

Fatty Ethyl Esters Production from Soybean Oil in Continuous Mode with Supercritical Ethanol and Propane as Cosolvent

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Abstract. This work aims to investigate a continuous supercritical process for the biodiesel production using propane as cosolvent, evaluating the production of fatty acid ethyl esters from soybean oil in supercritical ethanol using a continuous catalyst-free process. Experiments were performed in a tubular reactor evaluating the effects of temperature (523 K to 623 K), pressures up to 20 MPa, oil to ethanol molar ratio from 1:10 to 1:100, n-propane concentration up to 20 molar % in relation to ethanol, and reaction time from 3 to 30 min. Results showed that the best condition to produce ethyl esters from soybean oil was at 623 K, molar ratio of vegetable oil-to-ethanol of 1:40, reaction time of 30 min without using of cosolvent.

Keywords: Biodiesel, non-catalytic, supercritical, cosolvents.

1. Introduction

The ambient impact of petroleum production has induced the research of alternative sources of energy. Among these sources, the biodiesel has been received much attention in the last years. The biodiesel (fatty acid esters) from vegetable oil (soybean, sunflower, safflower, rapeseed, cottonseed, castor, among others) is an alternative to diesel of petroleum and comprise a non-toxic, biodegradable and renewable source (Ma and Hanna, 1999; Srivastava and Prasad, 2000; Fukuda et al., 2001; Altin et al., 2001). The transesterification of vegetable oils is currently performed using homogeneous acid or basic catalysts, but these processes are strongly dependent of raw-material purity, and present high ambient impact in the purification steps. Heterogeneous catalysts and enzymes are being investigated to suppress the inconvenient of these homogeneous processes (Ma and Hanna, 1999; Fukuda et al., 2001). On the other hand, the slow kinetic and high cost of these catalysts is the main reason for the limited used of these systems.

Saka and Kusdiana (2001), Kusdiana and Saka (2001a,b, 2004a,b) and Demirbas (2002) proposed a process for biodiesel production using supercritical methanol in batch mode. The main advantages of this process are the non dependence of the raw-material purity and the fast kinetics of the process. After these works, many investigations are available in the literature regarding the use of supercritical methanol in the biodiesel production, most of them in batch mode. In the last years, some works can be found regarding the development of continuous

process using methanol as solvent/reactant (Bunyakiat et al., 2006; He et al., 2007; Anitescu et al., 2008) and ethanol as solvent/reactant (Silva et al., 2007; Vieitez et al. 2008a,b).

In the supercritical process, high temperatures and pressures are the main limitation of the technique. Cao et al. (2005) and Han et al. (2005) reported that the addition of small amounts of cosolvents (propane and carbon dioxide) could improve the kinetic of the reaction and decrease the severity of process conditions for batch supercritical methylic biodiesel production. Although similar results were obtained for both cosolvents, results obtained in those works indicated that n-propane is a better cosolvent than carbon dioxide for this purpose. The main objective of this investigation is to develop a continuous supercritical process for ethylic biodiesel production using propane as cosolvent. The effects of temperature (523 to 623 K), residence time (3 to 30 minutes), oil to ethanol molar ratio (1:10 to 1:100), propane concentration (0 to 20 molar% in relation to ethanol) and distinct total volume of the tubular reactor were investigated on the esters conversion in the supercritical ethanol transesterification of soybean oil.

2. Materials and Methods

2.1. Materials

Commercial refined soybean oil (Soya), ethanol (Merck 99.9%) and n-propane (White Martins, 99.5% liquid phase) were used without further purification. For the chromatograph analyses, methyl heptadecanate (Sigma-Aldrich) was used as internal standards. Ethyl esters standards (ethyl palmitate, stearate, oleate, linoleate, and linolenate from Sigma-Aldrich) were used for the esters quantification.

2.2. Methods

The schematic diagram of the experimental unit used in this work is presented in Figure 1. The reactions were carried out using tubular reactor (stainless steel 316L, 1/8" OD) with capacity of 15 and 30 mL. The substrates, ethanol and oil, placed in container were mixed by means of a mechanical stirring device and then fed into the reaction system by a HPLC pump (Acuflo, Digital Series III). Cosolvent (propane) was added to the system by a syringe pump (Teledyne Isco, 260D). The tubular reactor was placed in an oven and the temperature was monitored by two thermocouples connected at the inlet and outlet of the reactor. The reaction temperature was controlled with a precision better than 1.5 K. The pressure was monitored by a back pressure regulator (Swagelok, KHB1WOA4C6P60000). The reactional mixture was pumped by the HPLC pump at a constant flow rate and once the whole system was stabilized, it was operated during at least two residence times, and then samples were collected for the chromatographic analysis.

