

## VENTURI TUBE AND SINGLE PIPE INLET AS GAS DISTRIBUTORS IN HYDROGENATION OF RAPE SEED OIL\*

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The effect of hydrogenation conditions on rate of hydrogenation of rape seed oil was studied in a laboratory stirred tank reactor of 250 ml volume, with nickel on kieselguhr catalyst within the range of conditions ( $150 \leq t(^{\circ}\text{C}) \leq 190$ ), ( $0.1 \leq P(\text{MPa}) \leq 1.0$ ), and ( $0.01 \leq c_{\text{Ni}}(\%) \leq 0.37$ ). On the basis of these results a comparison of the effect of a Venturi tube and single pipe gas inlet as gas distributors on hydrogenation rate was made in a bench scale unit of 5 l volume.

Venturi tube (VT) as gas distributors for *g-l* reactors were studied extensively at BASF (refs<sup>1-4</sup>) and some design aspects were considered by Henzler<sup>5</sup>. A considerable attention to this type of gas distributor has also been paid recently in our Institute<sup>6-9</sup>.

As concerns the use of VT as gas distributor in hydrogenation of edible oils very little is available in literature. This type of distributor has been used for many years by Co. Buss<sup>10</sup> which is at present the sole producer of this type of modern hydrogenation units.

As concerns modelling of the mechanism of hydrogenation of edible oils, the most extensive study has been published by Schön *et al.*<sup>11-15</sup> and other interesting studies were made by Wisniak<sup>16</sup>, Marangozis<sup>17</sup>, and Hančil<sup>18</sup>.

At the request of Czechoslovak industry of edible oils, which is preparing a reconstruction of most of its existing hydrogenation units (mostly batch type units of 5–10 tons of oil/batch with hydrogen inlet through a single pipe), this study has been performed with the aim to obtain information on possible improvement of the hydrogenation process (reduction of batch time or reduction of catalyst consumption). To make such a study possible, data had to be collected on basical behaviour of rape seed oil at hydrogenation within the range of industrially interesting conditions (temperatures, pressures, and catalyst concentrations).

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## THEORETICAL

With reference to the above quoted studies the complex mechanism of hydrogenation of edible oils is still not fully understood. In our case we were interested in a simple correlation of the overall reaction rate, *i.e.* reduction of the Iodine volume  $V_I$  and not in description of the mechanism of these reactions which were adequately treated elsewhere. Out of available literature the most suitable for our purpose was that by Bern, Hell and Schöön<sup>12</sup> who expressed the reaction rates of individual fatty acids by use of the power type equation with one exponent and the rate constant dependent on temperature. These effects were expressed in the form of tables. For our purpose we have not found this approach as suitable, moreover neither our  $V_I$  nor their log are linear in dependence on time.

For these reasons for description of the overall hydrogenation rate  $V_I$  the simplest linearisation method for the dependence of conversion on time was used which could have been found. For conversion expressed by the iodine volume  $V_I$

$$X_A = (V_{I,i} - V_{I,t})/V_{I,i} \quad (1)$$

all experimentally obtained conversions presented in this study were linearized by the relation

$$X_A^2 = k_1 t . \quad (2)$$

Coefficients  $k_1$  of this relation were obtained for time intervals acceptable with regard to the experimental unit and the accuracy of the analytical methods used (5–15 min) and which were measured up to hydrogenation times interesting from the point of view of the practical application of this process, *i.e.* up to about 2 h.

For the reaction rate, the following relation can be then written

$$r_{V_I} = dX_A/dt = -k_1/2X_A . \quad (3)$$

## EXPERIMENTAL

Two experimental units were used: laboratory stirred tank reactor operated batchwise (LSR) and the bench-scale unit (BSU).

LSR was a cylindrical vessel of diameter  $D = 54$  mm, length  $L = 200$  mm. The stirrer was driven by magnetic drive, so that no seals were needed. Speed of mixer rotation was constant and equal to 2 400 rpm.

