

PROCESS DESIGN FOR VEGETABLE FAT HYDROGENATION IN SCF: REACTOR OPERATION, CO-SOLVENT AND SAFETY

M.J. Mayorga, D. Cuevas, A.D. Bojarski, and F. Recasens*

Chemical Engineering Department, ETSEIB Diagonal 647,

08028 Barcelona, Spain

Conventional low-pressure hydrogenation of vegetable fats produces *trans* isomers that are suspect of inducing heart-diseases, so there is a nutritional risk associated to the ingestion of foods based on hydrogenated fats. In some EU countries (i.e., Denmark) *trans* isomers in food have been already banned by law. Technologies are needed for developing new processes providing very low *trans* fats (less than 2-3% *trans* material). High pressure, supercritical-fluid hydrogenation process provides an efficient method to reduce unwanted *trans* C18:1 triglyceride formation. The purpose of this paper is to provide a simulation study of a SCF process based on a catalyst developed in our laboratory. We show that the process is industrially feasible and relatively safe, and that the use of high pressure SC solvent does not involve an unfamiliar danger compared to the usual SCF mass transfer processes.

HYDROGENATION KINETICS IN SCF

A demonstration plant of 2000 metric ton/year of margarine will be considered, consequently a reactor for the provision of such capacity is considered. The catalyst is based on supported Pd and the catalysed reactions are depicted in **Figure 1**. The source of fat considered was sunflower oil with 6 wt% linoleic triester and 7% estearic acid. Supercritical solvents were either pure CO₂ or modified CO₂, or liquid hexane. The catalyst related and reaction kinetic data is summarized on **Table 1** based on the work of Santana et al. [1].

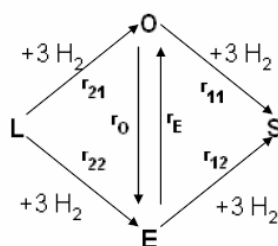


Figure 1. Simplified hydrogenation of sunflower oil

All the reactions are catalytic, first order in the triglyceride and half order in hydrogen, except reactions 11 and 12 that are first order in hydrogen. Kinetic expressions are of Langmuir-Hinshelwood type and are reported in mole concentrations. **Table 1** information is used in AspenPlus for reaction modeling.

Table 1. Kinetic parameters for two catalysts, Santana et al. [1].

Pd/C catalyst				Pd/Al ₂ O ₃ catalyst			
Factor preexp.		Activation energy		Factor preexp.		Activation energy	
mol ^{-1/2} (m ³) ^{3/2} kg ⁻¹ s ⁻¹		J/mol		mol ^{-1/2} (m ³) ^{3/2} kg ⁻¹ s ⁻¹		J/mol	
(*)mol ⁻¹ (m ³) ² kg ⁻¹ s ⁻¹				(*)mol ⁻¹ (m ³) ² kg ⁻¹ s ⁻¹			
A ₂₁	1.61	E ₂₁	3.59 × 10 ⁷	A ₂₁	8.21 × 10 ⁻³	E ₂₁	19.28 × 10 ⁶
A ₂₂	4.25 × 10 ⁻⁶	E ₂₂	1.47 × 10 ⁶	A ₂₂	67.90	E ₂₂	1.47 × 10 ³
A _O	3.84	E _O	3.50 × 10 ⁷	A _O	8.45 × 10 ¹¹	E _O	3.50 × 10 ⁴
A _E	1.48 × 10 ⁻³	E _E	6.97 × 10 ⁴	A _E	1.09 × 10 ¹⁷	E _E	6.97 × 10 ¹
A ₁₁	7.08 × 10 ²⁴ (*)	E ₁₁	2.66 × 10 ⁸	A ₁₁	1.70 × 10 ⁻³ (*)	E ₁₁	1.49 × 10 ⁵

Based on the reaction network shown on Fig 1., the following overall selectivity (s) and yield (y) were defined [2]. Selectivity s is the rate of H₂ reaction to oleate (O) with respect to reaction to stearate (s) which in terms of the reactor effluent (F_i) and feeds (F_i^0), renders Eqs. 1 and 2.

$$s = \frac{F_o - F_o^0}{F_S - F_S^0} \quad (1)$$

$$y = \frac{F_E}{F_{H_2}^0 - F_{H_2}} \quad (2)$$

In Eq. 2 y represents the yield in elaidate (*trans* isomer) relative to the total hydrogen uptake. In general, s should be large and y small. For a given space-time of the reactor, the values of s and y are calculated using the above equations from the model output.

