Hydrodesulfurization of Gas Oil, Reaction Rates in Narrow Boiling Range Fractions

The hydrodesulfurization of gas oil is treated as a sum of parallel reactions taking place in narrow boiling range fractions. The component reactions are approximately first order for fractions with boiling ranges of 20°C and mid boiling points between 250° and 350°C. The experimental procedure *involves desulfurization of the gas oil, fractionation* of samples of feed and products at various residence times, and determination of sulfur concentration in the fractions. The effect of the particle size of the catalyst and of the viscosity of the oil on the reaction rate can be assessed from Thiele's equation.

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SCOPE

The kinetics of the hydrodesulfurization of gas oil have been the subject of numerous investigations aimed at finding methods that could be used for predicting the degree of desulfurization at various conditions. The plots of the concentration of sulfur against the time were fitted by various empirical equations: first order (Van Zoonen and Douwes, 1963), second order (Beuther and Schmidt, 1963), and noninteger orders between 1 and 2 (Metzger et al., 1971). The reaction was also treated as the sum of two parallel first-order reactions with different rates (Van Deemter, 1965; Reitz, 1972; Schuit and Gates, 1973). But the usefulness of these treatments is limited, as the parameters, and often the form of the equations, change in a way which cannot be accurately predicted when the reaction conditions are varied or when the space velocity is changed. The rate is known to be affected by pore diffusion limitations, but the lack of a reliable kinetic expression makes it difficult to test the applicability of the common pore diffusion theories. In the present work, we examine the results of experiments, in which samples of feed and raffinates at various space velocities are fractionated and analyzed, and we treat the overall process as the sum of the processes taking place in the fractions. The diversity of the sulfur compounds in a narrow boiling range fraction is less than in the wide boiling range gas oil, and one can apply simple and significant equations with greater accuracy. Experiments were performed with catalyst of various particle sizes, and feeds of various viscosities and pore diffusion effects are treated.

CONCLUSIONS AND SIGNIFICANCE

It is advantageous to treat the hydrodesulfurization of gas oil as the sum of the processes taking place in the fractions. The rate equation in fractions with boiling ranges of 20°C and mid boiling points between 250° and 350°C closely approaches first order. Pore diffusion effects are taken care of by Thiele's equation and intrinsic rate constants, and diffusivities can be estimated. The treatment shows how the plots of the concentration against the residence time should be extrapolated; it also predicts the effect on the degree of desulfurization of such variables as the particle size of the catalyst, the viscosity of the treated oil, and its boiling range.

The kinetics of the desulfurization of gas oil are difficult to analyze rigorously. The process one actually measures, the rate of change of the sulfur content, is in fact the result of a multitude of chemical reactions involving a multitude of sulfur compounds with various reactivities and various mass transfer properties, and rigorous analysis implies monitoring the rate of disappearance of the individual sulfur compounds in the gas oil at reaction conditions.

There are grounds to assume that the individual compounds react according to first-order kinetics but have various rate constants. Desulfurization was performed with various sulfur compounds in the pure state, and the observed kinetics were either first order or of the Langmuir-

Hinshelwood type, approaching first order at low concentration (Satterfield and Roberts, 1968; Van Looy and Limido, 1958). If we assume further that the individual compounds in the gas oil react in parallel without interfering mutually, we can express the kinetics of the overall desulfurization reaction by

$$C = \Sigma C_i^o \exp(-k_i t) \qquad (1)$$

One cannot test this equation without monitoring the individual compounds, but it can be shown that it leads to a graph of ln C against t concave towards the ln C axis, in agreement with the curvatures usually found in actual measurements (Reitz, 1972; Van Deemter, 1965; Schuit and Gates, 1973).

