

KINETICS AND SOLUBILITY OF HYDROGEN
IN COAL LIQUEFACTION REACTIONS

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Introduction

There has been considerable interest in investigation of the kinetics of coal dissolution and heteroatom removal in the presence of donor solvents and hydrogen gas. This interest stems not only from an intrinsic desire to understand the process better from a fundamental viewpoint, but also from a need to obtain data and knowledge from which coal liquefaction processes may be intelligently designed. If reliable kinetics expressions can be obtained, the effects of various operating variables quantified, and the trends better established, then data taken in laboratory experiments can be more confidently extrapolated to other conditions with a minimum of experimental investigation.

From work in this laboratory (1,2) and that of others (3,4,5,6) a free radical mechanism for the dissolution of coal in hydrogen donor solvents can be postulated. The initial dissolution of the coal solid is thermally initiated; however, the net rate of depolymerization for a given coal depends upon the nature of the solvent and its effectiveness in stabilizing the free radicals. The higher the hydrogen donating ability of the solvent, the more effective the solvent is in terminating radicals and promoting coal solvation. This is shown by the fact that hydrogenated recycle solvent has been found to facilitate coal solvation much more readily than untreated solvent (18). The overall rate limiting step in the process appears to be the rehydrogenation of the donor vehicle. This latter process can, however, be aided significantly by the action of coal mineral matter (7,8). The separation of these two steps, hydrogen transfer and solvent rehydrogenation, may provide the key to an improved SRC type process, allowing greater reactor throughput and operation at lower temperatures and pressures. Such an arrangement would be similar to the coal conversion process at Cresap, West Virginia.

Considerable research has been conducted concerning the kinetics of coal solvation and sulfur removal. Although performed in the absence of a solvent, the recent study of the nonisothermal kinetics of coal hydrodesulfurization reported by Yervey, *et al.* (9) is of interest. These investigators divided the sulfur in coal into five classes of Organic I, II, III, Pyritic, and Sulfide, and determined pre-exponential and activation energies for the reaction of each of these five types. Of particular interest

was the reverse reaction of H_2S with the organic matter of coal to produce the Organic III class of coal-contained sulfur. Liebenburg and Potgieter (10), and Potgieter (11), have recently reported studies on the uncatalyzed hydrogenation of coal and on the kinetics of conversion of tetralin during the hydroliquefaction of coal. They concluded that heating and cooling could cause considerable spurious effects in batch autoclave kinetics studies and suggested sampling techniques to avoid these. Kinetic rate constants for the formation of asphalt and oil fractions from the uncatalyzed hydrogenation of coal in tetralin were reported and several different kinetic mechanisms were postulated. Wen and Han (12) have also determined rate constants using coal liquefaction and desulfurization data gathered primarily from studies by Pittsburgh and Midway Coal Mining Co., the University of Utah, and the Colorado School of Mines. These researchers were able to fit data from these sources with an empirical expression for the rate of coal dissolution; however, no kinetic expression was obtained for desulfurization, probably because of lack of sufficient data. Furthermore, the effect of hydrogen partial pressure was not firmly established, and it is likely that the different type reactors and experimental procedures employed in the three laboratories made the data correlation more difficult. Coal liquefaction data using creosote oil together with a CO -stream gas phase have been reported by Handwerk, et al. (13) at the Colorado School of Mines. In these experiments it was established that reaction temperature had a stronger effect on desulfurization than did hydrogen partial pressure; however, reaction rate expressions were not reported. Similar investigations employing synthesis gas, with the addition of an external catalyst, have been reported by Fu and Illig (14) and Appell, et al. (15). With regard to catalytic studies, the University of Utah studies on hydrocracking and heteroatom removal (16,17) are representative of batch autoclave studies in the presence of an added catalyst, although in these particular studies a coal-derived oil was used as a starting material rather than a coal-solvent slurry. Given et al. (18) at the Pennsylvania State University, in cooperation with Gulf Research and Development Company, have reported recent results of their efforts to correlate coal liquefaction behavior with chemical and physical characteristics of the coal. Although their results are enlightening, it appears that further work will be required to firmly establish the relation between different characteristics of the coal and liquefaction behavior, in view of the large number of interacting variables which are present. Thus, despite the fact that numerous studies have been reported concerning liquefaction kinetics, it appears that the reaction-dissolution process is still not completely understood and that further investigation is needed.

