Kinetics of Hydrogenation of Rapeseed Oil: I. Influence of Transport Steps in Kinetic Study

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ABSTRACT

The influence of mass transfer steps in the kinetic study of rapeseed oil hydrogenation in a laboratory reactor was estimated. Hydrogenations were carried out at 140-200 C and at 0.3-10 atm hydrogen pressure in the presence of 0.087% of commercial nickel-on-kieselguhr catalyst, corresponding to 0.05% of nickel. Despite intense mixing conditions on the macroscale of the bulk oil, corresponding to a reaction rate independent of further increase of the stirrer rate, the concentration differences across the liquid film surrounding the bubbles and the catalyst particles could not be neglected. The pore transport of triglycerides and hydrogen molecules was found not to be a slow step in most hydrogenations.

INTRODUCTION

The complexity of a chemical process will increase with an increase in the number of phases and coupled reactions involved. The fat hydrogenation process may, therefore, be considered as one of the most complicated chemical processes known in industry. Besides the fact that there are three phases involved in the process which give rise to mass transfer complications, the chemical part of the process consists of a network of parallel and consecutive reactions, resulting in a complex mixture of position isomers and *trans* isomers in the hydrogenated fat. It is also a well known fact that it is very difficult to scale-up the reaction conditions to obtain the same quality of the hydrogenated fat in the industrial plant as in the laboratory. Most of these difficulties are connected closely with the great difference in conditions between the laboratory and the industrial reactor regarding the transfer of hydrogen from the gas phase to the catalyst.

In kinetic studies on a laboratory scale, the mass transfer resistances are considered to be eliminated at a high gas flow rate and a high stirrer rate (1-4), since the rate of hydrogenation is not found to increase with an additional increase in mixing intensity. There are, however, other possible explanations for the observed limiting rate of hydrogenation. At intense mixing conditions with respect to macroscale of the bulk oil, it is probable that the small porous catalyst particles and the oil volume elements may behave as a homogeneous medium, which means that the catalyst particles move with nearly the same velocity as the oil. This opinion is supported by the result reported by Bieber and Gaden (5), who found that the liquid was practically stagnant relative to the solid particles at high stirrer rate and with very small particles (particle diameter 10-11 μ). This very low relative velocity on the microscale between the liquid and the solid particles obviously gives a limiting value of the mass transfer resistance, which may not be decreased easily with an additional increase in mixing intensity. It should be pointed out that the limiting resistance also includes the pore transport resistance which is not at all influenced by the mixing intensity.

In the present article, the magnitude of the limiting mass transfer resistances and the subsequent concentration differences caused by these resistances are estimated in rapeseed oil hydrogenation in a laboratory reactor.

EXPERIMENTAL PROCEDURES

Material

The hydrogenations were carried out with rapeseed oil with a high content of erucic acid in glycerides. More details concerning the fatty acid composition will be given in a future publication. The composition of triglyceride corresponds to a mol wt of 937 g/mol and a concentration of ca. 0.85 mol/liter at the reaction temperature.

The catalyst was a commercial nickel-on-kieselguhr G53-catalyst (Girdler-Süd Chemie Katalysator GmbH, Munich, West Germany) delivered as flakes suspended in hardened solid fat. The catalyst contained 58% nickel and 42% kieselguhr by wt. The total surface of the catalyst was 276 m^2/g, and the pore volume was 0.55 cm^3/g. These properties were measured using a Perkin-Elmer sorptometer 212 D. From these values, the mean cylindrical pore diameter and the apparent particle density were calculated to be 80 Å and 1.5 g/cm^3, respectively.

Analytical Methods

The rate of hydrogen mass transfer was calculated from the rate of iodine value decrease. The iodine value was calculated from the gas liquid chromatographic (GLC) determination of the fatty acid composition using a Perkin-Elmer 900 gas chromatograph.

Reactor

The reactor, 11 cm inner diameter and 20 cm ht, was provided with two baffles and a 5 cm turbine impeller with 6 blades (Fig. 1). The ht of the liquid-gas dispersion in the reactor was ca. 11 cm. The reactor was heated electrically and cooled by a spiral cooler. The gas inlet was placed directly under the impeller.

