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Thermodynamic balance in reaction system of total vegetable oil hydrogenation

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ABSTRACT

Total hydrogenation of vegetable oils to yield hydrocarbons is an emerging process for production of biofuels. Tristearate was chosen as a model compound to represent vegetable oils in the calculations. As its thermodynamic data were not available in literature, their values were estimated by using the Joback's contribution method. Based on the comparison to a relevant known system (butyl stearate) it was concluded that the chosen method is suitable for the assessment of thermodynamic data of triglycerides. A basic thermodynamic analysis of the reaction system was performed and the predictions of the derived thermodynamic model were compared to the experimental observations of rape-seed oil total hydrogenation into hydrocarbons. The model predictions were found to be in good agreement with experimental data. The estimations suggested that the reaction was limited by hydrogen diffusivity through the liquid film on catalyst particles.

1. Introduction

Partial hydrogenation of vegetable oils with the aim to improve their functional behaviour is a well-known and proven process [1–4]. It is performed under strictly defined reaction conditions and only non-saturated bonds of triglycerides, *i.e.* the almost exclusive compounds of vegetable oils, are hydrogenated. Typically, Ni or noble metals supported on silica support are used under mild reaction conditions (100–180 °C, 0.15–0.3 MPa) [4]. Other chemical processes using vegetable oils include hydrolysis, interesterification, transesterification, isomerization and polymerization [4]. In the recent years, particularly transesterification has become very important due to the environmental concerns that are major driving force of biofuels implementation. Biodiesel (methylesters of fatty acids, FAME) is the most common biofuel in Europe [5]. The physico-chemical properties of biodiesel are, however, not optimal for its use as diesel fuel. The main problems are caused by its low oxidation and storage stabilities and poor cold-flow properties [4]. Therefore, alternative routes for the production of diesel fuel components from vegetable oils are sought. A promising route appears to be the direct conversion of vegetable oils into hydrocarbons by their total hydrogenation [6–10].

Total hydrogenation of triglycerides yields hydrocarbons (n-alkanes) as the main products and propane, water, CO and CO_2 as by-products [7–10]. The hydrocarbons are produced by two reaction pathways: (i) hydrodeoxygenation (HDO) and (ii) hydrodecarboxylation (HDC). n-Alkanes originating from HDO have the same carbon number as the original fatty acid chain, *i.e.* even carbon number, typically 16 or 18. The main reaction by-products of this route are water and propane. On the other hand, HDC yield hydrocarbons with an odd carbon number; they have one carbon atom less in the molecule than the original fatty acid chain. The dominant by-products are CO, CO_2 and propane [8,9]. A process for production of diesel fuel components based on the total hydrogenation of vegetable oils has been recently developed and commercialized by the Finnish company NesteOil [10].

The prime motivation of this contribution is to investigate reaction pathways of rape-seed oil transformation into hydrocarbons and the effects of reaction parameters, such as temperature and pressure, on hydrocarbon distribution in the final product. The conversion of rape-seed oil into hydrocarbons was previously experimentally verified and a reaction scheme was proposed [14]. Rape-seed oil consists of triglycerides of fatty acids having predominantly 18 carbon atoms in the molecule (ca. 93%, m/m). Some C_{16} (ca 5%, m/m) and C_{20} (ca. 2%, m/m) fatty acids are found in the triglycerides in rape-seed oil as well. The major hydrocarbons produced by rape-seed oil conversion are n-octadecane and n-heptadecane; C_{16} and C_{15} alkanes are found only in low quantities [11–13,39]. The concentrations of C_{17} and C_{18} hydrocarbons, and C_{16} and C_{15} hydrocarbons correspond to the concentrations of C_{18} fatty acids and C_{16} fatty acids, respectively, in the triglycerides that make up rape-seed oil [14]. The formation of hydrocarbons with two different chain lengths suggests that two different reaction pathways

