



# Synthesis of maleated-castor oil glycerides from biodiesel-derived crude glycerol



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## ABSTRACT

Castor oil glycerides were obtained from the glycerolysis of castor oil or its methyl esters with alkaline-crude glycerol. High monoglyceride yields were obtained between 20–30 min and 180–200 °C with both substrates. The glycerolysis of castor oil afforded highest yield of products at 180 °C and 30 min (50.4 of monoglycerides and 35% of diglycerides). However, the glycerolysis of methyl esters was more selective toward the formation of monoglycerides. Castor oil glycerides were further esterified with maleic anhydride without catalyst. Reaction was followed by acid value and <sup>1</sup>H NMR. ca. 87% conversion of hydroxyl groups was obtained at 90 °C. The final product contained 2.6 maleate groups per glyceride molecule.

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## 1. Introduction

Industrial uses of vegetable oils in last years have increased due to concerns about depletion of fossil fuels and environmental issues (Biermann et al., 2011). The use of non-edible oils such as castor oil and jatropha oil in chemical purposes can reduce the consumption of edible oils for these applications (Biermann et al., 2011; Rios et al., 2013). Castor oil is one of the most valuable oils due to its high content of ricinoleic acid (ca. 90%). Ricinoleic acid has a double bond close to a hydroxyl group, which confers it special physical and chemical properties. Castor oil is a raw material with wide application in many chemical industries such as paints, coatings, inks, lubricants and a variety of other products (Dix et al., 1995).

An interesting strategy to obtain vegetable oil-based monomers consists of the attachment of readily polymerizable functional groups to the triglyceride structure forming vegetable oil macromonomers. Attachment of these functionalities can be done through unsaturations, allylic carbons, ester groups, hydroxyl groups and  $\alpha$  carbons to carbonyl groups (Mazo et al., 2012; Ronda et al., 2011). Hydroxylated and non hydroxylated oils such as castor oil, jatropha oil or soybean oil can be converted to hydroxyl derivatives through alcoholysis (transesterification) or epoxidation-hydroxylation (Can et al., 2001, 2006a; Echeverri et al.,

2010; Rios et al., 2011, 2013). The main advantage of the alcoholysis route is that it produces principally primary hydroxyl moieties.

Alcoholysis of vegetable oils can be accomplished with several polyols like glycerol, pentaerythritol and bisphenol-A propoxylate. However, considering the price of raw materials it is more convenient the use of glycerol. Price of glycerol has diminished due to the glut of crude glycerol from biodiesel production (Yang et al., 2012). Biodiesel-derived crude glycerol possesses very low value due to the impurities. Therefore, value-added uses of crude glycerol are convenient in order to improve economics of biodiesel. Use of alkaline crude glycerol in the production of mono- and diglycerides through glycerolysis of oils and their methyl esters is a promissory application because impurities in crude glycerol are catalysts of the reaction. A few works regarding to the glycerolysis of fats and methyl esters with alkaline crude glycerol has been reported (Chetpattananondh and Tongurai, 2008; Nouredini et al., 2004; Nouredini and Medikonduru, 1997; Echeverri et al., 2010, 2012).

Unsaturated monomers can be obtained by the attachment of maleate groups (maleinization) to hydroxyl functionalities of triglycerides or their derivatives. For instance, maleated castor oil has been obtained in high yields by catalyzed and thermal maleinization of castor oil by several authors (Can et al., 2006a; Wang et al., 2007). In addition, thermal and microwave assisted maleinization of castor oil were studied recently in our group (Mazo et al., 2012). It was observed that the reaction was complete within 7 h at 80 °C and within 3 h at 100 °C, regardless of the heating method used. Besides castor oil, ricinoleic acid has been esterified with maleic anhydride at 90 °C using toluene as solvent, as reported by Teomim et al. (1999). Catalyzed maleinization of

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hydroxyl-derivatives of soybean oil and castor oil has been conducted by Can et al. (2006a). Thus, maleated soybean oil glycerides were obtained at 100 °C using several catalysts such as sodium hydroxide, sulphuric acid, 2-methyl imidazole and p-toluene sulphonic acid. According to the results, the best catalyst was 2-methyl imidazole, which afforded a yield of 93% in 5 h. Likewise, castor oil derivatives of glycerol, pentaerythritol and bisphenol-A propoxylate were esterified with maleic anhydride at 98 °C, using N,N-dimethyl benzylamine as catalyst. These monomers were copolymerized with styrene affording hard rigid plastics (Can et al., 2006a). Properties of polymers were comparable to those of high-performance unsaturated polyester resins.

