
THE EFFECT OF BUBBLING REGIME AND MODE OF MECHANICAL AGITATING ON THE COURSE OF HYDROGENATION OF VEGETABLE OIL

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The effect of hydrogen distribution was studied on the rate and selectivity of hydrogenation of sunflower oil in a bubbled air-lift-type reactor and in a laboratory reactor with interchangeable agitators. It was found that the change of bubbling regime considerably influences character of the reaction. The hydrodynamic properties of agitators have even the surprising effect on the kinetics of hydrogenation. The rate and selectivity of the reaction is to be efficiently controlled by the intensity and mode of agitating in both types of reactors.

In recent years new non-traditional modes of mixing have begun to be applied on the laboratory and industrial scale in the fat hydrogenation technology. Several reasons lead to this trend. From the economical point of view we see an effort to accelerate the hydrogenation process, however, on keeping up the preferential selectivity and isomerization on a required level. From this view, great attention in partial hydrogenation of fats and oils was aimed at the development and selection of an active but selective catalyst or at a choice of reaction conditions. Neglecting the ticklish problem of the catalyst quality, there is a possibility to control the reaction course by changing the hardening conditions. To the main factors influencing the hydrogenation process pertain pressure, temperature, mixing but neglecting are neither the quality of inlet oil or hydrogen.

The effect of temperature and pressure has been comparatively well studied, and a number of studies offer very good orientation in this field¹⁻⁶. However, the problems of effect of mixing were practically limited to the investigation of the influence of mixing intensity on the hydrogenation kinetics under the given conditions only. The effect of macrokinetic properties of system on the level of hydrogen distribution and so also on the reaction rate and on the selectivity was in the past investigated quite sporadically. In several isolated cases, the effect of position of mechanical agitator on the rate of hydrogenation⁷⁻¹⁰ was investigated.

The use of mechanical agitators can be avoided by applying the constructionally easily feasible bubbled reactors where the mixing of reaction mixture is ensured

only by the stream of inlet gas. The quality of the gas-liquid layer is then a function of a number of macrokinetic elements, among them the distributor character, the equipment geometry and the gas velocity play an important role. The number of types of distributors applied is relatively high, the evaluation of their effect on the course of hydrogenation of vegetable oils is, however, with some exceptions¹¹⁻¹³, practically missing in the literature.

The common denominator of all these projects realized both in the mechanically agitated or bubbled reactors is the intensification of contact of single phases. The main parameter investigated during mixing is, besides the requirement of suspending the catalyst and sufficient heat transfer, the attainment of the maximum g-l interface surface.

The mass transfer from the gas (hydrogen) into the liquid (oil) is in most industrial but also laboratory reactors the decisive process influencing the overall reaction time¹⁴⁻¹⁶. Therefore it is necessary in the intensification of hydrogenation process to take the improvement of hydrogen distribution in the system as one of fundamental points of view. However, it is not possible to neglect the fact that the conditions leading to the increase in the reaction rate, decrease its selectivity.

The new view on the control of hydrogenation from the point of view of increasing or decreasing the hydrogen concentration on the catalyst surface by choosing the intensity and mode of agitating or bubbling-through appears as a perspective one, which foreshadow even the responses in the current literature¹⁷⁻¹⁸.

In this respect the submitted work is directed. The main attention was paid to the description of the effect of mode and intensity of agitating in mechanically agitated reactor and the regime of bubbling-through in a reactor without mechanical agitating on the course and selectivity of hydrogenation of sunflower oil.

EXPERIMENTAL

The work consists of two stages. First the effects of the bubbling regime and the catalyst concentration on the course of reaction were studied in a glass mechanically non-agitated reactor of the air-lift type with volume of 1 dm³. In the second stage, the hydrodynamic effects of different types of mechanical agitators were compared from the point of view of kinetics of hydrogenation in a steel reactor of volume 3.6 dm³. The agitator frequency of revolutions was scanned with a cell and evaluated by means of a digital revolution indicator. Parameters of both the experimental equipments are given for the sake of lucidity, in Tables I and II.

