• Technical

Mass Transfer and Scale-Up in Fat Hydrogenation

L. BERN, J.-O. LIDEFELT, and N.-H. SCHÖÖN,[1] Department of Chemical
Reaction Engineering, Chalmers University of Technology, Fack S-402 20 Göteborg 5, Sweden

ABSTRACT

The mass transfer of hydrogen in fat hydro-
genation was studied in two geometrically similar
reactors of 30 and 500 liter capacity equipped for
hydrogen recirculation. A scale-up rule was formu-
lated on the basis of the experiments and checked in
industrial hydrogenations with a 24 m³ reactor. The
scale-up rule found was similar to the equal mixing
time rule.

INTRODUCTION

It is a well-known fact that it is difficult to obtain the
same quality of hydrogenated fat in the industrial plant as
in the laboratory. This difficulty is closely connected to the
problem of finding the same reaction conditions in the two
scales with respect to the hydrogen transfer from the gas
phase to the solid catalyst. Only a few investigations (1-5)
have been published on mixing conditions and mass transfer
in fat hydrogenation, and these investigations were not
directed towards solving the scale-up problem. In fat
hydrogenation, the resistances of the liquid films near the
gas bubbles and near the external surface of the catalyst are
the only resistances which are influenced by the mixing
conditions. It is also these resistances which are of primary
interest in a scale-up study. The transport resistance near
the catalyst may be neglected in comparison to the resist-
ance near the bubble in industrial fat hydrogenation, so the
process may be looked upon as a pure gas-liquid process

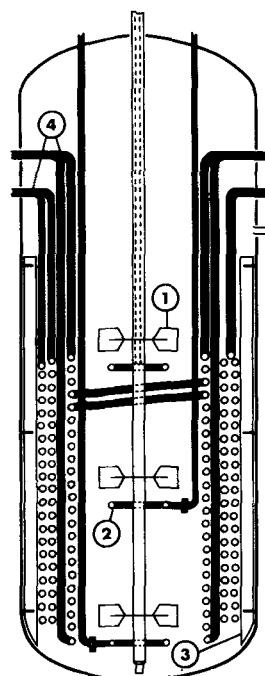[1] Author to whom correspondence should be addressed.

FIG. 1. Experimental arrangements: (1) turbine impeller, (2)
perforated ring for hydrogen supply, (3) baffle, and (4) cooling and
heating coils.

from a scale-up point of view.

In the present article, the mass transport properties were
studied in fat hydrogenations carried out in two geometri-
cally similar reactors of 30 and 500 liter capacity, equipped
for hydrogen recirculation. The scale-up criterion, formu-
lated on the basis of the experiments, was checked in fat
hydrogenations with an industrial reactor of 24 m³
capacity.

EXPERIMENTAL PROCEDURES

Reactor and Methods

The geometry and details of the reactors are given in
Figure 1 and Table I. The investigation was performed using
a laboratory reactor of 30 liter capacity and a geometrically
similar industrial pilot reactor of 500 liter capacity. The
result was checked in a geometrically similar 24 m³ indus-
trial reactor. In addition to the hydrogenations in these
three reactors, some hydrogenations were performed in a
conventional 1 liter reactor (6). This small reactor was not
geometrically similar to the other reactors.

It should be noted that the industrial reactors were
designed and used for daily production, so some instru-
ments and other auxiliary arrangements usually present in
laboratory experiments were not available, as may be clear
from the following. The reactors were provided with four
baffles and cooling and heating coils. The impeller was a
triplet turbine impeller with six blades in each turbine. The
hydrogen can be supplied through perforated rings under-
neath each impeller. In the present investigation, hydrogen
was supplied underneath the bottom impeller only. The
reactors were supplied with fresh gas only, and no recircula-
tion of hydrogen from the outlet was performed.

The volumetric gas flow rate was determined at the gas
inlet. Both the inlet and outlet gas tubes were provided
with pressure gauges. The gas flow rate and the hydrogen
pressure in the reactor were calculated on the assumption
that the reactor was equal to an ideal stirred tank reactor
with respect to mixing of the continuous gas flow (7). The
gas flow rate in the reactor and in the outlet was thus
obtained as the difference between the measured inflow
rate and the rate of hydrogen reacted in the reactor. The
reaction rate was calculated from the rate of iodine value
decrease. The power consumption by the impeller was not
measured owing to safety regulations at the industrial plant.

