

Biodiesel Purification using an Ion Exchange/Adsorbent Resin with Regeneration through Supercritical Fluids

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The glycerol desorption from the ion exchange and adsorbent resin Purolite[®] PD206 was studied using conventional and supercritical fluids techniques. Untreated biodiesel was purified by dry washing using the resin and, after purification, the glycerol desorption was carry out using three diferent solvents: absolute ethanol under atmospheric conditions at different mass flows (10 and 30 g/min), or supercritical CO₂, or ethanol-modified supercritical CO₂ (35:65 molar ratio of ethanol:CO₂). In the supercritical runs the pressure was 14 MPA, temperature was 110 and 130°C, and mass flow rates were 10 and 30 g/min. Results have showed that ethanol is an efficient co-solvent for this resin regeneration. Desorption kinetics showed that it is possible to carry out the resin regeneration in just seven minutes using supercritical fluids, while using absolute ethanol under atmospheric conditions it is necessary around 210 minutes.

INTRODUCTION

Once produced, the biodiesel needs a final purification step to be in accordance with the requirements laid down on the European Standard for biodiesel fuel (EN 14214).

Glycerol can be in biodiesel in the form of free glycerol or bound glycerol (mono-, di- and triglycerides). Total glycerol is the sum of free glycerol and bound glycerol. The amount of free glycerol is directly related to the purification process, whereas the total glycerol (free glycerol + bound glycerol) allows an evaluation of the transesterification process. One of the requirements specified in the EN 14214 standard relates to the free glycerol, which must be removed because it causes problems such as deposits in the engine injectors and crystallization [1]. Also, the glycerol burning in diesel engines generates acrolein, a toxic substance.

There are two generally accepted methods to remove glycerol from the biodiesel: water and dry washing. The more traditional water washing has some disadvantages, as the great generation of liquid effluents. In the other hand, dry washing has the advantages of eliminating the use of water and avoid the formation of emulsions, for example.

About dry washing, the performance of some commercial and alternative adsorbents has been reported in research papers [1, 2]. Among these, the commercial resin Purolite[®] PD206 is a material that has shown good capacity in the biodiesel purification. However, there are insufficient data regarding the regeneration (desorption of impurities after biodiesel purification) of these materials.

The regeneration of resins or adsorbents needs to be efficient to increase the contaminants removal and its life time. About the solvent, ethanol is an adequate solvent to carry out the glycerol desorption from resins or adsorbents, because it is a renewable material that has affinity for glycerol (polar compound) and has been used successfully in the biodiesel production [3-6].

Thus, the aim of this study is investigate the glycerol desorption from the resin using conventional and supercritical fluids techniques.

MATERIAL AND METHODS

Materials

Untreated biodiesel produced from used cooking oils was supplied by Stocks del Vallés S.A. (Montornés del Vallés, Spain). The biodiesel properties are showed in Table 1. Although the biodiesel properties do not fulfill the methyl ester content on EN 14214 Standard, this biodiesel has been used in the purification process in order to saturate the resin.

Table 1: Biodiesel properties.

Property	Test-Method	Result
FAME content (% w/w)	UNE EN 14103:2003	91.0
Water content (mg/kg)	UNE EN 12637:2001	6747
Monoglyceride content (% w/w)	UNE EN 14105:2003	0.47
Diglyceride content (% w/w)	UNE EN 14105:2003	0.21
Triglyceride content (% w/w)	UNE EN 14105:2003	0.85
Free glycerol content (% w/w)	UNE EN 14105:2003	0.12
Total Glycerol content (% w/w)	UNE EN 14105:2003	0.36

Purolite supplied samples of PD206 resin. Table 2 shows the PD206 basic features.

Table 2: PD206 basic features.