In contrast to the large amount of research on the kinetics of coal solvation and sulfur removal, there is a distinct lack of related information on the kinetics of hydrogen consumption during the coal solvation process. The rate of hydrogen consumption is important in the SRC process where it is desirable to minimize the consumption of costly hydrogen and maximize the yield of the SRC boiler fuel. The production of highly hydrogenated products including C_1 - C_4 gases decreases SRC yield and increases the consumption of hydrogen. The synthesis of boiler fuel for use in power plants does not require extensive hydrogenation. It is interesting to note that SRC product usually contains a slightly lower hydrogen/carbon ratio ($H/C = 0.75$) than the feed coal itself ($H/C=0.8$)(19,26). Thus, if the production of light gases ($H/C=6.6$), water, and light liquids ($H/C=1.5$) can be minimized, the SRC process has the potential to be self-sufficient in hydrogen which can be recovered from light liquids and gases by steam reforming, if necessary. The SRC pilot plants operated at

Wilsonville, Alabama, and Tacoma, Washington, currently consume about two weight percent of hydrogen per pound of HAF coal feed. Controlling solvent composition and process conditions to optimize selectively the production of SRC product would limit hydrogen consumption to a minimum and still produce an environmentally acceptable boiler fuel. Before optimum conditions can be selected, however, kinetic rate expressions are needed to provide models for process scale-up, simulation, and optimization. This work reports the development of such a model for hydrogen consumption in the dissolver stage of the SRC process.

Reaction Kinetics Experiments

Reagents and Materials. Kentucky No. 9/14 coal mixture was crushed; and the -170 mesh fraction - having the screen analysis shown in Table 1, and the elemental analysis in Table 2 - was used. The creosote oil used in this work was furnished by Southern Services, Inc., and was used as received from Wilsonville. Typical analysis of this creosote oil by gas chromatography is given in Table 1. The oil is distilled from coal tar in the boiling range 175° to 350°C. The oil was originally obtained from Allied Chemical Company as creosote oil 24-CB; and has a carbon-to-hydrogen ratio of 1.25 (90.72% C and 6.05% H), a specific gravity of 1.10 at 25°C, and a boiling point range of 350 to 650°F. A 3:1 solvent-to-coal weight ratio was used in all experiments reported, and all coal was dried overnight at 100°C and 25 inches of Hg vacuum before use. Hydrogen was obtained from Linde Hydrogen in 6000 psi grade and had a purity of 99.995%. Practical grade mesitylene was obtained from Matheson Coleman and Bell (MCB) and used without further purification.

Procedures. For each run, a 30 gm. of coal/90 gm of solvent slurry was charged into a 300 cc. magnedrive autoclave from Autoclave Engineers, Inc. Reactions were carried out at reaction times of 15, 30, 60, and 120 minutes and at reaction temperatures of 385, 400, 410, and 435°C; a stirrer setting of 1000 rpm was used in all the runs, with the exception of one run in which a stirrer setting of 2000 rpm was used to evaluate mass transfer effects. A heat-up rate of about 20°C per minute was used - requiring only about three minutes for heat-up within the zone in which significant reaction occurs (above 370°C) and a total heat-up time of about 30 - 35 minutes. Prior to heat-up 400 psig of hydrogen was charged to the reactor and at reaction temperature more hydrogen was added to give the desired initial hydrogen partial pressure. During each run reaction temperature was held constant within $\pm 3^\circ\text{C}$; and upon completion, the final hydrogen partial pressure (psia) was determined from gas analysis and total pressure measurement.

Solubility of Hydrogen in Coal Liquids

Data on the solubility of hydrogen in the coal-solvent slurry and a knowledge of the Henry's law constant is necessary in the kinetic modeling to follow hydrogen consumption. In addition, hydrogen solubility data are of importance for design and analysis of subsequent hydrogen recovery and downstream hydrogenation units in the coal processing train.

The coal-derived process solvent for liquefaction operations is typically a complex mixture consisting largely of partially hydrogenated polynuclear aromatic compounds, capable of transferring hydrogen to the coal structure. The exact chemical composition of the steady-state recycle solvent is dependent upon the characteristics of the feed coal and operational conditions. The creosote oil having the composition given in Table 1 was used as the start-up solvent at the SRC pilot plant in Wilsonville, Alabama, and is reasonably representative of the steady-state

recycle solvent. Solubility data for hydrogen in this oil are determined and used for the kinetics modeling in this investigation.

Determinations of the solubility of hydrogen in coal liquids have not been previously reported at coal liquefaction conditions. Peter and Weinert (20) have determined hydrogen solubility in slack wax, a paraffin oil, under similar conditions as encountered here. Eakin and Devaney (21) have measured hydrogen solubilities in paraffinic, naphthenic, and aromatic solvents as a ternary system with hydrogen sulfide in the temperature range from 100° to 400°F and a pressure range from 500 to 2000 psia. Chappelow and Prausnitz (22) have also made measurements of the Henry's law constants for hydrogen solubility in squalane and octamethylcyclotetrasiloxane between 25° and 200°C. The work presented here provides data on hydrogen solubility in creosote oil solutions at the high partial pressures of hydrogen and high temperatures used in coal liquefaction reactors. Thus, these data may be applied directly to coal conversion systems.

Hydrogen Solubility Experiments

The equilibrium cell used was a one gallon Autoclave Engineers 316 Stainless Steel magnedrive autoclave. Equilibrium pressures were monitored with a Heise Bourdon-tube gauge which had been calibrated against a deadweight gauge. The temperature of the cell was measured with a Type K thermocouple inserted into a thermowell extending into the liquid phase. Temperature was controlled within ±1%.

