COMPARATIVE SUSTAINABILITY STUDY BETWEEN THE TRADITIONAL BATCH AND THE SUPERCRITICAL CONTINUOUS SUNFLOWER OIL HYDROGENATION PROCESSES

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Introduction

Supercritical fluids are increasingly considered in the processing of some natural products, in the food, biotechnological, in the fragances, and fine chemical industries [1]. In these processes the supercritical fluid can be easily recovered from the reactor and recycled with minimal impact on the environment, very little energy expenditure, and without residual contamination in the product. Recently, an interesting account of the use of SCF in clean catalytic hydrogenation reactions has been published [2].Our purpose in this work is to evaluate the sustainability consequences that would involve the substitution of one part (1/6) of a discontinuous plant production for a supercritical continuous plant of the same output. We start with a traditional batch plant with a total capacity of about 76500 tonnes per year. The new supercritical plant will have a similar capacity in order to enable us to compare the total amounts of raw materials, water and energy consumed, as well as the incidences in toxicity, pollution and safety from both studied processes. To sum up, our main purpose is to evaluate the economical and ecological viability of this change from the results obtained, including the payback period.

1. THE PROBLEM

The present plant has a load of 5000 kg oil in each of 4 reactors. The resulting production is of 9555 kg/h for the present production schedule. In order to make the process comparable with the continuous production, the production has been optimized by reducing dead times performing 6 batch per lot. Production can be optimised by reutilization of some of the equipment (4 reactors and 2 filters) and carrying out operations in an out of phase mode. In this way a reduced cycle time with respect to the original for the traditional process is obtained. The production derived from this scheduling will be compared with the supercritical process,hence assuming a certain degree of optimization in the batch plant. The data for the batch process, including fire and explosion assessment, can be obtained from the author corresponding to the conditions of the plant with 4 reactors and two filters. This uses Ni Raney as a catalyst and sunflower oil as fat.

2. SELECTIVE HYDROGENATION OF EDIBLE OILS

The oils are hydrogenated to reduce colour and odour, to improve stability and mainly to increase the melting point, so that a solid or semisolid results at room temperature The main

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disadvantage is that certain nutritious losses take place, thin oils disappear (oleic, linoleic) and the formation of trans (C18:1, elaidate) and saturated products that are less healthy. With respect to the catalysts, nickel is used owing to the low cost, but its activity decays. With respect the isomer selectivity and trans, platinum and palladium are superior and they react to lower temperatures in comparison with nickel.

3. SUSTAINABILITY METRICS

We will use the following intensities based on Bridges methodology [3] for a unit mass of product. We consider the following indices:

1. Material Index
2. Energy Index
3. Water Index
4. Toxics Index
5. Pollutant Index
6. Dow´s Fire & Explosion Index to account for process safety.

These indices or intensities are constructed as a fraction with an impact in the numerator and an output in the denominator in kilograms of useful hydrogenated oil. Except for the Dow Index, which is not a ratio.

4. SUPERCRITICAL CONTINUOUS PROCESS

A bench-scale continous process has been developed in the UPC. The results given here were obtained with Hysys for separations. To design the reactor, an special solver with various reactor model combinations, was used. The total plant capacity is 12307 mt/year, based on a vapour phase hydrogenation using DME or propane as SC solvents. The pressure with CO2 to achieve SC conditions is larger than with C3 solvents (100 bar more). The following sections of the plant are:

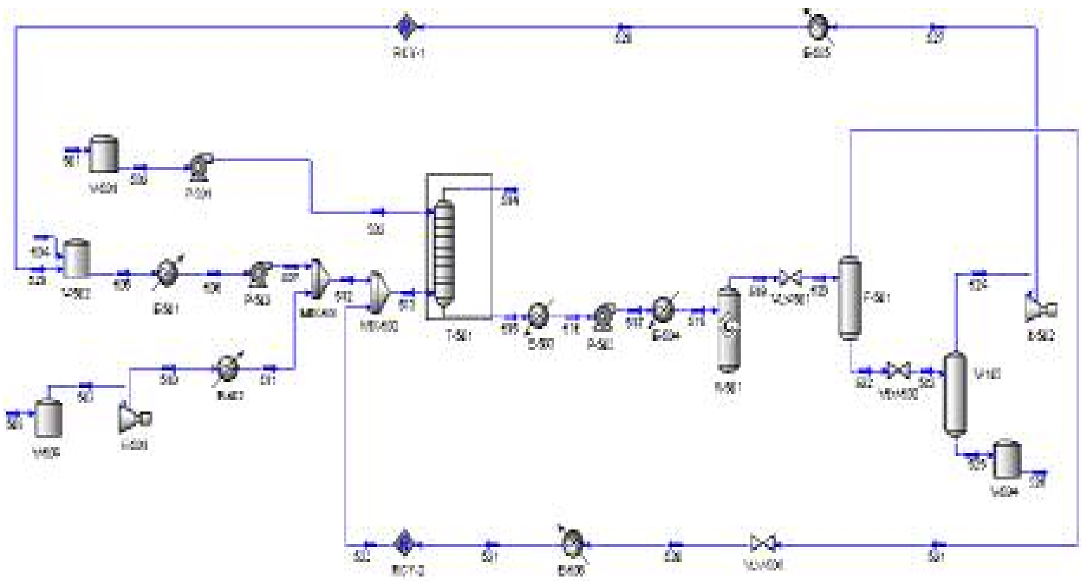

Fig 1. Process flow diagram of the SC process, J.Sans [5]

