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Biodiesel from Castor Oil: A Comparison of Ethanolysis versus Methanolysis

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The transesterification reactions of castor oil with ethanol and methanol as transesterification agents were studied in the presence of several classical catalytic systems. The effects of the nature of the alcohol and catalyst on the yields of monoalkyl fatty acid esters were evaluated. The results indicate that biodiesel can be obtained by transesterification of castor oil using either ethanol or methanol as the transesterification agent. Similar yields of fatty acid esters may be obtained following ethanolysis or methanolysis; however, the reaction times required to attain them are very different, with methanolysis being much more rapid.

Introduction

The use of vegetable oil derivatives as direct replacements for diesel fuel is not only environmentally advantageous but is rapidly becoming an economically viable strategy for sourcing part of the global fuel oil requirement. In this context, castor oil, derived from *Ricinus communis* by pressing and/or solvent extraction, has been identified as an important potential source of raw material for the local production of biodiesel in the northeast of Brazil.¹

Castor oil is comprised almost entirely (ca. 90%) of triglycerides of ricinoleic acid (12-hydroxy-*cis*-octadec-9-enoic acid) in which the presence of a hydroxyl group at C-12 imparts several unique chemical and physical properties. Thus, castor oil and its derivatives are completely soluble in alcohols and exhibit viscosities that are up to 7-fold higher than those of other vegetable oils.² Such properties are exploited in various industrial applications of castor oil including the production of coatings, plastics, and cosmetics.

Although a wide variety of vegetable oils, including castor oil, can be used directly to replace normal diesel fuel, the high viscosities of the crude vegetable oils themselves limit their application.² One approach to resolve this problem involves transesterification of the triglycerides (the major component present in the crude vegetable oil), in the presence of a short-length alcohol, such as methanol or ethanol, leading to less viscous methyl esters (FAMEs) or ethyl esters (FAEEs), respectively. This process can be catalyzed by acid, alkali, or enzymes.^{3–5}

Despite the fact that we have recently reported the results of some studies concerning the ethanolysis of castor oil,⁶ little information is currently available concerning the reaction parameters and the respective yields for the production of FAMEs or FAEEs by the methanolysis or ethanolysis of castor oil. With the aim of rectifying this situation, a systematic and comparative study has been carried out of the transesterification of castor oil with ethanol and methanol as transesterification agents in the presence of various conventional transesterification catalysts.

Experimental Section

Materials. Analytical-grade H₂SO₄ (purity > 99%) and HCl (37 wt %), KOCH₃ and NaOCH₃ (purities appropriate for synthesis), and anhydrous EtOH and MeOH (analytical grade; stored over MgSO₄ as a desiccant) were purchased from Merck. Reagent-grade KOH, NaOH, H₃PO₄, and NaHCO₃ were obtained from Vetec. All reagents were used without further purification. Castor oil (export type 1) was from Bioleo—Bariri Comercial de Óleos and was used as received. This product contained 1.2% free fatty acids (determined as oleic acid according to the AOCS official method Ca 5a-40).

Analytical Procedures. The FAMEs or FAEEs obtained from the transesterification reaction were analyzed by gas chromatography using a Varian 3400 CX instrument, equipped with an capillary injection system operating at 240 °C, with a split ratio of 100:1 and sample size of 1 µL. The capillary apolar column, with 2.2 m in length, 0.32 mm of internal diameter, and 0.1 mm film thickness, was employed, and the column temperature program was initial temperature of 50 °C (1 min), 15 °C/min to 180 °C, 7 °C/min to 230 °C, and 30 °C/min to 245 °C. The detection system

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was equipped with a flame ionization detector (FID) operating at 250 °C. The carrier gas was high-purity hydrogen.

Biodiesel yield, described as the amount of FAMES or FAEEs formed from the transesterification reaction, was quantified in the presence of tricaprylin as an internal standard. Approximately 0.15 g of the products, obtained according with the procedure described in the Transesterification Experiments section, was weighted in a vial. An amount of 1 mL of tricaprylin solution (0.01 g/100 mL of hexane) was added. This solution was injected in a chromatographic apparatus, and the peak areas of the compounds were integrated. Each experiment was evaluated twice, and each sample was evaluated as an average of two injections. The biodiesel yield (percent FAMES or percent FAEEs) was calculated as

$$\text{percent FAMES or percent FAEEs} = \frac{m_{\text{tricaprylin}} A_B f_{\text{tricaprylin}}}{A_{\text{tricaprylin}} m_s}$$

where $m_{\text{tricaprylin}}$ = weight of the internal standard, A_B = peak area of FAMES or FAEEs, $f_{\text{tricaprylin}}$ = response factor, $A_{\text{tricaprylin}}$ = peak area of the internal standard, and m_s = weight of the sample.