Performance of Experiments

The oil (0.7 kg) and the catalyst were added to the reactor at room temperature. Nitrogen was bubbled through the oil under vacuum during heating to the desired temperature. The inlet linear hydrogen gas velocity, based upon an empty cross-section of the reactor, was 0.68 cm/sec. The stirrer rate was 42 sec^{-1}. The gas velocity and the stirrer rate were chosen so that the rate of hydrogenation reached its limiting constant value. All hydrogenations were carried out at 0.087% catalyst loading, corresponding to 0.05% of nickel. Hydrogenations were carried out at different temperatures between 140-200 C and at different pressures between 0.3-10 atm. To decrease the mass transfer resistance in the gas phase, no inert gas was added to decrease the hydrogen pressure. Instead, the hydrogenations at the lowest pressures were carried out at reduced total pressure. The hydrogen pressure was measured at the outlet of the reactor, since the inlet gas may be mixed instantaneously with the entire volume of the reactor (6). The reactor may, thus, be looked upon as a continous perfect mixed reactor as far as hydrogen is concerned, which means that the hydrogen pressure is the same in the entire reactor and in the gas outlet.

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MODEL OF REACTION SYSTEM

The reaction system may be described as either pseudo-homogeneous (7) or heterogeneous (8). In the latter case, the different reaction steps are treated separately from one another and from the chemical steps. In the present study, the reaction system is described with a heterogeneous reaction model consisting of three steps in the liquid phase, i.e. the transport of hydrogen from the gas-oil interface to the bulk oil, the transport of hydrogen from bulk oil to the external surface of the catalyst, and, finally, the transport into the porous catalyst to the internal surface of the catalyst where the chemical reactions proceed. A similar transport takes place for the triglycerides, both into and from the catalyst. The present model does not include the gas phase, since it is most probable that the transport in the gas phase is very rapid under the prevailing reaction conditions.

Hydrogen Transfer from Gas-Oil Interface

Extensive studies have been carried out concerning the transfer of gas to the liquid in stirred reactors (9-14). Most of these investigations were concerned with model systems, however, and the results may be limited to these systems. Some studies deal with the hydrogen transport in liquid hydrogenations (7, 15-17), but only a few deal with the fat hydrogenation process (18).

The mass transfer phenomena in liquid phase hydrogenations are most often described in terms of the film model concept, where all the resistance to mass transfer is confined to a stagnant layer near the phase boundary. As is common practice in reactions systems where the interfacial area is difficult to determine, the rate of mass transfer in a gas-liquid dispersion is calculated per unit volume of dispersion or per unit volume of liquid instead of unit interfacial area. The molar rate of hydrogen transported per unit volume of oil (N) through the liquid film near the gas bubbles may, thus, be written as the product of the concentration difference of hydrogen across the liquid film (Δc_H), and the proportionality constant (ka) called the volumetric (liquid) mass transfer coefficient. This coefficient is a product of the mass transfer coefficient k and the specific interfacial area a. The mass transfer coefficient k, which includes the thickness of the stagnant layer, is dependent upon the physical properties of the dispersion and on the relative velocity between the gas and the oil, among other things. The interfacial area is dependent upon the process conditions and upon the physical properties as well.

Owing to the difficulty of using literature data in the estimation of mass transfer conditions in the present study, the volumetric mass transfer coefficient ka was determined for cottonseed oil in a separate study according to a method used by Pihl and Schöön (19). The volumetric mass transfer coefficient was found to be ka = 2.1 sec^{-1}. Moreover, this coefficient was found to be practically independent of the iodine values and of the temperatures of interest. By using this value, the concentration difference of hydrogen across the transport film near the bubbles may be calculated from the equation:

$$N = 2.1\ \Delta c_H, \qquad \text{(I)}$$

where the units of N and Δc_H are mol hydrogen/liter oil, sec, and mol hydrogen/liter oil, respectively.

Transport Conditions to External Surface of Catalyst in Slurry

The mass transfer to the solid particles in liquid-particle slurries in stirred reactors has been the subject of many studies. Among recent papers, the extensive works by Brian, et al., (20) Levins and Glastonbury (21), and by van den Berg (22) may be mentioned. Complete references can be found in these articles.