TABLE I

Dimensions of the Reactor Equipment

Equipment details	Lab reactor	Pilot reactor	Industrial reactor
Volume of vessel	30 liter	500 liter	24 m³
Volume of oil	20 liter	300 liter	11-15 m³
Diameter of vessel	25 cm	65 cm	2.4 m
Height of vessel	60 cm	155 cm	6.0 m
Diameter of impeller rotation	8.4 cm	22 cm	0.9 m
Type of impeller		6 blade turbine	
Number of impellers	3	3	3
Distance between impellers	15.5 cm	40.5 cm	1.6 m
Width of impeller blade	2.3 cm	6.0 cm	0.25 m
Length of impeller blade	2.4 cm	6.3 cm	0.25 m
Number of baffles	4	4	4
Width of baffles	1.3 cm	3.5 cm	0.13 m

Materials

The hydrogenations were performed with industrially refined rapeseed oil in the presence of such a high loading of catalyst that external mass transport steps were rate determining. At the prevailing reaction conditions, i.e., 180 C and 1.2-1.4 atm, a catalyst loading of 0.1% nickel was sufficient to fulfill these requirements. The catalyst was a commercial G53 nickel-on-kieselguhr catalyst with a mean particle size of 10^{-3} cm.

Calculation of $k_L a$

In a liquid phase hydrogenation the external resistances against the transport of hydrogen from the gas phase to the catalyst are often considered to be concentrated to the apparent thin liquid films near the gas bubbles and near the external surface of the catalyst. Owing to the high external surface of the catalyst compared to the interfacial gas-oil surface and also owing to the low relative velocity between catalyst particles and oil, the resistance against hydrogen transport near the catalyst surface may be neglected. As is common practice in reactions systems where the interfacial area is difficult to determine, the rate of mass transfer in a gas-oil dispersion is calculated per unit vol of dispersion or per unit vol of oil instead of unit interfacial area. At steady state the molar rate of hydrogen transported per unit vol of oil (N) may be written as a product of the concentration difference across the apparent liquid film surrounding the bubbles and the coefficient $k_L a$. This coefficient is called the volumetric (liquid) mass transfer coefficient and is a product of the mass transfer coefficient k_L and the specific interfacial area a. The mass transfer equation may thus be written:

$$N = k_L a(c^o - c) \qquad (I)$$

where

N	=	rate of hydrogen transfer, mol H_2 (sec 1 oil)$^{-1}$
k_L	=	mass transfer coefficient in the liquid film, near the bubbles, cm sec^{-1}
a	=	specific interfacial area, cm^2 (cm^3 oil)$^{-1}$
c^o	=	hydrogen concentration in the gas-oil interface, equal to the solubility of hydrogen, mol(1 oil)$^{-1}$
c	=	hydrogen concentration in the bulk oil, mol (1 oil)$^{-1}$

In the present investigation, the catalyst loading was chosen so high that the hydrogen concentration c, due to the very rapid chemical reaction, may be neglected compared to the hydrogen concentration c^o.

The volumetric mass transfer coefficient $k_L a$ may thus be calculated as

$$k_L a = N/c^o \qquad (II)$$

The solubility concentration of hydrogen c^o may be calculated from the relationship

$$c^o = K_H p \qquad (III)$$

where

p	=	hydrogen pressure in gas outflow, atm
K_H	=	equilibrium solubility constant, mol hydrogen (1 oil atm)$^{-1}$