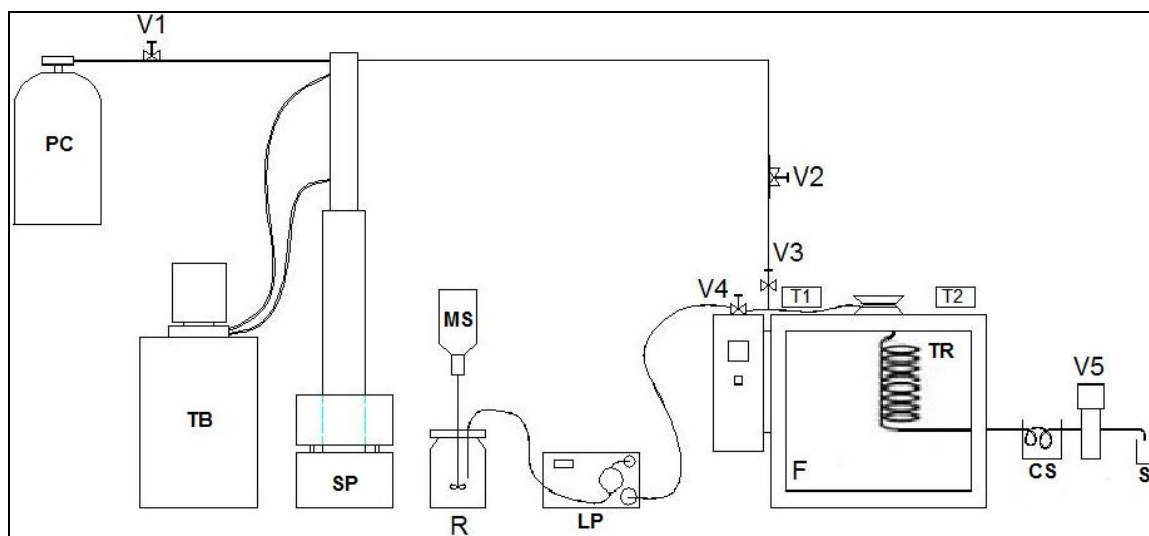


Figure 1. Schematic diagram of the experimental unit. PC–Propane cylinder; TB–Thermostatic Bath; SP–syringe pump; R–reactional mixture; MS–mechanical stirring; LP–high-pressure liquid pump; F–oven; TR–tubular reactor; T1–temperature indicator at the reactor inlet; T2–temperature indicator at the reactor outlet; CS–cooling system; V1,V2,V3 and V4 - feed valve; V5 - Back Pressure Regulator; S - sample collector.

2.3. Sample preparation and Chromatographic analysis

Around 500mg of the sample were collected and transferred for a test tube, where it was added 400 μ L of saturated solution of NaCl and 4 mL of hexane. The mixture was homogenized in a vortex by 1min and, after phase separation, the upper phase (esters) was transferred to a 10 mL calibrated flask and the volume completed with n-hexane. Afterward, 100 μ L of this solution was transferred to a 1 mL flask and added 250 ppm of the internal standard methyl heptadecanate.

1 μ L of the solution was injected in triplicate in a gas chromatograph (GC VARIAN CP-3800), equipped with a FID detector. A DB-WAX (30 m x 0.25 mm x 0.25 μ m) capillary column. The oven of the equipment was programmed from 443 K, holding 1 min, heating to 483 K at 283 K/min, holding 1 min, and to 503 K at 278 K/min, holding 2 min. Nitrogen was used as carrier gas, and the injection and detector temperatures were 503 K, using a split ratio of 1:20. Conversions were calculated based on the chromatographic areas of the compounds and the injection of authentic standards.

3. Results and Discussion

Figure 2 presents the effect of temperature for distinct residence times and total volume of the tubular reactor. It is important to mention that in this work the residence time was defined as the reactor volume (15 or 30 mL) by the volumetric flow rate of the HPLC pump. It can be observed in this figure that the conversion in esters is increased with the temperature independent of the reactor volume for both residence times and reactor volumes investigated.