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Nomenclature

Symbols

a, b, c, d	constants for c_p calculation (–)
c_p	thermal capacity (kJ/(mol K^{-1}))
Da,×Dd	atomic contribution groups for c_p calculation (–)
G	Gibbs free energy (kJ/mol)
H	enthalpy (kJ/mol)
K	equilibrium constant (–)
N	atomic group contribution (–)
p	pressure (bar)
R	gas constant (kJ/(kmol K^{-1}))
S	entropy (kJ/(kmol K^{-1}))
t	temperature (°C)
T	temperature (K)
ν	stoichiometric coefficient (–)

Prefix

Δ	difference of thermodynamic parameter

Subscripts

E	equilibrium
f	formation
I	component number, products
j	component number, reactants
r	reaction

Superscripts

$\circ$	standard conditions
P	pressure
T	temperature

are involved in the total hydrogenation of rape-seed oil. It was proposed [14] that these are hydrodeoxygenation, leading to C_{18} and C_{16} hydrocarbons, and hydrodecarboxylation, forming C_{17} and C_{15} hydrocarbons. The product distributions (C_{18} vs. C_{17} and C_{16} vs. C_{15}) are significantly affected by reaction temperature and pressure.

The aim of this paper is therefore to elucidate basic thermodynamic limitations in the reaction system of total vegetable oil hydrogenation. Principally this complex task can be divided into two basic steps – (i) saturation of double bonds and (ii) elimination of oxygen atoms. Since the first step is known from the industrial practice to be quantitative and selective, saturated triglycerides were considered to be raw materials in the thermodynamic study. As the vast majority of triglycerides in rape-seed oil contains C_{18} fatty acids, the thermodynamic study of the system was limited to the investigation of tristearate, *i.e.* triglyceride of stearic acid.

The role of thermodynamic prediction of the chemico-physical behaviour of the reaction system is unfortunately limited. The thermodynamic balance in the system can neither predict the process on the thin film on the catalyst contact, nor discuss the insufficiency of the hydrogen (or another reactant) in the system. The only benefit of thermodynamic approach is to define the boundary conditions of studied complex reactions with respect to idealised reaction conditions, if thermodynamic equilibrium is established. Therefore, predicted behaviour of the reaction system was a priori confronted with measured lab-scale data. The study should answer the basic question of the system balance – how far is the real system from the thermodynamic (idealised) equilibrium.

Presented paper is divided into two parts. In the first one, a thermodynamic model of the reaction system will be derived and an overview of the relevant thermodynamic data will be given. Due to the absence of almost all thermodynamic data of triglycerides in open literature and chemical databanks, a methodology of thermodynamic data estimation will be presented and the relevant data will be estimated. In the second part, a thermodynamic model will be derived and applied for the prediction of thermodynamic behaviour of the investigated hydrogenation system. Finally, the modelling results will be compared with the experimental results.

2. Thermodynamic balance of total triglyceride hydrogenation

A thermodynamic model for the total hydrogenation of tristearate was derived for temperatures between 250 and 450 °C and hydrogenation pressures ranging from 7 to 70 bar. Dilution of roughly 100:1 (mol/mol) for the reaction mixture with either hydrogen or an inert gas was assumed to enable isothermal reaction conditions. Phase equilibrium liquid–gas was considered in the model, too (Peng–Robinson and Ideal EOS = Equation of State) [15].

