Omega−3 fatty acid ethyl ester from a simple catalytic non-oxidative dehydrogenation of a biobased oleochemical

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Abstract

Essential fatty acids and derivatives, such as ethyl esters, have acquired an important interest, lately. The reactivity of ethyl linoleate (di-unsaturated fatty acid ethyl ester, FAEE), specially the catalytic reactions of non-oxidative dehydrogenation and isomerization, in a fixed bed reactor using active carbon as a catalyst has been studied. Active carbon presented dehydrogenation properties under non-oxidative conditions and in a temperature range of 70–120 °C. Omega−3 tri-unsaturated FAEE and aromatic FAEE were the detected dehydrogenation compounds. Mono-unsaturated FAEE and isomers of ethyl linoleate were the products of hydrogenation and isomerization reactions, respectively. The dehydrogenation activity of active carbon remained stable with time. The non-oxidative dehydrogenation to omega−3 tri-unsaturated FAEE becomes more important than the isomerization and hydrogenation reactions at lower temperatures such as 70 °C. Up to a 7.2% of omega−3 tri-unsaturated FAEE has been obtained synthetically for the first time.
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1. Introduction

Carbon materials are becoming increasingly important in catalysis, not only as supports, but also as catalytic active phases. Their performance is determined both by their texture and surface chemistry [1]. The application of carbon materials in dehydrogenation reactions has recently been studied by several research groups. Figueiredo and co-workers [2,3] studied the catalytic activity of activated carbons in the oxidative dehydrogenation (ODH) of ethylbenzene. Figueiredo and Schlögl and co-workers [4], correlated the surface carbonyl-quinone and hydroxyl groups with the ODH of ethylbenzene.

Essential fatty acids (EFAs) and their derivatives have recently acquired a growing interest [5–7]. They are necessary fats, since humans are not able to synthesize them. EFAs are made up of long-chain polyunsaturated fatty acids such as linoleic (two unsaturations) and linolenic (three unsaturations) acids, and their omega−3, omega−6, conjugated and non-conjugated isomers. The desaturation or dehydrogenation of fatty acids, such as the obtaining of linolenic acid, is usually performed by enzymes in plants and other organisms [8]. Research on alternate, man-made, economically feasible sources of EFA's is therefore becoming an important issue for both industry and academia [9].

Previous studies from our laboratory (and other workers) [10,11] agree on the easy oxidation of unsaturated fatty acid derivatives in the presence of oxygenates at temperatures higher than 80 °C, and also, the remarkable thermal stability of the corresponding fatty acid ethyl ester (FAEE) derivatives up to about 200 °C. Since, the thermodynamic feasibility to dehydrogenation increases with the degree of unsaturation, and the fact that temperature requirements for the dehydrogenation of ethyl linoleate are less demanding than those of ethylbenzene (justifying an oxidative dehydrogenation [2–4]), a catalytic non-oxidative dehydrogenation seems a suitable approach to our research.

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The main goal of this work is then to achieve the non-oxidative chemical dehydrogenation of ethyl linoleate (di-unsaturated FAEE) at temperatures lower than 130 °C, to obtain up-graded polyunsaturated products and isomers, using active carbon as catalyst in a fixed bed continuous flow reactor.

2. Experimental

Active carbon was supplied by Fluka (Germany). The feed consisted ethyl linoleate (>97%) supplied by Fluka (Germany). Gas Chromatography coupled to mass spectrometry (GC–MS) and ^{1}H Nuclear Magnetic Resonance (NMR) were used in order to identify the reaction products obtained. Ultraviolet (UV) analyses were also performed in order to detect the potentially present conjugated fatty acid esters. These analyses were performed using a spectrophotometer diode array Hewlett–Packard 8452 A.