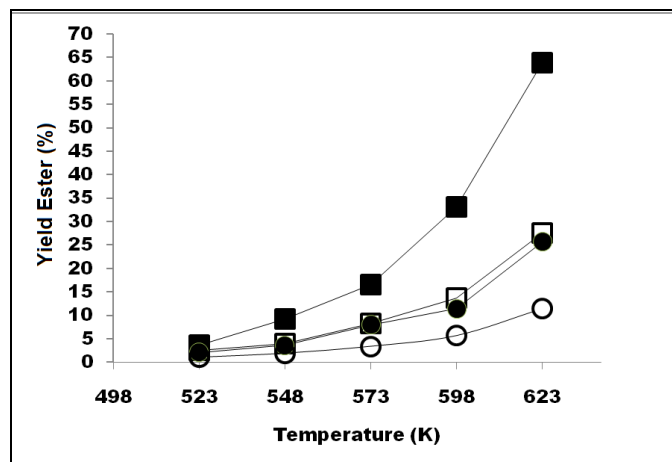


Figure 2. Effect of temperature on the conversion in ethyl ester at 20 MPa. Oil:ethanol molar ratio of 1:40 and 0% of propane. Reactor 30 mL: (■) 30 min and (□) 15 min. Reactor 15 mL: (●) 15 min and (○) 7,5 min.

Figure 3 presents the experimental results for distinct residence times, showing a continuous increase in the conversion to ethyl esters. The results suggest that the thermodynamic equilibrium was not attained in the experimental range investigated.

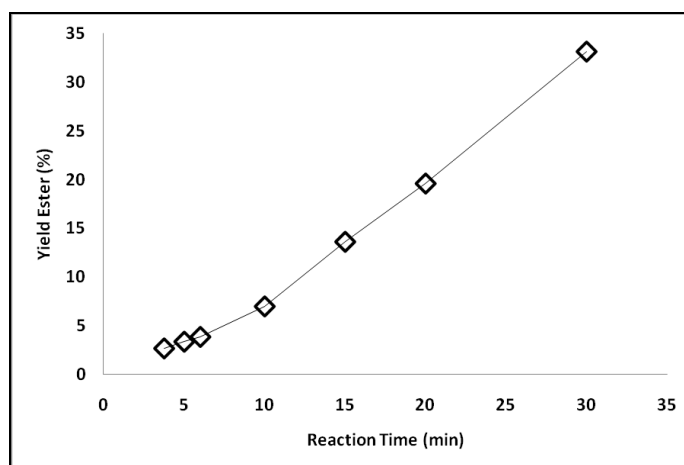


Figure 3. Effect of residence time on the soybean oil conversion in ethyl ester at 598 K, 20 MPa, oil:ethanol molar ratio of 1:40 and 0% of propane.

Figure 4 presents the effect of ethanol:oil molar ratio (MR) on the ethyl ester conversion. It can be observed a slight decrease in the esters conversion up to MR of 40 and then a stabilization of the conversion. Two antagonist effects are present and should be consider in the reaction conversion. In general, it should be expected an increase in the conversion as the MR is increased, as the higher concentration of the reactants should displace the reaction toward products side. On the other hand, the enhancement of alcohol content in the reaction mixture also dilutes the concentration of oil, and in this sense could decrease the reaction conversion.

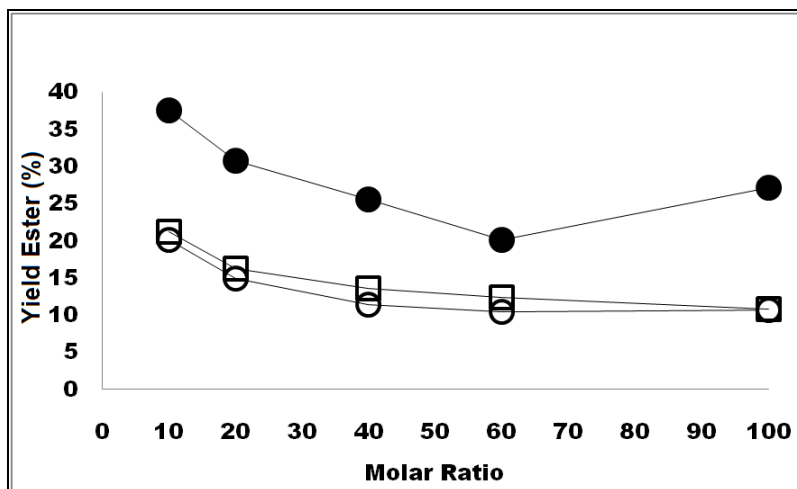


Figure 4. Effects of oil:ethanol molar ratio on the ethyl ester conversions at 20 MPa, residence time of 15 min and 0% of propane. Reactor 30 mL: (□) 598 K. Reactor 15 mL: (●) 623 K and (○) 598 K.

Figure 5 presents the results of propane addition for the reactor of 1/8" of external diameter with volumes of 15 and 30 mL. The results indicate that the propane addition up to 20% in molar basis leads to small reductions in the reaction conversion to ethyl esters. It is also observed that the reactors of 15 and 30 mL behave quite similar, with very good reproducibility. Similar results of decrease of conversion with the addition of a cosolvent in the non-catalytic continuous biodiesel production in supercritical ethanol was observed by Bertoldi et al. (2009), using carbon dioxide as cosolvent.

