THE EFFECT OF SCALLING-UP AND HYDRODYNAMIC PROPERTIES OF STIRRING SYSTEM ON THE KINETICS OF VEGETABLE OIL HYDROGENATION

Ivan DĚDEK
Institute of Chemical Process Fundamentals,
Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchdol

Received November 15, 1991
Accepted April 8, 1992

The stirring system of classical turbine agitator beside the anchor agitator system was studied from the point of view of the effect of their hydrodynamic properties on the kinetics of sunflower oil hydrogenation. It was found out that the anchor agitator makes up a higher gas hold-up than the turbine one and its efficiency from the view of reaction kinetics is higher. On changing the geometrical parameters of anchor agitator – by reducing its blade height – its hydrodynamic properties change considerably, and its efficiency decreases. The scaling-up of the stirring system did not manifest itself in the reaction rate in case of the turbine agitator. With the anchor agitator, the scaling-up resulted in the confirmation of its specific effect on the reaction kinetics, viz., on exceeding the limiting value of stirring frequency, the dramatic loss in efficiency took place.

Comparatively few papers[1 – 5] have hitherto been published on the problems of stirring in hydrogenation. The mechanical agitator in hydrogenation system plays a number of roles. Primarily it must intensively disperse the gas in the form of bubbles considering that the rate of process is proportional to the interfacial surface area. Simultaneously it is necessary to ensure a sufficient relative velocity of catalyst grains, oil and bubbles, which is immediately connected with the ability to renew the catalyst surface with the hitherto unreacted double bonds and to supply hydrogen for the reaction. The agitator must ensure the intensive charge circulation as well for, in this way, partly the gas hold-up increases, and so the average phase contact time and partly the catalyst is held in suspension, which may play an important role in the overall efficiency of some types of autoclaves where the catalyst bed remains unexploited on the tank bottom.

The requirements mentioned complicate the choice of the agitator type. For the case of hydrogen dispersion in oil, the agitators generating radial flow of reaction mixture (e. g., Rushton turbine) are convenient even if from some other points of view, also axial agitators can be suitable. For hydrogenation, the high-speed impellers mostly with d/D = 0.3 are often used. However, neither low-speed agitators, where this ratio is increased up to 0.5 and more, are exceptional. The up-to-date solution is the location of several agitators above each other, e.g., in the autoclaves supplied by Krupp or Votator Division, Chemtron Corporation.

In preceding papers we have studied the effect of hydrodynamic properties of agitators on the reaction kinetics in a small laboratory reactor[6,7] (0.0036 m^3; hereinafter reactor A). In this study, this investigation was extended to the experiments in a larger bench-scale equipment of 0.017 m^3 volume (hereinafter reactor B).

EXPERIMENTAL

The main parameters of hydrogenation steel reactors are given in Table I. The measurements were carried out with Nysel DM-3 catalyst supplied by Harshaw containing 25% (w/w) Ni and with reduction degree 65.4% (as determined by the Kraft method[8]). All the experiments were performed with sunflower oil whose chemical characteristic is given in preceding paper[6] and at the temperature of 180 °C and Ni concentration 0.05% (w/w). Electrolytic hydrogen was supplied below the agitator into the reactor centre with a tube distributor with free end and was bubbled through the reaction mixture against the normal atmospheric pressure (reactor A). In case of reactor B, we worked partly in the flow pressureless arrangement and partly in the dead end system under the overpressure of 0.1 MPa.

The measurement itself was carried out so that oil was sucked into the reactor and after heating under vacuum, at 160 °C the catalyst was inserted. After reaching the reaction temperature required (180 °C) and adjusting the stirring frequency, a sample was taken at the zeroth minute and the reaction was started by admitting hydrogen. Next intervals of sampling were determined with respect to the reaction rate found orientationally by measuring refractive index. In the samples taken, the composition of fatty acids was determined by gas chromatography, iodine volume by Hanuš and the contents of trans-isomers by the infrared spectroscopy method[9]. The gas hold-up was measured by reading the level height by means of a video-technique in glass vessels of the same parameters as the used reactors under the conditions as those in the reaction. On the basis of these visual measurements, the stirring frequences for the experiments were chosen. The power inputs of turbine agitator were calculated from literature[10].