The basic reaction mechanism of the proposed catalytic transformation is summarised in Eqs. (1–4) and consists of two main reactions [5,16,17]: hydrodecarboxylation (1) and hydrodeoxygenation (2), completed by water–gas-shift reaction and CO formation.

$$(CH_2)_2CH[(CH_2)_{16}]_3(COO)_3(CH_3)_3 + 3H_2 = 3\,C_{17}H_{36} + C_3H_8 + 3CO_2 \tag{1}$$

$$(CH_2)_2CH[(CH_2)_{16}]_3(COO)_3(CH_3)_3 + 12H_2 = 3\,C_{18}H_{38} + C_3H_8 + 6H_2O \tag{2}$$

$$CO_2 + H_2 = CO + H_2O \tag{3}$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{4}$$

Both C_{17} and C_{18} hydrocarbons were present in the products of rape-seed oil total hydrogenation and their concentration varied significantly with reaction temperature and/or pressure. That means that reaction conditions favour either hydrodecarboxylation of triglycerides, leading to formation of C_{17} hydrocarbons + CO_2 (Eq. (1)), or hydrodeoxygenation, characterised by the production of C_{18} hydrocarbons and water (Eq. (2)). These two parallel reaction steps and their extents are crucial for the final product distribution. In addition, the formed CO_2 (Eq. (1)) is converted under reaction conditions by consecutive reactions into CO (Eq. (3)) and methane (Eq. (4)). A by-product of both Eqs. (3) and (4) is water.

Description of the proposed reaction scheme from a thermodynamic point of view includes, besides the fairly simple description of the phase equilibrium, the definition of the chemical equilibrium [17–19,40]. The relation between equilibrium reaction (or system of equilibrium reactions) and predictive equilibrium model is the topic of next discussion, see Eqs. (5) and (6).

Chemical equilibrium in a reaction system is generally defined by the minimisation of Gibbs free reaction energy (5):

$$\Delta G_r^T = -RT \ln K_E(T) \tag{5}$$

where K_E represents a dimensionless equilibrium constant of the chosen reaction system (mass/mass) and T is the reaction temperature (K).

Additionally, Gibbs free reaction energy for any reaction system is defined by superposition of reaction enthalpy and the multiplication of temperature and entropy of the system (6):

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ \tag{6}$$

Eq. (6) allows a simple recalculation between Gibbs free energies and other basic thermodynamic data. If Eqs. (5) and (6) are combined, it is possible to predict an equilibrium of the chosen reaction system from tabulated enthalpies and entropies at a given reaction temperature. This algorithm is well-known and applied in almost all standard simulation machines like ASPEN+, PRO and HYSYS [20,21]. The only problem is the recalculation of ΔH and ΔS to the desired (reaction) temperature and, of course, the acquisition of the thermodynamic data if not tabulated.

2.1. Recalculation of basic thermodynamic data to reaction temperature

The Gibbs free energy is recalculated according to Eq. (6). Reaction enthalpy ΔH_r^T at temperature T is coupled with standard reaction enthalpy ΔH_r^0 by heat capacity (Eq. (7)):

$$\Delta H_r^T = \Delta H_r^\circ + \int_{298}^{T} c_{p,T}\,dT \rightarrow \Delta H_r^T = \Delta H_r^\circ + \overline{c_{p,T}}(T-298) \tag{7}$$

where $\overline{c_{p,T}}$ is an average thermal capacity, calculated as the arithmetical average of thermal capacities at higher and lower (standard) temperature.

For entropy of the reaction system, similar dependence can be defined (8).

$$\Delta S_r^T = \Delta S_r^\circ + \int_{298}^{T} \frac{c_{p,T}}{T}\,dT \rightarrow \Delta S_r^T = \Delta S_r^\circ + \overline{c_{p,T}}\ln\left(\frac{T}{298}\right) \tag{8}$$

Thus, to calculate ΔH and ΔS at desired (reaction) temperature where standard enthalpies and entropies are supposed to be known, "only" thermal capacities of the components are needed to solve Eqs. (7) and (8).

Generally, the enthalpies and entropies of many basic organic compounds are given in relevant chemical handbooks [20–23]. If not tabulated, two of the three already introduced thermodynamic parameters, *i.e.* ΔG, ΔH and ΔS, need to be estimated by a reliable and statistically proven method (see Eq. (6)). Moreover, the thermal capacities of unknown components need to be estimated as well to describe the reaction system at other temperature than the standard one.

