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Influence of vegetable oils fatty acid composition on reaction temperature and glycerides conversion to biodiesel during transesterification

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ABSTRACT

Presence of unreacted glycerides in biodiesel may reduce drastically its quality. This is why conversion of raw material in biodiesel through transesterification needs to readjust reaction parameter values to complete. In the present work, monitoring of glycerides transformation in biodiesel during the transesterification of vegetable oils was carried out. To check the influence of the chemical composition on glycerides conversion, selected vegetable oils covered a wide range of fatty acid composition. Reactions were carried out under alkali-transesterification in the presence of methanol. In addition, a multiple regression model was proposed. Results showed that kinetics depends on chemical and physical properties of the oils. It was found that the optimal reaction temperature depends on both length and unsaturation degree of vegetable oils fatty acid chains. Vegetable oils with higher degree of unsaturation exhibit faster monoglycerides conversion to biodiesel. It can be concluded that fatty acid composition influences reaction parameters and glycerides conversion, hence biodiesel yield and economic viability.

1. Introduction

Biodiesel is an alternative fuel that is usually produced from many vegetable oils and animal fats through the transesterification of large, branched triglycerides (TG) into smaller, straight-chain molecules of esters, usually aided by an alkali catalyst (Van Gerpen, 2005; Pinzi et al., 2009b; Luque et al., 2008; Granados et al., 2007). When the alcohol used is methanol, there are three stepwise reactions with intermediate formation of diglycerides (DG) and monoglycerides (MG) resulting in the production of 3 mol of methyl esters (ME) and 1 mol of glycerol (GL), as follows (Darnoko and Cheryan, 2000):

The overall reaction is:

$$TG + 3CH_3OH \xrightarrow{Catalyst} 3R'CO_2CH_3 + GL$$

The stepwise reactions are:

$$TH + CH_3OH \rightleftharpoons DG + R'CO_2CH_3$$
$$DG + CH_3OH \rightleftharpoons MG + R'CO_2CH_3$$
$$MG + CH_3OH \rightleftharpoons R'CO_2CH_3 + GL$$

The content of TG, DG and MG is mainly dependent on the technical process of transesterification. Moreover, glycerides content is the key parameter to define biodiesel quality. High contents of glycerides, especially triglycerides, may cause formation of deposits at the injection nozzles and in the valves (Mittelbach and Remschmidt, 2004). A low presence of glycerides can only be achieved by selecting the appropriate reagents (type and concentration) and reaction conditions, besides further distillation of the product (Mittelbach and Remschmidt, 2004). During the reaction, monitoring of these intermediate products is crucial to study both biodiesel conversion mechanism and quality of the final product. Kinetics study and monitoring of the transesterification reaction have been the subject of a number of recent publications (Dorado et al., 2004b, Vicente et al., 2005; Darnoko and Cheryan, 2000; Arzamendi et al., 2006), but a comparative study using different feedstocks is missing. The use of vegetable oils showing heterogeneous chemical composition is useful to determine the potential dependence between feedstocks fatty acid composition, transesterification mechanism and kinetics of the reaction.

It has been shown that several parameters related to biodiesel quality directly depend upon the fatty acid composition of biodiesel, hence influenced by the composition of the parent oil or fat. Among these specifications are cetane number, kinematic viscosity, oxidative stability, cold-flow properties in the form of cloud point or cold-filter plugging point, exhaust emissions, lubricity and heat of combustion (Pinzi et al., 2009b; Knothe and Steidley, 2005). To improve the quality of biodiesel through the optimization of the fats and oils with different chemical composition, several studies have been carried out (Canakci and Sanli, 2008; Knothe, 2005, 2008; Harrington, 1986; Ramos et al., 2009).

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However, there are also other important parameters that may be highly influenced by the fatty acid composition. Among them are the rate of FAME conversion and the optimal amount of reactants used in the transesterification reaction (Pinzi et al., 2009b; Dorado et al., 2004a). Those parameters are also important from the point of view of the economic viability of biodiesel production (Dorado et al., 2006). Stavarache et al. (2007) established the connection between yield of FAME during ultrasound-assisted transesterification and the composition of fatty acids of commercial edible oils, including corn, grape seed, canola and palm oils. They found that saturated fatty acids, that have a natural preference for the first and third positions in the triglyceride molecules (Richards et al., 2002), were transesterified mostly at the beginning of the reaction, while the amount of unsaturated fatty acids esters increased as the reaction progressed. Abreu et al. (2004) performed a heterogeneous metal–catalyzed transesterification and observed that both saturation degree and alkyl-chain length are determinant factors in the catalytic activity and, consequently, in the reaction yield.

The aim of this work was to study both the progress over the time of the products of the transesterification and the influence of the fatty acid composition on the optimization of the reaction temperature, as one of the main parameters involved in the transesterification process. To study this influence, a multiple regression model was proposed. To study the progress of glycerides (MG, DG and TG) over the time under optimal reaction conditions, different feedstocks (orujo olive, sunflower, maize, linseed, coconut and palm oils) were selected.