Transesterification Experiments. Transesterification reactions were performed in a 250 mL batch reactor equipped with a reflux condenser and a magnetic stirrer. The reaction mixture containing methanol or ethanol, castor oil, and the catalyst (KOH, NaOH, KOCH₃, NaOCH₃, H₂SO₄, or HCl), with a molar ratio of alcohol/oil/catalyst of 60:10:2, had been refluxed at the boiling point of the respective alcohol for an appropriate time. After this time, the alcohol was recovered by distillation, and the remained mixture was neutralized and washed 3 times with distilled water. The phase separation was carried out by gravity in a separatory funnel. The biodiesel yield was determined by gas chromatography and expressed in terms of the percentage (weight percent) of FAEEs or FAMES formed. Before chromatographic characterization, the mixture was dried in the presence of MgSO₄, as a desiccant agent, and centrifugated.

Results and Discussion

The quantification of biodiesel were conducted, after separation and purification steps, in terms of the yield (weight percent) in FAEEs or FAMES, obtained by transesterification of castor oil with EtOH and MeOH, respectively, in the presence of conventional catalysts, such as KOH, NaOH, KOCH₃, NaOCH₃, H₂SO₄, and HCl.

The workup procedure, for these reactions, involves neutralization and phase separation. The aim of the neutralization step is to deactivate the catalyst remaining in the medium. In the case of a basic catalyst, an aqueous solution of H₃PO₄ (5 wt %/vol) was used. For the acid catalysts, an aqueous solution of NaHCO₃ (5 wt %/vol) was employed. It is important to remark that, in all reaction, independent of the catalyst employed, the phase separation was difficult in the workup procedure. This is, in part, due to the singular chemical composition of the castor oil, as mentioned in the Introduction.²

The best yields of fatty acid esters were typically achieved when methoxide ion was employed as a catalyst (Figures 1 and 2). The catalytic efficiency of hydroxide ion was generally inferior to that of methoxide ion, even though, from a chemical standpoint, the active species present in both systems was the alkoxide ion formed in the presence of alcohol. The significant difference between the two catalytic processes is that molecules of water, produced during the formation of the active species in the presence of hydroxide ion, may hydrolyze or saponify the ester produced, hence, diminishing the yield.²

The ethanolysis or methanolysis of castor oil is effectively catalyzed by acids with very good yields, as is clearly demonstrated in Figures 3 and 4. It is reported that the acid-catalyzed transesterification reaction proceeds at rates that are

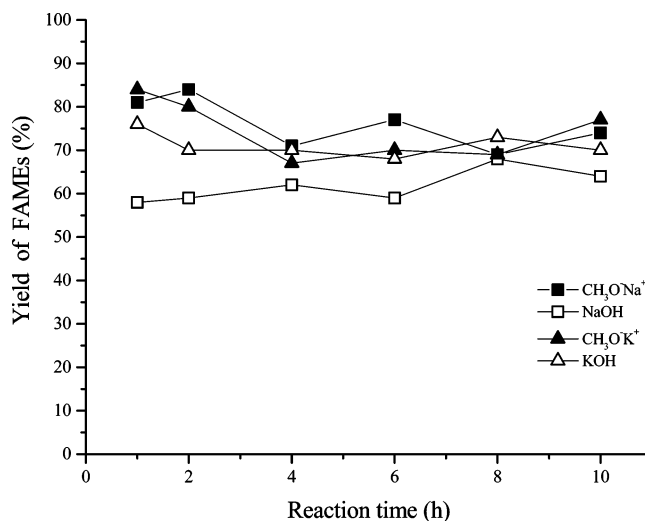


Figure 1. Production of FAMES (percent yield) by the methanolysis of castor oil in the presence of basic conventional catalysts. The reaction mixture contained MeOH/oil/catalyst in molar proportions of 60:10:2, and the reaction was carried out at 60 °C under reflux with constant magnetic stirring.

