

Synthesis of Triglycerides from Cinnamic Acid and Glycerol Using Supported Sulphonic Acids

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The esterification of cinnamic acid and glycerol can be a starting point of a promising new application of the biodiesel-based glycerol. In this work, the reaction was studied from a double perspective: On one hand, new catalysts based on TMOS and carbon were synthesized; on the other, kinetic data from the esterification runs were used to fit a three consecutive reactions kinetic model. Kinetic parameter values, as well as acidity to the catalyst, show that an amorphous mesoporous catalyst based on CSPTMS (a silane with a sulphonic moiety) can be a good alternative to *p*-toluenesulphonic acid when further oxidation of products is to be avoided and reuse of the catalyst is looked for.

1. Introduction

Nowadays, biodiesel is a promising new and renewable source of energy and many efforts are dedicated to the development of this green fuel trying to solve the logistic problems posed by raw material supply and by-products production (Dermibas, 2009).

The production of biodiesel has led to the increase in the production of glycerol and this polyol has become one of the drawbacks of the traditional process for biodiesel production, as well as a possible platform chemical and an energy source. As the glycerol market was saturated long time ago, a wide range of new applications are now in development, including chemicals, hydrogen from glycerol reforming with water, and additives for fuels (Zhou et al., 2008, Pagliaro et al., 2007).

Antioxidants with a controlled hydrophobic/hydrophilic balance are now looked for and can be obtained from carbohydrates, including glycerol, and fatty alcohols, on one hand, and phenolic acids, on the other hand. In fact, hydrophylation and/or lipophylation of such antioxidant acids can be the way of apply them in a wide range of materials of different polarity (Balasundram et al., 2007).

In this work, cinnamic acid esterification with glycerol is performed by using *p*-toluenesulphonic acid (PTSA), strong acid catalysts based on PTSA or phenylsulfonyl moieties heterogenized on mesoporous silicas. Furthermore, a kinetic model is used to fit experimental data from runs performed at 120 and 140°C .

Materials and methods

2.1 Materials

Analytical grade reagents (PTSA, sulphuric acid, *p*-formaldehyde) were from Aldrich, while chlorosulfonylphenyltrimethoxysilane –CSPTMS- 50% in dichloromethane was from Gelest Ltd. Amberlyst 36 dry, a strong acid resin functionalised with sulphonic groups, was kindly donated by Rohm and Haas Co.

2.2 Catalysts synthesis and acidity test

Reaction runs have been performed using strong Brönsted acid catalysts or without them. These catalysts were based on *p*-toluensulphonic acid or a silane containing a phenylsulfonyl chloride (chlorosulfonylphenyltrimethoxysilane –CSPTMS-) that was afterwards hydrolysed.

A siliceous mesoporous material of amorphous nature was obtained from TMOS and CSPTMS by a gelation process driven by NaF at 30-50°C (Reale et al., 2005). The solid were subsequently filtrated and dried in a vacuum furnace (60°C/0.1 mm/Hg) for 24h.

The acid active carbon was obtained by a chemical pirolysis, *p*-toluensulphonic acid, *p*-formaldehyde and sulphuric acid (10:2:0.2 on a mass basis) were mixed in a mortar and left with stirring in a round flask with reflux at 100°C for 48 h (Liang et al., 2008).

For estimating the real concentration of sulphonic acids on supports, 100 mg from each catalyst was stirred with 10 mL of a 7.5 g L⁻¹ KCl aqueous solution for 24 h, then filtered solution were titrated and tested by several pH measurements. In table 3.1, results from the acidity of the catalysts are shown on a support mass basis.

2.3 Esterification runs and kinetic modelling

Runs were performed in a temperature-controlled batch reactor with helix agitation, a spurger for nitrogen flushing, and a condenser. Samples were taken at several times and glycerides analysed by gel permeation chromatography in a 5000Å pore size phenogel GPC column. Data obtained at 254 nm in a diode-array detector were used to fit an adequate kinetic model, based on three consecutive reactions from glycerol and cinnamic acid to triglyceride via monoglyceride and diglyceride, as shown in the next figure:

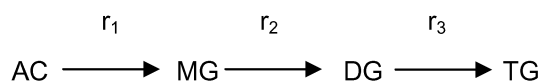


Figure 2.1.- Series reaction scheme for esterification of cinnamic acid and glycerol.

