Ethanolysis of Castor and Cottonseed Oil: A Systematic Study Using Classical Catalysts

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ABSTRACT: Several classical catalytic systems for the transesterification reaction have been used to produce FA ethyl esters (FAEE) from castor and cottonseed oils. The effects of the amount and nature of the catalyst, and of the reaction temperature, on the yields of FAEE were determined. The most efficient transesterification of castor oil was achieved in the presence of methoxide and acid catalysts, whereas for cottonseed oil, which has a composition that is much more similar to most vegetable oils than is castor oil, the highest yields of FAEE were obtained following base-catalysed ethanolysis.

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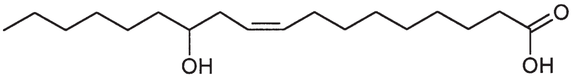
KEY WORDS: Biodiesel, castor oil, catalytic transesterification, cottonseed oil, ethanolysis.

The use of vegetable oil derivatives as direct replacements for diesel fuel not only is environmentally advantageous but also is rapidly becoming an economically viable proposition for the supply of energy in rural areas. As part of an initiative of the Brazilian government to stimulate the production of biodiesel for use in the northeast part of the country (1), two oleaginous plants have been identified as potential sources of appropriate oils.

Castor oil, obtained from seeds of *Ricinus communis* by pressing and/or solvent extraction, is constituted almost entirely (*ca.* 90%) of TG containing the unusual FA ricinoleic acid (12-hydroxy-*cis*-octadec-9-enoic acid) (Scheme 1). Owing to the presence of a hydroxyl group at C12 of ricinoleic acid, castor oil possesses several unique chemical and physical properties that are exploited in various industrial applications including the production of coatings, plastics, and cosmetics. Thus, castor oil and its derivatives are completely soluble in alcohols and present viscosities that are up to sevenfold higher than those of other vegetable oils (2).



Ricinoleic acid (**1**)

SCHEME 1

Cottonseed oil may be an alternative source of biodiesel in the northeast of Brazil. In comparison with castor oil, the FA composition of cottonseed oil resembles that of most other vegetable oils, consisting mainly of linoleic (54%), palmitic (22%), and oleic (19%) acids together with small amounts of stearic (3%), myristic (1%), palmitoleic (1%), and linolenic (1%) acids (3). Most of the physical and chemical properties of cottonseed oil resemble those of the major vegetable oils that also contain heterogeneous TG.

Although castor and cottonseed oils can be used directly to replace normal diesel fuel, the high viscosities of the crude oils limit their application (2). One strategy that can be used to overcome this problem is to convert the FA (free and bound) into either their methyl esters (FAME) or their ethyl esters (FAEE), derivatives that have greatly reduced viscosities. Transesterification of the crude oil can be carried out using acids, alkalis, or enzymes as catalysts for the reaction (4–8).

Very little information is available and, as far as the authors are aware, no in-depth studies have been carried out concerning the reaction parameters and respective yields for the production of FAME or FAEE from castor oil by transesterification. Thus, we have carried out a systematic study of castor oil ethanolysis in the presence of various conventional catalysts. To obtain information about the differential effect of TG composition on the transesterification reaction, we have also examined the ethanolysis of the more typical cottonseed oil under the same reaction conditions.

EXPERIMENTAL PROCEDURES

Materials. Analytical grade (purity >99%) H_2SO_4, HCl, K_2CO_3, and $CaCO_3$ were obtained from Merck (São Paulo, Brazil), and KOH and NaOH were from VETEC (São Paulo, Brazil). $KOCH_3$ and $NaOCH_3$ (at purities suitable for synthesis) were obtained from Merck, and anhydrous EtOH (analytical grade) was purchased from the same supplier and stored over $MgSO_4$ as desiccant. All reagents were used without further purification. Castor oil (export type 1) was from Bioleo – Bariri Comercial de Óleos (Bariri, São Paulo, Brazil), and cottonseed oil (commercial grade) was supplied by Bunge Alimentos (Gaspar, Santa Catarina, Brazil). Both oils were used

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as received. The FFA present in the oils [determined as % oleic acid, according to the AOCS official method Ca 5a-40 (9)] were equivalent to 1.2% for the castor oil, and 0.2% for the cottonseed oil.

Analytical procedures. The products of the transesterification reaction were analyzed, in the presence of methyl phthalate as internal standard, by GC using a Varian 3400 CX instrument equipped with an FID and a DB1 short capillary column purchased from J&W Scientific (Folsom, CA). The oven temperature was programmed from 150 to 260°C at a heating rate of 10°C/min, and the carrier gas was high-purity hydrogen. Aliquots (1 μL) of the samples were injected and the FAEE quantified using an internal standard method.

Transesterification experiments. All transesterification reactions (except for those in which the influence of the amount of catalyst was investigated) were carried out using EtOH/oil/catalyst in a molar ratio of 60:10:2. Reactions were performed at 80°C (except when the influence of the temperature of reaction was investigated) in a 250-mL batch reactor equipped with a magnetic stirrer. After an appropriate reaction time, the transesterification mixture was neutralized and subsequently washed three times with distilled water. In all cases it was found difficult to separate the phases during the workup procedure. The conversion yield was determined by GC and expressed in terms of the percentage of FAEE produced.

