J Am Oil Chem Soc (2011) 88:2023–2034
DOI 10.1007/s11746-011-1878-9

ORIGINAL PAPER

# Physical Properties of Nutritive Shortenings Produced from Regioselective Hardening of Soybean Oil with Pt Containing Zeolite

**An Philippaerts · Annika Breesch · Gert De Cremer · Pieterjan Kayaert · Johan Hofkens · Guy Van den Mooter · Pierre Jacobs · Bert Sels**

Received: 7 December 2010 / Revised: 26 April 2011 / Accepted: 1 June 2011 / Published online: 21 June 2011

**Abstract** Soybean oil was partially hydrogenated using Pt supported in microporous zeolite ZSM-5 and on mesoporous alumina at various IV. Their fatty acid and triacylglycerol composition were determined with GC and HPLC, respectively, and their physical characteristics were monitored by the slip melting point, solid fat content, melting and crystallization thermograms, polymorphism behavior, and the crystal and solid fat network formation. Both the chemical and physical properties were compared with commercial fat samples. Usage of Pt instead of Ni results in a significant reduction in *trans* fatty acids in the hardened fat. Moreover, the catalyst support of Pt, viz. zeolite ZSM-5 versus $\gamma$-alumina, markedly affects the TAG composition. Pt/alumina fats contain large amounts of SSS and polyunsaturates (PUFA), making them unsuitable for shortening application. Because of the (regio)selective hydrogenation property of Pt/ZSM-5, *sn*-2 unsaturates are hydrogenated faster, yielding an enrichment of intermediately reduced TAG. In addition, this unique fat composition shows a high nutritional added-value (high content of oleate, very low content of *trans* fatty acids, and low content of cholesterol-raising palmitate and myristate) and high thermal stability (very low in linolenate). Moreover, their melting characteristics perfectly match those of commercial shortenings. Pt/zeolite hardened soybean oil contains spherulitic crystals with orthorhombic $\beta'$ molecular packing, arranged in an open, flexible solid network, in accordance with their high plasticity.

**Keywords** Hydrogenation · Soybean oil · Pt/ZSM-5 catalyst · Shortening · Hardening · Melting behavior · Crystallization · Solid fat content · Polymorphism

## Introduction

Shortenings are fat products with a broad melting range and high plasticity, which are commonly used in the bakery industry as texture assisting agents. Three factors are very critical for their use in bakery foods: (1) the ratio of solid to liquid phase, (2) their plasticity, and (3) their oxidative stability [1]. The last issue refers to the high working temperature normally employed in bakeries, and thus to the high melting characteristics that are required. Since polyunsaturated fatty acids are highly thermo-labile, their level in bakery fat, especially that of linolenic acid (C18:3), needs to be very low.

Shortenings are usually prepared by partially hydrogenating vegetable oil in the presence of Ni catalysts at high temperature and low hydrogen pressure. These partially hydrogenated fats are known to contain high *trans* fatty acid levels as a result of a competitive double bond geometric isomerization on the Ni catalyst [2]. Despite their desirable

**Electronic supplementary material** The online version of this article (doi:10.1007/s11746-011-1878-9) contains supplementary material, which is available to authorized users.

A. Philippaerts · A. Breesch · G. De Cremer · P. Jacobs · B. Sels (✉)
Department of M2S, K.U.Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Leuven, Belgium
e-mail: bert.sels@biw.kuleuven.be

P. Jacobs
e-mail: pierre.jacobs@biw.kuleuven.be

P. Kayaert · G. Van den Mooter
Laboratory Farmacotechnology and Biopharmacy, K.U.Leuven, Herestraat 49, 3000 Leuven, Belgium

J. Hofkens
Department of Chemistry, K.U.Leuven, Celestijnenlaan 200F, 3001 Heverlee, Leuven, Belgium

effect on the melting profiles, *trans* fatty acids are associated with negative health impact. For instance, *trans* fatty acids consumption raise levels of low-density lipoproteins (LDL) and lower the levels of high-density lipoproteins (HDL) in humans. Moreover, *trans* fatty acids are considered to induce a higher risk to cardiovascular diseases than saturated fatty acids [3, 4]. There is currently a consensus to avoid high *trans* fatty acid levels in food [5, 6].

Recently, many efforts have been made to develop alternative technologies to produce essentially *trans* free shortenings. Numerous hydrogenation technologies are available for the production of low-*trans* fat products, including (1) changes in the conventional hydrogenation process (at the level of both operating conditions and the nature of the nickel catalyst) [7, 8], (2) the use of metal catalysts other than nickel, like platinum [9, 10], and (3) the application of alternative hydrogenation processes, like catalytic transfer hydrogenation [11, 12], electrocatalytic hydrogenation [13–15] and hydrogenation in supercritical conditions [16–19]. However, up to now, no hydrogenation process is able to convert vegetable oils, like soybean oil, in one step into a thermally stable, low-*trans* shortening, with desirable melting and crystallization properties. Despite the somewhat lower *trans* levels reported in the aforementioned reports, these hydrogenation technologies show very low hydrogenation selectivity, leading to unacceptably high levels of trisaturates (SSS). As SSS is associated with undesirable melting and crystallization trajects, the fatty products are not suitable as shortening in the bakery industry.

Interesterification of a hard fat (fully hydrogenated oil, palm stearine) with a liquid vegetable oil, might replace conventional hydrogenation as it yields fatty products with desirable physical properties without *trans* fatty acids [20–23]. However, as interesterification does not affect the content of thermally unstable and oxygen sensitive polyunsaturated fatty acids (C18:3), common vegetable oils like soybean oil can not be used directly for the production of bakery shortening, unless they are first hydrogenated or fractionated. Moreover, in order to obtain the desirable plasticity, high levels of saturated fatty acids with varying chain length (e.g., C12:0, C14:0, C16:0 and C18:0) are required. Tropical oils, like palm oil, are mostly used for this purpose. As a consequence, high levels of cholesterol-raising saturated fatty acids like myristic (C14:0) and palmitic (C16:0) fatty acids are present in the shortening [24]. The multiple step synthesis of interesterification in comparison to hydrogenation is another disadvantage: a fast hydrogenation or fractionation step is first required, followed by blending and interesterification of the different oils, making the overall process time consuming and expensive. Therefore, a reliable and economically viable hydrogenation process avoiding *trans* fatty acid formation, would out-perform existing Ni-based hydrogenation technology and be competitive with state-of-the-art interesterification processes.

In this context, we recently reported the hydrogenation of model triacylglycerols over ZSM-5 zeolite supported Pt, viz. Pt/ZSM-5 [25] into fats containing very low *trans* fatty acids. Moreover, the Pt/ZSM-5 catalyst shows a preferred reduction of the central fatty acid chain resulting in low trisaturates (SSS) levels and a preferred stepwise reduction of polyunsaturated fatty acids to the mono-unsaturated level with reduced formation of saturated fatty acids. While the presence of Pt considerably reduces the amount of *trans* fatty acids, the microporous pore architecture of the zeolite appeared essential for a low SSS content and for the consecutive reduction of *trans* fatty acids due to their preferred hydrogenation over the bend *cis* fatty acid in the zeolite pores [26]. Moreover, in contrast to classical hydrogenation examples, these partially hydrogenated fats contain surprisingly high levels of oleic acid (C18:1*c*), a compound with a beneficial effect on human health, which is much more stable against oxidation than linoleic and linolenic fatty acids [27]. Finally, the saturated fat fraction consists mainly of stearic acid (C18:0), which is unique among saturated fatty acids in terms of its low impact on coronary heart disease risk in contrast to other saturated fatty acids [28].

