

# TRANS-FREE HYDROGENATION USING SUPERCRITICAL CARBON DIOXIDE IN PRESENCE OF COSOLVENT

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**Abstract.** The hydrogenation of sunflower oil was carried out in fixed bed reactor in supercritical carbon dioxide – SC CO<sub>2</sub> (80%v/v) containing added hexane (20%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. The use of a small percentage of cosolvent, may provide additional lipid solubility at lower temperature and pressure conditions and allow use of supercritical carbon dioxide/hexane at lower pressures than pure carbon dioxide, an important consideration when designing large scale processing equipment. The results from this study show that the solubility of vegetable oils in SC CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> under mild conditions instead of some flammable solvents such as SC propane or DME.

**Keywords:** Supercritical hydrogenation, carbon dioxide, cosolvent, *trans*.

## 1. INTRODUCTION

Hydrogenation of fats and oils is the largest single reaction in the edible oil industries. 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.

Despite of the great potential that exhibits the use of SC propane or DME in an unique reactive single-phase as alternative process to obtain healthier raw materials for foodstuffs, the idea of using high flammable solvents in the presence of hydrogen under high pressure conditions leads to increase the risk of the process.

In the case of CO<sub>2</sub>, 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].

In the hydrogenation of fats and oils, CO<sub>2</sub> is not commonly used due to the low solubility of triglycerides in it. This fact leads to operate under two-phase conditions because, from an industrial point of view, the high pressure requirements to form a single-phase system become the process too expensive.

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 addition of an entrainer to CO<sub>2</sub> 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 CO<sub>2</sub>. The results obtained from this preliminary study showed that supercritical CO<sub>2</sub> hydrogenation in presence 20% v/v hexane presented low conversion with low *trans* and low stearic.

## 2. HYDROGENATION REACTOR SETUP

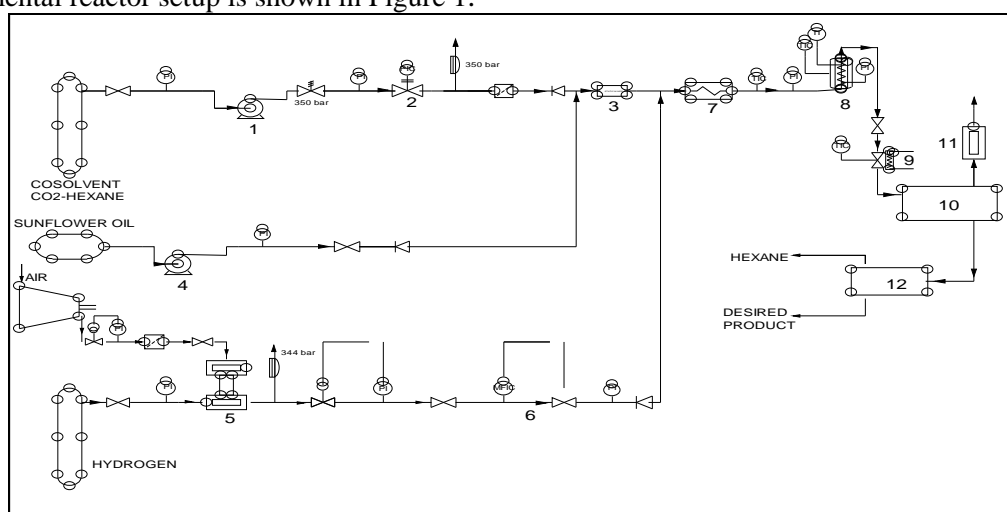
### 2.1 Raw Materials

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 = 320m<sup>2</sup>/g, pore volume = 0.45 cm<sup>3</sup>/g and bulk density = 750 kg/m<sup>3</sup>. The metal is deposited on an eggshell on the pellets) from Johnson Matthey (Barcelona, Spain).

### 2.2 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 H<sub>2</sub> was compressed by a gas booster system (AG-62, Haskel, Barcelona) equipped with a high-pressure gas reservoir. H<sub>2</sub> 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). H<sub>2</sub> 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.

The molar feed concentration (oil:H<sub>2</sub>:CO<sub>2</sub>+hexano) was 1:4:95 mol% and the mixture of supercritical carbon dioxide/hexane was (80:20 in volume ratio) respectively.

