalyst	Calcination		Oil type	Reaction temperature/ °C	Amount of catalyst (w/w oil)/%	Methanol:oil molar ratio	Reaction time/ h	Yield/ mass%	Reference
	Temperature/ °C	Time/ h							
KI/oyster shells	300	2	Soybean	60	3.5	6:1	4	85	Jairam et al. (2012)
KI/hydrotalcite/MgO	550	5	Soybean	70	5.0	20:1	8	90	Tantirungrotechai et al. (2010)
KI/m-SiO$_2$	600	3	Soybean	70	5.0	16:1	8	90.1	Samart et al. (2009)
KI/γFe$_2$O$_3$/a-SiO$_2$	500	1.5	Soybean	60	4.5	35:1	1.5	94.4	Macedo et al. (2016)
KI/γFe$_2$O$_3$/a-SiO$_2$	500	1.5	Macaúba Palm	60	4.5	30:1	8	94.1	Macedo et al. (2016)
KI/crystalline SiO$_2$	500	2	Soybean	60	5.0	100:1	7	95	This work

a: amorphous; m: mesoporous.
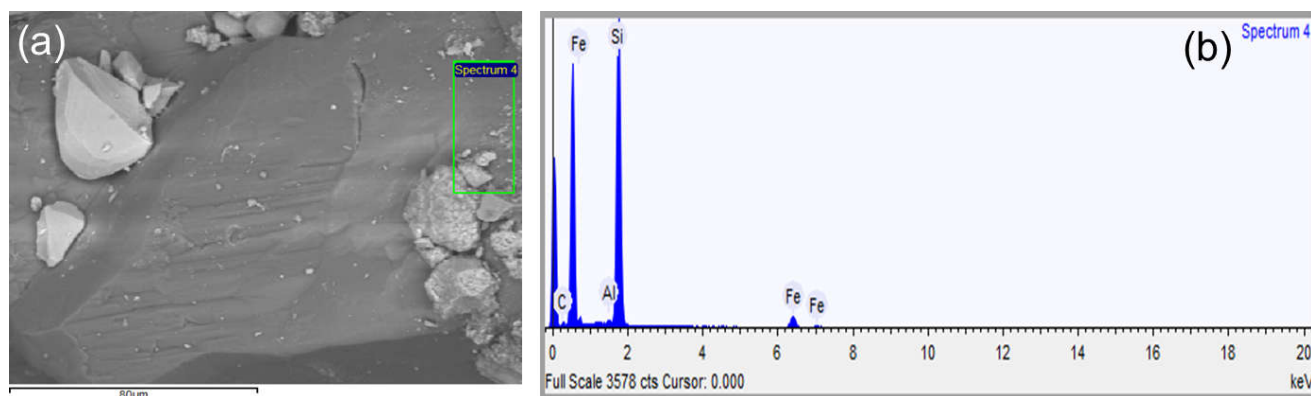
Figure 1. (a) SEM image (magnification, 5000x) and (b) EDX spectrum for the silica-rich material
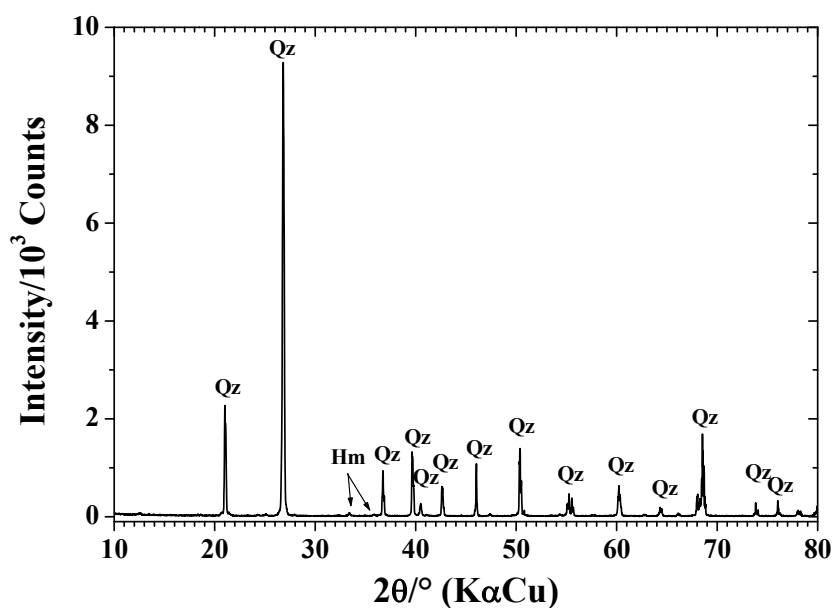
Figure 2. XRD pattern for the silica-rich material. Qz = quartz; Hm = hematite

