



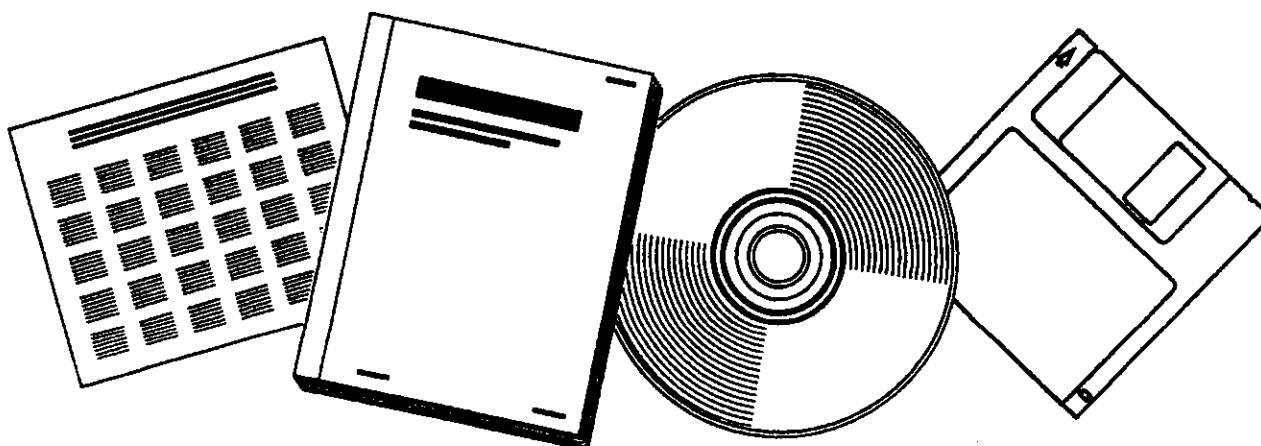
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SOLVENT REFINED COAL (SRC) PROCESS. EFFECT OF MIXING ENERGY ON HYDROGEN REACTION RATES IN SRC-II REACTORS

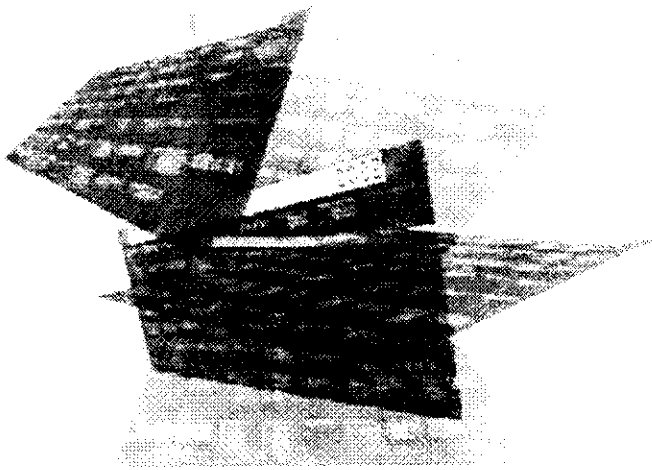
PITTSBURG AND MIDWAY COAL MINING CO.
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EFFECT OF MIXING ENERGY ON HYDROGEN REACTION RATES
IN SRC-II REACTORS

Solvent Refined Coal (SRC) Process

Volume V: Research and Development Technical Support Programs
Part 3: Modeling and Simulation

By
C. P. P. Singh
Y. T. Shah
N. L. Carr

January 1982

Work Performed Under Contract No. AC05-76ET10104

The Pittsburg and Midway Coal Mining Company
Englewood, Colorado



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Rates in SRC-II Reactors

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EFFECT OF MIXING ENERGY ON HYDROGEN REACTION
RATES IN SRC-II REACTORS

by

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ABSTRACT

This study attempted to analyze theoretically the conditions which may lead to hydrogen starvation in SRC-II reactors. Literature correlations for mass transfer coefficients in bubble columns were combined with experimental data from a stirred vessel (CSTR) on the basis of specific power consumption. Specific power consumption, i.e., consumption of mixing energy per unit volume per unit time, is proportional to N^3 , where N is the stirrer speed, and approximately proportional to superficial gas velocity (U_g) in a bubble column. For operating conditions selected to give maximum practicable reaction rate, i.e., under conditions of highest possibility of hydrogen starvation, results indicate that the fractional decrease in the rate of reaction would be insignificant (<4%) for superficial gas velocity, U_g , above 1 cm/s. Based on this result it can be claimed that in the SRC-II process, hydrogen starvation is unlikely.

The rate of reaction was shown to be sensitive to the value of the mass transfer coefficient, $K_L a$. A decrease in the rate of reaction due to lower value of mass transfer coefficient ($K_L a$) can be compensated by increasing the gas rate (superficial gas velocity). This shows that the possibility of hydrogen starvation would decrease with increase in the length of SRC-II reactors, since the superficial velocity in a taller reactor will have to be higher. Based on the present study, it is believed that the higher the gas velocity (the longer the reactor) in the large-scale reactor situation, hydrogen reaction rates will not be significantly influenced by mass transfer in normal operation of the reactor.

SUMMARY

The amount of hydrogen consumed per unit mass of MAF coal is a generally accepted indicator of the progress of coal liquefaction reactions. Since hydrogen is present in the gas phase, whereas all the reactions take place in the liquid or slurry phase, hydrogen has to enter, and be available at each point in the reacting slurry for the reaction to occur. Liquefaction reactions may be slowed down if the rate of transfer of hydrogen to the liquid phase is slow, i.e., the slurry is starved of hydrogen. This study attempts to analyze theoretically the conditions which may lead to hydrogen starvation in SRC-II reactors.

Kinetic rate expression for hydrogen consumption, developed in an earlier study, based on the once-through data from the A-1 unit, has been used here (Singh et al., 1980a). This rate expression has been successfully used to simulate various pilot plant runs with recycle and to predict effects of various variables on yields and buildup of solids in the SRC-II reactors (Singh et al., 1980b). Theoretical study of the thermal behavior of SRC-II reactors, based on this rate expression, indicated the reactor operation to be thermally unstable (Singh et al., 1981). A subsequent experimental study on P-99 substantiates this conclusion.

Correlations for evaluating mass transfer coefficients have been developed by using data on a tetralin-hydrogen system obtained from studies in a batch-stirred tank using special hydrogen probes (Kara, 1980-81, and available literature). Preliminary data on a coal liquid-hydrogen system, from the above experimental set-up, indicates that mass transfer properties of a tetralin-hydrogen system are the same as those of a coal liquid-hydrogen system.

The literature correlations for mass transfer coefficients in bubble columns are combined with experimental data from a stirred vessel (CSTR) on the basis of specific power consumption, to obtain a unified correlation which can be applied to SRC-II (bubble column) reactors. Specific power consumption, i.e., consumption of mixing energy per unit volume per unit time is proportional to N^3 , where N is the stirrer speed, and approximately proportional to superficial gas velocity (U_g) in a bubble column.

The developed correlation for mass transfer coefficient ($K_L a = b (P/V)^{0.84}$) has been used to simulate experimental runs in the A-1 unit. The agreement between calculated and measured hydrogen consumptions at different stirrer speeds validates the correlation. The latter is further used to evaluate the fractional decrease in the rate of reaction due to mass transfer effects and for evaluating the Hatta number using film theory concepts. For the operating conditions selected to give maximum practicable reaction rate, i.e., under conditions of highest possibility of hydrogen starvation or significant mass transfer effects, results from both the above mentioned approaches indicate that the fractional decrease in the rate of reaction would be insignificant (<4%) for superficial gas velocity, U_g , above 1 cm/s. Based on this result it can be claimed that in the SRC-II process, hydrogen starvation is unlikely. For analysis of mass transfer effects, the use of film theory is difficult in this case, since the mass transfer effects are insignificant only at very low values of the characteristic Hatta number, M . Therefore, direct evaluation of the fractional decrease in the rate of reaction is used, as it is more meaningful to our analysis.

In general, the rate of reaction is shown to be sensitive to the value of the mass transfer coefficient, $K_L a$. With decrease in the value of mass transfer coefficient ($K_L a$) the rate of hydrogen reaction decreases. However, a decrease in the rate of reaction due to lower value of mass transfer coefficient ($K_L a$) can be compensated by increasing the gas rate (superficial gas velocity). This shows that the possibility of hydrogen starvation would decrease with increase in the length of SRC-II reactors, since the superficial velocity in a taller reactor will have to be higher (in order to maintain a constant gas residence time).

Since no mass transfer studies in large bubble columns are reported in literature, the possibility that the above-developed correlation may not hold for large SRC-II reactors cannot be ruled out. However, it is significant to note that the gas dispersion coefficient for large size (3.2 m diameter, 18.9 m length) bubble columns showed the same dependence on gas velocity ($U_g^{3.56}$) as a small column (10 cm diameter) (Field and Davidson,

1981). Therefore, it is not likely that a large-size column will behave very differently with respect to mass transfer effects. The larger the size (length) of an SRC-II reactor, the smaller should be the effect of mass transfer resistance or the possibility of hydrogen starvation.

Based on this study, we believe the higher the gas velocity (the longer the reactor) in the large-scale reactor situation, hydrogen reaction rates will not be significantly influenced by mass transfer in normal operation of the reactor. Even if our best estimates are in error by a factor of ten, the above statement still holds.

INTRODUCTION

Coal liquefaction consists of innumerable reactions involving various coal constituents. It is known that a large number of these reactions consume hydrogen. Generally, the progress of coal liquefaction reactions is expressed in terms of the amount of hydrogen consumed per unit mass of coal. Since all the reactions take place in the liquid phase, whereas hydrogen is supplied in gaseous form, it is necessary that the latter enter liquid-phase for the reactions to take place. Also, the rate of hydrogenation reactions may depend on the availability, i.e., concentration of hydrogen in the liquid phase. This is shown by the fact that the rate of hydrogen consumption increases with an increase in the partial pressure of hydrogen. The latter can have only one effect which is to increase the concentration of hydrogen in the liquid or slurry phase. Concentration of hydrogen in the coal oil slurry also depends on the quality of the slurry, rate of hydrogen mass transfer to the slurry (liquid) phase and the rate of hydrogen consumption by reaction.

Quality of the slurry depends on the extent of liquefaction which is a function of many process and operating variables. No data on the mass transfer rate of hydrogen in coal liquids is reported in literature. Therefore, it has been difficult to determine the effects of variation in the properties of slurry on the rate of hydrogen consumption in the SRC-II process. In fact, the mass transfer correlations developed and used in the present study are based on data for cotton seed oil-hydrogen, anthracene oil-hydrogen and tetralin-hydrogen systems. However, it is important to mention that a preliminary evaluation from a most recent investigation of hydrogen mass transfer rates in coal liquid indicates that the tetralin-hydrogen system may be considered to give a reasonable representation of a coal oil-hydrogen system (Kara, 1980-81). On this basis, we generalize to claim that the mass transfer correlations, based on systems similar to coal oil-hydrogen, may be considered to give a reasonable representation of the coal oil-hydrogen system, i.e., the SRC-II process.