Previous works related with the use of biodiesel-derived crude glycerol and the residual catalyst in the glycerolysis of oils have been conducted only with soybean oil or palm. To the best of our knowledge, glycerolysis of castor oil or its methyl esters has not been evaluated before with crude glycerol, using alkaline impurities as the catalyst. On the other hand, the maleinization of castor-oil glycerides obtained from biodiesel-derived crude glycerol as well as data at different temperatures and reaction times have not been reported before. Moreover, the uncatalyzed maleinization of mono- and diglycerides of castor oil below 100 °C is not found in the literature.

In this work, the glycerolysis of castor oil and methyl esters derivative thereof were accomplished with crude glycerol, obtained from biodiesel production. Effects of the temperature and reaction time were evaluated. Reactions were followed by gas chromatography in order to determine influence of reaction conditions on monoglyceride and diglyceride content. In addition, these glycerides were esterified with maleic anhydride without catalyst. The effect of the temperature on the acid values as a function of the reaction time was analyzed. Conversions of hydroxyl groups as well as maleate and fumarate yields were analyzed by <sup>1</sup>H NMR.

## 2. Material and methods

### 2.1. Materials

Sodium hydroxide (>99%), methanol (≥99.8%), and maleic anhydride (≥98%) were obtained from Sigma-Aldrich (Sigma Aldrich, St Louis, MO). Refined soybean oil (acid value, 0.17 mg KOH/g) and technical grade castor oil (acid value, 1.96 mg KOH/g; hydroxyl value, 160 mg KOH/g) were purchased from a local distributor (Fig. 1).

### 2.2. Synthesis of castor oil glycerides (COG)

COG were obtained from the glycerolysis of castor oil and methyl esters derived thereof. Castor oil glycerolysis was conducted in a 250-mL round-bottom flask, equipped with a nitrogen inlet, mechanical stirring and heating mantle. Castor oil (150.0 g) was heated to the reaction temperature (180–220 °C) and then crude glycerol (42.35 g) was added in a 2.5/1 molar ratio of pure glycerol to oil according to the purity obtained by gas chromatography (88.1%). Once the reaction was completed, 2.0 mL of H<sub>2</sub>SO<sub>4</sub> solution in water (50%, w/w) was added to neutralize the catalyst. The mixture was allowed to cool to 100 °C to separate the neutralized catalyst and the most of the excess glycerol in the bottom of the flask.

Glycerolysis of castor oil methyl esters was carried out in a similar assembly as describe above, but in addition, a Dean-Stark-type condenser was connected to collect the methanol generated in the reaction. Molar ratio of glycerol to methyl esters was 1.25/1. Temperature ranged from 160–200 °C. The same procedure described for castor oil glycerolysis was followed, except that for a batch of

150.0 g of methyl esters and 63.25 g of crude glycerol, 3.0 mL of H<sub>2</sub>SO<sub>4</sub> solution in water (50%, w/w) were added.

Crude glycerol was obtained from the transesterification of soybean oil with methanol (methanol/oil molar ratio of 6/1), at 65 °C and catalyzed with 0.37% of NaOH respect to the oil, according to the procedure of Echeverri et al. (2010). No further purification step apart from methanol removal was accomplished for crude glycerol. The same procedure was followed for the transesterification of castor oil with methanol. Crude methyl ester phase was washed with hot-water until elimination of alkaline components (confirmed by titration with HCl) followed by heating at 100 °C under vacuum to remove water. The purity of castor oil methyl esters obtained by gas chromatography was 93%.