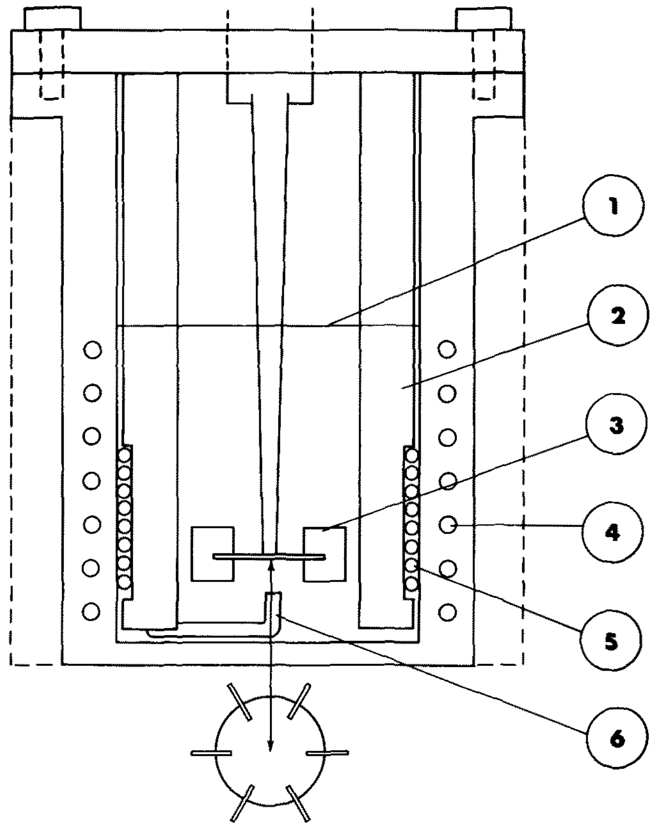

FIG. 1. Details of the reactor: 1 = ht of dispersion, 2 = baffle, 3 = impeller, 4 = cooling coil, 5 = heating coil, and 6 = gas inlet.

The estimation of the mass transfer coefficients k_H and k_G for the transfer of hydrogen and triglycerides, respectively, to the catalyst surface was based upon the results in (20-22). In these studies, the mass transfer coefficients are given as relationships between Sherwood number, Sh = k d_p/D, the specific power group $(\epsilon\, d_p^4/\nu^3)^{1/3}$, and Schmidt number, Sc = ν/D, according to the function:

$$\mathrm{Sh} - 2 = f([\epsilon d_p^4/\nu^3]^{1/3}, \mathrm{Sc}). \qquad \text{(II)}$$

The meaning of the introduced quantities are d_p = average diameter of catalyst particles, cm; D = molecular diffusivity, cm^2/sec; k = mass transfer coefficient, cm/sec; ϵ = energy dissipation rate in dispersion per unit mass, cm^2/sec^3; and ν = kinematic viscosity of the liquid phase, cm^2/sec.

The energy dissipation rate ϵ is defined as the power consumption (P) of the dispersion due to agitation/unit mass of dispersion. The power consumption may be calculated from the well known relationship (23):

$$P = N_p\, \rho_L\, n^3\, d_s^5, \qquad \text{(III)}$$

where: P = power consumption due to agitation, erg/sec; N_p = the power number, dimensionless; n = rotation speed of impeller, sec^{-1}; d_s = impeller diameter, cm; and ρ_L = density of the oil, g/cm^3.

For readers who are not familiar with the dimensionless numbers introduced, it may be mentioned that Sherwood number gives the ratio between the rate of total mass transfer and the rate of molecular diffusion. The specific power group is proportional to the fluid velocity and can be regarded as a Reynolds number for turbulent flow. Schmidt number, finally, gives the ratio between the momentum diffusivity and the molecular diffusivity.

The concentration difference across the transport film

TABLE I

Difference in Hydrogen Concentration across Transport Film near Gas Bubbles

Temperature (C)	Pressure (atm)	N x 10^3 mol/liter sec.	Relative concentration difference of hydrogen (%)
140	1.2	0.17	1.9
140	10.0	0.40	0.5
160	0.3	0.11	4.6
160	1.2	0.45	4.6
160	7.0	0.92	1.6
180	0.3	0.11	4.6
180	1.2	0.74	7.1
180	10.0	1.76	2.0
200	0.3	0.16	6.3
200	1.2	2.37	21.3
200	10.0	3.60	3.8

near the external surface of the catalyst particle then may be calculated from:

$$N = k(0.06\ w\ \rho_L/d_p\ \rho_p)\Delta c, \qquad \text{(IV)}$$

where k stands for k_H and k_G, and Δc stands for the concentration difference of hydrogen (Δc_H) and glycerides (Δc_G). The factor in parenthesis is the external surface of the spherical particles/unit volume of oil, where: w = catalyst loading, g/100 g slurry, and ρ_p = apparent density of the catalyst particles, g/cm^3.