BSU was a cylindrical vessel with  $D = 92$  mm and  $L = 590$  mm, and three types of distributors were tested: a) single pipe, where hydrogen was introduced into the oil bed through a pipe with  $d = 6$  mm; b) spider type cross distributor formed by two perpendicularly situated pipes ( $l = 80$  mm) at the end of the same pipe as used in the first case, with 8 equidistant holes drilled in their bottom side ( $d = 2$  mm), distances of holes were 10 mm; c) Venturi tube (VT) used as distributor which is demonstrated in Fig. 1. Oil from the reactor is here circulated through

the VT where hydrogen is sucked in from the upper part of the reactor. In cases *a*) and *b*) hydrogen is introduced in excess which is vented by the safety valve which retains also the required constant pressure in the vessel. In the case *c*) the system can be operated also without venting the excess hydrogen.

The same rape seed oil was used in each experiment. It has been heated with the known amount of catalyst to the required temperature. The reactor was connected to the vacuum pump and evacuated for 20 min. Then hydrogen was introduced into the reactor and parameters of the mixture were measured at fixed time intervals (operating conditions and primarily the change of iodine volume of the mixture with time).

In all experiments, a mixture of a fresh Ni catalyst on kieselguhr (containing 12.6% Ni) and spent catalyst (containing 24.2% Ni) was used at total Ni concentration 0.37%.

For determination of iodine numbers, the analytical method by Hanus<sup>19</sup> has been used.

## RESULTS AND DISCUSSION

### Laboratory Stirred Tank Reactor (LSR)

**Temperature.** Hydrogenations were performed at temperatures 150, 170, and 190°C at two pressures: 0.16 and 1.0 MPa. The results of both series of these measurements are given in Table I.

Within the range of temperatures studied (for the selected type of catalyst the hydrogenation temperature in industry is usually  $t \sim 180^\circ\text{C}$ ), the hydrogenation rate increases with temperature. In some experiments induction periods (IP) appear. The constants  $k_1$  (relation (2)) and IP obtained for these measurements are given in Table II.

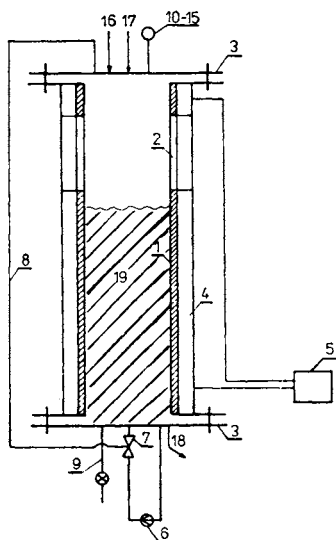


FIG. 1

Bench-scale unit (BSU). 1 reactor body, 2 sight glass, 3 reactor lids, 4 thermostatted reactor jacket, 5 thermostat with heating, 6 liquid pump, 7 Venturi tube (VT), 8 gas inlet to Venturi tube from the upper part of the reactor (gas layer-above liquid layer), 9 discharge pipe with valve, 10—15 manometer, thermometer, safety valve, hydrogen inlet, connections to vacuum and inert gas, 16 feeding of the oil, 17 catalyst feed, 18 product outlet, 19 three phase mixture

The dependence  $X_A^2$  vs  $t$  is reasonably linear (Table I). The effect of temperature on IP is plotted in Fig. 2.

Summarizing, the increase in temperature within the studied range (150–170–190°C) has, as concerns the hydrogenation rate, always a positive effect. First of all, it accelerates the reaction rate, secondly it shortens the induction period. These conclusions are evident from the results summarized in Table II.

*Pressure.* The effect of pressure has been measured at 180°C at three pressures: 0.16, 0.6 and 1.0 MPa. Results are listed in Table III.