The assessment of not-tabulated parameters is the most important task of this contribution, as the thermodynamic data for tristearate and their temperature dependencies are not readily available. Their estimation was also topic of several scientific contributions [24–30].

2.2. Thermodynamic data estimation of organic compounds by using the contribution method

The estimation of thermodynamic behaviour of organic compounds related to ideal gas state is mostly based on the molecular structure of the unknown component [31,32]. The contribution method by Joback [32] belongs to the most reliable and statistically proven methods due to its simplicity and high precision of the estimations for molecules with higher enthalpies [22,31,32]. According to Jobackĭs method, the reaction enthalpy of organic compounds can be estimated by Eq. (9):

$$\Delta H_r^{298,15} = 68.29 + \sum_{i=1}^{n} N_i \Delta_{H,i} \tag{9}$$

The atomic contribution parameter $\Delta_{H,i}$ is tabulated on the basis of statistical evaluation of large sets of experimental data [32] and can be used for data estimation for a wide range of organic compounds.

The same method enables the calculation of free Gibbs energy (Eq. (10)):

$$\Delta G_r^{298,15} = 53.88 + \sum_{i=1}^{n} N_i \Delta_{G,i} \tag{10}$$

In Eq. (10), the $\Delta_{G,I}$ represents atomic contributions of the individual chemical groups. The values for selected atomic groups, used in this paper, are listed in Table 1.

For solving Eqs. (9) and (10), a set of atomic contributions, which is usually tabulated, is needed. The same approach with other contribution parameters is used also by other authors, working on similar topics [24,31]. However, not the basic estimation of ΔG and ΔH for unknown components, but in many cases the assessment of thermal capacities is crucial for a proper calculation of the thermodynamic balance of the overall reaction system.

The most important scientific contributions to the prediction of thermodynamic data of vegetable oils, fatty acids and their derivatives have been given by Benson [19], Avaullée et al. [1] and Zhenyi et al. [31]. Zhenyi applied the Joback's contribution method for data prediction at standard conditions. However, the authors [31] used their own algorithm, based on the characteristic group values, for the recalculation of thermal capacities at higher reaction temperatures. Application of the Zhenyi's algorithm for the total hydrogenation of tristearate resulted in severe discrepancies in the estimated ΔG and ΔH at high reaction temperatures (up to 450 °C) mostly due to another recalculation of c_p values. Therefore, the standard Joback's method for c_p estimation was used.

Thermal capacity of organic compounds is according to ref. [32] calculated by using Eq. (11):

$$c_p^T = a + bT + cT^2 + dT^3 \tag{11}$$

where T represents the reaction temperature in K and constants a, b, c and d are further defined by individual atomic contribution.

2.3. Accuracy of the presented thermodynamic balance model

The accuracy of the chosen estimation method was tested on a similar reaction system, total hydrogenation of butyl stearate. This reaction system is well-known and all thermodynamic data are listed in many databanks, *e.g.* [19–23,33]. The comparison of tabulated data for butyl stearate and the results obtained by the method described by Zhenyi et al. [31] showed large deviations and, therefore, the use of this method was rejected for the calculation of the thermodynamic data of tristearate. On the contrary, the thermodynamic data calculated for butyl stearate by using the Jobackĭs method were in very good agreement with the tabulated ones. The standard reaction enthalpy of butyl stearate at 298 K gives −814.7 kJ/mol employing the Jobackĭs method. For the same compound the DECHEMA Databank [20] gives a value of −818.6 kJ/mol.

The discrepancy between the value obtained by using the contribution method of Joback and a reliable data source is in this example lower than 0.5%.