2. Methods

2.1. Vegetable oils

Biodiesel samples were produced after alkali-catalyzed transesterification of six different vegetable oils showing a wide range of fatty acids composition (Pinzi et al., 2009a). Sunflower oil (SFO), maize oil (MO) and orujo olive oil (OOO) were acquired from KOIPESOL (Sevilla, Spain), linseed oil (LO) was purchased from Guinama (Valencia, Spain), palm oil (PO) and coconut oil (CO) were acquired from Quimics Dalmau (Barcelona, Spain). Oils chemical composition is depicted in Table 1.

2.2. Reagents

KOH and methanol were the catalyst and alcohol used to produce biodiesel, respectively. KOH pellets [85% p.a. CODEX (USP_NF)] and methanol ACS-ISO were acquired from PANREAC (Barcelona, Spain).

To determine the content of TG, DG and MG in orujo olive oil methyl esters (OOME), sunflower oil methyl esters (SFME), linseed oil methyl esters (LME) and maize oil methyl esters (MME), the following internal standards were used as established in the EN 14105 standard: glycerine, monolein, diolein, triolein, monoglyceride stock solution and MSTFA purchased from Sigma–Aldrich (St. Louis, MO, USA), Tricaprin and 1,2,4 butanetriol acquired from Fluka (Steinheim, Germany).

To determine glycerides content in methyl esters with fatty acid short chains, i.e. coconut oil methyl esters (CME) and palm oil methyl esters (PME), size-exclusion chromatography (SEC) was used and the following analytical lipid standards were purchased from Larodan Fine Chemicals (Malmö, Sweden): monoglycerides mixture MG Mix 21 (monostearin, monoololein, monolinolein, monolinolenin), diglycerides mixture DG Mix 51 (distearin, diolein, dilinolein, dilinolenin), tripalmitin, triolein, trilinolein, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. Glycerol (99.5%, Sigma–Aldrich, St. Louis, MO, USA) and HPLC grade methanol from Scharlau (Barcelona, Spain) were used as reference standards (Arzamendi et al., 2006).

2.3. Instruments and apparatus

A Varian (Palo Alto, CA, USA) Star 3400 gas chromatograph equipped with a flame ionization detector (FID) was used for gas chromatographic determinations. A Supelco capillary column 12 × 0.32 mm, df 0.15 μm was used for the determination of glycerides in OOME, SFME, MME and LME. A Waters 510 HPLC pump, a Rheodyne 7725i manual injector, a Waters model 410 differential refractive index (RI) detector and a Viscotec TriSEC® model 270 dual detector were used for SEC determination of glycerides in PME and CME. Data collection and analysis were performed with TriSEC® GPC software (Arzamendi et al., 2006).

2.4. Analyses

The determination of TG, DG, MG and glycerol in SFME, MME, OOME and LME samples was performed according to the UNE EN 14105 standard. However, in the case of COME and POME, SEC method was used. The mobile phase was HPLC grade THF (Scharlau) at 1 ml/min. The columns were 300 × 7.8 mm Styragel® HR0.5, HR1 and HR2 columns (Waters) of 5 μm particles. The columns were protected with a Styragel® 30 × 4.6 column guard

Table 1
Raw materials chemical properties: total unsaturation degree (TUD), poliunsaturation degree (PUD), monounsatutation degree (MUD) and average of chain length (CL). (MO, maize oil; SFO, sunflower oil; OOO, orujo olive oil; CO, coconut oil; LO, linseed oil; PO, palm oil).

Property	MO	SFO	OOO	CO	LO	PO
Free fatty acid content (%)	0.15	0.20	0.40	1.20	0.23	0.85
Iodine value (gI/100 g)	118.1	134.7	99.8	33.5	189	58.32
Fatty acid composition (%)						
Caprylic (C8:0)				9.5		
Decanoic (C10:0)				8		
Lauric (C12:0)				41		0.5
Miristic (C14:0)	<0.1	<0.10		18		1.5
Palmitic (C16:0)	13.00	6.90	11	9	5.5	45.5
Palmitoleic (C16:1)			0.8	0		
Stearic (C18:0)	2	6	3	3.8	6	4
Oleic (C18:1)	33	26.5	75.2	7.5	21	38
Linoleic (C18:2)	50.8	66.5	9.5	2.7	14	10
Linolenic (C18:3)	1	0	0.5	0.5	53.5	0.5
CL (average number of carbons)	17.72	17.88	17.76	13.05	17.89	16.57
TUD	137.60	149.50	96.50	14.40	209.50	58.01
PUD	104.60	123.00	20.50	6.90	188.50	20.01
MUD	33.00	26.50	76.00	7.50	21.00	38.00