Production of diesel fuel from renewable feeds: Kinetics of ethyl stearate decarboxylation

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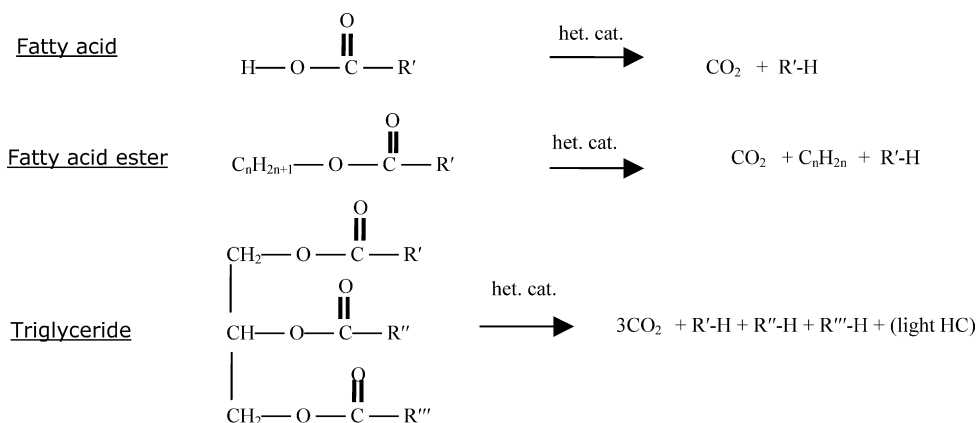
Abstract

The kinetics of liquid phase ethyl stearate decarboxylation for production of diesel fuel hydrocarbons was studied over a Pd/C catalyst in a semi-batch reactor. The kinetic behavior was tested in a wide range of temperature. Furthermore a supplementary investigation of the reaction intermediate, stearic acid, was performed. The main kinetic regularities were established in both cases. Finally successful kinetic modeling and parameter estimation was performed based on the proposed reaction route. The predicted results explained the experimental results well.
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Keywords: Decarboxylation; Stearic acid; Biodiesel

1. Introduction

The extreme increase in energy consumption in the past decade and the growing environmental concerns have made renewable fuels an exceptionally attractive alternative as a fuel for the future. Several methods of producing fuels from renewable resources are nowadays well established, however, new innovative solutions are needed to satisfy the increasing energy demand and the well-being of our ecological system.

A novel method for production of diesel-like fuel from renewable resources, like vegetable oils and animal fats, is being investigated at our laboratory. It has recently been demonstrated that renewable feeds over heterogeneous catalysts in liquid-phase tend to decarboxylate [1,2]. The production of a deoxygenated biodiesel fuel involves removal of the carboxyl group in the fatty acid structure via carbon dioxide and/or carbon monoxide release, thus producing a linear hydrocarbon originating from the fatty acid alkyl group (typically C_6–C_{22}) [3]. The catalytic decarboxylation of fatty acids, fatty acid esters and triglycerides (comprising of three fatty acids and a glycerol group) is schematically illustrated below.

Fatty acid

$$H-O-C(=O)-R' \xrightarrow{\text{het. cat.}} CO_2 + R'\text{-H}$$

Fatty acid ester

$$C_nH_{2n+1}-O-C(=O)-R' \xrightarrow{\text{het. cat.}} CO_2 + C_nH_{2n} + R'\text{-H}$$

Triglyceride

$$\begin{array}{l} CH_2-O-C(=O)-R' \\ CH-O-C(=O)-R'' \\ CH_2-O-C(=O)-R''' \end{array} \xrightarrow{\text{het. cat.}} 3CO_2 + R'\text{-H} + R''\text{-H} + R'''\text{-H} + (\text{light HC})$$

Since the method of producing biodiesel from renewable feedstocks via selective deoxygenation was only recently introduced, no kinetic study in this area has been reported. However,