The calculated and tabulated thermal capacities remain almost the same in the investigated temperature range, *i.e.* up to 370 °C. The standard deviation varies between 0.1% and 0.4%. Even though higher deviations between "real thermodynamic data" and the predicted ones can be expected for tristearate, as it is a more complex molecule than butyl stearate, the good agreement of thermodynamic data predictions for butyl stearate with measured (tabulated) data suggests that the chosen estimation method (Joback) is suitable for the assessment of thermodynamic data of esters of fatty acids. Moreover, it will be shown that in a real system, only thermodynamic data of tristearate

Table 1
Atomic contribution values for the estimation method according to Joback [32], extended by values for calculation of thermal capacities.

Atomic contribution N_i	$\Delta_{H,i}$	$\Delta_{G,I}$	D_a	D_b	D_c	D_d
$-CH_3$	−76.45	−43.96	19.5	$-8.08.10^{-3}$	$1.53.10^{-4}$	$-9.67.10^{-8}$
$-CH_2-$	−20.64	+8.42	−0.909	0.095	$-5.44.10^{-5}$	$1.19.10^{-8}$
>CH-in chain	+29.89	+58.36	−23.0	0.204	$-2.65.10^{-4}$	$1.20.10^{-7}$
–COO– (ester)	−337.92	−301.95	24.5	0.0402	$4.02.10^{-5}$	$-4.52.10^{-8}$

need to be estimated since the thermodynamic data of the remaining components (both reactants and products), are readily available from reliable sources (*e.g.* from databanks or scientific journals).

In addition to the validation of the thermodynamic data estimations over the whole studied temperature range, the accuracy of estimations at elevated pressure was investigated as well. It is well-known that the precision of all estimation methods based on molecular contributions is rather strictly limited to low pressures. However, hydrogenations are typically carried out at elevated pressures. In the presented case, hydrogenation pressure of 70 bar was used in the experiments. Thus, the dependence of thermodynamic data on pressure could not be neglected, as one of the aims of the work was to compare the experimental data with the modelled ones.

To estimate the accuracy of presented thermodynamic model (based on ideal gas approach) at higher pressure, the results were compared to calculation using Peng–Robinson EOS and tabulated data. The dependence of ΔG on temperature by Peng–Robinson at elevated pressure can be taken from literature or some standard calculation machine (ASPEN+). The resulting plot of ΔG vs. reaction temperature at the highest reaction pressure of 70 bar is given in Fig. 1. It can be seen that there is a systematic deviation between the results obtained by the two chosen approaches; the Gibbs free energy calculated by the ideal-gas-law approach at 70 bar is lower compared to the one calculated by Peng–Robinson EOS. Nevertheless, the discrepancy remains fairly low, namely 2–4%. Such accuracy of the predicted thermodynamic parameters is still acceptable, considering the basic problems with acquisition of all thermodynamic data of the system.

3. Total triglyceride hydrogenation experiments

The experiments were carried out in an electrically-heated fixed-bed reactor (i.d. 17 mm). The reaction temperature and pressure varied in the range of 240–360 °C and 0.5–8 MPa, respectively. The weight-hourly space velocity (WHSV) and the molar ratio of hydrogen to feedstock were kept constant at values 1 h^{-1} and 100 (mol/mol), correspondingly. Commercial hydrotreating and hydrogenation catalysts (Ni-Mo/Al_2O_3 and Ni/Al_2O_3, respectively) were used. In these experiments about 15 g of a catalyst were loaded in the reactor. Both catalysts were activated in-situ prior to the experiments, either using dimethyldisulfide (DMDS) for the NiMo catalyst or hydrogen for the Ni catalyst. Refined rapeseed oil was fed into the reactor.

