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Hydrocarbons for diesel fuel via decarboxylation of vegetable oils

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Abstract

Deoxygenation reaction of vegetable oils over a carbon-supported metal catalyst was studied as a suitable reaction for production of diesel-fuel-like hydrocarbons. Stearic acid, ethyl stearate, and tristearine have been used as model compounds. Catalytic treatment of all the three reactants resulted in production of *n*-heptadecane as the main product with high selectivity.

Keywords: Diesel fuel; Decarboxylation; Ethyl stearate; Stearic acid

1. Introduction

Conversion of vegetable oils and animal fats into diesel fuel of adequate quality is widely studied. Nowadays, the term biodiesel is mainly associated with mono-alkyl esters of long chain fatty acids, since transesterification represents the most common process [1]. However, several properties of mono-alkyl esters of fatty acids based fuels, such as higher viscosity and cloud point, and possible engine problems due to their higher acid number than that of conventional diesel fuels, limit their applicability in some areas. Removal of oxygen, e.g. via hydrodeoxygenation [2] or pyrolysis [3] reactions, represents an alternative route leading to a production of hydrocarbons fractions suitable for diesel fuel blending. Decarboxylation reaction has been reported to accompany reactions occurring during hydrodeoxygenation [2,4] and hydrocracking [5]. In the present work, a commercial metal supported catalyst was tested with the aim to convert oxygenated feedstocks to diesel-fuel-like hydrocarbons. The product distribution with respect to model compounds and reaction conditions were especially studied.

2. Experimental

The deoxygenation experiments were performed in a conventional Parr autoclave (300 ml) operating in a semi-batch mode. The pressure and the mass flow controllers placed at the inlet and the outlet of the reactor, respectively, maintained constant reaction pressure and gas flow through the reactor during the whole experiment. The reactor was provided by an electric heating jacket a thermocouple, a pre-heater, a cooling coil, and a liquid condenser placed on the outlet of the reactor, and baffles. Efficient agitating of the reaction mixture was achieved by an electric stirrer (1100 rpm). Under such conditions, the influence of external diffusion was sufficiently suppressed, as it was confirmed in a series of experiments with varying stirring speed and catalyst mass, respectively.

In each experiment, a commercial activated carbon supported palladium (5 wt.%, Aldrich) catalyst was employed. The catalyst (1 g, <90 μm) was placed into the reactor prior to the experiment and reduced in situ at 200 °C for 2 h in a constant flow of hydrogen. After the reduction, the activated catalyst was covered by solvent under a flow of inert gas and, consequently, the reactants (in solid state) were added into the reactor.

Stearic acid (Fluka, >98%), ethyl stearate (Aldrich, >97%), and tristearine (Fluka, techn.) representing model

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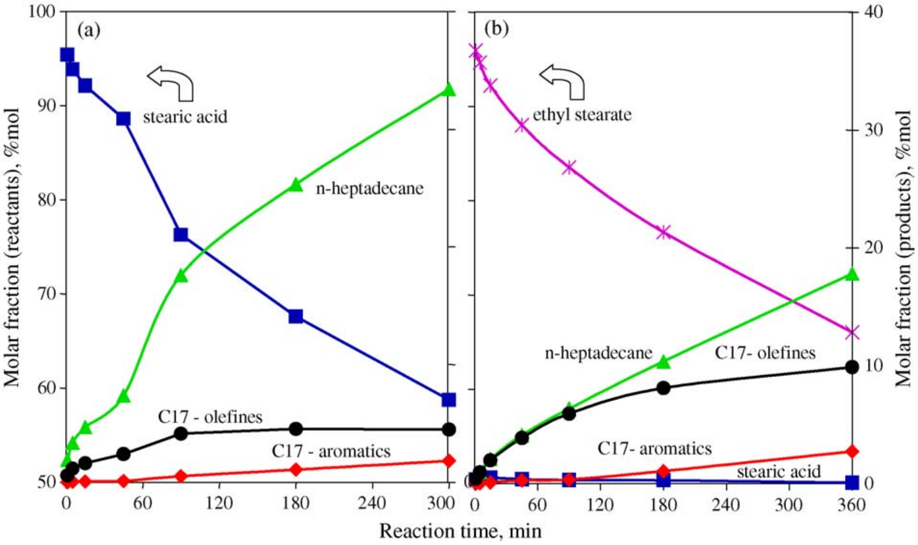

Fig. 1. Typical profiles of stearic acid (a), and ethyl stearate (b) consumption and products evolution as a function of reaction time; He atmosphere, 17 bar, 300 °C.

compounds of vegetable oils have been tested in separate deoxygenation experiments at 300–360 °C and overall pressure 17–40 bar. The masses of reactants (45, 50, and 47 g, respectively) were varied to maintain a constant catalyst/carboxylic group ratio in a reaction mixture. Dodecane was employed as a solvent. In order to determine the influence of hydrogen partial pressure on the conversion and products distribution, different reaction atmospheres, e.g. helium (He), hydrogen (H_2), and hydrogen (5 vol.%)–argon (H_2–Ar) mixture, were applied.