Pore Transport Criteria for Liquid-Filled Pores

To date, the pore transport criteria for liquid-filled pores have been comparatively little studied (24). Pore transport limitations in liquid phase hydrogenations have been reported recently by various authors (24-30). In those cases where the effective diffusivity is smaller than the molecular diffusivity, Satterfield, et al., (24) found that the effectiveness factor in liquid-filled porous catalytic processes could be calculated with the same methods as those developed for gas phase processes. Based upon this observation, the risk of pore diffusion limitation in the present hydrogenation of rapeseed oil may be tested by using the well known criterion by Weisz and Prater (31,32):

$$\Phi = (N'\ d_p^2/4\ c\ D_e) < 1, \qquad \text{(V)}$$

where: Φ = Weisz-Prater modulus, dimensionless; N' = rate of mass transfer, mol/sec cm^3 catalyst; c = concentration of hydrogen or glycerides at the external surface of catalyst, mol/cm^3 oil; and D_e = effective diffusivity of hydrogen or glycerides in the porous catalyst, cm^2/sec. The effective diffusivity D_e may be estimated from the relationship:

$$\log_{10}(D_e\ \tau/D) = -2.0\ \lambda, \qquad \text{(VI)}$$

recently given by Satterfield, et al., (28) where τ is the tortuosity factor and λ is the ratio between critical solute molecular diameter and pore diameter. The meaning of the inequality (V) may be summarized as follows. If $\Phi \ll 1$, the process is free of significant diffusion effects and the properties of the kinetics observed are representative for the chemical steps of the process. If, however, $\Phi \gg 1$, a definite existence of diffusion effects is proved, and the kinetical behavior of the process is not representative for the chemical steps.

To date, the influence of the pore transport resistance on the fat hydrogenation has been very little studied. Albright (33) discussed the role of the pore transport step in a review of the different steps involved in the fat hydrogenation, and Coenen, et al., (34) studied the selectivity in fat hydrogenation as a function of the pore size of various catalysts. A quantitative interpretation of the pore transport effect recently was given by van der Plank and co-workers (25). In a kinetic study directed to give information concerning the behavior of the chemical reactions, the problem is, in contrast to the above mentioned articles, to show whether the pore transport is a rate-determining step or not. This question has been difficult to answer hitherto, owing to the lack of a method for estimating the effective diffusivity in liquid-filled pores of very small particles. The recently reported correlation equation (VI) now has made it possible to clarify this question with respect to the fat hydrogenation.

RESULTS AND DISCUSSION

In all runs, the mixing conditions corresponded to those used in an ordinary kinetic study of fat hydrogenation, where the intention is to eliminate the transport resistances. This means that the stirrer rate and the gas velocity were chosen to give very high mixing intensity on the macroscale of the bulk oil with subsequently limited mixing intensity on the microscale of the oil films near bubbles and catalyst particles, as discussed above. In all runs, the reaction rate thus reached a limiting value and was not influenced by any small change in the mixing conditions.

Influence of Transport Resistance in Gas-Liquid Contact

The differences in the hydrogen concentrations across the liquid film surrounding the gas bubbles were calculated according to equation I for some typical rapeseed oil hydrogenations at different hydrogen pressures and different temperatures. As may be seen from Table I, only high reaction rates at moderate hydrogen pressure will give rise to high values of the relative concentration differences, i.e. the concentration difference in percent of the hydrogen concentration in the gas-oil interface. The concentration in the gas-oil interface may be equal to the solubility of hydrogen. The solubility was calculated from values given in a recent study (35). The equilibrium solubility constant K_H was found to follow the relationship:

$$K_H = 0.0203\ \exp(-710/T)\text{mol/liter atm} \qquad \text{(VII)}$$

between the temperatures 140-200 C, where T is the absolute temperature in Kelvin. The rate of hydrogen transport N in Table I was calculated from the rate of the iodine value decrease, since the transport rate is equal to the reaction rate in a process without accumulation effects. The rate given in Table I refers to the iodine value (I.V.) = 80. The mass transfer rate in the units mol H_2/sec liter oil may be obtained by multiplying the iodine value decrease/min with the conversion factor (0.032/60).

Influence of Transport Resistance of Film Surrounding External Surface of Catalyst Particles

The mass transfer coefficient and the average external surface must be estimated before the concentration differences can be calculated. The average external surface was calculated to be a_p = 2.78 cm^{-1} (equation IV). The mass transfer coefficients for hydrogen (k_H) and triglycerides (k_G) were calculated from equation II. This equation is a general form of the equations given in references (20-22). The specific forms of the equations may be found by consulting the original articles. The values of Sh_H, Sh_G, k_H, and k_G in Table II are arithmetic mean values based upon equations from the three above mentioned references. The mass transfer conditions are specified in Table II by the Schmidt number and the specific power group. In addition to these, the mean catalyst particle diameter was $d_p = 10^{-3}$ cm; the energy dissipation rate was $\epsilon = 2.17 \times 10^6$ cm^2/sec^3.

