

# Studying the Influence of Alumina Catalysts Doped with Tin and Zinc Oxides in the Soybean Oil Pyrolysis Reaction

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**Abstract** The pyrolysis of vegetable oils consists of cracking triglycerides to produce smaller molecules. A mixture of hydrocarbons and oxygenated compounds, such as carboxylic acids and aldehydes, is obtained as the product and which can be separated by fractional distillation. When the reaction is carried out in the absence of catalysts (thermal cracking), a great quantity of these oxygenated compounds is obtained. Thus, the presence of those oxygenated compounds in the products results in a high level of acidity, which can be a problem when using them as fuels in combustion engines. The aim of this work was to study the composition of the products obtained by cracking of vegetable oils assisted by  $\gamma$ -alumina doped with zinc and tin oxides. The products were analyzed by FT-IR, GC-MS and GC-FID and the acid number was determined by titration with alcoholic KOH solution. The acid number, infrared spectra and chromatograms of the resulting hydrocarbon mixtures indicated a significant reduction in oxygenated compounds when compared with the mixtures obtained by the thermal cracking process, thus decreasing the acidity of the mixture.

**Keywords** Cracking · Catalysts · Alternative fuels · Vegetable oils · Alumina · Tin · Zinc

## Introduction

Studies concerning alternative fuel sources have recently become more frequent, which can be explained by several economical, social, and ecological factors. In the isolated communities of Brazilian Savannah and Amazonian rainforest regions, as well as other tropical areas in the world, the use of alternative fuel sources is particularly important due to the difficult access to petroleum derived fuels, since they are situated far away from the production and distribution centers. It is worth mentioning that these communities use diesel engines for economical production, transport and to produce electricity. Thus, the use of biodiversity as energy source may represent an important way to provide sustainable development in regions such as these and elsewhere [1]. The mainly studied processes concerning the conversion of biomass into fuels suitable to use in diesel engines are the alcoholysis and pyrolysis of vegetable oils to produce, respectively, fatty acid methyl- or ethyl- esters and hydrocarbons [2]. Among these options, considering their great potential for obtaining vegetable oils from palm-trees and grains and the difficulty in obtaining dry alcohols, the pyrolysis or cracking of vegetable oils seems to be a simple and efficient method to produce fuels.

The pyrolysis of vegetable oils has been used for the fuels supply during war periods, for example, the production of hydrocarbons by thermal cracking of Tung oil in China during the Second World War [3]. Since then, numerous methods for thermal [4–7] and catalytic pyrolysis under inert [8–15] or reductive [16] atmospheres have been developed. For a recent review of the development of catalysts for fatty-based materials see reference [2]. In these works, the characterization of gas and liquid products indicated that not only the reaction affords the

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desirable linear and cyclic paraffins and olefins, but also undesirable oxygenated compounds are produced, such as aldehydes and carboxylic acids. It was suggested that these oxygenated compounds are produced when the glyceridic part of the triglyceride is cracked [17]. Indeed, it was proposed that the triglycerides are decomposed to give carboxylic acids, acrolein and ketenes [3]. In the reaction conditions, these oxygenated compounds are further decomposed, generating esters, carboxylic acids and hydrocarbons [16]. Finally, the carboxylic acids are decarboxylated or decarbonylated, producing, respectively, carbon dioxide and paraffins or carbon monoxide, olefins and water [16].

It was also pointed out that the composition of the pyrolysis product can be tuned by use of different raw-materials or by the presence of heterogeneous catalysts. For instance, it was observed that the pyrolysis of macauba oil affords hydrocarbons, aldehydes and carboxylic acids [6], whereas the pyrolysis of its calcium soap affords only hydrocarbons and ketones [5]. On the other hand, it was observed that the presence of different types of zeolites dramatically changes products formed by the decomposition of vegetable oils [8–10, 14, 15], affording essentially non-oxygenated compounds. Indeed, it was pointed out that the Brønsted acid sites of the zeolites induce the formation of aromatic compounds and short chain hydrocarbons in the range of gasoline proportionally to the amount of the alumino-silicate added to the reaction [11, 15].

The catalytic effect of activated alumina and their derivatives doped with transition-metals was also studied. It was reported that the pyrolytic products of soybean and babassu oils catalyzed by  $\gamma$ -alumina doped with nickel and molybdenum in hydrogen atmosphere were completely deoxygenated when the reaction was carried out in the presence of hydrogen pressure [16]. However, the need for hydrogen in the system makes the process complicated due to the difficult of handling this gas and also because of its high price. On the other hand, the decomposition of sewage sludge, composed basically of free fatty acids and some amounts of triglycerides, in the presence of activated alumina, yields predominantly hydrocarbons [18].

