

STUDY OF MELTING BEHAVIOUR OF HYDROGENATED VEGETABLE OILS IN SUPERCRITICAL PROPANE

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The melting profiles of six samples hydrogenated using supercritical propane on different operating conditions have been characterised. To determine characteristics of melting behaviour, sunflower oil was hydrogenated under supercritical conditions on 2% Pd/C to iodine values (IV) ranging from 85 to 115, temperatures ranging from 456 K to 484 K, pressures ranging from 20 MPa to 28 MPa and hydrogen mol content (%H₂) ranging from 4% to 8%. In addition, several amounts of palladium catalyst with different particle sizes (dp) were also tested. The melting behaviour of hydrogenated products was characterized by differential scanning calorimetry (DSC) that determines the solid fat content (SFC). These results of SFC relate the consistency of the fat and oil products in terms of their softness, plasticity, organoleptic, and other physical properties important for their use as an ingredient in prepared foods.

In this study, for a given temperature the melt point diminishes with pressure. The melting point of one hydrogenated product which was blended with sunflower oil resulted in an improved solid fat content profile.

INTRODUCTION

Hydrogenation is an extremely important process to modify the melting point of vegetable oils and to contribute important textural properties to food. The versatility of the hydrogenation process promotes the industrial development of fats to achieve specific physical and chemical characteristics in processed foods[1].

The physical and sensory properties of the final product strongly depend on the number of residual double bonds as well as on the *cis-trans* isomers present in the mixture. From nutritional point of view the *cis* isomer is more desirable. However, fatty acids with *trans* configuration affect the textural and melting properties of fat, increasing the stability and serving to extend the plastic range that are characteristics beneficial for margarine production and others products requiring a sharp melting point with good flavor stability while providing the required firmness at room temperature [2]. The consumption of *trans* fatty acids has been discussed in connection with an elevated risk of developing premature atherosclerosis as well as cardiovascular diseases [3]. The low *trans* C18:1 content is a desirable objective with respect to food health.

Melting behaviour of hydrogenated products is an important property for functionality in many prepared food products. The proportion of solid to liquid fat in a shortening, margarine, or specialty product at a given temperature has an important relationship to the performance of the product at that temperature. This proportion cannot be determined from single point melting analysis or other analysis of the physical properties. Estimates of the solids and liquids contents in a fat at different temperatures over the melting range can be made with calorimetric, dilatometric or nuclear magnetic resonance procedures [4]. This behaviour was

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monitored by differential scanning calorimetry (DSC). DSC is the most widely used thermo-analytical technique in oil and fat research [5]. DSC provides a more detailed analysis of the melting behaviour than either the slip melting point solid fat content measurements [2]. DSC offers a sensitive, rapid and reproducible fingerprint method for the identification of vegetable oils and fats.

Solid fat content (SFC) is responsible for many important characters of fat like physical appearance, organoleptic properties, and spreadability. SFC also influences the melting properties indicating the behaviour of a fat at different temperatures. Plasticity or consistency of an edible oil product depends on the amount of solid present [6]. The variation of SFC with temperature and the sharpness of melting range determine the range within which a fat could be considered plastic [7].

In this study, we carried out the hydrogenated of sunflower oil on 2% Pd/C with supercritical propane as solvent under several operating condition (temperature, pressure, particle sizes and hydrogen mol content) [8,9]. DSC was used to determine the SFC of hydrogenated vegetable oils. We studied how the reduction of formation *trans* C18:1 isomer and the operational variables of supercritical hydrogenation effect the melting profile, parameters that are necessary for further industrial food application.

1. EXPERIMENTAL PROCEDURES

Hydrogenation Reactor Setup

A sunflower seed oil from *Helianthus agnus* from Sigma Aldrich (Barcelona, Spain) that had an initial iodine value (IV) of 133 and a fatty acid composition [10,68% saturated (C16:0, C18:0), 22.23% *cis* C18:1, 64.65% C18:2 and 0.8% C18:3] was used in all experiments. Propane (99.5% minimum purity grade) and hydrogen (99.999% minimum purity grade) were purchased from Praxair (Barcelona, Spain).

Hydrogenation runs were carried out in an internal recycle, gradientless microreactor (Robinson, 1986) with catalyst held in an annular basket made of mesh screens. Recycle flow was delivered by a variable-speed stirring-shaft pumping radially through the bed. In order to avoid reactor wall effects the vessel was fabricated from a nickel-free, alloy bar (holding a free volume of 50 cm³). Blank runs showed no catalysis by the wall. Because of the large fan speeds used (up to 105 rad/s), well-mixed conditions prevailed. Liquefied propane was pumped using a high pressure diaphragm pump (Milroyal D, Dosapro Milton Roy, France) to the reactor in order to provide and maintain a system downstream pressure of 18–25 MPa, which was manually set with the high pressure regulator (Model PR57, GO, Euroval, Barcelona). The sunflower oil was pumped at constant flow rate using a HPLC pump (Gilson 305, France) and H₂ was compressed by a gas booster system (AG-62, Haskel, Barcelona) equipped with a high-pressure gas reservoir. H₂ flow was metered from the constant pressure reservoir through a mass-flow indicating-controller (Model 5850S, Brooks Instruments, Euroval, Barcelona).

