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**STUDIES IN COAL LIQUEFACTION WITH APPLICATION TO
THE SRC AND RELATED PROCESSES**

Quarterly Report for the Period August–October 1981

By
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Work Performed Under Contract No. AC22-79ET13397

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U. S. DEPARTMENT OF ENERGY

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WITH APPLICATION TO
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Period August, 1981 - October, 1981

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PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract No. DE-AC01-79ET13397

Objective and Scope

Scope:

The Auburn Coal Conversion Laboratory is engaged in a research program designed to investigate fundamental aspects of the Solvent Refined Coal (SRC) and other closely related coal liquefaction processes. The SRC process provides a method for liquefaction of coal, and removal of sulfur and ash pollutants which would results from direct combustion of the raw coal. If successful, the SRC process will permit the use of high sulfur coals as a boiler fuel, which otherwise could not be used under EPA regulations. This research program seeks to improve the economic attractiveness of the SRC process through the application of chemical engineering techniques.

Objective:

The objective of this research program is to systematically investigate, characterize, and delineate the effects of changes in process operating conditions, equipment configuration, and nature of raw materials upon the kinetics, mechanism, and extent of coal dissolution, heteroatom removal, and hydrogenation in the SRC and closely related processes, for the purpose of providing an increased fundamental understanding of SRC process chemistry as well as guidelines and recommendations leading to economic and technical improvements in SRC technology. The program objectives are being carried out in cooperation with the Southern Services' SRC pilot plant operation at Wilsonville, Alabama, and with the Rust Engineering subsidiary of Wheelabrator-Frye, Inc.

The research program is divided into three major tasks with several sub-tasks within each area. An outline of the program by tasks and subtasks is presented on the following page.

Program Task Outline

Task 1. Mechanistic Studies of Coal Particle Dissolution

- A. Dissolution Behavior as a Function of Coal Characteristics
- B. Effect of Solvent Type and Gas Phase Composition on Particle Dissolution
- C. Direct Visual Observation of In-situ Particle Dissolution

Task 2. Catalysis by Coal Mineral Matter

- A. Process Variable and Kinetics
- B. Characterization of Coal Minerals
- C. Regeneration/Pretreatment of Coal Minerals and Residue
- D. Effect on Individual Species in Coal Liquefaction Products
- E. Continuous Reactor Studies

Task 3. Analytical Support

- A. Fourier Transform Infrared Spectroscopy of Coal and SRC
- B. Energy Dispersive X-Ray Fluorescence of Coal and SRC

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SUMMARY

Model compound reactions were studied to evaluate the effects of mass transfer, solvent type, solvent blending, hydrogen partial pressure, temperature, reactant concentration, additive loading and its preparation, etc. Naphthalene hydrogenation and benzothiophene hydrodesulfurization were investigated under the conditions comparable to commercial coal liquefaction and related processes. Both of these reaction systems were observed to be surface reaction controlled under the reaction conditions used in this work. Certain aromatic compounds were observed to cause a reduction in the reaction rates of naphthalene and benzothiophene.

Single stage coal dissolution was investigated using tetralin as a hydrogen donor solvent and a commercial cobalt-molybdate catalyst. A spinning basket system was developed to allow injection of the catalyst at a desired time in the reaction cycle. This catalyst injection technique proved to be reliable for the exploratory work done here. The degree of catalyst deactivation was rated by comparing the activities of the spent catalyst for model compound (naphthalene and cumene) reactivities relative to those of the fresh catalyst. No substantial reduction in deactivation was observed to result with delayed contacting of the catalyst with the coal-tetralin reaction mixture. The effect of reaction temperature on the initial rate of catalyst deactivation was also studied.

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I. INTRODUCTION

Catalytic coal liquefaction deals with contacting the catalyst with a coal-solvent slurry in the presence of a hydrogen transfer medium, either a donor solvent or hydrogen gas or both. Interests in catalytic coal liquefaction are increasing because of its potential advantages over non-catalytic liquefaction. Some of these are a lower operating pressure (usually below 4000 psi), a shorter retention time, improved product selectivity, and greater ease of operation. Some disadvantages associated with catalytic liquefaction are catalyst cost and increased separation loads (3).

The deactivation of the catalyst in coal liquefaction is severe. This is evident from the high amounts of catalyst estimated to be required per unit of coal feed for the more prominent processes. The H-coal process, for example, is estimated to require one pound of fresh catalyst per ton of coal processed, whereas the synthoil process has been estimated to require four pounds of catalyst per ton of processed coal (4).

Not much is known about the exact mechanism by which deactivation takes place in coal liquefaction. It is believed that liquefaction catalyst deactivates primarily due to coke formation on its surface. Based on discussions with the Electric Power Research Institute (EPRI) staff (1), it was postulated that delayed contacting of the catalyst with a reacting coal slurry would extend catalyst longevity. This is

because the products formed during the early stages of liquefaction are felt to have a higher propensity for coke formation than those formed during the later stages of liquefaction. To verify this postulation, a spinning basket system was developed which allowed the injection of the catalyst at a desired time. Data were obtained regarding the activity of the spent catalyst, coal conversion to cresol solubles, and final product distribution.

Coal liquefaction involves both hydrogenation and hydrocracking reactions. Besides these types of reactions, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) reactions also occur. Coal liquefaction is a very complex reaction system. Model compounds are used here to study specific effects, i.e., changes in catalytic activity for specific types of reactions (hydrogenation and hydrocracking). This is to provide insight as to what might occur in the more complex real coal system.

In addition to delayed catalyst contacting studies, a detailed study of the response of benzothiophene (BT) hydrogenolysis and naphthalene (N) hydrogenation to changes in the diluent solvent properties was made. This is to some degree a continuation of two earlier works done at Auburn, that by Fan (36) and that by Au (37), particularly the work by Au. In these earlier works, the rate of agitation of the tubular bomb reactor appeared to have a significant effect on BT conversion. Also, differences in the volatility of the diluent solvent for BT appeared to have some effect on its conversion rate. Higher BT conversions were observed when highly volatile aromatic solvents (benzene

and toluene) as opposed to highly volatile aliphatic solvents were used. A purpose of part of this work was to verify these observations and to develop a better understanding of the underlying mechanisms.

II. LITERATURE REVIEW

An extensive amount of literature has been reviewed regarding coal liquefaction chemistry and the role of catalysts in coal liquefaction processes. Presented here is an overview of the literature that has been reviewed.

The development of catalytic coal hydrogenation began in 1924 with high pressure flow reactors containing 50 cc of catalyst. It continued with larger units and large scale semicommercial plants at Ludwigshafen/Rh (5). Up to the 1940's, extensive research was done in coal liquefaction technology, and from this, the first two stage process having hydrofining and hydrocracking steps was evolved. However, in the mid 1950's, large oil discoveries in the middle-east killed all interest in coal conversion developments due to economic reasons. At present, the only commercial coal conversion plant in the world is in Sasolburg, South Africa. Several pilot and demonstration plants have been sanctioned by the U.S. Department of Energy (DOE) and are scheduled for construction in the near future (6).

Numerous variables affect the distribution of products from coal liquefaction. Some of these are:

- (1) Temperature
- (2) Pressure
- (3) Reaction time (space velocity)
- (4) Solvent nature

- (5) Gas atmosphere
- (6) Catalyst and its properties
- (7) Catalyst loading
- (8) Agitation and mixing
- (9) Coal composition and history etc.