At pressure 0.16 MPa no inhibition period has been observed, although according to previous paragraph it should be about 7 min. In first 15 min the measured conver-

TABLE I

The effect of temperature. Dependence of  $X_A^2$  on time for LSR. Concentration of catalyst 0.07% Ni (fresh catalyst) + 0.3% Ni (used catalyst)

Hydrogen pressure MPa	Reaction temperature °C	$X_A^2$ at reaction time (min)			
		15	30	45	60
1.0	150	0.0041	0.031	0.055	0.068
	170	0.031	0.060	0.082	0.134
	190	0.106	0.154	0.237	0.275
0.16	150	0	0.001	0.0085	0.0225
	170	0.0014	0.012	0.0024	0.027
	190	0.042	0.086	0.151	—

TABLE II

Dependence of  $k_1$  values and induction periods (IP) on temperature  $t$  and hydrogen pressure  $P$  for hydrogenation of rape seed oil in LSR

Temperature °C	0.16 MPa		1.0 MPa		$k_{1.0}^1/k_{0.16}^1$
	IP	$k_1 \cdot 10^{3a}$	IP	$k_1 \cdot 10^{3a}$	
153	30	0.83	15	1.82	2.2
170	15	0.89	0	2.25	2.5
190	0	2.73	0	5.33	2.0

<sup>a</sup> Calculated using Eq. (2).

sion is higher at all studied pressures than that corresponding to linear dependence of  $X_A^2$  vs  $t$ ; further on, the form of this dependence is reasonably linear (Table III). By analysis of all the experimental data it has been found that at the beginning of all the measurements, fast increase in temperature took place, due to the exothermic reaction. This temperature rise was within 6–10°C, and was the most profound for the reaction rates measured at 1.0 MPa. In the next phase of hydrogenation the temperature was kept practically constant (with 0.16 MPa only the second point is higher). This partially explains the experimentally found higher conversions at the time  $t = 15$  min and also the above mentioned fact that no IP has been observed.

TABLE III

The effect of pressure. Dependence of  $X_A^2$  on time for LSR. Concentration of catalyst 0.07% Ni (fresh catalyst) + 0.3% Ni (used catalyst); reaction temperature 180°C

Hydrogen pressure MPa	$X_A^2$ at reaction time (min)			
	15	30	45	60
0.16	0.024	0.062	0.076	0.093
0.6	0.045	0.077	0.095	0.141
0.6 <sup>a</sup>	0.070	0.097	0.135	0.181
1.0	0.099	0.142	0.184	0.240

<sup>a</sup> Hydrogen vented.

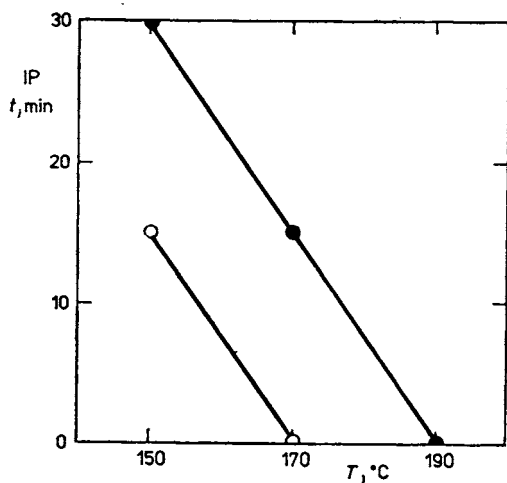


FIG. 2  
Temperature dependence of induction period for LSR.  $c_{cat} = 0.07\%$  Ni (fresh catalyst) + 0.3% Ni (used catalyst); hydrogen pressure ○ 1 MPa, ● 0.16 MPa

The dependence of constant  $k_1$  on  $P$  obtained for the measured dependences  $X_A^2$  vs  $t$  is listed in Table IV.

Three measurements presented in Table III were performed in a closed system to which only the consumed hydrogen was added. For pressure 0.6 MPa this measurement has been carried out also for excess of hydrogen. This excess hydrogen is vented by the suitably fixed safety valve.

