

# INTENSIFICATION OF MULTIPHASE REACTORS USING SUPERCRITICAL SOLVENTS

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## Summary

There is a strong emphasis on the development of more sustainable processes. Supercritical fluid technology can provide the basis for decentralizing chemical processes and for achieving material recycles for sustainable society. CO<sub>2</sub> is often promoted as a sustainable solvent, as CO<sub>2</sub> is non-flammable, exhibits a relatively low toxicity and is naturally abundant. Supercritical continuous hydrogenation of sunflower oil was carried out on supported Pd catalyst. The catalytic performance in three kinds of solvents (propane, DME and CO<sub>2</sub>+Hexane) was compared. The reaction rate and product distribution were strongly influenced by the type of reactor, solvent, total pressure, and feed composition.

## Keywords

Sustainability; Process intensification; Green CRE; Multiphase and particulate reactors.

## Introduction

In a slurry reactor, dissolving the liquid heavy-oil phase, allows to change H<sub>2</sub> concentration independently of the solubility limit (Henry's law) on the catalyst surface, so the oil and H<sub>2</sub> concentrations are only determined by their feed concentrations, their external mass transfer rates and by phase-equilibrium stability of the multicomponent mixture. So a slurry process can be converted in a vapor-phase continuous fixed bed process [1], applied this concept to fat oil hydrogenation. The intensified process has two advantages: reaction can be carried out in the solvent phase, thus a continuous process is possible, avoiding repetitive batch processing. Secondly, extremely large reaction rates are possible, compared to the slurry process.

Single-phase, continuous hydrogenations of sunflower oil on supported Pd catalysts were carried out in a gradientless microreactor using propane or DME as SC solvent or a CO<sub>2</sub>+Hexane mixture as SC modifier. Kinetics and intraparticle diffusion were studied as well as the effect of operating variables on sunflower hydrogenation process to assess the reduction in the formation of *trans* C18:1 isomer, an important parameter in industrial food application.

## Results and Discussion

The kinetics for three different sunflower oil hydrogenation systems: eggshell 0.5% Pd/Al<sub>2</sub>O<sub>3</sub>-SC DME, uniform 2% Pd/C-SC DME and uniform 2% Pd/C-SC propane was determined using an experimental design [2]. The operating conditions were chosen to ensure the presence of an unique single-phase (1 mol% of sunflower oil, 4-10 mol

% of H<sub>2</sub> and 89-95 mol% of solvent, 20 MPa, 443-513K). The stirrer speed was held constant at 157 rad/s.

The kinetic expressions follows the reaction network (See Fig. 1) proposed by Wisniak and Albright [3]:

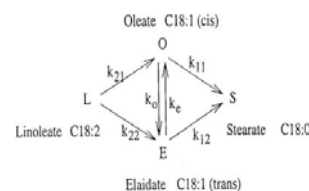


Fig. 1. Accepted triglyceride interconversion during hydrogenation of vegetable oils (H<sub>2</sub> not shown).

in which an order one-half with respect to hydrogen was considered for the reactions involving di- and mono-unsaturates and first order for the formation of saturates from oleic or elaidic fatty acids.

Table 1 establishes a comparison between the estimated constants for several reaction systems. It is noteworthy that for the same type of catalyst (uniform 2% Pd/C), the estimated rate constants values are higher in the case of DME as reaction medium than in propane whereas the isomerisation rate constants are about the same in both solvents. On the other hand, for the same operating conditions using DME as solvent, the estimated rate constants for uniform 2%Pd/C catalyst are somewhat higher than those for eggshell 0.5%Pd/Al<sub>2</sub>O<sub>3</sub>. The net rate of hydrogen uptake per active metal weight at similar conversion (around 20%) is slightly higher in the case of uniform 2%Pd/C catalyst irrespective of reaction solvent.

Table 1. Estimated rate constants for sunflower oil hydrogenation (at 483K and 20MPa).