The textural characterization of all materials was based on the N_2 adsorption isotherms, determined at 77 K with a Micromeritics Pulse Chemisorb ASAP 2010. The surface chemistry of carbon materials was studied by Fourier-transform infrared spectroscopy (FTIR) and Temperature Programmed Desorption (TPD) using a MS detector. CO and CO_2 desorbed from the carbon materials (0.8 g) were monitored using a Thermofinnigan TPDRO 1100 using a mass spectrometer (Pfeiffer Vacuum) as detector. FTIR analysis was performed with an infrared spectrophotometer FT Midac prospect. An elemental analyser Carlo Erba EA1108 was used to perform the elemental analysis of active carbon. The catalytic reaction has been carried out in a continuous tubular quartz reactor specially designed for this work. The reactor displays a double column which allows the preheating and evaporation of the starting material before the catalytic bed is reached. This reactor has been placed inside a temperature-programmed oven. Argon has been used as carrier gas (13.5 mL/min). The products of reaction have been analyzed by GC using a Flame Ionization Detector (FID) and a high polar column HP-FFPA. A reaction temperature range of 70–120 °C has been set in all cases. The catalyst weight in all cases has been 0.2 g. Under these experimental conditions no diffusion limitations were detected.

3. Results and discussion

3.1. Catalyst characterization

The surface chemistry of active carbon was studied by TPD using TCD-MS as CO and CO_2 detector. Fig. 1 shows the TPD, and Mass Spectra of CO and CO_2 desorption profiles from 35 °C to 995 °C using helium as a carrier.

The amount of CO desorbed at higher temperature is considerably higher than the amount of CO_2.

The overlapping of CO and CO_2 MS curves fit very well the TPD curve from active carbon, in Fig. 1. Some assign-
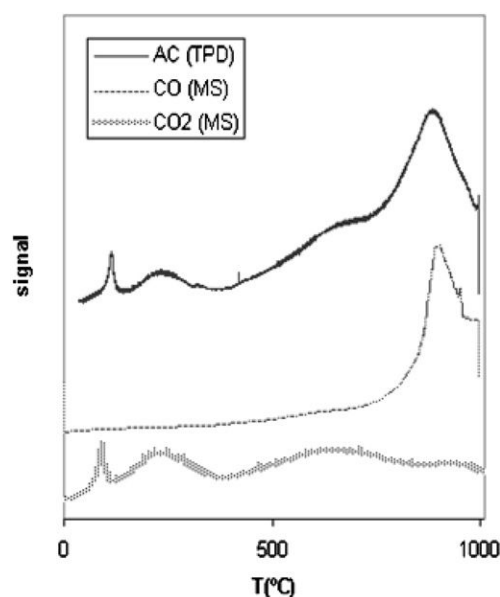

Fig. 1. TPD and mass spectra vs. temperature of desorbed CO and CO_2 from active carbon.

ments to the carbon surface functional groups can be done from the CO and CO_2 detected [12].

According to Ref. [12], the highest peak of TPD profile in Fig. 1 can be assigned to a surface carbonyl–quinone, the peak of desorbed CO_2 at 250 °C is assigned to carboxylic functionality and the CO_2 peak at 600–700 °C is assigned to lactone functionality on the carbon surface. The ash content of this active carbon is 7.1%. The X-ray diffraction and chemical analyses of the ash showed that the main element present was potassium.

The BET surface area and the micropore volume of the catalyst are 1400 m^2/g and 0.207 cm^3/g, respectively (Fig. 2). The isotherm of this active carbon exhibits a type I profile, which typically corresponds to microporous adsorbents.

The Fourier Transformed Infrared Spectra of the catalyst showed no clear peaks, possibly because of the low functionality content of the carbon. The FTIR spectrum of the carbon sample after TPD has been also performed. In this case, the general profile of the spectrum became
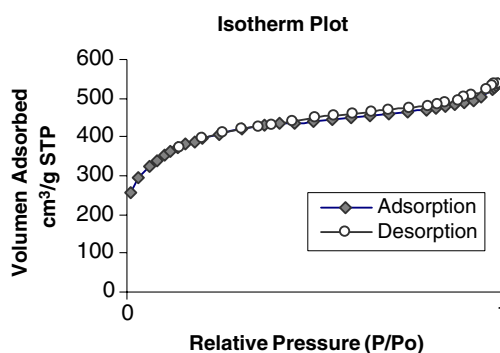