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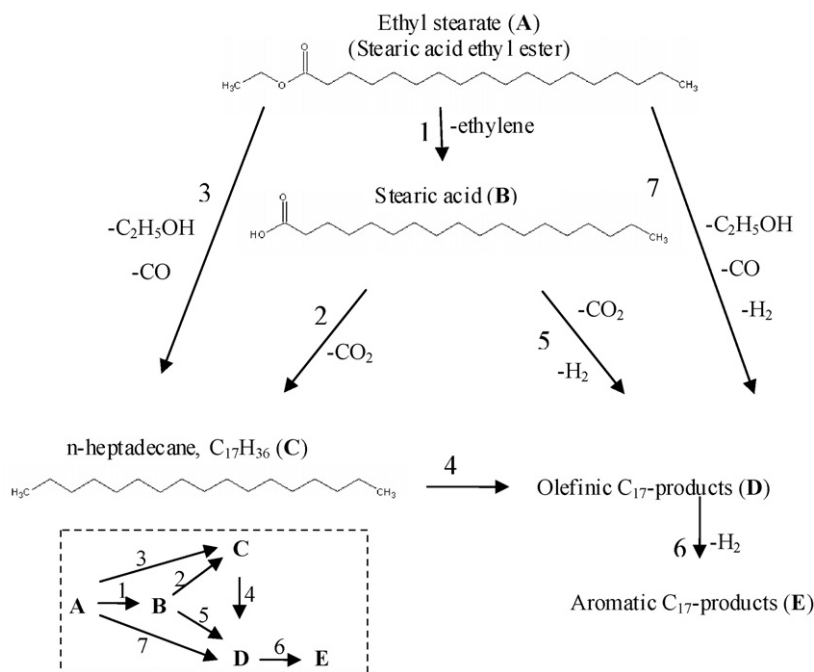*E-mail address:* dmitry.murzin@abo.fi (D.Yu. Murzin).

Fig. 1. Schematic and simplified deoxygenation network of ethyl stearate to diesel products.

several kinetic studies on decarboxylation of organic acids can be found in the literature [4–6].

In the present work the kinetic behavior of ethyl stearate decarboxylation over a heterogeneous catalyst was investigated with the aim to verify the reaction mechanism and further optimize the chemical process.

2. Experimental

The kinetic study was carried out in a semi-batch reactor (300 ml Parr autoclave) over a commercial 5% Pd/C catalyst (Aldrich). The catalyst powder (catalyst mass = 1 g) was placed into the reactor and reduced *in situ* with a flow of hydrogen at 200 °C for 2 h. By applying a fine catalyst powder (mean catalyst particle size = 15 μm) and evaluating the potential influence of internal diffusion by calculating the catalyst effectiveness factor ($\eta_{eff} = 0.999$) [7], the effect of mass transfer is supposed to be negligible. The impact of external diffusion was avoided by conducting experiments at a stirring speed of 1100 rpm, which was proven to be efficient enough to avoid mass transfer limitations. The reaction temperature and pressure were kept constant during the reaction, in the range of 270–360 °C and 17–40 bar (the reaction pressure was adjusted according to the vapor pressure of the reaction mixture), respectively. The reaction was performed in a solvent (n-dodecane) under inert (helium or argon) or argon- (5 vol%) hydrogen atmosphere, the total liquid volume in the reactor was 100 ml. The carrier gas was bubbled through the reaction mixture with the volumetric flow of 25 ml/min. The withdrawn liquid phase sample composition was determined by gas chromatography (GC) equipped with a Flame ionization detector (FID). The product identification was further verified by gas chromatography coupled to a mass spectrometer (GC–MS).

3. Results and discussion

The decarboxylation of the fatty acid ester, ethyl stearate (A), proceeds via its corresponding fatty acid (reaction (1), Figs. 1 and 2), stearic acid (B), which is subsequently decarboxylated (reaction (2)) to the desired paraffin n-heptadecane (C). The produced paraffin is, however, simultaneously dehydrogenated [8] to unsaturated olefins (D) and aromatics (E) (reactions (4) and (6), respectively). Furthermore, the direct formation of paraffin from fatty acid ester has as well been detected (reaction (3)) [9]. The formation of olefins seems to evolve not only from paraffins but can also proceed directly from the saturated fatty acid and/or fatty acid ester feedstock (reaction (5)). Chemically, this can be explained by initial dehydrogenation of a saturated fatty acid and/or a fatty acid ester to an unsaturated acid and/or ester
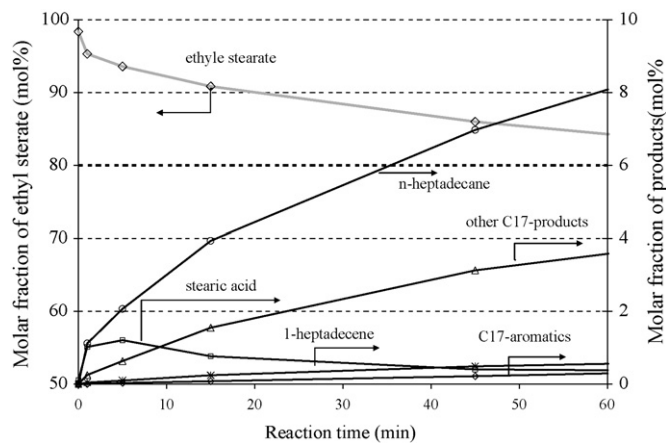