In a gas-liquid system the concentration of gas in the liquid in contact with the gas, i.e., at the gas-liquid interface equals the maximum possible concentration, i.e., the equilibrium concentration of the gas in the liquid. This equilibrium concentration depends on temperature pressure and properties of the system. At any interior point in the liquid phase, i.e., at any point away from the gas-liquid interface, the concentration of the gaseous reactant might be much smaller than that at the interface. If the rate of transfer of hydrogen to the point of reaction is slow, and the rate of reaction is fast, most of the gas can be consumed before it can reach an interior point in the liquid. On the contrary, if the rate of hydrogen mass transfer is very high, (the mass transfer resistance is very small), and the reaction is very slow, hydrogen may attain a uniform concentration throughout the liquid phase. The latter situation exists in normal SRC-II reactor operations.

The overall rate of mass transfer is proportional to the gas-liquid contact area, i.e., interfacial area, per unit reactor volume, \underline{a} , and to the rate of transfer per unit interfacial area, i.e., specific mass transfer coefficient K_L . Each of these two (\underline{a} and K_L) depend on the hydrodynamic conditions in the reactor. In case the reactor contents are very well mixed, gas will be very thoroughly distributed throughout the liquid in the form of small bubbles resulting in very large specific interfacial area, \underline{a} . Since the gas is very well distributed, no element of liquid will be far away from the gas-liquid interface and the gas molecules will have to be carried only a short distance to reach the farthest point from an interface. Also, fresh liquid will continuously be brought in contact with the gas bubble by thorough mixing in the liquid phase and the specific mass transfer coefficient will be high. Thus, better distribution of gas in a liquid leads to larger interfacial area, whereas better mixing in the liquid phase yields higher specific mass transfer coefficients. The net result of these two effects is higher overall mass transfer rate for higher levels of mixing in the reactor.

In case the extent of mixing in the reactor is small, the gas would exist in the form of large bubbles separated from each other by relatively large distances and the rate of renewal of liquid at the gas-liquid interface would be low. Therefore, in this case the specific interfacial area, a , as well as the specific mass transfer coefficient, K_L , would be small and the bulk of the liquid, away from the gas-liquid interface, may be starved of the gaseous reactant. In such a situation, the overall rate of reaction would be much smaller than what it would have been if the concentration of the gas throughout the liquid phase were the same as that at the interface. The reaction may be limited, i.e., rate may be reduced, due to insufficient transfer of gas through the gas-liquid interface. In other words, the resistance to transfer of gas to the liquid phase may limit the rate. In general, such a situation is described as mass transfer controlled reaction or reaction with significant mass transfer resistance. It is important to note here that for a very fast reaction the mass transfer effects may be significant even with very good mixing in the reactor.

The possibility of the SRC-II process being carried out under mass transfer controlled conditions cannot be ruled out a priori, since the partial pressure of hydrogen is known to have a significant effect on the rate of reaction. It is required that the effect of mass transfer resistances in the SRC-II process be evaluated over a large range of feasible operating conditions such that mass transfer controlled regions of operating conditions can be avoided. This will also help in selecting better or optimum operating conditions. The present study attempts to make such an analysis of the SRC-II process.

There are three theories, namely Film Theory, Surface Renewal Theory and Higbie's Penetration Theory, available in the literature, which can be used to estimate the role of mass transfer resistances on the overall reaction rate. The most simple and widely used "Film Theory" considers that all the changes, i.e., drop in the concentration of gaseous reactant, from gas-liquid interface to the farthest point in the liquid take place in a very thin film of liquid around the gas bubbles. In other words, except for a thin film

around the gas bubbles, the concentration of gaseous reactant throughout the liquid is considered to have a uniform value, C_l° , and the change in the concentration of gas in liquid, from the equilibrium value C_l^* to C_l° , is assumed to occur in the liquid film. Thickness of this liquid film around the gas bubbles depends on properties of the gas-liquid system, reactor configuration as well as the operating conditions. Though the Film Theory is relatively simple to use, it is important to mention that results from each of the three theories are almost identical in most of the situations of practical importance. One part of the present analysis is based on the Film Theory.

FIGURE 1

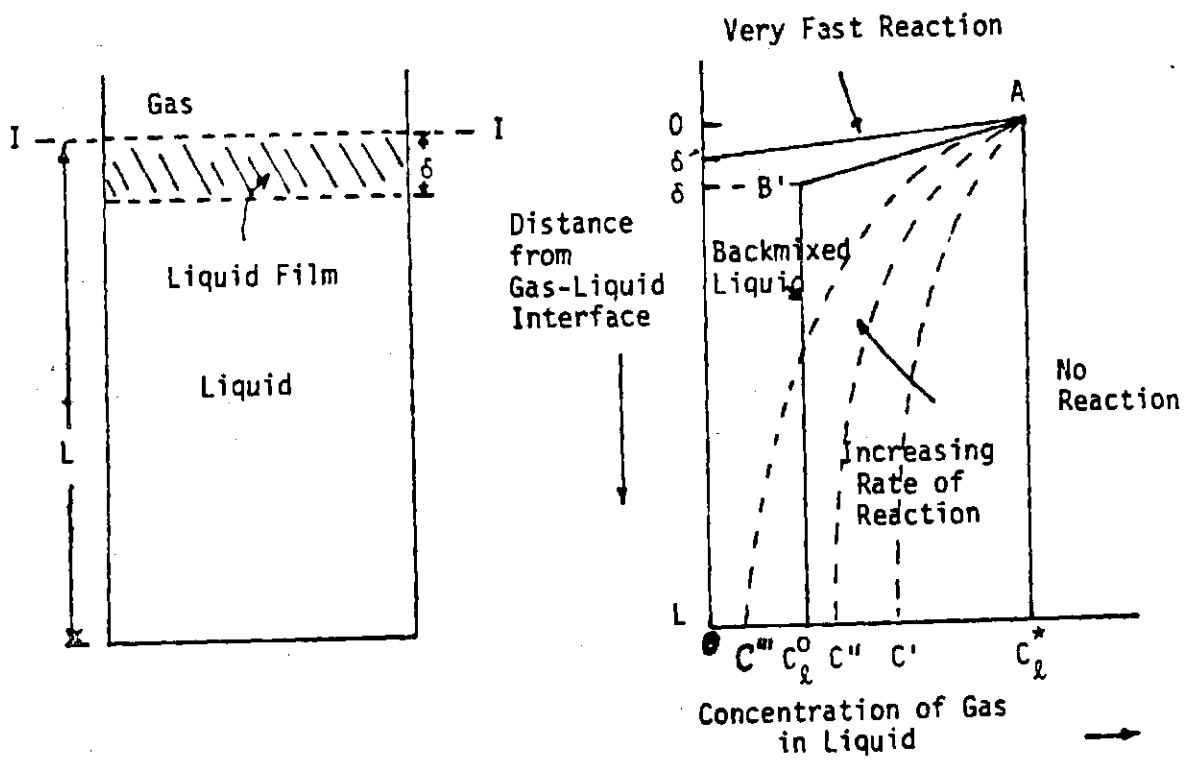


FIGURE 1: Concentration of Gas in Liquid Under Various Conditions

Effect of Mass Transfer

Let us consider a stagnant liquid separated from a gas by a well defined interface II (Figure 1). In case the two (gas-liquid) do not react the liquid would have a uniform distribution of the gaseous species and the concentration of gas in the liquid would correspond to its equilibrium value, C_l^* , which depends on its solubility under the prevailing pressure and temperature conditions. C_l^* in this case can be expressed by Henry's law.

$$C_l^* = H \cdot C_g \quad (1)$$

where C_g is the concentration of gas in the gaseous phase and H is the Henry's constant which depends on temperature. If the two (gas-liquid) react the concentration of the gas in liquid would be lower at larger distances from the gas-liquid interface. The magnitude of drop in concentration from C_l^* to C_l' , C_l'' , etc., would depend on the rates of diffusion of gas in liquid and its rate of reaction. If the reaction is very fast or instantaneous, the concentration of gas in the liquid phase would be insignificant at a very small depth or beyond a very thin (thickness δ') liquid film at the interface. The overall drop in concentration from the interface equilibrium value to the lowest concentration at the bottom as well as the concentration profile along the length would be dependent on the rates of reaction and diffusion. In case the liquid phase is well mixed, most of the concentration drop would occur in a thin liquid film close to the interface and bulk of the liquid would have a uniform concentration C_l^0 . The magnitude of the bulk liquid concentration, C_l^0 , and thickness of the liquid film, δ , would depend on the rate of the reaction and the extent of mixing, but the nature of variation in the concentration along the depth, AB'C, would be similar for various levels of mixing. The rate of reaction in this case can be expressed as

$$r = K f(C_l^0) \quad (2)$$

$$= K C_l^0 \quad (\text{for a first order reaction}) \quad (3)$$

and this must equal the rate at which the gaseous reactant is transferred through the interface, i.e.,

$$r = K_L \underline{a} (C_l^* - C_l^U) \quad (4)$$

where K_L is the specific mass transfer coefficient and \underline{a} is the specific gas-liquid interfacial area.

From equations (3) and (4), the rate of reaction can be expressed as

$$r = K \frac{K_L \underline{a}}{K + K_L \underline{a}} C_l^* \quad (5)$$

It is important to note that the above expression, for a first order reaction, is being used only for illustration. For complex reactions, such as coal liquefaction, it may not be possible to obtain an explicit relation as in equation (5).

In the case of a very high mass transfer coefficient, i.e., $K_L \underline{a} \gg K$, equation (5) reduces to

$$r = K C_l^* \quad (6)$$

and its comparison with equation (3) shows that it represents the rate of reaction when the concentration of the gas throughout the liquid equals the equilibrium concentration. In other words, it represents an insignificant or no mass transfer resistance situation.

When $K \gg K_L \underline{a}$, equation (5) reduces to

$$r = K_L \underline{a} C_l^* \quad (7)$$

The above equation is the same as equation (4), for $C_l^U = 0$. Thus, equation (7) represents a situation in which the concentration of the gaseous reactant

in the bulk liquid is insignificant i.e., the gas reacts completely in the liquid film itself. This represents a completely mass transfer controlled situation. For comparable mass transfer and reaction rates, the concentration of the gas in the bulk liquid C_{ℓ}^U would be comparable to the equilibrium concentration C_{ℓ}^* and also the reaction in the liquid film would constitute a significant part of the overall reaction. In case of a very slow reaction the concentration in the bulk, C_{ℓ}^U , is almost equal to that at the interface C_{ℓ}^* and the reactions take place essentially in the bulk liquid i.e., contribution of reactions in the liquid film is insignificant compared to the overall conversion.

