Hydroesterification of crambe oil (*Crambe abyssinica* H.) under pressurized conditions

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ABSTRACT

In this study the continuous production of esters from the hydroesterification (hydrolysis followed by esterification in two-step) of crambe oil was performed under pressurized conditions without a catalyst. For this purpose the effects of experimental variables were evaluated aiming to maximize the formation of free fatty acids (FFA) in the hydrolysis and the ester content in the esterification, keeping the pressure fixed at 15 MPa. Transesterification was also performed for comparative purposes. The results indicate that the combination of high temperature and the addition of a cosolvent (*n*-hexane), for a low oil to water mass ratio, favors the FFA formation. The kinetics reaction is fast and optimal conditions for the hydrolysis were identified as: temperature of 320 °C, water to oil mass ratio of 1:1, 75% of cosolvent and reaction time of 14 min. In the esterification step, increasing the temperature and molar ratio has a considerable effect and favors the FFA conversion and esters content for a residence time of $\leq$20 min, after which the thermodynamic equilibrium of the reaction was reached. The hydroesterification provided a higher esters content ($\sim$98%) compared to transesterification ($\sim$89%).

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1. Introduction

In the search for alternative raw materials the technological aspects of biodiesel production should be considered along with agronomic factors, such as the oil content, yield, production system and crop cycle (Rogério et al., 2013). Since the raw material represents around 75% of the total production cost, the selection of an oilseed with lower added value is vital to ensure a competitive cost for the biofuel (Atabani and César, 2014). According to the Brazilian National Petroleum Agency (ANP, 2015), most of the biodiesel produced in Brazil is obtained from soybeans and, since this is a crop mainly grown for human consumption, research on the exploitation of other oilseed crops with the potential to provide biodiesel has been identified.

Crambe oil (*Crambe abyssinica* Hochst) is an attractive option for biodiesel production because it is drought tolerant, has a cycle of approximately 90 days and the total seed yield is around 1000–1500 kg per hectare (Falasca et al., 2010; Viana et al., 2013). The oil content of crambe seed is 48–60% (Silva et al., 2013; Santos et al., 2015), and it has a high content of erucic acid (50–60%), which is toxic, causing heart disease through increased cholesterol levels and lipidosis in the heart tissues, and thus the oil is unsuitable for human consumption (No et al., 2013). Crambe oil can therefore only be used for industrial purposes such as biodiesel production.

Crambe oil is obtained by extraction through pressing and is not passed through a refining process. Thus, the free fatty acids (FFA) content is above that suitable for processing by the conventional biodiesel production method, which can be applied to raw materials containing up to 1% of FFA and 0.06% of water (Dermibas, 2009). For the processing of vegetable oils with high acidity, hydroesterification can be applied, since this process permits the use of low quality raw materials, which are completely converted into esters. Therefore, instead of decreasing the acidity of the feedstock through a refining process, in the hydrolysis step the acidity is increased.

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Subsequently, the hydrolyzate is esterified and fatty acid esters are obtained with water as a byproduct.

The processes generally employed in hydrolysis are catalytic, via chemical or enzymatic routes. The chemical process involves acid catalysis, generally conducted in the presence of sulfuric acid (Ngaosuwan et al., 2009), and alkaline catalysis using sodium and potassium hydroxide (Asai et al., 1997). The use of such catalysts requires long reaction times (20–48 h), besides causing oxidation and dehydration of the products obtained, resulting in a dark colored product, which requires purification to remove the color and excess catalyst (Castro et al., 2004). Enzymatic catalysis has recently been used in hydrolysis reactions. However, it presents several technical difficulties, including long reaction times, loss of enzyme activity with increasing temperature and contact with certain solvents, in addition to the high cost of the catalyst (Hama and Kondo, 2013).

The esterification of the hydrolyzate, which is rich in free fatty acids, is usually carried out via a catalytic route using homogeneous acid catalysts (Brinks et al., 2013). However, the use of this type of catalysts is associated with slower reaction rates and difficulties related to the separation and purification of the final product (Christopher et al., 2014). Enzymatic catalysis can also be applied in the esterification reaction, however, as mentioned above, the high cost of the enzymes and long reaction times are significant disadvantages. Moreover, studies have shown that the enzymes are easily deactivated by the alcohol used (Hama and Kondo, 2013).

To minimize the problems associated with the use of catalysts in reactions for biodiesel production, the recent literature reports the application of technology involving fluids under sub- or supercritical conditions, without the addition of a catalyst in the process (Minami and Saka, 2006; Silva and Oliveira, 2014). The properties of a fluid under these conditions are intermediate between a gas and a liquid and one of the advantages is that many of the physical properties, such as density, dielectric constant and solubility, can be easily adjusted through slight variations in the temperature and pressure (Wen et al., 2009).