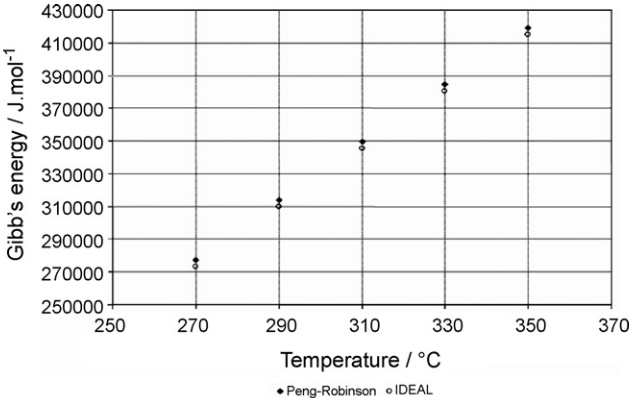

Fig. 1. Comparison of the Gibbš free energies calculated by the Joback's contribution method (ideal-gas approach) with tabulated values (by Peng–Robinson EOS) – temperature dependence at elevated pressure of 70 bar.

Samples of liquid as well as of gas phase were analyzed off-line by GC techniques. The gas-phase samples were analyzed by using the conventional three-column system equipped with both FI and TC detectors (Agilent). The liquid phase samples free from reaction water were analyzed by using on-column injection and a pre-column (deactivated capillary silica column, 2.5 m × 0.53 mm i.d.) connected to an analytical HP-5 column (10 m × 0.25 mm i.d., film 0.1 μm). The identification of liquid products was confirmed by GC-MS analysis.

4. Results and discussion

The Joback's contribution method has been demonstrated to estimate accurately the thermodynamic data of butyl stearate over the entire range of experimental conditions studied (*i.e.* up to 370 °C and 70 bar) and thus it could be safely applied for the assessment of the relevant thermodynamic data of tristearate. The calculated thermodynamic data were used to study the total hydrogenation of tristearate based on the derived thermodynamic model (Eqs. (1–4)) over the whole range of experimental temperatures and pressures. In Table 2, an overview of calculated standard thermodynamic properties of main reactants and products of the reaction system is presented.

4.1. Thermodynamic balance – the influence of temperature and pressure on the liquid product distribution

The main reactant of the total hydrogenation, tristearate, reacts according to reactions (1)–(4). The liquid phase (experimentally separated at 80 °C) consists of hydrocarbons and water. After separation of the water phase, the liquid phase comprises almost exclusively C_{15}–C_{18} hydrocarbons.

In agreement with the composition of rape-seed oil, C_{17}–C_{18} hydrocarbons are the major products and their concentration is more than 90%, m/m. Thus, the influence of temperature and pressure on the product distribution will be demonstrated only for these two representatives. Nevertheless, it could be shown that the trends for C_{15} and C_{16} hydrocarbons are similar to those of C_{17} and C_{18}

Table 2
Basic calculated thermodynamic data of tristearate hydrogenation system, standard conditions 25 °C = 298 K, 1 bar.

Component	Thermodynamic parameter	
	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
Tristearate	−2176.9	−504.5
$C_{17}H_{36}$	−394.2	92.3
$C_{18}H_{38}$	−414.9	100.7
Propane	−105.3	−25.6

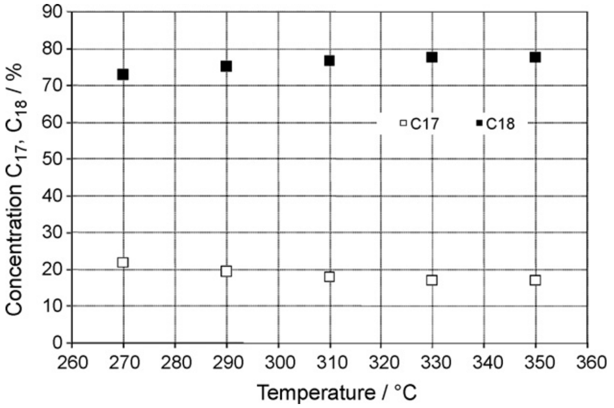

Fig. 2. Calculated concentration profiles of C_{17} and C_{18} hydrocarbons at 70 bar as a function of reaction temperature, reaction extent corresponds to 7 mol hydrogen per 1 mol tristearate in the feed. Total feed dilution is equal to 1:100 by hydrogen.

hydrocarbons [8,34]. In Fig. 2, the calculated mass concentrations of formed hydrocarbons are presented as a function of reaction temperature for the total pressure of 70 bar.

