



Hydrothermal conversion of linoleic acid and ethanol for biofuel production



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ARTICLE INFO

Article history:

Received 30 March 2016
Received in revised form 16 June 2016
Accepted 21 June 2016
Available online 21 June 2016

Keywords:

Hydrothermal conversion
Linoleic acid
Heptadecane
Biofuel
Pt/C catalyst
Kinetic model

ABSTRACT

The catalytic conversion of linoleic acid in ethanol/water mixtures (1:1 vol. ratio) was explored in a batch reactor using a Pt/C catalyst. Linoleic acid was converted into heptadecane with high yields (>80%) after 6 h at 350 °C under autogenous pressure. The reaction proceeded through consecutive steps: linoleic acid → stearic acid → ethyl stearate → heptadecane. Hydrogen was generated in-situ by oxidation of ethanol into acetaldehyde. A moderate sintering of platinum was evidenced after hydrothermal reaction.

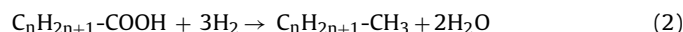
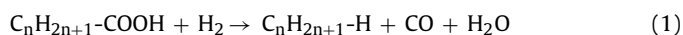
A reaction network based on products distribution and kinetic studies was proposed. It was found that the hydrogenation route proceeds via the free acids whereas the hydrogenation of the ethyl esters was negligible. The formation of heptadecane, on the other hand, proceeded via ethyl stearate and not via stearic acid.

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1. Introduction

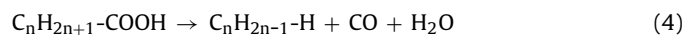
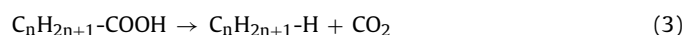
The production of biomass-derived fuels as alternatives to fossil fuels is an important research field in order to meet the European targets of 20% renewable energy by 2020, with a minimum of 2% for transportation energy needs [1]. Unlike ligno-cellulosic biomass, the structure and composition of vegetable oils are the closest to that of petroleum fuels, since they consist of triglycerides with long aliphatic chains essentially in the C₁₆–C₁₈ range [2,3]. The transesterification of triglycerides with methanol yields fatty acid methyl esters (FAME) that can be blended with mineral Diesel fuel in ratios ranging from 5% (B5 gasoil) up to 30% (B30) and burnt in Diesel engines. FAMEs, however, have a higher viscosity than Diesel fuel and a lower energy content, as the result of the oxygen atoms of the ester group [4]. They are also less stable regarding oxidation and can form peroxides and degradation products, which can polymerize in the fuel injector or corrode it.

Another approach to fatty acids valorisation consists in their deoxygenation into hydrocarbons. This can be achieved by hydro-deoxygenation (HDO) under high hydrogen pressure, using standard NiMo/Al₂O₃ hydrotreatment catalysts [5]:



Pure fatty acids, mixtures of them and various vegetable or microalgae oils have been deoxygenated under high pressures of hydrogen, using various heterogeneous catalysts. Mixtures of hydrocarbons and cracking products were obtained in variable yields [3,6–10].

Alternatively, fatty acids can be deoxygenated by direct decarboxylation (Eq. (3)) or decarbonylation (Eq. (4)) reactions, the latter reaction leading simultaneously to the formation of an olefinic bond:



These reactions are thermodynamically possible at 300 °C, the Gibbs enthalpies of reaction calculated for stearic acid (C₁₇H₃₅-COOH) are equal to –67.6 kJ/mol for Eq. (1), –86.1 kJ/mol for Eq. (2), –83.5 kJ/mol for Eq. (3) and –17 kJ/mol for Eq. (4) [11].