Various theories and reaction mechanisms have been presented for coal liquefaction reactions in the literature. Falkum and Glenn (10) have postulated that the initial liquefaction of coal involves depolymerization to form reactive unsaturated materials which are either stabilized by hydrogen or repolymerized. This free radical formation theory has been used by Berkowitz (11), Van Krevlen (12), Heredy et al. (13), Reuther (14) and Guin et al. (15) in their works.

The basic reaction scheme for coal liquefaction as suggested by Sternberg (27) is:

In practice however, instead of simple series reactions, various combinations of these reactions can occur. Oils are typically defined here as n-pentane or n-hexane soluble material; asphaltenes, as insoluble in n-pentane or n-hexane but soluble in benzene; preasphaltenes, as benzene insoluble but methylene chloride soluble (7-9). Mohan and Silla (28) presented an excellent review of the different models that have been proposed for coal liquefaction kinetics. They reviewed the works of Pelipetz et al. (7), Hill et al. (9), Falkum and Glenn (10), Struck et al. (60), Weller et al. (8), Liebenberg and Potgieter (58), Yoshida et al. (59), Cronauer et al. (16), and Shalabi et al. (61). Also, Mohan

and Silla proposed several new models based on a new separation scheme that they developed which uses liquid-solid chromatography (LSC) as opposed to conventional solvent extraction.

Coal liquefaction requires high temperatures because of the relatively high strengths of bonds that must be broken. However, at such temperatures many undesirable side reactions occur such as coking, char formation, and dehydrogenation. Catalysts are used to favor reactions by which heteroatom (S,N,O) removal and depolymerization occur over hydrocracking reactions which yield light hydrocarbon gases. Storch et al. (33) reported that the thermal decomposition of Bruceton coal occurred in the temperature range of 370°C to 415°C, and that excessive coke formation occurred above 440°C, even at very high hydrogen pressures.

Coal dissolution itself has been observed to occur rapidly at liquefaction temperatures. Tarrer et al. (34) concluded from their studies that complete disintegration of Kentucky No. 9 bituminous coal took place immediately upon heating to 360°C with none of the original coal particles remaining intact.

Cronauer et al. (16) indicate that the rate constants for oil production from coal and asphaltenes significantly increase when using a good hydrogen donor solvent. Guin et al. (34) and others have observed tetralin and hydrogenated cresote oil to be good hydrogen donors. Brunson (35) has presented a discussion of the fundamental chemical aspects by which tetralin functions as a donor solvent. Guin et al. (17) have suggested that the slower controlling steps in liquefaction may involve hydrogenation of the solvent to replenish hydrogen donor

species. Yen et al. (29) have studied catalytic liquefaction in a batch autoclave using a commercial catalyst such as Co-Mo-Al₂O₃. They have concluded that for better liquefaction and desulfurization, a hydrogen donor solvent is essential. They have also observed an increase in liquefaction and oil yield when the pore diameter of the catalyst was increased, even though surface area was lower compared to that of the other catalyst tested.

Quite a few researchers have tried to separate catalytic effects from thermal effects in coal liquefaction. Acorn et al. (32) among others, have batch screened coal liquefaction catalysts using a falling basket type of reactor. They have found that the conversion of the coal to asphaltenes involves thermal degradation, and the rate of asphaltene formation was about the same with or without catalyst present. Hydrogenation rates and heteroatom (S,N,O) removal rates, on the other hand, were observed to be much higher with a catalyst present.

A recent study of coal liquefaction within the temperature range of 390° to 410°C was performed by Gun et al. (18). They studied three different reaction systems: (1) coal-solvent with catalyst present (2) coal-solvent without catalyst present, and (3) coal and no solvent with catalyst present. For all three reaction systems, there was a hydrogen atmosphere. The activation energy when both solvent and catalyst were present (system (1)) was nearly half of that found for the other two systems (systems (2) and (3)). Based on these results, they concluded that either the role of the catalyst and that of the solvent are interrelated or the catalyst influences both direct hydrogenation with gaseous hydrogen and indirect hydrogenation via hydrogen donor

solvent. Also, Gun et al. (19) used free radical scavengers to investigate the basic coal liquefaction mechanism. From this investigation, they concluded that pyrolysis is the main driving force in coal liquefaction.

Both hydrogenation and hydrocracking reactions occur during coal liquefaction. Curran et al. (20) have mentioned that the rupture of covalent bonds is the rate determining step in coal liquefaction. Orchin and Storch (21) postulated that thermal treatment alone cannot break the types of bonds necessary to produce a liquid product. Collins et al. (22) considered c-c bond scission as an important factor in asphaltene formation. Mukherjee and Chowdhury (23) postulated that the addition of large amounts of minerals like kaolinite causes a higher conversion of coal because of their cracking properties.

In summary, much is not known about the role of a catalyst in coal liquefaction. It is not clear which activity is more critical to selectively produce more oil from coal: hydrogenation or hydrocracking.

Garg et al. (30) concluded that the selectivity for desulfurization in two stage hydrodesulfurization of coal is improved by using a high reaction temperature and a short residence time in the first stage. Here, the solid residue from the solvent refining of coal was used as a first stage catalyst, and a commercial Co-Mo- Al_2O_3 was used as a second stage catalyst. They also observed two stage catalytic coal liquefaction to be more selective for hydrodesulfurization than either catalytic or non-catalytic single stage coal liquefaction.

Shah and Cronauer (31) have reviewed a number of works concerned with heteroatom (S,N,O) removal in coal liquefaction. Their review

provides good insight with regard to the general coal chemistry, role of the catalyst, and basic reaction mechanism for heteroatom-removal reactions occurring during coal solvation.

It has been observed by Bhinde (24) that nitrogen containing compounds severely reduce the hydrogenation and hydrocracking activities of commercial catalysts such as Co-Mo-Al. This is attributed to the acidic nature of the catalysts and the basic characteristics of the nitrogen compounds (4). Gates and his coworkers (25) observed a drastic reduction in hydrogenation rates in the presence of quinoline, a basic nitrogen compound, when they studied hydrodesulfurization of dibenzothiophene. Mobil investigated mixtures of model compounds in a fixed-bed down flow reactor (26). They also observed a drastic reduction in hydrogenation, hydrocracking, and hydrofining activities of commercial catalysts such as Ni-Mo-Al, Co-Mo-Al etc; in the presence of basic nitrogen compound like quinoline. They observed this kind of catalyst inhibition to be reversible. The significance that inhibitors like quinoline have in coal liquefaction is not well understood.

Typically in model compound studies such as those made in this work, the model reactant is dissolved in a diluent solvent that is relatively unreactive at reaction conditions. The physical properties of this solvent can affect the state of the reaction system: the system can exist either as two-phases (gas-solid) or as three-phases (gas-liquid-solid) at reaction conditions. Fan (36), for example, studied the hydrogenolysis of benzothiophene (BT) at coal liquefaction conditions using pyrite as a catalyst and n-dodecane as a diluent solvent. He observed a reduction in the activation energy for BT hydrogenolysis

above reaction temperatures of 390°C . This was attributed to the phase change in the BT-dodecane reaction solution in this temperature range, i.e., the reaction solution possibly existing completely in the vapor state above 390°C .