Gases encountered in this experiment were analyzed for H₂, Air, CH₄, CO₂, H₂S, C₂H₆, C₃H₈, i-C₄H₁₀, n-C₄H₁₀, i-C₅H₁₂, and n-C₅H₁₂. Hydrogen analyses were carried out on a Varian Model 920 areograph using a 15 foot column packed with 75% molecular sieve 13X and 25% molecular sieve 5A. The column was operated isothermally at 100°C with nitrogen as a carrier gas (40 ml/min). The other gases were analyzed on a Varian model 1800 areograph using a 15 foot column packed with Porapak Q, 80-100 mesh. The column temperature was programmed between 40° and 230°C at approximately 12°C/min. Helium was used as a carrier gas (40 ml/min). Both chromatographs were equipped with thermal conductivity detectors.

The creosote oil was charged into the autoclave and the system purged by evacuation. The autoclave was then brought to the desired temperature and hydrogen added to an amount determined by observation of the pressure. Hydrogen pressure was found to reach an equilibrium state in less than 5 seconds by standard step-response testing. Stirring was carried on during the entire process (2000 rpm), except during sample withdrawal.

Samples of the vapor were withdrawn from the top of the autoclave and analyzed by gas chromatography. From the analysis of the vapor phase and the knowledge of the gauge pressure and the vapor pressure of the creosote oil (Figure 1), the partial pressure of hydrogen in the vapor was calculated.

Liquid samples were withdrawn from the bottom of the autoclave into a stainless steel bomb. The bomb was then fitted to an evacuated glass rack, (Figure 2), in which the volume of the dissolved gases were measured. After volume measurement the gases were passed to a gas chromatograph for analysis. From this analysis,

-knowing the barometric pressure, ambient temperature, and total gas volume - the weight of hydrogen dissolved in the creosote oil was computed using the ideal gas law. By weighing the loaded bomb the weight of the oil was determined inferentially, and the solubility calculated as grams H_2 /gram oil.

Result of Hydrogen Solubility Experiments.

To verify the liquid sampling and analytical procedures the solubility of H_2 in mesitylene was determined at 400°F (204°C) at partial pressures of hydrogen between 500 and 2000 psia. A comparison of the data obtained for solubility of hydrogen in mesitylene in this work to the literature values (21) is given in Figure 3. The measured values agree with the previously reported values within a few per cent, thus confirming the techniques used here.

Experimental data for the solubility of hydrogen in creosote oil were obtained at temperatures of 100°, 200°, 300°, and 400°C at partial pressures of hydrogen ranging from 500 to 3000 psia; and the resulting data is shown in Figure 4. Hydrogen solubility exhibits an interesting inverse temperature behavior, with solubility at 400°C being greater than values at 100°C at the same pressure.

The major sources of error in this work are associated with transfer of liquid sample from the autoclave to the gas burette. The sample bomb was massive and determination of the weight of oil withdrawn was the least accurate step in the experiment. Minor errors result from uncertainties in the temperature of the equilibrium cell and the measurement of dissolved gas volume. As a result of these factors, the present data are estimated from least squares analysis to have an experimental accuracy of 4-6% in solubility at a given partial pressure of hydrogen.

It is apparent from these data that hydrogen is appreciably soluble in creosote oil. Thus in a batch autoclave with equal volumes of gas and liquid at 400°C and 2000 psig approximately one-third of the total hydrogen gas present is dissolved in the liquid phase.

In order to determine the effect of coal on the hydrogen solubility, experiments were run in which a slurry of 3:1 ratio of solvent to coal was used instead of creosote oil. The data were taken at 400°C and 2500 psia total pressure after 30 minutes at temperature. Assuming all the organic coal matter to be in the liquid phase, the hydrogen solubility was essentially the same - that is, within experimental error - as that in creosote oil alone at the same conditions. Thus the hydrogen solubility data in Figure 4 may also be used in the subsequent study of coal liquefaction kinetics.

Controlling Regimes in Coal Liquids Hydrogenation

The three-phase - solid-coal, hydrogen-gas, and donor-solvent - reaction system present in the SRC process is subject to several possible mass transport effects. The fact that coal particles readily disintegrate in the presence of an appropriate donor solvent (1) and that initial particle size seemingly has little effect upon the rate of solvation (23) indicates that pore diffusion and fluid-solid mass transfer play minor roles in the SRC process - though additional research is desirable to fully substantiate this tentative conclusion. Nonetheless, the rate of gaseous hydrogen consumption might be controlled, at least partly, by