Fig. 2. Typical concentration profile of ethyle stearate and products in the decarboxylation reaction. The reaction conditions: $T = 300$ °C, $p = 17$ bar (Ar-(5 vol%) H_2), $c_{ethyl\ stearate} = 1.6$ mol/l, and $m_{catalyst} = 1$ g.
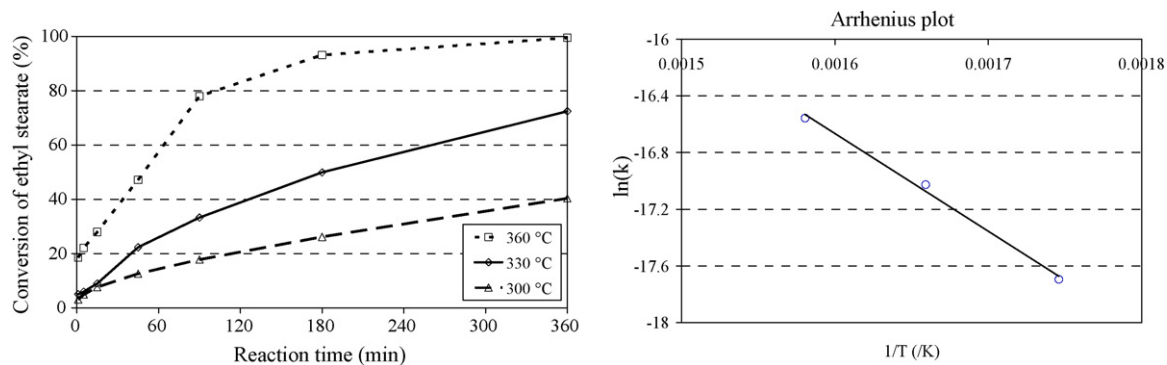
Fig. 3. Effect of reaction temperature in the decarboxylation of ethyl stearate and the Arrhenius dependence for the first order reaction constant. The reaction conditions: $c_{ethyl\ stearate} = 1.6$ mol/l, $m_{catalyst} = 1$ g, $T = 300$–$360\,°C$, $p_{300} = 17$ bar, $p_{330} = 27$ bar and $p_{360} = 40$ bar (Ar-(5 vol%) H_2).

intermediate following a fast decarboxylation producing an olefin. Direct decarboxylation of unsaturated fatty acids and fatty acid esters to olefin has recently been reported [10].

Paraffinic hydrocarbons are very suitable diesel fuel components, with high cetane number (cetane number of hexadecane, $C_{16}H_{34} = 100$) and chemical stability, while unsaturated products have a significantly lower cetane number and chemical stability [11,12]. Furthermore the environmental drawbacks of using aromatic fuel compounds in diesel engines substantiates, that the production of unsaturated hydrocarbon should be minimized.

The effect of reaction temperature in ethyl stearate decarboxylation was reported recently [13]. As expected, the reaction rate increased with temperature when decarboxylation was conducted in the temperature range of 300–360 °C. Analysis of the temperature dependency (Fig. 3) results in the value of apparent activation energy equal to 57.3 kJ/mol based on the Arrhenius equation and first order kinetics in respect to ethyl stearate.