The thermodynamic prediction for 70 bar shows that with increasing temperature, starting at 270 °C, the concentration of C_{18} hydrocarbon rises and finally, at 350 °C, reaches almost 80% in the liquid hydrocarbon product (Fig. 2). That means that, at elevated pressure of 70 bar and higher temperature, the hydrodeoxygenation reaction is preferred, resulting in the formation of C_{18} hydrocarbons. A plausible explanation of the product distribution can be derived from the already presented reaction scheme (Eqs. (1)–(4)) – at elevated pressure hydrodeoxygenation (Eq. (2)) will be preferred due to the fact that the number of moles of products is lower than that of reactants in hydrodeoxygenation (compare Eqs. (1) and (2)).

The hydrodecarboxylation reaction (Eq. (1)) is, on the contrary, accelerated by lowering the reaction pressure (as the number of moles of products is higher than that of reactants). The effect of reaction pressure is demonstrated on Fig. 3, which depicts the dependence of product distribution on reaction pressure at a medium temperature of 310 °C. At low pressure (*e.g.* 0.5 bar) the concentrations of C_{17} and C_{18} hydrocarbons are most equal, *i.e.* the extent of hydrodecarboxylation increases at the expense of hydrodeoxygenation. Furthermore, a comparison of Figs. 2 and 3 reveals that the effect of the change of reaction pressure on the product distribution is more pronounced than that of reaction temperature in the range of experimental conditions investigated here.

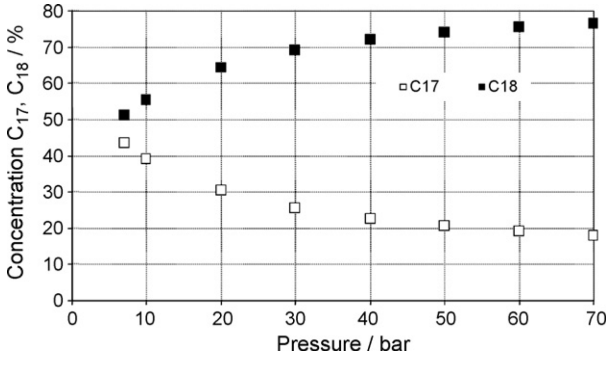

Fig. 3. Calculated concentration profiles of C_{17} and C_{18} hydrocarbons at 310 °C as a function of reaction pressure, reaction extent corresponds to 7 mol hydrogen per 1 mol tristearate in the feed. Total feed dilution is equal to 1:100 by hydrogen.

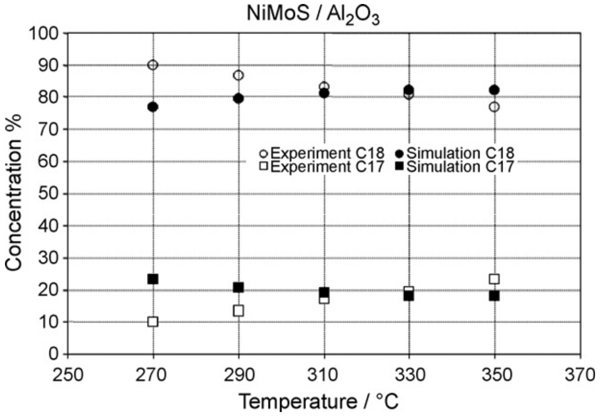

Fig. 4. Comparison of measured (open symbols) and calculated (filled symbols) concentrations of C_{18} and C_{17} hydrocarbons (including iso-derivatives) at 70 bar for total tristearate (calculation) and rape-seed oil (experiments) hydrogenation. Catalyst used in experiments: NiMoS on alumina. Reaction extent (calculations) corresponds to 7 mol hydrogen per 1 mol tristearate in the feed. Total feed dilution is equal to 1:100 by hydrogen.