Polymer Structure	Gel polystyrene crosslinked with divinylbenzene
Appearance	Hard Spherical beads
Functional group	Sulfonic Acid
Upper temperature limit (°C)	150
Average particle diameter (µm)	600

The ethanol-modified supercritical CO₂ (35:65 molar ratio of ethanol:CO₂) was supplied by Abello Linde S.A. (Germany). The methyl ester standards and methyl heptadecanoate internal standard for the chromatography analysis were purchased from Sigma Aldrich (Barcelona, Spain).

Adsorption

Resin was previously saturated by contact with biodiesel in batch mode, under magnetic stirring, at 25°C (room temperature) and atmospheric pressure (1 bar). Biodiesel samples were taken at 30 min intervals and analyzed for free glycerol. This procedure was continued until the free glycerol level of the three consecutive samples was constant. The total time of adsorption was 8 h. After this time, biodiesel samples were analyzed for mono-, di- and triglycerides and water content.

Conventional desorption

Conventional desorption was investigated in a continuous mode, by passing absolute ethanol through a column of saturated resin supported in a glass tube with 3.1 cm inner diameter. The flow was controlled by a peristaltic pump and samples were collected by an automatic fraction collector.

The sample mass used in each experiment was 40 g (ion exchange resin + glycerol + biodiesel traces). Experiments were conducted with flows of 10 and 30 g/min, at 25°C (room temperature).

Samples were taken at 2 minute intervals in the range of 1 to 7 min of extraction, 5 minute intervals in the range of 10 to 20 min, 10 minute intervals between 20 and 30 min and 30 minute intervals between 60 and 300 min. Samples were analyzed for free glycerol, until the free glycerol level was below the limit specified by the EN 14105 standard (0.005% w/w).

Supercritical desorption

Supercritical desorption experiments were carried out in continuous mode using an extractor purchased from Eurothecnica (Germany). Figure 1 shows a diagram of the experimental equipment. Liquid CO₂ or a liquid mixture of ethanol/CO₂ (35:65 molar ratio) was initially cooled and then pumped using a diaphragm metering pump through a column of saturated resin supported in a stainless steel cell with 3.2 cm inner diameter. The extractor pressure was controlled by a back-pressure valve and the temperature was monitored inside the reactor by a thermocouple. Mass flow was measured using a balance connected to a computer. The weight of the tank mixture was sent to the computer at 1 s intervals.

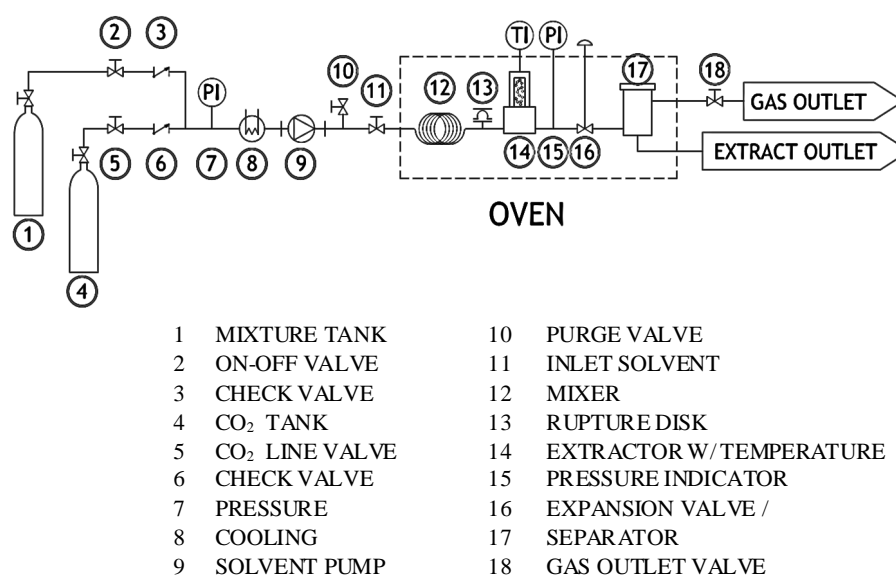


Figure 1: Supercritical desorption equipment.