The liquid reaction products were analyzed by gas chromatograph (HP 6890) equipped with a capillary column (DB 5, 60 m) and a flame ionization detector. Samples were dissolved either in pyridine (in the case of stearic acid deoxygenation), or 2-propanol (in ethyl ester experiments) and silylated by BSTFA to enable detection of fatty acids. In the case of tristearine, the composition of the liquid products at the end of the reaction time was determined by gel permeation chromatography. In selected experiments, the gaseous products were qualitatively analyzed by a gas chromatograph (HP 6890) equipped with a thermo-conductivity detector, a flame ionization detector, and a capillary column (Porapack Q, 30 m) coupled with molecular sieves (5 A, 30 m).

3. Results and discussion

The typical profiles of stearic acid consumption and the formation of *n*-heptadecane and unsaturated C17 hydrocarbons in a semi-batch reactor at 300 °C under helium are shown in Fig. 1a.

Stearic acid was converted with high selectivity to *n*-heptadecane. *n*-Heptadecane, the main product in the liquid phase, corresponded to direct decarboxylation of stearic acid, which is supported by formation of carbon dioxide, detected in the gas phase. In addition, other hydrocarbons containing 17 carbon atoms (C17), and carbon monoxide, were identified. Based on GC–MS analysis, C17 hydrocarbons included positional isomers of heptadecenes, and constitutional isomers of substituted aromatic hydrocarbons (undecylbenzenes).

The influence of the hydrogen concentration in the carrier gas on stearic acid conversion and products distribution was studied in a series of experiments. The turnover frequency (TOF) and final conversions (after 360 min) obtained under given conditions are listed in Table 1. Evidently, low partial pressure of hydrogen enhances the catalyst activity since TOF in the experiment performed under H_2–Ar atmosphere was the highest one while TOF values obtained in experiments carried out either under pure hydrogen atmosphere or without any hydrogen were clearly lower.

Fig. 2 depicts the molar selectivities (percentage of a particular product from total the amount of products) to *n*-heptadecane and to unsaturated C17 hydrocarbons as a function of conversions of stearic acid. The amount of unsaturated hydrocarbons directly correlated to the concentration of hydrogen in reaction atmosphere. The highest selectivity (e.g. 25.2% at conversion of 6.6%) giving the

Table 1
Influence of reaction atmosphere on stearic acid decarboxylation at 300 °C and 17 bar total pressure

Reaction atmosphere	Reaction time (min)	$p_{H_2,max}$ (kPa)	Conversion (%)	TOF ($\times 10^3\ s^{-1}$)
Helium	300	0	41	67
Hydrogen	360	1290	49	78
Hydrogen (5 vol.%) + argon (95 vol.%)	360	70	62	126

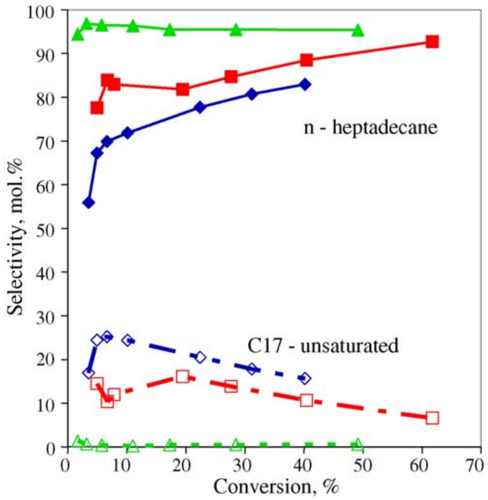

Fig. 2. Selectivities to the main reaction products as a function of conversion of stearic acid under different reaction atmosphere: (◆) He, (■) H_2–Ar, (▲) H_2; at 17 bar and 300 °C.

yield of 1.7% of unsaturated C17 was observed under helium, whereas under hydrogen it was almost negligible. The selectivity results (Fig. 2.) have indicated that heptadecenes were most probably the reaction intermediates since the selectivity to heptadecenes declined with reaction time (e.g. conversion of stearic acid). C17-olefins were probably partially hydrogenated into *n*-heptadecane; however, they also acted as intermediates in the formation of aromatic hydrocarbons which amount increased during the course of the reaction.