mass transfer across the gas-liquid interface. When gas-liquid mass transfer controls the overall reaction rate, the most important factor is the interfacial area, which is governed by the agitation rate. To test for the presence of mass transfer regulation, experiments were performed using autoclave stirring speeds of 1000 and 2000 rpm respectively (24). The experimentally measured gas phase composition indicated no difference in the net rate of hydrogen consumption, thus indicating the absence of mass transfer resistance for the hydrogenation reaction. Further evidence is provided by Figure 5 where, after injecting a pulse of hydrogen gas, a new quasi-equilibrium state is rapidly established, immediately following hydrogen saturation of the liquid phase. The data of Figure 5 were obtained by allowing the reaction mixture of equilibrate at 405°C and 700 psig hydrogen pressure. The pressure was then increased very rapidly to 1870 psig, by opening and closing the hydrogen inlet valve. The pressure rise and decay was followed by a Leeds and Northropp pressure transducer. The rapid approach to equilibrium shown in Figure 5 indicates that at any given time, the gas and liquid phases are in equilibrium with respect to hydrogen concentration, unless the reaction is very fast indeed.

A third and final criterion for the absence of mass transfer influence upon the hydrogen consumption rate is the magnitude of the activation energy subsequently determined. The activation energy of 21 kcal/mole determined experimentally is indicative of kinetic control rather than diffusional control. Thus, it appears that mass transfer is not rate controlling in the noncatalytic (except for mineral matter effects) hydrogenation of coal solutions and that lumped parameter, homogeneous-phase reaction rate expressions are adequate for kinetics modeling.

Reaction Kinetics Modeling

The purpose of this section is to determine the magnitude of the parameters in an appropriate kinetic rate expression for hydrogen consumption. Material balances for hydrogen in the gas and liquid phases in the batch autoclave may be written:

$$\frac{dH_g}{dt} = -\dot{m} \quad (1)$$

$$\frac{dH_L}{dt} = -r_A V_L + \dot{m} \quad (2)$$

The mass transfer term \dot{m} allows for the transfer of hydrogen from the gas to the liquid phase as the reaction proceeds and hydrogen is depleted. The form of the reaction rate r_A must be determined from experimental data. Addition of Equations 1 and 2 eliminates the mass transfer term \dot{m} and yields Equation 3 for the rate of disappearance of total hydrogen:

$$\frac{dH_T}{dt} = \frac{d(H_g + H_L)}{dt} = -r_A V_L \quad (3)$$

For a first order reaction of dissolved hydrogen in the liquid phase, the form of r_A is

$$r_A = k_L H_L / V_L \quad (4)$$

Using the solubility data presented in Figure 4 we may determine the Henry's law constants for use in the relation:

$$\beta = S/P_{H_2} \quad (5)$$

Representative values of β are given in Table 4. Equation 5 may be used together with the experimental parameters to yield Equation 6.

$$\alpha = H_L / H_T \quad (6)$$

Values of α for the experimental temperatures used herein are presented in Table 5. Employing the assumption of quasi-equilibrium discussed previously, Equations 3, 4, and 6 may be solved to yield the significant result:

$$\frac{H_L}{H_{L0}} = \frac{H_G}{H_{G0}} = \frac{H_T}{H_{T0}} = \exp(-\alpha k_L t) \quad (7)$$

Note that the solubility of hydrogen enters the kinetics model through the parameter α . Equation 7 gives the amount of hydrogen present in either the gas or liquid phase as a function of time during the reaction. A comparison of Equation 7 with the experimental data is presented in Figure 6. The satisfactory fit verifies the assumption of first-order kinetics made in Equation 4. Values of k_L obtained from the slopes are presented in the Arrhenius plot of Figure 7, where an activation energy of 21 kcal/mole for the hydrogenation reaction has been determined. The complete experimental data for this investigation is recorded elsewhere (25). The total amount of hydrogen consumed by the reaction at any time may be found according to

$$H_c = H_{T0} [1 - \exp(-\alpha k_L t)] \quad (8)$$

Conclusions

The rate of consumption of hydrogen in coal solvation can be adequately described by a homogeneous kinetic rate expression first-order in dissolved hydrogen concentration. Mass transfer influence appears to be negligible and the overall hydrogen consumption rate is governed by chemical kinetics alone.

The reaction rate constant has a frequency factor of 1.06×10^5 per minute and an activation energy of 21 kcal/mole. It is likely that these numerical values are affected by the mineral matter present in the coal, which can catalyze hydrogenation activity (8).

The solubility of hydrogen in coal liquefaction solutions is appreciable and may be represented adequately by a Henry's law coefficient. The solubility exhibits an inverse temperature-solubility behavior.