As discussed in the preceding paragraph the contribution of reactions in the liquid film to the overall conversion is a very clear indicator of the relative importance of mass transfer and kinetic rates. Criterion for insignificant or very significant mass transfer effects can therefore be based on the conversion in the liquid film. However, in many cases particularly when the reaction rate expression is of complex order it may be more useful to base all the analysis on a direct comparison of the rates of mass transfer and reaction. The analysis to follow uses both the approaches to evaluate the effect of mass transfer resistance in the SRC-II coal liquefaction process.

Criterion for Insignificant Effect of Mass Transfer

Slow reactions: In this case an appreciable amount of the absorbed gas reacts before leaving the reactor but a negligible proportion of the absorbed gas reacts in the liquid film. The process is essentially one of physical absorption followed by reaction in the bulk, or removal from the system by the outgoing liquid stream. For coal liquefaction the rate of hydrogen consumption can thus be expressed as

$$\underline{Ra} = K_L a (C_{H_{2\ell}}^* - C_{H_{2\ell}}^U) = \frac{1}{\tau} (C_{H_{2\ell}}^U - C_{H_{2\ell}}^i) + r_{H_2} \quad (8)$$

where R is rate of absorption per unit interfacial area, gm/cm^2 , a is the interfacial area per unit reactor volume, cm^2/cm^3 ; K_L is the mass transfer coefficient, cm/s ; $C_{H_2}^*$, $C_{H_2}^U$, and $C_{H_2}^i$ are concentrations of hydrogen at the gas-liquid interface, in the outlet liquid stream or bulk liquid and in the inlet stream respectively, $\text{gm}/\text{c.c.}$; τ is slurry residence time, s ; and r_{H_2} is the rate of hydrogen consumption $\text{gm}/\text{cm}^3\text{s}$.

The condition to be fulfilled, if no appreciable proportion of the absorbed gas is to react in the film, can be deduced as follows (the nomenclature of film theory is used for convenience, but the conclusions do not depend on the model). The concentration of hydrogen falls from $C_{H_2}^*$ to $C_{H_2}^U$ across the film, so the mean concentration in the film is less than $C_{H_2}^*$. Thus the average rate of hydrogen consumption per unit volume of the film is less than $r_{H_2}^*$, the rate at which hydrogen would be consumed if its concentration in bulk liquid were $C_{H_2}^*$. The rate of reaction of H_2 in the film associated with unit area of interface is therefore not more than $\delta r_{H_2}^*$, where δ is the film thickness, and since

$$\delta = \frac{D_{H_2l}}{K_L}$$

$$\frac{D_{H_2l}}{K_L} r_{H_2}^* \ll R = K_L (C_{H_2}^* - C_{H_2}^U) \quad (9)$$

is the condition that a negligible amount of the absorbed gas should react in the film. Equation 9 can be rearranged as

$$\frac{D_{H_2l}}{K_L^2} \frac{r_{H_2}^*}{C_{H_2}^*} \ll 1 - \frac{C_{H_2}^U}{C_{H_2}^*} \quad (10)$$

Since the expression on the right hand side is less than unity, the value of L.H.S. expression must be much less than unity in any case, so that

$$(M =) \frac{D_{H_{2\ell}} r_{H_2}^*}{K_L^2 C_{H_{2\ell}}^*} \ll 1 \quad (11)$$

is a necessary condition for insignificant reaction in the film, and it is usually sufficient. It is to be noted that if the rate of hydrogen reaction was first order with respect to $C_{H_{2\ell}}^0$, the condition in Equation 11 could reduce to the following explicit expression in terms of $D_{H_{2\ell}}$, K and K_L ,

$$\frac{D_{H_{2\ell}} \cdot K}{K_L^2} \ll 1 \quad (12)$$

where K is the first order reaction rate constant. Equation 12 gives the generally used criterion for determining whether the reaction is in the slow reaction regime for first order reactions. For the latter case, a more restrictive explicit analytical criterion is given by

$$\frac{D_{H_{2\ell}}}{K_L} \ll 1 \quad (13)$$

The above criterion, (Equation 13) represents the situation in which the liquid is uniformly saturated with the gas and the reaction is virtually homogenous. Since the rate of hydrogen reaction in SRC-II coal liquefaction is of complex order, an explicit analytical criterion, such as in Equation 13, cannot be obtained. However, the rate of reaction can be compared with the rate of mass transfer to obtain the ranges of operating conditions in which the effects of mass transfer resistances can be considered to be insignificant. Thus, the effect of mass transfer resistance can be expressed in terms of fractional decrease in the rate of hydrogen reaction due to lower concentration of hydrogen in the bulk liquid. The fractional decrease can be expressed as

$$f = \frac{r_{H_2}^* - r_{H_2}}{r_{H_2}^*} \quad (14)$$

In the present analysis, the effect of mass transfer resistance is considered to be insignificant if

$$f < 0.05$$

(15)

Thus, Equations 11 and 15 constitute the two criteria used in this analysis. It is important to note that the limiting value of f has been taken to be 5 percent since the accuracy of the data is not expected to be more than 95 percent. However, a smaller or larger value of f can also be selected and in that sense this value is arbitrary.

Various terms required for use of the criteria in Equations 11 and 15 are discussed in the following sections.

(A) Rate of hydrogen reaction, r_{H_2} ; This is given by (Singh, et al., 1980a)

$$r_{H_2} = 0.0009 \cdot CIN \cdot \rho_L + 13560 e^{-\frac{18900}{R_g T}} \cdot P_{H_2}^{0.28} \cdot x_{ash} \quad (16)$$

where r_{H_2} is the rate of hydrogen consumption or reaction, $gm/cm^3 S$; CIN is the coal inlet concentration, mass fraction; ρ_L is the density of the liquid, gm/cc ; P_{H_2} is partial pressure of hydrogen, atm.; x_{ash} is mass fraction of ASH in the reactor; T is the operating temperature, K and R_g is universal gas constant, cal/gmole K. It is important to note that the above Equation 16 gives the rate of hydrogen consumption in terms of partial pressure of hydrogen which is directly related only to $C_{H_{2l}}^*$, i.e., the hydrogen concentration at the gas (hydrogen) liquid interface. Since the above expression (Equation 16) was obtained from experiments in a CSTR under insignificant mass transfer effects (stirrer speed = 1000 rpm), the rate corresponds to $r_{H_2}^*$ which is dependent on $C_{H_{2l}}^*$. Thus, the above rate expression is valid under conditions of insignificant mass transfer effect in which the effect of hydrogen concentration is expressed in terms of P_{H_2} . However, to use the above expression under conditions of considerable mass transfer resistance, P_{H_2} should be expressed in terms of $C_{H_{2l}}$. In terms of $C_{H_{2l}}$, the above equation reduces to

$$r_{H_2} = 0.0009 \cdot \text{CIN} \cdot \rho_L + 4.05 \times 10^5 \times e^{-\frac{18900}{R_g T}} \left\{ C_{H_{2l}}^o e^{-\frac{1540}{R_g T}} \right\}^{0.28} \cdot x_{\text{ash}} \quad (17)$$

In obtaining Equation 17 from Equation 16, following relations have been used:

$$C_{H_{2l}} = H \cdot C_{H_{2g}} \quad (18)$$

where Henry's constant H is given by (Giun, et al, 1976)

$$H = 1.2 \exp(-1540/R_g T) \quad (19)$$

Hydrogen concentration (gm/cm³) in the gas phase is obtained by using the ideal gas law

$$C_{H_{2g}} = \frac{2 \cdot P_{H_2}}{82 \times T} \quad (20)$$

From mass transfer considerations

$$r_{H_2} = K_L a (C_{H_{2l}}^* - C_{H_{2l}}^u) \quad (21)$$

Value of $C_{H_{2l}}^o$ is obtained by trial and error using Equations 17 and 21, each of which yield the rate of hydrogen consumption. In the mass transfer equation for H₂, i.e., Equation 21, it is assumed that concentrations of hydrogen in the inlet and outlet streams are equal, i.e., $C_{H_{2l}}^u = C_{H_{2l}}^i$.

(B) Diffusion Coefficient of Hydrogen in Liquid, $D_{H_{2l}}$:

Marangozis, et al (1977) evaluated the diffusion coefficient of hydrogen in cotton seed oil using Scheibel's correlation and used these values in their study of the mechanism of cotton seed oil hydrogenation. The same

values are used in the present analysis. Figure 2 shows the $D_{H_{2l}}$ vs. $1/T$ as a straight line, on a log - log plot, which is used to obtain the following expression:

$$D_{H_{2l}} = 0.072 e^{-\frac{2548}{T}} \quad (22)$$

Satterfield and Huff (1980) suggest use of the following expression, based on Wilke-Chang correlation, for diffusivity of hydrogen in any hydrocarbon liquid:

$$D_{H_{2l}} = 7.35 \times 10^{-3} e^{-\frac{2285}{T}} \quad (23)$$

This expression yields a much smaller value of $D_{H_{2l}}$ compared to that obtained from Equation 22 (1/6 th at 440°C). Since higher values of $D_{H_{2l}}$ yield higher values of Hatta number, M , Equation 22 was used to have a conservative estimate of the region of insignificant mass transfer effects in terms of M .

(C) Overall mass transfer coefficient, $K_L a$:

Kastanek (1977) used Higbie's penetration theory and derived

$$K_L a = b U_g^n \quad (24)$$

where b is a parameter whose value depends on the distributor and the liquid media; n is another parameter having values in the range of 0.72 to 0.82 depending on the gas-liquid system but independent of sparger design and U_g is superficial gas velocity. The liquid velocity is found to have no effect on $K_L a$.