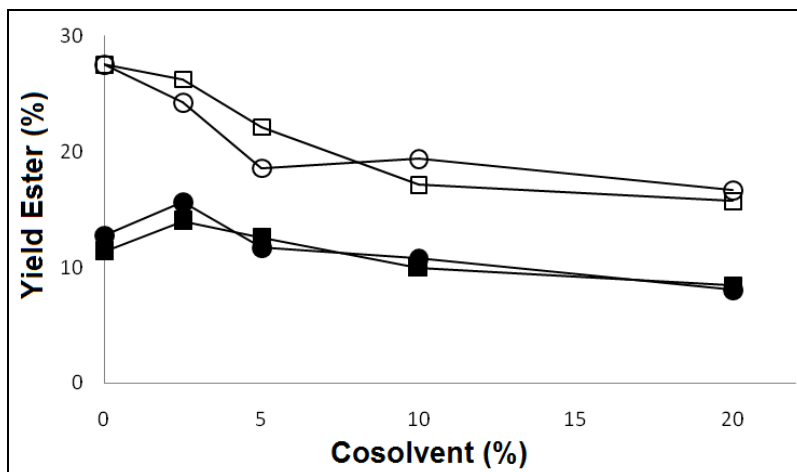


Figure 5. Effect of the propane addition on the ethyl esters conversion. MR 1:40, residence time of 15 min, 20 MPa. (■) 598K-30mL; (●) 598K-15mL; (□) 623K-30mL; (○) 623K-15mL.

Figure 6 presents the results of the propane addition in distinct residence times and temperatures. It can be observed in this figure that independent of temperature or residence time, the effect of the propane addition as cosolvent is quite similar, leading to a small decrease in the conversion with the increment of the concentration. The results presented by

Cao et al. (2005) and Han et al. (2005) indicated that the propane or carbon dioxide addition increase the reaction conversion, permitting to work at lower temperatures. On the other hand, the studies were performed with methanol and in mixed batch reactor, where possible phase separation effects are minimized. Some authors reported that phase separation could be present in the experimental reaction conditions investigated (Hegel et al., 2007; Anitescu et al., 2008). The results presented by Hegel et al. (2007), on the other hand indicated better results without using cosolvent. Bertoldi et al. (2009) investigated the addition of carbon dioxide as cosolvent for the non-catalytic production of ethyl esters of soybean oil in a tubular reactor and observed that the addition of this cosolvent (20% in mass) leads to an expressive decrease on the reaction conversion in esters. Although propane also promotes a decrease in the conversion, this effect is less pronounced than in the case of carbon dioxide.

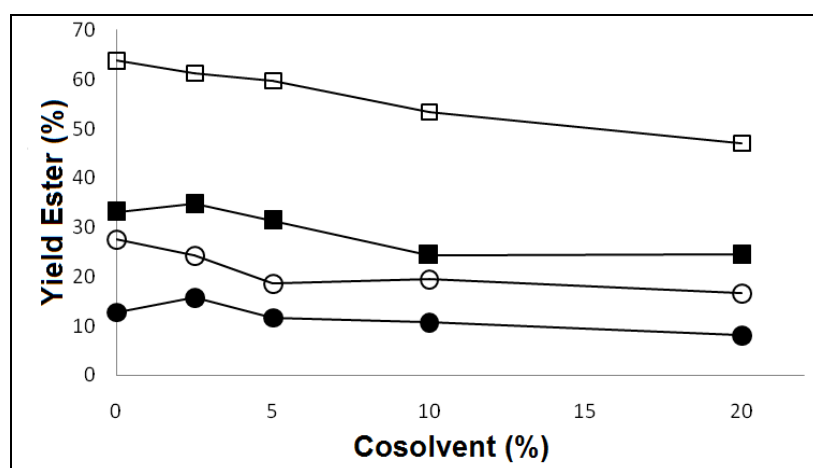


Figure 6. Effect of propane addition on the ethyl esters conversion. MR 1:40, 20 MPa and Reactor volume 30 mL. (■) 598K/30min; (●) 598K/15min; (□) 623K/30min; (○) 623K/15min.

4. Conclusions

This work reported experimental data on ethyl esters production from soybean oil in a continuous tubular reactor using propane as cosolvent, evaluating the influence of temperature, reaction time, oil to ethanol molar ratio, cosolvent concentration in relation to ethanol and reactor volume. In the experimental range investigated, reasonable yields were achieved at 623 K, 20 MPa, MR of 1:40, and without using propane. Results demonstrated that the conversion in esters decreased with increasing cosolvent addition, and that total volume of the 1/8" tubular reactor did not present effect on the conversion.

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