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Study of correlations between composition and physicochemical properties during methylic and ethylic biodiesel synthesis

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ABSTRACT

In this work, correlations between the physicochemical parameters (density and kinematic viscosity) and the composition of various samples, obtained during the biodiesel production process of methylic and ethylic soybean biodiesel, were investigated. The results point out that the composition of the medium in terms of remaining catalyst and its residues, alcohol and water content, among others variables, has no significant influence on the physicochemical properties studied. These findings are mainly influenced by the composition of the medium in terms of FAAE, TAG, DAG and MAG.

1. Introduction

The raw fat materials used for biodiesel production are mostly formed by triacylglycerides (TAG) that are converted to fatty acid alkyl monoesters (FAAE) and glycerol during the transesterification reaction. The transesterification process consists of three consecutive and reversible reactions that form diacylglycerides (DAG) and monoacylglycerides (MAG) as intermediate products (Suarez et al., 2007; Schwab et al., 1987).

Therefore, during biodiesel production, it is possible to detect the presence of unconverted TAG, DAG, MAG, alcohol, and the catalyst and its residues in the reaction medium in addition to FAAE and glycerol. Furthermore, if transesterification occurs using hydroxides or alkoxides as catalysts, water molecules are formed, which may also be present in the raw materials that are used. The presence of water causes the hydrolysis of TAG, DAG and MAG and leads to the formation of fatty acids (FA). The determination of the amount of each substance during the reaction process and its influence on the physicochemical properties is very important for the development and optimization of processes on both pilot and industrial scales.

Two situations can be observed during biodiesel production after a pre-determined reaction time and stirring ends: the formation of two phases or no phases. When two phases form, the top (oily phase) contains unconverted TAG, FAAE, DAG and MAG. In the lower stage (glycerol phase), it is possible to find glycerol, the catalyst and its residues, water formed or assigned to the process by the reactants, excess alcohol, and even smaller portions of esters and fatty acids. When there is no phase separation, all these substances are present as an emulsion, and it is possible to observe the formation of gels and soaps.

It has been established that the physicochemical properties of biodiesel are essentially determined by the composition of the reaction medium, and several studies revealed relationships between the properties and compositional features by studying mixtures of pure compounds (Knothe et al., 2005; Chuck et al., 2009; Su et al., 2011; Najafabadi et al., 2012). In this work, physicochemical parameters were determined to provide information that can be applied to the design and improvement of the process mostly used to obtain biodiesel (transesterification) and, consequently, to understanding the reaction medium behavior. To this end, samples that simulated actual reaction conditions were obtained and characterized by determining the amount of FAME (for methylic biodiesel) or FAEE

Abbreviations: FAAE, fatty acid alkyl monoesters; FAME, fatty acid methyl monoesters; TAG, triacylglycerides; DAG, diacylglycerides; MAG, monoacylglycerides; HPLC, high performance liquid chromatography; pH, potencial of hydrogen; FA, fatty acids.

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Table 1
Composition of the medium (FAME, TAG, DAG and MAG) and physicochemical properties (**phase separation**).

FAME[a] (wt.%)	MAG[a] (wt.%)	DAG[a] (wt.%)	TAG[a] (wt.%)	Viscosity ($mm^2 s^{-1}$)	Density ($kg m^{-3}$)	Water ($mg kg^{-1}$)	Acid number ($mg KOH g^{-1}$)	pH
35	6	20	39	17.56	0.920	10098	3.87	10.3
45	5	12	34	12.02	0.907	1866	0.50	9.4
49	7	12	35	12.01	0.909	[b]	[b]	[b]
50	4	12	34	10.02	0.897	[b]	[b]	[b]
51	3	11	35	8.50	0.899	[b]	[b]	[b]
52	3	11	34	10.52	0.897	[b]	[b]	[b]
54	4	12	31	8.64	0.896	[b]	[b]	[b]
55	13	7	25	8.79	0.903	7857	0.65	10.4
55	5	10	30	9.48	0.899	3409	0.45	9.3
57	6	11	27	8.84	0.904	5789	0.76	10.1
59	5	11	26	9.17	0.903	7048	3.19	9.8
60	3	11	27	9.57	0.899	10312	1.60	9.8
60	6	11	23	9.72	0.902	4726	0.62	[b]
79	2	5	14	5.71	0.889	1355	0.58	8.2
92	5	1	2	4.07	0.881	650	0.22	10.0
94	5	1	0	4.10	0.880	879	0.63	10.0

[a] Determined in purified oily phase.
[b] No determined.