Fig. 2. BET isotherm plot.

smoother which can be accounted for as a loss of the weak functionality after the TPD treatment.
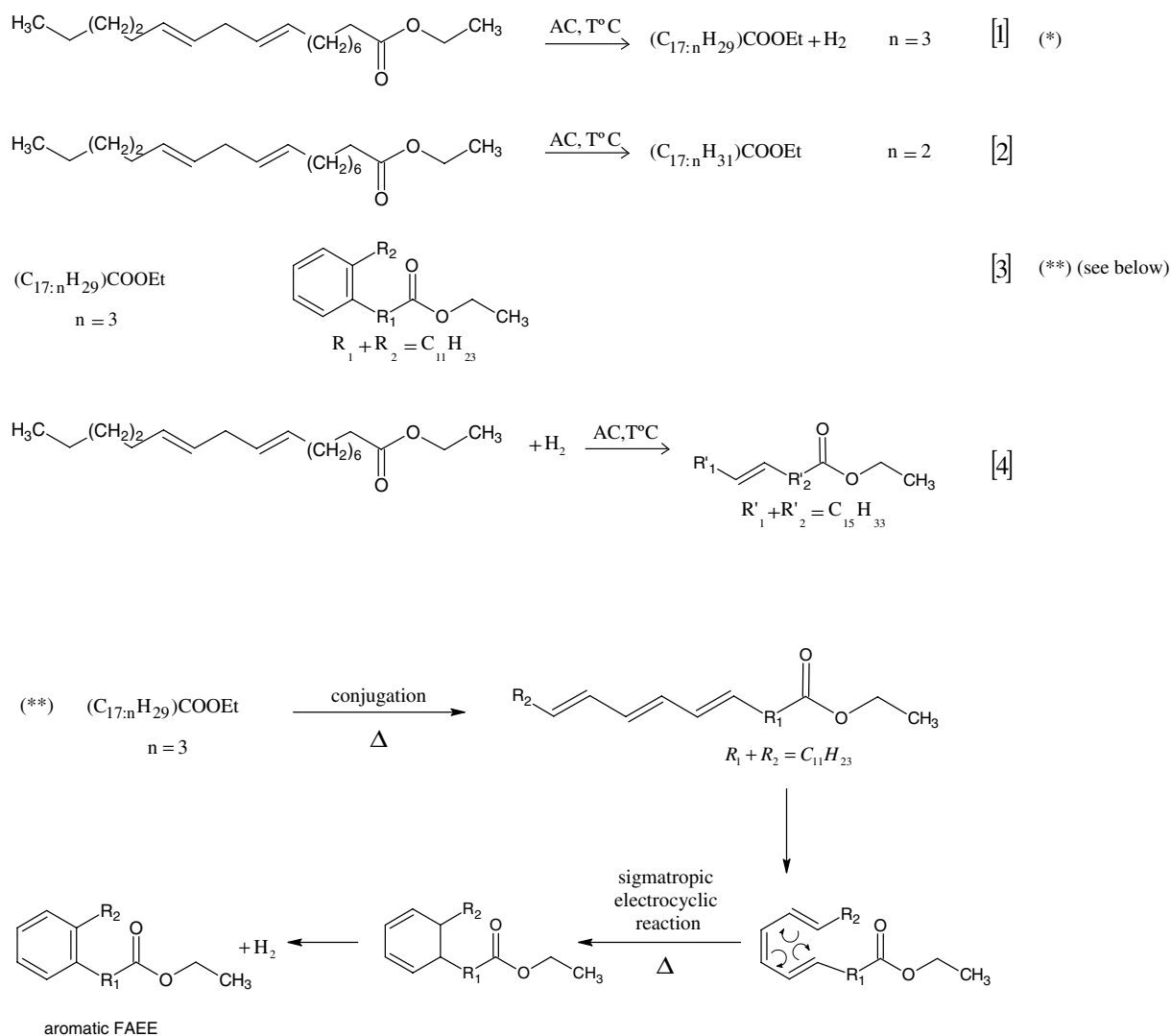
3.2. Catalytic activity