The starting equation for the selectivity calculation, which was defined as the ratio of rate constants of hydrogenation of linoleic acid and oleic acid, and also for calculating the rate constant of decrease of iodine volume are given in preceding paper[6].

RESULTS AND DISCUSSION

It follows from Figs 1 and 2 that the magnitude of gas hold-up is one of the factors positively influencing the reaction rate. After exceeding the limiting frequency of stirring (about 33 s^{-1}), further increase in the stirring intensity does not result in an

TABLE I
Geometric parameters of experimental apparatus

Reactor	h	$V \cdot 10^3$, m^3	$V_{oil} \cdot 10^3$, m^3	D, m	Agitator	d/D
A	0.1 D	3.6	1.5	0.126	turbine	1/3
B	0.1 D	16.8	12.5	0.258	anchor	2/3

increase of reaction rate any longer. In this region even the gas hold-up increases somewhat mildly with the mixing frequency than within the range of f 0 – 20 s^{-1}. At the same time it is possible to state that at higher stirring frequencies (above 26 s^{-1}) the increase in the hydrogen flow rate from 0.06 m^3 h^{-1} to 0.12 m^3 h^{-1} leads to a considerable increase in reaction rate. Apparently, it can be ascribed to the fact that there is its critical lack for the reaction even if the dispergation is more perfect. However, on the other hand, the hydrogen flow rate cannot be increased unlimitedly for the agitator flooding with gas may take place and so the loss of the agitator dispersing ability[11].

To be able to predict the behaviour of stirred reaction system (e.g., the reaction rate) as precise as possible, it is convenient to carry out the model experiments in a small as well as large equipment under defined conditions[12]. Such a comparison is summarized in Table II. Though only two parallel series of experiments were carried out, it appears

TABLE II

Results of model experiments with turbine agitator on reactor scaling-up

Quantity	Reactor			
	A	B	A	B
f, s^{-1}	21.0	13.3	39.2	24.5
$\dot{V}_g$, m^3. h^{-1}	0.10	0.85	0.09	0.72
P_g/V, W . m^{-3}	2 053	2 056	16 700	16 705
P_g, W	3.08	24.95	25.05	208.80
k . 10^3, min^{-1}	5.42	5.72	7.52	7.11

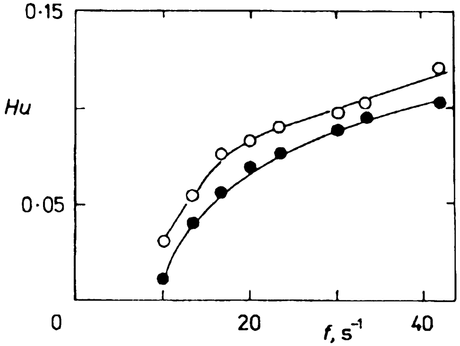

FIG. 1

The dependence of gas hold-up on the stirring frequency in the oil–hydrogen system for the set-up of turbine agitator in reactor A. ○ $\dot{V}_g$ = 120 m^3 h^{-1}, ● $\dot{V}_g$ = 60 m^3 h^{-1}