In addition kinetic decarboxylation experiments with the intermediate product, stearic acid, were performed. This study demonstrated that the reaction order of stearic acid is close to zero and the apparent reaction constant is approximately 0.0065 mol/l min. However, with high initial concentrations (1.54 mol/l) of stearic acid, catalyst deactivation is observed (Fig. 4), which is reflected in a lower value of the corresponding rate constant. An earlier study of decarboxylation in a tubular reactor showed that the catalyst is indeed deactivated with a fatty acid feedstock [14].
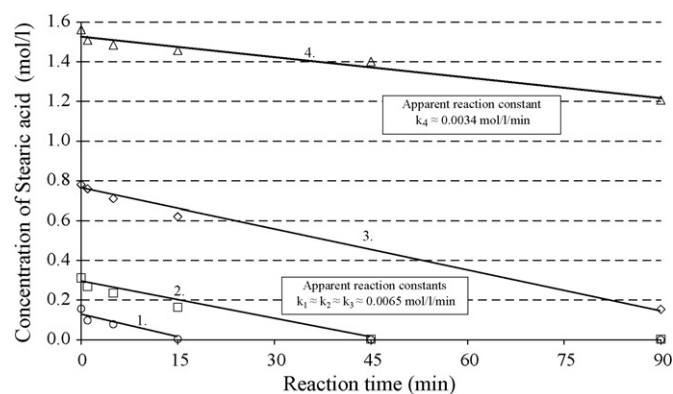

Fig. 4. Effect of reactant concentration in the decarboxylation of stearic acid. The reaction conditions: $c_{stearic\ acid,\ 1} = 0.154$ mol/l, $c_{stearic\ acid,\ 2} = 0.308$ mol/l, $c_{stearic\ acid,\ 3} = 0.77$ mol/l, $c_{stearic\ acid,\ 4} = 1.54$ mol/l, $m_{catalyst} = 1$ g, $T = 300\,°C$ and $p = 17$ bar (inert atmosphere).

A comparison of product ratios as a function of ethyl stearate (A) and the reaction intermediate, stearic acid (B) (concentration 1.6 mol/l) conversion at 300 °C under Ar + H_2 atmosphere, indicated that the parallel route, proposed in the reaction network (Fig. 1) was indeed in conjunction with empirically observed. Hence, the ratio of *n*-heptadecane/olefinic C17-products (C/D) seems to be rather constant. Nevertheless, the ratio between olefinic C17-products/aromatics C17-products (D/E) are decreasing, implying that it is a consecutive reaction (Fig. 5a and b).
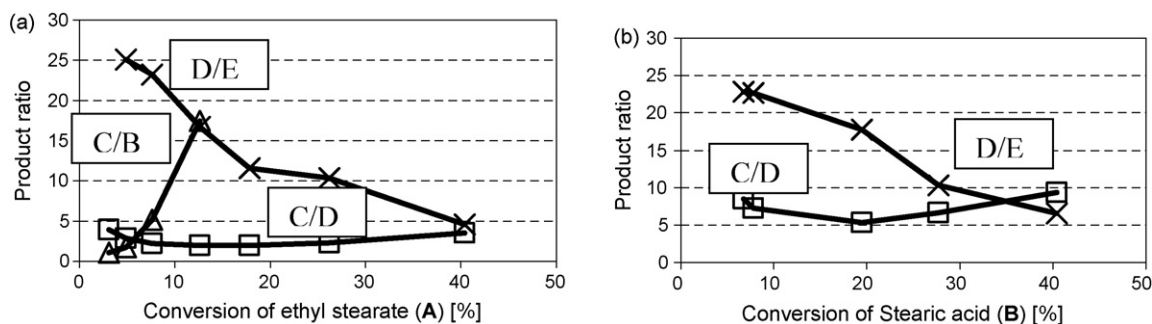

Fig. 5. Ratio of C_{17}-product concentration as a function of (a) ethyl stearate and (b) stearic acid conversion. Symbols: (×) D/E (olefinic C17-products/aromatics C17-products) and (□) C/D (*n*-heptadecane/olefinic C17-products). The reaction conditions: $c_{feed} = 1.6$ mol/l, $m_{catalyst} = 1$ g, $T = 300\,°C$ and $p = 17$ bar (Ar + H_2).