REACTOR OPERATION

A hierarchical decomposition of decisions approach was used for reactor operation (see as **Figure 2**). The decision variables considered were:

- Catalyst type: Pd/C or Pd/Alumina.
- Reactor type: PFR or CSTR.
- Reactor jacket: adiabatic or isothermal operation at different temperatures 170°C, 185°C and 200°C.
- H₂ partial pressure: 3%, 5%, 8% or 10%.

The simulation was run and the output values s and y were calculated. A constraint on the trielaidate concentration being below 9% was also considered (for maximum selectivity), a minimum value of tristestearate was also desired.

The former decomposition considers two binary variables: reactor geometry and catalyst type, while the other two decisions are continuous by modeling the required heat flow and inlet amount of H_2 . Through all the simulations it is considered that single-phase based on LVE is found see Figure 4 .

The selectivity and yield for various reactor space-time values were calculated (see **Figure 3**). It was found that the Pd/Al catalyst provides better results than the Pd/Alumina. Regarding reactor geometry it is found that the multi-tubular reactor behaves better than the CSTR. Both reactor types were tested and it was found that isothermal operation at the lowest temperature produces better results.

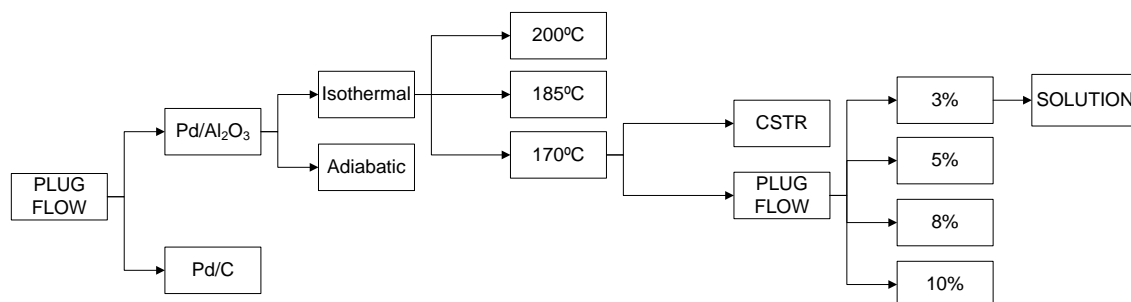


Figure 2. Proposed decision tree for reactor selection.

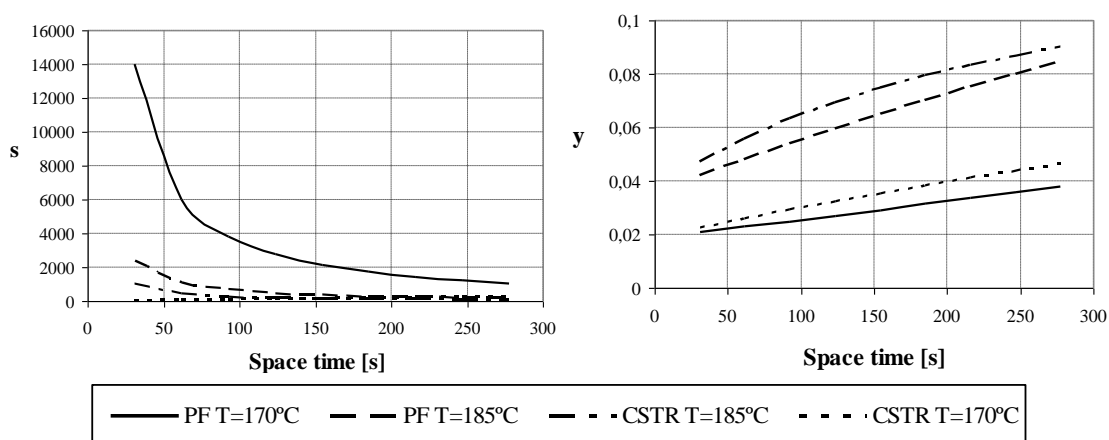


Figure 3. Selectivity and elaidate yield as a function of space-time for Pd/Alumina catalyst, SCF ($CO_2/Hexane$ 50%). Final IV = 80 (initial IV= 130).