Experimental conditions of temperature and pressure for the supercritical desorption were selected based on theoretical estimation of the critical properties of the mixture according to the Chueh–Prausnitz approximation [7, 8]. The upper temperature limit for the resin application (150°C) also was considered. The critical properties and other parameters of the pure components are listed in Table 3.

Table 3: Critical properties and substance parameters in equation of state.

Substance	Molar mass (kg.kmol ⁻¹)	Critical Temperature, T _c (°C)	Critical Pressure, P _c (bar)	Acentric factor, ω
Ethanol	46	241	61	0.644
CO ₂	44	31	74	0.239
Glycerol	92	453	67	0.516

The Peng-Robison equation of state (PR-EOS) was used to correlate the experimental data. The equation can be expressed as follows:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + 2bV - b^2}, \quad (1)$$

where P is the pressure (bar), R is the gas constant (8.314 J/mol.K), T is the temperature (K), and V is the molar volume (m³/mol). ω is the acentric factor. The parameters a and b are the energy and size parameters, respectively.

For a pure component i , the parameters a_i and b_i in the PR-EOS vary as a function of the critical temperature, critical pressure and acentric factor of the component. To model the molecular interactions between components i and j , the binary interaction parameters ($k_{a,ij}$, $k_{b,ij}$) are introduced through the mixing rules as follows [8]:

$$a = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{a,ij}) \quad (2)$$

$$b = \sum \sum x_i x_j \frac{b_i + b_j}{2} (1 - k_{b,ij}) \quad (3)$$

To ensure a single phase, the operating pressure and temperature for the extractor were held above the critical values for the mixture estimated using the Chueh–Prausnitz approximation [7, 8]. Figure 2 represents a pseudo-binary system where the component 1 is the supercritical solvent mixture (ethanol + CO₂ at fixed molar ratio of 35:65) and the component 2 is glycerol. The binary vapor–liquid equilibrium (VLE) diagram is shown in terms of the VLE constants as a function of pressure at constant temperature. The diagram was calculated for the CO₂+ethanol (1)–glycerol (2) system, estimating the K_i values from the fugacity coefficients calculated with the PR-EOS [9-11].

A constant operating pressure of 140 bar was selected with temperatures above 120 °C, to ensure the supercritical (single phase) condition, as seen in Figure 2, where the convergence pressure is approximately 130 bar. Experiments were carried out at the temperatures of 110 and 130°C and for the mass flows of 10 and 30 g/min, respectively. The weight of saturated resin (resin + glycerol + biodiesel traces) was 40 g.

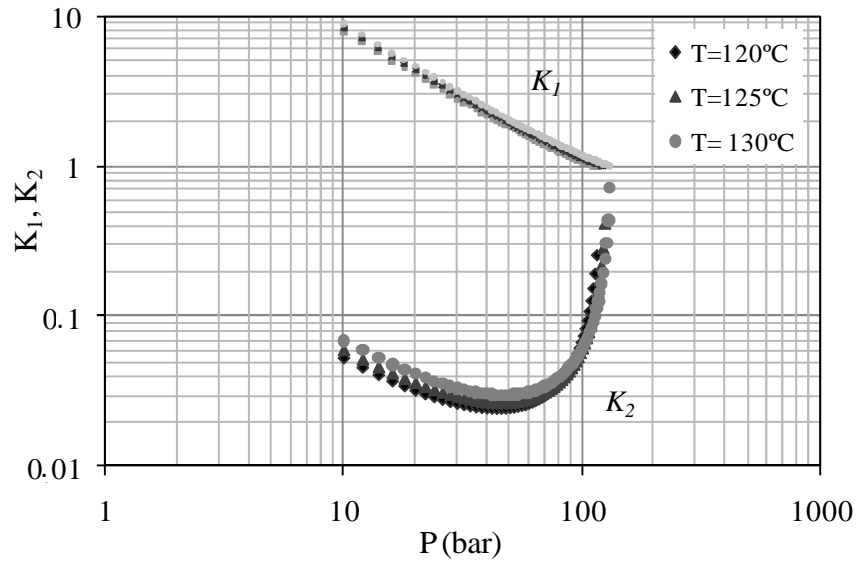


Figure 2. Pseudo-binary vapour liquid equilibrium diagram for the supercritical solvent mixture (ethanol + CO₂ - component 1) and the glycerol (component 2).