Notation

H = mass of hydrogen, g
K = first order rate constant, min^{-1}
m = rate of mass transfer from gas to liquid, g/min.
P = pressure, psia
S = solubility, g H_2 /g oil
 r_A = reaction rate of hydrogen in liquid phase, g/min-cc
T = temperature, $^{\circ}\text{K}$
t = time, min
V = volume, cc
 α = parameter defined by Equation (5)
 β = Henry's law constant, g H_2 /g oil-psia

Subscripts

c = amount consumed by reaction
g = in gas phase
L = in liquid phase
T = total amount in both places
o = amount at $t = 0$

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TABLE 1

Gas Chromatographic Analysis of Creosote Oil

Compound	Weight %
coumarone	.10
p-/cymene	.02
indan	.11
phenol	.12
o-cresol	.05
benzonitrile	.12
p-cresol	.37
m-cresol	.16
o-ethylaniline	.03
naphthalene	5.1
thianaphthene	.08
quinoline	.37
2-methylnaphthalene	1.3
isoquinoline	.30
1-methylnaphthalene	.38
4-indanol	.55
2-methylquinoline	.42
indole	.21
diphenyl	.49
1,6-dimethylnaphthalene	.39
2,3-dimethylnaphthalene	.19
acenaphthene	6.0
dibenzofuran	6.7
fluorene	10.3
1-naphthonitrile	.18
3-methyldiphenylene oxide	1.7
2-naphthonitrile	.14
9,10-dihydroanthracene	2.4
2-methylfluorene	.85
diphenylene sulfide	.52
phenanthrene	18.6
anthracene	4.3
acridine	.19
3-methylphenanthrene	.98
carbazole	2.2
4,5-methylenephenanthrene	2.5
2-methylanthracene	.24
9-methylanthracene	1.2
2-methylcarbazole	1.7
fluoranthene	5.5
1,2-benzodiphenylene oxide	.96
pyrene	2.6

Table 2. Screen Analysis of Bituminous Kentucky No. 9/14 Coal Mixture

Mesh Size of Screen	% Retention
170	1.23
200	1.92
230	1.09
270	4.30
325	17.94
400	10.86
-400	62.65
Total	99.99

Table 3. Chemical Analysis of Bituminous Kentucky No. 9/14 Coal Mixture

H	4.9
C	67.8
Total Sulfur	2.55
Organic Sulfur	1.63
FeS ₂	0.79
Sulfate Sulfur	0.13
Total Ash	7.16

Table 4

Henry's Law Constants for Hydrogen in Creosote Oil

T_1 °C	$\beta \times 10^7$, g H ₂ /g oil-psia
100 ^o	5.95
200 ^o	6.94
300 ^o	7.75
400 ^o	9.65

