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APPLICATION OF ALUMINA-SUPPORTED 12-MOLYBDOPHOSPHORIC ACID AS HETEROGENEOUS CATALYST FOR BIODIESEL SYNTHESIS FROM NON-EDIBLE OIL

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ABSTRACT – *This study focuses on the optimization of the ethyl biodiesel production from macaw palm oil via heterogeneous acid catalyst. H_3PMo/Al_2O_3 catalyst was prepared, characterized and tested for single-step simultaneous esterification and transesterification. A central composite design (CCD) combined with response surface methodology (RSM) was employed to statistically evaluate and optimize the biodiesel production. Effects of variables: reaction temperature (100 - 200 °C), ethanol-to-oil molar ratio (20:1 - 60:1) and catalyst concentration (5 - 15%) on response variables ester content and viscosity were appraised. The variance analysis (ANOVA) indicated that the proposed models are well adjusted and statistically significant. The process achieved an optimum level of 99.8% ester content and $4.1 \text{ mm}^2 \text{ s}^{-1}$ viscosity at 190 °C, 50:1 ethanol-to-oil and catalyst concentration of 13%. The reusability of the catalyst was successfully tested in four subsequent cycles. The fuel properties such as density, monoacylglycerol and diacylglycerol contents were found to be within the limits set by both USA (ASTM D6715) and Brazil (ANP 45/2014) standards.*

1. INTRODUCTION

Heterogeneous acid catalysts are recommended for a direct biodiesel production from oils and fats with high free fatty acids (FFAs) contents due to generating cost reduction by using low-cost feedstocks (Abdullah *et al.*, 2017). Thereby, heterogeneous acid catalysis becomes an attractive alternative on account of its ease of product separation, high tolerance to elevated FFAs levels, use of technologies that reduce the amount of chemical waste generated along the process and reuse capability (Malins *et al.*, 2015). Although such factors contribute to cheapening the biodiesel production process, a high-activity catalyst that can overcome the presence of water and present high thermal stability is required (Sani *et al.*, 2014).

Recently, many studies regarding the use of heterogeneous acid catalysts in a simultaneous esterification and transesterification of feedstocks with high FFAs contents have been developed. Among them, heteropolyacids (HPAs) with the Keggin structure stand out, such as $H_3PW_{12}O_{40}$ (H_3PW) and $H_3PMo_{12}O_{40}$ (H_3PMo), due to presenting elevated acidity (strong Brönsted acids) (Chen *et al.*, 2016). However, there are limited number of published works on using H_3PMo as catalyst for producing biodiesel, which attaches great relevance to this study.



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Therefore, this study aims to synthesize, characterize and optimize the performance of a 12-phosphomolybdic acid catalyst supported on aluminum oxide ($\text{H}_3\text{PMo}/\text{Al}_2\text{O}_3$) through simultaneous reactions of esterification and transesterification for producing biodiesel from macaw palm oil (*Acrocomia aculeata*). A face-centered central composite design (CCD) and the response surface methodology (RSM) was used to determine optimal variable conditions for biodiesel production, such as reaction temperature, alcohol-to-oil molar ratio and catalyst concentration, taking ester content and viscosity as response variables.