determined with a gas chromatograph coupled to a mass spectrometer, was 95 ± 2 mass%. These results suggest that while impregnation KI onto the silica-rich support leads to a chemically effective catalyst, additional efforts need to be made to reduce reaction time and optimize chemical yields.

The methanol:oil molar ratio 100:1 is recognizably and probably still high, if a larger scale production plant is envisaged. Previously reported data by Macedo *et al*. (2016) for a comparable catalyst with amorphous silica from a building sand, also prepared by impregnating with KI, revealed a chemical conversion, for a similar transesterification reaction

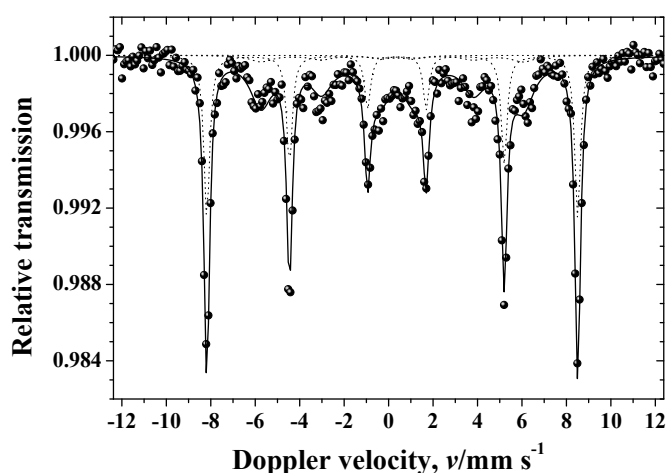at a methanol:soybean oil molar ratio 35:1, of 94.4% biodiesel, in 1.5 h.

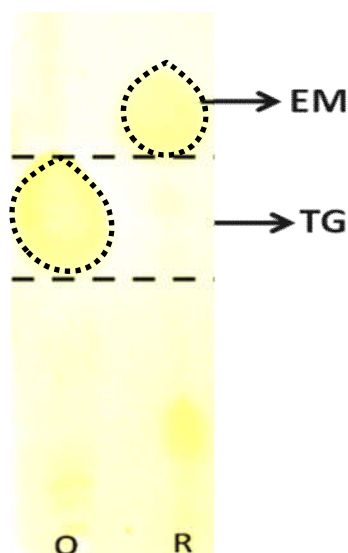**Figure 3. 298 K-^{57}Fe-Mössbauer spectrum for the silica-rich geomaterial**

Figure 4. Chromatographic thin-layer plate for the liquid medium after 7 h reaction with the silica-rich heterogeneous catalyst 5 wt% and methanol:oil molar ratio 100:1. Legend: O = soybean oil (reference); R = product of the catalyzed reaction; TG = triglycerol and EM= methyl esters

This may mean that the KI-impregnation on amorphous silica renders a chemically more active catalyst than on this more crystalline support. Also, the solid phase preparation and the reaction conditions are to be continuously optimized, in order to gain further potentiality towards scaling up the technology based on this heterogeneous catalyst process to produce biodiesel in any intended industrial scale. A more extensive data concerning the reported data related to similar processes with heterogeneous catalysts are listed in Table 2. The actual prospects for this KI-impregnated iron-containing species and crystalline quartz-rich geomaterial as an effective heterogeneous catalyst for the industrial production of biodiesel is indicated by these results.

