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Hydrogenation of edible oils and fats

Jonker, Geert Hilbertus

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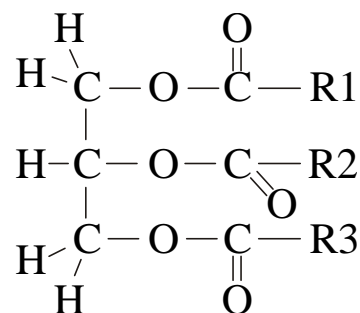
1. Introduction

In the labyrinth of the porous catalyst particle, the edible oil molecules diffuse through channels and adsorb on active sites where they react with hydrogen to saturated components or where they are converted to other isomers. The catalysed process investigated in this thesis: the hydrogenation of edible fats and oils, has been applied for over 90 years on a large industrial scale, but the understanding of the process is far from complete. This thesis investigates the fundamentals of edible oil hydrogenation on supported nickel catalysts, by studying intrinsic surface kinetics, intraparticle diffusion limitation, and adsorption. Chapter 1 is a general introduction to the thesis and a definition of the problem area to be covered by this thesis.



1.1. Background

An edible oil consists of a mixture of triacylglycerides (TAGs). These are triesters of glycerol and three fatty acids, with typical chain lengths of 18 carbon atoms and degrees of unsaturation varying between 0 and 6. Typical fatty acids are stearic (octadecanoic), oleic (*cis*-9-octadecenoic), elaidic (*trans*-9-octadecenoic), and linoleic (*cis,cis*-9,12-octadecenoic). To improve oil features (odour, melting point), the hydrogenation is usually carried out in a three-phase semibatch reactor over a porous nickel catalyst at 0.1–0.6 MPa and around 443 K (Coenen, 1976). Besides saturation, also migration and isomerization of double bonds occur, the latter of which is undesirable in food applications (Katan et al., 1994; Emken, 1994).



Oil molecule; R = alkyl chain

At industrially applied conditions, $373 < T < 473$ K and $0.1 < P_{\text{H}_2} < 1.0$ MPa, polyunsaturated fatty acids (in this thesis also referred to as polyenes) are hydrogenated preferentially over the monounsaturated species (monoenes). This selectivity increases with increasing temperature and decreases with hydrogen pressure; unfortunately, this also applies to the production of *trans* isomers. The kinetics of hydrogenation and isomerization of edible oils are poorly understood, and general rate equations are not available (Albright, 1985). Because of their relevance to industrial applications, particularly polyunsaturated oils were investigated aiming at selectivity improvement, which resulted in apparent rate equations containing many fit parameters. For the selection of the optimal process conditions, knowledge of the fundamental process steps is desired (see for a recent review Veldsink et al., 1997).

In the elaborate literature about the hydrogenation of edible oils, the kinetics are often assumed to be first order in the concentration of unsaturated bonds and based on the degree of saturation: diene \equiv monoene \equiv saturated (Veldsink et al., 1997). The application of Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetics is a more fundamental approach, which consists of a rate determining reaction step (usually a surface reaction step), combined with Langmuir adsorption of reactants and products (Weller, 1992). Hashimoto et al. (1971), Gut et al. (1979), and Grau et al. (1986, 1988) applied LHHW kinetics to oil hydrogenation, based on apparent kinetics. However, a thorough investigation of the rate determining steps in edible oil hydrogenation is not available from open literature.

A thorough investigation of the elementary reaction steps should start with the kinetics of monoene hydrogenation to serve as a key component in the elaborate reaction scheme of the polyene hydrogenation, because the latter implies a large amount of various side products (Coenen, 1986). The *cis-trans* isomerization is commonly explained from the formation of a half-hydrogenated surface intermediate by its easy rotation at the surface, whereas migration occurs via the π -allyl intermediate, the latter being mainly present at hydrogen pressures below industrially applied values. In the range of $0.1 < P_{\text{H}_2} < 1.0$ MPa, the formation of the half-hydrogenated intermediate, which is the key component of the well-known Horiuti–Polanyi mechanism, forms the basis of the reaction scheme for the mono- and double-unsaturated oil molecules (Van der Plank and Van Oosten, 1975).

Usually, different adsorption strengths of fatty acids on the catalyst surface are mentioned as the explanation for the difference in reaction rates of different types of unsaturated methyl esters. Coenen and Boerma (1968) and Heertje and Boerma (1971) concluded, that if linoleic acid was present, hardly any of the monoenic acid in the liquid bulk could adsorb on the catalyst surface. However, adsorption of unsaturated oil molecules or their fatty acids has been scarcely investigated up to now (Albright, 1985; Veldsink et al., 1997). The Horiuti–Polanyi mechanism enables a straightforward implementation of the competitive adsorption of diene relative to monoene.

In the hydrogenation of edible fats and oils over porous nickel catalysts, intraparticle mass transfer limitations not only reduce catalyst effectivities, but also may change the product selectivities (Tsuto et al., 1978; Coenen, 1986; Colen et al., 1988). Information from open literature on the possible role of intraparticle diffusion limitation in oil hydrogenation is very limited (Veldsink et al., 1997). Preferably, the intraparticle effective diffusion coefficient, D_e , should be determined under reaction conditions, which requires a thorough knowledge of the intrinsic kinetics. Additional data on D_e can be obtained from independent experiments in the absence of reaction (Haynes, 1988).