2. MATERIAL AND METHODS

Macaw palm oil (acidity of $39.0 \text{ mg KOH g}^{-1}$) was obtained from Association of Small Farmers D'Antas (Minas Gerais, Brazil). Aluminum oxide (Calcined Alumina A-1) was donated by Alcoa Alumínio S.A. This compound, containing 98.8% Al_2O_3 and surface area of $67.70 \text{ m}^2 \text{ g}^{-1}$, was calcined at $300 \text{ }^\circ\text{C}/3 \text{ h}$ before use. 12-molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$), was purchased from the Vetec[®] Sigma-Aldrich. The catalyst $\text{H}_3\text{PMo}/\text{Al}_2\text{O}_3$ was prepared via incipient-wetness impregnation by dissolving the heteropolyacid mass in an alcoholic solution $70\% \text{ m m}^{-1}$ at room temperature, transferred to a ceramic crucible containing the support (Al_2O_3) and then mixed. The solid formed was dried ($100 \text{ }^\circ\text{C}/30 \text{ min}$), followed by calcination at $300 \text{ }^\circ\text{C}/1 \text{ h}$ in a muffle furnace, being this step repeated two additional times with a final calcination at $300 \text{ }^\circ\text{C}/3 \text{ h}$. Different impregnations, 10, 20 and 30% (m m^{-1}) H_3PMo relative to the support (Al_2O_3) were performed. The resulting catalysts were subjected to the analysis of surface acidity and preliminary catalytic tests performed under fixed conditions: $175 \text{ }^\circ\text{C}$, ethanol-to-oil molar ratio of 40:1 and catalyst concentration of 10%) to evaluate the catalyst activity and determine the best impregnation concentration of the catalyst to be employed throughout the study. These tests were also used to select the experimental range in the experimental design. The catalyst was characterized as described by Conceição *et al.* (2017). The catalyst activity was evaluated by simultaneous esterification and transesterification reaction of macaw palm oil with ethanol. Before the reactions, the catalyst was thermally activated at $120 \text{ }^\circ\text{C}$ for 2 h. All tests were performed on pressurized stainless-steel reactor (Parr Series 5500 HPCL Compact Reactors) equipped with an electrical heating jacket covering the reaction vessel. Reaction time and agitation parameters were set at 4 h and 700 rpm, respectively. The effects of the independent variables: temperature, ethanol-to-oil molar ratio and catalyst concentration on the response variables (ester content and viscosity) were evaluated employing central composite design 2^3 with four repetitions at the central point (Table 1). At the end of each run, the catalyst was recovered and the raw biodiesel purified by traditional procedure. The ester content was determined by gas chromatography (Varian, model CP 3800) according to Conceição *et al.* (2017) using methyl heptadecanoate (C17) as an internal standard reference. Ester content was expressed as mass fraction in terms of percentage. The catalyst regeneration and reusability were evaluated under consecutive batch runs. At the end of each run, the catalyst was recovered from the reaction medium by single filtration, washed three times with *tert*-butanol alcohol (10 mL) thermally activated at $120 \text{ }^\circ\text{C}/2 \text{ h}$ and used for another catalytic cycle, under the optimized reaction conditions.

3. RESULTS AND DISCUSSION

According to the initial tests, the $\text{H}_3\text{PMo}/\text{Al}_2\text{O}_3$ catalyst with 30% of H_3PMo impregnation showed the highest efficient, obtaining a product with better ester content (>



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80.0%) and viscosity ($6.7 \text{ mm}^2 \text{ s}^{-1}$). The XRD pattern presented the amorphous phase of alumina (amorphous halos) as well as characteristic peaks of H_3PMo crystalline phases. Moreover, the presence of such peaks in the $\text{H}_3\text{PMo}/\text{Al}_2\text{O}_3$ catalyst demonstrates that the heteropolyacid was dispersed on the alumina support, which was confirmed by SEM analysis showing that the H_3PMo was highly dispersed upon on all support surface leading to reduction of the specific surface area and evidences the success of impregnation. FTIR spectrum exhibited four bands in the range $1100\text{-}750 \text{ cm}^{-1}$. These bands are assigned at 1065 , 960 , 870 and 795 cm^{-1} , which are characteristics of the Keggin structure. The band at around 1635 cm^{-1} was equally pronounced in both materials, this band was attributed to O–H stretching vibration. The values of BET indicate a remarkable decrease between the BET surface area value of the Al_2O_3 support ($67.70 \text{ m}^2 \text{ g}^{-1}$) and $\text{H}_3\text{PMo}/\text{Al}_2\text{O}_3$ catalyst ($31.66 \text{ m}^2 \text{ g}^{-1}$) after impregnation. This reduction was attributed to the effect of H_3PMo deposition on the support, which resulted in partial blocking of the porous network, however, this is not a surprise when regarding the high H_3PMo loading of 30 wt%. The adsorption-desorption isotherms of N_2 and pore size distribution for the $\text{H}_3\text{PMo}/\text{Al}_2\text{O}_3$ showed typical characteristics of mesoporous material.