The constant K_H was found to follow the relationship (6)

$$K_H = 0.0203 \exp(-710/T) \qquad (IV)$$

where T is absolute temperature in Kelvin.
The rate of hydrogen transfer may be calculated from

$$N = -\frac{0.039}{60} \rho \, d(IV)/dt \qquad (V)$$

where

d(IV)/dt	=	iodine value change per min
ρ	=	density of the oil, g cm^{-3}

Since all hydrogenations were performed at 180 C, where the oil density may be approximated to be $\rho = 0.8$ kg 1^{-1}, Eqs. II-V will be summarized to be

$$k_L a = -0.12(1/p)d(IV)/dt \qquad (VI)$$

Correlations Between $k_L a$ and Process Variables

A correlation between $k_L a$ and the process variables may be easily formulated if all experiments are performed in a reactor of one single size. If the correlation instead is intended for scaling-up calculations, it is a delicate task to find the right type of correlation. Although much work has been carried out in this field, there does not seem to exist any general rule of design for stirred gas-liquid contactors at present. Moreover, opinions concerning the best scaling-up rule have been strongly contradictory. It should also be noted that tests of scaling-up rules on industrial reactors are seldom reported in the literature, and the explanation may be that the industrial reactor is more complex than reactors used in the experiments. Moreover, it is difficult to determine the necessary data in the industrial process.

In stirring operations in general, the rule of constant agitation power consumption per liquid vol is frequently applied in scaling-up. This rule is also often used in scaling-up the mass transfer properties in stirred gas-liquid dispersions (8). This so-called "constant (P_g/V) rule," where P_g is the power input to the gas-liquid dispersion by the impeller and V the volume of liquid, may be slightly modified when introducing an exponent α giving (P_g/V^α). The modified rule is called "the equal mixing time rule." The exponent is dependent on the type of impeller and was found to lie between 1.4 and 1.9 (9). Other scaling-up rules of interest are the so-called "constant impeller tip speed rule" (10) and a rule based on the Gilliland-Sherwood equation (11).

The aim of the present work is not to take sides with some of these rules. Since the "equal mixing time rule" seems to include most degrees of freedom, this rule was used in the present work.

A correlation between $k_L a$, the power input by the impeller, and the linear gas velocity (v_s) may thus be written:

$$k_L a = \text{const} \, (P_g/V^\alpha)^\beta \, v_s^\gamma \qquad (VII)$$

where α, β, and γ are the exponents to be determined. The influence of physical properties such as diffusivity, density, surface tension and so on are not included in Eq. VII, since all experiments were carried out at the same temperature and with the same oil. The power input by the impeller (P_g) was not determined during current industrial runs. however, so the power input was instead estimated from the equation given by Michel (12):

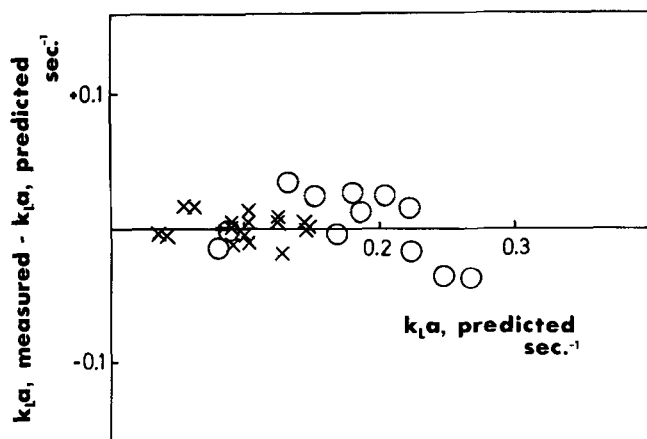$$P_g = \text{const} \, (P^2 \, nd_s^3/Q^{0.56})^{0.45} \qquad (VIII)$$

FIG. 2. Residuals vs. predicted volumetric mass transfer coefficient. (k_La)-values: (x) runs in 30 liter reactor, (o) runs in 500 liter reactor.

where Q is the volumetric gas flow rate, P is the power input in the gas-free liquid, n is the rotation speed of the impeller, and d_s is the diameter of impeller blade rotation. Eq. VIII seems to be the best known equation for correlating the power input in liquid-gas dispersions with the corresponding power input in gas-free liquid (8).