From the process point of view, the product distribution is significantly affected by the choice of reaction conditions and this fact could be thus used for tailoring the process to suit different local conditions.

4.2. Thermodynamic balance vs. lab-scale experiment

The ultimate (and most challenging) task is to discuss the reliability of the presented thermodynamic model by comparing its predictions to the results of lab-scale experiments. Details of the experimental procedure and of the product analysis are given in Section 3 [16,34]. The comparison of the thermodynamic predictions (based on tristearate) with experimentally performed conversion of rape-seed oil is given in Fig. 4 for reaction temperature ranging from 270 to 350 °C at total reaction pressure equal to 70 bar.

For both C_{18} and C_{17} hydrocarbon concentrations, an acceptable agreement between experiment and model can be observed for temperatures above 300 °C. Below 300 °C, the discrepancy of the measured and predicted hydrocarbons concentration is increased and at reaction temperature of 270 °C, the deviation of C_{18} concentration amounts to ca. 9.2% (relative). The thermodynamic predictions show that in excess of hydrogen n-octadecane is the exclusive hydrocarbon product. In order to account for the observed formation of n-heptadecane the H_2/oil ratio was varied until reasonable agreement with the experimental data was found. It was at the value of H_2/oil ratio equal to 7.

It can be therefore suggested that under the reaction conditions the reaction can be limited by hydrogen diffusion to the active sites, *i.e.* by hydrogen mass transfer through the stagnant liquid film formed by reactants and/or products on the outer surface of catalyst particles. The diffusion limitations in similar systems (Ni catalyst, FAME/triglycerides, H_2) were studied in detail by Junker [35]. The authors have found that the hydrogenation is limited by hydrogen diffusion as well as by triglyceride diffusion [35]. The vegetable-oil-hydrogenation-rate limitations by low concentrations of hydrogen on the catalyst surface, which is caused by low hydrogen solubility in vegetable oils, were reported by others as well [36–38]. As the diffusion is affected by temperature, it may also explain the discrepancy between the model predictions and experimental results. Moreover, further peculiarities, such as n-alkane isomerization and possibly also cracking, have to be considered at elevated temperatures.

Generally, it can be concluded that the thermodynamic model describes rather well the experimental data and that the observed discrepancies are due to the complexity of the reaction system involving a heterogeneous catalyst and the mass effects. The model distribution of both hydrocarbons with temperature (and pressure) reflects the limits of the system from thermodynamic point of view. Considering the complexity of the system, the accuracy of the model is relevant for a basic process layout. Hence, the obtained results confirmed the basic reaction dependencies observed experimentally.

5. Conclusions

A basic thermodynamic model was derived for the total hydrogenation of tristearate and its predictions were compared to the experimental observations of rape-seed oil transformation into hydrocarbons. As the basic thermodynamic data for tristearate were not available in literature, their values were estimated by using the Joback's contribution method. Based on the comparison to a relevant known system (butyl stearate) it was concluded that the chosen method is suitable for the assessment of thermodynamic data of triglycerides. The accuracy of the estimates is within 5% for elevated pressures and temperatures for butyl stearate and it can be assumed that it is of the same magnitude for, the chemically similar, tristearate (there is no relevant measured data to compare directly to).

The thermodynamic balance of the system was used to predict the composition of the liquid phase, namely to predict the distribution of C_{17} and C_{18} hydrocarbons. The predictions suggest that C_{18} hydrocarbons are the main reaction products and that their concentration is affected by temperature and particularly by pressure. Moreover, the model predictions are in a good agreement with experimental data. Additionally, the estimations suggest that the reaction is limited by hydrogen transfer. This finding is currently being examined experimentally.

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