All the experiments were carried out with sunflower oil whose chemical characteristics are given in Table III. The heterogeneous Ni-catalyst Nysel DM-3 supplied by Harshaw containing 25.0 mass % Ni and with the reduction degree 65.4% (as determined by the Kraft method¹⁹) was used. The temperature in both the reactors was maintained isothermally at $180 \pm 1.5^\circ\text{C}$. Hydrogen used was electrolytical from pressure cylinders. Its consumption was measured with a gas meter and a flow meter. All the experiments were carried out in the normal pressure arrangement and hydrogen was bubbled through the reaction mixture against atmospheric pressure. The samples of oils taken were analyzed after filtering by common methods (iodine volume by Hanuš, determination of fatty acid composition by the GLC method^{20,21}).

The measured analytical data were then processed by means of a computer. Primarily the rate constant of the iodine volume decrease was evaluated from the generally used relation

$$IV = IV_0 \exp(-kt) . \quad (I)$$

The calculation of rate constant of hydrogenation of individual fatty acids stemmed from the model of the 1st order consecutive reactions²³

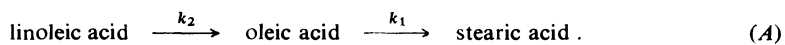


TABLE I
Geometric parameters of bubbled reactor with air-lift

Parameter	Size, cm
Reactor height	35
Reactor diameter	6
Diameter of inner cylinder	4
Fritted glass S1 diameter	2

TABLE II
Geometric parameters of mechanically agitated system

Parameter	Size, cm
Steel reactor	
Diameter	12.6
Height	29.9
Oil level height	12.6
Tube distributor inside diameter	0.4
Agitators used	
Turbine – radial flow	4.2
Propeller – axial flow	4.2
Paddle-wheel – axial-radial flow (3 blades)	4.2
Agitator producing tangential flow (2 blades)	8.2

This scheme is described by the system of differential equations whose integrated form is as follows

$$L = L_0 \exp(-k_2 t), \quad (2)$$

$$O = O_0 \exp(-k_1 t) + L_0 [k_2 / (k_1 - k_2)] [\exp(-k_2 t) - \exp(-k_1 t)]. \quad (3)$$

To evaluate the rate constants of the above-mentioned functional dependences, the optimization simplex method²⁴ was chosen. The advantage of the program made-up is its easy adaptability to different functional dependences or other kinds of oils. Its disadvantage consists in a great number of steps leading to the attainment of the minimum sought. Selectivity S_1 is defined as the ratio of rate constants of hydrogenation of linoleic and oleic acid

$$S_1 = k_2 / k_1. \quad (4)$$

RESULTS AND DISCUSSION

The hydrogen distribution in common industrial autoclave is ensured above all by mechanical agitating. However, at lower frequencies of agitator revolutions, even the type and location of distributor may exhibit a significant contribution to the overall gas distribution and agitating effect. The air-lift system was chosen as a perspective type of distributor. The advantage of this system compared to the other usual distributors consists in the fact that it can bring about recirculation of hydrogen supplied. So, in fact, the elongation of the bubble path takes place which positively reflects in an increase of the gas hold-up.

TABLE III
Main parameters of sunflower oil used

Iodine volume	136.2
Acid number	0.25
Saponification number	189.0
H ₂ O content in mass % by Fischer method	0.02
Phospholipide content in mass %	0.01
Composition of fatty acids by GLC method in %	
16 : 0	6.1
16 : 1	trace amounts
18 : 0	4.4
18 : 1	20.8
18 : 2	68.1
18 : 3	0.1
20 : 0	0.2
20 : 1	0.1

Choosing the rate constant of decrease of iodine volume k (see Eq. (1)) as an arbitration parameter, we can draw several conclusions from the data summarized in Table IV. In the measured range of gas flow rates or gas linear velocities, the qualitative change of bubbling regime takes place above the sintered glass distributor.