In a bubble column, the energy for mixing is supplied by the gas. The gas enters the column at the bottom which is at a higher pressure, due to the liquid column above it, and leaves at the top at a lower pressure. The loss in pressure energy of a unit volume of gas, P_e , can be calculated from

the pressure drop in the column by assuming that the latter is insignificant in comparison to the total pressure in the column. Thus,

$$P_e = p_{\text{bot}} - p_{\text{top}} = \Delta p_{\text{col}} \quad (25)$$

where p_{bot} and p_{top} are pressures at the bottom and top of the column, respectively and Δp_{col} is the pressure drop in the column. Δp_{col} which can be expressed as

$$\Delta p_{\text{col}} = \rho (1 - \epsilon_g) g h_c \quad (26)$$

where ϵ_g is the gas holdup and h_c is the height of the column. Total pressure energy per unit time or power, P , supplied by the gas to the column can be expressed, in terms of volumetric flow rate of gas, as

$$P = \frac{\pi}{4} D_c^2 U_g \rho (1 - \epsilon_g) g h_c \quad (27)$$

P divided by volume of the reactor ($V = \pi/4 D_c^2 h_c$) yields the power per unit volume, i.e.,

$$P/V = U_g \rho g (1 - \epsilon_g) \quad (28)$$

In addition to being a function of superficial gas velocity, ϵ_g depends on various properties of the gas and liquid as well as the reactor dimensions. For simplicity of analysis, we use a high value of ϵ_g ($=0.2$) to have a conservative estimate of the specific power for mixing supplied by the gas. Figure 3 shows (P/V) as a function of U_g for two limiting ($0 < U_g < 15$ cm/sec) values of ϵ_g (0 and 0.2). The actual values corresponding to any gas velocity would lie in the shaded area (Figure 3).

From Equations 24 and 28

$$K_L a = b' (P/V)^n (1 - \epsilon_g)^{-n} \quad (29)$$

The values of b and n in the above expression were determined by using the data on rate of hydrogen transfer to tetralin at various levels of specific power input. The measurements were carried out at 348°C and 1200 psig (1150-1160 psig H_2 partial pressure) in a one liter CSTR using a special hydrogen probe (Kara, 1980-81). In all the experiments gas and liquid were separated by an unbroken interface (i.e., no bubbling of gas occurred during the experiments). Therefore, gas hold up, $\epsilon_g = 0$ and for this particular case,

$$K_{L,a} = b (P/V)^n \quad (30)$$

Power supplied by stirrer is obtained from the following relation (Perry, 1973)

$$P = K N^3 D_a^5 \rho_l \quad (31)$$

where P is in ergs/S; N is the stirrer speed rps; D_a is the impeller diameter, cm; and K is a characteristic constant which depends on the nature of the stirrer, baffle, etc. For the above referred experimental system, $K=6.3$. Figure 4 presents P/V vs N for a stirred reactor.

Figure 5 shows the relation between $K_{L,a}$ and (P/V) on a log-log plot. From this figure, the following correlation is obtained

$$K_{L,a} = 4.15 \times 10x^{-5} (P/V)^{0.84} \quad (32)$$

This corresponds to $n=0.84$ in Equation 24. This value of n is in very good agreement with those reported by Kastanek (1977) and Deckwer (1980). Deckwer (1980) suggests that value of b' is not influenced by column geometry, direction of flow, i.e., cocurrent or countercurrent, but depends strongly on the type of gas distributor (Figure 6). It also depends on the properties of the gas liquid system. The values of b' (Equation 24) reported by Deckwer (1980) correspond to $b=3.8 \times 10^{-5}$ and 1.04×10^{-4} (Equation 32) for 1 mm nozzle and sintered plate sparger, respectively. It is important to note

that for the same system, the value of b (or b') for sintered plates is three times that for 1 mm nozzle sparger. The value of b obtained for tetralin-hydrogen system (Equation 32) is in this range (Figure 6). In spite of all the approximations, the agreement can be considered excellent in view of the large variations in the value of b for the same system. Thus, it can be concluded that same correlation for mass transfer coefficient, based on (P/V) , can be used for bubble columns as well as stirred vessels.

It is assumed that the dependence of $K_L a$ on temperature is the same as that of K_L , i.e., a is independent of temperature and dependence of K_L on temperature for coal liquids is the same as that for cotton seed oil. The latter can be expressed as

$$K_L = c e^{-\frac{2248}{T}} \quad (33)$$

where c is a constant. The above expression is based on data of Marngozis (1977) which is plotted in Figure 2.

Using Equations 28 and 29 and the $K_L a$ values for hydrogen tetralin system (Kara, 1980-81), following expression for overall mass transfer coefficient is obtained.

$$K_L a = 1.532 \times 10^{-3} e^{-\frac{2248}{T}} \cdot (P/V)^{0.84} \quad (34)$$

(D) Specific Interfacial Area: On the basis of Kolmogoroff's theory of isotropic turbulence, Nagel and Kurten (1976) and Nagel, et al., (1979) derived the following expression for the specific interfacial area

$$\underline{a} = K (P/V)^{0.4} (1 - \epsilon_g)^n \quad (35)$$

The above correlation is based on sulfite oxidation method (Nagel, et al. 1972, 1973, 1976, 1978) for determining (experimentally) the interfacial area. The exponent of the power consumption or energy dissipation per unit volume, i.e., P/V is evaluated between 0.25 and 1 by several other workers

(Calderbank, 1958, 1959, 1960; Yoshida and Miura, 1963; Akida and Yoshida, 1973). Published correlation of \underline{a} versus (P/V) for a bubble column (Shah and Deckwer, 1980) shown in Figure 5 is used in this work. It can be expressed analytically as

$$\underline{a} = 0.05 (P/V)^{0.34} \quad (36)$$

(E) Specific Mass Transfer Coefficient: This is obtained from Equations 30 and 32.

$$K_L = 3.056 \times 10^{-2} e^{-\frac{2248}{T}} (P/V)^{0.5} \quad (37)$$

Calderbank's correlations (1958, 1959, 1960) show K_L to be independent of (P/V) for agitated as well as non-agitated gas-liquid systems. It is, however, noteworthy that theoretical considerations (Calderbank, 1960 and Calderbank and Moo Yong, 1961) for high mixing rates yield

$$K_L \propto (P/V)^{0.25} \quad (38)$$

Studies of Davis, Kilner, and Ratcliff (1964), Yoshida and Miura (1963) show the exponent of (P/V) to range between 0.14 to 0.25. In view of the reported literature information, the dependence of K_L on (P/V) is stronger in the present analysis (Equation 37). However, it should be noted that the scatter of data in all the empirical correlations is rather large and therefore Equation 37 can be considered to be more reliable.

RESULTS AND DISCUSSION

To check the validity of the correlation for K_{La} (Equation 34) experimental measurements of hydrogen consumption, in A-1 unit at different stirrer speeds are simulated. In these experiments gas was bubbled through the stirred liquid. It is known that appreciable reduction in stirrer power input takes place when gas is introduced in a mechanically agitated liquid. However, additional power for mixing is supplied by the incoming gas. Using the correlation of Michel and Miller (1962), for calculating the reduction in stirrer power input, the total power input to the reactor is expressed as

$$P = 0.1063 \left\{ \frac{P_o^2 N D_a^3}{Q^{0.56}} \right\}^{0.45} + Q_g (1 - \epsilon_g) \rho_g h_c \quad (39)$$

where P_o is the stirrer power input in the absence of bubbles in liquid, lrgs/sec; N is the stirrer speed, rps; D_a is impeller diameter, cms; Q_g is the volumetric flow rate of gas, cm^3/sec and h_c is the height of the reactor, cm^2 . Using equations 17, 21, 34 and 39, hydrogen consumption in A-1 unit is evaluated. Figure 7 shows the measured and calculated values at different stirrer speeds. Process and operating conditions are listed on the figure. The correlation for K_{La} is validated by the good agreement between measured and calculated values. Figure 8 shows evaluated hydrogen consumption for a different set of process and operating conditions as a function of power per unit volume.

It can be noted from conditions in Equation 11 and 15 that the effect of mass transfer resistance is more important at higher rates of reaction. Therefore, operating conditions for maximum feasible rate of hydrogen reaction are used in generating values of M and f shown in Figure 8 as functions of (P/V) (Figure 9). Correlation of Satterfield and Huff (1980) for $D_{H_{2l}}$, has also been used to show the effect of diffusion coefficient on values of M (Figure 10). Figure 9 shows that in the range of practical importance ($U_g > 1\text{cm/s}$), the fractional decrease in rate of hydrogen consumption due to mass transfer resistance is less than 0.0372 or 3.72 percent. Thus, the mass transfer effects can be considered to be insignificant in all operations of SRC-II reactors. The corresponding values

of M evaluated from the two correlations for D_{H_2} (Equations 22 and 23) are 0.0034 and 0.0005 (Figure 10). This shows the sensitivity of M with respect to the values of D_{H_2} obtained from different correlations and the difficulty in pre-assigning any value to M below which the effect of mass transfer resistance could be considered insignificant. This also indicates magnitudes of possible error in the evaluation of $K_L a$ from different correlations.

Figure 11 shows the effect of variations in $K_L a$ values on the significance of mass transfer resistance. For comparison, actual value of $K_L a$ is taken as a fraction of that evaluated from Equation 34 (Figure 5) by defining

$$\gamma = \frac{(K_L a) \text{ actual}}{(K_L a) \text{ evaluated}} \quad (40)$$

It can be noted from Figure 11 that for $\gamma=0.5$, i.e., the actual value of $K_L a$ is only half of that evaluated from the correlation (Equation 34), over the entire region of practical importance the effect of mass transfer resistance is less than 7.5 percent ($f=0.075$) and for $U_g > 2$ cm/s, the mass transfer resistances would reduce the rate of hydrogen consumption by less than 4.2 percent ($f=0.042$). However, if the overall mass transfer coefficient is only 1/10th of the calculated value ($\gamma=0.1$) the superficial gas velocity will have to be more than 10 cm/s such that the mass transfer resistance reduces the rate by less than 5 percent.