### 2.3 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.

## 3. THERMODYNAMIC MODELING

### 3.1 Selection of Potential Cosolvents

The selection of the possible modifiers to add to SC CO<sub>2</sub> 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.

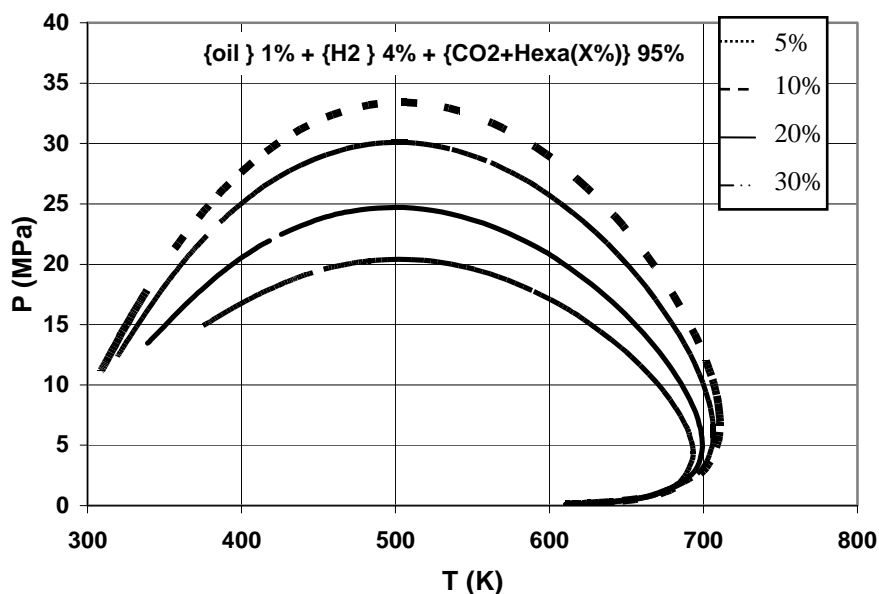
**Table 1.** Extraction solvents which use are the product or fractionation of fats and oils [21].

Solvent	T <sub>c</sub> (K)	P <sub>c</sub> (Mpa)	ω	Dipole Moment (D)
Hexane	508	3.00	0.305	0
Ethylmethylketone	536	4.15	0.324	2.76

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 (See table 1).

## 4. PHASE EQUILIBRIUM ESTIMATION

The addition of a modifier to CO<sub>2</sub> increases the single-phase region for the reaction due to the improvement of triglycerides solubility in SC CO<sub>2</sub>. Therefore, the temperature and pressure dependence of the solvent power are enhanced. This fact makes possible to operate under milder conditions (e.g. lower pressures 20- 30 MPa) in comparison to those with pure CO<sub>2</sub> (75 Mpa).



**Figure 2.** PT-envelope at constant mol composition (1%oil:4% $H_2$ :95% $CO_2$ +hexane) for different composition of hexane

To investigate the influence of modifier (hexane) on phase behaviour of the reactive mixture Sunflower oil/SC  $CO_2/H_2$  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  $H_2$  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  $CO_2$  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.

## 5. RESULTS

The supercritical hydrogenation was carried out with a molar feed concentration (oil: $H_2$ : $CO_2$ +hexano) was 1:4:95 mol% and the mixture of supercritical carbon dioxide/hexane was (80:20 in volume ratio) respectively. The operating variables are shown in Table 2.

The results obtained from this preliminary study showed that  $CO_2$  supercritical hydrogenation in presence 20% v/v hexane presented low conversion with low *trans* and low stearic (see Table 3). 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 2.** Operating of sunflower oil hydrogenated on 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> with supercritical CO<sub>2</sub>+hexane as medium

Sample	Temperature	Pressure	H <sub>2</sub> %mol
A	210	250	4
B	190	250	4
C	190	300	4

**Table 3.** Fatty acid composition (as weight percentage) of hydrogenated products

Sample	C18:0%	<i>trans</i> C18:1%	IV
A	7.34	3.45	120.59
B	7.81	4.94	117.57
C	10.4	4.28	114.78

## 6. CONCLUSIONS

The results from this study show that the solubility of vegetable oils in SC CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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% H<sub>2</sub>, and 95 % CO<sub>2</sub>+hexane. The reaction is run continuously in a single-fluid phase, using a laboratory setup. The catalyst is 0.5% Pd/Al<sub>2</sub>O<sub>3</sub>.

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.

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