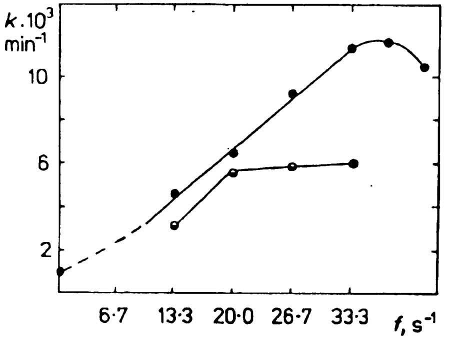

FIG. 2

The dependence of rate constant k on the stirring frequency for turbine agitator. Reactor A: ○ $\dot{V}_g$ = 60 m^3 h^{-1}, ● $\dot{V}_D$ = 120 m^3 h^{-1}

that the rate constants differ within 5%, which is satisfactory for orientation when designing or modelling the equipment. Therefore the conclusion is offered that scalling-up under the conditions of hydrogenation in a reactor stirred with a turbine does not reflect in the reaction rate on keeping the conditions of modelling a constant power input on a volume unit in the reactor, P_g/V. The reaction rate in both the equipments remains comparable.

After this verification of rightness of this procedure on scaling-up in a standard stirred system, further attention was paid to the anchor agitator generating tangential flow of reaction mixture which appeared to be very efficient even in foregoing experiments[6,7]. With this agitator whose set-up is non-standard, the gas hold-up increases nearly linearly in the range of Reynolds number investigated and is nearly threefold compared to the turbine agitators. By comparing the effect of stirring intensity on the reaction rate (Fig. 3), it can be observed that the reaction rate maximum for the anchor agitator is attained at the half stirring frequency (20 s^{-1}) than for the turbine agitator. Nevetheless, the Reynolds number value is twofold at these stirring frequencies as compared to the turbine agitator (Fig. 4).

Scaling-up resulted in the decrease of needed stirring frequency for attaining the maximum reaction rate down to 6 s^{-1} (Fig. 5), which is about four times lower frequency than that in the small reactor. Considering that the agitator diameter in the large reactor is twofold compared to the small one and consequently the turbulence formed by it is fourfold, therefore the comparable stirring frequency in the great reactor

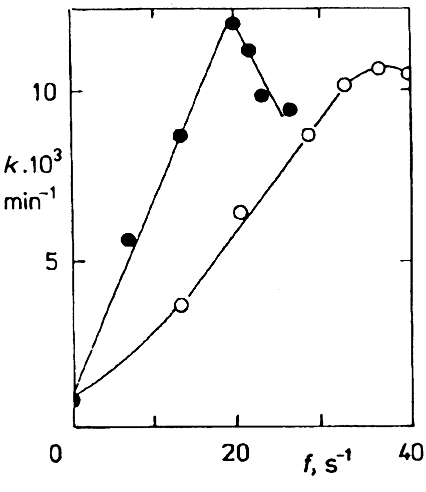

FIG. 3

The dependence of rate constant k on the stirring frequency. Reactor A, $\dot{V}_g$ = 120 m^3 h^{-1}: ○ turbine agitator, ● anchor agitator

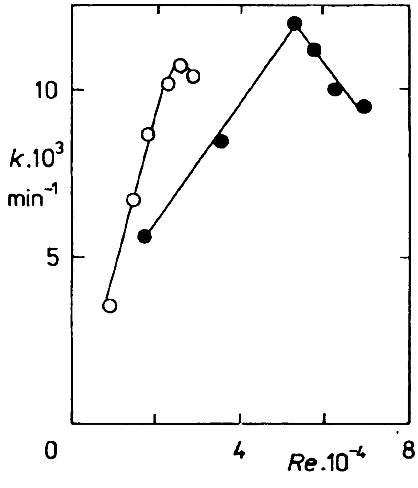

FIG. 4

The dependence of rate constant k on the Reynolds number. Reactor A, $\dot{V}_g$ = 120 m^3 h^{-1}: ○ turbine agitator, ● anchor agitator is then four times lower. It signals a good transferability of measured data to other larger equipments on keeping the modelling conditions.

It is well-known that the anchor-shaped agitators generate a relatively high resistance during stirring, and so the demands on the motor input are increased. The agitator resistance can be diminished among others by decreasing the length of vertical arm. As it follows from Fig. 5, decreasing the *h*/*d* ratio has the decisive influence on the efficiency of this agitator. On reducing the arm by half, the reaction rate decreased also nearly by 1/2, and on reducing the arm by 2/3, the complete loss of agitator efficiency took place.