Thus, we think there is still a long way to go in order to develop an efficient and cheap process to produce hydrocarbons suitable to be used as fuel in diesel engines. Indeed, the main goal in this field is developing a catalytic system active for deoxygenating the products during the pyrolysis of triglycerides without the presence of hydrogen and also enable the cracking or aromatization of the hydrocarbon chains.

Recently we observed that it is possible to isolate a fuel with physical-chemical properties comparable to those specified for petroleum diesel by pyrolysis of soybean oil and palm-tree oil [19]. Indeed, a diesel-like fuel was

obtained by fractional distillation of the resulting mixture of hydrocarbons and oxygenated compounds, by the adequate choice of temperature intervals. Nonetheless, the resulting fuel possesses some residual undesirable carboxylic acid content (acid number, AN, 116.2, ASTM D465-9). In this work, we studied the catalytic influence of alumina doped with tin and zinc oxides in the composition of the pyrolysis products of soybean oil. The main goal of this study was to identify the potential of these Lewis acid solids in the deoxygenation of the products without hydrogen. Indeed, we studied the pyrolysis of soybean oil in the presence of the solids  $(\text{SnO})_2(\text{Al}_2\text{O}_3)_8$ ,  $(\text{SnO})_1(\text{ZnO})_1(\text{Al}_2\text{O}_3)_8$  and  $(\text{ZnO})_2(\text{Al}_2\text{O}_3)_8$ , and, after adequate distillation, analyzed the pyrolytic products by GC-FID, GC-MS and the acid number in order to determine the catalyst with best product deoxygenating efficiency.

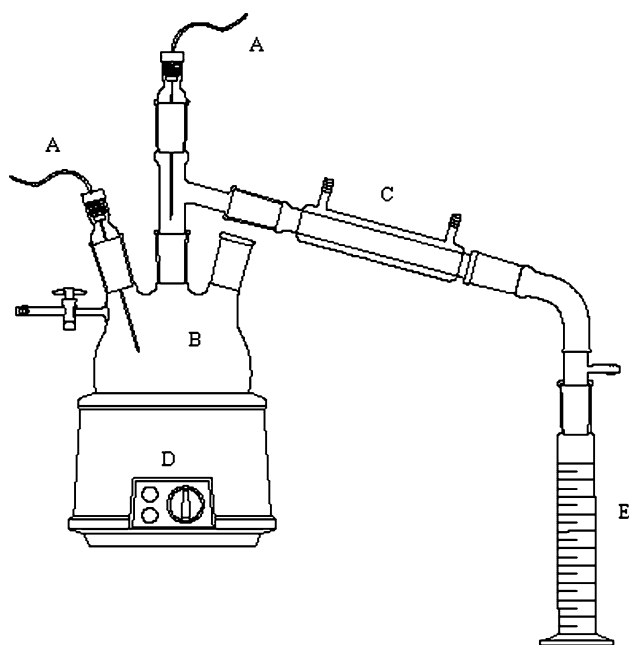
## Experimental Section

### Materials

The refined soybean oil (*Soya* brand) was obtained from commercial sources (Bunge, Brazil) and was used without further treatment. The solids  $(\text{SnO})_2(\text{Al}_2\text{O}_3)_8$ ,  $(\text{SnO})_1(\text{ZnO})_1(\text{Al}_2\text{O}_3)_8$  and  $(\text{ZnO})_2(\text{Al}_2\text{O}_3)_8$  were prepared by co-precipitation as described in the literature [20].

### Pyrolysis Experiments

The pyrolysis experiments were carried out in temperatures ranging from 350 to 400 °C using a 250-mL Pyrex round bottomed flask as represented in Fig. 1. Both the vegetable oil (100 g) and the catalyst (1 g) were introduced into the flask and then heated by an electric resistance. The temperature was measured with thermocouples in the flask and in the gas flow all along the experiment. When the temperature in the flask reached approximately 350 °C, the vegetable oil underwent pyrolysis and the products vaporized. The vapors left the flask at temperatures between 200 and 250 °C and were then condensed in a common glass condenser. The reaction was consistently stopped when approximately 75 mL of the condensed products had been recovered. These products consisted of two distinct layers: an aqueous phase and an organic one. After decantation of the two phases, the organic products were isolated and stored under refrigeration. Each pyrolysis reaction was done in duplicates and the organic products of both runs were distilled and separated into four fractions accordingly to their distillation temperature (DT) intervals: (a)  $\text{DT} < 80$  °C (fraction 1); (b)  $80$  °C  $\leq \text{DT} < 140$  °C (fraction 2); (c)  $140$  °C  $\leq \text{DT} < 200$  °C (fraction 3); (d)  $200$  °C  $\leq \text{DT}$  (fraction 4 or diesel fraction). The different



**Fig. 1** Scheme of the pyrolysis apparatus used in the experiments: A thermocouples; B round-bottom three-necked flask; C condenser; D electric resistance; E graduated collector

fractions were weighed, analyzed by GC and FT-IR and their acid numbers (AN) were determined.