It is known from the literature^{13,22} that on getting over the critical value $u_{o\text{crit}} \sim 0.09 \text{ m s}^{-1}$, the encroachment of the stability of the distributor output takes place, and the homogeneous bubbling regime changes into the heterogeneous one. The distribution of bubble size under this regime is wide and so the g-l interphase surface regularly decreases.

From the results in Table IV discussed clearly follows that just on surpassing $u_{o\text{crit}}$ given, the considerable decrease of the reaction rate takes place. The results of all three blocks of measurements carried out at three different catalyst concentrations prove the outlined findings. The increase in the catalyst concentration under constant hydrodynamic conditions manifests itself in the increase of values of rate constant. It appears that the reaction selectivity at reduced reaction rate in the region

TABLE IV

Values of rate constants of decrease in iodine volume k and selectivities S_1 at various flow rates of hydrogen or linear velocities of gas on fritted glass u_o and catalyst concentrations. Bubbled reactor with air-lift

Hydrogen flow rate $\text{dm}^3 \text{ h}^{-1}$	u_o m s^{-1}	Catalyst concentration mass % Ni/oil	$k \cdot 10^3$ min^{-1}	S_1^a
30	0.02	0.05	3.85	32.6
60	0.05	0.05	5.76	11.7
80	0.07	0.05	6.59	10.6
120	0.11	0.05	8.42	8.1
180	0.16	0.05	4.75	15.8
30	0.02	0.2	4.10	27.1
60	0.05	0.2	6.84	13.1
120	0.11	0.2	9.60	8.9
180	0.16	0.2	6.43	12.6
240	0.22	0.2	5.50	18.0
30	0.02	0.3	4.60	30.8
60	0.05	0.3	7.42	14.6
120	0.11	0.3	11.18	6.0
240	0.22	0.3	5.24	16.3

^a Selectivity S_1 is defined as a ratio of rate constants of hydrogenation of linoleic and oleic acids.

of heterogeneous regime increases and on the contrary, decreases with increasing values of rate constant.

An important conclusion following from the discussed results above is that the character of the gas-liquid layer strongly influences the course of hydrogenation reaction and that the change in the bubbling regime results in the step change in the reaction rate.

The mechanically agitated system became the subject of further research. The distributor was formed in this case by a tube with free and led radially under the agitator axis. This distributor was selected purposefully on the basis of foregoing

TABLE V

Values of rate constants of decrease in iodine volume k and selectivities S_I at various frequencies of agitating f or Re numbers. Mechanically agitated reactor, hydrogen flow rate $360 \text{ dm}^3 \text{ h}^{-1}$, catalyst concentration $0.2 \text{ mass } \% \text{ Ni/oil}$

Agitator	f s^{-1}	$Re \cdot 10^{-4}$	$k \cdot 10^3$ min^{-1}	S_I
Turbine — radial flow	6.7	0.46	3.07	32.4
	13.3	0.92	8.05	22.0
	20.0	1.39	10.47	13.2
	26.3	1.83	13.18	8.4
	41.7	2.89	18.53	7.6
	66.7	4.63	19.60	5.7
Propeller — axial flow	13.3	0.92	4.10	29.1
	20.0	1.39	7.51	18.3
	41.7	2.89	15.00	8.5
	66.7	4.63	18.9	8.3
Paddle-wheel — axial-radial flow	10.0	0.69	3.42	24.7
	13.3	0.92	4.41	18.6
	20.0	1.39	7.21	11.6
	33.3	2.31	13.96	8.3
	41.7	2.89	15.58	8.3
	103.3	7.18	19.7	4.9
Agitator producing tangential flow	3.3	0.87	1.97	31.0
	6.7	1.77	10.50	14.3
	10.0	2.65	19.30	9.4
	13.3	3.52	27.13	8.6
	16.7	4.42	33.57	7.6
	20.0	5.29	37.90	6.2
	26.7	7.07	34.40	7.9
	33.3	8.82	18.63	8.4

results²⁵ as comparatively rather little efficient. The reason of this choice was an effort to limit the effect of the gas distributor on the overall hydrogen distribution to enable to evaluate objectively, for the agitators studied, their dispergation effects.