NOMENCLATURE

A	Cross sectional area of the stirred reactor, cm^2
$\frac{a}{C_l^0, C_l^*}$	Specific interfacial area, cm^2/cm^3 Concentration of dissolved gas in bulk liquid phase and in equilibrium gm/cm^3
$C_{H_{2l}}^i, C_{H_{2l}}, C_{H_{2l}}^*$	Concentration of hydrogen in inlet and bulk liquid and at the interface, gm/cm^3
$D_{H_{2l}}, D_c$	Diffusivity of hydrogen in liquid phase, cm^2/sec Diameter of the column, cm
δ	Liquid film thickness, cm
f	Fractional decrease in hydrogen consumption
γ	Ratio of actual and calculated overall mass transfer coefficient
H	Henry's constant
h_c	Height of column, cm
K	Reaction rate constant
K_L	Specific mass transfer coefficient, cm/sec
P	Pressure, $\text{gm}/\text{sec}^2 \text{ cm}$
Pe	Pressure energy, ergs
Δp	Pressure drop
P_{H_2}	Partial pressure of hydrogen, atms
R	Rate of absorption per unit area, gm/cm^2
r_{H_2}	Rate of hydrogen consumption, $\text{gm}/\text{cc sec}$
T	Temperature, K
U_g	Superficial gas velocity, cm/s
V	Volume, cm^3
b, b' and n	constants

REFERENCES

1. Akita, K and Yoshida, F., I&EC Proc. Des. Div., 12, 76 (1973).
2. Calderbank, P. H., Trans. Inst. Chem. Engrs., 36, 443 (1958).
3. Calderbank, P. H., Trans. Inst. Chem. Engrs., 37, 173 (1959).
4. Calderbank, P. H., F. Evans, J. Rennie, Parts I and II, p. 51, Proceedings of the International Symposium on Distillation, Brighton, Inst. Chem. Engrs., London (May 1960).
5. Calderbank, P. H. and M. B. Moo Young, Chem. Eng. Sci., 16, 39 (1961).
6. Davis, Kilner and Ratcliff, Chem. Eng. Sci. 19, 583 (1964).
7. Deckwer, W. D., "Access of Hydrodynamic Parameters Required in the Design and Scale Up of Bubble Column Reactor," ACS Annual Meeting, San Francisco, August 1980.
8. Field, R.W. and J.F. Davidson, Trans Inst. Chem. Engrs. 58,228 (1980).
9. Guin, J. A., A. R. Tarrer, W. S. Pitts and J. W. Prather, ACS Fuel Chem. Preprints, 21, 170 (1976).
10. Kara, M., PhD Thesis, "Hydrodynamics & Mixing in a Three-Phase Bubble Column," University of Pittsburgh (1981).
11. Kastenak, F., Coll. Czechoslov. Chem. Commun., 42, 2491 (1977).
12. Marangozis, J., I. B. Keramidas and G. Papisvas, I&EC Proc. Des. Div., 16, 361 (1977).
13. Michel, B. J. and S. A. Miller, AIChEJ, 8, 262, (1962).
14. Nagel, O., H. Kurten and R. Siem, Chem. Eng. Tech., 44, 367 and 899 (1972).
15. Nagel, O., H. Kurten and B. Hegner, Chem. Eng. Tech., 45, 913 (1973).
16. Nagel, O., H. Kurten, Chem. Eng. Tech., 48, 513 (1976).
17. Nagel, O., B. Hegner and H. Kurten, Chem. Eng. Tech., 50, 934 (1978).

18. Nagel, O., H. Kurten and B. Hegner in "Two-Phase Momentum, Heat and Mass Transfer in Chemical Process and Engineering Systems," ed. by F. Durst, G. V. Tsiklauri and M. H. Afgan, Vol. 2, p. 834, Hemisphere Publ. Corp., Washington, D.C. (1979).
19. Perry, R. H., Chemical Engineers Handbook, McGraw-Hill, 5th Edition, New York (1973).
20. Satterfield, C. N. and G. A. Huff, Chem. Eng. Sci. 35, 195, (1980).
21. Shah, Y. T., W. D. Deckwer, "Fluid-Fluid Reaction," a chapter to be published in "Scaleup Problems in Chemical Industries," John Wiley & Sons, New York (1981).
22. N. L. Carr et.al., "A New Model for Coal Liquefaction," Report No. 627RL041, DOE/ET/10104-5 (Vol. 2), April 1981.
23. Y. T. Shah et.al., "Simulation of an SRC-II Recycle System," Report No. 627RL039, DOE/ET/10104-5 (Vol. 2), April 1981.
24. Singh, C. P. P., Y. T. Shah and N. L. Carr, "Thermal Behavior of SRC-II Reactors," Report No. 627RM055, DOE/ET/10104-34, 1981.
25. Vermeulen, T., G. M. Williams and G. E. Langlois, Chem. Eng. Progr., 51, 85 (1955).
26. Yoshida, F. and Y. Miura, I&EC, Proc. Des. Div., 9, 263 (1963).

FIGURE 2: D_{H_2L} and K_L as Functions of Temperature (Cottonseed Oil-Hydrogen System, Marangozis et al., 1977)

