

Comparison of soybean oil and castor oil methanolysis in the presence of tin(IV) complexes

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ARTICLE INFO

Article history:

Received 5 September 2010
Received in revised form 23 January 2011
Accepted 20 February 2011
Available online 3 March 2011

Keywords:

Biodiesel
Tin catalysts
Methanolysis
Transesterification
Castor oil

ABSTRACT

In this paper we present and discuss the results obtained from the methanolysis of two vegetable oils with very distinct triglyceride composition, castor oil and soybean oil, using Lewis acid Sn(IV)-based compounds as catalysts. For all transesterification reactions, two different types of reactors were employed; an open glass (OG) reactor equipped with a reflux condenser, and a closed steel (CS) reactor. The results indicated that in all reactions assayed, regardless of the Sn(IV)-based catalyst employed, the yields obtained with the methanolysis of castor oil are generally lower than those carried out with soybean oil. Furthermore, independently of the oil used, the reaction yields tend to be higher when the CS reactor was employed.

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1. Introduction

Biodiesel represents today an alternative solution to meet the increasing demand for energy with environmental quality and considering economical aspects [1–3]. When compared with petroleum fuels, biodiesel is advantageous, not only because it is renewable, but its use allows reductions in CO_x, SO_x and particulate matter exhaust emissions into the atmosphere. Another important factor is that biodiesel has a higher flash point than diesel, ensuring higher levels of safety in its transport and storage [4].

The transesterification of vegetable oils in the presence of a short chain alcohol, such as methanol, leads to biodiesel (a mixture of alkyl monoesters) and glycerol as the final products. This reaction is conventionally catalyzed by chemical species that may act as enzymes, or Brønsted acids or bases [5]. Many vegetable oils can be employed as source to obtain biodiesel, and the right choice of raw materials should always be based on the technical and economical aspects. For example, particularly in Brazilian in subtropical areas, soybean oil is already used in large scale for biodiesel production. In Brazilian semi-arid lands, castor oil, obtained from *Ricinus communis* by pressing and/or solvent extraction, can be an appropriate choice of raw material for biodiesel production.

Castor oil is comprised almost entirely (ca. 90%) of triglycerides containing the unconventional fatty acid, known as ricinoleic acid

(12-hydroxy-*cis*-octadec-9-enoic acid, Fig. 1). Due to the presence of a hydroxyl group at C12, castor oil possesses unique chemical and physical properties that are exploited in diverse industrial applications including the production of coatings, plastics and cosmetics. For example, castor oil and its derivatives are completely soluble in alcohols and feature viscosities that are up to seven times higher than those of other vegetable oils [6].

Soybean oil, in contrast to castor oil, has physico-chemical properties that are common to most vegetable oils. Its composition in terms of fatty acids consists mainly of linoleic (54%), oleic (24%), palmitic (11%), linolenic (7%) and stearic (4%) acids [7].

As we can see, the fatty acid composition of the oil employed is a variable feature that must be seriously considered on catalytic biodiesel production processes. In an earlier study, we determined the effect of triglyceride composition on transesterification reactions [8]. Therein, cottonseed and castor oils were subjected to ethanolysis in the presence of commonly used basic and acid catalysts. At that opportunity, it was observed that under base catalysis the ethanolysis of castor oil leads, in general, lower yields of biodiesel as fatty acid ethyl esters (FAEE). At that opportunity, we concluded that this tendency is related to the fact that, in the presence of a Brønsted base catalyst (NaOH), the hydroxyl group at C12 of ricinoleic acid can be converted into an alkoxide derivative, which competes with the generation of ethoxide species and, consequently, inhibits the conversion reaction [8]. It worth noting that the ricinoleic alkoxide derivative formed displays only a weak nucleophilic character, and thus no products derived from the transesterification of the ricinoleic alkoxide derivatives were observed.

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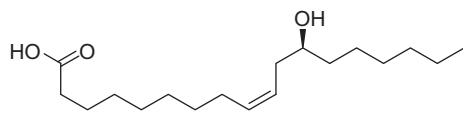


Fig. 1. Ricinoleic acid.

In order to increase the yields of the transesterification reaction, develop new biodiesel industrial processes, and minimize the waste production and treatments diverse catalytic systems have been proposed and studied [9].

An approach that has been adopted in the development of new classes of catalysts for biodiesel production is that based on complexes exhibiting Lewis acid sites [10–12], and potential candidates are tin(IV) complexes. In the industry, tin(IV)-based compounds function as catalytic homogeneous or heterogeneous precursors in esterification, transesterification and polycondensation reactions, with the purpose of generating polymeric and intermediate materials [13–15]. However, as far as we are aware, no information is available about the performance of these class of catalysts face to different source of vegetable oils with very dissimilar chemical structure, like castor and soybean oils.