The catalytic deoxygenation of fatty acids by direct decarboxylation/decarbonylation routes in the absence of reductant has also been investigated by several authors. Snåre et al. [11] studied the conversion of stearic acid (C₁₇H₃₅-COOH) at 300 °C in dodecane as solvent in the presence of various heterogeneous catalysts. Among the 20 catalysts screened, a 5%Pd/C commercial catalyst was found the most active and selective towards C₁₇ hydrocarbons, the selectivity into heptadecane + heptadecene reaching 99% at 100% stearic

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acid conversion. In a comparative study of the conversion of stearic acid ($C_{17}H_{35}-COOH$) and oleic acid ($C_{17}H_{33}-COOH$, with one $C=C$ bond) under similar conditions (5% Pd/C catalyst, in dodecane, no H_2 added), the reaction of oleic acid was found very slow relative to stearic acid and decarboxylation was the main reaction pathway [12]. The solvent (dodecane) was also shown to undergo partial dehydrogenation and to transfer hydrogen to the reactants. Under H_2 pressure, oleic acid and linoleic acid ($C_{17}H_{31}-COOH$, two $C=C$ bonds) were first hydrogenated into stearic acid before decarboxylation could proceed at a significant rate [12].

The catalytic hydrothermal conversion of fatty acids has also been studied in supercritical water in the absence of reductant. Watanabe et al. reported that zirconia promoted the decarboxylation of stearic acid in supercritical water; the main products formed were CO_2 and C_{16} -alkenes, and presumably acetic acid [13]. Oleic acid has also been converted in sub- and supercritical water in the presence of Ni-based catalysts [14]. The conversion of oleic acid was 13–15% at 350 °C (sub-critical conditions) and 30–33% at 400 °C (supercritical conditions) with heptadecenes as the main products; decarboxylation was proposed as the main reaction pathway. The addition of glycerol to provide in-situ H_2 improved the conversion of oleic acid and the selectivity for heptadecane [14]. Similarly, the hydrothermal conversion of triglycerides into C_{17} hydrocarbons over a 5 wt.%Pd/C catalyst was improved when glycerol or methanol were added as reagents providing in-situ hydrogen through aqueous phase reforming [15]. Savage and co-workers obtained high yields (>80%) in C_{n-1} hydrocarbons from different saturated fatty acids, stearic ($C_{17}H_{35}-COOH$), palmitic ($C_{15}H_{31}-COOH$) and lauric ($C_{11}H_{23}-COOH$), in water at 330 °C using a 5%Pt/C commercial catalyst [16,17]. However, only low yields of hydrocarbons (<20%) were formed from unsaturated C_{18} fatty acids (oleic and linoleic), while heptadecane was the main product. The authors showed that a fraction of oleic acid decomposed into H_2 , CO_2 , CH_4 and C_2H_6 , and the hydrogen formed in-situ allowed the reduction of oleic acid into stearic acid, which subsequently underwent decarboxylation to yield heptadecane. $PtSn_x/C$ catalysts were also developed for the hydrothermal conversion of stearic, oleic and linoleic acids in the absence of reductant [18]. Nearly quantitative yields of heptadecane were obtained from stearic acid, but oleic and linoleic acids were found more difficult to convert into hydrocarbons than stearic acid, i.e. the yield in hydrocarbons did not exceed 15% with linoleic acid.

Cyclohexene, tetralin, formic acid and organic alcohols have been known for a long time as hydrogen-donor compounds, that can be used as solvents to perform liquid phase catalytic transfer hydrogenation reactions such as the reduction of organic multiple bonds (alkenes, alkynes, carbonyls, nitriles) and hydrogenolysis [19]. More recently, catalytic transfer hydrogenation has been shown to convert efficiently biomass-derived compounds, such as levulinic acid, 5-hydroxymethylfurfural (HMF), glycerol, to partially deoxygenated compounds [20]. Carbonyl groups are selectively hydrogenated into alcohols, but the hydrogenolysis of $C-O$ bonds can also lead to partial deoxygenation through elimination of CO_2 or CO . Using H-donor solvents for hydrogenation is an attractive alternative to using high-pressure hydrogen, which presents important safety and handling issues. In addition, alcohols, and particularly ethanol, can be produced from renewable sources.