(for ethylic biodiesel), MAG, DAG and TAG present. The density, kinematic viscosity, pH, acid number, water and alcohol contents were also determined.

More specifically, the physicochemical parameters were obtained during the biodiesel production process of methylic and ethylic soybean biodiesel by alkaline transesterification to: (i) simulate the reaction process on a laboratory scale; (ii) analyze the density, kinematic viscosity, pH and acid number; (iii) determine the composition of the medium in terms of water, alcohol, FAAE, TAG, DAG and MAG content, and (iv) define possible correlations between the physicochemical parameters for the various samples obtained during the reaction process and their composition.

2. Material and methods

2.1. Transesterification process

To obtain various samples that represent the process, methylic and ethylic transesterifications of soybean oil were performed in several reaction conditions. Sodium hydroxide was used as the catalyst (see Tables S1 and S2 in Supplementary material). In a typical experiment, a 2.0-L glass reactor that was fit to a mechanical stirring, heating and a condenser system was employed. After the established reaction time, the mixture was transferred to a 2.0-L separatory funnel, where it remained at rest for 3 h at 25 °C. After this time, two situations were observed: (i) a two phases formed or (ii) no phases formed. The samples were stored to determine their physicochemical properties.

To determine the composition of the TAG, DAG, MAG and FAAE (by HPLC) contents as well as the acid number, a sample was purified from the oily phase (phase separation) or from the mixture (no phase formation) by neutralization with 5% phosphoric acid (v/v), followed by washing with a brine until it reach a pH of 7.0.

2.2. Determination of physicochemical parameters and composition of samples

The properties were determided according to standard method: kinematic viscosity ($mm^2 s^{-1}$) by ASTM D445-15a, acid number ($mg KOH g^{-1}$ oil) and pH by ASTM D664-11a, density at 20 °C ($kg m^{-3}$) by ASTM D4052-15 and water content using ASTM D6304-07. The alcohol content was determined by a gravimetric test; 5 g of the sample was placed into a rotaevaporator with a water aspirator (vacuum system) for 45 min at 25 °C, and the mass loss (determined until weight constant) was calculated. All results were calculated based on the average of three samples.

The amount of FAAE, TAG, DAG and MAG was determined by HPLC using the method described in the literature (Carvalho et al., 2012) and one example is presented on Supplementary material (see Fig. S1).

The repetibility of the method was assessed by having one operator analyzing ten times the same sample on the same day, using the same apparatus. The standard deviation was 0.02 $mm^2 s^{-1}$ for kinematic viscosity, 0.001 $kg m^{-3}$ for density, 0.03 $mg KOH g^{-1}$ oil for acid number, 10 $mg kg^{-1}$ for water and 0.5% for alcohol content. In the case of FAAE% the value was 4% and for TAG, DAG and MAG was 2%, respectively. The mathematical tool used was Excel – Microsoft Office Professional Plus 2010, version 14.0.4760.1000.

In order to outline possible correlations between the physicochemical parameters for the various samples (simulating reaction process) and their composition, regression analysis were calculated using Origin®, version 6.0, Microcal (TM) Software, Inc. The values of coefficient of correlation (r) and coefficient of determination (r^2) are presented in Tables S3 in Supplementary material. Whenever the coefficient of correlation value is found between ±0.500 and ±0.749 the correlation is considered moderate and, if between ±0.750 and ±1.000, then it is an indicative of strong correlation (Colton et al., 1982). In the case that is possible to establish correlation, the linear regression equations are presented (Table S3).

3. Results and discussion

3.1. Correlations between the composition of the reaction medium and physicochemical parameters during methylic soybean biodiesel (FAME) obtention

Several samples that exhibited FAME ratios from 29 to 94% were obtained to represent the reaction process. It is important to highlight that the purpose of this work was not to determine the influence of reaction conditions on the amount of chemical species formed (FAME, TAG, DAG, MAG, water, etc.) because this issue has already been exhaustively discussed in the literature, and many reviews address this theme (Datta and Mandal, 2016; Hoekman et al., 2012; Knothe, 2005). As was mentioned in the experimental section of this paper, some reaction conditions and results in terms of the composition are presented in Supplementary material.

Tables 1 and 2 presents the results, which were calculated from the average of a triplicate analysis. These characterizations were