Thus, the evolution of the involved compounds follows the next differential equations, rate expressions and stoichiometric relationships:

$$\frac{dn_{\text{AC}}}{dt} = -r_1 - r_2 - r_3 \quad (1)$$

$$\frac{dn_{\text{MG}}}{dt} = r_1 - r_2 \quad (2)$$

$$\frac{dn_{\text{DG}}}{dt} = r_2 - r_3 \quad (3)$$

$$\frac{dn_{\text{TG}}}{dt} = r_3 \quad (4)$$

$$r_1 = k_1 \cdot n_{\text{AC}} \cdot n_{\text{G}} \quad (5)$$

$$r_2 = k_2 * n_{MG} * n_{AC} \quad (6)$$

$$r_3 = k_3 * n_{DG} * n_{AC} \quad (7)$$

$$n_G = n_{G0} - (n_{MG} + n_{DG} + n_{TG}) \quad (8)$$

Results

Esterification of cinnamic acid and glycerol was performed in an inert atmosphere by flushing nitrogen during the reaction in order to efficiently remove produced water. Even on those conditions, when the reaction was carried out without catalyst, scarce activity is observed at 140°C and none at 120°C. However, when using strong acid catalysts, both homogeneous and supported, the esterification reaction takes place.

It can be seen that the mesoporous amorphous acid catalyst is ten times less strong than the others (Table 3.1). However, as it is shown in Figures 3.1 and 3.2, its activity is comparable to the acid PTSA-carbon.

When using the proposed kinetic model to fit experimental data, the parameter values observed in Table 3.2 are obtained. While further supporting the high activity of the mesoporous catalyst, these values show that higher rates are obtained in the first step, decreasing with the increase of the esterification degree of the glycerol. However, this is much more obvious when using PTSA solved in the reaction media, so mass-transfer hindrance is expected with the supported catalysts. The possible exception can be the siliceous sulphonic catalyst, which shows a very high activity at 140°C (almost 10 times higher than the carbonaceous sulphonic catalyst).

Table 3.1.-Acid pH measure and concentration of Brönsted acid sites in the tested catalysts

Catalyst	pH	C _{acid sites} (mmol/g)
PTSA-carbon	1.48	3.31
Strong acid resin	1.38	4.16
PTSA	1.55	2.82
mesopo-sbuOH	2.38	0.42

Table 3.2.-Kinetic model fitting parameters for the esterification of cinnamic acid and glycerol at several temperatures and in the presence of acid catalysts