Table 5

T_1 °C	α
385 ^o	0.183
400 ^o	0.193
410 ^o	0.196
435 ^o	0.211

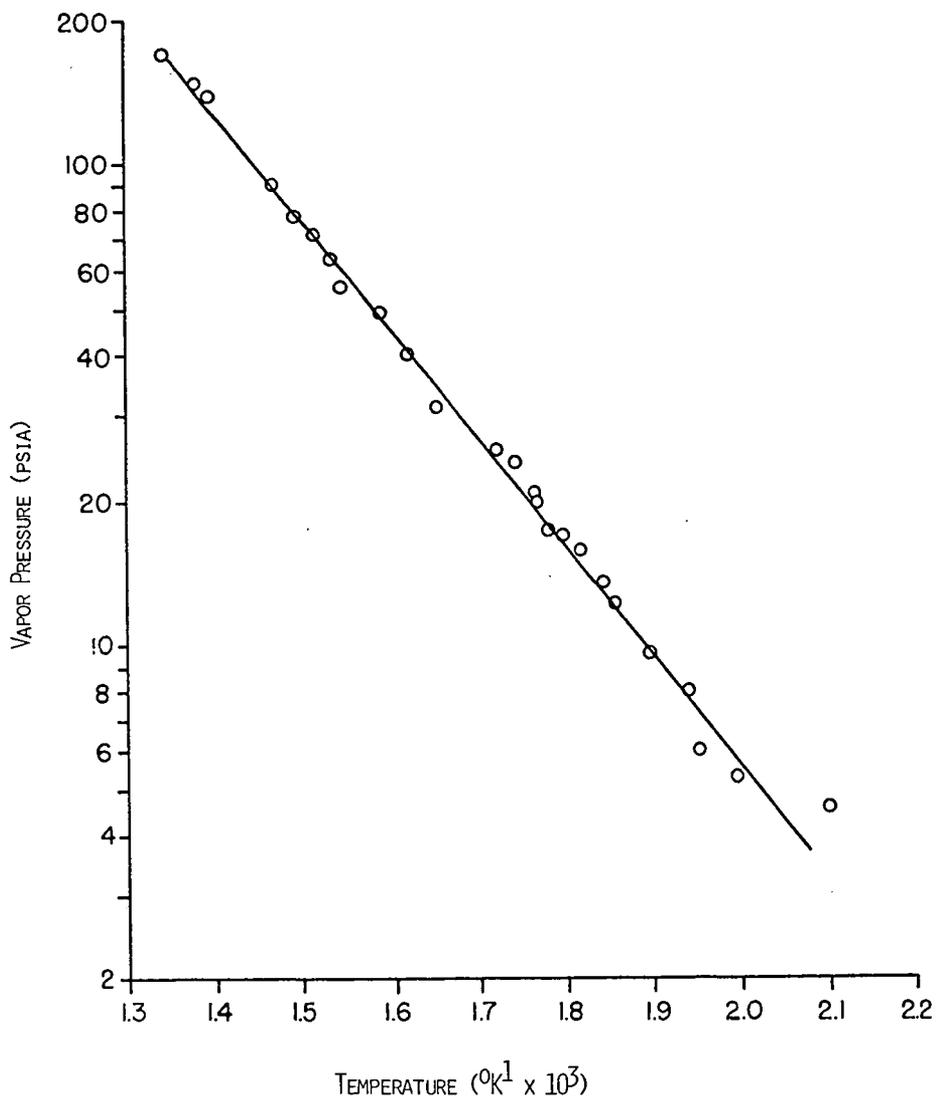


FIGURE 1. VAPOR PRESSURE OF CREOSOTE OIL

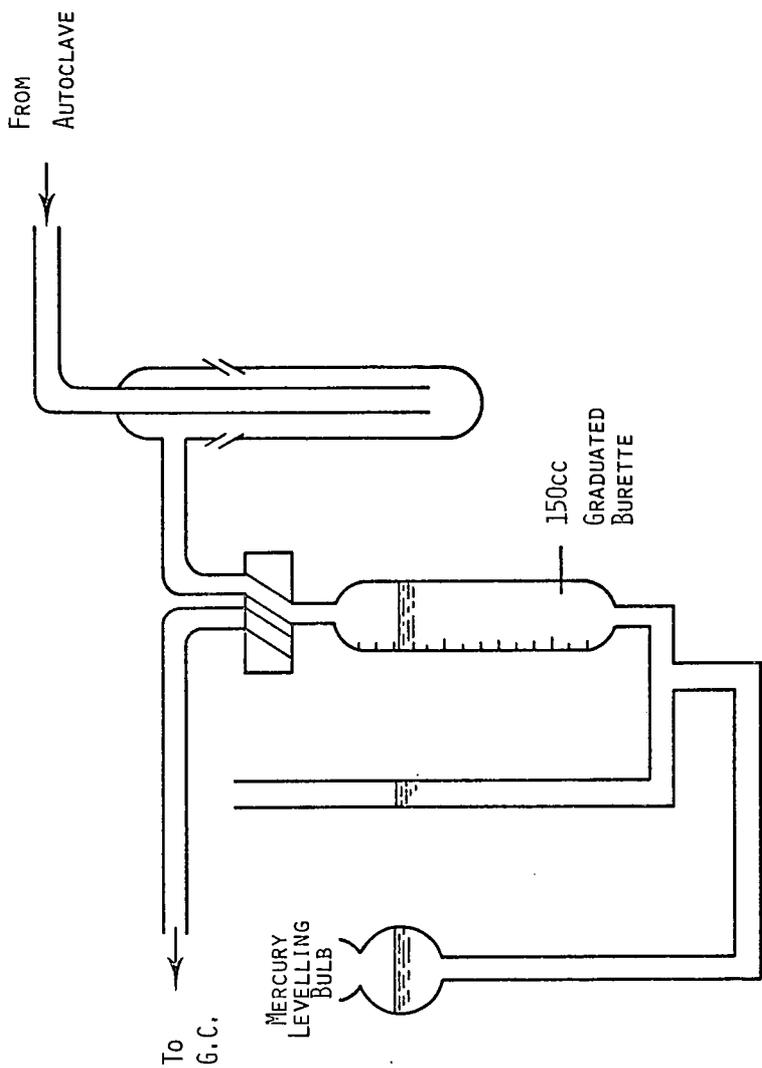


Figure 2. Gas Solubility Measurement Apparatus.