In this context, we carried out a systematic study on the methanolysis of castor and soybean oil in the presence of Sn(IV) complexes as catalysts, aiming to acquire further data on the transesterification reactions using molecular Lewis acid catalysts. Furthermore, in order to evaluate to which extent reaction parameters like time and temperature influence the transesterification reactions of the two oils, several reaction conditions were applied. In addition, two classes of reactors were employed, one open glass reactor (OG), where the reactions were carried out under methanol reflux condition at atmospheric pressure, and a closed steel reactor (CS), where the reactions were carried out at different temperatures, and different endogenous pressures [16,17].

2. Materials and methods

2.1. Materials

Dibutyltin diacetate, $(C_4H_9)_2Sn(C_2H_3O_2)_2$ – DBTDA; butylstannic acid, $(C_4H_9)SnO(OH)$ – BTA; di-*n*-butyl-oxo-stannane, $(C_4H_9)_2SnO$ – DBTO; and dibutyltin dilaurate, $(C_4H_9)_2Sn(C_{12}H_{23}O_2)_2$ – DBTDL, were purchased from Sigma–Aldrich. Castor oil (export type 1) was purchased from Bioleo – Bariri Comercial de Óleos (Brazil), and soybean oil (commercial grade) was supplied by Bunge Alimentos. All chemicals were used as received, without further purification. Methanol was commercially acquired from Merck (analytical grade) and stored over $MgSO_4$ as a desiccant.

The free fatty acids present in the oils (determined as % oleic acid according to the AOCS official method Ca 5a-40) were equivalent to 1.2% for castor oil and 0.1% for soybean oil.

2.2. Transesterification experiments

Two types of reactors were employed to carry out the transesterification reactions: an open glass (OG) reactor equipped with a reflux condenser and a closed steel (CS) reactor. Both reactors have been previously described elsewhere [17]. In the case of OG reactor the reactions were performed at the reflux temperature of the methanol and for CS reactor the employed temperatures were 80 °C, 120 °C and 150 °C.

Regardless of the reactor employed, all reactions were performed using a methanol:oil:catalyst molar ratio of 400:100:1. In the case of the experiments carried out under diluted conditions, 10 wt.% toluene solutions of castor or soybean oil were used.

After the set reaction time (1, 2 and 4 h), the reaction mixture was washed three times with distilled water and the mixture was dried over $MgSO_4$ and centrifuged. The reaction yields were determined by GC and expressed in terms of the percentage of fatty acid methyl esters (% FAMES), according to a procedure described elsewhere [17].

3. Results and discussion

This study aimed to expand the discussion regarding the catalytic properties exhibited by Sn(IV) complexes in the transesterification of two dissimilar vegetable oils with alcohols [16,17]. To this end, we carried out a systematic study on the methanolysis of castor oil and soybean oil in the presence of Sn(IV) molecular catalysts. It is important to note that, as far as we are aware, no information is available concerning castor oil transesterification in the presence of these metal complexes as catalysts.

As detailed in Table 1, the castor oil and soybean oil methanolysis reactions were carried out using different reaction times and temperatures. Also, the different reaction conditions were assessed using CS or OG reactors.

The results show that, under the reaction condition carried out with the OG reactor, *i.e.* at atmospheric pressure and methanol reflux temperature (*ca.* 65 °C), only two Sn(IV) complexes (DBTDL and DBTDA) were relatively catalytically active, and just for soybean oil methanolysis. On the other hand, in all reaction conditions assayed, employing the CS system, better yields were obtained for both vegetable oils used. Indeed, with the CS reactor, higher reaction temperatures can be achieved, resulting in an increase in the reaction yield, except when reversible reactions were attained [10,11,18]. In addition, under high reaction temperature in CS reactors, high concentrations of methanol in the liquid phase can be reached, leading to high reaction rates in methanolysis [17].

Furthermore, at higher reaction temperatures the catalysts can be effectively activated [19,20], and their solubility in the reaction medium can be improved [16]. It should be noted that BTA and DBTO present significant catalytic activity only at high temperatures [16]. Complexes like BTA and DBTO are insoluble in a series of solvents, and organized as stable oligomeric structures at room temperature [21]. However, on increasing the temperature these particular arrangements can be destabilized, resulting in more active molecular species.

With a 100-mL CS reactor, the endogenous reaction pressure significantly increased at high temperatures. Measuring the pressures, it was possible to estimate the methanol concentration in the liquid phase, using the Peng–Robinson equation of state. It should be noted that, according to our experiments, the methanol concentration in the liquid phase using the OG reactor remained at around 35 wt.%, which is very low when compared to that using the CS reactor (*ca.* 90 wt.%) [17].

One can also verified that, regardless of the catalyst employed or the reactor used, the yields obtained in the transesterification of castor oil were lower than those obtained when soybean oil was employed as the triglyceride source. The lower reactivity of castor oil in comparison to soybean oil in transesterification has been previously observed using conventional Brønsted base catalysts [8,18,22]. Clearly, this behavior can be related to the dissimilar chemical composition of the two oils.