The present contribution presents the one-step hydrogenation of soybean oil, including an extensive study of the physical properties of the Pt/ZSM-5 (Z) hardened fat to demonstrate its potential as a new generation of stable, highly nutritive shortenings for bakery and other related applications. Fat samples were analyzed for their fatty acid composition, solid fat content, melting and crystallization behavior, polymorphic forms and crystal morphology. Fat products such as commercial high-*trans* shortenings (prepared with a commercial Ni catalyst, CP), fat samples containing low *trans*, but high levels of trisaturates (prepared with a Pt/alumina catalyst, AL), and some recently reported interesterified shortenings were used as reference. The hydrogenated fat samples compared at two IV levels, with IV 90 and 65, are further denoted as CP90 and CP65, respectively, for hydrogenated fat samples obtained by the commercial Ni-catalyzed process; as AL90 and AL65 in case of hydrogenated fat samples obtained with a Pt/alumina catalyst, and as Z90 and Z65 in case of hydrogenated fat samples obtained with the Pt/ZSM-5 zeolite catalyst.

## Materials and Methods

### Materials

RBD soybean oil was kindly provided by Oleon (Belgium). The commercial Ni catalyst was PRICAT 9910 (22% Ni/

silicate coated with hardened vegetable oil, from Johnson Matthey). $NH_4$-ZSM-5 zeolite powder was from Zeolyst, having an Si/Al ratio of 138. $\gamma$-Alumina was purchased from Aldrich (Type 507C).

### Synthesis of Pt Catalysts

Pt/alumina catalyst was prepared by incipient wetness impregnation as described elsewhere [25]. 0.6 mL/g of a 40.7 mM aqueous solution of $Pt(NH_3)_4Cl_2$ with a volume equal to the total water sorption capacity of the in vacuo-dried alumina, was added dropwise to the dry powder. The catalyst was further dried overnight at 110 °C.

Pt/ZSM-5 catalyst was prepared by competitive ion-exchange under stirring for 48 h of the zeolite suspension, containing the required amount of Pt precursor ($Pt(NH_3)_4Cl_2$) and Na ions (NaCl) in a 200 mL aqueous solution per gram of dry zeolite (0.128 mM). The Na/Pt atomic ratio of the exchange solution was 25. Prior to metal loading, the zeolite was brought in the Na-form via two successive ion-exchange steps at room temperature for 16 h with 200 mL of a 1 M aqueous NaCl solution per gram of dry zeolite. After each exchange step, the slurry is filtered, and the solids are washed three times with distilled water and dried at 100 °C. All samples were loaded with 0.5 wt% of Pt.

Pt catalysts were activated by successive calcination and reduction at 350 and 500 °C, respectively. Prior to activation the dry powders were compressed, crushed and sieved. The 0.25–0.50 mm fraction was retained for further use. Calcination was conducted under flowing oxygen (120 mL/min/g), whereas reduction was done under flowing hydrogen (120 mL/min/g) applying heating rates of 0.3 °C/min and 0.4 °C/min, respectively. After calcination the catalyst was cooled to room temperature under flowing nitrogen before it was reduced. After reduction, the acid sites formed by reducing $Pt^{2+}$ to $Pt^0$, were neutralized under a flow of 5% dry ammonia in $N_2$. A full physico-chemical characterization of the catalysts can be found in an earlier publication [26].

### Hydrogenation

Hydrogenation of soybean oil was carried out in a 100-mL Parr-autoclave with sampling device. Hydrogenation reactions with the Pt catalysts, viz. Pt/ZSM-5 and Pt/alumina, were conducted at 65 °C and 60 bar $H_2$ pressure under constant stirring (500 rpm). To mimic the industrial process, hydrogenation reactions using the Ni catalyst were conducted at 180 °C and 1 bar of $H_2$ pressure under constant stirring (500 rpm). In a typical experiment, 40 g soybean oil and an amount of catalyst at a concentration of 0.2, 0.005 and 0.002 wt% (g metal/g oil) for the commercial Ni, Pt/ZSM-5 and Pt/alumina catalyst, respectively.

### Fatty Acid Composition

The fatty acid composition of the samples was determined by analyzing the corresponding fatty acid methyl esters (FAME) by gas chromatography. The triglycerides are first converted to FAME by methanolysis. In this reaction, a sample of 300 µL is dissolved in 3 mL diethylether and reacted with a solution of 3 mL 5% KOH in methanol. After 15 min the transesterification reaction is stopped through addition of 3 mL octane. The formed methyl esters migrate to the octane phase, which is subsequently washed three times with 3 mL distilled water in order to remove glycerol and $K^+$ soaps. The FAME were analyzed by a Hewlett Packard HP 6890 gas chromatograph with a split injection system (split ratio = 100:1) and $N_2$ as the carrier gas. A 60 m BPX-70 (SGE) highly polar capillary column with an internal diameter of 320 µm and a film thickness of 0.25 µm is used for separation. Initially, the column temperature is kept at 180 °C for 40 min, and then raised at 10 °C/min to 260 °C and held for 5 min. The FID detector used was kept at 280 °C. Heptadecane was used as external standard for quantification. FAME were identified based on retention times, using a FAME MIX C14-C22 reference from Supelco.

The degree of hydrogenation was also monitored by determining the iodine value (IV) of the products. Iodine values (g of iodine necessary for complexation with the double bonds present in 100 g of fat substrate) were calculated from the GC composition.

Stereospecific analysis of triglyceride molecules is carried out using a *sn*-1,3 specific pancreatic lipase according to the procedure of Luddy et al. [29]. A 50 mg fat sample was dissolved in 0.25 mL hexane and 1 mL of a 1 M aqueous tris(hydroxymethyl)-amino methane was added to obtain a pH of 7–8. Then 0.1 mL of a 22% aqueous $CaCl_2$ solution, 0.25 mL of 0.1% bail salts and 9 mg lipase (porcine pancreatic lipase type II) were added. The lipolysis reaction was carried out at 40 °C for 5 min under constant stirring. Afterwards the reaction was stopped by the addition of 5 mL ethanol. Extraction of the reaction products was carried out with diethylether. The ether extract was washed thoroughly by addition of distilled water. The *sn*-2 mono-acylglycerols are separated by means of TLC with chloroform/acetone/formic acid (85/15/1) as the mobile phase. Twenty dots of 40 µL were separated, and the mono-acylglycerol fraction was scraped off, dissolved in diethylether, converted to FAME by means of methanolysis and analyzed by GC as described above. Despite the intrinsic high specificity of the lipase used in the method, some acyl migration can not be avoided completely.

### Triacylglycerol Composition

Triacylglycerol (TAG) composition was determined by Reversed-Phase high performance liquid chromatography (RP-HPLC), using a Supelcosil TM LC-18 column (25 cm × 4.6 mm; 5 μm). The column temperature was kept at 40 °C. The mobile phase was a mixture of 70% (v/v) methanol and 30% (v/v) chloroform, and was used at a rate of 1.5 mL/min. 10 μL samples prepared at 0.07 g/mL concentration with chloroform as the solvent, were injected. Quantification of triacylglycerols was based on relative peak areas. Identification of triacylglycerols was carried out by comparison of retention time and equivalent carbon number (ECN) based on commercial standards. The compounds are separated by the chain length of their fatty acids as well as by their degree of unsaturation. Each double bond reduces the retention by the equivalent of two carbon atoms. This is reflected in the ECN, which is defined as CN—2*n*, in which CN is the sum of the carbon atoms in the fatty acid residues of a TAG molecule and *n* is the number of double bonds in a TAG molecule. Triacylglycerol molecules with identical ECN will co-elute.

### Slip Melting Point

The slip melting points (SMP) were determined according to AOCS Method Cc 3-25. An open capillary tube was dipped in the molten fat sample, so that the fat rises for about 10 mm in the tube. After overnight storage in a refrigerator, the sample tube was heated in a water bath at 0.5 °C/min and the temperature at which the solid fat column rises in the tube was determined. Each sample was measured in triplicate and the average was reported as the slip melting point.