Catalyst	T (°C)	k ₁	k ₂	k ₃	SQR	F																																				
PTSA-carbon	120	3.1·10 ⁻² ±	7.4·10 ⁻³ ±	1.9·10 ⁻³ ±	1.8·10 ⁻²	554																																				
		5.4·10 ⁻³	9.9·10 ⁻⁴	5.1·10 ⁻⁴			Strong acid resin	120	4.1·10 ⁻³ ±	1.1·10 ⁻² ±	1.1·10 ⁻³ ±	1.7·10 ⁻²	649	7.3·10 ⁻⁴	5.9·10 ⁻³	8.7·10 ⁻⁴	PTSA	120	1.6·10 ⁻¹ ±	3.1·10 ⁻² ±	4.9·10 ⁻³ ±	1.0·10 ⁻²	1848	1.4·10 ⁻²	2.7·10 ⁻³	7.1·10 ⁻⁴	mesopo-sbuOH	140	1.7·10 ⁻¹ ±	1.2·10 ⁻¹ ±	2.5·10 ⁻² ±	4.2·10 ⁻³	5833	7.74·10 ⁻³	6.4·10 ⁻³	3.3·10 ⁻³	PTSA-carbon	140	2.0·10 ⁻¹ ±	1.5·10 ⁻¹ ±	3.3·10 ⁻² ±	1.0·10 ⁻²
Strong acid resin	120	4.1·10 ⁻³ ±	1.1·10 ⁻² ±	1.1·10 ⁻³ ±	1.7·10 ⁻²	649																																				
		7.3·10 ⁻⁴	5.9·10 ⁻³	8.7·10 ⁻⁴			PTSA	120	1.6·10 ⁻¹ ±	3.1·10 ⁻² ±	4.9·10 ⁻³ ±	1.0·10 ⁻²	1848	1.4·10 ⁻²	2.7·10 ⁻³	7.1·10 ⁻⁴	mesopo-sbuOH	140	1.7·10 ⁻¹ ±	1.2·10 ⁻¹ ±	2.5·10 ⁻² ±	4.2·10 ⁻³	5833	7.74·10 ⁻³	6.4·10 ⁻³	3.3·10 ⁻³	PTSA-carbon	140	2.0·10 ⁻¹ ±	1.5·10 ⁻¹ ±	3.3·10 ⁻² ±	1.0·10 ⁻²	1154	2.0·10 ⁻²	1.6·10 ⁻²	3.2·10 ⁻³						
PTSA	120	1.6·10 ⁻¹ ±	3.1·10 ⁻² ±	4.9·10 ⁻³ ±	1.0·10 ⁻²	1848																																				
		1.4·10 ⁻²	2.7·10 ⁻³	7.1·10 ⁻⁴			mesopo-sbuOH	140	1.7·10 ⁻¹ ±	1.2·10 ⁻¹ ±	2.5·10 ⁻² ±	4.2·10 ⁻³	5833	7.74·10 ⁻³	6.4·10 ⁻³	3.3·10 ⁻³	PTSA-carbon	140	2.0·10 ⁻¹ ±	1.5·10 ⁻¹ ±	3.3·10 ⁻² ±	1.0·10 ⁻²	1154	2.0·10 ⁻²	1.6·10 ⁻²	3.2·10 ⁻³																
mesopo-sbuOH	140	1.7·10 ⁻¹ ±	1.2·10 ⁻¹ ±	2.5·10 ⁻² ±	4.2·10 ⁻³	5833																																				
		7.74·10 ⁻³	6.4·10 ⁻³	3.3·10 ⁻³			PTSA-carbon	140	2.0·10 ⁻¹ ±	1.5·10 ⁻¹ ±	3.3·10 ⁻² ±	1.0·10 ⁻²	1154	2.0·10 ⁻²	1.6·10 ⁻²	3.2·10 ⁻³																										
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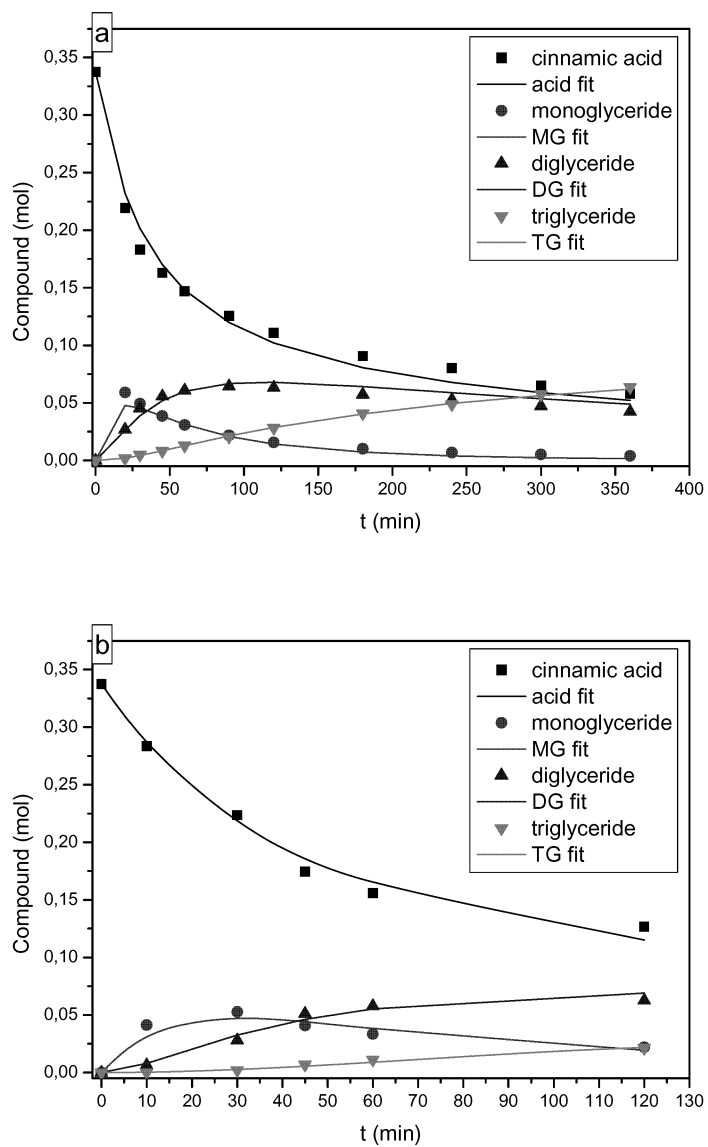


Figure 3.1.- Esterification of cinnamic acid and glycerol with PTSA-carbon (a) and with amorphous mesoporous silica from TMOS, CPGTMS and *s*-BuOH at 140°C: fitting of the kinetic model to the experimental data.