The presence of the hydroxyl group at C12 of the ricinoleic acid derivative in castor oil (12-hydroxy-*cis*-octadec-9-enoic acid, Fig. 1) increases the solubility of methanol in castor oil, which improves the contact between the two reactants (oil and alcohol). However, this hydroxyl group is also responsible for the high viscosity of the oil, causing mass transfer problems. We previously

Table 1

Production of FAMEs (percentage yield) by the methanolysis reaction of castor oil and soybean oil in the presence of several Sn(IV) catalysts, at different temperatures and using OG and CS reactors. The reaction conditions were: molar proportions of MeOH:oil:catalyst = 400:100:1 and constant magnetic stirring (1000 rpm).

T (°C)	Reaction time (h)	Catalysts							
		DBTDA		DBTDL		DBTO		BTA	
		Soybean oil	Castor oil	Soybean oil	Castor oil	Soybean oil	Castor oil	Soybean oil	Castor oil
OG	1	8	<5	7	<5	<5	<5	<5	<5
	2	13	<5	11	<5	<5	6	<5	<5
	4	23	<5	20	<5	7	<5	<5	<5
CS 80 °C	1	32	<5	47	6	35	<5	11	<5
	2	63	<5	48	7	48	12	10	<5
	4	75	<5	62	8	64	16	9	<5
CS 120 °C	1	56	28	70	19	45	8	40	<5
	2	73	47	77	23	83	23	76	14
	4	77	64	76	36	85	46	60	35
CS 150 °C	1	69	41	98	47	75	31	70	39
	2	65	45	98	52	95	50	73	53
	4	79	56	80	57	74	50	74	61

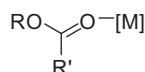


Fig. 2. Schematic illustration of carboxylic group activation via acid–base Lewis type interaction.

reported that alcoholysis under conventional base-catalyzed reactions [8,18,22] can converted the hydroxyl group of the ricinoleic fragment into an alkoxide derivative, which competes with the generation of methoxide species, compromising, consequently, the production of the monoester, i.e., biodiesel [8].

In this context, we decided to verify whether the low reactivity of the castor oil in methanolysis, using Sn(IV) complexes as catalysts, is related to mass transfer problems, or if there is a significant chemical contribution from the particular chemical composition of the castor oil in the deactivation of the catalyst.

Thus, experiments were conducted under diluted conditions. Two different solutions containing 10 wt.% in toluene of each triglyceride, castor and soybean oil, were prepared. At this concentration the viscosity differences between the two solutions are minimized (viscosity of both solutions was $0.7 \text{ mm}^2 \text{ s}^{-1}$), and differences related to mass transfer problems are minimized. These solutions underwent transesterification reactions with methanol, using DBTDL as catalysts (molar ratio of methanol:oil:DBTDL = 400:100:1, 120 °C, 4 h of reaction using CS reactor). The biodiesel yields attained were 80% and 30% for the system containing soybean and castor oil, respectively. From these results it can be assumed that the mass transfer is not the factor responsible for the lower yields observed in the methanolysis of castor oil, but indeed the intrinsic chemical structure of castor oil is the main factor for its lower activity. It appears to be highly probable that the ricinoleic fragment has a strong influence on the formation of the active species in the reaction medium, i.e., the Lewis acid–base complex formed by the interaction between the acylglycerides (mono, di, or tri) or the fatty acids at the metal center via the oxygen of the carbonyl group, see Fig. 2 [23]. Therefore, it is possible to envisage that the hydroxyl group at C12 of ricinoleic acid may also interact with the metal centre of the catalyst, inhibiting the faster progression of the reaction.

It is worth noting that, for all of the reaction conditions employed, no products derived from the transesterification reaction of ricinoleic alkoxide derivatives were observed, confirming the low nucleophilic character of the hydroxyl group at C12 of the ricinoleic fragment.

4. Conclusions

The results indicated that, regardless of the Sn(IV) catalyst employed, the methanolysis of the castor oil leads to lower yields than those observed when soybean oil is adopted as the triglyceride source. This lower reactivity of the reaction systems based on castor oil, regardless of the Sn(IV) catalyst employed, is not due to mass transfer problems, but rather to the singular chemical composition of this oil. This observation indicates the influence of the chemical composition of the triglycerides on the activity of catalytic systems based on Lewis acid sites. Another important finding is that the use of a CS rather than an OG reactor, and increases in the reaction temperature, lead to higher reaction yields for all Sn(IV) complexes studied. The high activity of the closed reaction system is due to the high temperatures that can be achieved with this type of reactor, and to the higher concentration of methanol in the reaction medium.

Acknowledgments

The authors wish to thank FINEP, CAPES, CNPq and FAPESP for financial support. TMS, DRM and JPVS express their appreciation for fellowships granted by CAPES and CNPq. SMPM and MRM thank CNPq for research fellowships.

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