Parameters	DME		Propane
	0.5 % Pd/Al <sub>2</sub> O <sub>3</sub>	2% Pd/C	2% Pd /C
k <sub>21</sub>	9.27x10 <sup>-4</sup>	2.46x10 <sup>-2</sup>	9.17x10 <sup>-3</sup>
k <sub>22</sub>	2.01x10 <sup>-3</sup>	8.75x10 <sup>-3</sup>	1.53x10 <sup>-4</sup>
k <sub>11</sub>	3.05x10 <sup>-3</sup>	3.93x10 <sup>-2</sup>	3.04x10 <sup>-2</sup>
K <sub>12</sub>	6.22x10 <sup>-3</sup>	3.95x10 <sup>-3</sup>	9.94x10 <sup>-4</sup>
k <sub>0</sub>	7.25x10 <sup>-3</sup>	2.83x10 <sup>-2</sup>	2.63x10 <sup>-2</sup>
k <sub>E</sub>	7.85x10 <sup>-2</sup>	1.47x10 <sup>-1</sup>	1.09x10 <sup>-1</sup>
χ <sup>2</sup>	1.91x10 <sup>-4</sup>	4.85x10 <sup>-4</sup>	2.28x10 <sup>-5</sup>
-r <sub>H<sub>2</sub></sub> <sup>c</sup>	0.88	1.1	0.99

<sup>a</sup> mol<sup>-1/2</sup> (m<sup>3</sup>)<sup>3/2</sup> kg Pd<sup>-1</sup> s<sup>-1</sup>; <sup>b</sup> mol<sup>-1</sup> (m<sup>3</sup>)<sup>2</sup> kg Pd<sup>-1</sup> s<sup>-1</sup>; <sup>c</sup> Total H<sub>2</sub> uptake rate in mol s<sup>-1</sup> kg Pd<sup>-1</sup>

It is worth mentioning the great potential of SC continuous hydrogenation as compared with the conventional batch process, as it allows using a final product with the required plasticity as well as a low *trans* % value by properly choosing the reaction conditions. It is seen that for the same degree of hydrogenation (IV=90-110), the *trans* % obtained in this work (2-6 wt %) is quite lower than that obtained in the conventional process (11-30 wt%).

Despite that propane and DME are considered a green solvent, they are flammables, this is the main drawback in comparison with CO<sub>2</sub>. 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 and the safety in the processes.

The Table 2 shows the comparison between solvents and selectivities. The selectivity values for eggshell Pd/Al<sub>2</sub>O<sub>3</sub> in DME as solvent are better than those for uniform Pd/C irrespective of solvent. The operation conditions on CO<sub>2</sub>+Hexane are milder than in the other solvents. The difference of temperature of the two processes is 153 K where the cost and safety for the hydrogenation process are decreased.

Table 2. Linoleic selectivity and trans yield in the partial hydrogenation of sunflower oil.

Catalizador (dp)	Proceso	T (K)	P (MPa)	S <sub>Lo</sub>	S <sub>i</sub>
25% Ni-Silica (powder) [4]	Batch/slurry	393	0.3	10.8	2.5
Uniform 2% Pd/C (0.92 mm)[5]	Continuous Recycle Reactor	483	20 Propano	4	0.14
Uniform 2% Pd/C (0.47 mm) [5]	Continuous Recycle Reactor	483	20 DME	2	0.4
Eggshell 0.5 Pd/Al <sub>2</sub> O <sub>3</sub> (2mm) [5]	Continuous Recycle Reactor	483	20 DME	9	0.13
Eggshell 0.5 Pd/Al <sub>2</sub> O <sub>3</sub> (2mm) [6]	Continuous Recycle Reactor	333	25 CO <sub>2</sub> +Hex	4.14	1.8

$S_i = -100(AC_{r,max}/A(IV))$ ,  $S_{Lo} = AC_o/AC_s$ .

The comparative sustainability study [7] between the traditional batch and the supercritical continuous hydrogenation using propane as solvent was carried out based on Bridges methodology [8]. The sustainability impacts of

supercritical process showed in the figure 2 were practically the same comparing the impacts of conventional process except the toxicity index (low index for supercritical process) and the Dow's fire & explosion Index.

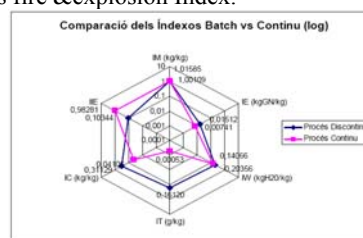


Fig. 2. Ecological footprint of supercritical (continuous) and conventional (discontinuous) hydrogenation processes, log. scales.

## Conclusion

The main benefits of continuous supercritical hydrogenation are process intensification (smaller reactors and reaction with extraction) and improved selectivity due to the independent control of operation variables. The superior heat and mass-transport properties of supercritical fluids, on the other hand, allow the use of continuous reactors in place of the traditional batch units.

Application of supercritical solvents in a continuous flow reactor seems to be attractive for new sustainable, continuous vapour phase process.

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