#### Analysis of the Products

The pyrolysis products were analyzed by GC, FT-IR and AN. The GC analyses were carried out with a Shimadzu GC-17A chromatograph equipped with an FID detector and a Shimadzu GCMS-QP5050 equipped with a mass spectrometer, both containing a polydimethylsiloxane column 50 m, 0.25 mm id and 0.2  $\mu\text{m}$  thin layer (CBPI PONA-M50-042), operating between 50 and 250  $^{\circ}\text{C}$  with a heating rate of 10  $^{\circ}\text{C min}^{-1}$ . The FT-IR spectra were obtained on a Bruker Equinox 55 with a thin liquid layer NaCl window. The FT-IR spectrum corresponds to the sum of 64 scans with a spectral resolution of 4  $\text{cm}^{-1}$ . The AN was determined by the titration of the products with a methanol/KOH solution, according to a standard method (ASTM D465-9). The titration of each sample was conducted in triplicates with a negligible error of  $\pm 0.3$  mL for  $V_f$ .

## Results and Discussion

Soybean oil was pyrolyzed in the presence of different  $\gamma$ -alumina catalysts doped with tin (II) and zinc (II) that we had prepared and described in a previous work [20]. The chemical compositions and surface areas of these catalysts are depicted in Table 1.

Table 2 shows the reaction yields obtained for the different catalytic pyrolysis fractions of soybean oil with the different alumina catalysts. For all the catalysts tested, very similar yields of the recovered organic phase and fraction 4 ( $>200$   $^{\circ}\text{C}$ ) were obtained. Nevertheless, the distribution of the other fractions was different for each catalyst. It can be clearly seen that the presence of  $(\text{SnO})_1(\text{ZnO})_1(\text{Al}_2\text{O}_3)_8$  favored conversion to fraction 3 (140–200  $^{\circ}\text{C}$ ), while catalyst  $(\text{ZnO})_2(\text{Al}_2\text{O}_3)_8$  favored conversion to fraction 1 ( $<80$   $^{\circ}\text{C}$ ) and catalyst  $(\text{SnO})_2(\text{Al}_2\text{O}_3)_8$  equally favored conversion to fractions 1 and 3.

All the fractions were analyzed by gas chromatography (GC-FID and GC-MS) and, as an example, the chromatograms (GC-FID) for the four different fractions obtained in the presence of  $(\text{SnO})_2(\text{Al}_2\text{O}_3)_8$  are shown in Fig. 2. As can be depicted from these chromatograms it is really complicated to identify and quantify all this peaks. However, comparing GC-MS with the Wiley Library CLASS-5000 (6th Edition) with more than 95% similarity it was possible to determine that the pyrolysis results in a mixture of hydrocarbons with linear and saturated or unsaturated chains and oxygenated products, such as linear carboxylic acids, aldehydes and ketones. As we have already seen in a previous work [19], the length of the chains depends on the fractions. In the diesel-like fraction the hydrocarbons exhibits from 11 to 15 carbons and the carboxylic acids from 7 to 11 carbons. The presence of 2-propenal (acrolein) was also seen in the lightest fractions (fractions 1 and 2).

Figure 3 shows the FT-IR spectra of the diesel fraction components (distillation temperature,  $\text{DT} \geq 200$   $^{\circ}\text{C}$ ) for the different metal oxides supported in alumina catalysts. It is worth noting that the spectra were normalized taking into account the 1,459  $\text{cm}^{-1}$  signal ( $\text{CH}_3$  bending). Absorption signals in the region 1,000–1,250  $\text{cm}^{-1}$  associated with C–O stretching were also noticed. A very broad feature, changing the baseline profile in the 2,500–3,500  $\text{cm}^{-1}$  spectral region can be associated with the OH stretching

