

CATALYTIC HYDROGENATION IN MODIFIED DENSE CO₂

A.Santana, A. Huguet, B. Pina, F. Recasens, M.A. Larrayoz*
Chemical Engineering Department, Universitat Politècnica de Catalunya.
Av. Diagonal 647, ETSEIB. Pab. G-2. 08028. Barcelona, Spain.
m.angeles.larrayoz@upc.edu

The key factor in the use of supercritical solvent in vegetable oil hydrogenation is that under certain conditions, the concentrations of H₂, triglycerides and solvent can be varied independently over the external catalyst surface, without any limitation. Using SC propane or CO₂ as reaction solvents increases the rate of reaction (more in the case of propane than in CO₂) and reduces the *trans* fatty acid content in the final hydrogenated product. The process with CO₂ has a tendency towards to split up into a two- phase reactive system under until very high pressures whereas in the case of propane, which presents completely miscibility with triglycerides, the system can operate in a unique reactive phase (gaseous) into the reactor under mild operating conditions but the offset is its high flammability. The feasibility of continuous single-phase hydrogenation increases because of the minimization the risk due to the use of modified SC CO₂ under mild conditions instead of some flammable solvents such as SC propane or DME. The hydrogenation of sunflower oil was carried out in fixed bed reactor in supercritical carbon dioxide – SC CO₂ (80 - 60% v/v) containing added hexane (20 – 40% v/v). The specific objective for the research presented here was the determination of supercritical carbon dioxide/hexane cosolvent mixture over a range of pressure and temperature settings to obtain an estimate of the temperature-pressure parameters that would be best for obtaining low *trans* fatty acids in the hydrogenated products.

1. INTRODUCTION

The production of margarine and shortenings from vegetable is one typical heterogeneous catalytic hydrogenation process. Its purpose is provides products with the desired melting profile and texture, according to their final use. The hydrogenated oil is more stable and less sensitive to oxidation [1].

The low rate of reaction of the conventional process [2] as well as the rise of *cis-trans* isomerization [3] is consequence of the low solubility of hydrogen and the high mass-transfer resistance in the liquid phase. Commercial oils, which are partially hydrogenated, contain normally 30-40 % *trans*-fatty acids [4]. This isomer has shown to have similar effects as saturated fats increasing serum cholesterol levels in the blood, believed to be a major cause of heart disease [5].

The transport properties and the favourable solvent of supercritical fluids make them an adequate medium for chemical reactions and offer great opportunities for process improvement [6-7]. The application of a suitable supercritical fluid to a gas-liquid hydrogenation process can bring all reactants and products into a homogeneous fluid phase. Under these conditions the problems of hydrogen solubility and gas-liquid mass-transfer resistance are removed and reaction rates are greatly increased. The main benefits of supercritical hydrogenation are process intensification (small reactors) and improved selectivity due to the independent control of temperature, pressure, and composition of the reactants at the catalyst surface.

Tacke *et al.* [8-9], Harrod *et al.* [10-12], and Ramírez *et al.* [13-14] have been reported on the last decade, that continuous single-phase process of hydrogenation on supported Pd using

supercritical propane as reaction solvent increases dramatically the rate of reaction in comparison to the traditional gas-liquid process as well as reduces the *trans* fatty acid content (less than 3 wt%) in the final hydrogenated product.

In the case of CO₂, there are many significant advantages as it is naturally occurring, inexpensive, colourless, odourless, tasteless, non-flammable, non-ozone depleting and nontoxic. It is by far; the most widely used SCF [15]. It has been employed in the hydrogenation of a wide variety of substrates where the reactive system was operated at two-phase conditions [16].

The process with SC propane or DME as solvent presents completely miscibility with triglycerides [17], which allow operating in a unique reactive gas phase into the reactor under mild operating conditions but Bonanza and Recasens [18] found by means of the evaluation of the DOW's Fire and Explosion Index (FEI) [19].