The mixing conditions corresponded to fully developed turbulent flow and the power number N_p was estimated to be N_p = 9.5 (29). This value was found to be influenced only slightly by the gas flow rate at the present stirrer rate according to correlations given by Calderbank (9) and by

TABLE II

Mass Transfer Coefficients for Transport of Hydrogen and Triglycerides across Film Surrounding External Surface of Catalyst Particles in Rapeseed Oil Hydrogenation[a]

Temperature (C)	Sc_H	Sc_G	Specific power group[b]	Sh_H	Sh_G	k_H cm/sec	k_G cm/sec
140	350	26200	0.25	4.5	12.2	0.68	0.024
160	260	15000	0.30	4.3	10.9	0.73	0.032
180	180	9900	0.36	4.1	10.1	0.82	0.036
200	110	6800	0.45	3.9	9.6	1.1	0.040

[a] See text for definition of column headings.

[b] Specific power group, $(\epsilon\, d_p^4/\nu^3)^{1/3}$.

TABLE III

Concentration Differences across Transport Film near External Surface of Catalyst Particles

Temperature (C)	Pressure (atm)	N x 10^3 mol/liter sec.	Relative concentration difference of hydrogen (%)	Relative concentration difference of triglyceride (%)
140	1.2	0.17	2.1	0.3
140	10.0	0.40	0.6	0.7
160	0.3	0.11	4.9	0.1
160	1.2	0.45	4.9	0.6
160	7.0	0.92	1.6	1.2
180	0.3	0.11	4.5	0.1
180	1.2	0.74	7.0	0.9
180	10.0	1.76	1.9	2.1
200	0.3	0.16	4.8	0.2
200	1.2	2.37	19.4	2.5
200	10.0	3.60	2.9	3.8

TABLE IV

Test of Pore Transport Limitations in Rapeseed Oil Hydrogenation[a]

Temperature (C)	Pressure (atm)	D_{eH} x 10^5 cm^2/sec	D_{eG} x 10^7 cm^2/sec	N' x 10^3 mol/sec cm^3 catalyst	Φ_H	Φ_G
140	1.2	3.2	2.8	0.37	0.7	0.4
140	10.0			0.86	0.2	0.9
160	0.3	3.6	4.1	0.24	1.7	0.2
160	1.2			0.97	1.7	0.7
160	7.0			1.99	0.5	1.1
180	0.3	4.3	5.1	0.24	1.3	0.1
180	1.2			1.60	2.2	0.9
180	10.0			3.80	0.5	2.2
200	0.3	5.8	5.9	0.35	1.4	0.2
200	1.2			5.12	7.1	2.7
200	10.0			7.78	0.9	4.1

[a] D_{eH} and D_{eG} refer to an average pore, since the porosity is not included in equation (VI).

Michel and Miller (36). The value of N_p is somewhat uncertain, since it was based upon experiments using a reactor with somewhat different geometry than the present one. An error in N_p will, however, influence the mass transfer coefficient very little since this coefficient depends upon the one-third order of N_p at most (equations II and III).

As may be seen from Table II, the mass transfer coefficient for hydrogen is much larger than that for triglycerides. This difference is explained by the great difference in the diffusivities between hydrogen and triglycerides. The low specific power group values given in Table II indicate that the relative velocity between the oil and the particles is low.

The relative concentration differences near the external surface of the catalyst, i.e. the concentration differences in percent of the concentrations in the bulk oil, are given in Table III.

As may be seen from Table III, the differences in the triglyceride concentration are low even at high reaction rates, whereas this is not the case for the hydrogen concentration differences. Especially at medium hydrogen pressure, the concentration differences may not be neglected in a kinetic study of the chemical steps in the process. The relative concentration differences of hydrogen pass through a maximum upon increasing the hydrogen pressure owing to the simultaneously increasing solubility of hydrogen. The bulk oil concentrations of hydrogen were calculated from the solubility (equation VII) with correction for the concentration difference across the liquid film near the gas bubbles.