RESULTS AND DISCUSSION

The transesterification of castor oil in the presence of EtOH to yield FAEE was investigated using various reaction times and temperatures and different amounts and types of catalyst. To verify the effect of TG composition on FAEE formation, we also examined the transesterification of cottonseed oil.

Transesterification of castor oil in the presence of acid and alkali. Several conventional catalytic systems were used (including KOH, NaOH, $KOCH_3$, $NaOCH_3$, H_2SO_4, HCl, K_2CO_3, and $CaCO_3$) to obtain an overview of the typical yields of FAEE obtainable from the transesterification of castor oil. In all cases the highest conversion yields were achieved following long (>5 h) reaction times (Fig. 1). Among the catalytic systems studied, the use of methoxides or acids produced the highest yields of FAEE, and such reactions attained reversibility after *ca.* 6–8 h, as has already been reported (10).

Methoxide ions appeared to be more efficient catalysts than hydroxide ions although, from a chemical standpoint, the active species in both systems were the ethoxide ions formed by virtue of the large excess of EtOH in the medium. The significant difference between the two catalytic systems is that with hydroxide catalysts, water molecules are produced during the formation of the active species; as a consequence, side reactions, such as hydrolysis and saponification, may diminish the yield of ester (2).

The results clearly show that acid catalysis is relatively effective for the ethanolysis of castor oil, particularly at short reaction times (Fig. 1). Homogeneous acid-catalyzed transesterification has hitherto been considered unattractive for commercial applications, as it reportedly proceeds at a rate some 4000 times slower than its base-catalyzed counterpart (4). Such findings relate, however, to typical vegetable oils containing heterogeneous TG, such as cottonseed oil, and are obviously not applicable when castor oil is substrate.

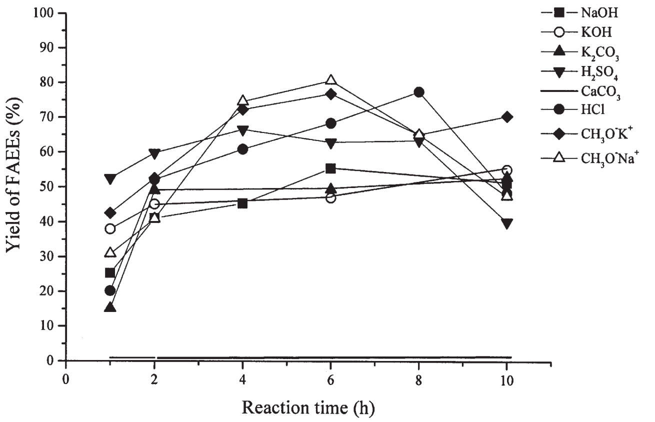

FIG. 1. The production of FA ethyl esters (FAEE) (percentage yield) by the ethanolysis of castor oil in the presence of conventional catalysts. The reaction conditions were: molar proportions of EtOH/oil/catalyst (60:10:2); temperature 80°C; constant magnetic stirring.

Potassium and calcium carbonates were also tested as catalysts. Although both compounds were insoluble in the reaction medium, the former was a relatively effective catalyst whereas the latter showed no catalytic activity even after 10 h of reaction (Fig. 1). The catalytic site of potassium carbonate is unknown; however, the compound may function as a Brønsted base, or traces of oxide present on the surface of the solid material could be responsible for the transesterification reaction (11).

The influences of the concentration of catalyst and the reaction temperature on transesterification were evaluated in the presence of sodium hydroxide and hydrochloric acid. As shown in Figure 2A, the amount of catalyst present did not affect remarkably the yield of FAEE obtained. For sodium hydroxide, however, the highest conversion was obtained when the catalyst was present at a concentration of 0.2 mmol. The use of higher concentrations led to a reduction in the yield of product, probably as a result of an increase in the occurrence of side reactions (2). The effect of temperature on the yield of FAEE in the presence of sodium hydroxide was insignificant (Fig. 2B). In contrast, higher reaction temperatures produced significant increases in the reaction yield when hydrochloric acid was used as the catalyst. Thus, at 100°C the HCl-catalyzed yield of FAEE was *ca.* 80% compared with only 54% at 80°C.

Comparison between the ethanolysis of castor and cottonseed oil in the presence of acid and alkali. To determine the effect of the TG composition on transesterification, cottonseed oil was subjected to ethanolysis in the presence of acid, base, and methoxide catalysts, and the yields of FAEE were determined. The results (Fig. 3) indicate that base catalysis is very much more efficient than acid catalysis. In the presence of sodium hydroxide, a yield of *ca.* 80% FAEE was obtained after