Water in the subcritical state (10–20 MPa and 270–350 °C) has recently been used in hydrolysis reactions. Since the water temperature is high there is a reduction in the polarity, which is due to a decrease in the dielectric constant. In addition, the kinetic energy of water also increases, resulting in a greater distance between the molecules. In the subcritical region, water has properties (density and dielectric constant) similar to an organic solvent at room temperature. This allows an increase in the reaction rate without using a catalyst (Carr et al., 2011). Subcritical water is a technically feasible and environmentally acceptable alternative in comparison with water in the supercritical state, which is associated with serious hazards since it is toxic, flammable, explosive and corrosive (Shin et al., 2012; Kansedo and Lee, 2014).

In the esterification step, the alcohol used under pressurized conditions shows an autocatalytic mechanism due to dissociation of the free fatty acids in the reaction medium under these conditions (Akgün et al., 2010). Thus, catalysts are not used in the process, eliminating their cost and the need to remove them from the final product (Pinnarat and Savage, 2010). The use of elevated temperatures and pressures in the method leads to a higher reaction rate compared to the conventional alkaline method due to decreased mass transfer limitations resulting from the high miscibility between the substrates (Alenezi et al., 2010a; Abdala et al., 2014a).

In this context, the aim of this study was to evaluate the continuous production of esters from the hydroesterification of crambe oil under pressurized conditions. The effects of the experimental variables were investigated in the hydrolysis step in order to maximize the production of free fatty acids, and the residence time was also studied. In the esterification step the effects of the temperature, ethanol to FFA molar ratio and residence time on the FFA conversion and esters content were investigated. Transesterification was also performed for comparison purposes. The results of this study contribute to research on the production of crambe biodiesel and the use of hydroesterification under pressurized conditions, for which there are very few reports available in the literature.

2. Materials and methods

2.1. Materials

Crambe oil, donated by the MS Foundation, and water, from a Millipore (ZICW300UK) deionization system, were used as substrates in the hydrolysis reactions. Ethanol (JT Baker, 99.8%) was used in the esterification and transesterification reactions. n-Hexane (Anidrol) was used as a cosolvent in the hydrolysis and transesterification reactions. In the determination of the FFA content and composition and the glycerol and ethyl esters content as well as the qualitative analysis by thin layer chromatography the following reagents were used: sodium hydroxide (Anidrol, 97%), ethyl ether (Anidrol), ethanol (Anidrol, 95%), phenolphthalein (Nuclear), the derivatizing agent BF_3-methanol (Sigma-Aldrich), sodium periodate (Vetec), ethylene glycol (Vetec, 99.5%), sulfuric acid (Anidrol, 98%), bromothymol blue (Synth), heptane (Anidrol), n-hexane (Anidrol), acetic acid (Nuclear), silica-coated plates (Polygram Sil G), solid iodine (Synth, 99.8%), 3 Å molecular sieves (Sigma-Aldrich) and methyl heptadecanoate (Sigma-Aldrich, 99.9%).

2.2. Oil characterization

The crambe oil used was characterized in terms of the free fatty acids content, fatty acids composition and water content, using the official methods recommended by the AOCS (1990): Ca 5a-40, Ce 2-66 and 984.20, respectively. After derivatization, the fatty acids composition was determined using the method described by Trentini et al. (2016).

2.3. Experimental procedure

The reactions were carried out in a tubular reactor with a packed bed, the specifications for which are given in detail by Abdala et al. (2014b). The reactor had a void volume of 60.7 mL and was made of stainless steel tubing (6 m, 316 L 1/4 in outer diameter (OD) and inner diameter (ID) 3.2 mm HIP) and stainless steel tubing (0.15m, 304 L 30.5 mm OD and ID 13 mm HIP). Fig. 1 shows the schematic diagram of the experimental apparatus used. The substrates were kept under constant stirring using a mechanical stirrer (IKA® RW 20 D) and pumped through an isocratic pump (Waters, 515 HPLC) at a given volumetric flow rate until the reactor was filled. The reaction temperature was monitored using three thermocouples (Salvi Casagrande) coupled to the reactor and the system pressure was controlled by a pressure control valve (Swagelok) and monitored by a pressure indicator (Record). The residence time was computed by dividing the void volume of the reactor (mL) by the flow rate of the substrates (mL min^{-1}). After passing through the reactor the reaction mixture was sent to a cooling system maintained at 10 °C by a thermostatic bath with circulation (Tecnal, TE-184).

At the end of the hydrolysis reaction, samples were placed in a centrifuge (Quimis, Q222E) and submitted to centrifugation for 15 min at 3500 rpm, to remove the glycerol. The oil phase was again transferred to a sample bottle and left in an oven with air circulation (Marconi, MA035) at 80 °C until constant weight. For the samples taken during the esterification and transesterification steps and at the end of the reaction, unreacted ethanol was removed in an oven with circulation (Marconi, MA035). Next, 2 mL