

Research article

Production of esters from soybean oil deodorizer distillate in pressurized ethanol



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ABSTRACT

The aim of this study was to obtain esters from soybean oil deodorizer distillate (SODD) in pressurized ethanol without the use of a catalyst. Experiments were carried out to evaluate the effects of the operating variables (pressure, temperature, residence time and ethanol to free fatty acids molar ratio) using a minimum factorial experimental design. The results indicate that increasing the temperature, pressure and residence time in the reactor enhanced the conversion of free fatty acids (FFA) while increasing the ethanol to FFA molar ratio decreased the conversion. The experiment carried out under optimum conditions (20 MPa, 275 °C, 20 min and ethanol to FFA molar ratio of 7:1) reached ~87% of FFA conversion. The reaction kinetics was investigated at different temperatures and the results obtained reveal that a high rate of FFA consumption and conversions close to the thermodynamic equilibrium were quickly reached. At high temperatures (325 and 350 °C) the conversion decreased with increasing residence time, indicating that the reverse reaction occurred. The reaction in two steps increased the FFA conversion, indicating that the conversions obtained were close to the thermodynamic equilibrium and the removal of water between the steps shifted the equilibrium, making it possible to achieve higher FFA conversion and ester yields.

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1. Introduction

Soybean oil deodorizer distillate (SODD) is one of the by-products generated during the soybean oil refining process [1]. This residue contains high levels of free fatty acids (3 to 60%) and triacylglycerols (45 to 55%), tocopherols and sterols [2–4]. Its generation reaches values of 0.3 to 0.5% of the crude oil processed and since SODD has no application in the soybean oil industry it is treated as a waste product [5].

The presence of high concentrations of free fatty acids and triglycerides makes SODD attractive for the production of esters (methyl or ethyl). In addition, considering the low value associated with this residue, it is competitive when compared to the refined vegetable oils used in food products, such as soybean oil, thus avoiding competition between the food and biofuels industries for arable land [6,7].

Ester production from SODD cannot be performed using alkaline homogeneous catalysis, since a high concentration of free fatty acids in the residue results in the saponification reaction which inhibits the separation processes and reduces the reaction yield. The esterification of free fatty acids can occur in the presence of a homogeneous catalyst with

acid activity, such as sulfuric acid [8]. Unlike alkaline catalysts, the use of acid catalysts does not lead to the saponification of free fatty acids, but rather to their esterification. However, the rate of ester formation in processes employing acid catalysts is lower than in those using alkaline catalysts [9]. Furthermore, the use of any type of homogeneous catalyst generates charge neutralization and the removal of the residual catalyst increases the total production costs [1]. This can be solved by the use of heterogeneous acid catalysts such as ion exchange resins [10] which are easily separated from the reaction medium, however, the reaction time of the process could be > 5 h.

The use of an alcohol in the reaction under sub- or supercritical conditions avoids the use of a catalyst and reduces the time required for high conversions to be achieved, enabling the use of fats and oils with high acid content [11–14]. The main advantages of using pressurized conditions to obtain esters are: increased solubility of the free fatty acids and triacylglycerols in alcohol; facilitated mixing of the reactants; improved mass transfer in the system; and ease of separation and purification of the products after the process [14].

In Brazil, the production of ethanol is high and it is obtained from renewable sources, adding to its attraction as a biodiesel [13]. The use of ethanol makes biodiesel production more environmentally friendly, reducing the need for fossil fuels [15]. Furthermore, with the use of ethanol under pressurized conditions for biodiesel production yields similar

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to those obtained using methanol can be attained [16]. However, the processing of SODD in pressurized ethanol to obtain esters is still little explored in the literature.

In this context, the aim of this study was to investigate the effect of the operational variables (temperature, pressure, ethanol to FFA molar ratio and residence time) on the conversion of the FFA in SODD, to obtain the kinetics of the reaction at different temperatures and to perform the reaction in two steps with the intermediate removal of water.

2. Materials and methods

2.1. Materials

The substrates used were soybean oil deodorization distillate (SODD) donated by Cocamar Cooperativa Agroindustrial (Maringá-PR) and ethanol (JT Baker, 99.8% purity). In the analysis for the SODD characterization and the determination of the FFA conversion and ester content the following reagents were used: hydrochloric acid (Synth, 38%), potassium hydroxide (Anidrol, 85%), *n*-hexane (Anidrol, 98.5%), silica gel 60 (Macherey-Nagel), methanol (Panreac, 99.9%), ethyl ether (Anidrol, 99.5%), ethanol (Anidrol, 95%), sodium hydroxide (Anidrol, 97%), phenolphthalein (Nuclear) and methyl heptadecanoate (Sigma-Aldrich Chemical Co, >99% purity).