**Table 1** Chemical analysis and BET surface area determined for the catalysts [20]

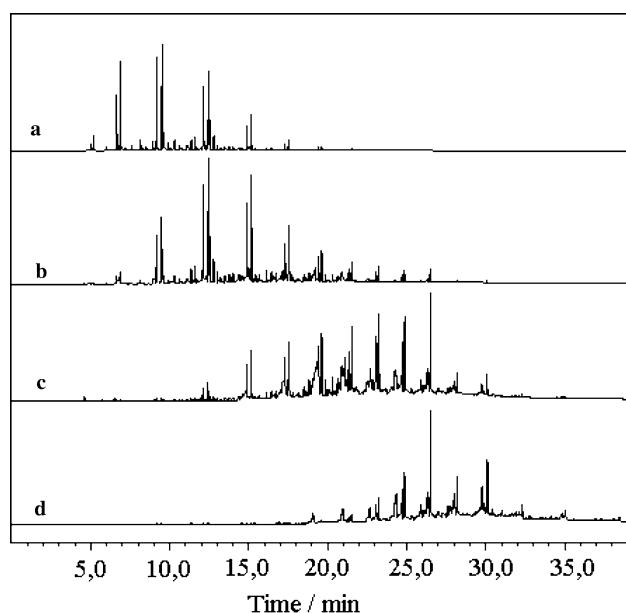
Catalyst	Chemical composition <sup>a</sup>			BET surface area ( $\text{m}^2 \text{g}^{-1}$ )
	Al	Sn	Zn	
$(\text{SnO})_2 \cdot (\text{Al}_2\text{O}_3)_8$	8.13	1.87	–	12.54
$(\text{SnO})_1(\text{ZnO})_1(\text{Al}_2\text{O}_3)_8$	8.20	1.00	0.8	42.62
$(\text{ZnO})_2 \cdot (\text{Al}_2\text{O}_3)_8$	8.00	–	2.0	82.42

<sup>a</sup> Determined by ICP-IOIS

**Table 2** Soybean oil pyrolysis yields with different alumina doped with tin and zinc<sup>a</sup>

Catalyst	Recovered organic phase (g)	Distillation temperature fraction (°C) yield (wt%)			
		<80 °C	80–140 °C	140–200 °C	>200 °C
–	60.0	9.81	15.46	14.91	59.82
	60.5	9.77	15.12	15.21	59.90
(SnO) <sub>1</sub> (ZnO) <sub>1</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>8</sub>	62.0	9.66	10.86	19.05	60.81
	62.3	11.33	10.48	18.46	60.98
(ZnO) <sub>2</sub> · (Al <sub>2</sub> O <sub>3</sub> ) <sub>8</sub>	66.5	21.42	7.40	11.85	59.33
	67.2	21.25	6.86	12.64	59.25
(SnO) <sub>2</sub> · (Al <sub>2</sub> O <sub>3</sub> ) <sub>8</sub>	65.0	17.20	6.16	20.45	56.19
	65.7	17.02	6.42	20.40	56.16

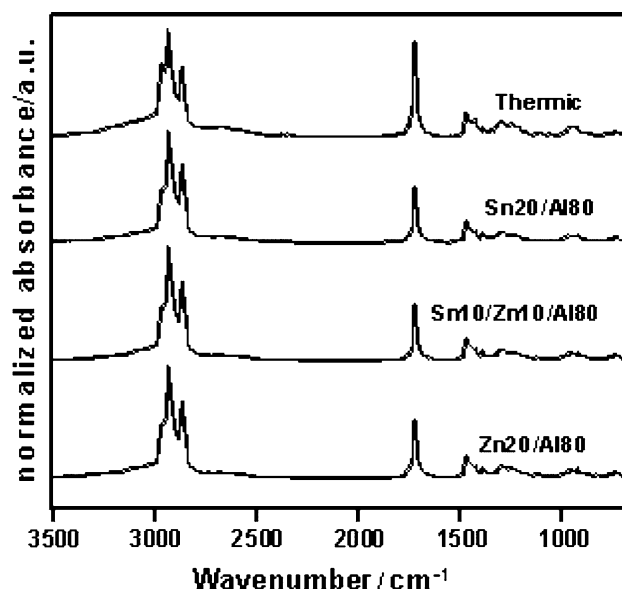
<sup>a</sup> Reaction conditions: (i) temperatures ranging from 350 to 400 °C; (ii) 100 g of vegetable oil and 1 g of catalyst



**Fig. 2** GC-FID chromatograms for the four fractions obtained after distillation of the organic fraction produced by pyrolysis of soybean oil in the presence of (SnO)<sub>2</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub> according to their distillation temperature (DT) intervals: (a) DT < 80 °C; (b) 80 °C ≤ DT < 140 °C; (c) 140 °C ≤ DT < 200 °C; (d) 200 °C ≤ DT (diesel fraction)

modes of carboxylic acids. The 1,700 cm<sup>-1</sup> signal refers to the stretching of C=O bonds in carboxylic acids.