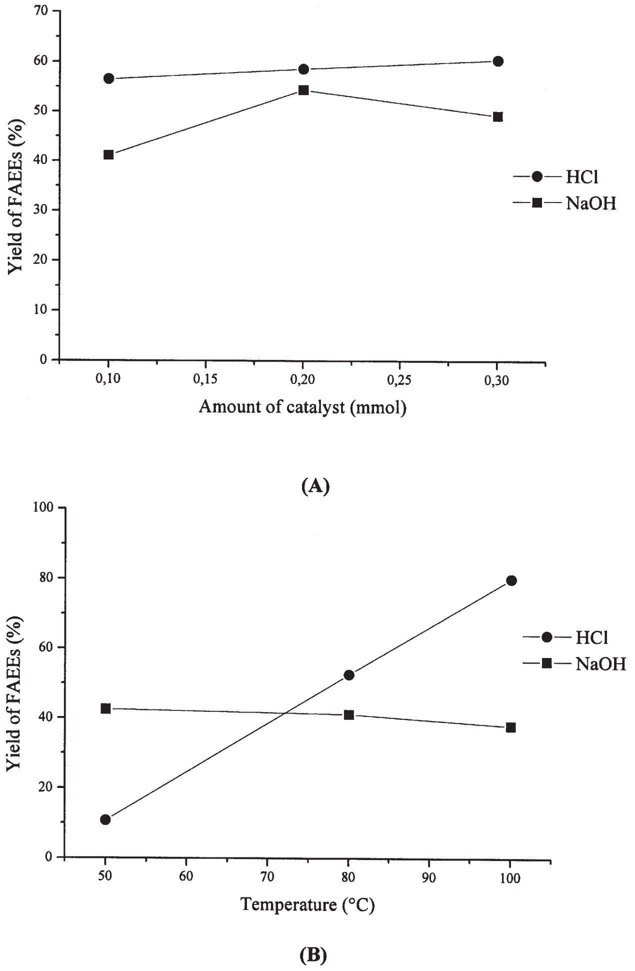

FIG. 2. The influence of the amount of catalyst (A) and reaction temperature (B) on the production of FAEE (percentage yield) by the ethanolysis of castor oil in the presence of HCl and NaOH as catalysts. Reaction conditions were the same as those in Figure 1 where appropriate. For abbreviation see Figure 1.

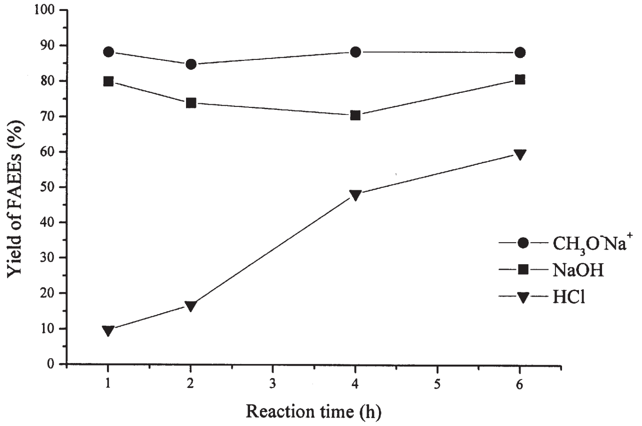

FIG. 3. The production of FAEE (percentage yield) by the ethanolysis of cottonseed oil in the presence of NaOH, $NaOCH_3$, and HCl. Reaction conditions were the same as those in Figure 1. For abbreviation see Figure 1.

1 h of reaction time whereas with hydrochloric acid less than 10% of ester was produced in the same time. These results are in line with those reported for other vegetable oils that exhibit the typical FA composition (4,12,13). On the other hand, acid-catalyzed transesterification of castor oil provides better rates of conversion at short reaction times (Fig. 1). For example, the yield of FAEE after 2 h of reaction was 52% for castor oil but only 17% for cottonseed oil.

The lower yields of FAEE obtained following base-catalyzed conversion of castor oil compared with cottonseed oil may be the result of two factors. First, the high acid value exhibited by castor oil may lead to the neutralization of part of the catalyst present, thus reducing the formation of ethoxides and producing soaps within the reaction medium. Soap formation would not only reduce mass transfer during the reaction but also exacerbate the problem of phase separation at the stage of product recovery (14). Second, in basic medium, the hydroxyl group at C-12 of ricinoleic acid is converted into an alcohoxide derivative that can compete with the generation of ethoxide species and consequently compromise the conversion reaction (15).

Based on the results presented, one may conclude that the production of biodiesel by ethanolysis of castor oil may be improved through further development and optimization of appropriate catalytic systems and processes. Strategies involving acid catalysis might provide a promising solution to this problem since it has recently been demonstrated that on an industrial scale acid-catalyzed production of biodiesel can compete economically with base-catalyzed processes (16). Moreover, acid-catalyzed transesterification reactions exhibit an important advantage in that the performance of the acid catalyst is not strongly affected by the presence of FFA in the oil. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification (15).

Reports (9,16,17) of new catalytic systems containing metal complexes exhibiting Lewis acid sites that can be used in transesterification reactions appear very encouraging and offer further avenues of research. However, the intrinsic high viscosity of castor oil and the FAEE derived from them can lead to some problems in their application as a biodiesel. It may be necessary to use the product from castor oil in admixture with low-viscosity biodiesel from different sources or to modify the diesel motor to overcome these technological barriers.

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