

# Adsorptive Properties of Silica Gel for Biodiesel Refining

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The refining of biodiesel by adsorption over silica gel was assessed. Silica gel samples were used for the adsorption of glycerol and monoglycerides. Room-temperature isotherms for the adsorption of glycerol were measured for biodiesel samples containing only fatty acid methyl esters or samples spiked with contaminants, such as water, methanol, monoglycerides, and soaps. The results indicate that adsorption of glycerol and monoglycerides contained in biodiesel over silica is very efficient and robust. Adsorption of glycerol is not influenced by the presence of small amounts of water and soaps. The presence of monoglycerides lowers the adsorption capacity of glycerol because of the competition of monoglycerides for the same adsorption sites. Methanol adversely affects the adsorption in a different way. It increases the activity of glycerol in the liquid phase and reduces the adsorption affinity and adsorption capacity of silica. Conventional refining downstream transesterification reactors currently performed by decanting/washing or centrifugation/washing can be conveniently replaced by simple decanting and silica adsorption, thus preventing the issue of excessive amount of effluent waters.

## Introduction

Biodiesel is a diesel fuel substitute produced by the transesterification of fatty substances, such as oils and fats. Its production has increased steadily over the last few years. Only in Argentina, the installed capacity has grown from practically zero to one million tons per year in half a decade. The advantages of biodiesel compared to petroleum-derived diesel include reduction of most exhaust emissions, biodegradability, high flash point, inherent lubricity, and domestic origin.<sup>1</sup>

In the Americas, one of the main raw materials for biodiesel manufacture is soy oil. The two main subproducts of the production of biodiesel from soy beans are the expeller and glycerol. These two are also commercial products and help with the economy of the whole process. The expeller is the solid residue obtained after crushing and pressing the soy beans to obtain the oil and is a valuable protein-rich subproduct used for formulating cattle meal. Glycerol is produced during the transesterification of the major triglyceride fraction of the oil.

All soy biodiesel is produced by base-catalyzed transesterification with dissolved homogeneous catalysts, such as sodium or potassium hydroxide. The reaction is carried out in two steps with intermediate removal of glycerol. In this way, the equilibrium-limited reaction can be driven to completion. Complete conversion is needed to attain the purity limits established by the quality standards for the fuel. After the reaction has been completed and the main subproduct, glycerol, has been removed by gravity settling or centrifugation, some impurities still remain in the fuel. These impurities are glycerol itself, soaps, catalyst, water, methanol, and mono-, di-, and triglycerides. In the usual industrial practice, the impurities are removed by washing with water. Packed washing towers, mixers-settlers, and centrifuges are commonly used with this purpose.

Removal of glycerol and glycerides from biodiesel is especially important because the quality of the fuel strongly depends upon the content of free and bound glycerol. ASTM D6751 and EN 14214 standards establish a maximum amount of 0.02% free glycerin and 0.25% total glycerol (free and bound). Glycerol is especially undesired in the fuel because when heated it tends to polymerize by condensation with other molecules of glycerol or glycerides. The result is the formation of coke and tarnish on injectors and cylinders. Glycerides also increase the cloud point of biodiesel by forming small crystals at low temperatures. The equilibrium glycerol content in biodiesel issuing from a decanter is a function of the residual methanol acting as a co-solvent, but when this is completely removed, the free glycerin content only depends upon the temperature. It is approximately 0.2% at 25 °C and increases linearly at higher temperatures.<sup>2</sup> Even if methanol is not present, hydrophilic glycerol can be solubilized in the oily phase by the mediation of amphiphilic mono- and diglycerides.

Biodiesel refining by water washing has been lately critically objected on an environmental basis because of the relatively large amounts of process water that are issued as effluents. Karaosmanoglu et al.<sup>3</sup> investigated the refining step of biodiesel and concluded that a minimum of 3–5 g of water/g of biodiesel at 50 °C was needed to remove the impurities of the fuel. A substantial reduction of the amount of effluents of the process could be obtained if water washing is replaced by glycerides removal by adsorption. It has been recently proposed<sup>4</sup> that the level of glycerol in biodiesel could be adjusted to values within quality standard limits by adsorption over silica beds. Özgül

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**Table 1. Physical Properties of the Silica Gel Adsorbent as Measured by Nitrogen Physisorption at 70 K**

property	value
Brunauer–Emmett–Teller (BET) specific surface area	330 m <sup>2</sup> g <sup>-1</sup>
Wheeler's mean pore radius	40.6 Å
pore volume	0.67 cm <sup>3</sup> g <sup>-1</sup>
particle radius	75–180 μm

and Turkay<sup>5</sup> proposed to retain biodiesel impurities over rice hulls. Adsorption-based purification of biodiesel has lately been incorporated into some commercial processes. Bournay et al.<sup>6</sup> used adsorption tower downstream methanol evaporators to remove glycerides.