The bulk oil concentrations of the triglycerides may be commented upon. It is a well known fact that fatty acids in glycerides with two and three double bonds are hydrogenated more rapidly than those with only one double bond. At the beginning of the hydrogenation, it is, therefore, expected that only linoleic and linolenic acids in glycerides are responsible for the transport of triglycerides to the catalyst. Since the wt of these acids in the original rapeseed oil glycerides is only 14.3 + 9.7 = 24%, the bulk oil concentration of interest would be 0.24 x 0.85 = 0.20 mol/liter, which means that the relative concentration differences would be 4 times those given in Table III. However, when inspecting the composition changes of the fatty acids at the beginning of the hydrogenation, it was found that the decrease of the wt fraction of the sum of linoleic acid and linolenic acid was ca. the same as the decrease in the wt fraction of erucic acid. The wt fraction of euric acid in glycerides was as high as 48.4% in the original rapeseed oil. From this observation, it is obvious that the triglyceride molecules may be looked on as a single type of molecule from a mass transport point of view.

Influence of Pore Transport Resistance

The pore transport resistance may not be influenced by the external mixing conditions; and, therefore, this resistance may be high even under intense mixing conditions. The reaction conditions in the pores of the catalyst are given in Table IV at different hydrogen pressures and different temperatures in some rapeseed oil hydrogenations. Before a discussion of the results in Table IV is undertaken, the calculation procedure and the values used in equations V and VI should be commented upon for sake of clarity.

The effective diffusivities in Table IV, D_{eH} and D_{eG} for hydrogen and triglycerides, respectively, are calculated from equation VI using the molecular diffusivities of hydrogen and glyceryl trioleate in cottonseed oil, determined in a separate study (35). The average pore diameter of 80 Å was estimated for the present catalyst, and the tortuosity factor was assumed to be $\tau = 4$ (8,24). The critical solute molecular diameter was calculated in the same way as in ref. 28. Two diameters may be possible for the triglyceride, depending upon whether the molecules are transported lengthwise or breadthwise. It should be observed, however, that equation VI for the calculation of the effective diffusivity is based upon the smallest critical diameter of the solute molecule. It is obviously not possible to estimate the effective diffusivity for the breadthwise transport by this equation. The critical diameter of triglycerides may be estimated to be 10 Å (37,38), and the critical diameter of hydrogen was estimated to be 2.7 Å.

In Table IV, the mass transfer rate N′ is calculated from the rate N by multiplying with the factor $\rho_p/10\ w\ \rho_L$ to give the mass transfer rate in the desired units mol/sec cm^3 catalyst.

Now, let us return to the results in Table IV. From this table, it is clear that the process is free from significant diffusion effects with respect to the triglyceride molecules in most runs. At high reaction rates, the pore transport may be a slow step of the process, as indicated by the Φ-value. In experiments carried out under conditions similar to those used in the present work, van der Plank and co-workers (25) found effective diffusivities much smaller than those given in Table IV. This indicates a more pronounced effect of the pore diffusion than found here. The effective diffusivities were estimated with quite another method than the one used here. It is also clear from Table IV that the hydrogenation may not be affected to any appreciable extent by the pore diffusion of hydrogen molecules.

Corrections for Transport Resistance

If the parameters in the rate equation of the chemical reaction are to be calculated, the concentration of hydrogen at the external surface of the catalyst (c_H) may be calculated in the usual way from the following equation:

$$c_H = c_H^o - N([1/ka] + [1/k_H\ a_p]), \qquad \text{(VIII)}$$

where c_H^o is the solubility concentration of hydrogen in the oil. The first term within parenthesis is the transport resistance in the liquid film near the bubbles, and the second term is the transport resistance near the external catalyst surface. Owing to the low pore resistance against the hydrogen transport, c_H also will be the hydrogen concentration in the pores. Since the hydrogen pressure is determined experimentally more often than the hydrogen concentration, the rate equation may be written in terms of hydrogen pressure, and equation VIII may be rewritten to give the decrease in hydrogen pressure. It is also appropriate to write the mass transfer rate in terms of the rate of iodine value decrease, since this rate is directly determined. Equation VIII will thus be rewritten in the following form:

$$p = p^o + (0.032/K_H)\ (dIV/dt)\ ([1/ka] + [1/k_H\ a_p]), \qquad \text{(IX)}$$

where p^o is the hydrogen pressure in the gas phase and p is the equilibrium hydrogen pressure corresponding to the hydrogen concentration c_H. In equation IX, the pressure is given in atm and the decrease in iodine value in (I.V.)/sec.

A corresponding correction for the triglyceride concentration is not necessary owing to the relatively low concentration differences in the external transport step.

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