The dehydrogenation of hydrocarbon chains in stearic acid occurred in the beginning of the reaction followed by the decarboxylation of such products. These reactions might partially contribute to the formation of C17 hydrocarbons other than *n*-heptadecane.

The selectivity for the formation of direct hydrodeoxygenation product of stearic acid – *n*-octadecane – was also followed; however, it was found to be negligible even in the experiment performed under hydrogen atmosphere (0.50% at stearic acid conversion of 49%).

The presence of hydrogen in the reaction atmosphere particularly diminished the undesired, consecutive aromatization. At 40%-conversion of stearic acid, the selectivities to olefins were 11.1 and 9.3 mol% under He and H_2–Ar, respectively. The selectivity to aromatic hydrocarbons was, however, three times lower under H_2–Ar (1.4%) than under He (4.5%).

Ethyl stearate was initially converted into stearic acid, which subsequently decarboxylated into *n*-heptadecane (Fig. 1b). The gas phase contained carbon dioxide, and carbon monoxide, as well as ethane and ethylene originating from the decomposition of ethyl stearate. Since stearic acid was an intermediate in the deoxygena-tion of ethyl stearate, the same C17 products as in experiments discussed previously were identified in the liquid phase.

Table 2
Temperature dependence of ethyl stearate deoxygenation; under H_2–Ar atmosphere and selectivity to *n*-heptadecane at 40% conversion

Reaction temperature (°C)	Total pressure (bar)	Conversion[a] (%)	Selectivity (mol%)	TOF ($\times 10^3\ s^{-1}$)
300[b]	17	32		32
300	17	40	70	64
330	27	72	55	125
360	40	100	45	200

[a] After 360 min.
[b] under He atmosphere.

The TOF and conversion of ethyl stearate after 6 h of reaction at different reaction atmospheres and temperatures are given in Table 2. The dependency of ethyl stearate conversion on reaction atmosphere showed a similar trend as stearic acid: the TOF was doubled when He was replaced by H_2–Ar. Note, the TOF in ethyl stearate deoxygenation is approximately the same as that of stearic acid, under both reaction atmospheres.

The apparent activation energy calculated based on the initial rates in the temperature range 300–360 °C was 57 kJ/mol. As expected, higher temperature favoured conversion of ethyl stearate; however, increasing the temperature caused a decrease of the selectivity towards *n*-heptadecane (Table 2, Fig. 3.) and particularly promoted aromatization. As a result, the yield of aromatics was enhanced nine-fold when the reaction temperature was risen from 300 to 360 °C. Note that aromatics are not suitable diesel fuel components and they contribute to catalyst deactivation as well.

Similarly to other tested feedstocks, tristearine deoxygenation led to formation of C17 hydrocarbons, with *n*-heptadecane being the main decarboxylation product.

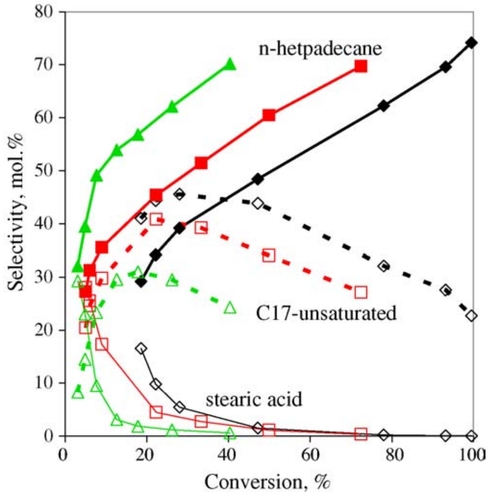

Fig. 3. Selectivities to the main reaction products as a function of conversion of ethyl stearate; H_2–Ar atmosphere: (◆) 300 °C, 17 bar; (▲) 330 °C, 27 bar; (■) 360 °C, 40 bar.

4. Conclusions

Stearic acid, ethyl stearate, and tristearine representing vegetable oils were almost exclusively converted to the same final product—*n*-heptadecane. The side products consisted of positional isomers of heptadecenes and constitutional isomers of undecylbenzenes.

Ethyl stearate transformation occurs via stearic acid as an intermediate. Gas phase products in this reaction contained carbon dioxide, carbon monoxide, along with ethane and ethylene originating from the decomposition of ethyl stearate. The product distribution, more particularly the concentration of unsaturated C17 hydrocarbons, which was significantly higher than in case of stearic acid, showed a pronounced dependency on the reaction conditions. Under slightly higher hydrogen pressure the formation of aromatic hydrocarbons was suppressed. Further increase of the hydrogen partial pressure, however, suppressed the stearic acid conversion. Increasing the reaction temperature significantly improved the conversion of ethyl stearate, leading at the same time to enhanced formation of undesired aromatics.

Acknowledgments

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