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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