Based on the above observation Au (37) investigated the response of conversion rate for BT hydrogenolysis to changes in properties of the diluent solvent, which in Fan's study was dodecane. Ferric oxide was used, in Au's study, as a sulfur scavenger to accelerate desulfurization rates and improve selectivity for the desulfurized product, ethyl benzene, over the hydrogenation product, dihydrobenzothiophene. Au observed higher rates of BT hydrogenolysis with dodecane than those with less volatile hexadecane in the temperature range of $> 390^{\circ}\text{C}$ to 400°C . Both Fan and Au showed the apparent kinetics for BT hydrogenolysis to be first-order with respect to hydrogen concentration and first-order with respect to BT concentration. Au determined the activation energy for BT hydrogenolysis, even in the temperature range of $> 390^{\circ}\text{C}$, to be about or greater than 10 kcal/g-mole. This was interpreted to suggest that the reaction was surface reaction controlled as opposed to mass transfer controlled. Both Au and Fan observed agitation rate to have a strong influence on BT conversion rate; in fact, in Fan's study the effect was linear, i.e., BT conversion rate increased in linear proportion with an increase in agitation rate. From the results of these studies, it was not clear why BT conversion rate was sensitive to agitation rate or why it varied with diluent solvent properties.

III. SOLVENT EFFECTS IN NAPHTHALENE HYDROGENATION

Introduction

Based on the results of the studies by Fan (36) and Au (37) for BT hydrogenolysis, it was decided to do a similar study for a different model compound reaction: Naphthalene (N) hydrogenation. The response of N hydrogenation rate to changes in reaction temperature, agitation rate, and diluent solvent properties were studied. The results of this part of this thesis work provided the impetus for that described in Chapter IV.

Materials Used

The diluent solvents used in this study were benzene, hexadecane, and cyclohexane. Specifications for these and the model reactant, naphthalene, are as follows:

Naphthalene: Pure crystals from Fisher Scientific Company.

Benzene: Nanograde from Fisher Scientific Company.

Hexadecane: Research grade from Pfaltz and Bauer.

Cyclohexane: Research grade from Fisher Scientific Company.

Quinoline: 97% pure from Aldrich Chemicals, Inc.

Catalyst: Harshaw Co-Mo-Al 0402T (3% CoO, 14.7 MoO₃) presulfided by insitu sulfiding techniques.

Catalyst Preparation

Generally, the sulfided form of a hydrogenation catalyst (e.g. Co-Mo-Al) is more active than its oxide form. In this work, the Co-Mo-Al catalyst was presulfided using techniques developed at Auburn (45). The Harshaw 0402T Co-Mo catalyst, ground to -325 mesh, was spread uniformly in a pyrex tube. It was treated with hydrogen sulfide at a flow rate of approximately 20 c.c. per minute. Heat-up, reaction temperature, and times were approximately as follows:

Heat up from room temperature to 300°C (60 minutes)

300°C to 350°C (30 minutes)

350°C to 410°C (30 minutes)

After reaching 410°C, heating was discontinued and the reaction tube was air-cooled to room temperature while maintaining a constant H₂S flow. After cooling, the sulfided catalyst was stored in a closed glass bottle placed in vacuum desiccator. Normally a Co-Mo-Al catalyst sulfided by this procedure contains 7 to 9 wt. % sulfur. The same batch of sulfided catalyst was used throughout this work.

Experimental Procedure

The reactions were carried out in microreactors (tubing bomb) made from SS316. The tubing bomb was constructed from s.s. tubes having a 0.5 inch OD and a 0.035 inch wall thickness and are 6 inches in length. It was equipped with a fine metering valve connected via 0.125 inch and 0.25 inch tubes to the reactor body. The whole unit was assembled using swagelock fittings and reducing unions.

The reactants were charged in the tubing bomb along with the catalyst (if any). When powdered catalyst was used, two steel ball agitators of 0.125 inch diameter were used to ensure good end to end mixing during reaction. The bomb was sealed, and hydrogen gas was charged via the metering valve, and finally, the bomb was tested for leaks. Figure 1 shows the shaker assembly. The temperature of the sand bed was monitored using a multipoint omega digital indicator.

When the temperature of the fluidized sand bed reached about 6°C above the desired reaction temperature, the tubing bomb was quickly immersed in the sand bed. Heat up of the contents in the tubing bomb was usually achieved in less than 30 seconds. The temperature of the sand bed was controlled within $\pm 1^{\circ}\text{C}$ steadily after approximately one minute of an initial period of transient temperature, within which it varied less than $\pm 3^{\circ}\text{C}$. At the end of the desired reaction time, the bomb was quenched in cold water. After cooling, the gases were vented and liquid sample was collected in small glass vials after removing the solid catalyst by filtration.

The liquid samples were analysed using a Varian 3700 gas chromatograph with helium as the carrier gas and with a ionization detector. Separation of the products was achieved by using a six foot, 0.125 inch OD stainless steel column packed with 3% SP-2250 on 100/120 supelcoport.

Results and Discussion

Hydrogenation of naphthalene has been studied by many researchers. The reaction scheme has been reported (25,48,49) to be as follows:

Effect of Agitation on Naphthalene Conversion

A direct method for evaluating the importance of gas-liquid mass transport is to measure the response of conversion rate to changes in

Figure 1. Reactor-Shaker System Used in Model Compound Experiments

Table 1. Naphthalene Conversion at Different Agitation Rates both with Benzene and with Hexadecane as the Diluent Solvents

RPM	Benzene System		Hexadecane System	
	GC peak area ratio, T/N	% Naphthalene conversion	GC peak area ratio, T/N	% Naphthalene conversion
275	0.05	5.0	0.29	23.4
450	0.15	13.6	0.88	48.1
600	0.35	26.9	1.0	51.3
800	0.48	33.6	1.12	54.1
900	0.53	35.8	1.2	55.8

Reaction conditions: 5 minutes, 380 °C, 1250 psig H₂ at RT., 0.25 g Co-Mo-Al (presulfided), 5.0 g. reactant mixture containing 10 wt.% naphthalene in solvent, two steel ball agitators, 15 ml. tubing bomb reactor

Refer Table 1. for reaction conditions

Figure 2. Effect of Agitation Rate on Naphthalene Conversion

agitation rate. A high sensitivity of conversion with respect to agitation usually indicates that gas-liquid mass transport is controlling. To evaluate the intrinsic kinetics, the reaction system should be operated in a range of agitation speed such that conversion rate is insensitive to agitation. Table 1 and Figure 2 show the sensitivity of N conversion to agitation rate when using benzene and hexadecane as diluent solvents and presulfided Co-Mo-Al catalyst.

As can be seen in Figure 2, below 500 RPM, conversion appears to be very sensitive to agitation rate. With hexadecane, the N conversion appears to be fairly insensitive to agitation rate above 600 RPM. In this agitation range, N conversion may be slightly increasing as agitation rate is increased. However, it is difficult to ascertain whether this trend is real because of experimental error. One possible explanation for sensitivity of N conversion rate to agitation rate has to do with catalyst dispersion. That is, the catalyst becomes more dispersed with increasing agitation up to some critical amount of agitation above which dispersion remains essentially the same. Moniz (62) has also evaluated the sensitivity of N conversion to agitation rate (Figure 3). He used molybdenum octoate to catalyze N hydrogenation. Carbon disulfide was added to react with hydrogen and form H_2S . The H_2S is assumed to react with the molybdenum octoate to form molybdenum sulfide, which is an effective hydrogenation catalyst. The molybdenum sulfide catalyst formed by this assumed reaction sequence appeared to be a fine powder and was assumed to be easily dispersed. From Figure 3, N conversion appears to be insensitive to agitation rate in the range above about 400 rpm. This range of insensitivity extends to a lower value of

Reaction conditions: 30 minutes, 410 °c, 1250 psig H_2 at RT., 0.1 % catalyst Moly-Octoate in 10 wt.% solution of naphthalene in solvent, two steel ball agitators, 15 ml. tubing bomb reactor.