The oil substrate was mixed with propane in a 20-cm long, 1/4" OD, static mixer (37-04-065, Kenics, Barcelona). H₂ was added downstream of mixer. The reactant mixture was preheated to the desired operating temperature before entering the reactor. The reactor (Robinson-Mahoney reactor, AE, Pa, USA) was equipped with a fan shaft (MagneDrive, AE, Pa, USA), which created a flow through the basket to the reactor wall for upward-downward deflection and a fixed annular catalyst basket (52x52 mesh, catalyst volume= 8.6 cm³), which had baffles inside and outside the basket to prevent vortexing. The reactor was heated with an electrical heating jacket. Control thermocouples were located in the outside skin of the reactor body. Internal reactor temperature was monitored with a thermowell located in the bottom.

After leaving the reactor, the effluent was continuously expanded to atmospheric pressure on an externally heated needle valve in order to control the total flow of the reactor mixture.

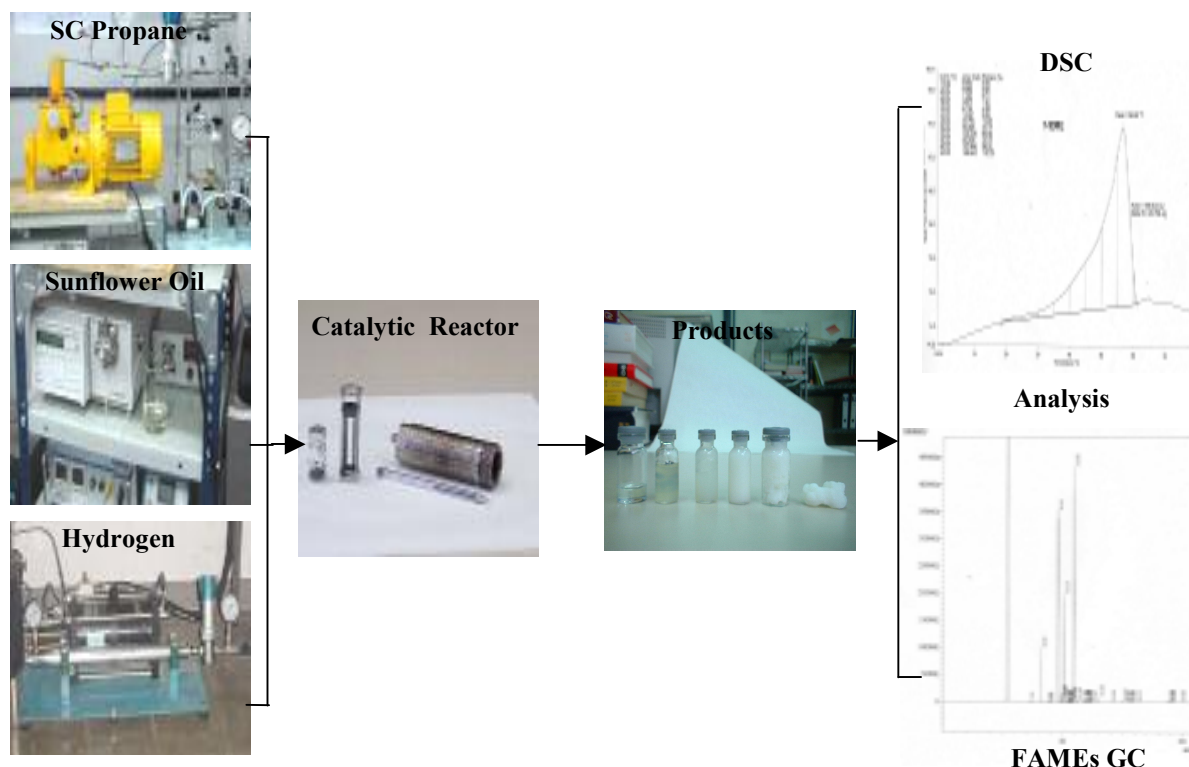


Figure 1. Simplified Process Diagram

This effluent was then sent to a series of glass U-tubes, immersed in an ethylene glycol–water (40% v/v) bath held at 249 K in order to condense the oil from the propane and unreacted H₂ mixture. The flow rate of exhaust gas was measured with a rotameter (2300, Tecfluid, Spain) and sent to an explosion-proof absorption system. In Figure 1, a simplified process diagram is presented.