If it can be proven that solid adsorbents can retain glycerol and all of the other biodiesel contaminants, then conventional water washing could be replaced by fixed bed adsorption with the associated reduction of the issue of effluent waters.

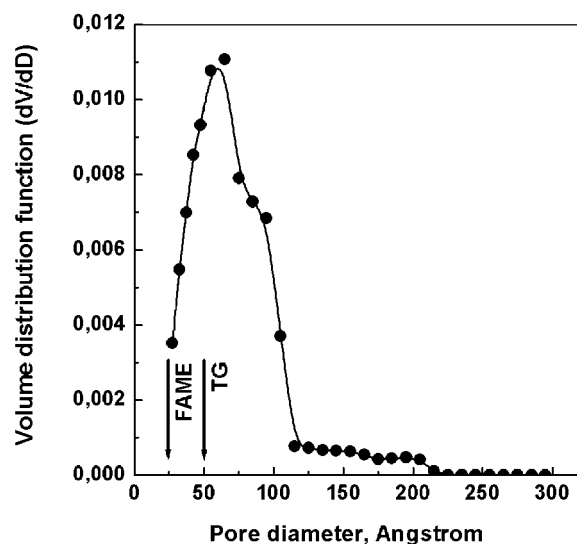
A study on the properties of silica gel for the adsorption of biodiesel impurities was performed in this work. The main focus was put on the elimination of glycerol and the influence of other components on the adsorptive properties of the support. Room-temperature isotherms for the adsorption of glycerol were measured for biodiesel samples containing only fatty acid methyl esters or samples spiked with contaminants, such as water, methanol, monoglycerides, and soaps. Basic information was obtained in the form of room-temperature isotherms at different conditions of the biodiesel phase.

### Experimental Section

**Materials.** Methyl soyate was prepared according to a method described elsewhere.<sup>7</sup> Biodiesel was further purified from glycerol and glycerides by repeated cycles of washing with distilled water and centrifugation, until the glycerol concentration was lower than 0.004% by gas chromatography analysis. Biodiesel/glycerol solutions were prepared using this biodiesel and pure glycerol. Pure glycerol was supplied by Sintorgan (>99.5%). Solutions with variable contents of soaps, monoglyceride, water, and methanol were prepared by the addition of trace amounts of these compounds. Sodium estearate (99%) was chosen as a model soap and was supplied by Serisa S.A. Analytical-grade methanol (99.9%) was supplied by Dorwil. Glyceryl monoestearate (98%) was used as a model monoglyceride and was supplied by Cloretil SACIF. White silica gel was supplied by W. R. Grace and Co. in the form of amorphous granules. It was ground and sieved to 35–80 meshes, dried in a stove at 110 °C, and stored in a desiccator before its use.

**Adsorption Measurements.** In a typical adsorption experiment, 100 mL of pure biodiesel was placed in a flask. Dissolved gases and water were then removed by stripping the liquid solution with nitrogen (10 mL min<sup>-1</sup>) for 1 h at 80 °C. The concentration of the solution with respect to each impurity was adjusted by adding small amounts of the liquid impurities (glycerol, methanol, and water) with a micropipette. The concentration of solid impurities (monoglyceride and soap) was adjusted by weighing small aliquots and adding them to the solution. The solution was then stirred and stabilized at 25 °C by placing the flask in a thermostatted bath. Then, a carefully weighed variable amount (0.5–3.0 g) of silica was added to the solution, and the thus formed slurry was stirred for 2 h. Then, the solid was let to decant, and the liquid phase was sampled for analysis. The steps of silica addition, stabilization, and sampling were repeated several times to have points with different liquid-phase compositions.

The glycerol amount adsorbed on silica gel (glycerol<sub>ads</sub>) was calculated with a mass balance. The glycerol on silica is equal to



**Figure 1.** Pore size distribution of the silica gel adsorbent, with comparison to the molecular size of adsorbates.

the total glycerol originally present in the solution minus the final glycerol content remaining in the solution after the adsorption test (glycerol<sub>liq</sub>). Glycerol saturation capacity was determined from the adsorption experiments by fitting the isotherm data with a multi-component Langmuir equation (see the footnote of Table 2). The parameters of the equation were obtained by minimization of the sum of squares of the deviation between the model and the data using a Marquardt nonlinear algorithm included in the Microcal Origin for Windows software.