The intensity of the C=O stretching (integrated signal), the AN (mg of KOH g<sup>-1</sup>) of diesel-like fractions obtained with different catalysts, and the yield in water obtained during the pyrolysis process are presented in Table 3. It can also be seen that the nature of the solid influences the quantity of acid products, which can be related to the activity of the catalyst in deoxygenating the pyrolysis products. The IR results presented in Table 2 and Fig. 3 suggest the following order for the activity of the catalysts towards the decomposition of the carbonyl compounds during pyrolysis: (SnO)<sub>1</sub>(ZnO)<sub>1</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub> > (SnO)<sub>2</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub> > (ZnO)<sub>2</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub>. On the other hand, regarding specifically the decomposition of carboxylic acids, which is



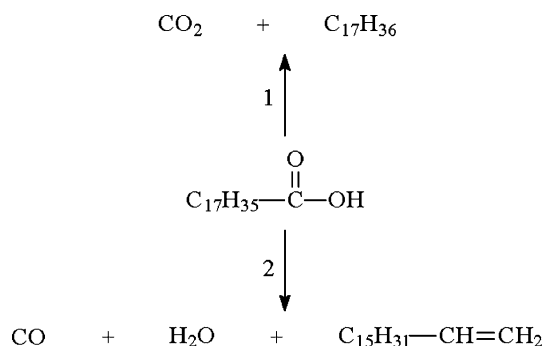
**Fig. 3** FT-IR spectrum of diesel fractions obtained with the soybean oil pyrolysis assisted by metal oxides supported in alumina catalysts

closely related to AN, the following catalytic activity order can be established (SnO)<sub>1</sub>(ZnO)<sub>1</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub> > (ZnO)<sub>2</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub> > (SnO)<sub>2</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub>. However, it can be said that, when compared to the thermal cracking, all the catalysts are active in deoxygenating the products but among the three solids tested, (SnO)<sub>1</sub>(ZnO)<sub>1</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub> is the most active of all.

It was also observed that when using alumina doped with tin, the percent conversion to water is higher than when using zinc doped alumina or the thermal cracking process. It has been proposed in the literature [16] that the thermal decomposition of carboxylic acids occurs by the decarboxylation or decarbonylation reactions, as depicted in Fig. 4. The higher production of water obtained for the tin-based catalyst might suggest that the decarbonylation reaction is preferentially taking place when these catalysts are used. Besides, the presence of saturated hydrocarbons detected by GC-MS in all the pyrolysis products suggests

**Table 3** Integrated intensity of C=O stretching signal at 1,710 ( $I_{\text{C=O}}$ ), acid number (mg KOH/g) of diesel fractions obtained with different catalysts and the water yield obtained during the pyrolysis process

Catalyst	Integration of C=O (1,710 $\text{cm}^{-1}$ )	AN (mg KOH/g)	Yield in water (% wt)
—	73.6	116.14	1.0
	73.7	117.20	0.9
(SnO) <sub>2</sub> · (Al <sub>2</sub> O <sub>3</sub> ) <sub>8</sub>	43.2	99.84	3.0
	43.1	99.73	3.0
(SnO) <sub>1</sub> (ZnO) <sub>1</sub> (Al <sub>2</sub> O <sub>3</sub> ) <sub>8</sub>	42.3	82.34	3.0
	42.0	82.04	3.4
(ZnO) <sub>2</sub> · (Al <sub>2</sub> O <sub>3</sub> ) <sub>8</sub>	47.3	86.65	1.0
	47.3	86.26	1.0

**Fig. 4** Thermal degradation of carboxylic acid pathways: (1) decarboxylation reaction and (2) decarbonylation reaction (adapted from reference [16])

that both pathways (decarboxylation and decarbonylation) occur in the studied systems.

In summary, we have shown that the products of the catalytic pyrolysis of soybean oil consist mainly of a mixture of linear hydrocarbons and oxygenated compounds, such as carboxylic acids. It was observed that the presence of alumina doped with tin and zinc during the pyrolysis can reduce the amounts of carboxylic acids up to 30%. The higher deoxygenating activity was achieved when the solid (SnO)<sub>1</sub>(ZnO)<sub>1</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>8</sub> was used as catalyst. Small differences in the distillation temperature fraction distribution were observed, especially for the diesel-like fraction, which probably means that these catalysts are not active in the carbon chain cracking process. However, more studies are still needed in order to improve the catalytic activity of doped alumina in the deoxygenation of the pyrolysis products of triglycerides and also to determine the possibility of recovering these catalysts, and these are currently being carried out in our laboratory.

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