The safety and loss prevention guide developed by the Dow Chemical Company gives a method for evaluating the potential hazards of a process and assessing the safety and loss prevention measures needed. A numerical Fire and Explosion Index is calculated, based in the nature of the process and the properties of the materials. The larger the value of the index, the more hazardous is the process [20].

The effect of several entrainers, allowed to foodstuff processing (e.g. ethanol, propane, butane, acetone, etc.), on the continuous vegetable oil hydrogenation in SC CO₂ was theoretically studied in order to increase the process feasibility.

The selection of the possible modifiers to add to SC CO₂ was made in accordance with the EC Council directive [21] which states the regulations regarding the use of solvents in the production of foodstuffs and food ingredients within the CE.

The use of a small percentage of cosolvent may provide additional lipid solubility at lower temperature and pressure conditions, allowing use of supercritical carbon dioxide/hexane at lower pressures than pure carbon dioxide. Among the cosolvents under study, hexane appears to be the most appropriate. The hexane was chosen as the cosolvent because it has not reacted with hydrogen compared with Ethylmethylketone and the hexane is the less reactive solvent due to fact that it is a hydrocarbon

The addition of an entrainer to CO₂ dramatically increases the solubility of triglycerides in the reaction medium. This fact would offer the possibility to hydrogenate in a unique-single phase into the reactor under mild operating conditions in comparison to those with pure CO₂. The results obtained from this preliminary study showed that supercritical CO₂ hydrogenation in presence 20% v/v hexane presented low conversion with low *trans* and low stearic.

2. MATERIALS AND METHODS

2.2. HYDROGENATION REACTOR SETUP

Raw Materials

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. The mixture dioxide carbon/hexane (80:20 v/v) used in this work was supplied by Abello Linde S.A. (Barcelona, Spain). The hydrogen (99.999% minimum purity grade) was purchased from Praxair (Barcelona, Spain).

The catalyst used was 0.5% Pd on alumina (spheres of 2 mm, surface area = 320m²/g, pore volume = 0.45 cm³/g and bulk density = 750 kg/m³. The metal is deposited on an eggshell on the pellets) from Johnson Matthey (Barcelona, Spain).

Equipment

Hydrogenation runs were carried out in a microreactor (Eurothechnica, 2007), the maximum pressure supported is 500 bar and 250°C of temperature. The reactor material is titanium. The experimental reactor setup is shown in Figure 1.

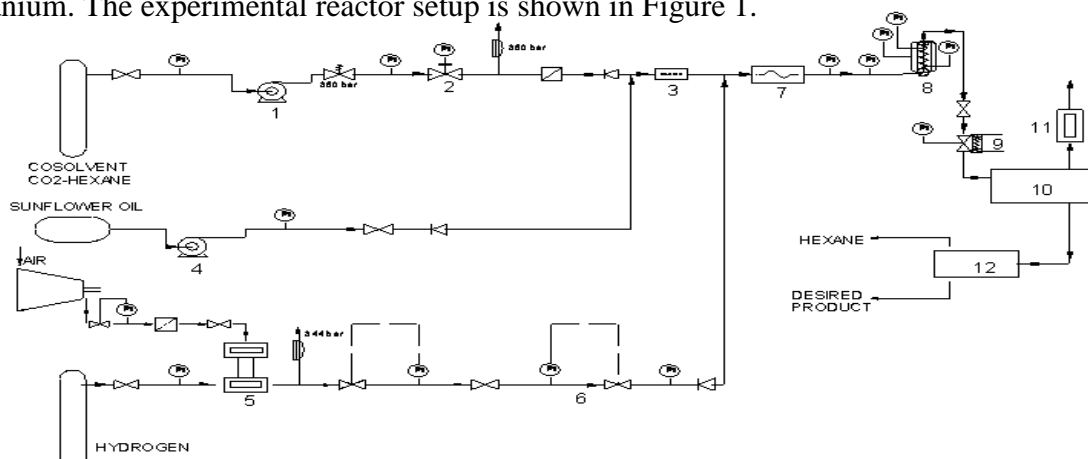


Figure 1. Continuous hydrogenation reactor setup: (1) diaphragm pump MILROYAL D; (2) back pressure; (3) static mixer; (4) piston pump; (5) HASKEL gas booster AG-62; (6) Brooks Smart 5850-S; (7) heating device; (8) reactor HPA 500; (9) autoclave engineers needle-valve; (10) ethylene glycol bath; (11) rotameter; (12) Rota-vapor.

