

Pd-CATALYSED HYDROGENATION OF SUNFLOWER OIL IN SC PROPANE: DESIGN OF EXPERIMENTS IN A WELL MIXED CONTINUOUS REACTOR

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In this paper, we report on a study of the effect of the supercritical-solvent process conditions (temperature, H₂ mol composition, liquid hourly space velocity (LHSV) and stirrer speed) on the *trans* acid content and the extension of single phase sunflower hydrogenation (expressed by the iodine value) in a CSTR reactor using a 2 % Pd/C as catalyst and SC propane as a reaction medium in order to assess them. 155-215 °C, 30-70 h⁻¹, 2-10 H₂ mol %, 500-2500 rpm were the experimental ranges of the operational variables. The observed trends shown the great influence of variable interactions (e.g. LHSV-H₂ % and T-H₂ %) on the desirable responses whereas the stirrer speed is negligible for the velocity range studied.

INTRODUCTION

In vegetal oil hydrogenation processes, unsaturated fatty acid chains of triglycerides are reacted with hydrogen in the presence of a catalyst in order to convert liquid oils to the semi-solid form mostly for greater utility in certain food uses (e.g. margarine and shortenings) thus increasing the stability of the fat to oxidative rancidity [1].

Common problems present in multiphase catalytic hydrogenations (such as H₂ mass transport limitations, limited rates of reaction, temperature control due to heat of reaction) are eliminated when a SC fluid is used as the reaction solvent e.g. CO₂ or C₃H₈ [2-5].

In a previous work [6], we presented preliminary experimental data on SC single-phase hydrogenation of sunflower oil. It was shown that is possible to obtain different characteristics of the final hydrogenation products using different reaction conditions.

In the present work we study how the operational variables affect sunflower hydrogenation in order to assess the iodine value and the *trans* content at the same time for a further industrial food application.

MATERIALS AND METHODS

The experiments were performed in a Robinson-Mahoney type, gradientless, fixed bed, annular flow reactor (total volumen ca. 50 cc) working isothermally in well-mixed flow and fed with the supercritical single phase mixture of the vegetal oil (SIGMA, IV = 130), propane (Praxair, 99.5% purity) and hydrogen (GC grade, 99.9999% purity). The catalyst used was 2 wt % Pd/C (Degussa-Hüls AG) with uniform metal loading. The experimental setup has been reported previously [6].

The catalytic hydrogenation rates and the *trans* fatty acid content were determined by the measurements of the iodine value (IV) using Wijs titration method and by high performance liquid chromatography (2410, Waters) respectively from the recovered product.

The experiments were carried out according to a central composite design (2^4 factorial design + star points (SP) = (2×4) + center point (CP) = 25 experiments) [7]. We varied the reaction temperature (158-217 °C), hydrogen molar composition (2-10%), liquid-oil hourly space velocity (LHSV) ($30-70 \text{ h}^{-1}$) and the stirrer speed (500-2500 rpm). The total system pressure, the molar oil concentration and the catalyst mass were kept constant at 200 bar, 1 % and 0.1085 g, respectively. The calculations were done using the statistical software package Minitab [8].

RESULTS

Table 1, shows the experimental reaction conditions along with the values of the iodine value (IV) and the *trans* acid content.

Table 1. Central composite experimental design

Experiment	Temperature (°C)	LHSV (h^{-1})	H2 mol %	Stirrer speed (rpm)	IV	<i>Trans</i> wt %
1	175	46	4	1000	95.80	2.34
2	205	46	4	1000	112.22	2.42
3	174.5	60	4	1000	119.58	4.41
4	200.5	60	4	1000	120.31	2.32
5	170.5	40	8	1000	119.81	2.82
6	203.5	40	8	1000	111.78	6.20
7	172	60	8	1000	118.57	1.85
8	203.5	60	8	1000	110.65	2.64
9	173	46	4	2000	116.33	1.85
10	203.5	40	4	2000	112.52	3.39
11	172	60	4	2000	122.35	4.04
12	200.5	60	4	2000	126.29	2.52
13	171	40	8	2000	121.87	2.53
14	203.4	40	8	2000	112.47	3.30
15	172.5	60	8	2000	121.24	1.65
16	201.5	60	8	2000	110.30	3.19
17(CP)	188	50	6	1500	117.59	2.32
18(SP)	158	50	6	1500	120.3	1.10
19(SP)	217	50	6	1500	95.17	4.62
20(SP)	185	30	6	1500	119.44	2.12
21(SP)	187.5	70	6	1500	113.15	2.37
22(SP)	186	50	2	1500	121.04	2.26
23(SP)	186.5	50	10	1500	110.66	3.11
24(SP)	186.5	50	6	500	121.34	2.55
25(SP)	187.5	50	6	2500	117.20	2.18

The collected response data were fit a full mathematical model using the Minitab software, which includes the four main effects (T, LHSV, % H₂ and rpm), six two-way interactions, and four quadratic-way interactions. Using the values in the p factor (< 0.05) of the estimated effects and coefficients table was determined which of the effects are significant: LHSV- H₂ % and T- H₂ % interactions more than the main effects for T, LHSV or H₂ % whereas the stirrer speed was the minor importance.

The estimated standard deviation (S) of each one of the final polynomial regression models (S = 6 for IV and S= 0.73 for *trans* content) were considered low. These deviations were due mainly to some experimental (e.g. fluctuations in the gas feed flows) or analytical (lack of precision) problems.