The second derivative of the function ln $C(t)$ is

$$d^2(\ln C)/dt^2 = (1/C)(d^2C/dt^2) - (1/C)^2(dC/dt)^2 \qquad (2)$$

Substituting C, dC/dt and d^2C/dt^2 by their values according to Equation (1), we get

$$C^2[d^2(\ln C)/dt^2] = [\Sigma C_i^o k_i^2 \exp(-k_i t)] \\ [\Sigma C_i^o \exp(-k_i t)] - [\Sigma - C_i^o k_i \exp(-k_i t)]^2 \qquad (3)$$

Effectuating the multiplications in the right-hand side of the equation, one obtains

$$C^2[d^2(\ln C)/dt^2] = \Sigma(k_i - k_j)^2 \\ C_i^o C_j^o \exp(-k_i t) \exp(-k_j t) \qquad (4)$$

Each term in the summation is formed by combining k_i and C_i^o for a compound with k_j, C_j^o for another compound, and the summation comprises $n(n-1)/2$ terms for a gas oil containing n different sulfur compounds. Equation (4) can also be written in terms of C_i, C_j, the concentrations of the compounds at time t:

$$d^2(\ln C)/dt^2 = (1/C^2)\Sigma(k_i - k_j)^2 C_i C_j \qquad (5)$$

It is obvious that all the terms in the summations in Equations (4) or (5) are positive, and it follows that the curve of ln C against t is concave towards the ln C axis in agreement with the experimental results found in the literature. The curvature is large if the constants vary widely; that is, if $k_i - k_j$ have large values, it is zero, if all the compounds react according to identical rate equations $k_i - k_j = 0$, and in this case the rate equation for the overall process is first order.

A simplified treatment is to group the compounds together with close values of k and to consider the resulting groups as homogeneous species. Equation (1) becomes

$$C = \Sigma C_\nu^o \exp(-k_\nu t) \qquad (6)$$

with the subscript ν referring to the groups, and it contains a consistently smaller number of terms. The groups ν can be considered homogeneous within a desired accuracy, if one can neglect in Equations (4) or (5) the terms in which k_i and k_j belong to the same group. In that case, the groups fulfill the condition

$$C_\nu = C_\nu^o \exp(-k_\nu t) \approx \Sigma C_{i\nu}^o \exp(-k_{i\nu} t) \qquad (7)$$

and obey first-order kinetics.

The experimental procedure associated with this treatment involves the use of an adequate separation method capable of separating the gas oil into fractions containing the sulfur compounds with values of k sufficiently close. Desulfurization is performed on the overall gas oil, and separation into fractions is performed on samples of the feed and of the product at various retention times. The separated fractions are finally analyzed for their sulfur content, and graphs of ln C_ν against t for the fractions are drawn. The separation procedure is adequate if these graphs are linear. It is presumable that the best separation procedures are those in which the sulfur compounds are separated according to their structures as well as according to their molecular weights. We found, however, that the simplest of the separation procedures, fractional distillation, gave fairly good results when applied to oils with a boiling range between 240° and 360°C.

MATERIALS AND PROCEDURE

The assessments in this work are based on unpublished data privately communicated as well as on experimental work we performed. Wide boiling range fractions were submitted to hydrodesulfurization at 350° to 360°C in trickle-bed reactors of pilot plant size. Samples of feeds and products were fractionated and analyzed. The catalysts used contained 4 to 5% cobaltous oxide and 12 to 13% molybdenum oxide on γ alumina support and had surface areas around 240 m^2/g and porosities around 0.5. In experiments 1, 2, and 3, the pressure was 30 atm and the hydrogen to oil ratio was 200 m^3/m^3. In experiment 4, the pressure was 48 atm and the hydrogen to oil ratio 500 m^3/m^3. It is assumed that at any of these conditions desulfurization is zero order in relation to hydrogen. The nature and boiling range of the feed and the particle size of the catalyst were varied.

Experiment 1

The feed had a wide boiling range encompassing the gasoline and the gas oil ranges (see Table 1 and Figure 1). The particle size of the catalyst was 3 mm. Measurements were performed at two different LHSV; 2.5 hr^{-1} and 4.0 hr^{-1}.