### Differential Scanning Calorimetry

A differential scanning calorimeter (TA Instruments) was used to obtain melting and crystallization characteristics of the samples. About 5–10 mg of molten sample was accurately weighed and sealed in an alodined pan. An empty sealed alodined pan was used as a reference. The sample was heated rapidly to 80 °C for 10 min to ensure homogeneity and removal of residual crystal nuclei. The samples were further cooled to −60 °C at a rate of 10 °C/min, and held there for 5 min. Subsequently, the melting thermogram was recorded from −60 to 80 °C at a rate of 5 °C/min. All samples were analyzed in triplicate and average values were used. Crystallization and melting peaks were analyzed using TA Instruments Universal Analysis 2000 software.

### Polymorphism by X-Ray Diffraction Spectroscopy

The polymorphic forms of the fat samples were determined by X-ray diffraction using a X'Pert Pro diffractometer (PANalytical, Almelo, The Netherlands) configured for transmission measurements and equipped with a focusing mirror. Cu $K_\alpha$ radiation was used with $\lambda$ equal to 1.540598 Å, operating at 45 kV and 40 mA. A $2\theta$ scan from 4° to 40° at a step size of 0.0334° with a step time of 1,200 s was performed at ambient temperature on samples mounted between two Kapton foils. Data collection was controlled by X'Pert Data Collector software (version 2.2c) from PANalytical. Before the XRD analysis, the fat samples were preheated at 80 °C, allowed to crystallize at room temperature and stored in a dark at room temperature for 7 days. The obtained data were analyzed with X'Pert Data Viewer (version 1.2a).

### Solid Fat Content

The solid fat content (SFC) of the samples was measured by low-resolution NMR (Bruker Minispec) according to AOCS Official Method Cd 16b-93. Samples were previously conditioned at the desired temperature for 30 min. Measurements were made at 10, 20, 25, 30, 35, 40, 45 and 50 °C. Duplicate measurements were obtained.

### Crystal Morphology by Optical Microscopy

Optical microscopy images were taken using an Olympus FluoView FV-500 confocal laser scanning microscope, operated in transmission mode. The optical transmission images were generated by evaluating the transmission of a focused 488 nm laser beam, pixel by pixel, using a PMT detector. By scanning the laser position over the sample a complete transmission image was generated. An Olympus LUCPlanFLN air objective (20× magnification, 0.45 N.A.) with a long working distance was used. The sample consisted of a drop of fat sandwiched between two 170 μm thick cover glasses, mounted inside a Linkam THMS 600 heating stage, which allowed accurate control over the sample temperature. Before recording the images the fat was melted inside the heating stage at 60 °C. Transmission images were taken after slow (approx. 1 °C/min) or fast cooling (approx. 7 °C/min) to room temperature.

## Results and Discussion

### Fatty Acid Composition

The fatty acid composition of virgin soybean oil and the hydrogenated fat samples obtained by the three different procedures, viz. with Ni (CP), Pt/alumina (AL) and Pt/ZSM-5 (Z) are compared in Table 1. The starting soybean oil has high contents of unsaturated fatty acids, viz. 84.0%, with oleic acid (C18:1*c*, 55.4%) and linoleic acid (C18:2*c*, 22.4%) as main constituents, along with a considerable amount of linolenic acid (C18:3, 5.8%). In agreement with earlier reports [30, 31], the commercial hydrogenation process with Ni (CP) very selectively reduces the polyunsaturated fatty acid fraction into mono-unsaturates without a noticeable raise in saturated fatty acid (SFA) content. As an example, hardening the oil to IV 65 increases the mono-unsaturates from 22.4 to 61.2%, while the total SFA remains almost constant (15.9 vs. 18.0%). As expected, high contents of *trans* fatty acid (TFA) levels were present in the hydrogenated fat. For instance, 36.8 wt% of C18:1*tr* was found in the CP65 hardened fat product. Due to its negative health impact, the TFA fraction needs to be reduced essentially to zero.

The use of Pt supported on mesoporous alumina (AL) instead of Ni greatly diminishes the TFA content. In the hydrogenation conditions applied, only 0.8% C18:1*tr* was found in the AL65 fat product. Besides the low TFA levels, hydrogenation with Pt on alumina unfortunately proceeds with very low hydrogenation selectivity, i.e. high levels of saturates are formed at incomplete conversion of the oxidation-susceptible polyunsaturated fatty acids (PUFA). The AL65 sample for instance contains 48.9% saturates in addition to 1.6% linolenic acid.

The hydrogenated fat prepared by Pt, hosted in the micropores of ZSM-5 zeolite, not only shows very low TFA levels, but also very selective hydrogenation. A combination of very selective hydrogenation with low isomerization activity is unique in literature, as they usually have an inverse relationship. Sample Z65 with IV of 62.7 contains only 2.0% C18:1*tr* and almost no linolenic acid (0.2 wt%). Based on the fatty acid composition, Pt/ZSM-5 hydrogenated fats can be regarded as thermally stable, low-*trans* shortenings.

Table 1 also summarizes the fatty acid composition of some promising shortenings, obtained by interesterifying fully hydrogenated soybean oil (HSBO), rapeseed oil (RSO) and palm stearine (PS) blends [23]. Interestingly, a comparison of these compositional data with these of the zeolite (Z) samples at similar melting points clearly points to a higher nutritional value of the Pt/zeolite-hardened fat products. The following major differences are obvious and in favor of the partially hydrogenated soybean oil with respect to health aspects: (1) the yield of total saturates, viz. C16:0 and C18:0, is significantly lower (38.5 vs 50.5%) for the Pt/ZSM-5 hydrogenated fats; (2) the level of cholesterol-raising palmitate (C16:0) is much lower (12.7 vs 33.5%); (3) the susceptibility of the fat to oxidation as expressed by the content of C18:3, is substantially inferior (0.2 vs 4.0% C18:3), and (4) the content of physiologically desirable fatty acid chains, viz. C18:1*c* and C18:2*c*, shows enhanced values (58.1 vs 45.1%).

**Table 1** Fatty acid composition (wt%) and slip melting point (SMP, °C) of soybean oil, hydrogenated fat samples with IV 90 and 65, respectively, obtained according to the commercial process (Ni catalyst, 180 °C, 1 bar, Ni/lipid = 0.2 wt%) (CP90 and CP65), with Pt/alumina catalyst (65 °C, 60 bar, Pt/lipid = 0.002 wt%) (AL90 and AL65) and Pt/ZSM-5 catalyst (65 °C, 60 bar, Pt/lipid = 0.005 wt%) (Z90 and Z65) and interesterified fat blends of fully hydrogenated soybean oil (HSBO), rapeseed oil (RSO) and palm stearine (PS), mixed in different ratios (15:40:45 and 15:20:65), obtained via lipase-catalyzed interesterification

| Fatty acid | Soybean oil | Ni (CP) | | Pt/alumina | | Pt/ZSM-5 | | HSBO:RSO:PS[a] | |
|---|---|---|---|---|---|---|---|---|---|
| | | CP90 | CP65 | AL90 | AL65 | Z90 | Z65 | 15:40:45 | 15:20:65 |
| C16:0 | 12.1 | 13.0 | 12.8 | 12.7 | 13.0 | 12.5 | 12.7 | 33.5 | 44.6 |
| C18:0 | 3.5 | 4.6 | 8.9 | 22.8 | 35.6 | 16.3 | 25.4 | 15.7 | 16.2 |
| C18:1*c* | 22.4 | 41.8 | 38.9 | 26.4 | 27.9 | 36.5 | 48.2 | 33.4 | 27.5 |
| C18:1*tr* | 0.0 | 19.4 | 36.8 | 0.5 | 0.8 | 0.9 | 2.0 | / | / |
| C18:2*c* | 55.4 | 16.6 | 0.7 | 34.0 | 20.3 | 30.9 | 9.9 | 11.7 | 8.0 |
| C18:2*tr* | 0.4 | 4.0 | 1.5 | 0.4 | 0.5 | 1.0 | 1.2 | / | / |
| C18:3*c* | 5.8 | 0.2 | 0.0 | 3.1 | 1.6 | 1.7 | 0.2 | 4.0 | 1.9 |
| C20:0 | 0.3 | 0.4 | 0.4 | 0.2 | 0.3 | 0.4 | 0.4 | 0.5 | 0.4 |
| ∑SFA[b] | 15.9 | 18.0 | 22.1 | 35.7 | 48.9 | 29.2 | 38.5 | 50.5 | 62.3 |
| ∑TFA[c] | 0.4 | 23.4 | 38.3 | 0.9 | 1.3 | 1.9 | 3.2 | / | / |
| IV | 131.7 | 88.7 | 68.7 | 90.5 | 64.6 | 91.3 | 62.7 | 59.7 | 42.6 |
| SMP (°C) | | <20 | 34.4 | 53.5 | 57.4 | 42.9 | 44.3 | 42.3 | 45.5 |