Liquid samples (ethanol + desorbed material) were taken at 1, 3, 5, 7, 10, 20 and 30 min and analyzed for free glycerol, until the free glycerol level was below the limit specified by the EN 14105 standard (0.005% w/w).

Analytical methods

Free and total glycerol and mono-, di-, triglyceride contents were analyzed by gas chromatography with on-column injection (Shimadzu, GC-2010, PTV/On-Column OCI 2010). The equipment was assembled with a flame ionization detector (FID) and capillary column (Teknokroma, model TRB-Biodiesel, 10 m length, 0.32 mm inner diameter and 0.10 μm film thickness) with a pre-column (Teknokroma, 2 m length, 0.53 inner diameter, attached using INOX connector). The chromatographic conditions were selected according to European standard EN 14105:2003. The temperature of the flame ionization detector was 380°C and helium was used as the carrier gas at a column head pressure of 21.3 kPa. Two internal standards are used, butanetriol for glycerol and tricaprín for the glycerides. The analysis was carried out by derivatizing 100 mg of each homogenized sample, dissolving it in 8 mL of heptane and then injecting 1 μL of this solution into the GC. Free and total glycerol and mono-, di-, triglyceride contents were expressed as weight percent (% w/w). The instrument was calibrated using glycerol, monoolein, diolein and triolein solutions in accordance with the standard EN 14105:2003.

Water content was determined by the Karl-Fischer method (standard EN 12637:2001).

RESULTS AND DISCUSSION

Adsorption

After reaching the equilibrium, the adsorption capacity was 0.71 g of free glycerol per gram of resin PD206. No difference was found between the levels of the mono-, di- and triglyceride before and after adsorption. Similar results have been reported by Berrios and Skelton [1].

Desorption using supercritical CO₂

Desorption kinetics of glycerol using supercritical CO₂ are showed in Figure 3.

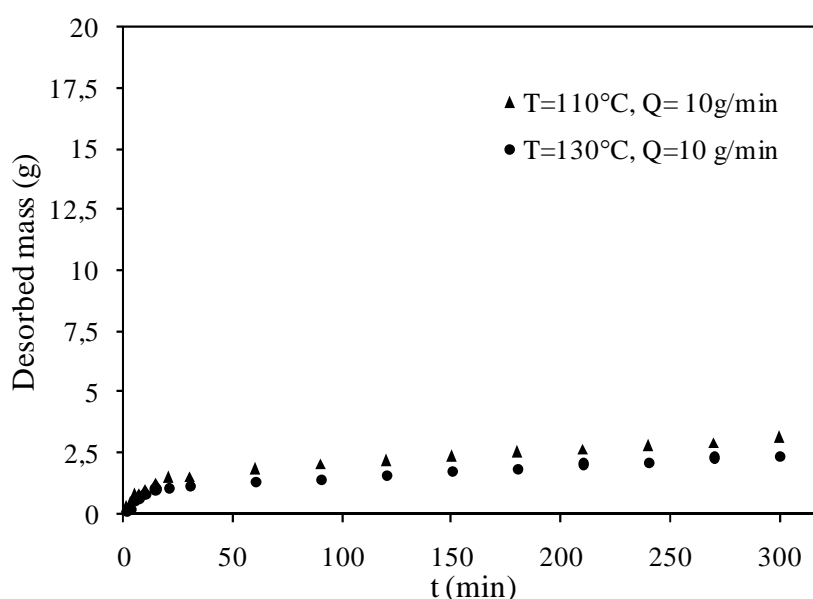


Figure 3: Glycerol desorption from the resin using supercritical CO₂.