2.2. SODD characterization

The FFA content was determined according to AOCS method Ca 5a-40 [17] and the water content was quantified using a Karl Fischer titrator (Orion, AF8). Hydrolysis of the SODD was conducted to determine the maximum FFA content that can be obtained from the mono-, di- and triglycerides present in the residue, as reported by Salimon et al. [18]. The polar compounds were determined using a methodology adapted from Dobarganes et al. [19], in silica gel, activated at 400 °C for 4 h and quenched with 5% water, as the stationary phase.

2.3. Experimental procedures

The experimental apparatus used in this study (Fig. 1) was previously employed in the studies by Doná et al. [20] and Abdala et al. [21]. 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. [21]. To carry out the reactions, the substrates were kept under constant stirring (IKA RW20) and pumped using a high pressure liquid pump (Waters 515 HPLC) for the time needed to fill the reactor. The reaction

temperature was monitored by three thermocouples (Salvi Casagrande) coupled to the reactor. The 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). Before sampling, the reaction mixture passed through the cooling system which consisted of a serpentine submerged in a bath with water circulation at 10 °C connected to a thermostatic bath (Tecnal, TE-184).

The unreacted ethanol was evaporated in an oven with air circulation (Marconi, MA035) at 80 °C. In the next step, 2 mL of *n*-hexane and 2 mL of distilled water were added to the samples, which were transferred to centrifuge tubes and separated by centrifugation (Quimis, Q222E) under rotation at 3500 rpm for 15 min. The supernatant was transferred to sample vials and kept in an oven at 80 °C until constant weight.

For the determination of the optimum levels of the variables, in order to maximize the FFA conversion, a minimum factorial experimental design with three levels was used, including three runs at the central point, generated by Statistica® 8.0 software. The levels employed for the independent variables are shown in Table 1.

Analysis of variance was used to evaluate the effect of independent variables on the responses and experimental data were fitted to second-order polynomial model including interaction effect of linear terms. The generalized model used was expressed by Eq. (1).

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^4 \beta_{ij} X_i X_j \quad (1)$$

where β_0 , β_i , β_{ii} and β_{ij} are regression coefficients (β_0 = constant term; β_i = linear effect; β_{ii} = quadratic effect; β_{ij} = linear interaction term) and Y is the response variable (conversion) observed in the experiments. X_i and X_j are the independent variables: temperature, pressure, residence time and ethanol to FFA molar ratio.

Experiments to obtain the reaction kinetics were carried out at different temperatures (from 250 to 350 °C), maintaining the ethanol to FFA molar ratio fixed at 7:1 and the pressure at 20 MPa, based on the results obtained from the experimental design conducted.

To carry out the reaction in two steps a sufficient amount of sample was collected at the reactor outlet after reaching the steady state. After the sample collection, the residual ethanol and water formed were removed following the procedures described above for the treatment of the sample for analysis. Ethanol was added to the sample obtained and the reaction was carried out as described above.

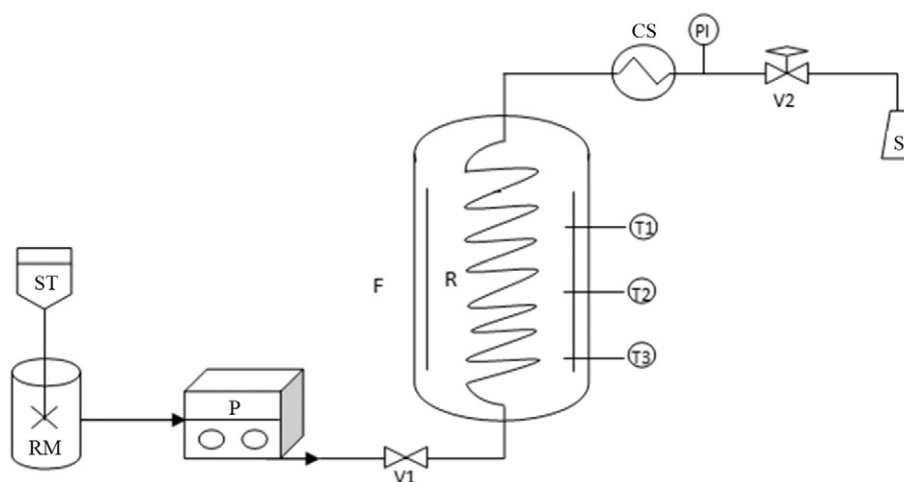


Fig. 1. Experimental apparatus for reactions under pressurized conditions (ST – stirrer; RM – reaction mixture; P – high pressure pump; F – furnace; R – reactor; CS – cooling system; S – sample).

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