The selected operating conditions for the reactor can be summarized as follows: Pd/Alumina catalyst, using a multitubular reactor with isothermal operation at $170^\circ C$, and 3% H_2 (1mol% oil). The operating space-time is around 100 s, while the operating pressure is 20 MPa, the selectivity obtained is around 400 and the elaidate production is 3%. The calculation is based on a run with SCF propane, but the plant is simulated with other fluids.

LIQUID-VAPOUR EQUILIBRIUM

In order to check for condensation in the reactor under the operating conditions, a two phase flash unit was studied prior to running the reactors. The LVE was modeled with

the Peng-Robinson EOS as modified by Aspen operated fixed at the temperature and pressure of interest, for different feed conditions. In this way, different critical envelopes were obtained, see **Figure 4**

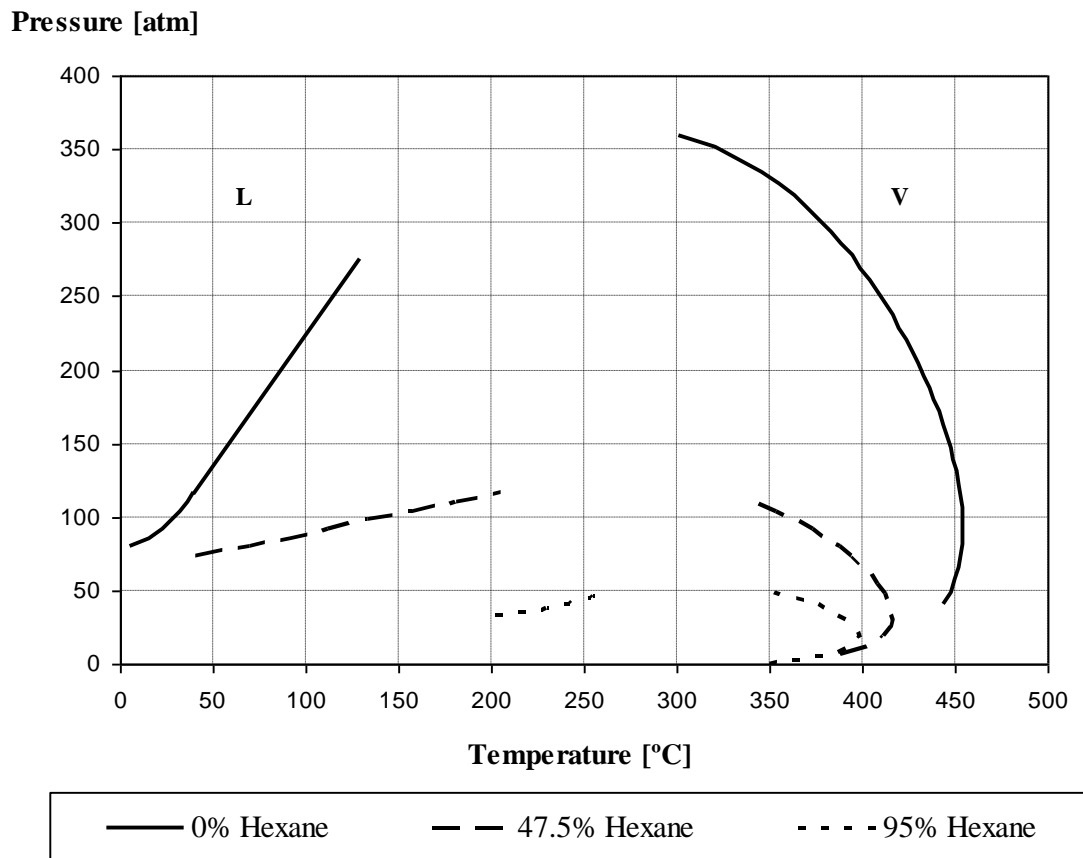


Figure 4. Critical envelopes for the reactor inlet mixture (CO₂ with hexane as a cosolvent), with the saturated liquid and vapor branches. Aspen PR-EOS

Qualitatively, the critical lines calculated using the PR EOS are seen to decrease by increasing the fraction of cosolvent, which is in the expected behaviour. On the other hand, precise convergence is not good at the critical point.