1. Makeup section (Oil, hydrogen, DME), pumping and heating to SC conditions.
2. Reactor section. This is a packed bed reactor filled with supported Pd catalyst.
3. Separation DME/Oil and unreacted H2. Two stage separators for H2 and DME recovery.
4. Recycle streams of H2 and DME

In order to adjust pressure and temperature conditions at reactor feed, the critical points of the multicomponent mixtures was calculated to avoid condensation using the Peng-Robinson EOS with simplifications (Sans, 2004). Safe operation conditions are about 200 bar and 183º-200ºC, with 1 mol% oil, 9% H2 and 90% DME. The catalyst is 0,5%Pd on γ-alumina. The packed bed is cooled with coils inmersed in the catalyst mass (1314 kg) for easy catalyst removal. Space time is 517 s, and exit iodine value = 95 (inlet = 130). Reactions runs were tried first on a Robinson-Mahoney gradientless reactor. Details on reaction conditions are given in Ramírez et al. (2003) for SC propane. Reaction rate in DME, are somewhat faster than in propane , depending on the catalyst.

The advantage of the SC reaction medium is less trans fatty esters (about 3% trans C18:1 on Pd vs 35% trans for the conventional process on Ni) compared with a larger solubility of lipids of reaction products together with the advantages of a continuous process over the batch process. With the above conditions, the composition of the hydrogenated sunflower oil is glycerol triolinoleate 53%, trioleate 23% and tristearate
18,5% (initial 15%). The rest are tripalmitate (7%), etc. Trielaidate is close to 0-2% in certain runs.

5. CALCULATION OF SUSTAINABILITY IMPACTS

Material Index. This is defined as kilograms of raw materials wasted, hence not converted into useful product or not used in reaction, per kg of useful product. In the batch process, H2 not consumed is recycled making the process more profitable. There is a oil waste of 5% per lot, due to insufficient cleanup. The hydrogenated oil from the reactor is filtered to recover the catalyst. There is a 21 kg catalyst in a reactor load (0,07%). From this the waste is 8%. In the continuous process the unreacted H2 is recycled completely. A small amount of DME, on the other hand, is vented to the atmosphere or to a torch. The evaporation is rather small, and it accounts for 60 kg DME/year. This can be reduced using VOC adsorption. The amount of catalyst loss is small.

Energy Index. Mass of natural gas per unit product mass. The fuel conversion of energy/mass is 52000 kJ/kg fuel. The kilograms of steam or the kWh of electricity are converted assuming the following factors: 0,92 kJ/kJ of fuel and 0,31 kWe/kW of heat (that is 92% combustion efficiency and 31% thermoelectric conversion efficiency). In the batch process, natural gas is spent to generate steam in the boiler. This is used to heat up the reactors to reaction temperature. Mechanical agitators use electricity. This is used also in the refrigeration machine and auxiliary pumps. In the continuous process, heat is used in the thermal oil heaters, with a high conversion efficiency (95%). A total of 15 kg/h natural gas is consumed. The heat flows and the electric powers determine the consumed energy. The thermal fluid in the hydrogenation reactor usually releases heat since the hydrogention is exothermic. A steam flow of 167 kg/h is recovered from the reactor, that represents a saving of 7 kg/h of natural gas in the boiler (this is considerd negative in the energy bill). In the continuous process, the high pressure pump is the item that uses more energy.

Water Index. In the batch process, water is used as a coolant in the reactor. Cooling tower water is used. So the net water expenditure is the waste evaporation of into the environment. This represents 2% of the cooling water flow.

Toxicity Index. In the batch process, there is a higher relative toxicity due to the nickel losses. An advantage of the SC process is that no losses are expected from the Pd catalyst.

Pollutant Index. This refers to greenhouse gases.Thus corrresponding to annual CO2 emissions from the boiler as well as the electrical energy or kWh/y taken from the electrical company supplier. For the supercritical process, we also consider the solvent emitted that cannot be adsorbed and the CO2 from electrical energy generation.

6. SAFETY

Low pressure hydrogenation plants and supercritical process plants require attention to personal risks due to high pressure and fire. Additionally, solvents like DME are compressed gases that may have anesthetic effects and are flamable. Even carbon dioxide (not flammable) may involve Bleve accidents. Also above 8% vol in air, may be toxic. Burns may result from exposure to dryice temperatures.

In order to measure the Safety Index, the Dow index has been calculated. This is relative to a maximum (maximum danger). The Dow index has become popular for process safety assessment worldwide.