Experiment 2

Same feed as in experiment 1. The particle size of the catalyst was 5 mm. The same LHSV were used, 2.5 and 4.0 hr^{-1}.

Experiment 3

The gasoline fraction was removed from the wide boiling range oil used as feed in experiments 1 and 2, and the remaining gas oil was treated. A single run was performed at LHSV = 2.5 hr^{-1}. The particle size of the catalyst was 5 mm.

Experiment 4

The feed was a gas oil in the 200° to 350°C range (see Figure 2), and the catalyst had a particle size of 1.5 mm.

THE FRACTIONATION

The fractionation in experiments 1, 2, and 3 was performed at intervals of 20°C, and the resulting fractions were weighed. In experiment 4, the samples were separated into ten fractions of equal volume, and the mid boiling points were determined. The cumulative weight percent or volume percent of the vaporized fractions is plotted against the boiling points in Figures 1 and 2. The plots are mostly linear, indicating that for the oils examined in the work, the two separation procedures are approximately equivalent.

In order to treat the overall desulfurization process as a sum of the processes taking place in the fractions, it is essential that the fractions in the product closely correspond to those in the feed. Table 1 and Figures

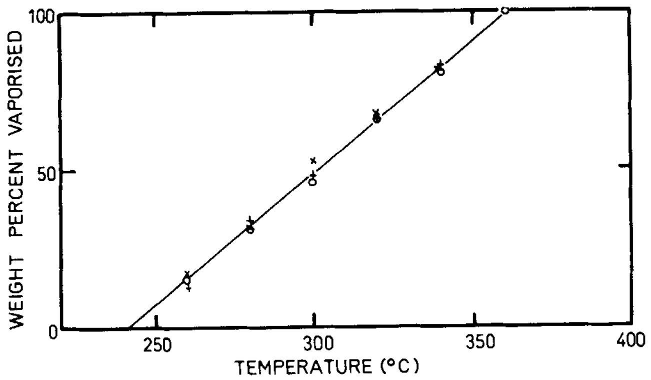

Fig. 1. Composition of the 240° to 360°C fractions in experiments 1 and 2. The cumulative weight percent vaporized at a given temperature is plotted against the temperature: ○ feed; X product, experiment 1; + product, experiment 2. The composition of the products at t = 0.25 hr^{-1} and at 0.4 hr^{-1} are undistinguishable.

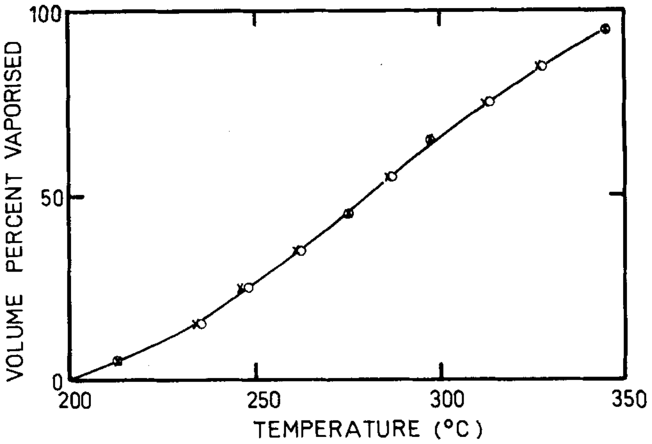

Fig. 2. Composition of oil in experiment 4. The cumulative volume percent of liquid vaporized at a given temperature is plotted against the temperature: ○ feed, X product.