**Biodiesel Analysis.** Each liquid sample was analyzed by different techniques. The water content was assessed by means of a Karl Fischer potentiometric titration. The Karl Fischer reagent was supplied by Merck, and the titration was performed with an Altronix apparatus with a glass electrode. The soap content was indirectly assessed by means of the ASTM D874 test for sulfated ash content and directly by means of an acid–base titration method based on the hydrolysis of the soap with mineral acid and the subsequent titration of the remaining acid. The concentration of glycerol, methanol, mono-, di-, and triglycerides, and fatty acid methyl esters was determined by means of the chromatographic method of Plank and Lorbeer.<sup>8</sup> Pyridine (Merck, 99.9%) was used as a solvent and silylation catalyst for the preparation of the samples. These were derivatized with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MST-FA, Aldrich). 1,2,4-Butanetriol (>95%, Fluka) and tricaprins (>99%, Fluka) were added as internal standards. After 15 min at room temperature, the silylated samples were dissolved in *n*-heptane (Merck, 99.5%) and injected in the GC for their analysis. The analysis was performed with a Varian Star 3400 CX gas chromatograph equipped with an on-column Supelco injector and a flame ionization detector (FID). The column was a Zebron ZB-5 (Phenomenex), 25 m × 0.25 mm inner diameter fused-silica capillary column. The samples were injected manually at an oven temperature of 50 °C. After an isothermal period of 1 min, the chromatograph oven was heated at 15 °C min<sup>-1</sup> to 180 °C, at 7 °C min<sup>-1</sup> to 230 °C, and ballistically to 300 °C (held for 20 min). Nitrogen was used as a carrier gas at a flow rate of 3 mL min<sup>-1</sup>. The detector temperature was 350 °C; nitrogen served as the detector make up gas at an inlet pressure of 0.5 bar. The total run time was 90 min.

### Results and Discussion

Figure 1 contains the pore size distribution of the adsorbent silica used. The silica was mainly mesoporous, with a main maximum at 60 Å and a shoulder at about 80 Å. The main

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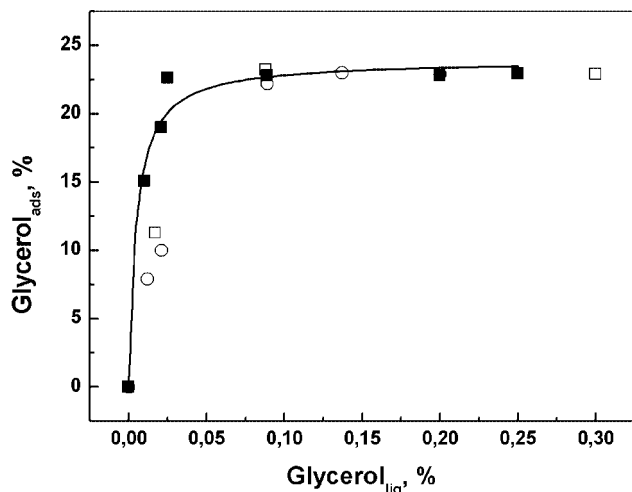
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**Table 2. Measured Values of the Adsorption Constants for Glycerol Adsorption over Silica<sup>a</sup>**

adsorbate	Langmuir constant, <i>K</i>		glycerol saturation capacity, <i>A<sub>Gly</sub></i>	
	(% <sup>-1</sup> )	(cm <sup>3</sup> μmol <sup>-1</sup> )	(%)	(mmol g <sup>-1</sup> )
glycerol (in pure biodiesel)	211	2.20	23.9	2.59
glycerol (in biodiesel with 944 ppm of water)			24.0	2.60
glycerol (in biodiesel with 270 ppm of soaps)			23.8	2.58
methanol	37	0.134		
glyceryl monoestearate	13	0.573		

<sup>a</sup> Multicomponent Langmuir formula: ( $K_{\text{water}} \approx K_{\text{soaps}} \approx 0$ ):  $Q_{\text{Gly}} = A_{\text{Gly}} K C_{\text{Gly}} / (1 + K_{\text{Gly}} C_{\text{Gly}} + K_{\text{MeOH}} C_{\text{MeOH}} + K_{\text{MG}} C_{\text{MG}})$ , where  $Q_{\text{Gly}}$  is in % (w/w),  $C_{\text{Gly}}$  is in % (w/w),  $A_{\text{Gly}}$  is in % (w/w), and  $K$  is in %<sup>-1</sup> (w/w) or  $Q_{\text{Gly}}$  is in mol<sub>Gly</sub> g<sub>silica</sub><sup>-1</sup>,  $C_{\text{Gly}}$  is in mol cm<sup>-3</sup>,  $A_{\text{Gly}}$  is in mol<sub>Gly</sub> g<sub>silica</sub><sup>-1</sup>, and  $K$  in cm<sup>3</sup> mol<sub>Gly</sub><sup>-1</sup>.