<sup>1</sup>H NMR spectra of the glycerolysis products showed the following signals:

<sup>1</sup>H NMR [CDCl<sub>3</sub>, δ (ppm)]: 5.54 (m,  $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{OH})-$ ), 5.37 (m,  $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{OH})-$ ), 5.08 (m,  $-\text{CH}(\text{OC}=\text{O})-$ ), 4.25–4.05 (m,  $-\text{CH}_2(\text{OC}=\text{O})-$ ), 3.98–3.84 (m,  $-\text{CH}-\text{OH}$ ), 3.76–3.52 (m,  $\text{CH}_2\text{OH}$ ), 2.34 (t,  $-\text{CH}_2(\text{C}=\text{O})\text{O}-$ ), 2.20 (m,  $\text{CH}-\text{CH}_2-\text{CH}(\text{OH})-$ ), 2.02 (m,  $-\text{CH}_2-\text{CH}=\text{CH}-$ ), 1.58 (t,  $-\text{CH}_2-\text{CH}_2-(\text{C}=\text{O})\text{O}-$ ), 1.45 (m,  $-\text{CH}_2-\text{CH}_2-\text{CH}(\text{OH})-$ ), 1.42–1.14 (m,  $n\text{CH}_2-$ ), 0.85 (t,  $\text{CH}_3-$ ).

### 2.3. Synthesis of maleated castor oil glycerides (MACOG) (Fig. 1)

Reaction was carried out in test tubes closed with rubber stoppers, according to the time intervals to be evaluated. 10-mL magnetically stirred test tubes was used. COG (0.2 g) was mixed with maleic anhydride (0.3 g) in each test tube. The tubes were stirred in a heating bath at the reaction temperature (80, 90 and 100 °C). The tubes were withdrawn from the heating bath at 10, 30, 45, 60 and 120 min and cooled in a water container to stop the reaction quickly before the chemical characterization.

<sup>1</sup>H NMR spectrum of the maleinization products showed the following signals:

<sup>1</sup>H NMR [CDCl<sub>3</sub>, δ (ppm)]: 6.89 (m,  $-\text{CH}=\text{CH}-$ , from fumarate moieties, 0.1 H), 6.32 (m,  $-\text{CH}=\text{CH}-$  from maleate moieties, 5.2 H), 5.48 (m,  $-\text{CH}(\text{OC}=\text{O})-$ , 1.6 H), 5.30 (m,  $-\text{CH}=\text{CH}-$ , from fatty acid chain, 1.8 H), 5.02 (q,  $-\text{CH}_2-\text{CH}(\text{OC}=\text{O})-\text{CH}_2-$ , 0.8 H), 4.50–4.05 (m,  $-\text{CH}_2(\text{OCO})-$ , 4 H), 2.34 (m,  $-\text{CH}_2(\text{C}=\text{O})\text{O}-$ , 5 H), 2.01 (m,  $-\text{CH}_2-\text{CH}=\text{CH}-$ , 2.9 H), 1.58 (t,  $-\text{CH}_2-\text{CH}_2(\text{C}=\text{O})\text{O}-$ , 5.5 H), 1.41–1.14 (m,  $-\text{CH}_2-$ , 22.3 H), 0.85 (t,  $\text{CH}_3-$ , 4.3 H).

### 2.4. Characterization

Glycerol in crude glycerol as well as diglycerides and monoglycerides in the glycerolysis products were determined by a standardized method (Brüschweiler and Dieffenbacher, 1991). Methyl esters in glycerolysis products were determined by gas chromatography according to BS EN14103 method. An Agilent 7890A with flame ionization detector was used. A DB5-HT with a length of 15 m, an inner diameter of 0.32 mm and a film thickness of 0.1 μm was used. Tetradecane was employed as internal standard for the quantification of products. Helium was used as carrier. Contents of NaOH and soap in crude glycerol were determined by modified AOCs method Cc 17-79 (Van Gerpen et al., 2004).

Reactions were followed by acid value titration and <sup>1</sup>H NMR. For the determination of acid value of the maleinization samples, same procedure of Wang et al. (2007) was followed. This procedure consists in hydrolysis of excess of maleic anhydride and titration with KOH ethanol solution. <sup>1</sup>H NMR (300 MHz) spectra were obtained using a Bruker AMX400 spectrometer with Fourier transform and CDCl<sub>3</sub> as solvent.

Data plotted in the accompanying figures correspond to the means of triplicate experiments with a relative standard deviation < 5% in all cases.

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