In the laboratory, the critical locus conditions calculated with Aspen correctly predicts condensation in the reactor.

OPTIMIZATION OF PRODUCT QUALITY

As seen, the best product quality is obtained when the *trans* yield, y , is minimum, together with maximum selectivity, s , to minimize stearate. Therefore, in order to optimize quality, the following objective function is defined,

$$Fo = a(1/y) + bs$$

where a and b are scaling factors (in our case $a = b = 1$ is acceptable). The function Fo , depends on a number of factors, each considered at two levels in the optimization procedure. The design factors are given in Table 5,

Table 5. Two-level variables

Factors	Level	
	Lower	Upper
Reactor type	CSTR	PF
T	170°C	200°C
Catalyst	Pd/Al ₂ O ₃	Pd/C
Heat transfer	Adiabatic	Isothermic
Mole fraction H ₂	1%	4%
W/F	100 s	300 s

A possible experimental design consists of $2^6 = 64$ runs, which are easily done as it requires only running the reactor model programs a certain number of times. The results of the effects, based on the Yates algorithm (this not shown), are summarized on **Figure 5**.

The conclusions of the composite optimization are as follows. The best operating conditions are: plug flow, Pd/Alumina catalyst, low temperature 170°C, with 4% H₂ in the feed, with a space-time of about 100 s. These conditions are close to those predicted before from the prior algorithm, and agree well to those reported by Harrod [4], for the same process. This fact validates the kinetic constants reported in **Table 1**. Probably, there exists a better catalyst that gives less elaidate yield, but the overall rate seems correct, at least as far as the space-time is concerned. A Pt catalyst operating at a much lower temperature would yield still less *trans* [2].

PROCESS SIMULATION AND PLANT DESIGN

One base-case simulation was done with a process based on SC propane (with data from Santana et al [1]). The AspenPlus simulation allows to calculate the stream compositions, the utilities, and the recirculations and to define a final process flowsheet, as well. Other cases were done with solvents based on carbon-dioxide modified with cosolvent (hexane) and a 3rd case in which the solvent is liquid hexane, as a superheated liquid. The hypothesis made, is that the kinetic coefficients are independent of any solvent used. This is not critical as a first approximation, because we wanted to see the effects of the solvent in the operating pressures and the separation schemes or the process operations. The utility costs are taken from the current practice in Spain.