First, a blank experiment of running ethyl linoleate without catalyst at 120 °C was run giving no conversion at all, under the conditions given in the experimental section. Another blank running a mixture of ethyl linolenate and ethyl linoleate without catalyst at 120 °C gave traces of aromatic FAEE and mono-unsaturated FAEE. These previous runs, in the absence of catalysts, conclude that the aromatic FAEE only results from the tri-unsaturated ethyl linolenate.

The reaction, using active carbon as a catalyst, was performed at a temperature range between 70 °C and 120 °C. The conversions of ethyl linoleate according to equations [1–4] in Scheme 1 are shown in Table 1 and plotted vs. the reaction temperature in Fig. 3. Then, conversion of

ethyl linoleate to tri-unsaturated FAEE follows an increase on lowering temperature from 100 °C–70 °C. The non-oxidative dehydrogenation to omega−3 tri-unsaturated FAEE becomes more important than the isomerization and hydrogenation reactions at 70 °C. The conversion to isomers presents a maximum value at the higher temperature and a minimum value at the lower temperature with a plateau region in between, the conversion to aromatic FAEE yields a maximum value at 120 °C, and conversion to mono-unsaturated FAEE gives a maximum value at 120 °C (Fig. 3).

The values of total conversion increase, as expected, with temperature rise (Fig. 3). At 120 °C, the conversion reaches a value of 59%. At the lowest temperature of 70 °C, the conversion is 20%. The reaction rates of conversion of ethyl linoleate at 70 °C and 120 °C were $0.007 \, \mu mol \, g_{cat}^{-1} \, s^{-1}$ and $0.02 \, \mu mol \, g_{cat}^{-1} \, s^{-1}$, respectively. All products were identified by GC–MS and/or ^1H NMR techniques according to Christie [13,14] as given in the

Scheme 1. General mechanism. (∗) n = number of unsaturations.

Table 1
Catalytic activity of active carbon

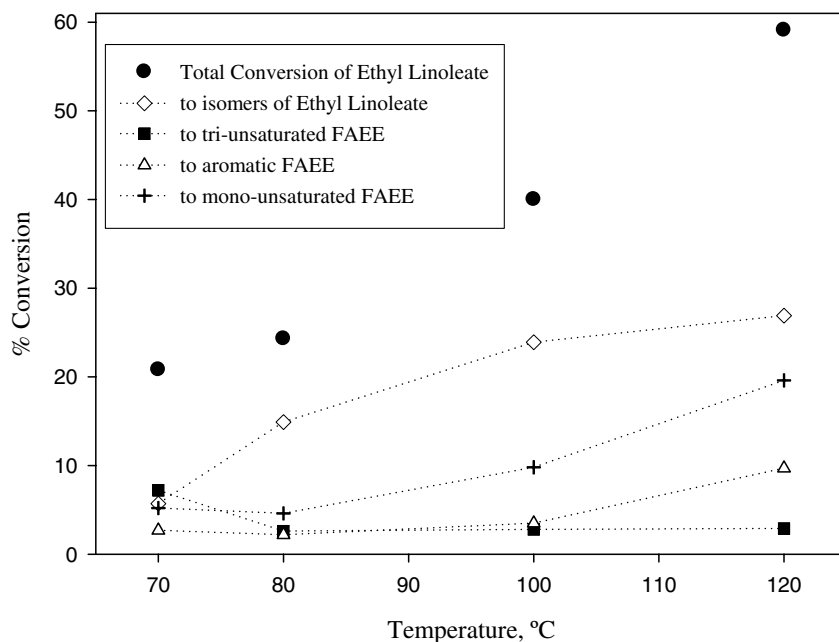| Temperature, °C	Total conversion of ethyl linoleate, %	% Conversions of ethyl linoleate to			
		Isomers of di-unsaturated FAEE	Tri-unsaturated FAEE	Aromatic FAEE	Mono-unsaturated FAEE
70	20.8	5.7	7.2	2.7	5.2
80	24.3	14.9	2.6	2.2	4.6
100	40.0	23.9	2.8	3.5	9.8
120	59.1	26.9	2.9	9.7	19.6