4. Kinetic modeling

The kinetic modeling was based on the proposed reaction network in Fig. 1 assuming a Langmuir–Hinshelwood type mechanism. A reasonable simplification is that adsorption constants for gaseous products (i.e., CO_2, ethylene, etc.) can be disregarded in the denominator. The surface reactions were assumed to be rate limiting, while the adsorption steps were assumed to be rapid compared to surface reactions. In the equation below K_i, k_j, and c_i denote the equilibrium adsorption constant, reaction constant, and the concentration for the arbitrary compounds, respectively. The equilibrium adsorption constant, K_i, and reaction constant k_j were lumped together as an apparent reaction constant denoted as k_i' giving the rate expression

$$r_1 = \frac{k_1' c_A}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E},$$
$$\text{where } k_1' = k_1 K_A \tag{1}$$

$$r_2 = \frac{k_2' c_B}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E},$$
$$\text{where } k_2' = k_2 K_B \tag{2}$$

$$r_3 = \frac{k_3' c_A}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E},$$
$$\text{where } k_3' = k_3 K_A \tag{3}$$

$$r_4 = \frac{k_4' c_C}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E},$$
$$\text{where } k_4' = k_4 K_C \tag{4}$$

$$r_5 = \frac{k_5' c_B}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E},$$
$$\text{where } k_5' = k_5 K_B \tag{5}$$

$$r_6 = \frac{k_6' c_D}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E},$$
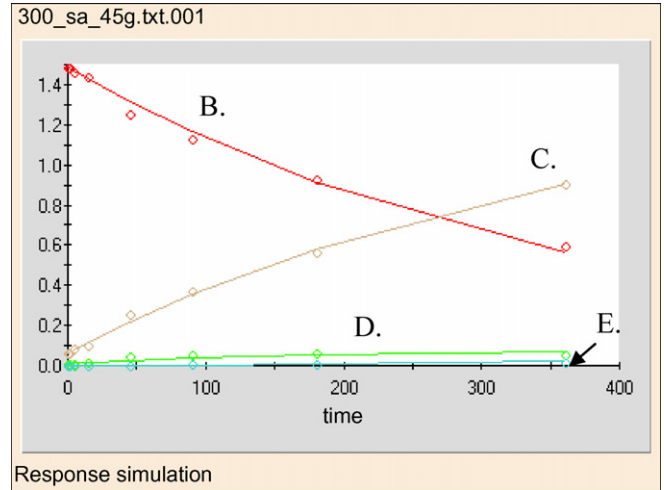$$\text{where } k_6' = k_6 K_D \tag{6}$$

Fig. 6. Kinetic modeling of stearic acid decarboxylation at 300 °C. Stearic acid = B, *n*-heptadecane = C, olefinic C_{17}-products = D and aromatic C_{17}-products = E (calculations = smooth lines and experimental results = symbols).

$$r_7 = \frac{k_7' c_A}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D + K_E c_E},$$
$$\text{where } k_7' = k_7 K_A \tag{7}$$

By implementing the kinetic rate expressions into the mass balances of components and taking into account the reaction stoichiometry (Fig. 1), a system of ordinary differential equations (ODE) is obtained,