Table 1. Composition of Feed and Products in Experiments 1, 2, and 3

	Vaporized below 240°C*, %	Vaporized between 240° and 360°C†, %	Liquid at 360°C, %	Unrecovered, %
Expt. 1				
Feed	47.0	40.4	11.9	0.7
Product, LHSV = 4 hr^{-1}	52.4	39.5	8.1	0.0
Product, LHSV = 2.5 hr^{-1}	52.2	41.6	5.9	0.3
Expt. 2				
Product, LHSV = 4 hr^{-1}	49.2	39.4	11.1	0.3
Product, LHSV = 2.5 hr^{-1}	46.9	41.5	11.3	0.3
Expt. 3				
Feed	19.0	61.2	16.1	3.7
Product, LHSV = 2.5^{-1}	19.5	64.0	15.2	1.3

* This column shows the cumulative weight percent of the eight lighter fractions; the first one was vaporized at 100°C and the others at 20°C interval between 100° and 240°C.

† This column shows the cumulative weight percent of six fractions. Detailed composition is given in Figure 1 for experiments 1 and 2.

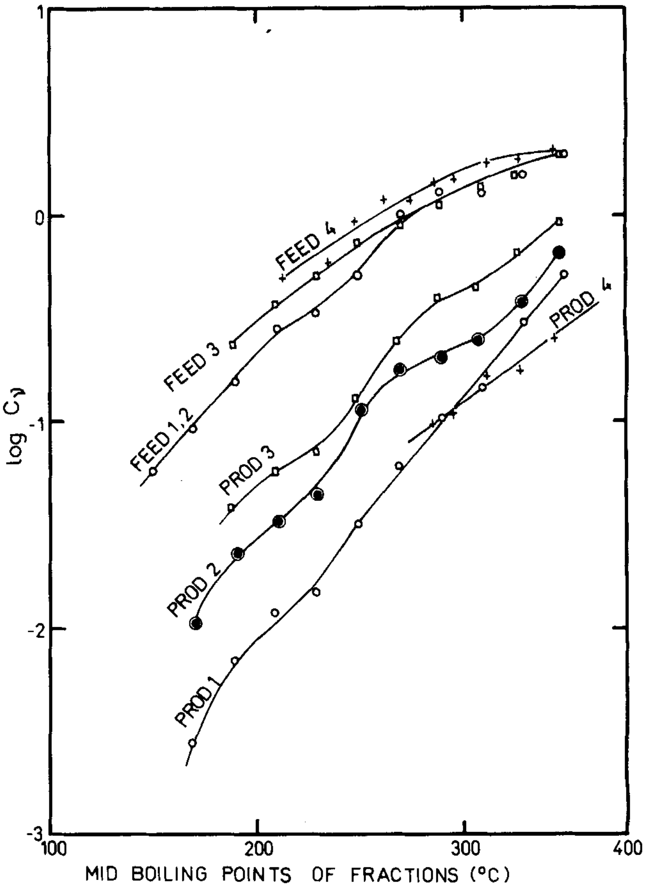

Fig. 3. Sulfur content of the fractions. Feeds and products at LHSV = 2.5 hr^{-1} (experiments 1, 2, and 3) and 2.2 hr^{-1} (experiment 4).

1 and 2 show that the desulfurization reaction causes a slight increase in the percentage of the lighter hydrocarbons, and this interferes with the reproducibility with which the fractions are defined. In Figure 1 the points referring to the products are higher than those referring to the feeds, and in Figure 2 the mid boiling points for the products are displaced to lower values. Most of the cracking occurs early during the process, and the plots are identical for products at different retention times. However, the shifts in the distributions are not considerable and should not lead to serious errors in the treatment of the data concerning the 240° to 360 deg fractions. The error is presumably large for the gasoline range fractions, as they may become enriched in sulfur by including fragments from the sulfur rich, high boiling point fractions.

The specific gravities of the fractions were also determined, and characterization factors (cubic root of mid boiling point in °*R* divided by specific gravity at 15°C) were calculated. In all the experiments, the characterization factors were between 11.6 and 11.8.