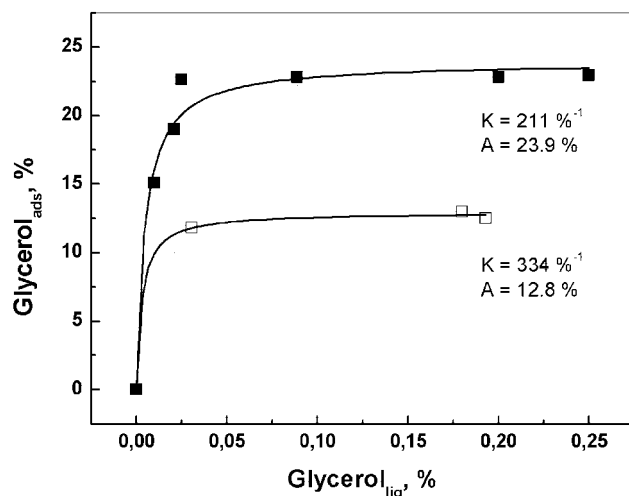


**Figure 2.** Adsorption isotherms of glycerol dissolved in the blank (pure biodiesel, ■) and in the blank spiked with soaps (270 ppm, ○) or water (944 ppm, □).

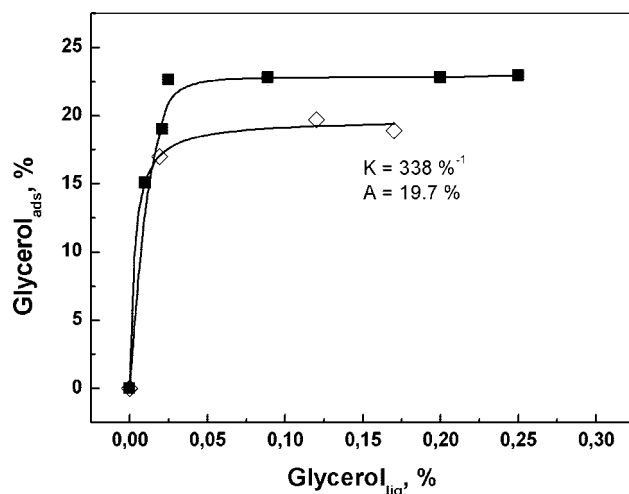
peak in the distribution was lower than the diameter calculated by Wheeler's formula (80.2 Å). This was due to the skewness of the distribution that had a tail in the zone of big mesopores (100–300 Å). The wide pore network of the silica was thought to present no problems for diffusion of the adsorbates. The approximate length of the molecules was included in Figure 1. It can be seen that the sizes of fatty acid methyl esters (FAME) and triglycerides (TG) are smaller than the average pore diameter of the silica network (Table 1).

The synthesized and purified biodiesel had a content of 99% FAME, 0.027% soaps, 20 ppm water, 0.016% free glycerol, 0.16% monoglycerides, and 0.057% total (free and bound) glycerol. The content of methanol and tri- and diglycerides was negligible. The density was 0.881 g cm<sup>-3</sup>. The residual acidity was 0.038 mg of KOH g<sup>-1</sup>.

The results of adsorption are plotted in Figures 2–4. The isotherm of the blank biodiesel sample is plotted in Figure 2. The saturation capacity (0.239 g g<sup>-1</sup>) is high and also almost equal to the monolayer value, as reported elsewhere.<sup>4</sup> The value of the Langmuir constant  $K$  is also high and determines that, for practical uses, the data can be approximated by a square isotherm. When the biodiesel was spiked with water to a final content of 944 ppm of water and the isotherm was measured again, the same isotherm was obtained within experimental error. The same occurred when soaps were added to the biodiesel; practically, the same curve was found upon addition of soaps to a final content of 270 ppm. Greater soaps contents, such as



**Figure 3.** Adsorption isotherms of glycerol dissolved in the blank (pure biodiesel, ■) and in the blank spiked with methanol (12 000 ppm, □).



**Figure 4.** Adsorption isotherms of glycerol dissolved in the blank (pure biodiesel, ■) and in the blank spiked with glyceryl monoestearate (7500 ppm, ◇), with Langmuir constants ( $K$ ) and saturation capacities ( $A$ ).