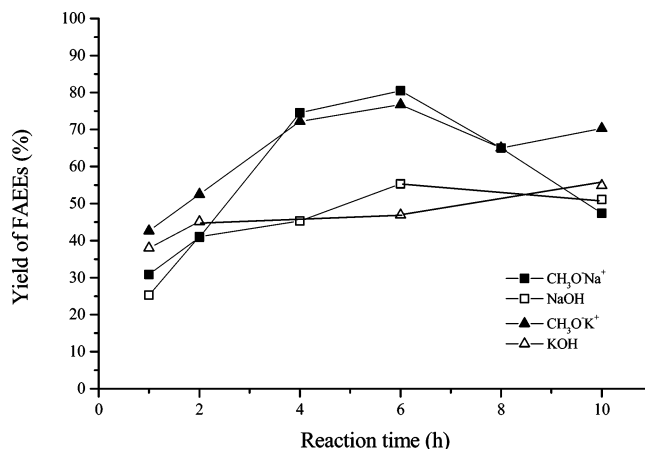


Figure 2. Production of FAEEs (percent yield) by the ethanolysis of castor oil in the presence of basic conventional catalysts. The reaction mixture contained EtOH/oil/catalyst in molar proportions of 60:10:2, and the reaction was carried out at 80 °C under reflux with constant magnetic stirring.

ca. 4000 times slower than the equivalent base-catalyzed reactions⁴ and, for this reason, have not been considered commercially viable. Such conclusions, however, are related to typical vegetable oils containing heterogeneous triglycerides, without or with a very low content of hydroxyl fatty acid derivatives. These are obviously not applicable when castor oil is the substrate.

An important aspect should be considered, in acid or basic catalytic transesterification of the castor oil: in both conditions, they occur in homogeneous phase because of the high solubility of the reagents in the castor oil, which is not verified when typical vegetable oils are used. Also, as it will be discussed later, it has been observed that, in basic condition, there are some drawbacks that are not present in the acid one.

It is known that the rate of transesterification reactions of vegetable oils shows a strong dependence on the nature of the transesterification agent.^{7–9} As shown in Figures 1–4, the

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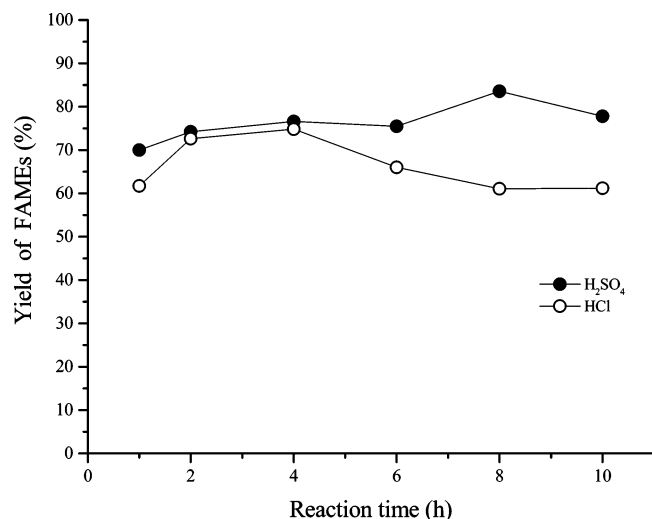


Figure 3. Production of FAMES (percent yield) by the methanolysis of castor oil in the presence of acid conventional catalysts. The reaction mixture contained MeOH/oil/catalyst in molar proportions of 60:10:2, and the reaction was carried out at 60 °C under reflux with constant magnetic stirring.

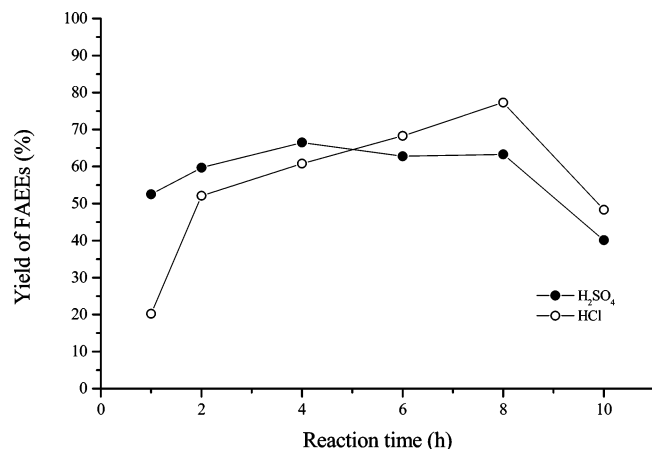


Figure 4. Production of FAEs (percent yield) by the methanolysis of castor oil in the presence of acid conventional catalysts. The reaction mixture contained EtOH/oil/catalyst in molar proportions of 60:10:2, and the reaction was carried out at 80 °C under reflux with constant magnetic stirring.