CONCENTRATION OF SULFUR AND RATE OF DESULFURIZATION IN THE FRACTIONS

The distribution of sulfur is depicted in Figure 3 as plots of the logarithms of the concentrations in the frac-

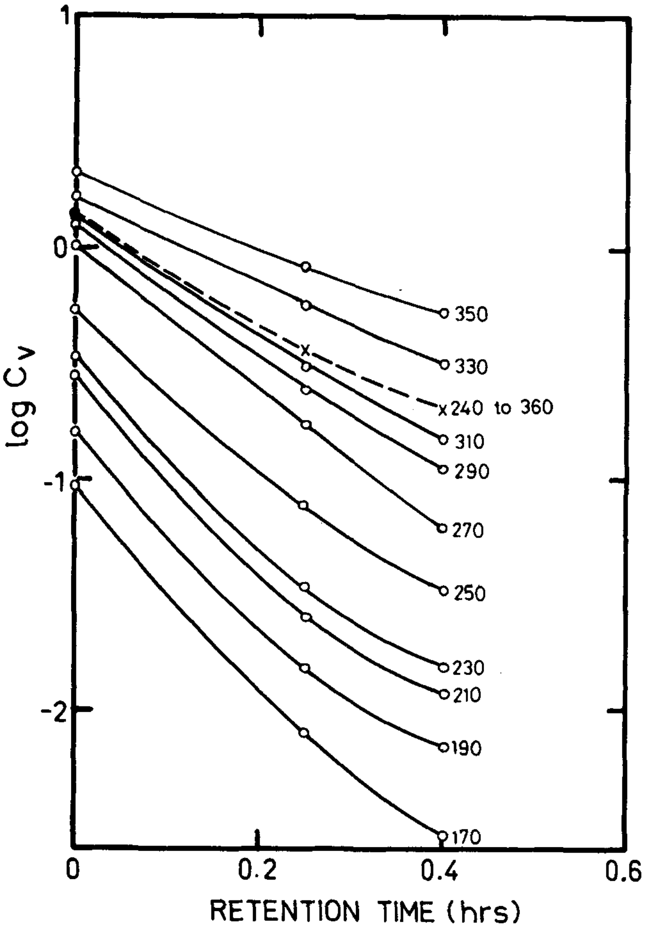

Fig. 4. Plots of log C_ν against the retention time (experiment 1). The mid boiling points (°C) of the fractions are indicated. The dotted curve refers to the wide boiling range fraction 240° to 360°C.

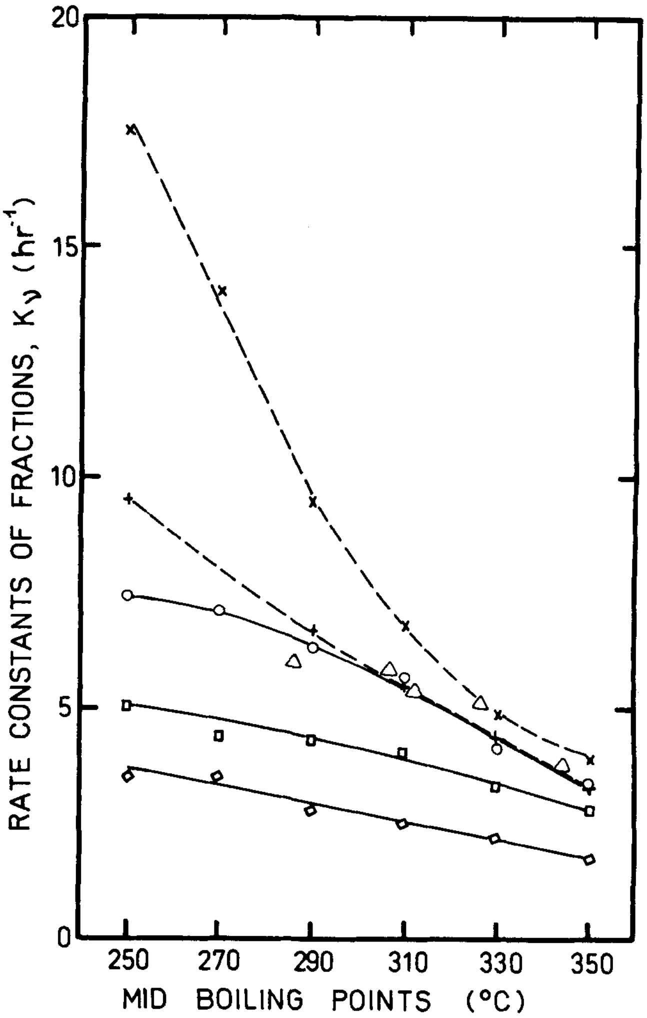

Fig. 5. Plots of the rate constants in the fraction against the mid boiling points.