Liquefied dioxide carbon and hexane were 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 dioxide carbon/hexane 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 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. This effluent was then sent to a series of glass U-tubes, immersed in an ethylene glycol bath held at 224 K to condense the oil from the hexane.

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.

Phase Equilibrium Estimation

To investigate the influence of modifier (hexane) on phase behaviour of the reactive mixture Sunflower oil/SC CO₂/H₂ for a defined composition, the phase envelopes were modelled using the standard Peng-Robinson equation of state (PR-EOS) with one *k_{ij}* binary parameter.

The mixture composition was set at typical values for the reaction under supercritical conditions: The molar oil and H₂ concentration were kept constant at 1 and 4 mol %, respectively. Though high substrate loadings and low concentration of hydrogen are desirable. The entrainer composition in the mixture was set at 20 % hexane of the CO₂ mol concentration because higher values can make the process potentially risky due to the inherent flammability character of the most of the substances selected as potential modifiers. PT-diagrams were generated by means of ASPEN PLUS® simulation software [22]. Each isopleth plotted in these diagrams represents the phase limit between the two-phase and the one-phase regions. The temperature and pressure dependence of the solvent power are enhanced (See figure 2). We have chosen the composition 20% v/v hexane due to the conditions of equipments. The operating conditions were between 250 – 300 bars and.

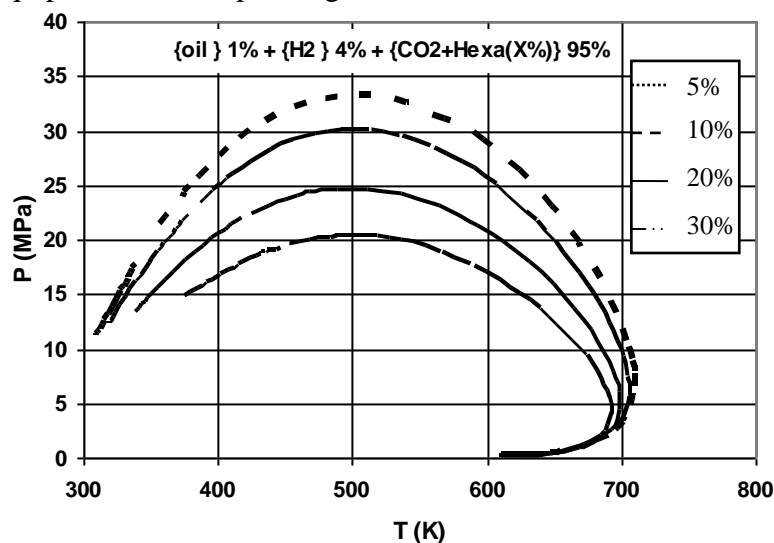


Figure 2: PT-envelope at constant mol composition (1%oil:4%H₂:95%CO₂+hexane) for different composition of hexane

3. RESULTS

The supercritical hydrogenation was carried out with a molar feed concentration (oil:H₂:CO₂+hexano) was 1:4:95 mol% and the mixture of supercritical carbon dioxide/hexane was (80:20/60:40 in volume ratio) respectively. The operation conditions were 2% Pd/C (1g), pressure 250 bar, the total volumetric flow was 0.28kg/h and supercritical CO₂+hexane as medium. The temperatures were shown in table 3.