$$\frac{1}{\rho_B} \frac{dc_A}{dt} = -r_1 - r_3 - r_7 \tag{8}$$

$$\frac{1}{\rho_B} \frac{dc_B}{dt} = r_1 - r_2 - r_5 \tag{9}$$

$$\frac{1}{\rho_B} \frac{dc_C}{dt} = r_2 + r_3 - r_4 \tag{10}$$

$$\frac{1}{\rho_B} \frac{dc_D}{dt} = r_4 + r_5 - r_6 + r_7 \tag{11}$$
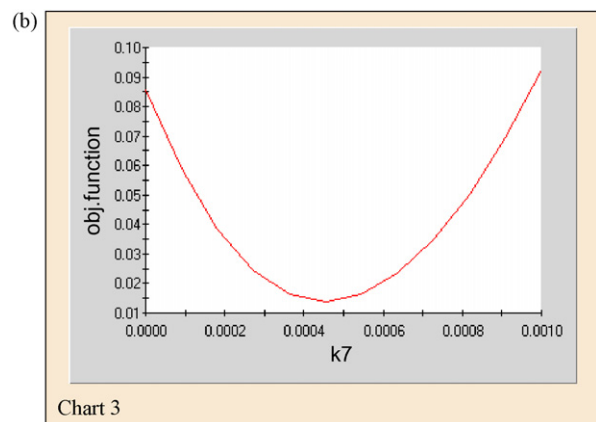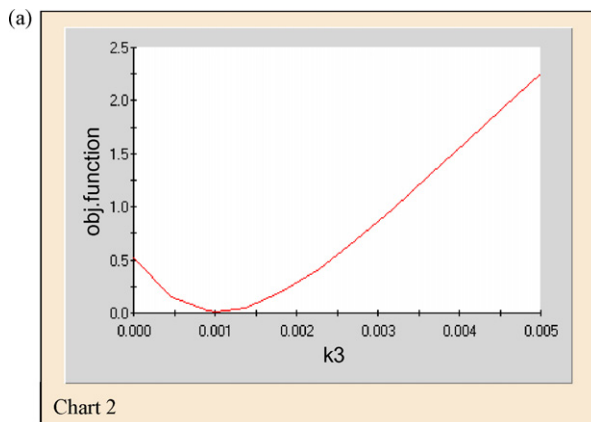
$$\frac{1}{\rho_B} \frac{dc_E}{dt} = r_6 \tag{12}$$

Fig. 7. Parameter sensitivity analysis for (a) k_3' and (b) k_7'.

where ρ_B denotes the catalyst mass-to-liquid ratio, i.e., the catalyst bulk density.

The evaluation of the proposed model was based on the results obtained from a parameter estimation program, ModEst 6.1 [15] integrated with an ODE solver (Odessa). The modeling was performed at all temperatures together by minimizing the residual sum of squares (Q) between experimental and calculated results with the simplex method.

$$Q = ||c_{exp} - c_{est}||^2 = \sum_t \sum_i (c_{exp,it} - c_{est,it})^2 \qquad (13)$$

where the subscript t and i denote time and compound, respectively.

The goodness of the model is described by the residual of experimental and estimated results in square and the residual of experimental and mean experimental values in square given the degree of explanation, R^2.

$$R^2 = 100\% \times \left[1 - \frac{(c_{exp} - c_{est})^2}{(c_{exp} - \bar{c}_{exp})^2} \right] \qquad (14)$$

The apparent kinetic parameters, consisting of rate and equilibrium constants, in the derived expressions follow an Arrhenius temperature dependency and the law of van't Hoff, respectively. Hence an apparent activation energy and apparent pre-exponential factor were estimated. The apparent parameters, E'_{act}, and k'_o, are defined as

$$E'_{act} = E_{act} - \Delta H_{ad} \qquad (15)$$

and

$$k'_o = k_o K_o \qquad (16)$$

where E_{act}, ΔH_{ad}, k_o and K_o denote activation energy, heat of adsorption, pre-exponential factors for the rate and equilibrium constant, respectively.

Preliminary results showed that the equilibrium constants could be neglected, thus the denominator in equation (1)–(7) is equal to 1. Since the model depicted by Fig. 1 is rather complex, the mathematical treatment becomes challenging. Therefore, separate modeling of the intermediate product, stearic acid, decarboxylation was performed. By simplifying the system to comprise only of stearic acid reactions the calculations converged giving an excellent fit (degree of explanation 99.86) to the proposed reaction scheme (Fig. 6). However, the system was still overparametrized, thus giving no physico-chemical relevance of the information obtained.