In the present work, the deoxygenation of linoleic acid into hydrocarbons has been investigated. The reactions were run in water/ethanol mixtures, ethanol being used as hydrogen-donor solvent, in the presence of Pt/C or Ru/C catalysts, which were previously found the best catalysts under similar reaction conditions [21]. The hydrogenation process using ethanol was found highly selective towards the formation of hydrocarbons. The reaction time was accurately controlled by injecting the reactants under pressure in a pre-heated autoclave, which allowed carrying out kinetic

studies. A kinetic model of the reaction is proposed, that provides relevant insight in the reaction pathway leading to the observed reaction products.

2. Experimental

2.1. Catalyst preparation

Pt/C and Ru/C catalysts were prepared by wet impregnation of $Pt(NH_3)_4(OH)$ and Ru(III) nitrosylnitrate precursors (Alfa Aesar). The carbon support (Engelhard, surface area $1000\text{ m}^2\text{ g}^{-1}$) was previously calcined at 500 °C under N_2 for 5 h. The metal precursors dissolved in water were deposited on the supports by wet impregnation in order to obtain a similar molar loading, close to 0.01 mol.% for both metals (1 wt.% of Ru and 2 wt.% of Pt on carbon). Water was evaporated in a rotatory evaporator and the catalyst was calcined at 500 °C in air to decompose the metal salts. The metals were then reduced under hydrogen at 300 °C for 2 h.

2.2. Catalyst characterization

The Ru and Pt loadings on the carbon support were analysed by ICP-OES. The 2 wt.% Pt/C catalyst used in kinetic studies had a specific surface area of $970\text{ m}^2\text{ g}^{-1}$, with a mean particle size of 16 μm (measured by Laser diffraction particle size analysis). The catalyst porosity was characterized by nitrogen physisorption using a 3Flex Micromeritics analyzer. The catalyst was essentially microporous ($\approx 80\%$ of BET surface area, pore size around 0.6 nm) with a small amount of mesopores with a pore size around 2.3 nm, actually very close to micropores. Pt leaching was assessed by hydrothermal ageing of Pt/C catalyst in water at 320 °C for 3 h. The Pt content in water after ageing analysed by ICP-OES was 0.1 ppm, which represented less than 0.006% of the total Pt amount. HAADF-STEM micrographs were obtained with a FEI Titan ETEM microscope.

2.3. Reactor and kinetic studies

Linoleic acid (>99%, Sigma-Aldrich) and ethanol (99.8%, Sigma-Aldrich) were used as received. The reactions were performed in a 250 mL Hastelloy autoclave (Parr) equipped with high-pressure valves for liquid or gas introduction and sampling, under autogenous pressure. In a typical experiment, the reactor was loaded with water and the desired amount of catalyst, then purged by bubbling nitrogen in the water for 10 min in order to remove gaseous air and dissolved oxygen. The heating system was then started and stabilized at the desired temperature in about 30 min. The mixture of linoleic acid in ethanol was injected in the autoclave using a preparative HPLC pump. Injection time was set to 2 min. The total liquid volume loaded in the autoclave was always 150 mL. The stirring rate was set at 300 rpm. In tests performed at 600 rpm the linoleic acid disappearance rate was not modified, showing therefore that the reaction was not limited by external mass transfer at 300 rpm.

The Weisz-Prater criterion, calculated at 300 °C using a diffusion coefficient of $3.87 \cdot 10^{-10}\text{ m}^2/\text{s}$ for linoleic acid in water [22], was found <0.05 indicating that internal diffusion limitations were negligible.

Kinetic studies were carried out between 250 and 350 °C, with a linoleic acid concentration between 1 and 2 g/L and using a catalyst/linoleic acid ratio between 0.0625 and 0.125. The initial volume of solution was always 150 mL. Liquid samples (1 mL) were periodically collected through a liquid sampling valve and were analyzed by GC-MS.

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