	Experiment No.	Material processed	Catalyst particle size
○	1	Gasoline-gas oil	3 mm
□	2	Gasoline-gas oil	5 mm
◇	3	Gas oil	5 mm
△	4	Gas oil	1.5 mm
+	Calculated	Gas oil	1.5 mm
×	Calculated, no diffusion resistance ($k_{o\nu}$)		

tions log C_ν against the mid boiling points. The plots are drawn for the feeds and for the raffinates at LHSV—2.5 hr^{-1} (experiments 1, 2, and 3) and 2.2 hr^{-1} (experiment 4). In the two oils examined, the sulfur content increases rapidly with the boiling point of the fraction. The curves for the products are nearer to straight lines than those for the feeds and have greater slopes. The dissimilarity of the curves feed 1, 2 and feed 3 stresses the fact that the sulfur content of the fractions depends on the way the feed is prepared. Curve feed 3 refers to the liquid product resulting from the removal of gasoline as a single fraction at 180°C. This procedure strips the liquid from low, boiling point hydrocarbons and sulfur compounds more efficiently than the multiple fraction procedure represented by feed 1, 2 and it produces a gas oil richer in high boiling point components and consequently richer in sulfur. Measurements of specific gravity confirmed this assumption.

In order to test if the sulfur compounds in a fraction can be considered as a homogeneous group reacting according to first-order kinetics, we plotted log C_ν against the retention time t. Results for the fractions in the gas-oil range in experiment 1 are shown in Figure 4. The plots are slightly concave towards the log C_ν axis, and they approach straight lines as the boiling point of the fraction becomes higher. The rate constants k_ν were calculated for the fractions between 240° and 360°C from the slopes of the corresponding curves and are depicted in Figure 5. The results in Figure 4 suggest that the rate constants for individual sulfur compounds of high molecular weight primarily depend on the molecular weight, and, therefore, separation according to the boiling points produces fairly homogeneous groups. The lower molecular weight compounds have rate constants that depend on the structure as well as on the molecular weight, and the lower boiling point fractions comprise wider ranges of k.

The results of experiment 2 followed the same pattern; the plots for the fractions with mid boiling points above 250 appeared to be fairly linear, and the values of k_ν could be estimated with a relative error of less than ±5% (see Figure 5). The data for the fractions in the gasoline range in both experiments were inconsistent; the sulfur concentration in the products was too low to be measured accurately, and cracking is likely to have affected the results consistently. Experiments 3 and 4 were conducted at a single LHSV, and the k_ν (in Fig. 5) were estimated on the assumption of linearity of the ln C against t plot.

The plot of ln C against t for wide boiling range fractions is concave towards the ln C axis as expected. The plot for the fraction ranging from 240° to 360°C in experiment 1 is depicted in Figure 4; it is concave in contrast with the plots for the component narrow fractions.

DIFFUSION EFFECTS

Figure 5 shows that the rate constant for any given fraction decreases with increase of the particle size of the catalyst (compare k_ν for experiments 1 and 2) and with increase of the viscosity of the processed liquid (compare experiments 2 and 3). The rates apparently depend on pore diffusion resistance. Taking advantage of the fact that the rates are first order, one can estimate the intrinsic rate constants $k_{o\nu}$ and the diffusivities D_ν with Thiele's equation

$$k_\nu = k_{o\nu}(3/\phi_\nu)[1/\tanh \phi_\nu - 1/\phi_\nu] \quad (8)$$

where the modulus

$$\phi_\nu = r[k_{o\nu}/D_\nu]^{1/2} \quad (9)$$

$k_{o\nu}$ and D_ν for the low viscosity, gasoline-gas oil mixture were estimated from k_ν of experiments 1 and 2. The calculated $k_{o\nu}$ were combined with k_ν of experiment 3 to give D_ν for the more viscous pure gas oil.