Nonetheless, by implementing and fixing the obtained parameters from the stearic acid case into the modeling of ethyl stearate decarboxylation, an excellent fit (99.85) was attained. Furthermore, the rate constants for reaction number 3 and 7 at 300 °C could be reliably determined (Table 1).
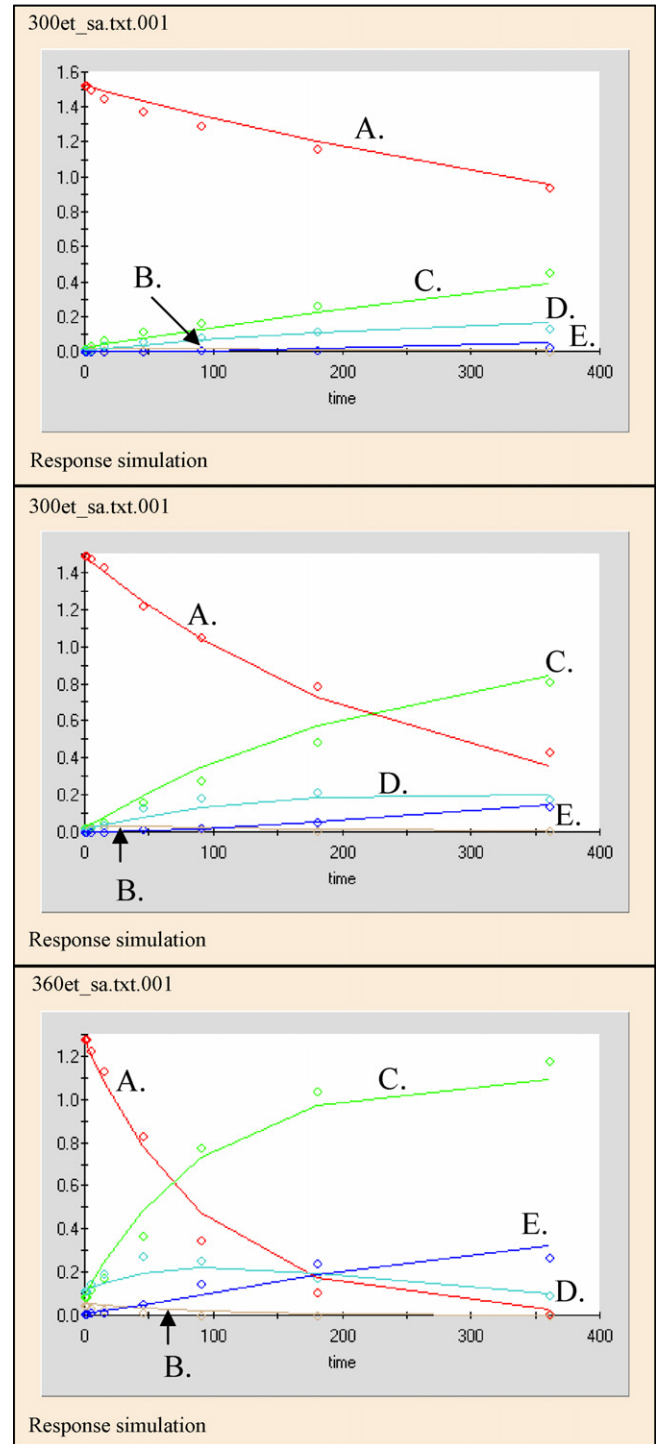

Fig. 8. Kinetic modeling of ethyl stearate deoxygenation at different temperatures (300–360 °C). Ethyl stearate = A, stearic acid = B, *n*-heptadecane = C, olefinic C_{17}-products = D and aromatic C_{17}-products = E (calculation = smooth lines and experimental results = symbols).

Table 1
Estimated rate constants for ethyl stearate decarboxylation at 300 °C

Parameter	Rate constant at 300 °C (min^{-1})
k'_1	6.27×10^{-12}
k'_2	$1.31^* \times 10^{-3}$
k'_3	1.01×10^{-3}
k'_4	$1.45^* \times 10^{-12}$
k'_5	$2.47^* \times 10^{-3}$
k'_6	$2.31^* \times 10^{-4}$
k'_7	4.55×10^{-4}

* Fixed values based on modeling of stearic acid.

Parameter sensitivity analysis was performed by investigating the behavior of objective function as a function of the kinetic parameters k_3' and k_7'. The sensitivity analysis for the rate constants is illustrated in Fig. 7. As can be seen from the figures, the kinetic parameters exhibit evident minima's. Conclusively the physico-chemical significance of the obtained results is important.

Modeling of temperature dependence (300–360 °C) of ethyl stearate decarboxylation demonstrated an excellent fit to experimental data (Fig. 8), 99.28% degree of explanation. The standard error of estimate was 0.039. The experimental and predicted concentration profiles of reactants and products at different temperatures are illustrated in Fig. 8.

5. Conclusions

The kinetics of ethyl stearate decarboxylation was studied in a broad range of temperatures and pressures over a Pd/C catalyst. Additionally decarboxylation of the intermediate product, stearic acid, was investigated. The main kinetic regularities were established. The kinetic modeling based on the proposed reaction mechanism of stearic acid and ethyl stearate decarboxylation was performed successfully.

Acknowledgements

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