Table 1 presents the experimental matrix and results of ester content and viscosity. Analysis of variance (ANOVA) was performed for fitting second-order response surface model by least square method. Models were generated at 95% of confidence level for both variable responses, presenting values of R^2 and R^2_{Adj} higher than 97%.

Table 1 – Experimental design matrix for the transesterification of macaw palm oil

Run	Variable						Response	
	Temperature (°C)		Molar Ratio		Catalyst concentration (%)		Ester content (%)	Viscosity ($\text{mm}^2 \text{ s}^{-1}$)
1	100	-1	20	-1	5	-1	3.2	38.5
2	100	-1	20	-1	15	1	12.7	29.9
3	100	-1	60	1	5	-1	12.9	27.9
4	100	-1	60	1	15	1	14.7	29.4
5	200	1	20	-1	5	-1	90.5	6.3
6	200	1	20	-1	15	1	95.7	6.0
7	200	1	60	1	5	-1	96.5	5.4
8	200	1	60	1	15	1	98.8	5.2
9	100	-1	40	0	10	0	13.7	31.4
10	200	1	40	0	10	0	96.0	5.9
11	150	0	20	-1	10	0	93.2	6.4
12	150	0	60	1	10	0	96.2	6.5
13	150	0	40	0	5	-1	59.5	11.5
14	150	0	40	0	15	1	86.8	6.5
15	150	0	40	0	10	0	81.7	6.9
16	150	0	40	0	10	0	82.0	6.7
17	150	0	40	0	10	0	83.0	6.9
18	150	0	40	0	10	0	81.2	7.2

Based on the RSM analyses and the desirability results, the optimum conditions of the biodiesel production over the studied variables were: reaction temperature of $190 \text{ }^\circ\text{C}$, ethanol-to-oil molar ratio of 50:1 and catalyst concentration of 13%. Values of the ester content and viscosity predicted under these conditions were 99.8% and $4.1 \text{ mm}^2 \text{ s}^{-1}$, respectively. In addition to these excellent values, low values of monoacylglycerol (0.87%) and absence of diacylglycerol are extremely important for the product quality and indirectly shows the



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optimal conversion of macaw palm oil into esters. The values of these contaminants are very low and do not affect properties such as density, which presented the value of 880 kg m^{-3} , within the limits specified by the ANP Resolution N^o 45/2014 standard. Finally, three consecutive catalytic cycles of simultaneous esterification and transesterification reactions were carried out under the established optimal conditions. The $\text{H}_3\text{PMo}/\text{Al}_2\text{O}_3$ catalyst showed good catalytic stability maintaining ester content of over 87.0%, a reduction of approximately 12% from its original ester content and biodiesel viscosity below $6.0 \text{ mm}^2 \text{ s}^{-1}$ after the fourth cycle. These results are consistent with data from an investigation conducted by Talebian-Kiakalaieh et al. (2013), whereby the catalyst was reused in four cycles for producing biodiesel from waste cooking oil with high free fatty acid content, revealing an overall reduction of 15%.

4. CONCLUSIONS

The catalyst prepared from supporting H_3PMo in Al_2O_3 showed excellent activity in simultaneous esterification and transesterification reactions of macaw palm oil. The quality properties of the biodiesel obtained in this work were in good agreement with ANP specifications. In addition, the catalyst presented good regeneration and can be reused for up to four reaction cycles.

5. ACKNOWLEDGEMENTS

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