The stirrer speed has a non-significant effect on the expected responses IV and *trans* content at all experimental values of H₂, LHSV and temperature which is inferred also from results of Table 1.

In general, the increase of temperature or LHSV or H₂ mol composition at medium values of the other variables increases the extent of hydrogenation and the *trans* content as could be expected (see Table 1, experiments 17 to 25) but in other cases the effect of each one of variables on the responses isn't so clear due to the existing interactions among them. For example, Figure 1 represents IV as a function of LHSV and H₂ at constant temperature. The

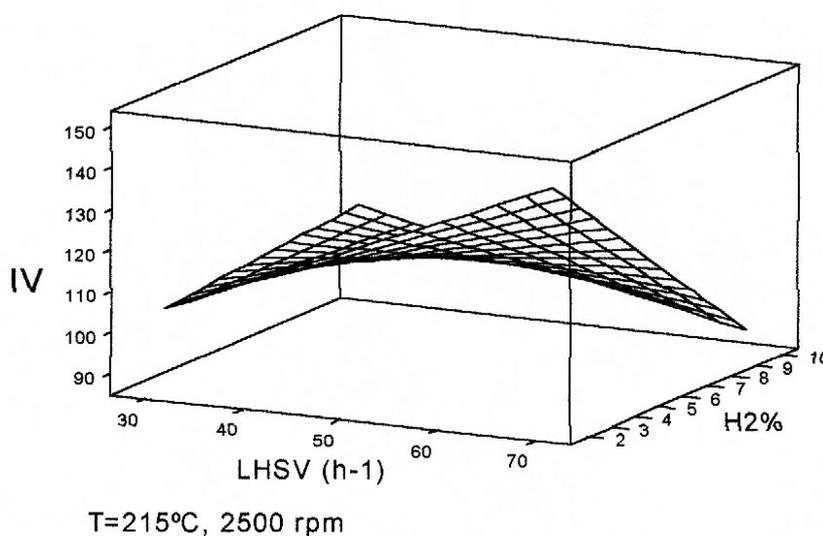


Figure 1. Iodine value as a function of LHSV and H₂% at 215°C and 2500 rpm.

increase of H₂ mol %, at any value of LHSV and high temperature, increases the extension of the hydrogenation. However this behavior does not show up for an increasing value of LHSV at any % H₂, since conversion can increase or decrease depending on the value taken by H₂.

As far as *trans* % is concerned, the increase in LHSV for any H₂ % makes the *trans* content to go down (see set of experiments 2-4 and 6-8, respectively) while the opposite effect is observed for the increase in %H₂ for any LHSV and high temperature (e.g. experiments 2-6 and 4-8).

The temperature-%H₂ interaction indicates that either factor improves the extension of reaction irrespective of the other operating variables (set of experiments 12-16 and 15-16). The *trans*-content as a function of T and %H₂ is shown at Fig. 2. The *trans* acid content at high LHSV (> 60 h⁻¹) decreases with the temperature increase at H₂ % < 7 or when the H₂% increases at any value of temperature.

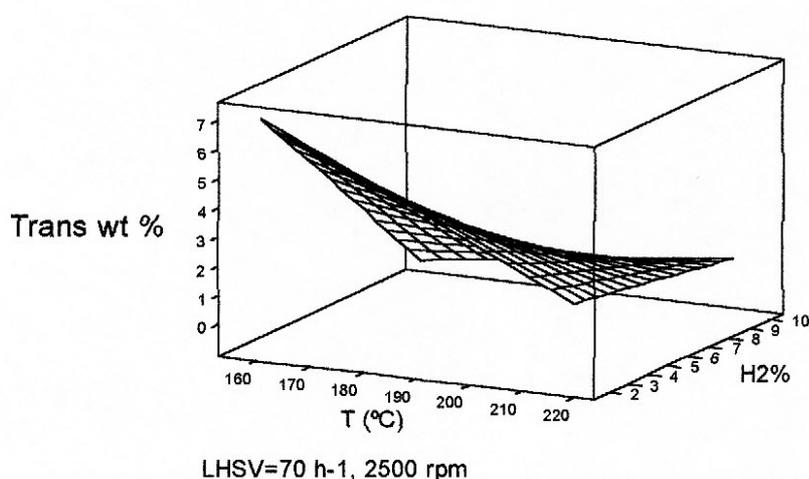


Figure 2. *Trans* fatty acid content as a function of temperature and hydrogen content at 70 h⁻¹ and 2500 rpm.

From the study of these two interactions, it is possible to determine the operating conditions that provide a moderate hydrogenation extent (IV <100) together with a *trans* content below practical limits (<3%), e.g. with large settings for the variables (T > 195 °C, LHSV > 60h⁻¹, H₂ mol % >8).

CONCLUSIONS

The results show that IV and the *trans* content depend mainly on the liquid oil space velocity (LHSV)-hydrogen composition interaction and on the temperature respectively. While the effect of stirrer speed is less significant in a recycle reactor, this is important in an integral, packed-bed bed without recycle. The trends observed indicate that it is possible to obtain a final hydrogenation product with a low *trans* content (lower 3 wt %) and a moderate hydrogenation extent (IV = 90-110) using different sets of operational conditions e.g. high

values of temperature, LHSV and hydrogen molar composition ($T > 200$ °C, LHSV = 60 h^{-1} and H_2 molar % = 9).

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