kinetic profiles of ethanolysis and methanolysis of castor oil in the presence of conventional catalysts are very different, a finding that is in accordance with a previous report relating to soybean oil.^{7,8} In the present study, the maximum yields of FAEs and FAMES obtainable with a reaction mixture containing alcohol/oil/catalyst in a molar ratio of 60:10:2 were, respectively, 80% (ethanolysis at 80 °C) and 90% (methanolysis at 60 °C). It noteworthy that higher yields have been reported for transesterifications carried out under similar reaction conditions with other vegetable oils as substrates.⁶

At least with respect to base catalysis, two factors may be responsible for the observed yields attained with castor oil. In the first place, the free fatty acids present in the castor oil used may have led to the neutralization of part of the catalyst present, thus reducing the formation of ethoxides and producing soaps within the reaction medium. Not only would mass transfer during the reaction be reduced by the formation of soaps, but also their presence during the product recovery step would

exacerbate the problem of phase separation.⁸ Second, the hydroxyl group at C-12 of ricinoleic acid may be converted, in basic medium, to an alkoxide. The generation of this anionic species may compete with the formation of ethoxide species and consequently reduce the yield of ester.¹⁰ It is important to mention that this alkoxide probably is not effective for the transesterification reaction, using conventional catalysts.^{10,11}

As expected, the obtention of biodiesel from castor oil, in the presence of any of the catalysts studied, was faster with methanol as the transesterification agent compared with ethanol. Thus, maximum yields of esters could be obtained following a reaction time of 1 h with methanol or of 5 h with ethanol. While transesterification is an equilibrium reaction between esters and alcohols,¹⁰ the reaction may be under kinetic control before thermodynamic equilibrium is achieved, and this would favor the formation of monoalkyl esters. This behavior may be observed in Figures 2 and 4 for the ethanolysis reaction in which the best yields were achieved after ca. 7 h of the reaction in the presence of methoxides or HCl as a catalyst; after this time, the reaction clearly attained reversibility, as has already been reported.^{6,7} For ethanolysis, the nature of the catalyst is very important in determining the overall yield of monoalkyl esters. With respect to methanolysis, however, the effect is not as marked because thermodynamic equilibrium of the transesterification reaction is achieved very rapidly (<1 h). Studies are on course in our group to obtain the entire kinetic profile of these transesterification reactions, through the determination of tri-, di-, and monoglyceride and glyceride content, besides FAEs and FAMES.

Conclusions

On the basis of the results of the present study, it is concluded that biodiesel can be obtained by transesterification of castor oil using either ethanol or methanol as the transesterification agent. However, while similar yields of fatty acid esters may be obtained following ethanolysis or methanolysis, the reaction times required to attain them are very different, with methanolysis being much more rapid. However, all studied systems presented difficulties with respect to the separation and purification of the biodiesel produced. Clearly, transesterification of castor oil via ethanolysis or methanolysis must be improved through the development of more efficient catalytic systems and processes, to maintain kinetic control of the reaction, and by optimization of purification procedures.

At light of these results, acid catalysis appears to offer a number of important advantages with respect to the transesterification of vegetable oils. For example, acid catalysts are not strongly affected by the presence of free fatty acids in the oil, and they can catalyze simultaneously both esterification and transesterification reactions.¹² Furthermore, it has recently been demonstrated that on an industrial scale acid-catalyzed production of biodiesel can compete economically with base-catalyzed processes.¹² Developments in this area may involve the application of catalytic systems containing metal complexes exhibiting Lewis acid sites, the potential of which has already been noted.^{13,14}

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A further problem that requires detailed consideration, however, relates to the high viscosities of castor oil and the FAMEs and FAEEs derived from them. The values of kinematic viscosity were, attaining at 38.7 °C, 17.02 and 19.75 for the

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FAMEs and FAEEs, respectively.^{15,16} It may be necessary to modify the current generation of diesel engines to accept such biodiesel, or alternatively, the properties of the castor oil product may need to be improved, perhaps by admixture with low-viscosity fuels derived from different sources.

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