[a] After ref [23]

[b] Saturated fatty acids

[c] *Trans* fatty acids

Table 2 presents the positional fatty acid composition for the starting soybean oil and some samples hydrogenated at IV 105. The saturated fatty acids are mainly located at *sn*-1,3 in the virgin soybean oil. After partial hydrogenation, the cholesterol-raising palmitate (C16:0) remains exclusively located at *sn*-1,3 positions (as in the virgin soybean oil), where it is less absorbed by the human organism [32]. The palmitate content at *sn*-2 is thus very low, viz. ~2.5%, in all hydrogenated fat samples regardless of the IV, while high contents, viz. up to 58.3%, due to fatty acid randomization were encountered in interesterified shortenings [23]. Hydrogenated fat products are thus favorable for food applications, provided *trans* fatty acid values are very low. After hydrogenation, an unprecedented influence of the catalyst support on the hydrogenation regioselectivity along the glycerol backbone was also noticed. Pt on alumina, viz. AL105, shows a significantly higher saturation level at the *sn*-1,3 position than Pt on zeolite, viz. Z105 (36.1 vs 29.8%), suggesting that the latter catalyst more preferably hydrogenates unsaturates at the *sn*-2 position.

## Triacylglycerol Composition

Triacylglycerol(s) (TAG) compositions of hydrogenated fat samples are collected in Table 3 in terms of their equivalent carbon number (ECN). Common TAG with ECN number are given in Table 4. Virgin soybean oil contains mainly ECN 42 (mainly LLL and OLLn), 44 (mainly OLL and PLL) and 46 (mainly PLO and OOL). ECN 46 and 48 (mainly OOO) are the main constituents of the CP fat samples suggesting that the industrial process using Ni hydrogenates in a selective way. Indeed, as both samples, CP90 and CP65, show very low levels of TAG with low and high ECN, poly-unsaturates such as LLL (ECN 42) have been selectively converted into TAG of the middle-melting range mainly containing OOO and mono-saturates, viz. SUU and USU (ECN 46 and 48), without forming large amounts of di- and trisaturates, viz. SSU, SUS and SSS (ECN 50, 52 and 54). As an example, less than 1% SSS (ECN 54) is present in highly hydrogenated fat samples, viz. CP65.

Totally different TAG compositions at the same IVs are found with Pt/alumina. The AL fat samples, AL90 and AL65, show very high levels of undesired SSS (ECN 54) along with low ECN values, corresponding to considerable levels of poly-unsaturated TAG. AL65 for instance contains 16% ECN 54 (SSS) and 7% ECN 42 (mainly LLL). Such TAG analysis corresponds to unselective hydrogenation, i.e. without differentiation in double bond reactivity neither due to their position on the glycerol backbone nor in degree of unsaturation. Unfortunately, high SSS and poly-unsaturation levels are unwanted in most food

**Table 2** *Sn*-2 and *sn*-1,3 positional fatty acid composition (wt%) of soybean oil, soybean oil hydrogenated with Pt/alumina (AL105) and with Pt/ZSM-5 (Z105)

| Fatty acid | Soybean oil | | AL105 | | Z105 | |
|---|---|---|---|---|---|---|
| | *sn*-2 | *sn*-1/3 | *sn*-2 | *sn*-1/3 | *sn*-2 | *sn*-1/3 |
| C16:0 | 1.9 | 16.9 | 2.4 | 17.3 | 2.5 | 17.7 |
| C18:0 | 1.5 | 4.5 | 8.1 | 18.8 | 9.4 | 12.1 |
| C18:1c | 21.1 | 22.8 | 29.1 | 25.2 | 32.9 | 29.2 |
| C18:1tr | 0.0 | 0.0 | 0.6 | 0.5 | 0.6 | 0.7 |
| C18:2c | 70.1 | 48.6 | 56.2 | 33.4 | 51.6 | 35.4 |
| C18:2tr | 0.5 | 0.3 | 0.5 | 0.4 | 0.6 | 0.6 |
| C18:3c | 4.9 | 6.4 | 3.1 | 3.8 | 2.4 | 3.5 |
| ∑SFA | 3.4 | 21.4 | 10.5 | 36.1 | 11.9 | 29.8 |
| ∑TFA | 0.5 | 0.3 | 1.1 | 0.9 | 1.2 | 1.3 |
| IV | 152.8 | 120.8 | 131.5 | 90.3 | 125.1 | 96.3 |

**Table 3** Triacylglycerol composition according to ECN

| ECN | 40 | 42 | 44 | 46 | 48 | 50 | 52 | 54 |
|---|---|---|---|---|---|---|---|---|
| Soybean oil | 7.0 | 25.2 | 32.6 | 23.0 | 10.2 | 2.12 | 0.0 | 0.0 |
| CP90 | 0.0 | 1.7 | 10.7 | 33.6 | 45.0 | 7.3 | 1.3 | 0.5 |
| CP65 | 0.0 | 0.0 | 0.0 | 7.4 | 70.4 | 18.8 | 2.6 | 0.9 |
| Al90 | 3.4 | 14.1 | 20.5 | 18.2 | 15.5 | 9.8 | 9.5 | 9.0 |
| Al65 | 1.5 | 7.0 | 12.1 | 13.9 | 18.0 | 15.2 | 16.3 | 16.0 |
| Z90 | 0.8 | 6.8 | 19.1 | 28.2 | 24.9 | 11.1 | 5.2 | 3.9 |
| Z65 | 0.0 | 0.0 | 3.1 | 15.8 | 38.4 | 26.5 | 11.0 | 5.0 |

**Table 4** Common triglycerides and their Equivalent Carbon Number (ECN)

| ECN | TAGs[a] |
|---|---|
| 40 | PLnLn, OLnLn, LLLn |
| 42 | LLL, OLLn, SLnLn, PLLn |
| 44 | OLL, OOLn, SLLn, PLL, POLn, PPLn |
| 46 | SLL, OOL, SOLn, POL, PSLn, PPL |
| 48 | OOO, SOL, PPP, PPO, POO, SSLn, PSL |
| 50 | OSO, SSL, PPS, PSO |
| 52 | OSS, PSS |
| 54 | SSS |

[a] *P* palmitate (C16:0), *S* stearate (C18:0), *O* oleate (C18:1; *cis* 9), *L* linoleate (C18:2; *cis* 9,12), *Ln* linolenate (C18:3; *cis* 9,12,15)

For all positional isomers (e.g. OSO and OOS) only a single combination of fatty acid chains is presented

applications because of undesirable melting- and crystallization properties (vide infra) and oxidative (thermal) instability. Despite of the extremely low *trans* fatty acid content, AL samples are thus not good candidates to replace current shortenings.