Summarizing, due to the higher temperature at which these measurements were performed ( $T = 180^\circ\text{C}$ ), the problem of inhibition periods has been avoided. The presented results prove the positive effect of pressure increase on the rate of hydrogenation, at least for the studied experimental conditions without considering its effect on selectivity.

*Catalyst quantity.* Catalyst quantity affects both the constant  $k_1$  and the induction period IP. The results of experiments at  $170^\circ\text{C}$  for the hydrogen pressure  $P = 1$  MPa are plotted in Fig. 3.

TABLE IV

The effect of pressure. Dependence of  $k_1$  on pressure for LSR, reaction temperature  $180^\circ\text{C}$ ; concentration of catalyst: 0.07% Ni (fresh catalyst) + 0.3% Ni (used catalyst)

$k_1 \cdot 10^3$	1.6	2.4	4.3
$P, \text{MPa}$	0.16	0.6	1.0

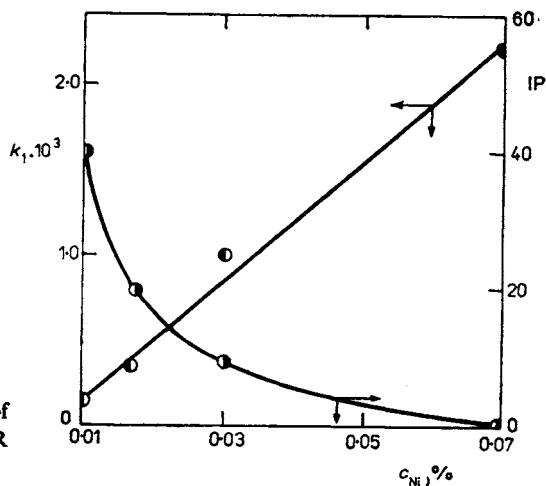


FIG. 3

Dependence of induction period (IP) and of  $k_1$  on catalyst concentration ( $c_{\text{cat}}$ ) for LSR (fresh Ni catalyst)

It is obvious from Fig. 3 that for the studied catalyst, the dependence of  $k_1$  on  $c_{\text{cat}}$  is practically linear, IP strongly decreases with increasing  $c_{\text{cat}}$ . On the basis of this dependence it would be possible to optimise the costs of needed catalyst and filtration costs for catalyst separation after hydrogenation. In this relation activity of the applied catalyst and hydrogen concentration play a decisive role.

*Desactivation of catalyst during hydrogenation.* On the basis of experience from the industry, the hydrogenation of rape seed oil is accompanied by accumulation of sulphur compounds in the gaseous phase, which are responsible for desactivation of the catalyst. To evaluate this effect, two measurements were performed at identical conditions ( $T$ ,  $P$ , and catalyst concentration) where in the first case the system was closed and hydrogen has been introduced only at the rate at which it is consumed at a constant pressure in the system. In the second case hydrogen has been introduced in excess and a constant pressure in the system has been kept by operation of the safety valve. Both these measurements are compared in Table III from which it is obvious that the hydrogenation rate is significantly lower in the closed system compared to the system with flushed excess hydrogen. This behaviour has been also confirmed by measurements performed in the following part of this study.

Summarizing, as concerns practical application of these results, decisive factors will be practical aspects of this behaviour — possible purification of hydrogen during hydrogenation, the required degree of hydrogenation, *etc.* It is possible that with other vegetable oils this problem might not be of such an importance.