Figure 3. Effect of Agitation Rate on Naphthalene Conversion, Reference (62).

agitation rate (400 rpm) with the molybdenum octoate/molybdenum sulfide than was observed with the ground Co-Mo-Al catalyst (600 rpm). The difference in the range of insensitivity observed between these two catalytic reaction systems could be due to differences in the ease of dispersion of the two types of catalyst. More work is needed before any definitive conclusions can be made.

It should be noted that Gollakota (65) has observed that the gas-liquid mass transfer coefficient is low at an agitation rate of 400 rpm for the tubing bomb reactor system used here. However, even at 400 rpm, the gas-liquid mass transfer coefficient is greater than that typically reported for bubble column, which are assumed to represent an actual liquefaction reactor (Figure 4). Therefore, the agitation rate range of < 400 rpm appears to be of commercial importance. The reason for the high sensitivity of N conversion to agitation rate in this agitation range, as stated above, is not clear, and more work is needed to better understand these observations.

Benzene has a high volatility as compared to hexadecane. Au (37) observed higher conversions for benzothiophene hydrogenolysis with benzene as the diluent solvent than those obtained with hexadecane. For these reasons, N conversions at different agitation rates were determined with benzene as the diluent solvent. The results are given in Table 1 and Figure 2. Lower rather than higher conversions were obtained at all agitation rates with benzene as compared to hexadecane. Also, N conversion with benzene appears to be more sensitive to agitation rate. As pointed out above, the difference in conversion and in

Figure 4. Comparison of Mass Transfer in Different Reactor Types, Reference (65)

sensitivity to agitation rate observed here could simply be due to differences in dispersion of the catalyst.

A computer program supplied by Prausnitz (63) was used to estimate the vapor-liquid distribution for various reaction systems. The program is based on correlations developed by Lee and Kesler for thermodynamic properties of normal fluids. Prausnitz applied these correlations to mixtures. Relations for vapor-liquid equilibria at high pressures used in the program are based on one-fluid theory and a new mixing rule developed by Prausnitz for estimating the pseudo-critical properties of the mixture. Based on observations made by Prausnitz, the mixing rule appears to be applicable to asymmetric mixtures. Input data for the program include pure component critical properties, acentric factors, and a binary interaction constant for each binary combination of the components. When pure component critical properties and acentric factors were not available, the estimation methods outlined by Prausnitz (57) were used. The binary interaction parameters were presented in the publication by Prausnitz (63) which describes the computer calculations used here.

The estimated vapor-liquid distributions for the reaction systems used here are given in Table 2. These estimations were made by Poliyedath (66) using the program described above. Apparently, from these estimations, the H_2 gas, N, benzene system exists completely in the vapor phase at reaction conditions ($410^{\circ}C$, 1250 psi initial hydrogen pressure). The H_2 gas, N, hexadecane system, on the other hand, exists in both the vapor and liquid phases at the reaction conditions. So, with hexadecane as opposed to benzene, more mass transfer resistance

Table 2.

Estimated Phase Compositions for The
Naphthalene Reaction System

System	Weight of Reactants	Feed Mole Fraction	Temp. °C	Pressure atm	Vapor Fraction	Initial Phase Compositions	
						liquid	vapor
10-90 N-HD and H ₂	5	Z _{HD} =0.3695 Z _N =0.0725 Z _{H₂} =0.5580	410	150	0.6038	X _{HD} =0.8003 X _N =0.1543 X _{H₂} =0.0454	Y _{HD} =0.0867 Y _N =0.0188 Y _{H₂} =0.8944
10-90 N-B and H ₂	5	Z _B =0.6102 Z _N =0.0413 Z _{H₂} =0.3485	410	350	1.0	--	Y _B =0.6102 Y _N =0.0413 Y _{H₂} =0.3485
10-90 N-CH and H ₂	5	Z _{CH} =0.6106 Z _N =0.0446 Z _{H₂} =0.3448	410	300	1.0	--	Y _{CH} =0.6106 Y _N =0.0666 Y _{H₂} =0.3448

would be expected since there is a liquid phase. However, for the same reason, better dispersion of the catalyst might be expected. There are other factors than these that may be dominating. Generally, the adsorptivity of a compound on an acid catalyst site is related to its basicity (4). The basicity of naphthalene is greater than that of benzene (50). However, there is much more benzene than naphthalene present in the reaction system, and as a result, benzene may interfere with naphthalene adsorption and inhibit its reaction.

Effect of Temperature on Naphthalene Conversion

The mass transfer rate parameters are weak functions of temperature. The sensitivity of reaction rates to changes in temperature provides a direct indication of rate-controlling phenomena. Typically the dependence of reaction rates on temperature follows the Arrhenius relation

$$k = k_0 e^{-\Delta E/RT} \quad (1)$$

where k is the reaction rate constant; k_0 , the frequency factor; R , the universal gas constant; T , the reaction temperature; ΔE , the activation energy. For mass transfer controlled reaction systems, the activation energy is usually less than 5 kcal/g-mole; whereas, for surface reaction controlled reactions, the activation energy is usually greater than 10 kcal/g-mole (40). Table 3 shows the N conversions obtained at different reaction temperatures.

Shridharani (45) and Moniz (62) have both observed the kinetics for N hydrogenation to be first order with respect to naphthalene

Table 3.

Effect of Temperature on Naphthalene Conversion

Temp., °C	$1/T \times 10^3, ^\circ\text{K}^{-1}$	Hexadecane System		Benzene System	
		% Naphthalene Conversion	First Order $K \times 10^2$ min^{-1}	% Naphthalene Conversion	First Order $K \times 10^2$ min^{-1}
350	1.6051	34.5±0.02	8.4624	26.4±0.2	6.131
380	1.5314	56.2±0.06	16.5107	37.1±0.07	9.273
410	1.4641	77.0±0.1	29.394	64.8	20.88
450	1.3831	82.2	34.54	75.3	27.97

Reaction Conditions; 5 min., 860 rpm, 1250 psig H_2 at RT, 0.25 g Co-Mo(sulfided), 5 gm reactant mixture containing 10 wt.% Naphthalene in solvent, 2 Steel Ball Agitators, 15 ml tubing bomb reactor.

Refer Table 3. for reaction conditions

Figure 5. Arrhenius Plot for Naphthalene Hydrogenation.

concentration. The activation energy for N hydrogenation was determined from regression analysis of the $\ln k$ versus $1/T$ data-set where k is the first order rate constant. (Table 3). The activation energy was computed to be about 17.6 kcal/g-mole for the N-hexadecane reaction system, and $E = 17.2$ kcal/g-mole for the N-benzene system. The correlation coefficients for the regression analyses were 0.999 and 0.978, respectively. The Arrhenius plots for the two reaction systems are given in Figure 5. The magnitudes of the activation energies are sufficiently high as to indicate the reaction systems to be kinetically controlled.

The liquid-solid mass transfer coefficient was estimated for the N-hexadecane system using correlations given by Brian and Hales (40) and Lemcoff and Jameson (64). These correlations relate the mass transfer coefficients to certain physical properties of the reactant species and the solvent. The required physical properties (e.g. diffusivities) were estimated by methods outlined by Prausnitz et al. (57). The liquid-solid mass transfer coefficients for hydrogen and for N with hexadecane as the diluent solvent were computed to be 1.39 and 1.0 cm/sec, respectively.