The results obtained from this preliminary study showed that CO₂ supercritical hydrogenation in presence 20% v/v hexane presented low conversion with low *trans* and low stearic (see Table 4). The final product can have suitable plastic properties. This study

showed that it is possible to determine the optimum operating conditions to obtain a final hydrogenated product of immediate food application (such as for margarine/shortenings production) such that it has a low trans content (> 3%) and a moderate IV reduction together with a relatively low stearic content.

Table 1: Fatty acid composition (as weight percentage) of hydrogenated products

Sample	Temperature	C18:0%	<i>trans</i> C18:1	C18:1%	IV
A	200	6.40	2.40	24.77	123
B	185	7.50	4.00	25.17	117
C*	120	32.30	19.70	22.01	67
D*	100	26.70	17.20	24.70	77
E*	60	10.61	5.12	31.70	112

*Near critical CO₂+hexane

It was not possible to analyze the supercritical hydrogenation in presence 40% v/v hexane due to the pressure did not remain constant. A possible explanation would be an increase of the viscosity of the mixture. The viscosity of 20% v/v hexane is $1.5 \cdot 10^{-4}$ and the viscosity of 40% v/v hexane is $2 \cdot 10^{-4}$.

The Table 5 shows the results obtained under supercritical fluids and near critical fluids, where the pressure remained constant and the temperature was varied. The sample A and B under supercritical conditions presented low conversion and low trans content. The experiment C, D and E were carried out under near critical conditions. The hydrogenation under low temperature resulted in a reduction of isomer *trans* and stearic contents but the oleic content was higher. No reaction was observed at temperature lower than 60°C.

4. CONCLUSIONS

The results from this study show that the solubility of vegetable oils in SC CO₂ can be increased due to the addition of an appropriate cosolvent e.g. hexane which allows a reduction in operating pressure which assures complete miscibility in the reactive mixture for a given temperature and feed composition in comparison with the system using only SC CO₂ as solvent. On the other hand, the feasibility of continuous single-phase hydrogenation increases because of the minimization the risk due to the use of modified SC CO₂ under mild conditions instead of some flammable solvents such as SC propane or DME.

In this work we report in the fluid-phase hydrogenation on sunflower oil in supercritical dioxide carbon/hexane with 1 mol % vegetable oil, 4% H₂, and 95 % CO₂+hexane. The reaction is run continuously in a single-fluid phase, using a laboratory setup. The catalyst is 0.5% Pd/Al₂O₃. A wide range of hydrogenation products can be obtained with certain plastic characteristics for further food application by tuning the reaction conditions. The experimental results show that one principal advantage of using supercritical carbon dioxide in presence of the cosolvent hexane is the low *trans* acid content.

5. ACKNOWLEDGMENTS

A fellowship to A. Santana from the FPI program (Spanish Ministry of Science and Technology) is acknowledged. The project of CiCYT-FEDER (Madrid,Spain) Project Number AGL 2006-05156 provided funds for a fellowship to A. Huguet and B.Pina. Financial support to this work was received from the same research project.