Although the same hydrogenation conditions were applied, Pt/zeolite samples, viz. Z90 and Z65, show a markedly different TAG composition, very unusual for a hydrogenation process conducted at this high hydrogen pressure and low temperature. At similar IVs, they span a much larger range of middle ECN values, roughly from ECN 44 to 50. For instance, the ECN range corresponds to 84.0% in case of fat sample Z65. These TAG compositional data can be easily explained taking into account the aforementioned unique regioselective hydrogenation property of Pt/zeolite. Because of the higher double bond reactivity of the central (*sn*-2) fatty acid, partially hydrogenated fat products are enriched in USU levels, corresponding to e.g. LOL (ECN 44), LSL (ECN 46), OSL (ECN 48), and OSO (ECN 50). More fundamental support for the unique hydrogenation selectivity of Pt/zeolite has been reported elsewhere [25].

## Slip Melting Points

Table 1 shows slip melting points of hydrogenated samples and two shortenings. As expected, SMPs increase with decreasing IV for all hardened fat products. However, SMP of commercially prepared fat samples, viz. CP90 and CP65, are too low (<20 and 34.4 °C, respectively) for shortenings, generally requiring melting points above 38 °C [19, 20]. The low SMPs are in accordance with the high levels of low-melting TAG such as OOO (see Tables 3, 4).

In contrast, SMP of AL90 and AL65, viz. 53.5 and 57.4 °C, respectively, are high due to the presence of high SSS contents (ECN 54 in Table 3).

SMPs of Z90 and Z65 show intermediate values, viz. 42.9 and 44.3 °C, respectively.

In summary, as their intermediate SMPs are in fair agreement with interesterified shortenings (Table 1) and with commercial shortenings obtained with hydrogenated soybean oil [22], hardened fat products obtained with Pt/zeolite appear potential candidates for shortening applications.

## Melting and Crystallization Characteristics

The melting and cooling curves of the partially hydrogenated fat samples, viz. CP, AL and Z, at IV 90 and 65 were determined with differential scanning calorimetry (DSC). The melting curves of all samples (Fig. 1) show discrete endotherms. As expected, the melting profiles shift to higher temperature with decreasing IV due to the formation of high-melting TAG upon hydrogenation. In a broad melting range, stretching from about −15 to 40 °C, fats obtained with the commercial process, viz. CP90 and CP65, show sharp minima at −8 (with a broad envelope at higher temperature) and 29 °C (with a broad shoulder at lower temperature), respectively. Such profiles underscore the high selectivity of hydrogenation with Ni; indeed, no peaks of remaining LLL or formed SSS expected at around −20 and 60 °C, respectively, are observed in the melting curves.

The melting curves of Pt/alumina fat products show several endothermic peaks. A distinct endotherm of a low-melting fraction around −28 °C for AL90, corresponding to the presence of LLL, disappears when the fat is more saturated (AL65). Meanwhile, the sharp peak at around 59 °C, reflecting the presence of high-melting SSS, increases in intensity while shifting towards a slightly higher temperature. These melting characteristics are in agreement with the overall fatty acid and TAG compositional data, supporting the unselective hydrogenation property of Pt/alumina (*vide supra*).

The melting curves of Pt/zeolite fat samples, viz. Z90 and Z65, show less intense minima at the high and low temperature extremes, while more discrete peaks are present in the middle temperature range (approx. −20 to 47 °C for Z90; approx. −10 to 47 °C for Z65), indicating a softer fat product. The end-melting points around 45 °C are ideal for application as bakery fats for cakes and doughnuts. The absence of high and low-melting peaks indicates that low-melting TAG, viz. LLL, have been replaced by medium-melting TAG, without forming high-melting TAG such as SSS. Thus, these melting profiles support the unusual TAG composition for a one-step hydrogenation process, as explained earlier in this contribution taking into account the unique regioselectivity of the Pt/zeolite hydrogenation. Literature survey reveals similar melting

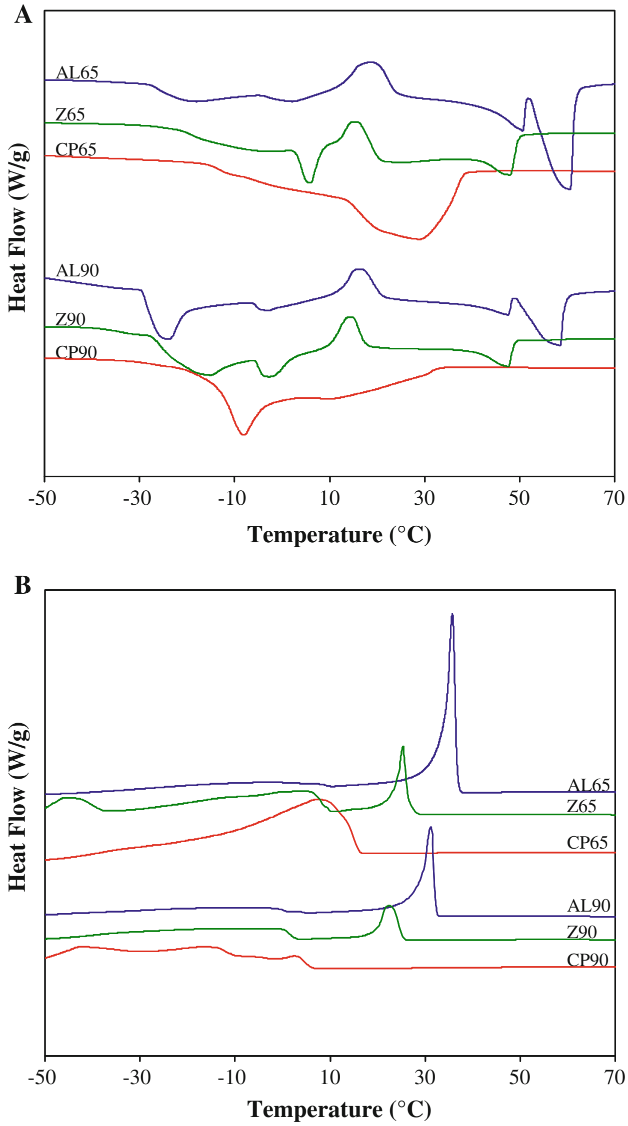

**Fig. 1** DSC melting (**a**) and crystallization (**b**) curves for fats from soybean oil hydrogenated till IV 90 and 65 with the industrial Ni catalyst (CP90 and CP65), Pt/alumina catalyst (AL90 and AL65) and Pt/ZSM-5 catalyst (Z90 and Z65) (exothermic heat flow upwards)

profiles for interesterified fats from fully hydrogenated soybean, rapeseed and palm oil, which are claimed to be very interesting shortenings [23].

The corresponding crystallization thermograms are presented in Fig. 1. The cooling curves of the commercially hydrogenated samples, viz. CP90 and CP65, show no obvious sharp exotherm. A broad crystallization envelope is observed in the range from −40 to 5 °C and from −10 to 15 °C for CP90 and CP65, respectively.

Samples hydrogenated with Pt/alumina, viz. Al90 and AL65, exhibit one sharp exothermic peak in the thermogram, indicative of an instantaneous nucleation and related to the presence of high amounts of SSS. As expected, the crystallization peak clearly shifts to higher temperatures (from 30 to 37 °C), increasing in intensity with decreasing IV, i.e. with increasing amount of saturates.

The crystallization behavior of the fat products from Pt/zeolite was different. The sharp exotherm at high temperature is accompanied with a broad feature in the lower temperature range. For instance, Z65 has a broad crystallization characteristic in the range of −10 to 10 °C, and a distinct larger exotherm at 26 °C. The thermogram indicates that most TAG crystallize at medium temperature, while only a small fraction starts crystallization at low temperature. Such dual crystallization behavior is also observed for many shortenings [22, 23]. The lower temperature of the high-end crystallization peak suggests less SSS in the fat product, in agreement with the TAG composition (vide supra). Also for the Z samples, crystallization features shift to higher temperatures (and increase in intensity) with increasing degree of hydrogenation.