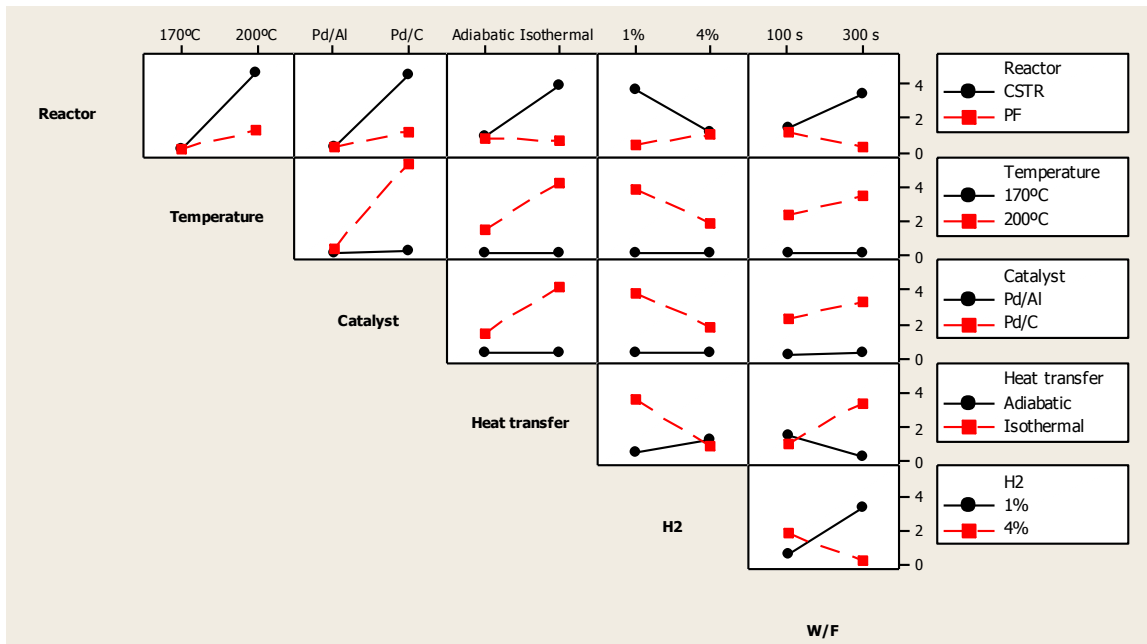
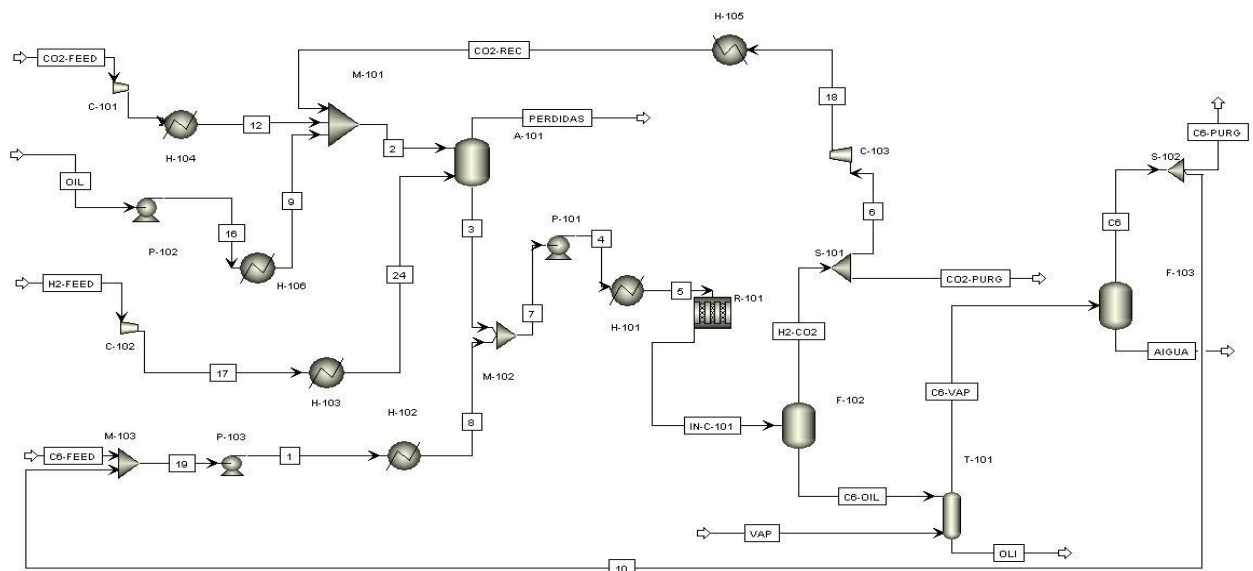


Figure 5. Interactions of the effects

The plant for the more complex case, which considers CO₂ with cosolvent, is given in the flowsheet of **Figure 6**, that involves a recycle of CO₂ and H₂, and that of hexane. The investment costs and operating cost for a plant producing 2000 metric tons/year are considered in the cash-flow analysis. The investment costs evaluated in the development of this work agree well with those suggested by Harrod, by adjustment of the plant capacities [4].