For geometrically similar reactors, the volumetric gas flow rate may be written

$$Q = const \ v_s \ d_s^2 \qquad (IX)$$

Considering fully baffled reactors in the turbulent mixing range we have, moreover (13)

$$P = const \ n^3 \ d_s^5 \qquad (X)$$

Insertion of Eqs. VIII-X in Eq. VII gives

$$k_La = const \ (n^{3.15}d_s^{5.35}/V^\alpha)^\beta v_s^\gamma \qquad (XI)$$

RESULTS AND DISCUSSION

Hydrogenations in 30 and 500 liter Reactors

Twenty-eight runs were performed at 180 C, 1.2-1.5 atm pressure of the outlet gas, and at linear gas velocities of 3.5-5.5 cm sec⁻¹ (30 liter reactor), 10-30 cm sec⁻¹ (500 liter reactor), and at stirrer rates at 240-750 rpm (30 liter reactor), 180-480 rpm (500 liter reactor).

It should be pointed out that the runs should be carried out at the same degree of bubble-shrinking. Linek (14) showed that different degrees of bubble-shrinking affected the specific mass transfer properties determined. He used the ratio between the gas inflow rate and the outflow rate as a measure of the bubble shrinking. In the present runs, this ratio was between 0.85 and 0.95, so the difference in bubble shrinking may be neglected.

The parameters of Eq. XI were estimated by the method of least squares. The adequacy of the fit was tested with a residual analysis, and a scale-up test of the equation is given below.

The result of parameter estimation may be summarized in equation

$$k_La = 0.326(n^{3.15}d_s^{5.35}/V^{1.41})^{0.37}v_s^{0.32}sec^{-1} \qquad (XII)$$

The constant 0.326 is valid when the length unit is meter.

The standard deviation between predicted and experimental k_La-values was s = 0.015 sec⁻¹. Within a 95% confidence interval the exponents were found to be α = 1.41 ± 0.08, β = 0.37 ± 0.02, and γ = 0.32 ± 0.10.
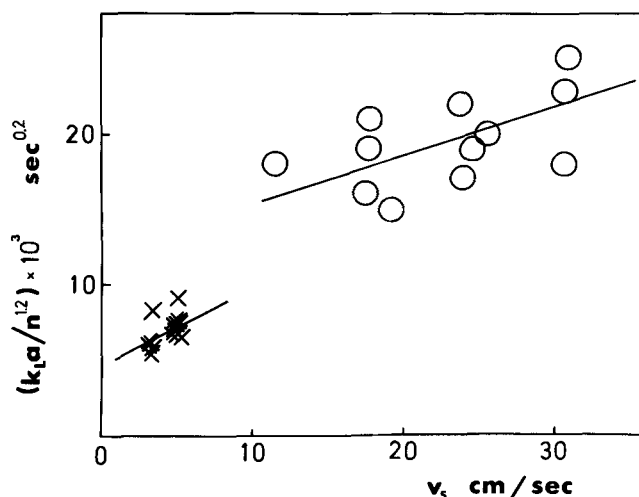

FIG. 3. Influence of the linear gas velocity (v_s) on the volumetric mass transfer coefficient (k_La): (x) runs in 30 liter reactor, (o) runs in 500 liter reactor, (–) predicted values.

TABLE II

Check of Mass Transfer Equation
under Industrial Conditions[a]

Reaction parameters	Run no. I	Run no. II	Run no. III
Temperature (C)	180	180	180
Pressure in reactor and gas outlet (atm)	1.4	1.4	1.4
IV (decrease/min)	0.50	0.61	0.65
Stirrer rate (n) (rpm)	75	75	75
Oil volume (V) (m³)	11.06	14.74	11.67
Linear gas velocity in reactor (v_s) (cm/sec)	7.1	8.7	6.4
k_La experimental (sec⁻¹)	0.043	0.052	0.056
k_La predicted (sec.⁻¹)	0.042	0.039	0.039

[a]k_La = volumetric mass transfer coefficient.

It may be observed that the confidence intervals of the exponents are rather small. As also seen from the residual analysis in Figure 2, where the differences between measured and predicted values of k_La are plotted vs. k_La predicted, the residuals are randomly distributed along the abscissa indicating that Eq. XII may be accepted. It is also seen from Figure 2 that the k_La-values obtained from 30 and 500 liter runs overlap.

There are two properties of special interest from a scaling-up point of view. First, the exponent α on the vol V is rather high, indicating that a scaling-up rule similar to "the constant mixing time rule" is the most probable rule for the present reactors. The obtained value α = 1.41 is in good agreement with the result presented by Nordwood and Metzner (9), as reported above.