## Polymorphism

As fats are able to crystallize in different molecular packings [33], they exhibit polymorphism, which is easily investigated by X-ray diffraction (XRD) in the $2\theta$ range of 12°–30°. The most important polymorphic forms are $\alpha$ with hexagonal packing, $\beta'$ with orthorhombic packing, and $\beta$ with triclinic packing. The $\alpha$ polymorph has a single short spacing at ca. 4.15 Å. The $\beta'$ phase usually shows two strong spacings at ca. 3.80 and 4.20 Å or three short reflections at ca. 4.34, 3.97 and 3.71 Å. A very strong short spacing at ca. 4.60 Å is characteristic of the $\beta$ polymorph [34]. Differences in polymorphism greatly affect the physical properties. Polymorph $\alpha$ typically shows the lowest melting point, while it easily transforms into metastable $\beta'$, which melts at intermediate temperatures. A high melting feature is characteristic of the $\beta$ polymorph. For most fat applications $\beta'$ crystals give rise to fats with a smooth texture and excellent plasticity at higher temperature, while undesired grittiness and crumbliness occurs when large, needle-like $\beta$ crystals are dominant [34, 35].

The reflection patterns with short spacings and polymorphism of the three types of partially hydrogenated soybean oil (with IV of 65), viz. CP65, AL65 and Z65, are illustrated in Fig. 2. The commercially produced fat sample, CP65, shows four distinct short spacings, namely at 4.37, 4.24, 4.07 and 3.85 Å, indicative of solids consisting of $\beta'$ crystals.

The Pt/alumina fat sample, AL65, has a very intense reflection at 4.59 Å, as well as some weaker short spacings at 3.87 and 3.73 Å. Such reflection pattern is typical of the dominant presence of $\beta$ crystals. Due to the unselective hydrogenation process with Pt/alumina, AL65 contains high levels of $\beta$ promoting TAG such as SSS (with ECN of

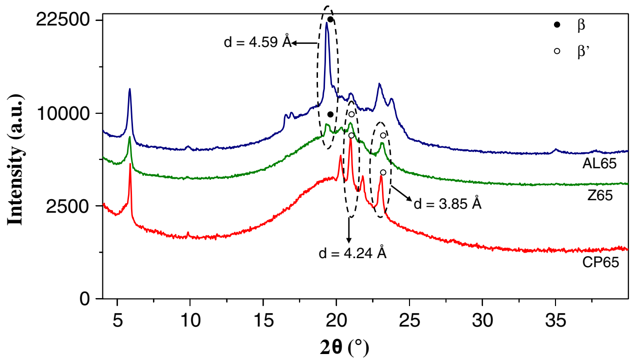

**Fig. 2** XRD of partially hydrogenated soybean oil with IV of 65 using Ni (CP65), Pt/alumina (AL90) and Pt/ZSM-5 (Z90) as catalyst

54). For many fat applications, such *β* crystal formation needs to be avoided in the fat product. The sharp *β* reflection is clearly much less apparent in the diffractogram of the Pt/zeolite sample, Z65. Instead, other intense spacing peaks coexist at 4.36, 4.23 and 3.85 Å, indicative of *β′* polymorphs. As the *β′* form is more favorable for bakery applications, the polymorphism in Pt/zeolite hardened fat is suitable for bakery fats such as shortenings.

## Crystal and Network Morphology

High plasticity, being essential for shortenings, involves two major properties of the microstructure of the solid fat: a proper proportion of solid and liquid phases, and a sufficiently fine dispersion of the solid phase in a loosely packed structure. Optical microscopy was therefore used to study in more detail the crystal and network morphology of the solids in the liquid phase. The faster cooling rates obviously lead to smaller crystals and a denser crystal network, compared to slow cooling rates (Fig. 3). The main differences in crystal and network morphology are evident in both sets of images.

Images of partially hydrogenated fat samples Z and AL at two different IVs, viz. 65 and 90, are presented in Fig. 3. As expected, less liquid phase exists between the solid networks with decreasing IV. Pt/alumina samples display considerable amounts of needle-shaped like crystals, while spherulitic-like crystals are obvious for the crystallized Pt/zeolite fat samples at room temperature. In addition, the crystals in Pt/alumina samples, in particular obvious in AL65, display more compact network structures with little space between adjacent crystals, while the network morphology of Pt/zeolite samples, viz. Z65 and Z90, exhibits a more open dendritic structure. The latter organization of solid–liquid phases is a prerequisite for high plasticity.

Movies of the crystallization process of the four different hydrogenated soybean oil samples, viz. AL90, AL65, Z90 and Z65 are available in the supplementary information. The samples were cooled (~7 °C/min) till the crystallization temperature (38 °C for AL90, 43 °C for AL65, 31 °C for Z90 and 34 °C for Z65). The individual images

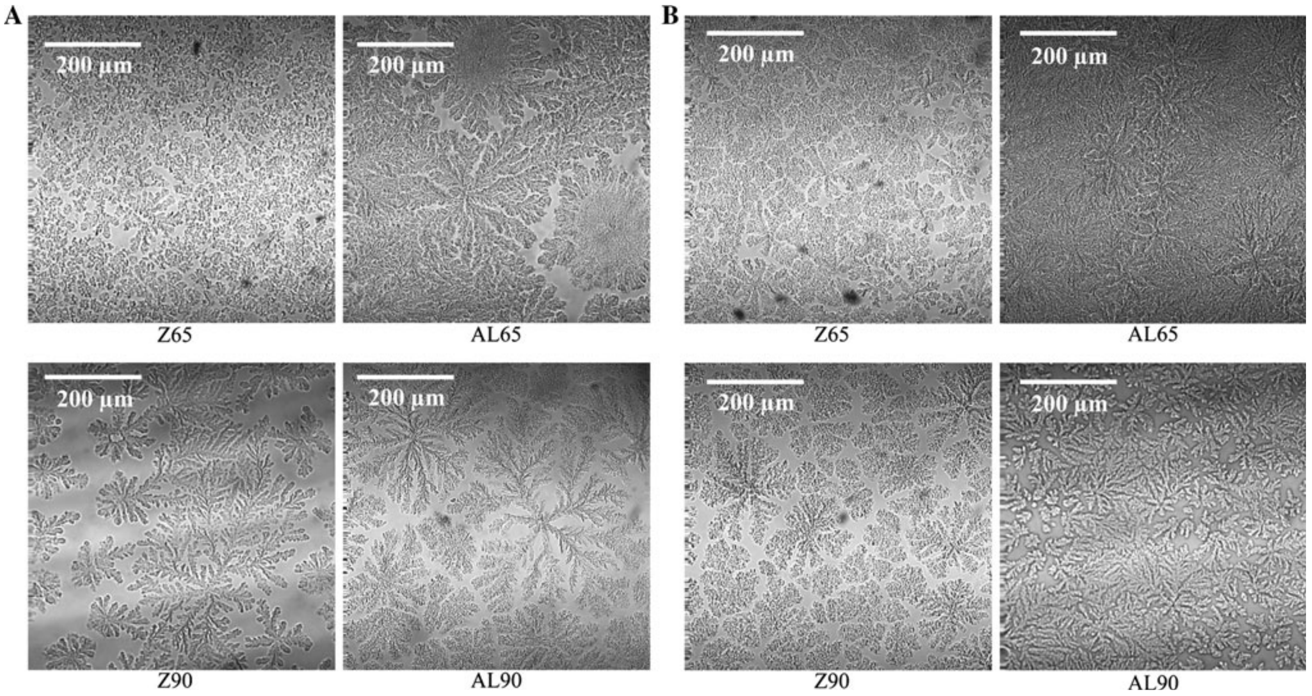

**Fig. 3** Microscopy images of partially hydrogenated fats after slow cooling (1 °C/min from 60 °C to room temperature) (**a**) and after fast cooling (7 °C/min from 60 °C to room temperature) (**b**)

were taken after 0.5, 1, 2, 3, 5, 7, 10, 15, 20 and 30 min at the crystallization temperature. These images clearly show that during the crystallization period, crystal growth takes place mainly by the addition of crystallized material on the crystals. However also the formation of new crystals in between the existing crystals can be observed. The crystallization process of sample AL65 clearly leads to large, dense crystals, owing to the high SSS level, whereas the other samples crystallize in a more branched crystal network with more liquid oil between the crystal aggregates.