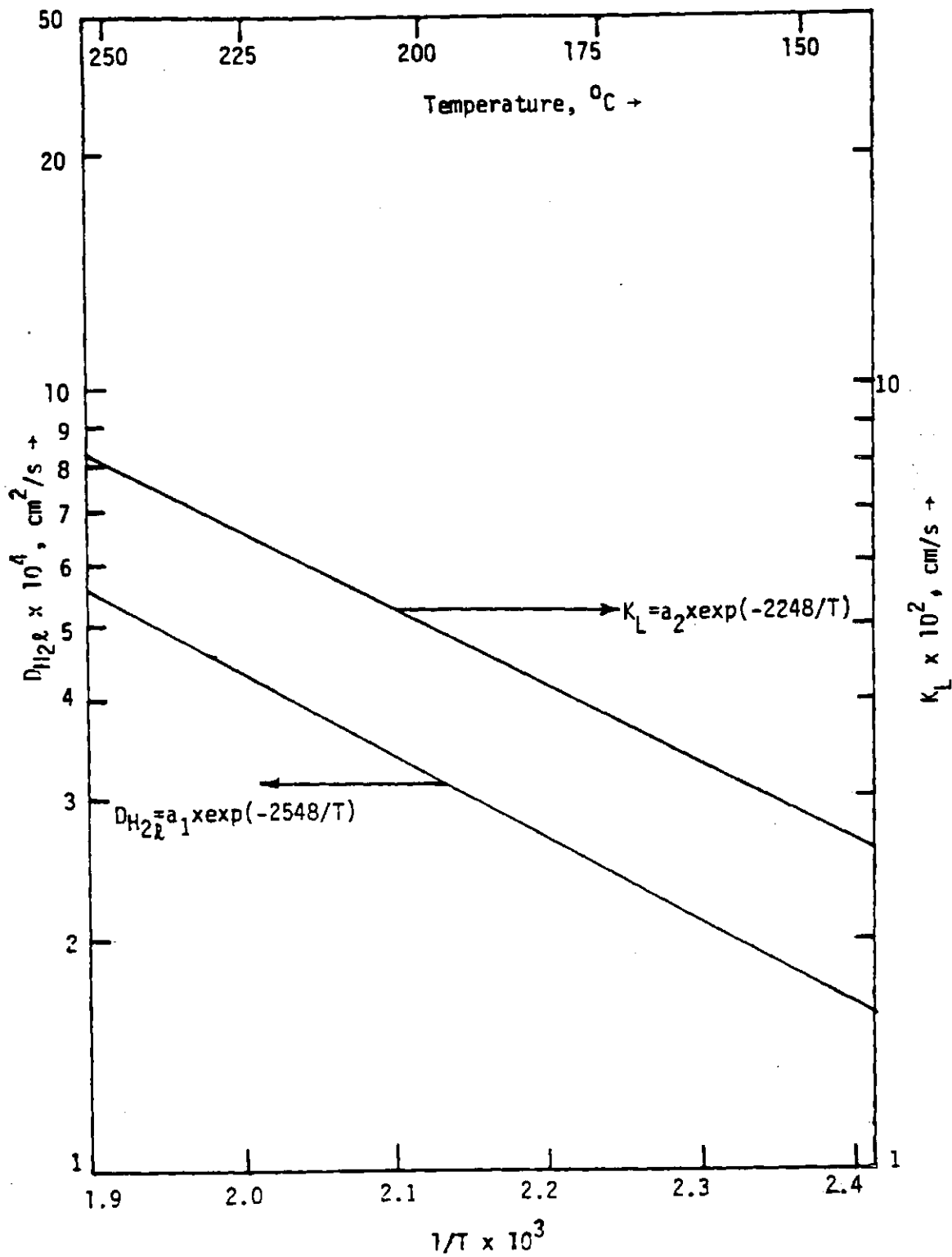


FIGURE 3: Specific Power Consumption as a Function of Superficial Gas Velocity

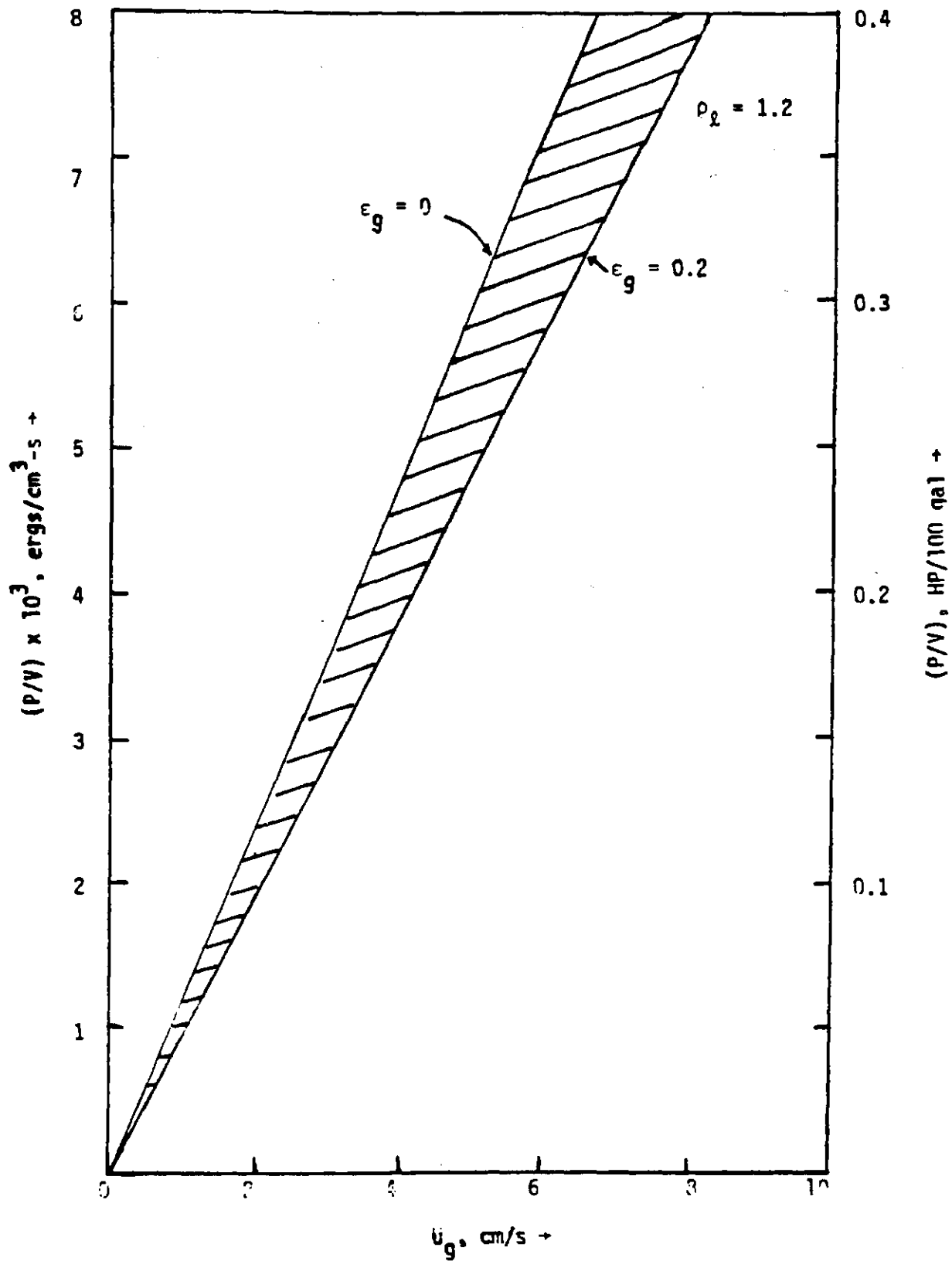


FIGURE 4: Power Consumption as a Function of Stirrer Speed

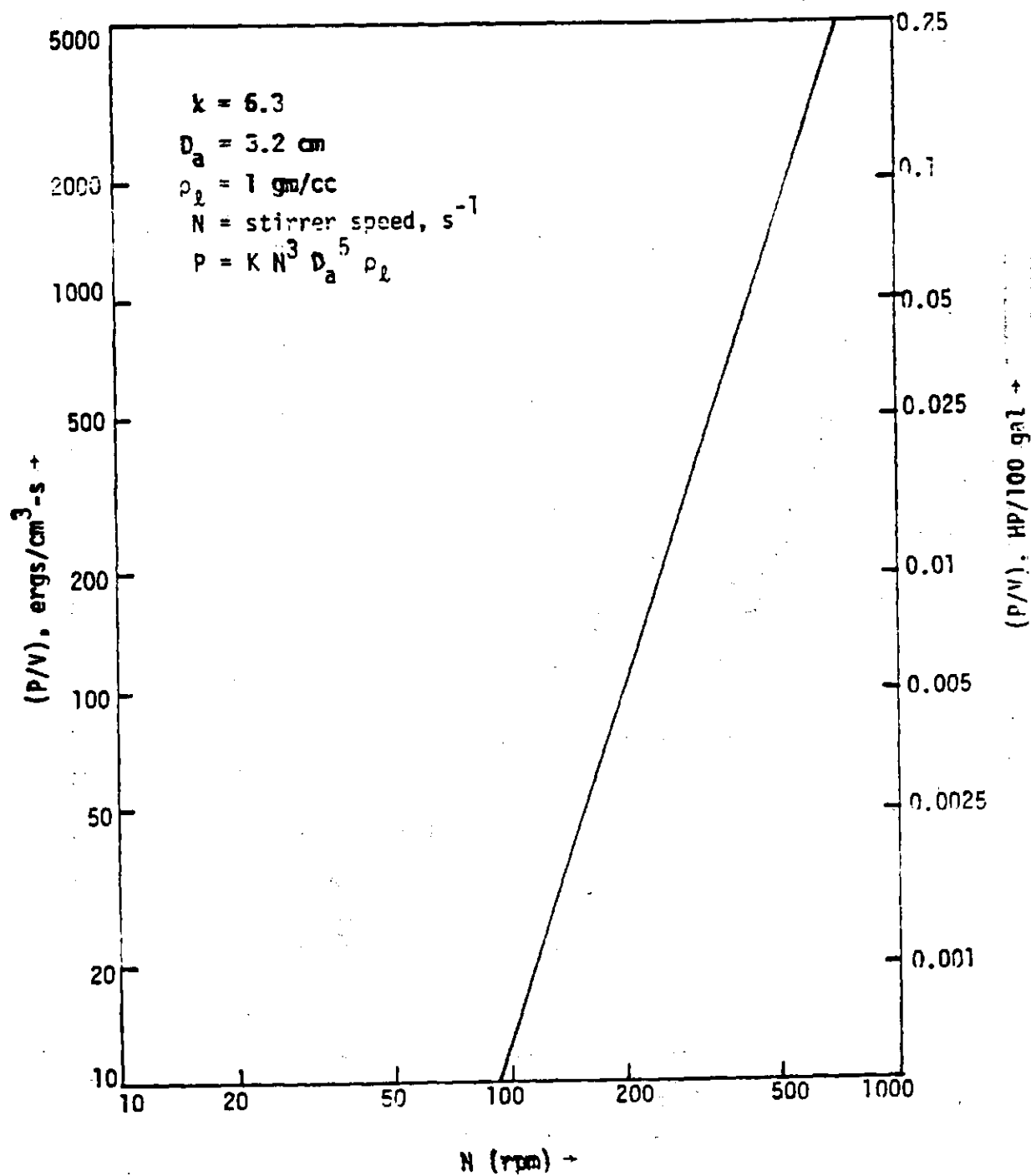


FIGURE 5: $K_L a$, K_L and a as Function of Specific Power Consumption

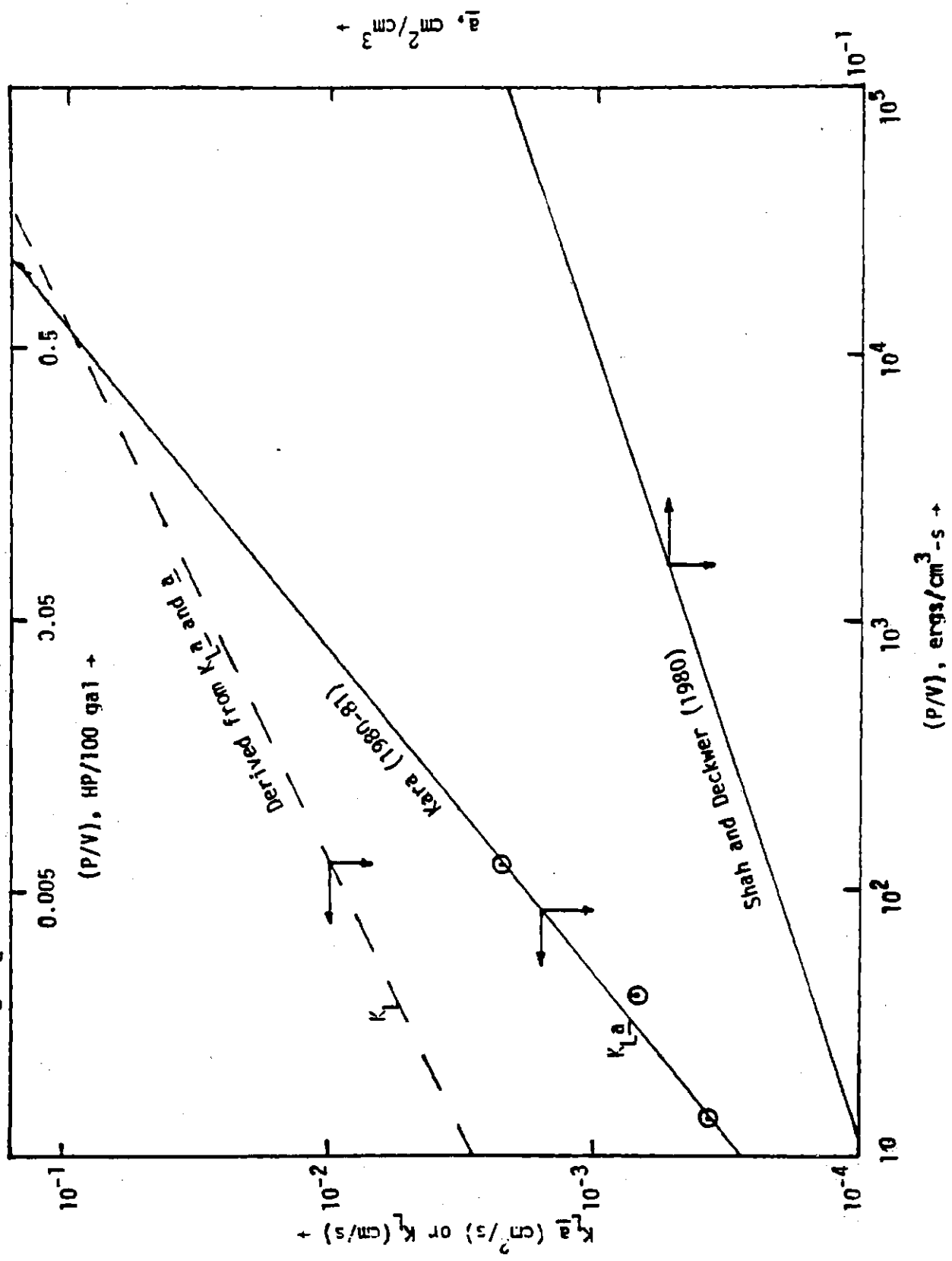


FIGURE 6: K_{La} as a Function of Specific Power Consumption

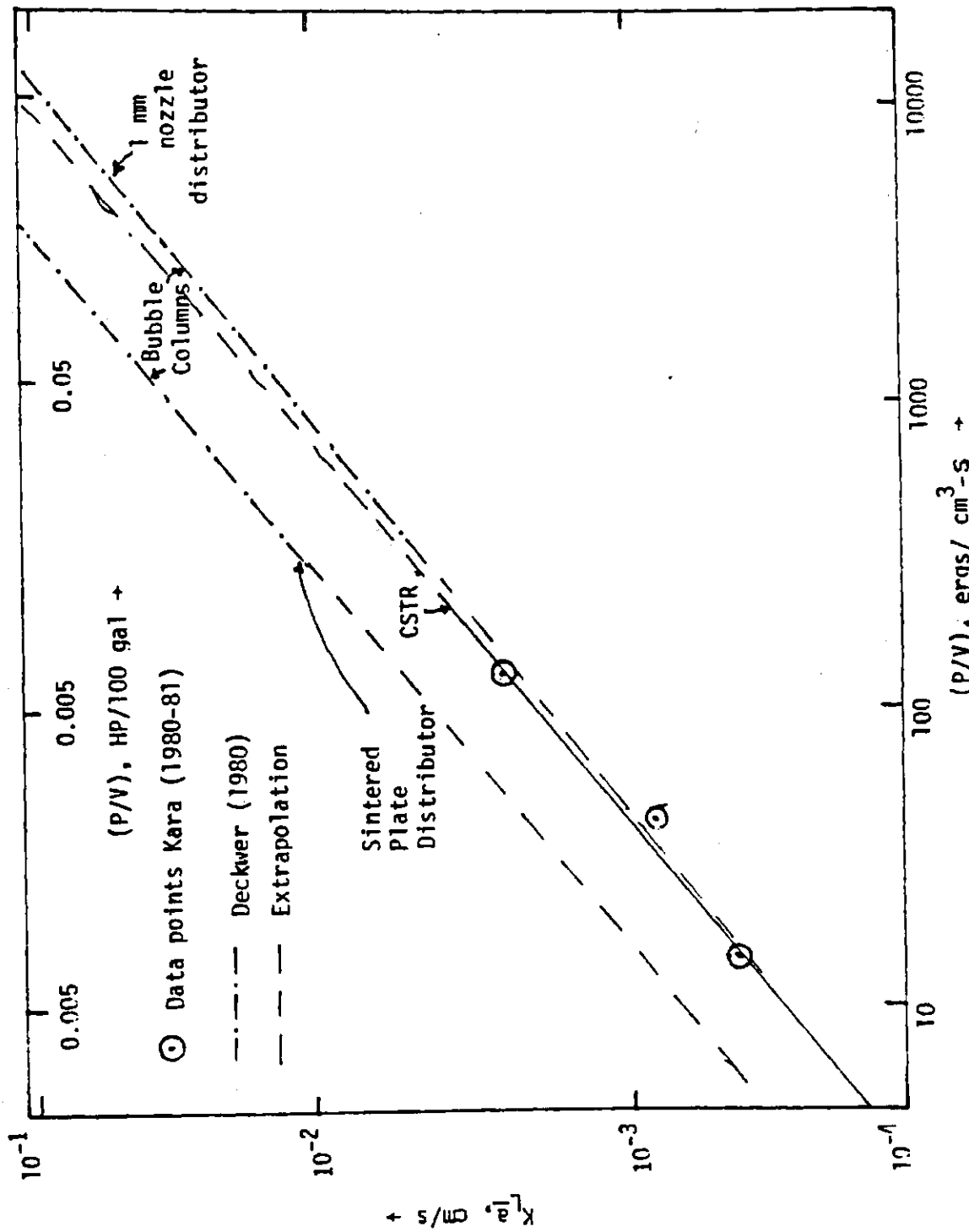


FIGURE 7: Comparison of Experimental and Calculated H₂ Consumption at Different Stirrer Speeds

