Thermocatalytic cracking kinetics of myristic acid adsorbed on catalysts with different acidity

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ABSTRACT

Mass losses related to the vaporization/decomposition of myristic acid, either pure or adsorbed on SiO_2, γ-Al_2O_3, SiO_2-Al_2O_3 and HZSM-5 catalysts were obtained by non isothermal thermogravimetric analysis from room temperature up to 650 °C. The adsorption of myristic acid on catalysts greatly changed the mass loss behavior of myristic acid, suggesting a significant decomposition of this fatty acid during heating as compared to its essentially simple volatilization in absence of catalyst. A model-free kinetic was used to estimate the values of apparent activation energy of the mass losses from experiments performed at heating rates of 3, 7, 10 and 15 °C min^{-1}. In absence of a catalyst, myristic acid presented a single mass loss event with an activation energy value of ~87–90 kJ mol^{-1}. In the case of myristic acid adsorbed on SiO_2, γ-Al_2O_3, SiO_2-Al_2O_3 and HZSM-5 at least two different mass loss events occurred during linear heating, associated to myristic acid volatilization/decomposition. The activation energies calculated for both these events, with the exception of myristic acid adsorbed on silica, exhibited values much higher than 90 kJ mol^{-1}. The apparent activation energy of the second mass loss events was always higher than that of the first mass loss events. Activation energy of the second mass loss reached a value as high as 190 kJ mol^{-1} at which point myristic acid was strongly adsorbed on HZSM-5. Such a high value suggests C—C and C—H bond ruptures and not only decarboxylation often described as the main reaction path when saturated fatty acids are pyrolyzed.

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1. Introduction

Increased demand for liquid fuels together with the necessity to decrease the environmental impact of gases produced during combustion has led to the increase of studies dealing with the transformation of renewable biomass into bio fuels and chemicals [1,2]. Among the products obtained from biomass, vegetables oils and fatty acids are excellent precursors of liquid fuels [3,4]. In order to find ways to avoid competition with edible feedstock, studies have been focused on used vegetable oils and fats [5] and on non-edible oils such as jatropha oil [6]. These vegetable oils can be employed to obtain biodiesel via transesterification [7]. However, highly acidic feedstocks are not appropriate for the conventional biodiesel process. Thus, the cracking of these feedstocks is an alternative of interest for the production of chemicals and liquid fuels suitable to use either as gasoline, jet fuel or diesel [8–10].

Before using these new feedstocks on an industrial scale, kinetic models need to be developed for the degradation of high acidic oils [11,12]. Model-free kinetics have been used to predict the conversion of complex molecules and optimize reactions such as cracking [13–15]. These kinetic methods have been used to estimate the apparent activation energy for the degradation of different molecules, either pure [16–19] or in the presence of catalysts [13–15]. Table 1 summarizes literature reports of activation energy values obtained from mass loss in thermogravimetric studies during linear heating treatment of vegetable oils [20–26].

The data from Table 1 are rather disperse [20,21–24], and do not lead to clear trends. For example, during the decomposition of sunflower oil, the presence of HBeta catalyst [23] led to a strong decrease of the Ea value, whereas the presence of catalysts such as MCM-41 and AlMCM-41 led to Ea values rather close to the ones obtained in absence of a catalyst.

During the cracking of fatty molecules, deoxygenated products can be obtained such as alkanes, mono and diolefins, and aromatics, together with oxygenated compounds such as ketones, aldehydes, carboxylic acids and alcohols [26]. The use of a catalyst during the cracking of fatty acids induces the production of

Table 1
Activation energies reported in the literature for the conversion of vegetable oils, obtained from thermogravimetric experiments.

References	Vegetable oil	Catalyst	N° of steps	Ea (kJ mol^{-1})
Font and Rey [20][a]	Olive	no	2	112 (1st step)-195 (2nd)
Santos et al. [21][b]	Sunflower	no	1	170–210
Santos et al. [22][c]	Palm	no	2	185(1st step)-191(2nd)
Melo et al., [23][d]	Sunflower	no	1	193
Melo et al. [23][d]	Sunflower	H-Beta	1	88
Melo et al. [24][e]	Sunflower	AlMCM-41	1	167
Melo et al. [24][e]	Sunflower	MCM-41	1	172
Chouhan et al. [25][f]	Jatropha	no	1	42
Biswas and Sharma [26][g]	Jatropha	no	2	114(1st step)-222(2nd)

Kinetic models: [a]Semi-global, [b,d,e]Vyazovkin, [c] Ozawa-Flyn-Wall (1st step) and Vyazovkin (2nd step), [f]Coats and Redfern, [g] Friedman.

more deoxygenated products when compared to simple thermal decomposition [27,28].

Many catalysts have been used in the production of biofuel derived from the cracking of vegetable oils and animal fats. Among these catalysts, zeolites, metal oxides, silica, alumina and mixtures of these are reported in the literature [29–33]. The catalyst has a key role in the composition of the cracked products. HZSM-5, due to its highly acidic nature, favors a high degree of aromatization, and high production of benzene, toluene and xylenes. The silica-alumina catalyst, with less acidity and crystallinity when compared to HZSM-5, favors the production of short-chain hydrocarbons and a rather high amount of aliphatic molecules [34,35]. Silica with no or limited acidity favors the production of linear olefins [28,29].