In summary, the microscopic observations are in accordance with the composition of the respective fats and their polymorphism. Since Pt/ZSM-5 fat samples contain low levels of SSS, they have lower tendency to crystallize in the $\beta$-phase compared to the Pt/alumina samples and show a more open network structure. As a result, hydrogenated Pt/zeolite fat products are interesting candidates for shortenings with high plasticity.

## Solid Fat Content (SFC)

The plasticity or melting range of fats can also be studied by SFC. The SFC curves show the percentage of solid fat at the various temperatures in the range 10–60 °C, and the values provide an additional understanding of the melting properties of solid fat products. Solid fat contents (SFC) of the different hydrogenated samples, viz. CP, AL and Z, at IV 90 and 65 were determined at several temperatures, and they were compared with some commercial shortenings and interesterified shortenings. The data are summarized in Table 5.

As expected, more solids are observed over the whole temperature region for the higher degree of hydrogenation. For instance, CP90 exhibits 16.0 and 0.6% solids at 10 and 30 °C, respectively, and they were increased to 62.5 and 10.2% for the more hydrogenated CP65 fat. Of all samples measured, CP65 shows the highest solid content in the lower temperature range, for instance more than 60% being solid at 10 °C. The commercial Ni CP samples contain very low solid fat contents at the higher temperatures. At 40 °C only 0.1 and 0.5% of solids were observed for CP90 and CP65, respectively. The SFC contents are in agreement with the low content of high-melting TAG in the CP samples.

Shortenings obtained by interesterifying fully hydrogenated soybean oil, rapeseed oil and palm stearin show high SFC values at lower temperature range, similar to the CP samples.

Pt/alumina samples generally have slightly lower solid contents at lower temperature, but considerably higher contents in the high temperature region. For instance, 16.1% of the lipids were solid at 50 °C for AL65, while only 0.1% was measured for CP65 at the same temperature. As presented before, the TAG composition of AL65 contains a lot of high-melting compounds such as SSS, crystallized in stable $\beta$ phase, which remain solid at the temperature applied. These AL fats are thus not interesting for shortening applications, since SFC at 35 °C should be below 10% in order to show complete melting in the mouth without leaving a waxy coating on the palate [21].

Replacement of the Pt/alumina catalyst by the Pt/ZSM-5 in the hydrogenation experiment of virgin soybean results in a decrease of the corresponding SFC curves at all temperatures, and a significant reduction of high-melting fats. For instance, the solid content at 20 °C is 27.6 and 46.4%

**Table 5** Solid Fat Content (SFC) of hydrogenated soybean oil hydrogenated (IV of 90 and 65) with an industrial Ni catalyst (CP90 and CP65), Pt/ZSM-5 (Z90 and Z65), Pt/alumina (AL90 and AL65), and of commercial shortenings obtained via classic hydrogenation and via an interesterified mixture of fully hydrogenated soybean oil (HSBO), rapeseed oil (RSO), and palm stearine (PS) (after ref. [23]) at comparable melting points

| Sample | Trans (wt%) | T (°C) | | | | | | | | | | | Ref |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 21.1 | 25 | 26.7 | 30 | 33.3 | 35 | 40 | 45 | 50 | |
| CP90 | 23.4 | 16.0 | 4.5 | | 1.9 | | 0.6 | | 0.2 | 0.1 | 0.3 | 0.3 | |
| Z90 | 1.9 | 20.5 | 13.6 | | 11.0 | | 9.1 | | 7.2 | 5.5 | 4.2 | 2.2 | |
| AL90 | 0.9 | 32.5 | 26.9 | | 24.2 | | 20.7 | | 17.4 | 14.3 | 10.8 | 7.2 | |
| CP65 | 38.3 | 62.5 | 34.9 | | 21.5 | | 10.2 | | 2.6 | 0.5 | 0.5 | 0.1 | |
| Z65 | 3.2 | 42.2 | 27.6 | | 22.0 | | 16.5 | | 12.5 | 8.6 | 5.2 | 2.8 | |
| AL65 | 1.3 | 55.3 | 46.4 | | 42.6 | | 36.8 | | 32.6 | 25.7 | 21.1 | 16.1 | |
| Shortening | 12–25 | 23–37 | | 16–23 | | 13–27 | | 9–16 | | 3–9 | | | [36] |
| Solid frying shortening | 11.3 | 33 | 22 | | 19 | | 17 | | 12 | | 9 | 0 | [22] |
| Crisco | 10.6 | 21.4 | | 15.6 | | 14.5 | | 11.5 | | 6.2 | | | [36] |
| 15/20/65[a] | | 62.9 | 42.0 | | | | 26.3 | | | 11.6 | | | [23] |
| 15/40/45[a] | | 51.1 | 29.6 | | | | 14.2 | | | 5.9 | | | [23] |

[a] Respective HSBO/RSO/PS ratios

for Z65 and AL65, respectively, while the value considerably reduces to 8.6% for Z65 at 40 °C, but the amount of solids is still high in the AL65 sample (25.7%). In addition, the SFC curves of Pt/zeolite samples, viz. Z65 and Z90, show gradual slopes over a wide temperature range from 10 to 40 °C, indicating that these fats could be used as bakery shortenings. To further strengthen this statement, SFC curves of three commercially available shortenings, containing high *trans* fatty acids contents [22, 36], and two interesterified fat products [23] were included for comparison in Table 5. Clearly, SFC properties of the Pt/ZSM-5 hydrogenated fat sample, viz. Z65, excellently agrees with that of the commercial samples, with the advantage that it contains significantly lower *trans* fatty acids amounts (3% for Z65 vs 11–25% for the commercial shortenings). Moreover, the SFC of Z65 in the temperature region from 10 to 40 °C is flatter than interesterified shortenings. The conclusion that partial hydrogenation of soybean with Pt/ZSM-5 catalyst produces low-*trans* fats suitable for various shortening bakery applications is thus valid.

## Conclusion

A single hydrogenation process of soybean oil at low temperature and high hydrogen pressure, using Pt hosted in a microporous ZSM-5 zeolite, results in thermally stable, highly nutritive and healthy, plastic fat products, suitable for shortening applications. Hydrogenation with Pt/zeolite proceeds fairly selectively, resulting in fast conversion of polyunsaturates. Low contents of e.g. C18:3*c* therefore agrees with the high thermal (oxidative) stability of the fat products. Pt on alumina does not hydrogenate selectively, leading to thermally unstable fat products. In addition, hydrogenation with Pt/zeolite occurs in a regioselective way, i.e. double bonds at the *sn*-1,3 position are less reactive, resulting in a unique mixture of intermediately melting TAG without formation of large amounts of SSS. As a result of the latter, low contents of $\beta$ crystal phases appear in the solid, with absence of pronounced high-melting characteristics. Moreover, the unique mixture of TAG enriched in e.g., LOL, LSL, LSO and OSO, provides an almost horizontal slope in the solid fat curve, indicative of its high plasticity. The fat crystals mainly constitute an orthorhombic molecular packing ($\beta'$ phase), spherulitic in shape, macroscopically arranged in open dendritic-like solid networks, also in accordance with the high plastic properties. Partial hydrogenation with Pt on alumina does not proceed in a regioselective way, resulting in large amounts of high-melting $\beta$ phase-promoting SSS. Thus, according to the various physical properties, fat solids obtained by hydrogenation of soybean oil with Pt/zeolite, in contrast to Pt/alumina, are interesting candidates for shortening applications. In addition to the physical characteristics, various nutritional and health aspects also suggest replacement of current hydrogenation shortenings and interesterified shortenings by fat samples obtained with Pt/zeolite. The latter solid fat contains (1) high levels of oleic (C18:1*c*) and linoleic acid (C18:2*c*); (2) very low levels of *trans* fatty acids; and (3) low levels of cholesterol-raising fatty acids such as myristic (C14:0) and palmitic acid (C16:0).