In the supercritical procedure, an important point is the pressure release. High pressure considerations in the Dow evaluation imply a relief-valve opening pressure of 360 bar. This give a penalty factor of 1. In our case, gases are flammable, therefore the factor to use is 1,3. On the other hand, in the batch process the maximum pressure is 6 bar (at most), therefore the penalty factor is only 0,3. Since H2 is a compressed gas, a factor = 1,2 must be used. Why do we use DME or propane instead of CO2:

1. DME is a solvent already used in skin and hair care as propellant, so studies should soon be available for food usage.
2. The required CO2 pressure is about 100 bar higher than DME or propane
3. DME is a better oil solvent than C3 and much better than CO2.
4. Fat hydrogenation on Pd is a somewhat faster in DME than in propane

7. ECONOMIC ASSESSMENT

For the two plants, a discounted cash flow study was made. The results are the profitability and the payback period. The investment for the SC plant is 15 MEur (12000 mt/y), whereas for the conventional equivalent plant the investment is only 10 MEur. The difference in production costs is 20 Eur/mt sales more expensive for the batch process.

The payback time is 7 years for the SC plant, and 4 years for the batch plant. Therefore the SC plant is economically viable, but more investment for unit otput is needed. This should be justified in terms of the product quality.

CONCLUSIONS

The results of the impacts are given in the following Table 1.

Table 1. Comparison of Impacts for Hydrogenation in batch and continuous process (SCF)

Vegetable Hydrogenation Plant, Batch process

Material (kg/kg)	Energy (kgGN/kg)	Water (kg/kg)	Toxics (g/kg)	Pollutant (kg/kg)	IIE (%)
1,01586	0,01512	0,20256	0,16120	0,31129	10,3

Vegetable Hydrogenation Plant (same output), Continuous supercritical process

1,001109	0,00741	0,140066	0,00053	0,04106	98,3

IIE = Dow F&E Index as % of maximum

The traditional process has a higher material index because of loading-unloading-cleaning cycle in the reactor, and due to the catalyst recovery from it. The energy impact is also higher in the conventional plant. The energy recovery at the reactor is easiest for the continuous process. The wastes (toxics and pollutants) as well as water usage are less for the SC process. Instead, the Dow F&E index is higher as expected for the SC process. As we

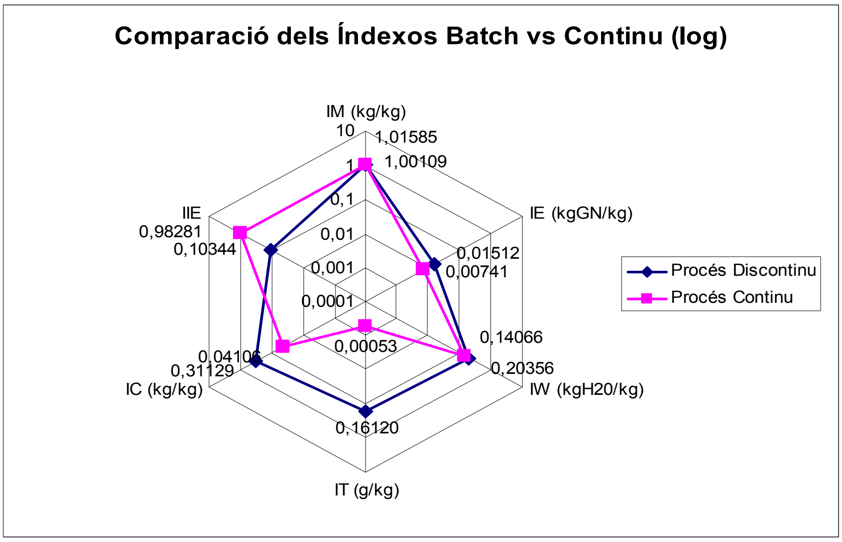

Fig 2. Ecological footprint of supercritical (continuous) and conventional (discontinuous) hydrogenation processes (IIE is Dow Fire & Explosion Index), logarithmic scales.

see, the SC process emits less greenhouse gases and it is less toxic. On the other hand the payback time is more than double than that of the batch process.

The final conclusion is that we can introduce the SC plant as a test plant to check the effciciencies and the utilities that we have found. The driving force for the investment is the increased quality of the margarines. The SC process is more sustainable but less profitable.

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REFERENCES

[1] Perrut, M., , *Ind. Eng. Chem. Res*., 2000, 39 (12) 4531.
[2] E. Ramírez, S. Zgarni, M.A. Larrayoz, F. Recasens, *Eng. Life Sci.*, 2002 (2) 257
[3] Schwarz et al., *Chem Eng Progress* June 2002
[4] Ramírez, E., F. Recasens, M. Fernández, MA.Larrayoz, *AIChE J*, 2003
[5] Camps,S. , Sans, J. , PFC, ETSEIB-UPC, June 2003, Barcelona, Spain