#### *Bench Scale Unit (BSU)*

This unit has been operated with hydrogen introduced *a)* by a single pipe, *b)* by a spider type distributor with drilled holes, and *c)* with the VT used as a distributor. The experiments with arrangements according to *a)* and *b)* were made so that the

TABLE V

Comparison of various distributors for BSU  $c_{\text{cat}} = 0.37\% \text{ Ni}$  (0.07% fresh + 0.3% used catalyst) reaction temperature 175°C, hydrogen pressure 0.16 MPa

Type	$X_A^2$ at reaction time (min)				
	15	30	60	90	120
One tube	0.0037	0.0142	0.044	—	0.075
Spider type cross	0.0030	0.0177	0.038	—	0.075
VT, closed system	0.011	0.034	0.061	0.074	0.094
VT, hydrogen vented	0.015	0.037	0.084	0.117	0.149

excess hydrogen was vented by the safety valve at a fixed internal reactor pressure. By calculation it has been determined that this quantity of hydrogen is about 10 times greater than the hydrogen consumption for hydrogenation.

The experiments with VT were performed: a) with the closed system without venting the excess of hydrogen and b) with venting of the excess hydrogen. The results obtained are listed in Table V.

The time needed for hydrogenation of rape seed oil by use of the VT distributor to the same hydrogenation degree is about half of that for the hydrogen fed through a single pipe or the spider cross distributor. There is again a considerable difference between the hydrogenation performed in a closed system and in the system with venting of the excess hydrogen (Table V). Superficial velocities of hydrogen were identical for both these measurements.

#### *Comparison of Results from LSR and BSU*

Two experiments were also performed in the BSU with the VT distributor for comparing the effect of temperature, pressure and catalyst quantity with the results obtained in the laboratory stirred tank reactor. The results of these two measurements are in the form of calculated  $k_1$  and IP given in Table VI.

On basis of the results of measurements of hydrogenation rates in the LSR and BSU operated with the VT as a distributor, it is possible to state that the hydrogenation rates are practically identical in both these measurements. This is a very promising result as concerns possible scale-up of the results to industrial size of units.

TABLE VI

Comparison of the results obtained in laboratory stirred reactor (LSR) and in bench scale unit with Venturi tube as a distributor (BSU(VT)) for hydrogenation of rape seed oil at temperatures 170 and 180°C

Reactor	$p(\text{H}_2)$ , MPa	$k_1 \cdot 10^{3a}$	IP, min <sup>a</sup>
170°C			
LSR	0.16	0.89	15
BSU(VT)	0.12	0.88	15
180°C			
LSR	0.5	2.51	0 <sup>b</sup>
BSU(VT)	0.5	2.83	0

<sup>a</sup> For designation see Table I. <sup>b</sup> The value obtained by extrapolation from Fig. 6.



The condition for their use is the need to obtain additional data on the hydrogenation in industrial units.

BSU has been equipped with three inspecting windows located on opposite sides of the unit in the upper part of the reactor for observation on foaming of the system. Stable foam has formed usually during the first 10 to 15 min of hydrogenation. After this period the foam subsided and has not appeared again.

## CONCLUSIONS

The obtained experimental results have demonstrated, that substitution of a single pipe inlet (or similar pipe distributor) by a Venturi tube results in considerable acceleration of the hydrogenation process which might be performed with the aim to speed-up the process or reduce the catalyst consumption. Further improvement might be achieved by operation at higher pressure, purification of the recycled hydrogen, etc.

## LIST OF SYMBOLS

BSU	Bench scale unit
$c_{\text{cat}}$	catalyst concentration (fresh), mass %
$d$	internal diameter of pipe or hole through which hydrogen enters the bed, mm
$D$	diameter of unit, mm
IP	induction period, min
$k_1$	coefficient in Eq. (2), $\text{min}^{-1}$
$l$	length of arm of the spider distributor, mm
$L$	height of unit, mm
LSR	laboratory stirred tank reactor
$P$	pressure at which hydrogenation is performed, MPa
$r_{V_1}$	reaction rate expressed by use of iodine values Eq. (3), $\text{min}^{-1}$
$t$	time, min
$T$	temperature, °C
$V_1$	iodine volume
VT	Venturi tube
$X_A$	conversion defined by Eq. (1)

## Subscripts

$i$	initial
$t$	at time $t$

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