Myristic acid is a useful model fatty acid for cracking studies because it is hardly degraded by pure thermal cracking when there are no catalysts present [29]. The products of catalytic cracking of myristic acid are often rich in 1-monoolefins (C5-C13) depending on the catalyst used [29]. These 1-monoolefins are possible precursors of alkylated fuels [36,37] and lubricants obtained from olefin metathesis [38]. Among the main natural sources of myristic acid, coconut oil (18.8–19.7 mass% of MA) [39,40], palm oil (15.3–16.0 mass%) [41,42], babassu oil (11–27 mass%) [43] and macauba oil (8.8 mass%) [44] can be cited.

The present work is part of a larger project aiming at studying the cracking behavior of different vegetable oils and their fatty acid constituents in the presence of catalysts. The general goal of the project is to define experimental conditions and catalysts allowing the obtaining of aromatics, mono-olefins and saturated products that can be added as "drop in" compounds in liquid fuels. The present contribution deals with a comparison of the activation energies measured during cracking of myristic acid (C14:0) either pure or adsorbed on catalysts with different acidity SiO$_2$, γ-Al$_2$O$_3$, SiO$_2$-Al$_2$O$_3$ and HZSM-5.

2. Experimental

2.1. Materials

All catalysts were obtained in powdered form. These were: silica (Kali Chemie AF125), γ-alumina (Oxiteno), silica-alumina (Si:Al = 9:1) (Sigma Aldrich, Grade 135). HZSM-5 was obtained by heating NH$_4$ZSM-5 (Sentex Industrial, SAR = 23.8) at 5 °C min^{-1}, up to 650 °C, for 4 h under air. Myristic acid (MA) (99%) was obtained from Sigma Aldrich.

Mixtures of previously dried catalysts at 120 °C and MA were obtained by hand grinding, at 50 °C, followed by a short heating time at a temperature of 10 °C higher than the MA fusion temperature, in order to allow a uniform spreading of the liquid MA on the catalyst surface. The catalyst:MA mass ratio was 5:1. The sample preparation used 100 mg of dried catalyst in powdered form and 20 mg of myristic acid.
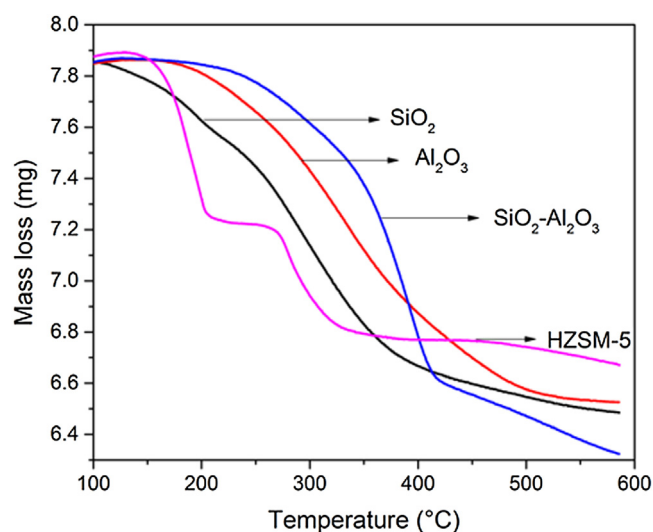

Fig. 1. TG of the mixtures myristic acid and catalysts under air flow.

In order to confirm the content of MA adsorbed on the catalysts, TG experiments of approximately 7.8 mg of each MA/catalyst under air were performed. Fig. 1 shows the MA mass loss after subtraction of the humidity of each pure catalyst under the same condition. Mass losses show that the contents of MA in the mixture were 17.4 mass% for MA/SiO2, 17.0% for MA/γ-Al$_2$O$_3$, 18.6% for MA/SiO$_2$-Al$_2$O$_3$, and 15.5% for MA/HZSM-5. These values correspond to a catalyst:MA mass relation of approximately 5:1 (varying from 4.4:1 to 5.4:1).

2.2. Characterization of the catalysts

Textural and acidic properties of the catalysts were measured. Nitrogen adsorption and desorption isotherms were obtained at −196 °C, using an ASAP 2420 apparatus (Micromeritics). Before adsorption, the catalyst samples were outgassed at 250 °C under vacuum. Relative pressure P/P$_0$ varied from 0.01 to 0.98 with 36 points for adsorption and from 0.98 to 0.20 with 18 points for desorption. Specific surface areas were calculated by using the BET model. The pore volumes were calculated by the BJH model, except for HZSM-5 where the t-plot model was used.

Total acidity was measured by a thermogravimetric technique using a Perkin Elmer STA 6000 instrument. After pre-treatment of the catalyst at 550 °C, pyridine was adsorbed at 120 °C on the catalyst surface. Excess pyridine was purged under a 20 mL min^{-1} nitrogen flow for 60 min, and thermal desorption of pyridine was performed up to 550 °C. The amount of pyridine desorbed between 120 and 550 °C was taken as a comparative estimate of the catalyst acidity [28].