If liquid-solid mass transfer of either reactant, hydrogen or N, is limiting, then the reaction rate can be computed using the respective mass transfer coefficient. Here, by definition of mass transfer being limiting, it is assumed that other resistances to reaction are negligible; that is, the gas-liquid mass transfer, pore diffusion, and surface reaction are relatively insignificant. Making the hypothesis that mass transfer of one or the other reactant is limiting, the

reaction rate based on the respective mass transfer coefficient was computed. The respective reaction rates were 0.091 g-moles/sec with mass transfer of hydrogen being limiting and 0.052 g-moles/sec with N limiting. Experimental reaction rates for N hydrogenation to form tetralin and for the corresponding hydrogen consumption were 0.00001 and 0.00002 g-moles/sec, respectively. Thus, the hypothesis that liquid-solid mass transfer of either reactant is limiting does not appear to be valid, for the experimental reaction rates are several orders of magnitude less than the computed rates.

The surface reaction is affected by the resistances associated with pore diffusion and chemical reaction. The significance of pore diffusion can be determined by estimating the effectiveness factor η . The value of η is usually between zero and one. Pore diffusion does not significantly affect the reaction rate when η is close to one. Neglecting the temperature gradients within the pore structure of the catalyst, η becomes a function of the reaction order and the Thiele modulus ϕ . ϕ is defined as

$$\phi = \frac{d_p^2}{D_A \theta} \times \frac{-r_A \rho_p}{w} \times \frac{1}{C_{A,\ell}} \quad (2)$$

where d_p is the catalyst particle diameter; D_A the diffusivity of component A; θ , the porosity of the catalyst; r_A , the reaction rate; ρ_p , the catalyst density; w , the catalyst weight; $C_{A,\ell}$, the concentration of component A in the bulk liquid. Substitution of the appropriate values for these parameters or conservative estimates given in Appendix A yields $\phi = 0.05$. This corresponds to $\eta = 1$ for a first order

reaction (40). Similarly, the effectiveness factor for the N-benzene system was found to be about one. Thus, pore diffusion does not appear to be significant for either reaction systems. This is generally the case for powdered catalysts as is used here.

Based on the above computations and the earlier discussion regarding gas-liquid mass transfer, it appears that N hydrogenation is surface reaction controlled for the reaction conditions used here. The differences in reaction rates observed here between the two reaction systems, N-hexadecane and N-benzene, is not clear. It could be due to differences in the adsorptivity of the solvents on catalyst sites with benzene being more strongly adsorbed and more inhibiting to N-hydrogenation. Or, the differences could simply be due to differences in dispersion of the catalyst with the powdered catalyst being more poorly dispersed in the lower density N-benzene system.

Additional studies were made to provide further insight with regard to the effects of the diluent solvent properties on reaction rates observed above. The response of N-hydrogenation rate to changes in solvent composition was determined with binary hexadecane-benzene mixtures as the solvent. The results are shown in Table 4. As stated earlier, Shridharani (45) and Moniz (62) have shown N-hydrogenation to be first order with respect to naphthalene concentration. Assuming Langmuir-Hinshelwood Kinetics apply here to N-hydrogenation, reaction rate

$$\frac{dC_N}{dt} = \frac{-K K_N K_H C_N C_H^m}{1 + K_N C_N + K_H C_H + K_B C_B} \quad (3)$$

Table 4. Effect of Changes in Hexadecane-Benzene Compositions on Naphthalene Conversion

Benzene concentration, $C_B \times 10^4$, g-mole/cc	Mole % benzene in feed	Experimental % naphthalene conversion	Predicted % naphthalene conversion	% Error
0.0	0.0	77.0 ± 0.1	77.1	- 0.13
7.69	36.8	75.0 ± 0.4	74.2	1.1
19.24	67.6	69.4 ± 0.1	70.2	- 1.2
30.77	85.4	66.1 ± 0.1	66.5	- 0.61
38.46	93.7	64.8	64.2	0.93

Reaction conditions: 5 minutes, 41C °C, 860 RPM, 1250 psig H_2 at RT, 0.25 g. Co-Mo-Al (sulfided), 5.0 g. reactant mixture containing 10 wt.% naphthalene in solvent(s), two steel ball agitators, 15 ml. tubing reactor

where C_N , C_H , C_B are the concentrations of naphthalene, hydrogen, and benzene, respectively; K_N , K_H , and K_B are the adsorption coefficients for naphthalene, hydrogen, and benzene, respectively; and K is the intrinsic reaction rate constant. More than three times the stoichiometric amount of hydrogen was charged initially into the reactor; therefore the hydrogen concentration C_H is assumed to remain constant with reaction. If $K_N C_N + K_H C_H \ll 1 + K_B C_B$, then equation 3 reduces to

$$\frac{dC_N}{dt} \cong \frac{K_1^* C_N}{1 + K_B C_B} \quad (4)$$

where $K_1^* = K K_N K_H C_H^m$. Separating the variables t and C_N , equation 4 becomes with integration

$$\ln \left(\frac{C_N}{C_{No}} \right) = \ln(1-x) = - \frac{K_1^* t}{1 + K_B C_B} \quad (5)$$

where $x = (C_{No} - C_N)/C_{No}$ and C_{No} is the initial concentration of naphthalene. Rearranging equation 5,

$$\psi = \frac{1}{-\ln(1-x)} = \frac{1}{K_1^* t} + \frac{K_B}{K_1^* t} C_B \quad (6)$$

For $t = \text{constant}$, a plot of ψ versus C_B should thus be a straight line, which as shown in Figure 6 is the case. K_1^* and K_B can be computed from the ordinate intercept and the slope of the ψ versus C_B curve. The values of K_1^* and K_B determined in this manner were 0.295 min^{-1} and $112 (\text{g-moles/cc})^{-1}$, respectively. A comparison of

Figure 6: Langmuir-Hinshelwood Model Fit for Naphthalene Hydrogenation in Presence of Benzene

Figure 7: Comparison of The Experimental and Predicted Naphthalene Conversions in The Presence of Benzene

Figure 8: Comparison of The Experimental and Predicted Naphthalene Conversions in The Presence of Quinoline, Reference (45).

experimental N conversions and predicted values using equation 6 is shown in Figure 7. The agreement with each experimental point is within the experimental error (± 2.0 wt %).

An analysis similar to that above was done by Shridharani (45) for N-hydrogenation with a binary mixture of hexadecane and quinoline as the diluent solvent. Quinoline is a basic nitrogen compound and is known to adsorb strongly to the surface of acidic catalysts and thus inhibit reaction. The values for K_1^* and K_Q (the adsorption coefficient for quinoline) were computed to be 0.0973 min^{-1} and $44500 \text{ (g-moles/cc)}^{-1}$, respectively. A comparison of experimental and predicted N conversions is shown in Figure 8. Again, the agreement is within experimental error. The experiments made by Shridharani (45) were done at a lower reaction temperature (380°C versus 410°C) and a longer reaction time (15 minutes versus 5 minutes) and with a slightly different Co-Mo-Al catalyst. Apparently, the kinetic model (equation 3) does describe both reaction systems reasonably well.

To estimate the adsorption coefficient for quinoline for the catalyst used here, a naphthalene hydrogenation run was made at 350°C and 15 minutes of reaction. Assuming Langmuir-Hinshelwood kinetics (equation 3), the adsorption coefficient for quinoline was estimated to be $1.5 \times 10^5 \text{ (g-moles/cc)}^{-1}$. A run was made with a benzene-quinoline mixture as the diluent solvent at 350°C and 15 minutes of reaction. The adsorption coefficient for benzene was assumed to be the same as that determined earlier from the run made at 410°C ; i.e., it was assumed not to vary with temperature. The N-conversion was estimated with the benzene-quinoline mixture as the solvent to be 21%; the

actual N-conversion was 15% (Table 5). The 6% difference could be due to synergistic effects, or more likely, to experimental error. The N-conversion was lower with benzene-quinoline (1 wt.%) as opposed to hexadecane-quinoline (1 wt.%) as the solvent (15 versus 23%, Table 5).