500 or 1000 ppm, were not feasible because of the segregation of a soap phase. 206

The influence of methanol addition to a final 12 000 ppm in biodiesel is seen in Figure 3. Methanol addition reduced the effective saturation capacity to about one half. The effect must be the result of both the affinity of methanol for the silica surface and the increase of the affinity of glycerol for the fluid phase when methanol is present. The latter effect has been theoretically assessed in a previous report<sup>4</sup> by considering a constant activity of glycerol on silica and by assuming that the activity coefficients are well-represented by the UNIFAC model. The increase of the activity coefficient of glycerol in the fluid phase was mainly due to the role of the –OH group interaction term in the UNIFAC formulation that reflected the interaction between glycerol and methanol through hydrogen bridge bond interaction. Both effects result in a diminished adsorption equilibrium capacity of silica. 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222

The competitive adsorption of glycerol and methanol can be taken into account by using a multicomponent Langmuir equation (see footnote of Table 2). Inspection of this equation reveals that the maximum capacity for silica will be a function of the  $K_{\text{Gly}}/K_{\text{MeOH}}$  ratio, i.e., for the relative affinity for the silica surface of both adsorbates. In a general model, both  $K_{\text{Gly}}$  and  $K_{\text{MeOH}}$  are a function of the concentration of methanol and 223 224 225 226 227 228 229

glycerol, as in the UNIFAC model of ref 4. In a simpler approximate model,  $K_{\text{Gly}}$  and  $K_{\text{MeOH}}$  can be supposed as independent of the concentration of the adsorbates. In this case,  $K_{\text{Gly}}$  is constant and its value is the same determined in the adsorption experiment with no methanol or monoglycerides ( $K_{\text{Gly}} = 2.20 \text{ cm}^3 \mu\text{mol}^{-1}$ ). Regression of this multicomponent model with the data of Figure 3 indicates that  $K_{\text{MeOH}} = 0.134 \text{ cm}^3 \mu\text{mol}^{-1}$ .

The influence of the addition of monoglycerides to biodiesel can be seen in Figure 4. The maximum adsorption capacity was reduced by 18% upon the addition of glyceryl monoestearate. The effect was less negative than that of methanol for a similar concentration on a mass basis (12 000 and 7500 ppm). However, on a mole basis, the higher affinity of monoglycerides is reflected by the value of  $K_{\text{MG}} = 0.573$ . In fact,  $K_{\text{Gly}} > K_{\text{MG}} > K_{\text{MeOH}}$ , probably reflecting the order of decreasing interaction through hydrogen bridge bond on a mole basis. This is evidence that, in this system, polar interactions prevail over those of molecular size.

The co-adsorption of MG was clearly revealed by the measurement of the MG concentration before and after silica addition in the adsorption tests. To elucidate the way that MG was adsorbed, their effective surface area in the adsorbed state must be known. Some reports<sup>9</sup> indicate that the effective surface area of monopalmitin monolayers is  $0.8\text{--}1.0 \text{ m}^2 \text{ mg}^{-1}$ . The value for glyceryl estearate should be similar. When a calculation is made with the effective size of glycerol and glyceryl estearate, it turns out that the surface in the plateau region of the adsorption isotherm is completely saturated; i.e., there are no more sites available, and a full monolayer of mixed glycerol and MG is formed. Therefore, the hypotheses of a unique constant value for  $K$  seems to be true in the case of MG. MG adsorption interferes with glycerol adsorption by mainly blocking adsorption sites and not reducing the affinity of glycerol for the silica surface.

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The results found have some practical consequences. The main products of the transesterification of fats and oils are glycerol and monoglycerides. The concentration of di- and triglycerides at high values of conversion (>97%) is much lower than that of monoglycerides. Therefore, silica adsorption is a robust way of reducing both free and total glycerol in the final biodiesel fuel. It is not much affected by water and soaps and can adjust biodiesel parameters to fit into the ranges established by nowadays strict quality standards.

## Conclusions

Glycerol has a great affinity for the silica surface and is selectively adsorbed from biodiesel solutions. The Langmuir adsorption constant and the saturation capacity constants were found to be equal to  $2.22 \text{ cm}^3 \mu\text{mol}^{-1}$  and  $0.239 \text{ g g}^{-1}$ , respectively.

During the adsorption of glycerol from biodiesel solutions and over silica gel samples, soaps do not interfere with the adsorption. Dissolved methanol produces a decrease of the adsorption capacity by increasing the activity of glycerol in the solvent and by competition for the adsorption sites on silica. Monoglycerides also produce a decrease of the saturation capacity as a consequence of their competitive co-adsorption over silica.

Conventional refining downstream transesterification reactors currently performed by decanting/washing or centrifugation/washing can be conveniently replaced by simple decanting and silica adsorption, thus preventing the issue of an excessive amount of effluent waters.

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