Using supercritical CO₂, the desorbed mass of glycerol was very small. This occurs because glycerol is a polar compound, and thus has low affinity for CO₂. Therefore, it is necessary to use a co-solvent.

Comparison of conventional and supercritical desorption of glycerol

Desorption kinetics of glycerol for the processes using conventional and supercritical fluids are shown in Figure 4. Conventional desorption was carried out with absolute ethanol, while in the supercritical desorption was used ethanol-modified supercritical CO₂ (35:65 molar ratio). For each run, the weight to saturated resin was 40 g (resin + glycerol + biodiesel traces). The total mass desorbed was calculated from the mass balance.

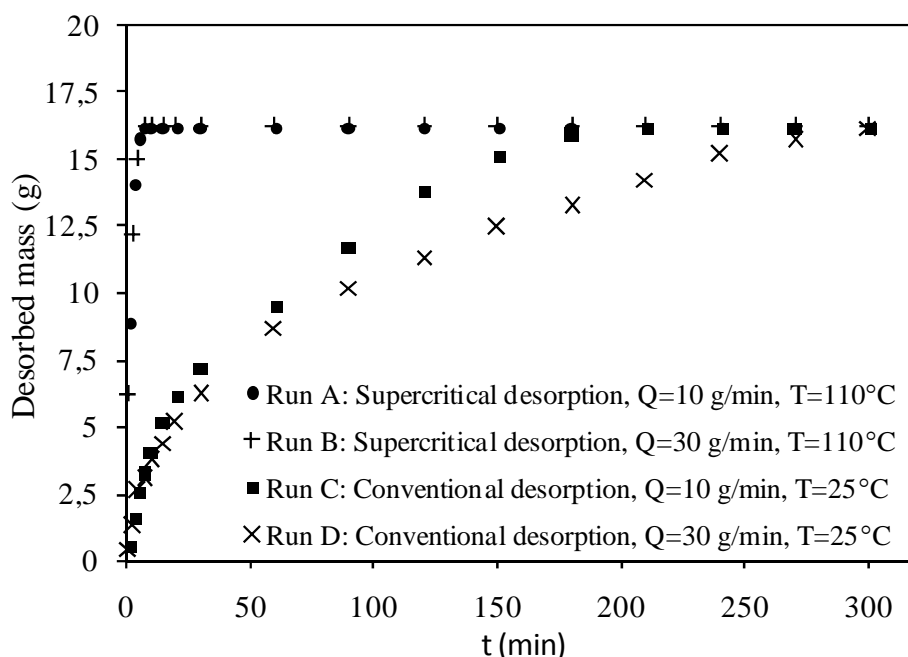


Figure 4: Glycerol desorption from the resin using conventional desorption and supercritical fluids.

Kinetics showed in Figure 4 have demonstrated that both desorption methods can remove glycerol from the resin. However, using supercritical fluids, the complete desorption of glycerol was significantly faster. Using supercritical, regeneration occurred in the range of 7 to 10 minutes (runs A and B), whereas using absolute ethanol under atmospheric conditions the resin regeneration was achieved between 210 and 300 minutes (runs C and D). The supercritical desorption can achieve higher rates due to the excellent properties of heat and mass transfer associated with SCF. The increase in the diffusivity, decrease in the viscosity and high penetration ability in porous structures are features that lead to the diffusion rate being higher in SCFs than in liquids [12].

Effect of temperature and mass flow rate on the glycerol desorption using supercritical fluids

In Figure 5 are showed the desorption kinetics of glycerol from the resin using supercritical fluids at different temperatures and mass flows. Desorption runs were carried using ethanol-

modified supercritical CO₂ (35:65 molar ratio). For each run, the weight to saturated resin was 40 g (resin + glycerol + biodiesel traces).