Pressure considerably increases the reaction rate in the system with anchor agitator. For instance, for $f = 5.8\ s^{-1}$, the increase in pressure to 0.1 MPa resulted in up to twofold increase of reaction rate. However, it is further apparent from Fig. 5 that after shortening the vertical agitator arm, the change of pressure had substantially lower effect on reaction rate.

The breaks in dependences in Figs 3 – 5 are characteristic of this type of agitator as otherwise followed from the preceding measurements[6,7], and it is evident that scaling-up has no effect on these hydrodynamic specifics. This phenomenon is caused by the tangential vortex which originates after reaching these critical frequencies when oil is driven along the vessel walls by the centrifugal force and hydrogen as the light phase

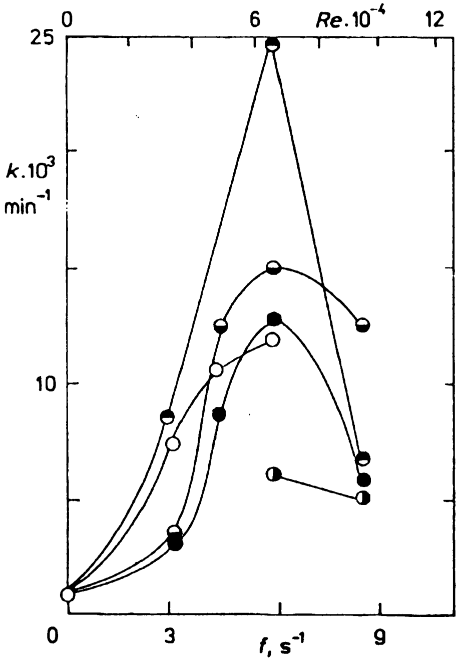

FIG. 5

The dependence of rate constant *k* on the stirring frequency and/or Reynolds number. Reactor B, $\dot{V}_g = 720\ m^3\ h^{-1}$, flow system, dead end system designated by (*p*) – pressure 0.1 MPa. Agitators: ○ *h*/*d* = 0.95, ◓ *h*/*d* = 0.95(*p*), ● *h*/*d* = 0.47, ◒ *h*/*d* = 0.47(*p*), ◑ *h*/*d* = 0.31

passes without being dispersed in oil through the reactor centre above the level despite the baffles.

The high efficiency of anchor agitator in the region of stirring frequencies lower than critical ones may be caused, among others, by its suction effect. That is to say, partly the hydrogen brought and dispersed at the reactor bottom and partly the hydrogen sucked into oil from head space is utilized in the reaction. Besides, the tangential flow results in an increase of gas hold-up as it has been stated above (Fig. 6). In the region of blades there are suitable conditions for hydrogen dispersion with respect to the high shear forces. These tangential agitators can therefore replace the systems with several

TABLE III
Effect of stirring on the reaction selectivity

Reactor	$\dot{V}_g$, m^3 h^{-1}	Agitator	f, s^{-1}	$k \cdot 10^3$, min^{-1}	Se
A	0.12	anchor	6.7	5.6	63.2
			13.7	7.3	20.9
			20.0	12.0	18.4
			21.7	11.3	12.4
			23.3	9.8	23.0
			26.7	9.5	22.0
A	0.12	turbine	13.3	3.7	19.1
			20.0	6.7	8.9
			26.6	8.7	5.1
			33.3	10.2	5.9
			37.5	10.7	5.2
			41.7	10.4	5.9
B	0.72	anchor	3.0	7.5	41.8
			4.3	10.6	25.4
			5.8	11.9	22.9
B	0.72	anchor[a]	3.0	3.9	38.2
			4.3	8.7	17.9
			5.8	12.7	21.0
			8.3	5.9	58.0
B	0.72	anchor[b]	5.8	6.8	20.6
			8.3	5.0	infinity

[a] h/d = 0.47; [b] h/d = 0.31.

agitators above each other. The intensive mixing of the charge bulk and the geometrical arrangement of anchor agitator moreover ensures the perfect heat transfer.