Stream	1	2	3	4	5	6	7	8	9	10	12	16	19	AIGUA
P (bar)	90	90	105	100	100	10	90	90	90	1	90	90	1	1
T (°C)	147	90	20	54	170	100	53	80	80	20	80	25,5	139	20
Mass Flow (kg/s)	0,14	0,14	0,14	0,28	0,28	0,06	0,28	0,14	0,07	0,12	0,01	0,07	0,14	0,14

Stream	C6	C6-FEED	C6-OIL	C6-PURG	C6-VAP	CO2-FEED	CO2-PURG	CO2-REC	H2-CO2	H2-FEED	IN-C-101	OIL	OLI
P (bar)	1	1	10	1	5	1	10	80	10	2	100	1	5
T (°C)	20	20	100	20	89	25	100	80	100	20	170	25	69
Mass Flow (kg/s)	0,13	0,02	0,20	0,01	0,27	0,01	0,02	0,06	0,08	0,00001	0,28	0,07	0,08

The cashflow study for the 3 plants gives the Net Present Value (NPV) calculations shown in **Figure 7**. The internal rate of return (IRR) are 13,99% for the pure hexane plant and 10,9% for the pure CO₂ plant. But for solvent mixtures based on CO₂ and hexane, the IRR is only 8,7%, see abscissa of **Figure 7**. The most profitable process is hydrogenation in liquid hexane, when the investment costs of the plants are considered.

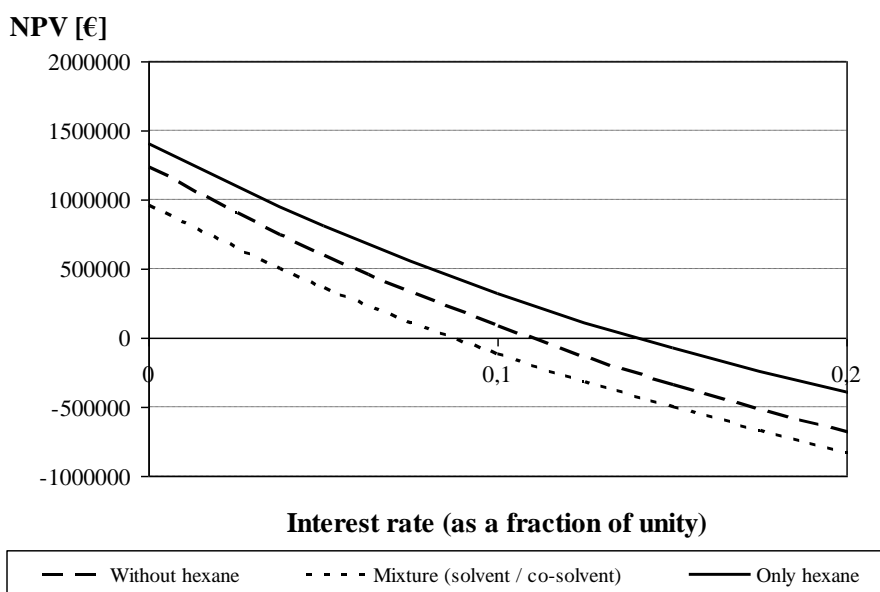


Figure 7. Plants of 2000 metric ton/y. NPV as a function of the internal rate of return for the 3 plants. Initial ordinates are the investment costs (depreciation rate = 7%/y).

SAFETY CONSIDERATIONS

Process safety is usually assessed using the Dow Fire and Explosion index (F&EI),[5] or a similar safety parameter. Perrut [6] has reported the hazards of SCF extraction plants based on his experience. Usually high pressure is accepted as hazard, provided that pressure vessel standards (i.e., ASME code) are met. When using the Dow F&EI the material factor for CO₂ is zero, because it has no risk of flammability, nor toxicity, although fatal BLEVE accidents with CO₂ may occur [6]. In practice the risks shown by Perrut [6] require consideration, but they are not critical in qualifying a SCF process. The degrees of Dow F&EI are given in Table 6 [5].

The F&EI was calculated for the three proposed processes: (i) process with neat CO₂, (ii) process with neat *Hexane* and (iii) process with a mixture of CO₂-Hexane. The unit chosen to quantify the risk was the reactor setup because it is the most critical plant unit (exothermic reaction occurs), and because its operation is known in detail from the laboratory runs under H₂ and CO₂ pressure.

The results of our calculation are shown in Figure 8, where the different processes are considered (see operating pressures on the right). The Dow F&EI reaches the highest rating for the pure propane process because of the propane flammability. Pure hexane comes next with an index of 90-60, either pure or mixed with CO₂. And finally, the least hazardous process is the pure CO₂ process, at the cost of a very high pressure (35 MPa), which is obviously too high. Likely, the most interesting process as far as hazard is concerned is *Hexane*-CO₂ process, with about the same hazard of a standard hydrogenation plant.