Conclusions

This KI-impregnated crystalline quartz-rich geomaterial containing a residual amount of iron oxides, mainly hematite

(αFe_2O_3) and goethite ($\alpha FeOOH$), was found to be a chemically active heterogeneous catalyst to produce fatty acid methyl esters (FAME; biodiesel). The catalyst promoted a significant chemical conversion of triacylglycerols present in soybean oil to FAME, after 7 h, of about 95 ± 2 mass%. These results show advances in the use of low-cost SiO_2-rich waste materials, which are available in relative abundance in mining areas, to produce biodiesel in economically and environmentally from more sustainable chemical processes. Further chemical tests with this and other similar silica-rich geo- or synthetic-materials are now in progress, in an attempt to better identify the quantitatively most relevant chemical parameters involved in this heterogeneously catalyzed transesterification reaction of triacylglycerols in bio-oils,which govern the optimization of the industrial production of biodiesel.

REFERENCES

Anuar, M.R., Abdullah, A.Z., 2016. Challenges in biodiesel industry with regards to feedstock, environmental, social and sustainability issues: A critical review. Renew. Sustain. Energy Rev. 58, 208-223. doi:10.1016/j.rser.2015.12.296

Cornell, R.M., Schwertmann U., 2003. The iron oxides: structure, properties, reactions, occurrences and uses. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. ISBN 3-527-30274-3

Garcia, C.M., Teixeira, S., Marciniuk, L.L., Schuchardt, U., 2008. Transesterification of soybean oil catalyzed by sulfated zirconia. Bioresour. Technol. 99(14), 6608-6613. doi:10.1016/j.biortech.2007.09.092

Jairam, S., Kolar, P., Sharma-Shivappa, R., Osborne, J.A., Davis, J.P., 2012. KI-impregnated oyster shell as a solid catalyst for soybean oil transesterification. Bioresour. Technol. 104, 329-335. doi:10.1016/j.biortech.2011.10.039

Janaun, J., Ellis, N., 2010. Perspectives on biodiesel as a sustainable fuel. Renew. Sustain. Energy Rev. 14(4), 1312-1320. doi:10.1016/j.rser.2009.12.011

Ji, X., Long, X., 2016. A review of the ecological and socioeconomic effects of biofuel and energy policy recommendations. Renew. Sustain. Energy Rev. 61, 41-52. doi:10.1016/j.rser.2016.03.026

Liew, H.W., Hassim, M.H., Ng, D.K.S., 2014. Review of evolution, technology and sustainability assessments of biofuel production. J. Clean. Prod. 71, 11-29.doi:10.1016/j.jclepro.2014.01.006

Macedo, A.L., Fabris, J.D., Pires, M.J.M., Oliveira, W.L., Ardisson, J.D., Augusti, R., Aragón, F.H., Santos, R.S., Oliveira, L.C.A., Pereira, M.C., 2016. A mesoporous $SiO_2/\gamma Fe_2O_3/KI$ heterogeneous magnetic catalyst for the

green synthesis of biodiesel. J. Braz. Chem. Soc. 27(12), 2290-2299. doi:10.5935/0103-5053.20160124

Meher, L.C., Sager, D.V., Naik, S.N., 2006. Technical aspects of biodiesel production by transesterification – a review. Renew. Sustain. Energy Rev. 10(3), 248-268. doi:10.1016/j.rser.2004.09.002

Tantirungrotechai, J., Chotmongkolsap, P., Pohmakotr, M., 2010. Synthesis, characterization, and activity in transesterification of mesoporous Mg-Al mixed-metal oxides. Micropor. Mesopor. Mat. 128(1-3), 41-47. doi:10.1016/j.micromeso.2009.08.001

****