Table III illustrates the effect of stirring on the selectivity of reaction. The validity of knowledge is confirmed that the selectivity decreases with increasing reaction rate and efficiency of stirring[13 – 15]. The concentration of trans-isomers expressed as percent of methyl elaidate was within 20 – 35% (w/w) in the range of iodine volumes 60 – 80, which corresponds to the used type of catalyst under these conditions.

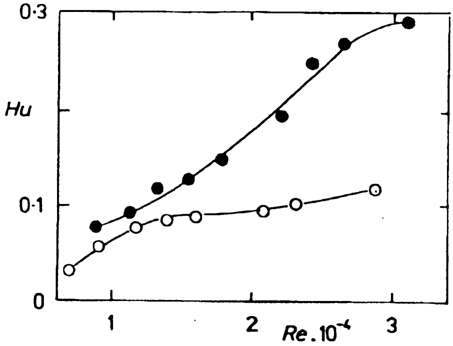

FIG. 6

The dependence of gas hold-up on the Reynolds number in the hydrogen–oil system for the hydrogen flow rate $\dot{V}_g$ = 120 m^3 h^{-1}. Reactor A: ● anchor agitator, ○ turbine agitator

SYMBOLS

d	agitator diameter, m
D	reactor diameter, m
h	height of agitator arm, m
Hu	gas hold-up
k	constant of iodine volume decrease, min^{-1}
n	baffle width, m
f	stirring frequency, s^{-1}
P_g	input power of agitator during aeration, W
Se	selectivity of hydrogenation – ratio of rate constants of hydrogenation of linoleic and oleic acids
V	reactor volume, m^3
V_{oil}	oil volume in reactor, m^3
$\dot{V}_g$	volumetric flow rate of hydrogen, m^3 h^{-1}

REFERENCES

1. Bern L., Lidefelt J. O., Schöön N. H.: J. Am. Oil Chem. Soc. *53*, 463 (1976).
2. Beal R. F., Lancaster E. B.: J. Am. Oil Chem. Soc. *31*, 619 (1954).
3. Boerma H., Lancaster E. B.: Chem. Eng. Sci. *23*, 794 (1968).
4. Wisniak J., Stefanovic S., Rubin E., Hoffman Z., Talmon Y.: J. Am. Oil Chem. Soc. *48*, 379 (1971).
5. Oldshue J. Y.: Chem. Eng. Progress *76*, 60 (1980).

6. Dědek I.: Collect. Czech. Chem. Commun. *55*, 1721 (1990).
7. Zajíc J., Dědek I., Lávičková H., Bareš M.: Fat-Sci. Technol. *90*, 189 (1988).
8. Kraft G.: Fresenius Z. Anal. Chem. *209*, 150 (1965).
9. *Standard Methods for the Analysis of Oils, Fats and Soaps*, IUPAC, 5th ed., Suppl. 2 Met. II. D. 7. Butterworths, London 1973.
10. ON 691001, Chepos Brno, 1986.
11. Mikulcová E., Kudrna V., Vlček J.: Sb. Vys. Sk. Chem.-Technol. Praze, K1, 167 (1967).
12. Strek F.: *Míchání a míchací zařízení.* SNTL, Praha 1977.
13. Coenen J. W. E.: J. Am. Oil Chem. Soc. *53*, 382 (1976).
14. Lefebvre J., Dizier J.: Rev. Fr. Corps Gras *31*, 69 (1984).
15. Klauenberg G.: Fette, Seifen, Anstrichm. *86*, 513 (1984).

Translated by J. Linek.