It was assumed that cyclohexane being a saturated compound would have a lower adsorptivity than benzene, an unsaturated compound. That is, the adsorption coefficient for cyclohexane would be less than that of benzene, and the N-conversion would be higher with it as opposed to benzene as the solvent. As shown in Table 5, this is indeed the case; in fact, the N-conversion is the same as that obtained with solvent hexadecane. It should be noted that, at the reaction conditions used here, the N-cyclohexane mixture was estimated to exist completely in the vapor phase (Table 2). More than ninety wt. % of the N-hexadecane mixture, on the other hand, would exist in the liquid phase.

Summary of Results

(1) Neither gas-liquid nor liquid-solid mass transfer appear to be controlling in the naphthalene-hexadecane-hydrogen reaction system under the experimental conditions studied here.

(2) Gas-solid mass transfer does not appear to be controlling in the naphthalene-benzene-hydrogen reaction system under the experimental conditions studied here.

(3) In both reaction systems studied here, pore diffusion was not significant.

Table 5.

Solvent Effects in Naphthalene Hydrogenation

Reactant System	% Naphthalene conversion
10 wt.% N in benzene	59.6
10 wt.% N in cyclohexane	70.3 $\pm$ 0.6
10 wt.% N in hexadecane	71.6
10 wt.% N and 1.0 wt.% quinoline in hexadecane	22.5
10 wt.% N and 1.0 wt.% quinoline in benzene	14.8

Reaction conditions : 15 minutes, 350 °C, 860 RPM., 1250 psig
H₂ at RT., 0.25 g. Co-Mo-Al (sulfided),
5.0 g. reactant mixture, two steel ball
agitators, 15 ml. tubing bomb reactor.

(4) The apparent sensitivity of reaction rate to changes in the agitation rate, for naphthalene hydrogenation, is believed to be due to differences in the dispersion of the catalyst particles.

(5) Benzene appears to cause a reduction in naphthalene hydrogenation rate. This may be due to benzene being adsorbed competitively to naphthalene on the active sites of the catalyst.

A Langmuir-Hinshelwood type of kinetics fits the data well. However, a detailed study is needed to further understand the phenomenon in general.

IV. EFFECT OF SOLVENT PROPERTIES ON HYDRODESULFURIZATION OF BENZOTHIOPHENE

Introduction

As outlined earlier, desulfurization is important not only from environmental pollution point of view, but also to reduce catalyst deactivation in subsequent steps of refining and upgrading of the coal liquids. Benzothiophene, which is one of the principal organo sulfur compounds in coal liquids, was chosen as the reactant. The major objective of this model compound work was to verify and extend the work done by Fan (36) and Au (37). This involved further testing of the first order kinetic model used by Fan and Au and studying the mass transfer effects in heterogeneous catalysis concerning hydrodesulfurization (HDS) of benzothiophene (BT) over different catalysts.

Materials Used and Experimental Procedure

The diluent solvents used in this study were hexadecane, dodecane, undecane, and tetralin. Specifications for these chemicals are as follows:

- (1) benzothiophene: 97% pure, from Aldrich Chemicals
- (2) hexadecane, dodecane, and undecane: as received from Pfaltz and Bauer, Research grade, or 99% pure from Aldrich Chemicals
- (3) tetralin: 99% pure, from Aldrich Chemicals
- (4) ferric oxide: as received from Fisher Scientific Co.

Iron oxide was used in this work as a sulfur scavenger. Normally, the iron oxide was dried overnight in a vacuum oven at 100°C and 25 inches Hg, and stored in vacuum desiccator. Essentially the same experimental apparatus and procedure described in Chapter III were used here. The analytical procedure were also the same except a different temperature program was used during the chromatographic analysis. A Varian CDS-111 automatic integrator-computer rather than a simple linear integrator was used. For chromatographic analysis the solvent was used as an internal standard and a carbon material balance was performed for benzothiophene and its reaction products to assure accountability (Refer to Appendix B for an example of this material balance).

Results and Discussion

From the experimental results from Fan's work, the HDS of BT appears to proceed either in parallel or by one of two reaction paths: (1) the hydrogenation of BT to form 2,3 dihydrobenzothiophene (DHBT) followed by desulfurization to form ethyl benzene (EB) and/or (2) direct desulfurization via C-S bond cleavage to produce intermediate styrene (no styrene was detected in this study probably because of the high hydrogen partial pressure) with subsequential hydrogenation to yield EB. These reaction pathways are illustrated in Figure 9.

Rollman (41) reported that the rate determining step in HDS is the initial ring opening of the s-heteroring and not the reaction of any mercaptan or thiophenol type intermediate. Fan (36) observed some 1 phenylethanthiol (PHET) formation which he attributed to result from

Figure 9: Mechanism of Benzothiophene Hydrogenolysis;
 (A) General Scheme (B) Pyrite Reduction
 (C) Overall Reaction with Iron Oxide

the back reaction of H_2S product with the intermediate product styrene. Styrene as an intermediate product in BT hydrogenolysis has been detected before by Dally and Furimsky (42,43). However, here the iron oxide appears to react relatively fast with the H_2S and only a small (undetectable) H_2S partial pressure exists. It is believed that this is why no PHET formation was observed in this work.

As stated earlier, Fan observed a decrease in the activation energy above $386^{\circ}C$ for HDS of BT over pyrite. This shift was thought to be associated with a possible change in state of the reaction mixture. Based on this observation, Au (37) evaluated the response of BT hydrogenolysis in the presence of iron oxide to the use of different solvents like dodecane, hexadecane, benzene, n-hexane etc. Both Fan and Au observed the BT hydrogenolysis to follow first order kinetics with respect to BT concentration and with respect to hydrogen concentration. Table 6 compares the preliminary studies regarding effects of initial benzothiophene concentration and type of solvent on BT conversion. There seems to be a lot of variation between the data with dodecane as the solvent. Data with hexadecane as solvent agree within the limits of experimental errors.

If BT hydrogenolysis is indeed first order with respect to BT concentration, then BT conversion should be independent of the initial BT concentration, i.e., provided the kinetics of the reaction is controlling. As shown in Table 6, Au observed BT conversion to be independent of initial BT concentration with hexadecane as the solvent. However, with dodecane as the solvent, BT conversion varied with initial BT concentration. The reason for this observed variation was

Table 6.

Effect of Initial Benzothiophene
Concentration on its conversion

Initial BT concentration wt.%in solvent	Au (36)		% Benzothiophene Conversion Shridharani (45)		This work	
	with solvent DD	with solvent HD	with solvent DD	with solvent HD	with solvent DD	with solvent HD
4	92	72	-	-	-	-
5	-	-	73.9±0.5	70.1	70.1±0.8	70.0
10	90	72	79.0±7.3	68.3	69.2±2.0	73.6±0.1
15	-	-	74.9	-	69.2±2.8	65.5
20	85	72	68.0	70.4	-	-
30	75	72	61.0	57.8	-	-

Table 6. (contd.)

Reaction conditions : 5 minutes, 405 °C, 1250 psig H₂ at RT., 1000 RPM., 0.5 g. iron-oxide,
4.5 g. reactant mixture, two steel ball agitators, 15 ml. tubing bomb
reactor.

not clear from Au's work, for the activation energy for the BT hydrogenolysis with solvent dodecane, at the reaction conditions used for Table 6, was about 9.6 kcal/g-mole. Typically, if the activation energy is of the order or greater than 10 kcal/g-mole, the reaction system is considered to be kinetically controlled. It is not strongly evident here whether the reaction is mass transfer or kinetically controlled. With solvent hexadecane, the activation energy for BT hydrogenolysis was 18.9 kcal/g-mole.