The intrinsic rate constants are depicted in Figure 5 as plots against the mid boiling points of the fractions. The diffusivities could not be determined accurately, and it was not possible to detect differences that could be related to the boiling points of the reacting sulfur compounds. They were around 4×10^{-5} cm^2/s for all the fractions with the mixture gasoline-gas oil and around 0.8×10^{-5} cm^2/s for all the fractions with pure gas oil. The ratio between these figures seems higher than the ratio between the viscosities of the processed liquids, but it is of the same order. The charts in Maxwell (1950) give μ_L for gas oil 200° to 350°C about 0.21 centipoise and for gasoline-gas oil 100° to 350°C around 0.1 centipoise.

The low magnitude of the diffusivities indicates that in trickle-bed desulfurization, the pores are filled with liquid rather than with gas. One can estimate the order of magnitude of the diffusivity in liquid filled pores according to the Wilke-Chang equation (Wilke and Chang, 1955)

$$D = 7.4 \times 10^{-8}(T/\mu_L)(M_L{}^{0.5}/V_b{}^{0.6})(\theta/\tau_p) \quad (10)$$

and in gas filled pores according to the Lennard-Jones expression (Satterfield, 1970)

$$D = 1.86 \times 10^{-3}T^{3/2}(M_1 + M_2)^{1/2}/(M_1M_2)^{1/2}p\sigma_{12}{}^2\Omega_b \quad (11)$$

We assume that the properties of the sulfur compounds are represented by those of dibenzo-thiophene:molecular weight 184 and molecular volume 190 cm^3/mole and that the gas phase, in the case of gas filled capillaries, is a binary mixture of hydrogen and of dibenzo-thiophene. We also introduce $M_L \approx 210$, $\theta/\tau_p \approx 0.1$, $\sigma_{1,2} \approx 6$, and $\Omega_b \approx 1$. We obtain a diffusivity of the order of 10^{-5} cm^2/s for the liquid filled pores and 10^{-3} cm^2/s for the gas filled pores. The diffusivities obtained experimentally are close to the diffusivity for liquid filled pores.

Figure 5 also comprises a calculated graph for 1.5 mm pellets and gas oil feed. This graph was calculated from $k_{o\nu}$ and D_ν based on the data of experiments 1, 2, and 3. It is found that the calculated graph matches fairly well with the results of experiment 4. This agreement is a confirmation of the applicability of Thiele's equation if we assume that the two oils used in experiments 1, 2, 3, and 4 have similar distributions of the intrinsic rate constants. The two oils have similar characterization factors, and the assumption that oils with similar characterization factors would have similar distributions of rate constants is plausible but needs further investigation. The k_ν for corresponding fractions in two different oils depends on the structures of the sulfur compounds present. This property is presumably related to the aromaticity and therefore to the characterization factor.

NOTATION

C = concentration, wt%
C^o = concentration in feed, wt%
D = diffusivity, cm^2/s
k = rate constant, l/hr
k_o = intrinsic rate constant, l/hr
M = molecular weight
P = pressure, atm
r = radius of particle, cm
T = temp, °C
t = time, hr
V = molecular volume, cm^3/g-mole

Greek Letters

μ_L = viscosity, centipoise
τ_p = tortuosity
ϕ = Thiele modulus
θ = porosity, cm^3/cm^2
$\sigma_{1,2}$ = effective molecular diameter

Subscripts

i, j = individual sulfur compounds
ν = group of sulfur compounds with close values of k
$i\nu$ = compound i in the group ν

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