**Acknowledgments** A.P. acknowledges the F.W.O.-Vlaanderen (Research Foundation—Flanders) for a doctoral fellowship and P.K. the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT—Vlaanderen) for a Ph.D. grant. The authors acknowledge the Flemish government for a long term sponsoring (Methusalem, CASAS). We are grateful to Vandemoortele (Izegem, Belgium) for measuring the solid fat content of the hydrogenated fat samples.

## References

1. Ghotra BS, Dyal SD, Narine SS (2002) Lipid shortenings: a review. Food Res Int 35:1015–1048
2. Albright LF (1963) Mechanism of hydrogenation of triglycerides. J Am Oil Chem Soc 40:16
3. Clifton PM, Keogh JB, Noakes M (2004) Trans fatty acids in adipose tissue and the food supply are associated with myocardial infarction. J Nutr 134:1848
4. Mozaffarian D, Katan MB, Ascherio A, Stampfer MJ, Willett WC (2006) Medical progress—*trans* fatty acids and cardiovascular disease. New Engl J Med 354:1601–1613
5. US Department of Health and Human Services FaDA, 21 CFR Part 101 [Docket No. 94P-0036], Food labeling: *trans* fatty acids in nutrition labeling, nutrient content claims and health claims, Washington, 2003, p. 254
6. EFSA (2004) Opinion on the scientific panel on dietetic products, nutrition and allergies on the request from the commission related to the presence of trans fatty acids in foods and the effect on human health of the consumption of trans fatty acids (Request No.° EFSA-Q-2003-022). EFSA J 81:1–49
7. Patterson HBW (1994) Hydrogenation of fats and oils: theory and practice. AOCS Press, Illinois
8. Cizmeci M, Musavi A, Kayahan M, Tekin A (2005) Monitoring of hydrogenation with various catalyst ratios. J Am Oil Chem Soc 82:925–929
9. Berben PH, Borninkhof F, Reesink B, Kuijpers E (1994) Production of low trans-isomer-containing products by hydrogenation. Inform 5:516
10. Beers A, Mangnus G (2004) Hydrogenation of edible oils for reduced trans-fatty acid content. Inform 15:404–405
11. Smidovnik A, Kobe J, Leskovsek S, Koloini T (1994) Kinetics of catalytic transfer hydrogenation of soybean oil. J Am Oil Chem Soc 71:507–511
12. Ju JW, So WS, Kim JH, Bae BJ, Choi EN, Kwon YH, Chung IM, Yoon SH, Jung MY (2003) Effects of alcohol type and amounts on conjugated linoleic acid formation during catalytic transfer hydrogenation of soybean oil. J Food Sci 68:1915–1922
13. Yusem GJ, Pintauro PN (1992) The electrocatalytic hydrogenation of soybean oil. J Am Oil Chem Soc 69:399–404

14. An WD, Hong JK, Pintauro PN, Warner K, Neff W (1998) The electrochemical hydrogenation of edible oils in a solid polymer electrolyte reactor. I. Reactor design and operation. J Am Oil Chem Soc 75:917–925
15. Mondal K, Lalvani SB (2003) Mediator-assisted electrochemical hydrogenation of soybean oil. Chem Eng Sci 58:2643–2656
16. King JW, Holliday RL, List GR, Snyder JM (2001) Hydrogenation of vegetable oils using mixtures of supercritical carbon dioxide and hydrogen. J Am Oil Chem Soc 78:107–113
17. Ramirez E, Recasens F, Fernandez M, Larrayoz MA (2004) Sunflower oil hydrogenation on Pd/C in SC propane in a continuous recycle reactor. AIChe J 50:1545–1555
18. Santana A, Larrayoz MA, Ramirez E, Nistal J, Recasens F (2007) Sunflower oil hydrogenation on Pd in supercritical solvents: Kinetics and selectivities. J Supercrit Fluids 41:391–403
19. Piqueras CA, Tonetto G, Bottini S, Damiani DE (2008) Sunflower oil hydrogenation on Pt catalysts: comparison between conventional process and homogeneous phase operation using supercritical propane. Catal Today 133:836–841
20. Khatoon S, Reddy SRY (2005) Plastic fats with zero trans fatty acids by interesterification of mango, mahua and palm oils. Eur J Lipid Sci Technol 107:786–791
21. Siew WL, Cheah KY, Tang WL (2007) Physical properties of lipase-catalyzed interesterification of palm stearin with canola oil blends. Eur J Lipid Sci Technol 109:97–106
22. Chu BS, Ghazali HM, Lai OM, Man YBC, Yusof S, Tee SB, Yusoff MSA (2001) Comparison of lipase-transesterified blend with some commercial solid frying shortenings in Malaysia. J Am Oil Chem Soc 78:1213–1219
23. Lee JH, Akoh CC, Lee KT (2008) Physical properties of trans-free bakery shortening produced by lipase-catalyzed interesterification. J Am Oil Chem Soc 85:1–11
24. Katan MB, Zock PL, Mensink RP (1994) Effects of fats and fatty-acids on blood-lipids in humans - an overview. Am J Clin Nutr 60:S1017–S1022
25. Philippaerts A, Paulussen S, Beersch A, Turner S, Lebedev OI, Van Tendeloo G, Sels B, Jacobs P (2011) Unprecedented shape selectivity in hydrogenation of triacylglycerol molecules with Pt/ZSM-5 zeolite. Angew Chem Int Ed 50:3947–3949
26. Philippaerts A, Paulussen S, Turner S, Lebedev OI, Van Tendeloo G, Poelman H, Bulut M, De Clippel F, Smeets P, Sels B, Jacobs P (2010) Selectivity in sorption and hydrogenation of methyl oleate and elaidate on MFI zeolites. J Catal 270:172–184
27. Kris-Etherton PM, Pearson TA, Wan Y, Hargrove RL, Moriarty K, Fishell V, Etherton T (1999) High-monounsaturated fatty acid diets lower both plasma cholesterol and triacylglycerol concentrations. Am J Clin Nutr 70:1009–1015
28. Kelly FD, Sinclair AJ, Mann NJ, Turner AH, Abedin L, Li D (2001) A stearic acid-rich diet improves thrombogenic and atherogenic risk factor profiles in healthy males. Eur J Clin Nutr 55:88–96
29. Luddy FE, Magidman P, Herb SF, Riemenschneider RW, Barford RA (1964) Pancreatic lipase hydrolysis of triglycerides by semimicro technique. J Am Oil Chem Soc 41:693
30. Hastert RC (1996) Hydrogenation. In: Hui YH (ed) Bailey's Industrial Oil & Fat Products. Wiley, New York, p 679
31. Chu YH, Lin LH (1991) An evaluation of commercial nickel-catalysts during hydrogenation of soybean oil. J Am Oil Chem Soc 68:680–683
32. Linderborg KM, Kallio HPT (2005) Triacylglycerol fatty acid positional distribution and postprandial lipid metabolism. Food Rev Int 21:331–355
33. Hernqvist L (1984) Polymorphism of fats. Lund University, Lund
34. Dsouza V, Deman JM, Deman L (1990) Short spacings and polymorphic forms of natural and commercial solid fats—a review. J Am Oil Chem Soc 67:835–843
35. Watanabe A, Tashima I, Matsuzaki N, Kurashige J, Sato K (1992) On the formation of granular crystals in fat blends containing palm oil. J Am Oil Chem Soc 69:1077–1080
36. List GR, Jackson M, Eller F, Adlof RO (2007) Low trans spread and shortening oils via hydrogenation of soybean oil. J Am Oil Chem Soc 84:609–612