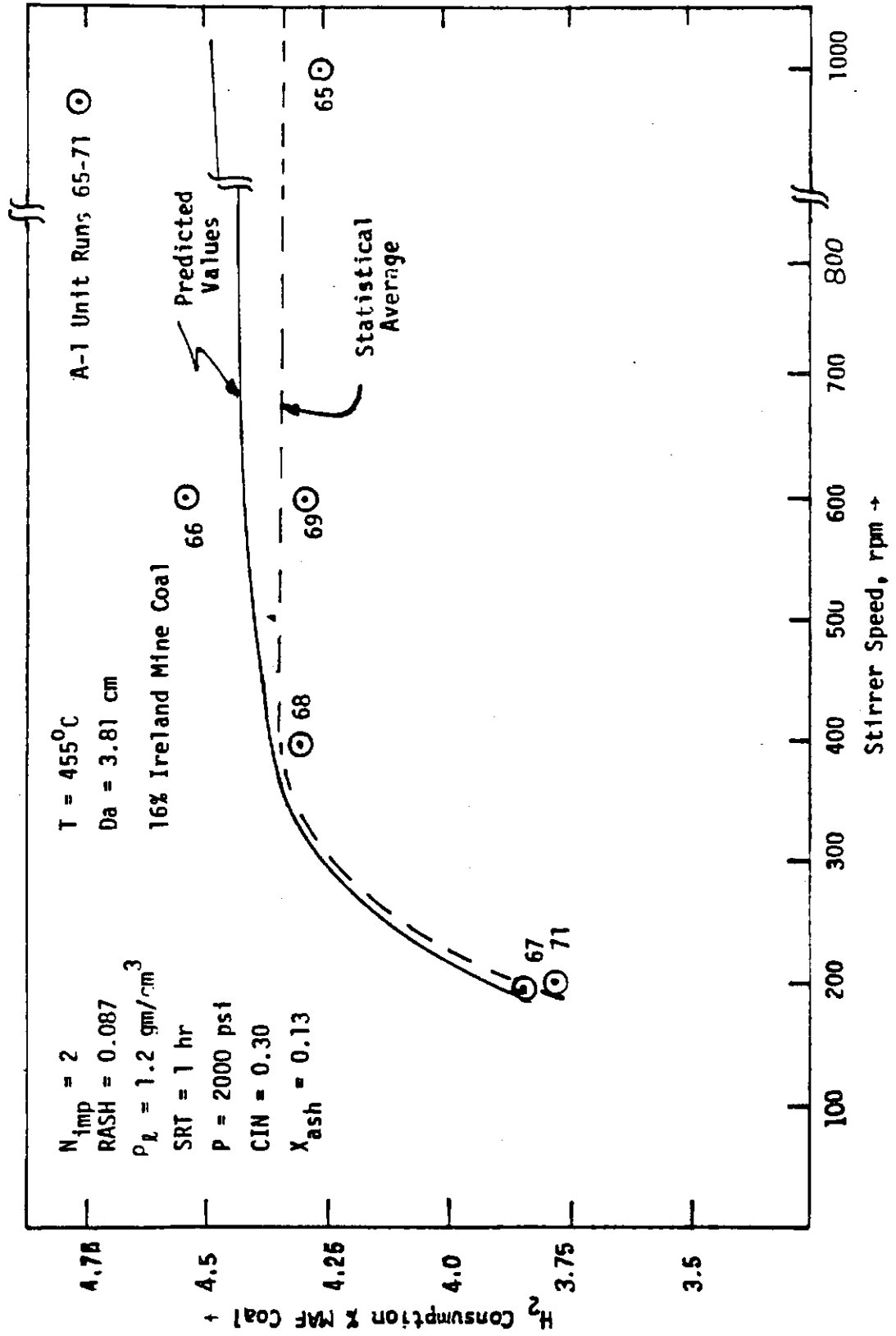


FIGURE 8: Hydrogen Consumption (% MAF Coal) as a Function of Power Consumption

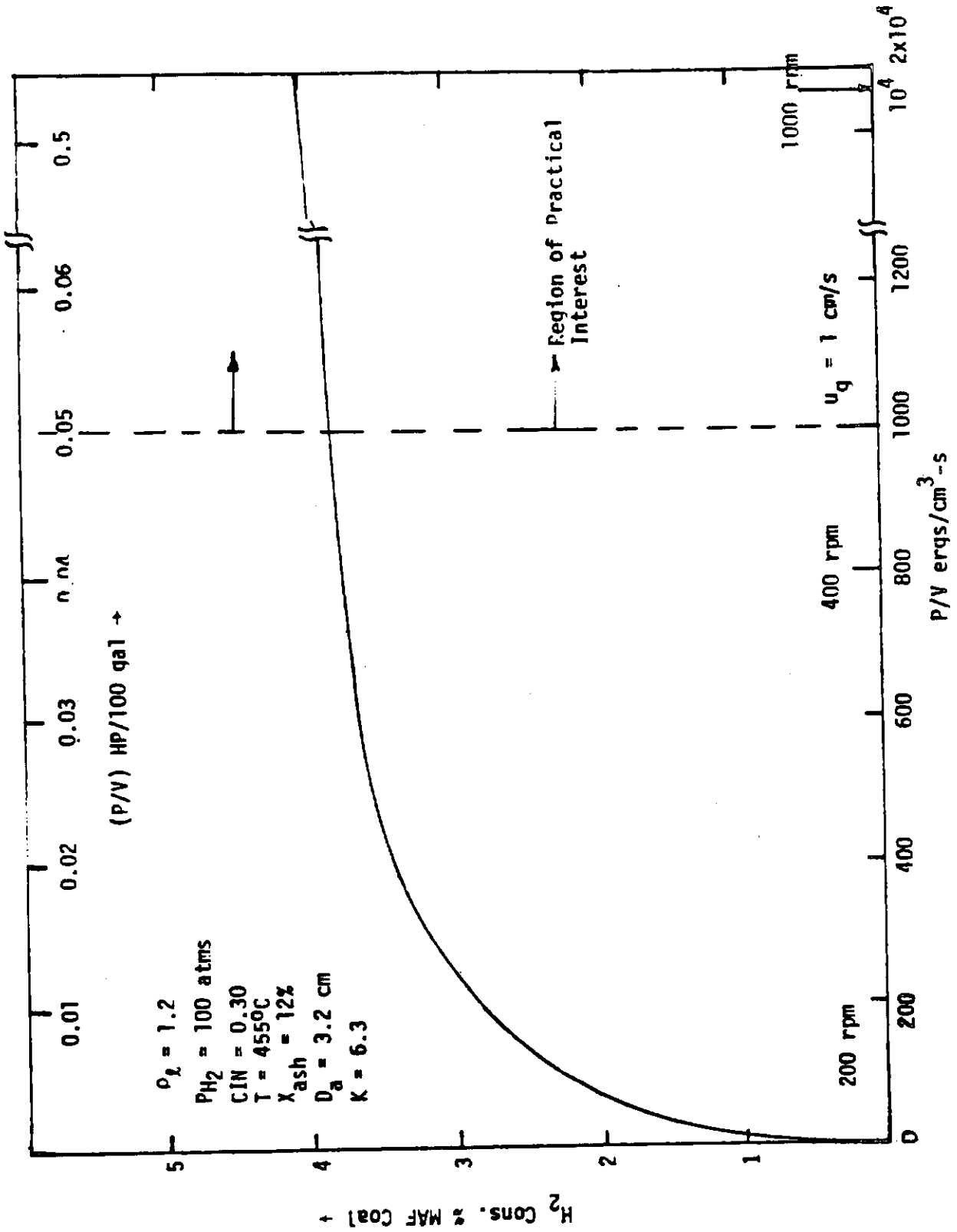


FIGURE 9: M and f as Functions of Specific Power Consumption

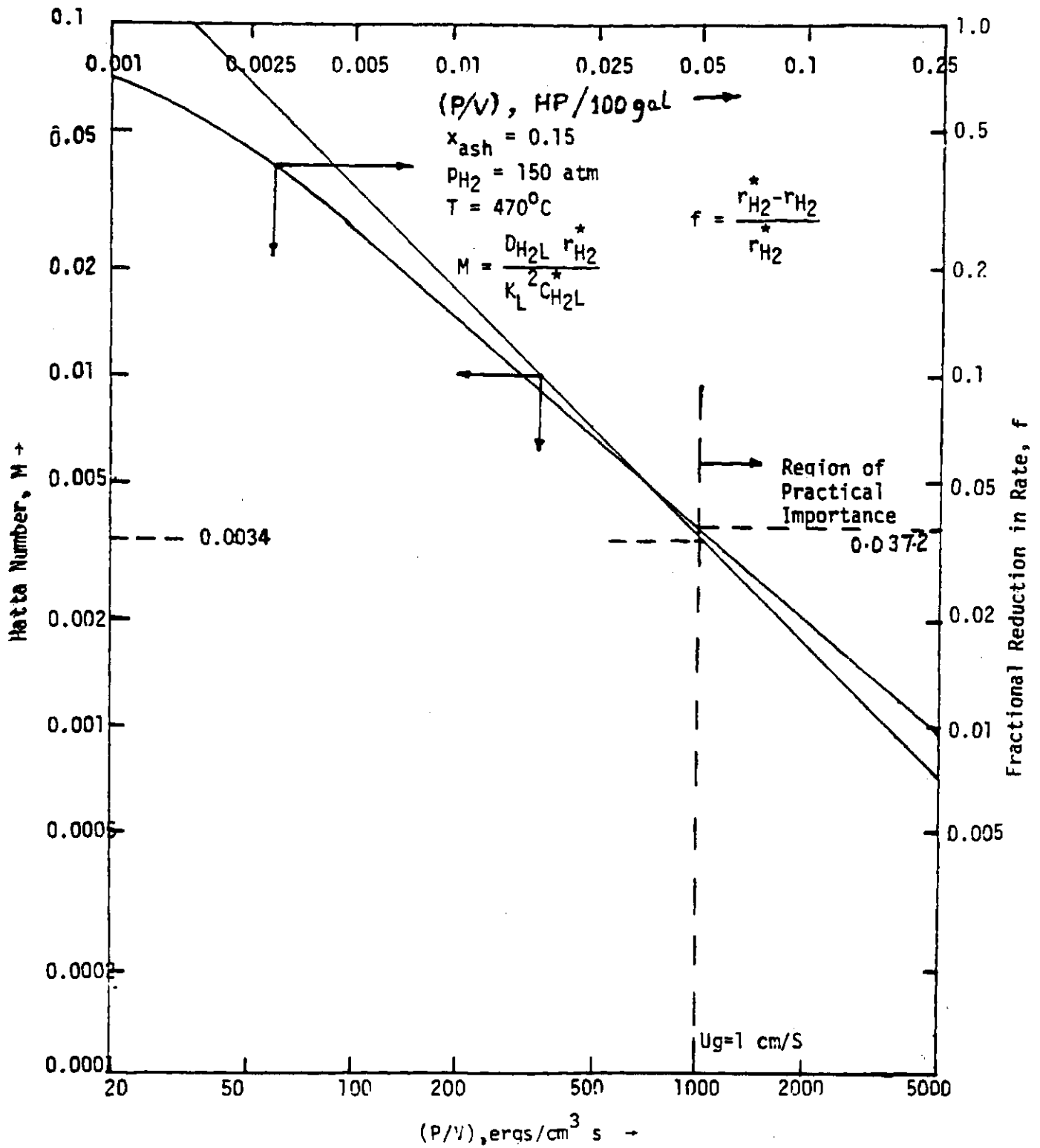


FIGURE 10: Effect of D_{H_2L} on M (Hatta Number)