Recent literature data showed the possibility of investigating the pore structure by applying various experimental techniques for measuring D_e (Park and Kim, 1984; Garc a-Ocoa and Santos, 1994). D_e should be measured with different experimental techniques: under inert (non-reaction) and reaction conditions, because the difference in these values reflects the influence of the pore structure in terms of micro- and macropores and their connectivity (McGreavy et al., 1994).

Because of the large influence of intraparticle diffusion limitation on the reaction products, methyl esters of fatty acids (FAME) are preferred relative to triacylglycerides (TAG) in kinetic studies, because the smaller FAME molecules are less subject to pore hindrance. TAG and FAME hydrogenation kinetics are believed to be the same, because the reaction kinetics appear to be influenced by the direct surroundings of the double bond in the fatty acid chain only (Van der Plank, 1972a,b; Grau et al., 1988). Further, FAMEs can be analysed directly on isomer formation and degree of saturation by high temperature gas chromatography. Especially these recent developments in analytical techniques, such as capillary gas chromatography enabled systematic quantitative analysis of geometrical (and to some extent positional) isomers, which were subsequently included in rate equations (Gut et al. 1979; Grau et al. 1988).

1.2. This Thesis

The thesis is an investigation of the edible oil nickel-catalyzed hydrogenation in order to improve reaction selectivities. The research was especially focused on a careful investigation of all subparts of the hydrogenation process, starting from the kinetics of monounsaturated FAMEs, which can be considered as the basis of the reaction mechanism. Experimentally, the role of intraparticle diffusion limitation could be ruled out, so we obtained the intrinsic or true surface reaction kinetics for monoenes. These kinetics were used in the investigation of the next step in the complex reaction network: the hydrogenation of double unsaturated FAMEs, dienes. Also, the monoene kinetics were used to study intraparticle diffusion limitation of TAG molecules and hydrogen.



In **Chapter 2** “Monoene kinetics” the rate determining reaction steps in the hydrogenation of monoene FAME are studied with the aim to obtain mechanistically realistic, LHHW based, intrinsic rate equations. *Cis-trans* isomerization is considered only, following the Horiuti–Polanyi mechanism, because at most conditions, the migration products appear to be minor only, relative to *cis-trans* isomerization products.

Various sets of rate equations are systematically derived, each with a unique set of rate-determining steps. The rate equations are subsequently evaluated for a wide range of experimental data obtained with an industrial nickel-based catalyst (Pricat 9910).



Chapter 3 “Diene kinetics” is an extension of the rate equations for the hydrogenation of monoenes to the hydrogenation and isomerization of dienes. Here, it will be tested whether the same (Horiuti–Polanyi) reaction mechanism that proved successful in describing the monoene hydrogenation is applicable. This procedure proved to be successful: this approach yields a repetitive scheme of hydrogenation and isomerization reactions where the kinetic rate constants are taken from the monoene kinetic study and where the adsorption constant of dienes, K_D , remains the only new parameter to be determined experimentally. The resulting rate equations are tested on a set of batch linoleate hydrogenation experiments with varying temperature and hydrogen pressure.



In **Chapter 4** “Intraparticle diffusion” the intraparticle liquid diffusion coefficients of FAME, TAG, and hydrogen are investigated for small nickel-on-silica industrial catalysts under reaction conditions and by applying tracer pulse column experiments in the absence of the hydrogenation reaction. The true intrinsic hydrogenation kinetics obtained in chapter 2 for monoene FAME are used to investigate the effects of intraparticle hydrogen and FAME or TAG diffusion on the hydrogenation rate under reaction conditions. Also, by applying recent improvements in the column packing techniques and realising various improvements in experimental accuracy, first data are reported on effective intraparticle liquid diffusion coefficients of FAME and TAG in porous non-zeolite nickel-on-silica catalysts from tracer pulse column experiments in the absence of hydrogenation. The D_e values obtained from these two methods will be compared.



Chapter 5 “Adsorption” contains a first independent determination of the adsorption phenomena of unsaturated versus saturated FAMEs. For this purpose, batch adsorption experiments are used, as well as the results of the HPLC experiments. The results are compared with the adsorption coefficients from literature and those obtained in Chapters 2 and 3.

Finally, **Chapter 6** “Conclusions” gives an overview of the stepwise construction of the complex catalytic reaction system of the hydrogenation of vegetable oils.

1.3. Research group

This thesis started as an independent research project with Unilever Research Laboratories, but was later brought under the scope of the ASHLI (Advanced Selective Hydrogenation of Lipids) project which ran from 1992 to 1997. This European AIR-project (number AIR1-CT92-513) was a co-operation between Chalmers university of technology (Göteborg), the Technische Hochschule Darmstadt, the University of Groningen, Fima Portugal (an edible oil processing industry), Degussa AG Hanau (a catalyst manufacturer), and the research institutes of Unilever (Vlaardingen) and SSOG (Milan). The project has yielded an understanding of many aspects of nickel catalyzed partial hydrogenation. These include the chemical kinetics, effective pore diffusion coefficients, adsorption on the surface, the influence of mass transfer and the effects of additives on the catalyst.