Fatty acid content of the fully hydrogenated fats

The fatty acid methyl esters (FAMES) were prepared by the method described in the French Standard (NF T 60-233, 1977). FAMES were analyzed by capillary gas chromatography (Shimadzu GC-2010, Barcelona, Spain). Fused silica capillary column 0.25 mm X 60 m (Restek Corporation, PA, USA) was used. The injector and detector temperatures were kept at 220 °C and 250 °C respectively. The initial temperature of the column was 180 °C and it was programmed to increase at the rate of 5 °C/min to 250 °C.

The calculated iodine value (IV) was determined simply by multiplying the percentage of each unsaturated fatty acid by its constant and addition of the results.

Thermal behavior

Differential scanning calorimetry (DSC model Pyris 1, Perkin-Elmer, Spain) was used to determine the thermal profile and solid fat content of hydrogenated products. Nitrogen was the purge gas and flowed at approximately 20 ml/min to avoid thermal currents in the cell. The DSC instrument was calibrated using indium. Samples of 5-10 mg of hydrogenated product were weighed into aluminium pan and covers were hermetically sealed into place. An empty, hermetically sealed, aluminium pan was used as reference, and prior to the analysis of samples, the baseline was established with the reference pan. Sample analysis was carried out according to the AOCS recommended DSC procedure CJ 1-94 [10]. Experimental factors such as melting range, and holding time were selected carefully. Perkin Elmer software was used for the calculate peak areas and the partial areas. The percentage SFC was

determined from the melting profiles and the plastic range of each fat was determined from its SFC.

2. Results and Discussion

The complexity of the thermal profiles of hydrogenated oils is essentially due to the great variety of triglycerides as principal constituents. Therefore, hydrogenated oils do not have specific melting temperature; rather, they melt over a temperature range, as long as a dynamic method is used to measure the melting process. This change may not be visible to the eye, but it can be studied by physical means such as in a DSC instrument. The application of DSC method for studying the melting behaviour of vegetal oils has proved very useful [11].

When hydrogenated experiments were carried out at different pressures, temperatures and particle sizes of the catalysts, the melting profile was considerably affected. For the study of the melting behaviour of six runs under different operating conditions were used. The operating variables are shown in Table 1, and the Figure 2 illustrates the melting curves of the hydrogenated products for these experimental runs.

The fatty acid compositions and IV are given in Table 2. The hydrogenated samples were coded as A, B, C, D, E and F.

Table. 1 Operating of sunflower oil hydrogenated on 2% Pd/C with supercritical propane as medium.

Run	Temperature (K)	Pressure (MPa)	H ₂ mol %	Weight of catalyst (g)	dp (mm)
A	484	20	4	0.25	0.28
B	484	20	8	0.25	0.55
C	484	20	4	0.25	0.55
D	484	28	4	0.8	2
E	456	28	4	0.8	2
F	456	20	4	0.25	0.28

Table. 2 Fatty acid composition (as weight percentage) of hydrogenated products.

Sample	C18:0 %	<i>trans</i> C18:1 %	<i>cis</i> C18:1 %	C18:2 %	IV
A	33.15	2.23	17.62	38.14	86.93
B	20.47	3.38	22.03	42.73	100.22
C	21.46	3.68	21.83	42.62	100.12
D	12.22	4.28	23.03	49.65	114.58
E	29.19	6.61	21.87	31.51	82.69
F	22.92	6.78	24.16	36.57	94.06