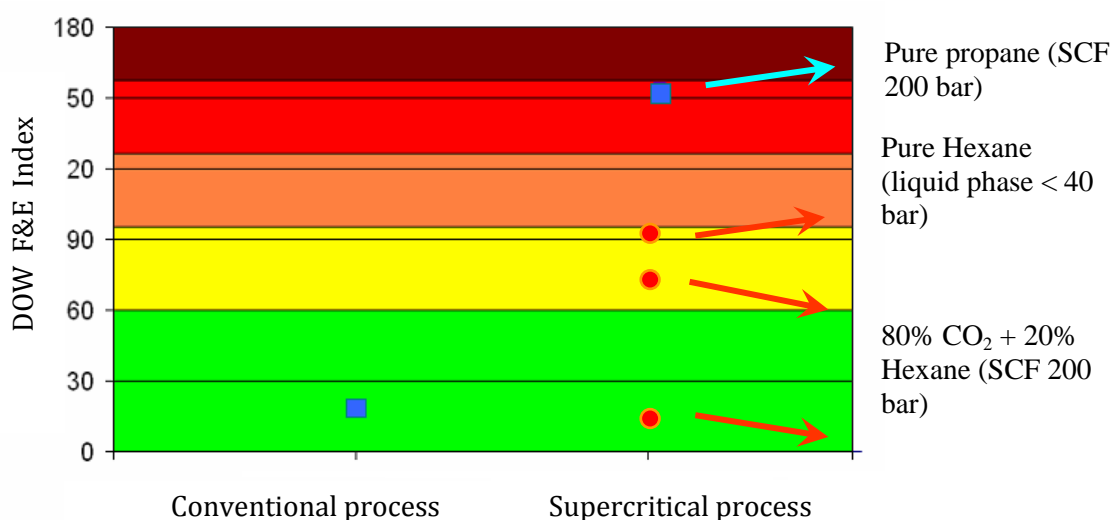


Figure 8. Dow F&E Index for different SCF processes

CONCLUSIONS

A process design study on the vegetable fat oil hydrogenation has been done making an estimate of three different plants operating with SCF. One plant was with neat CO₂, another with superheated liquid hexane, and a third with CO₂ and co-solvent (hexane). Based on the Dow F&EI, the process using only solvent presents a high value. For this process, the risk is reduced by using cosolvent, but less risk is obtained with a larger investment (and a lesser return on investment). At the beginning of the research, it was believed that there would be an optimum mixture of co-solvent in which economy and safety would equilibrate. But later, it was seen that the more inexpensive process was not the safer one. Probably the process with only hexane (as a superheated liquid) would provide the best compromise between cost and quality of the product. For the liquid hexane process a further study would be needed to select a lower-temperature, high activity catalyst.

ACKNOWLEDGMENT

The research presented here has been supported by the Ministry of Education and Science, Madrid, Projects nº CICYT AGL 2006-05156/ALI, through personal contracts with MJ. Mayorga and D.Cuevas.

REFERENCES

- [1] SANTANA, A, M.A. LARRAYOZ, E. RAMÍREZ, J. NISTAL, F. RECASENS, Sunflower oil hydrogenation on Pd in supercritical solvents: Kinetics and selectivities. *J. of Supercritical Fluids* 41 (2007) 391–403
- [2] FOGLER, H.S., *Elements of Chemical Reaction Engineering*, 4th Ed., Pearson, 2006
- [3] VAN DEN HARK, S.; HÄRRÖD, M. (2001) Hydrogenation of Oleochemicals at Supercritical Single-Phase Conditions: Influence of Hydrogen and Substrate Concentrations on the Process. *Appl. Catal. A: General* 210, 207-215
- [4] HÄRRÖD, M., Low *trans* frying oils by Selective Supercritical Single Phase Hydrogenation. 97th AOCS Annual Meeting & Expo, St Louis, 30 April – 3 May, 2006.
- [5] Dow Fire & Explosion Index, 7th Ed., AIChE, New York, 1994
- [6] PERRUT, M., Private Communication