Because of the difficulty in interpreting the above observation, it was decided to repeat the experiments to evaluate whether the observations were an artifact of the experimental procedure. It appeared from the results obtained that indeed the variation of BT conversion with its initial concentration was within experimental error (Table 7). The experimental results were triplicated and also checked by Shridharani (45) in a parallel experimental evaluation. The decrease in BT conversion for initial BT concentrations greater than 20 wt.% is due to stoichiometric limitations; i.e., stoichiometrically there is not enough iron oxide present to react with all the H_2S product.

The response of BT conversion to changes in its initial concentration was evaluated at a lower initial hydrogen pressure than that used in Table 6 (800 psi as opposed to 1250 psi). This was to slow the BT conversion rate and allow the use of longer reaction times; at which it was thought that better reproducibility could be attained. BT conversions were determined for reaction having different initial BT concentrations for reaction times of 3, 5, and 7 minutes. The

Table 7.

Effect of Initial Benzothiophene Concentration
on its Reaction Rate

Initial BT concentration, wt. %	5	10	15	average		5	10	15	average	
Reaction time, minutes	% Benzothiophene Conversion dodecane as internal std.				First order k,min. ⁻¹	% Benzothiophene Conversion undecane as internal std.				First order k,min. ⁻¹
3	43.9	44.8	33.4	40.7±6.3	0.174	43.6	44.4	32.8	40.3±6.5	0.172
5	60.0	52.3	50.7	54.3±5.0	0.157	58.8	52.1	50.2	53.7±4.5	0.154
7	62.4	61.7	55.5	59.9±3.8	0.131	62.2	61.4	55.0	59.5±4.0	0.129

Reaction conditions : 405 °C, 800 psig H₂ at RT., 1000 RPM., 0.5 g. iron-oxide, 4.5 g. reactant mixture, two steel ball agitators, 15 ml. tubing bomb reactor.

Refer Table 7 for Reaction Conditions

Figure 10: First Order Plot for Benzothiophene Hydrodesulfurization.

Refer Table 8 for Reaction Conditions

Figure 11: Effect of Temperature on HDS of Benzothiophene using Dodecane as Diluent Solvent.

Refer Table 8 for Reaction Conditions.

Figure 12: Effect of Temperature on HDS of Benzothiophene using Hexadecane as Diluent Solvent.

Table 8.

Effect of Temperature on BT Conversion

Temperature, °C	1/T x10 ³ , °K ⁻¹	Dodecane System		Hexadecane System	
		%BT conversion	First-order kx10 ² , min ⁻¹	%BT conversion	First-order kx10 ² , min ⁻¹
388	1.5125	51.8	19.25	63.0	19.89
395	1.4966	59.3	17.98	65.0	21.0
405	1.4746	69.2±2.0	23.55	73.6±0.1	26.64
410	1.4638	74.3±0.1	27.17	78.2	30.47

Reaction conditions : 5 minutes, 1250 psig H₂ at RT., 1000 RPN., 0.5 g. iron-oxide,
4.5 g. reactant mixture containing 10 wt. % benzothiophene in solvent,
two steel ball agitators, 15 ml. tubing bomb reactor.

Refer Table 8 for Reaction Conditions.

Figure 13: Arrhenius Plot for Benzothiophene Hydrodesulfurization.

results are shown in Table 7. Assuming BT initial concentration to have no effect on reaction rate, the standard deviation among the rate data were computed. The standard deviation with seven minutes of reaction is slightly less (3.8% as opposed to 6.3 and 5%). Normally, the solvent dodecane was used as an internal standard for G.C. analysis. To assess whether this was a source of error, the analyses were repeated using undecane as an internal standard; the deviation from the analyses as determined by the normal procedure was much less than the experimental error, i.e., essentially the same BT conversion was obtained.

It was decided to repeat an evaluation of the response of BT conversion to changes in reaction temperature made by Au (37). A comparison of the results is given in Figures 11 and 12. The difference in BT reactivity Au observed with solvent dodecane as opposed to solvent hexadecane could not be verified. Instead essentially the same BT conversion was obtained with either solvent.

BT hydrogenolysis was assumed to follow first-order kinetics with respect to BT concentration, as was observed to be true by Au (37). The activation energy for the reaction was computed to be 15.3 kcal/g-mole with solvent dodecane and 17.8 kcal-g-mole with solvent hexadecane. The difference here is assumed to be due to experimental error. The Arrhenius plot is shown in Figure 13. These activation energy values compare with what Au reported for the reaction with solvent hexadecane (18.9 kcal/g-mole) and solvent dodecane (9.6 kcal/g-mole). The reaction does appear to be kinetically controlled.

Table 9.

Effect of H₂ Partial Pressure on HDS of Benzothiophene

Initial BT concentration wt. %	5	10	15			
Initial H ₂ pressure, psig	% benzothiophene conversion			Average % conversion	First- order k, min ⁻¹	Average H ₂ pressure, psia
0	-	0.0	-	0.0	0.0	0.0
250	17.0	12.5	17.5	15.7	0.034	238
500	40.3±1.5	36.0	37.0	37.8	0.095	451
750	56.0	51.0	51.2	52.7	0.150	676
800	60.0	52.5	51.0	54.5	0.158	723
1000	68.2	66.5	69.0	67.9	0.227	901
1250	70.1±0.8	69.2±2.0	69.2±2.8	69.5	0.238	1148

Table 9. (contd.)

Reaction conditions : 5 minutes, 405 °C, 1000 RPM., 0.5 g. iron-oxide, 4.5 g. reactant mixture, two steel ball agitators, 15 ml. tubing bomb reactor.

Refer Table 9 for Reaction Conditions.

Figure 14: Effect of Hydrogen Partial Pressure on the Rate of Benzothiophene Hydrogenolysis.

Effect of Initial Hydrogen Partial Pressure

Au (37) observed BT hydrogenolysis to be first order with respect to hydrogen concentration. It was decided to verify this observation. The response of BT conversion to changes in initial hydrogen concentration was determined. To interpret the data, define K^* as

$$K^* = -\ln(1-x)/t \quad (7)$$

where t is reaction time and x is BT conversion. K^* is plotted versus initial hydrogen partial pressure in Figure 14. The plot gives a straight line. Au (37) also observed a straight line with his data. The reason is as follows:

$$R = \frac{dC_{BT}}{dt} = K C_{BT} C_{H_2} / (1 + \sum K_i C_i)^n \quad (8)$$

As discussed earlier, with solvent hexadecane $K_i C_i \ll 1$ and

$$\frac{dC_{BT}}{dt} = K C_{BT} C_{H_2} \quad (9)$$

Hydrogen is present in excess, and if C_{H_2} is assumed to remain constant at some mean value, then with integration equation 9 becomes

$$\ln(C_{BT}/C_{BT_0}) = K \hat{C}_{H_2} t \quad (10)$$

This can be rearranged to yield

$$K^* = K \hat{C}_{H_2} \quad (11)$$

Thus, K^* varies directly with $\hat{C}_{H_2}$ and the slope of the straight line in Figure 14 is the intrinsic kinetic rate parameter, K . From this development which is essentially the same as that used by Au, the

Note: Reaction Time with Molybdenum-Octoate Catalyst was 5 minutes.