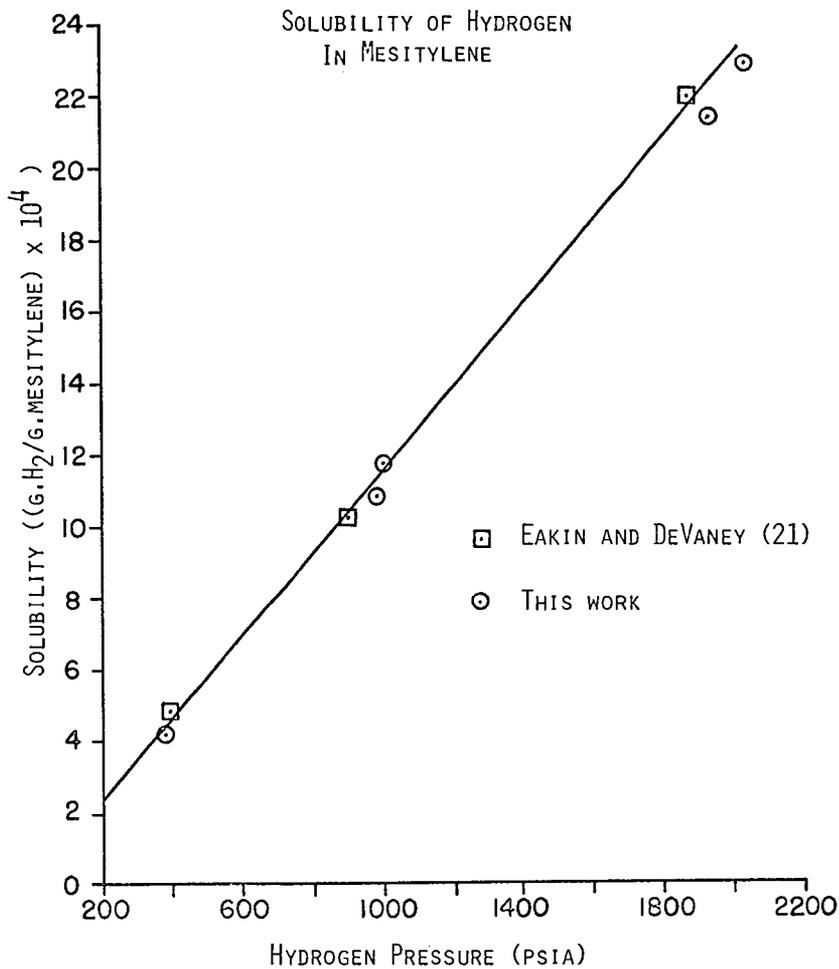


Figure 3. Comparison of this data with previous data for hydrogen solubility in Mesitylene