Fig. 3. Conversions of ethyl linoleate vs. temperature, according to Scheme 1.

experimental section. Up to a 7.2% of omega−3 tri-unsaturated FAEE has been obtained synthetically at 70 °C, to our knowledge, for the first time. The increase in the concentration of tri-unsaturated FAEE can be associated to the decrease of isomerization of ethyl linoleate.

Scheme 1 shows the overall mechanism of reaction that consists of two dehydrogenation reactions, the isomerization reaction and a hydrogenation reaction. The proposed mechanism of obtaining the aromatic FAEE is also developed in Scheme 1.

The first step in the mechanism shows the dehydrogenation of ethyl linoleate to give ethyl linolenate. The next step consists of the thermodynamically favourable isomerization or conjugation of ethyl linolenate and its ulterior electrocyclic sigmatropic reaction as a result of the exposure to temperature [15]. The ulterior dehydrogenation reaction to give the aromatic FAEE is given in Scheme 1, based on the amount of hydrogen used for obtaining mono-unsaturated FAEE. Such aromatic FAEE has acquired some important applications in printing inks, lately [16].

The amount of mono-unsaturated FAEE obtained, may be accounted for the hydrogenation of ethyl linoleate,

using the hydrogen from reactions [1, 3]. Therefore, either the formation of tri-unsaturated FAEE or the detection of mono-unsaturated FAEE proves the capability of active carbon to dehydrogenate FAEE. The mono-unsaturated compounds can either come from the hydrogenation of the starting material, ethyl linoleate, or the hydrogenation of the previously formed tri-unsaturated FAEE or from both hydrogenation reactions. Some hydrogenation experiments performed at 120 °C using active carbon as a catalyst and ethyl linoleate (di-unsaturated FAEE) as starting material in one case, and ethyl linolenate (tri-unsaturated FAEE), in the other case, showed that ethyl linoleate hydrogenates kinetically easier that the tri-unsaturated ester. Moreover, the hydrogen balance is consistent with this fact: on one hand, the formation of one mol of aromatic FAEE implies the formation of two moles of hydrogen. On the other hand, the hydrogenation of ethyl linoleate to give a mono-unsaturated FAEE uses one mol of hydrogen. So, the formation of one mol of aromatic FAEE gives enough hydrogen to form two moles of mono-unsaturated FAEE from ethyl linoleate, which may explain the fact that the conversion to mono-unsaturated

FAEE is about double than the conversion to aromatic FAEE.

The observed catalyst stability for a long time and the fact that the dehydrogenation takes place under non-oxidative conditions seem to indicate that the surface functionality of the catalyst (Fig. 1) does not play a crucial role (it is not spent), in this case. Therefore, due to its complexity, the study of the dehydrogenation mechanism at the catalyst active centres is the matter of a future work.

4. Conclusions

Active carbon showed dehydrogenation activity at low temperatures such 70–120 °C under non-oxidative conditions. Active carbon kept its dehydrogenation activity (zero conversion from a blank non-catalyzed reaction) at least after 24 h.

The dehydrogenation of ethyl linoleate gives tri-unsaturated FAEE, isomers of ethyl linoleate, aromatic FAEE and mono-unsaturated FAEE.

The conversion of ethyl linoleate to the tri-unsaturated FAEE is favoured at lower temperatures.

The non-oxidative dehydrogenation to omega−3 tri-unsaturated FAEE becomes more important than the isomerization and hydrogenation reactions at lower temperatures such as 70 °C.

Up to a 7.2% of omega−3 tri-unsaturated FAEE has been obtained synthetically for the first time.

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