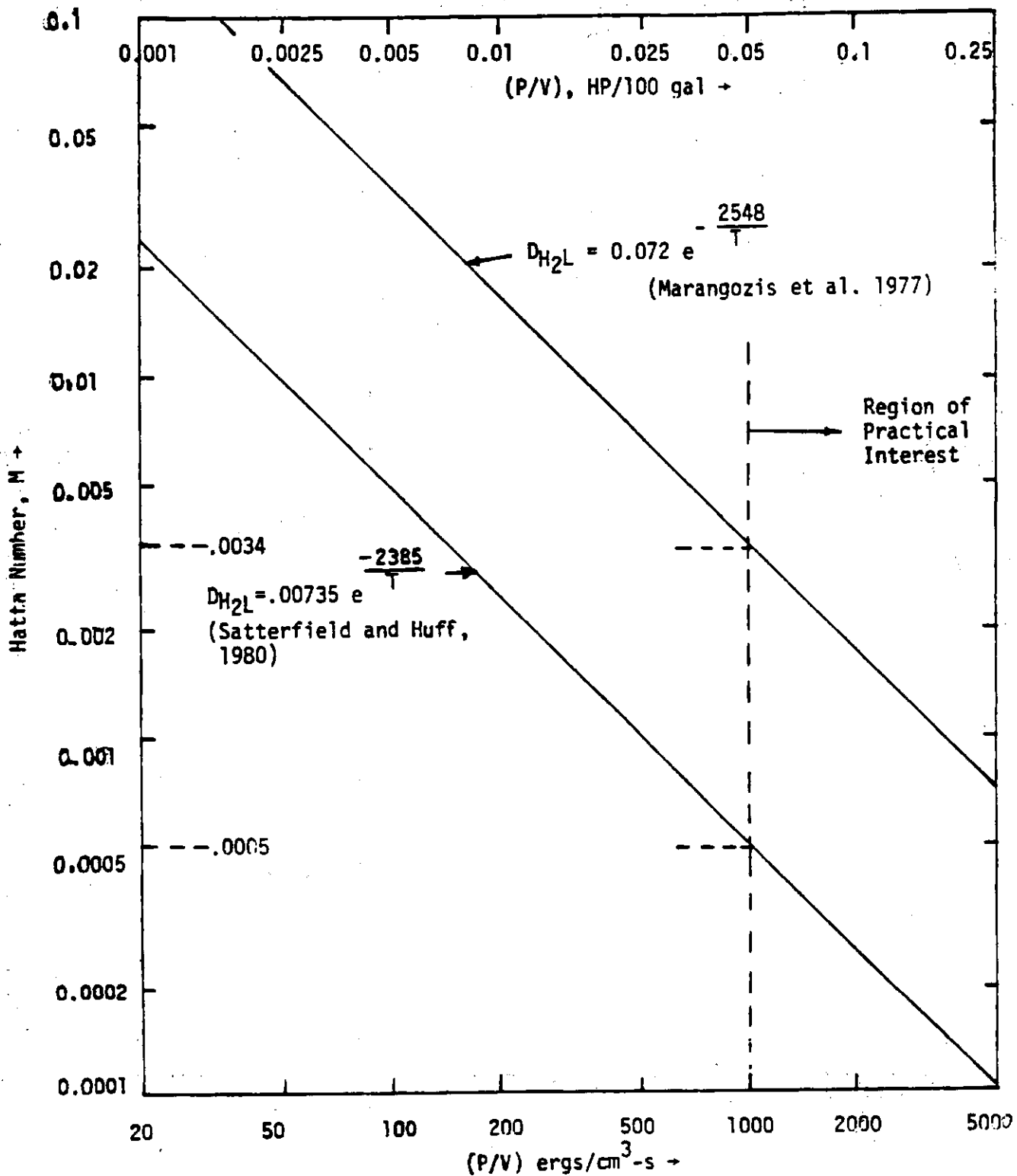
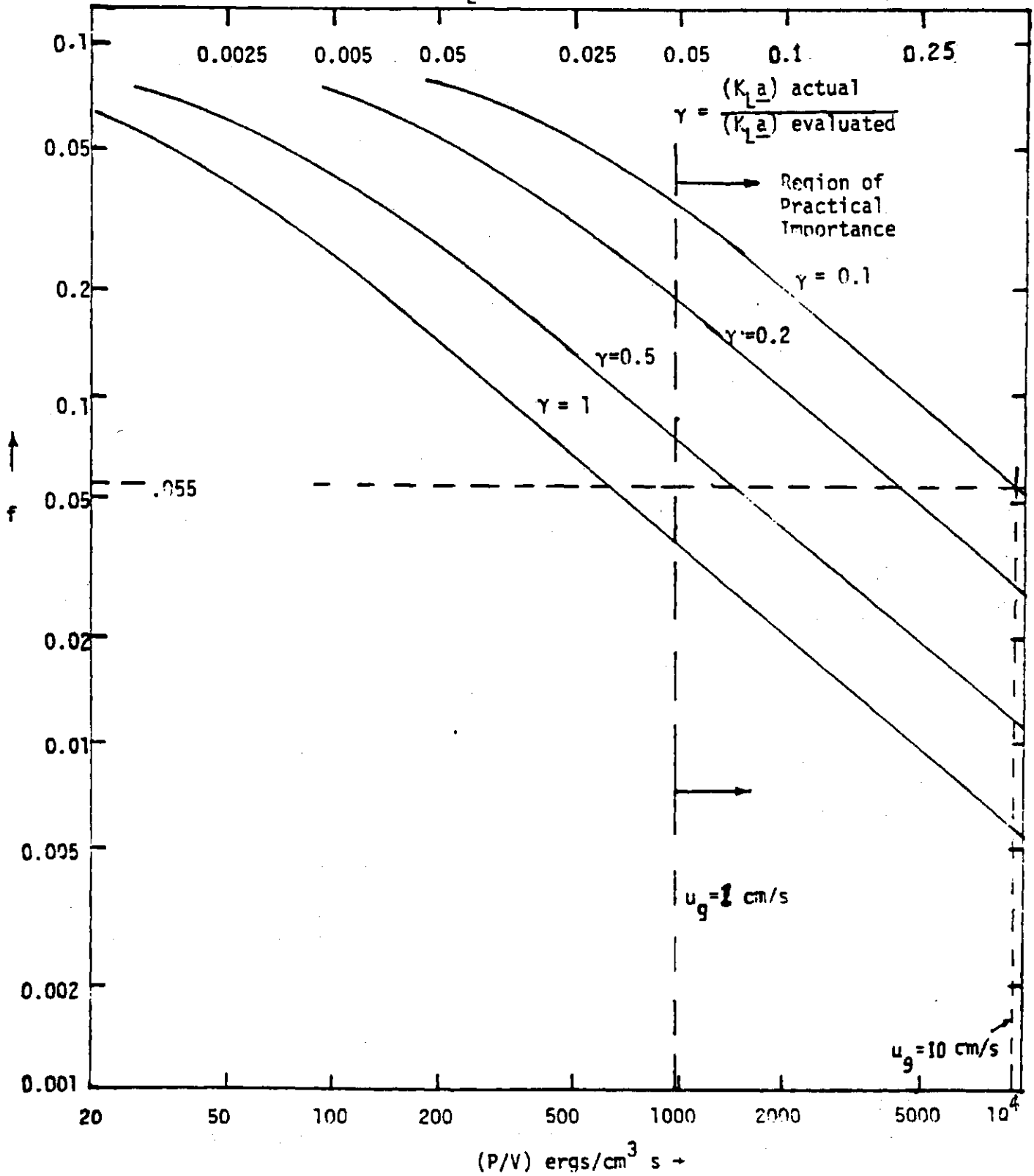


FIGURE 11: Fractional Decrease in Rate of Hydrogen Consumption (f) as a Function of $\gamma (= \frac{(K_L a)_{\text{actual}}}{(K_L a)_{\text{evaluated}}})$



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