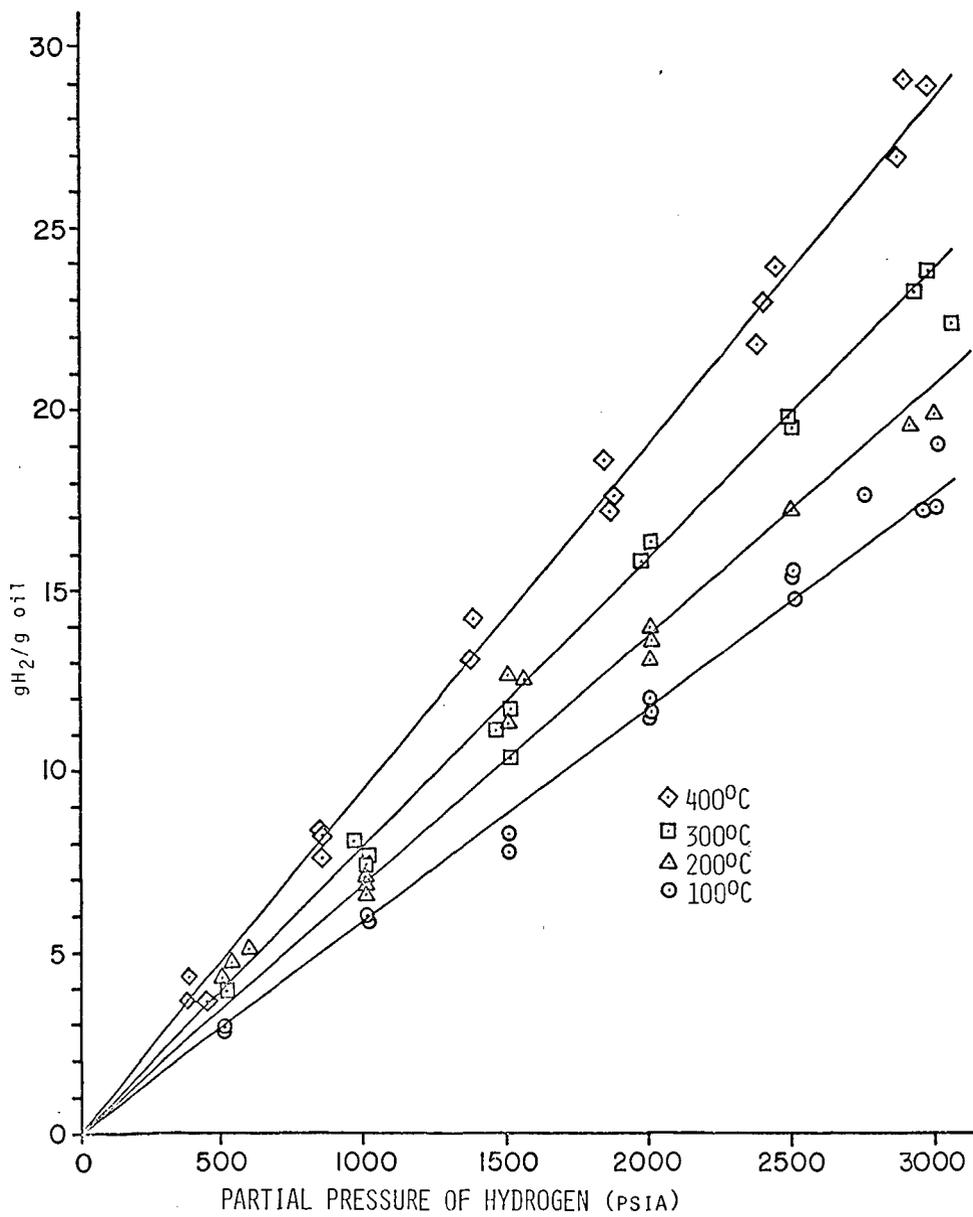


Figure 4. Solubility of H₂ in Creosote Oil

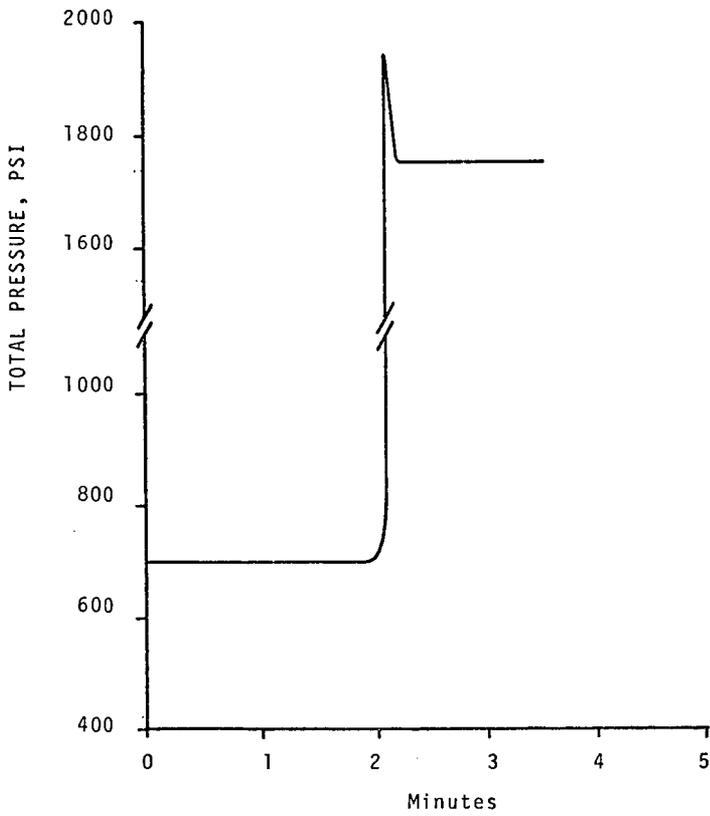


Figure 5. Rate of Approach to Gas + Liquid Equilibrium

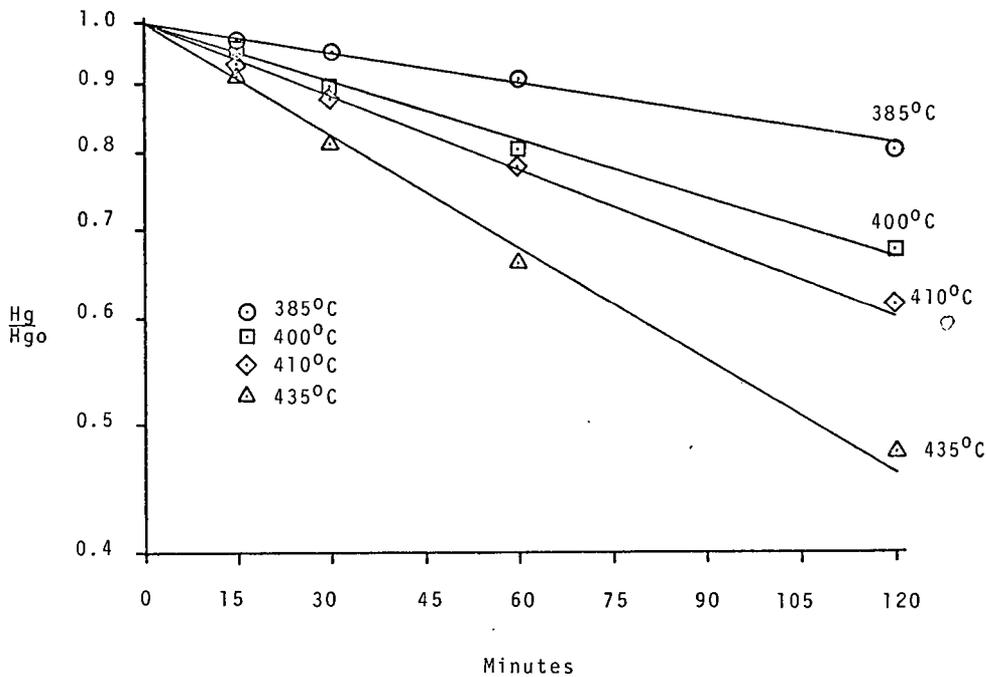


Figure 6. Verification of Hydrogenation Model

Figure 7. Arrhenins plot for hydrogen transfer rates to coal.