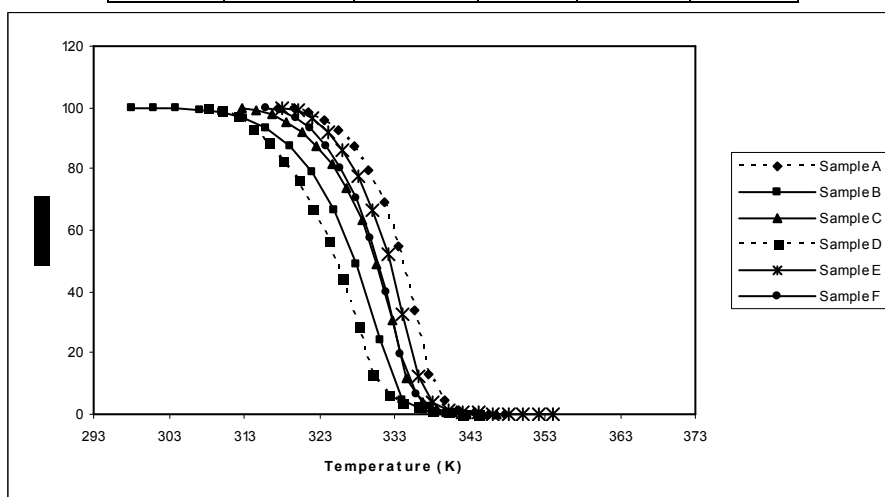


Figure. 2 Melting characteristics of the hydrogenated sunflower oils

Effect of temperature and pressure: The hydrogenation under low temperature and low pressure leads to greater contents of isomers *trans* whereas the production of stearic is less. Therefore, one sample under these conditions has a better melting behaviour than the other obtained under high temperature. This effect can be observed with the samples A and F, where sample F is that it has the best melting profile in this case (see Figure 2). The increase in the temperature resulted in a reduction of isomer *trans* and stearic contents. The sample melts faster than the sample E. (see table 2).

Effect H₂ mol content: Despite of the fact that the reaction conversion is the same under different H₂ mol contents, the production distribution is slightly different. In the case of high H₂ mol content, the reaction is more selective because of the distribution is richer in unsaturated compounds as shows Table 2. So, under this reaction condition a lower melting profile is obtained (see Figure 2).

Effect particle size: Sample C has a greater size of particle than sample A. Apparently, sample C has a melting point better than sample A, but it is a logical result due to the less conversion obtained for the former sample (see Table 2). Therefore, there is not possible to make a concluded explanation about the effect of particle size.

Based on the facts mentioned above, the better melting behaviour for the hydrogenated product may be obtained under high temperature, high pressure, and H₂ mol content. Our melting profiles are so far of the melting profile for hydrogenated food products. Margarine oil or other hydrogenated products must provide somewhat unique physical requirements, it must have a plastic consistency with a relatively sharp melting point. These characteristics most of the time are provided blending liquid with selectively hydrogenated basestock. Sample A has the highest % stearic, and consequently its melting point is the higher than others sample, because it had been made blends of the sample A and sunflower oil to verify the melting profile. The composition of each blend is shown in Table 3. In the Figure 3, the melting profile of three blends of sunflower oil and hydrogenated product are shown. The weight for sunflower oil compositions were 75%, 60% and 25%.

Table 3. Sunflower oil and hydrogenated basestock blends composition

Sample A	Blend 25%	Blend 40%	Blend 70%
Sunflower oil	75	60	30
Final IV	117.43	110.44	92.76

The melting point of these blends was slightly better than those of hydrogenated samples, Figure 3 shows the SFC curve for the blends.

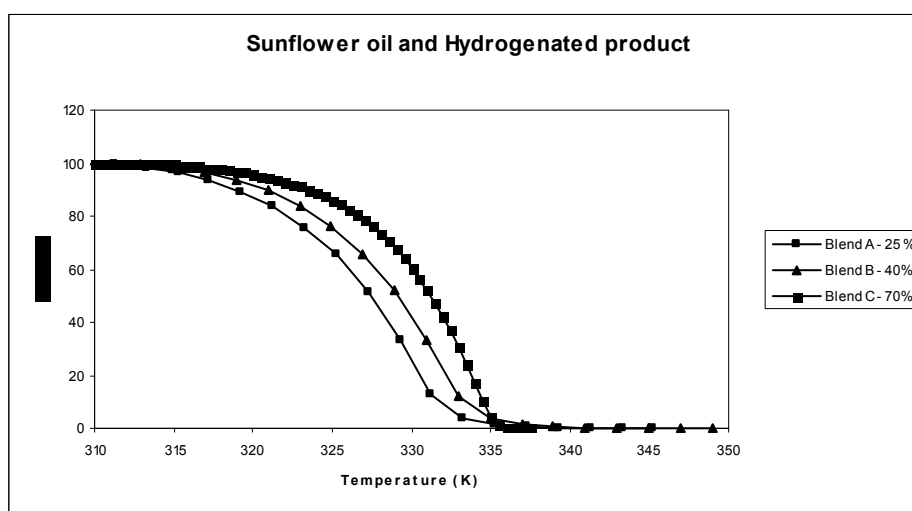


Figure 3. Melting characteristics of sunflower oil blends with hydrogenated products

It has been concluded the melting behaviour of triglycerides must be studied, in order to provide a better explanation of the melting behaviour of hydrogenated products.

CONCLUSION

The results obtained from the present study showed that supercritical hydrogenation under high pressure, high mol hydrogen content and high temperature leads to an improved melting profile of hydrogenated products. Even the melting behaviour of the blends prepared with different weight compositions of hydrogenated product and sunflower oil is improved, the final melting points are higher than those expected for hydrogenated basestock.

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