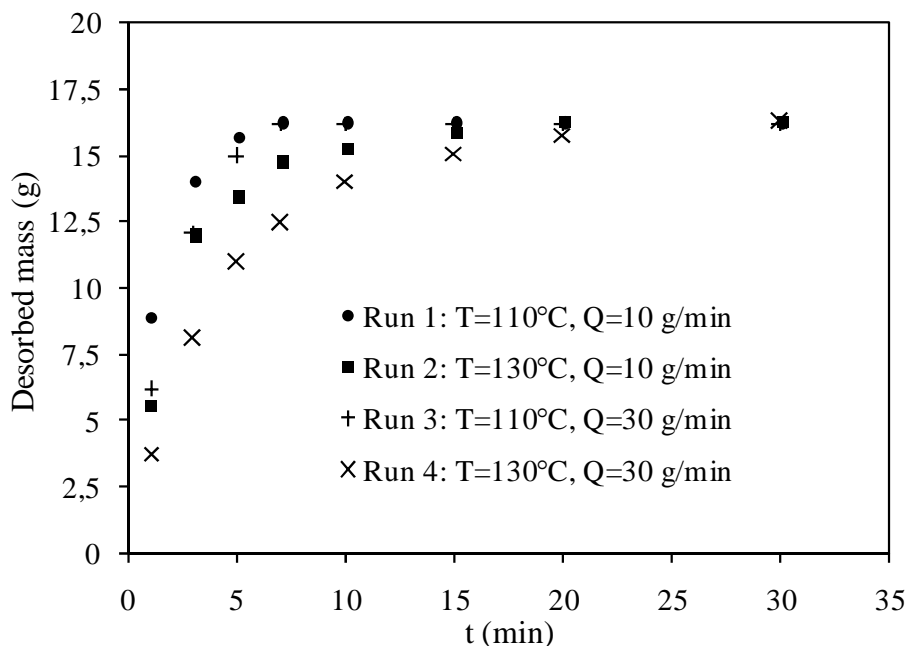


Figure 5: Glycerol desorption from the resin at different temperatures and mass flows.

In the run 2 the resin regeneration (complete glycerol desorption) was achieved in 20 minutes, while in the run 1 the regeneration was achieved in just 7 minutes. Likewise, in the run 3 the regeneration was faster than in the run 4 (10 and 30 minutes, respectively). Thus, an increase in temperature, keeping the mass flow constant, resulted in longer time for resin regeneration. The process of glycerol desorption was faster at lower temperature due to increase in the supercritical fluids density, which caused an increase in the solubility.

Now, comparing runs 1 and 3, and runs 2 and 4, it can be verified that an increase in mass flow, keeping the temperature constant, resulted in a longer time for resin regeneration.

Therefore, the resin regeneration was faster using the lower temperature (110°C) and mass flow (10 g/min) investigated in this work.

CONCLUSIONS

In this work, the glycerol desorption from the resin PD206 was investigated using absolute ethanol, supercritical CO₂ or ethanol-modified supercritical CO₂ (35:65 molar ratio of ethanol:CO₂).

The desorbed mass of glycerol obtained using pure CO₂ was very small, because glycerol (polar compound) has low affinity for CO₂.

Then, conventional desorption using absolute ethanol under atmospheric conditions and supercritical desorption using ethanol-modified supercritical CO₂ were compared and it was verified that supercritical desorption is much faster than conventional desorption. Under atmospheric conditions the resin regeneration was achieved between 210 and 300 minutes, whereas using supercritical fluids the regeneration occurred in the range of 7 to 30 minutes.

By investigating the glycerol desorption using ethanol-modified supercritical CO₂ at different temperatures and mass flows was verified that the resin regeneration was faster using the lower temperature (110°C) and mass flow (10 g/min) investigated.

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