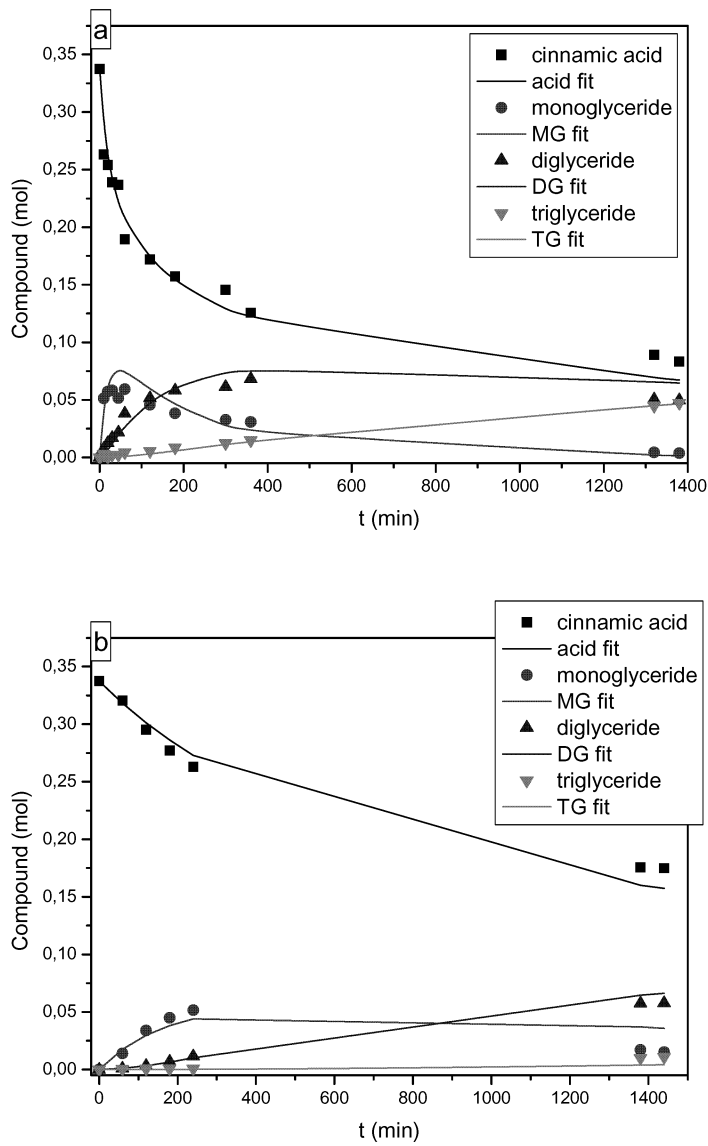


Figure 3.2.- Esterification of cinnamic acid and glycerol with PTSA (a) and with an strong acid resin – Amberlyst 36 dry- at 120°C: fitting of the kinetic model to the experimental data.

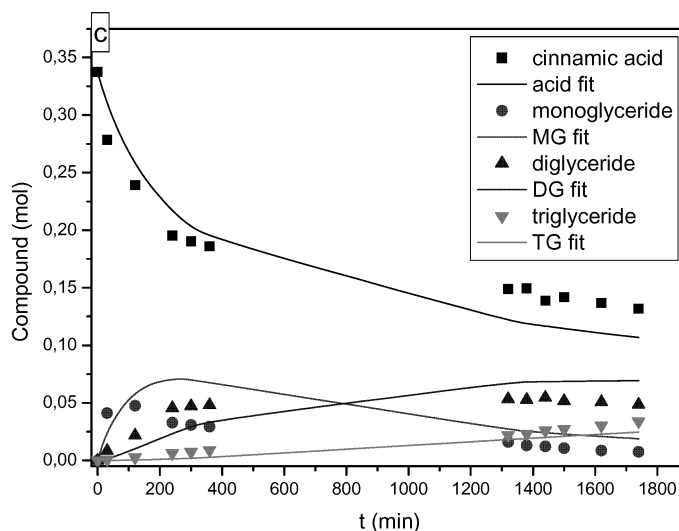


Figure 3.2 (cont.)- Esterification of cinnamic acid and glycerol with PTSA-carbon (c): fitting of the kinetic model to the experimental data.

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