The comparative experiments with these agitators in a laboratory steel reactor brought a number of interesting results (see Table V). The main reaction parameter investigated was, as in the preceding part of the work, rate constant k . It is evident at first glance that an agitator producing the tangential flow has as much as several times higher effect on the reaction rate than the other high-speed agitators. No less remarkable is the fact that in the region of frequency of agitator revolutions $f \sim \sim 20 \text{ s}^{-1}$, called the critical frequency of agitating f_{crit} (or $Re_{\text{crit}} = 5.3 \cdot 10^4$) a sharp break in efficiency occurs for this agitator. Consequently further increase in frequency of agitator revolutions above f_{crit} results in a sharp decrease of reaction rate.

This phenomenon seems to be analogous to the preceding finding, when, on changing the bubbling regime, a rapid decrease in the distributor efficiency took place as well. However, the conditions in the gas-liquid layer are different in the mechanically agitated reactor. Here a so-called "centrifuge effect" takes place owing to the strong centrifugal influence of agitator when the light phase (hydrogen) accumulates at the agitator axis and the heavier phase (oil and catalyst) are pushed to the wall. Contact between the phase is so considerably limited.

Table V provides orientation to judge the effect of the other agitators on the reaction course. It is evident that the axial and axial-radial agitators have practically the same effect on the reaction rate. This identical characteristic can perhaps be assigned to the fact that both the agitators have the same number of blades. On the other hand, the agitator producing radial flow (Rushton turbine) is somewhat more efficient.

Characteristic for these three agitators is the finding that the increase of agitation intensity above $f_{\text{crit}} > 40 \text{ s}^{-1}$ or $Re > 4 \cdot 10^4$ leads practically no more to the increase of reaction rate and it remains nearly constant. This fact is in good agreement with the results given in literature when the hydrogenations with turbine²⁶, propeller²⁷, and paddle-wheel²⁸ agitators were carried out. However, the literature data do not enable to compare mutually the effects of single agitators because the experimental conditions were considerably different. Similarly the selectivity of reaction which decreased with increasing hydrogenation rate, remains in this region above f_{crit} substantially constant.

From both tables of results it is evident that in the mechanically agitated systems, the rate of reaction is higher than that in bubbled systems. Higher values of rate constants k are, however, in mechanically agitated systems, reached on exerting the considerable energy of agitating, i.e., at relatively high frequencies of agitator revolutions $f > 20 \text{ s}^{-1}$. On the technological scale, the real boundaries of frequency of revolution are around $f < 13 \text{ s}^{-1}$. In this range are the efficiencies of air-lift and mechanical agitators practically comparable.

CONCLUSION

In the bubbled reactor, the hydrodynamic but also geometric conditions play significant role in the distributor efficiency. A change in the character of gas-liquid layer reflects considerably on the rate of hydrogenation and its selectivity. The agitation mode has even surprising effect on the course of hydrogenation. Flow properties, frequency of revolution and geometric conditions are decisive factors for the character of reaction. Both the rate and selectivity of reaction can be controlled by these variables. In the region of agitator revolutions, reaction rates in mechanically agitated reactors are comparable with the bubbled system of the air-lift type.

SYMBOLS

IV	iodine volume
f	frequency of agitator revolutions, s^{-1}
k	rate constant of decrease in iodine volume, min^{-1}
k_1	rate constant of hydrogenation of oleic acid, min^{-1}
k_2	rate constant of hydrogenation of linoleic acid, min^{-1}
L	concentration of linoleic acid, mass %
O	concentration of oleic acid, mass %
Re	Reynolds number
S_1	$= k_2/k_1$ selectivity
t	time, min
u_0	linear velocity of gas (gas velocity in cross section unit), $m s^{-1}$

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