6. REFERENCES

- [1] RASE, H. F., Handbook of Commercial Catalysts: Heterogeneous Catalysts, CRC Press, Boca Raton, FL (2000).
- [2] FARRAUTO, R. J. AND C. H. BARTHOLOMEW, Fundamentals of industrial catalytic processes, Chapman & Hall, Great Britain (1997).
- [3] HORIUTI, J., AND M. POLANYI. "Exchange reactions of hydrogen on metallic catalysts", Trans. Faraday Soc., 30, 1164 (1934).
- [4] KING, J. W., R. L. HOLLIDAY, G. R. LIST AND J. M. SNYDER, "Hydrogenation of vegetable oils using mixtures of supercritical carbon dioxide and hydrogen", JAOCS, 78 (2), 107 (2001).
- [5] OOMEN, C. M., AND M. C. OCKE, "Association between *trans* fatty acid intake and 10-year risk of coronary heart disease in the Zutphen elderly study: A prospective populationbased study", Lancet, 357, 746 (2001).
- [6] BAIKER, A., "Supercritical Fluids in Heterogeneous Catalysis", *Chem. Rev.*, 99, 453 (1999).
- [7] SAVAGE, P. E., S. GOPALAN, T. I. MIZAN, C. J. MARTINO, AND E. E. BROCK, "Reactions at Supercritical Conditions: Applications and Fundamentals", *AIChE J.*, 41, 1723 (1995).
- [8] TACKE, T., S. WIELAND, AND P. PANSTER, "Hardening of Fats and Oils", Proceedings of The 3rd International Symposium on High-Pressure Chemical Engineering, Zurich, Switzerland, p.17 (1996).
- [9] TACKE, T., WIELAND, S. AND PANSTER, P. Selective and Complete Hydrogenation of Vegetable Oils and Free Fatty Acids in Supercritical Fluids, in Green Chemistry Using Liquid and Supercritical Carbon Dioxide, ed. J. M. De Simone, Oxford University Press, Oxford (2003).
- [10] HARROD, M., M. MACHER, S. VAN DEN HARK, AND P. MOLLER, "Hydrogenation at supercritical conditions" Proceedings of Fifth Conference on Supercritical Fluids and their Applications, Garda, Italy, p.319 (1999).
- [11] HÄRRÖD, M., S. VAN DEN HARK, M.-B. MACHER AND P. MOLLER, Hydrogenation at supercritical single-phase conditions, In High Pressure Process Technology: Fundamentals and Applications, Eds. Bertucco and Vetter, Elsevier, New York (2001).
- [12] HÄRRÖD, M., VAN DEN HARK, S., "Hydrogenation of oleochemicals at supercritical at supercritical single-phase conditions: influence of hydrogen and substrate concentrations on the process", *Appl. Catal. A: Gen.*, 210, 207 (2001a).
- [13] RAMÍREZ, E., F. RECASENS, M. FERNÁNDEZ, AND M. A. LARRAYOZ, "Hydrogenation of Sunflower Oil on Pd/C in Supercritical Propane: Operating Conditions in a Continuous Internal Recycle Reactor", *AIChE Journal*, 50, 6 (2004).
- [14] RAMÍREZ, E., M. A. LARRAYOZ AND F. RECASENS, "Intraparticle Diffusion Mechanisms in Supercritical Sunflower Oil Hydrogenation on Pd/C Catalyst", *AIChE Journal*, 52, 4, 1539-1553 (2006).
- [15] JESSOP, P. G. AND W. LEITNER, Chemical Synthesis Using Supercritical Fluids, Wiley-VCH, Weinheim (1999).
- [16] HITZLER, M.G., F. R. SMAIL, S. K. ROSS, AND M. POLIAKOFF, "Selective Catalytic Hydrogenation of Organic Compounds in Supercritical Fluids as a Continuous Process", *Org. Process Res. Dev.*, 3(2), 137 (1998).
- [17] PETERS, C. J., H. J. VAN DER KOOI, J. L. DE ROO, J. DE SWAAN ARONS, J. S. GALLAGHER, AND J.M. H. LEVELT SENGERS, "The search for tricritically in binary mixtures of near-critical propane and normal paraffins", *Fluid Phase Equilibria*, 51, 339 (1989).
- [18] BONANZA, N. AND RECASENS, F. (2005). In Proceedings of The 10th Meeting on Supercritical Fluids: Reactions, Materials and Natural Product Processing, Strasbourg/Colmar, France, p.215.
- [19] Dow's Fire and Explosion Index Hazard Classification Guide. 7th ed. The Dow Chemical Company, American Institute of Chemical Engineers (1994).
- [20] COULSON, J. M. AND J. F. RICHARSON, Chemical Engineering Vol. 6, Pergamon, Great Britain (1983).
- [21] EC, EC directive 84/344/EEC (1984).
- [22] Aspen Plus® Version 2004.1 (2006).