The influence of the linear gas velocity (v_s) has been the subject of much discussion in connection with scaling-up of gas-liquid dispersions. One opinion is that the linear gas velocity does not influence the mass transfer conditions (10). The value γ = 0.32 of the exponent on the linear gas velocity indicates that the gas flow rate may not be neglected. The influence of the linear gas velocity in the present experiments is also clear from Figure 3, where $k_La/n^{1.2}$ is plotted vs. v_s. The exponent 1.2 was obtained as the product β x 3.15.

The main process factor from a mass transfer point of view, however, is not the gas flow rate but rather the impeller rate. The exponent on the rotation speed of impeller n is more than 3 times that on v_s.

Check of the Mass Transfer Equation

Correlations intended for scale-up are very often checked for pilot plant operations only. In the present investigation, it was possible to carry out fat hydrogenations industrially in a 24 m³ reactor at the same high catalyst loading as in the other hydrogenations to guarantee a dominating transport resistance. For economical reasons, only three hydrogenations were studied. The reaction conditions and the experimental and predicted values of k_La are given in Table II. As may be seen from the experiments with the oil vol 11.06 m³, the k_La-value found agrees well with the predicted value. In the experiments with the oil vols 11.67 and 14.74 m³, the agreement is not equally good. It is difficult to explain this deviation due to the fact that only one run was performed at each oil vol.

It may be observed that the difference in vol between the industrial reactor and the pilot plant reactor was greater than is generally recommended for a satisfactory scaling-up. As in many industrial situations, it was not possible to design the pilot plant reactor with regard only to these specific demands. With those facts in mind, the agreement between experimental and predicted values of k_La may be accepted.

Comparison Between the Mass Transfer Resistances of Different Scales

The mean values of k_La under the prevailing mixing conditions were 0.07 sec⁻¹ (30 liter reactor), 0.16 sec⁻¹ (500 liter reactor), and 0.05 sec⁻¹ (24 m³ reactor). As is obvious from these values, the mixing conditions of the 30 and 500 liter reactors may be easily changed to give the same k_La-value and thus the same quality of hydrogenated fat as with the industrial 24 m³ reactor. The corresponding values of stirring rate and linear gas velocity to give the desired value $k_La = 0.05$ sec⁻¹ may be estimated from Eq. XII.

It is obvious from the above that the greatest difference in hydrogenation conditions is not to be found between the pilot plant reactor and the industrial reactor but between the bench scale reactor and the pilot plant reactor. Some runs were undertaken with a laboratory reactor (1 liter capacity) under conditions corresponding to an ordinary kinetic study of fat hydrogenation to demonstrate this difference. Under the intense mixing conditions in the laboratory reactor, the mass transfer properties corresponded to $k_La = 2.1$ sec⁻¹. It follows from this value that the resistance against the hydrogen transport is ca. 40 times greater in the 24 m³ reactor than in the 1 liter reactor.

The mixing in the industrial reactor cannot be increased to the same high mixing intensity as in the bench scale reactor for practical reasons (very high power input by the impeller and limited cooling capacity), so a scaling-up from a small reactor to full industrial scale is not possible in an ordinary way. The reverse can always be done.

Use of the Mass Transfer Equation to Plan the Industrial Hydrogenation

The starting point in planning the industrial hydrogenation is to choose type of catalyst, hydrogen concentration in the oil, temperature, catalyst loading, and time of reaction. This choice may be based on kinetic experiments in which the chemical properties of the reaction are studied without interference from mass transfer steps. The temperature and hydrogen concentration required to obtain the desired hydrogenated fat within a certain time of reaction are then calculated from the resultant rate equations of the kinetic experiments. From the calculated hydrogen concentration and the reaction rate (estimated from the decrease in iodine value and time of reaction), it is now possible to calculate the hydrogen concentration in the gas-oil interface, the hydrogen pressure (cf. Eqs. II and III), and the value of k_La. The hydrogen pressure and k_La may not be chosen independently. A low value of k_La may be compensated for by a high hydrogen pressure, and the reverse. After the k_La-value is chosen, it is possible to calculate, from Eq. XII (or a similar equation for other reactor geometries), the corresponding rotation speed of the impeller and the linear gas flow velocity.

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