Figure 15: Response of Benzothiophene Conversion Rate to Changes in Agitation Rate, Reference (62) and (36).

apparent kinetics for BT hydrogenolysis is evidently first-order with respect to hydrogen concentration.

Because the activation energy for BT hydrogenolysis is relatively high (~15 to 18 kcal/g-mole) compared to 10 kcal/g-mole, it appeared that the reaction is kinetically controlled. Fan and Au (36,37), however, both observed BT conversion to be sensitive to agitation rate. This usually indicates that gas-liquid mass transfer is important. On the other hand, this could be the result of better catalyst dispersion with increased agitation. Moniz (62), for example, observed BT conversion to be insensitive to agitation rate over the agitation range of 400 to 900 rpm's. Figure 15 gives a comparison of the response of BT conversion rate to changes in agitation rate with catalyst iron pyrite as opposed to that with catalyst molybdenum octoate. Molybdenum octoate is assumed here to react with reactant hydrogen and product hydrogen sulfide to form molybdenum sulfide, which is a good hydrogenation catalyst. The molybdenum sulfide product forms as a very fine powder and is assumed to be easily dispersed. The BT conversion is only about 50% in the flat region where it is insensitive to agitation rate with catalyst molybdenum octoate. The reaction time as indicated in Figure 15 for this reaction system was only 5 minutes; thus, it is assumed that this conversion is not an equilibrium amount, and BT conversion would increase with increasing reaction time in accordance with first order kinetics. It is believed that the difference in sensitivity of BT conversion rate to agitation observed in Figure 15 is due to differences in the ease of dispersion of the two catalyst: iron pyrite and molybdenum octoate (molybdenum sulfide). It is not

clear then exactly what phenomena is controlling the reaction. To provide further insight with regard to the rate controlling phenomena, the response of BT conversion to changes in iron oxide loading, w , was evaluated. The magnitude of this response typically indicates the significance of liquid-solid mass transfer.

First, the BT-hexadecane system will be considered. For this reaction system, the reaction mixture is estimated to remain mostly in the liquid phase at reaction conditions. (Refer to Chapter III for details concerning the computer routine used to estimate the vapor-liquid distribution at reaction conditions.) The rate of transfer of BT from the bulk liquid reaction mixture to the external iron oxide surface is given by:

$$-r_{BT} = K_{ls} A_{ls} (C_{BT,l} - C_{BT,s}) \quad (12)$$

The intrinsic rate for BT hydrogenolysis is taken, to be first-order with respect to BT concentration, and as shown above, first-order with respect to hydrogen concentration. That is,

$$-r_{BT,s} \equiv -\frac{dC_{BT,s}}{dt} = \eta K_r w C_{BT,s} C_{H_2,s} \quad (13)$$

where η is the effectiveness factor; K_r , the intrinsic rate parameter; w , the iron oxide loading per unit volume of reaction mixture (gms/cc).

Hydrogen is present in excess in the reactions made here; thus, $C_{H_2,s}$ is assumed to remain constant throughout reaction as $\bar{C}_{H_2,s}$. This term is incorporated into the rate constant K_r , and

$$-r_{BT,s} = \eta K_r' w C_{BT,s} \quad (14)$$

Rearranging equation 12,

$$C_{BT,s} = \frac{K_{ls} A_{ls} C_{BT,l} + r_{BT,l}}{K_{ls} A_{ls}} \quad (15)$$

substituting this expression for $C_{BT,s}$ into equation 14 and rearranging and assuming $r_{BT,s} = r_{BT}$, (quasi-steady state),

$$-r_{BT,l} = \frac{w C_{BT,l}}{\frac{1}{\eta K_r'} + \frac{w}{K_{ls} A_{ls}}} \quad (16)$$

For this slurry reaction system (iron oxide-BT-hexadecane), if the solid particles (iron oxide) are assumed to be spherical and completely dispersed with no particle-particle contact, then

$$A_{ls} = \frac{6w}{d_p \rho_p} \quad (17)$$

where ρ_p is the particle density (gm/cc) and d_p is the particle diameter (cm). Substitution of this relation into equation 16 yields

$$-r_{BT} = \frac{-dC_{BT}}{dt} = \frac{w C_{BT}}{\frac{1}{\eta K_r'} + \frac{d_p \rho_p}{6K_{ls}}} \quad (18)$$

Table 10. Effect of Iron-Oxide Loading on Benzothiophene Conversion using Hexadecane as Solvent

Iron-Oxide loading, $w \times 10^2$, g/cc	% benzothiophene conversion	First-order rate constant $k \times 10^4$, sec ⁻¹
0	6.8	2.35
1.67	54.0	25.83
3.33	70.5 $\pm$ 3.3	40.67
5.0	82.0	57.17
6.67	78.0	50.50
10.0	78.5	51.17

Reaction conditions : 5 minutes, 405 °C, 1250 psig H₂ at RT.,
1000 RPM., 4.5 g. reactant mixture
containing 5 wt.% benzothiophene in
hexadecane, two steel ball agitators,
15 ml. tubing bomb reactor

Refer Table 10 for Reaction Conditions.

Figure 16: Effect of Iron Oxide Loading on Benzothiophene Conversion using Hexadecane as Solvent.

Integrating and rearranging in terms of BT conversion $X = (C_{BT} - C_{BT0})/C_{BT0}$ where C_{BT0} is the initial BT concentration,

$$K = -\ln(1-X)/t = \frac{w}{\frac{1}{\eta K_r} + \frac{d_p \rho_p}{6K_{ls}}} \quad (19)$$

where K is the apparent rate constant.

A plot of K versus w should thus be a straight line with a slope of $\left(\frac{1}{\eta K_r} + \frac{d_p \rho_p}{6K_{ls}}\right)^{-1}$. Below $w \approx 4$ to 5 gm/cc, as shown in Figure

16, the plot is a straight line having a slope of 0.11 cc/gm-s as determined by regression analysis with a correlation coefficient of 0.99. It is assumed in the above development (equation 19) that there is a sufficient supply of reactant BT for mass transfer to each particle to be independent of the number of particles. As the scavenger (iron oxide) concentration increases to higher values, there is competition between particles for reactant, and the rate asymptotically approaches a constant limit (2). This is the reason for the decreased sensitivity of reaction rate to w for values of w greater than 4 to 5 gms/cc.

The liquid-solid mass transfer coefficient, K_{ls} , was estimated for the BT-hexadecane system using a correlation given by Brian and Hales (40). A correlation developed by Lemcoff and Jameson (64) was also used to estimate K_{ls} ; but, it was found to be higher than the other estimate, and the lower, more conservative estimate was used, i.e., $K_{ls} = 0.601$ cm/sec. The calculative procedure is outlined in Appendix A. The effectiveness factor was estimated using the same

Table 11. Effect of Iron-Oxide Loading on Benzothiophene Conversion using Dodecane as Solvent

Reactant system	Iron-Oxide loading, $w \times 10^2$, g/cc	% BT conversion	First-order rate constant, $K \times 10^4$, sec^{-1}
5 wt.% BT in dodecane	1.67	55.5	26.99
	3.33	69.5	39.58
	4.13	78.0	50.47
	5.0	75.0	46.21
	5.87	73.1	43.77
	6.67	56.5	27.75
	10.0	35.5	14.62
15 wt.% BT in dodecane	3.33	71.0	41.26
	4.13	74.0	44.9
	5.0	75.5	46.88
	5.87	72.9	43.52
	6.67	63.5	33.6
	10.0	42.5	18.45

Refer Table 10 for Reaction Conditions.

Figure 17: Effect of Iron Oxide Loading on Benzothophene Conversion using Dodecane as Solvent.

approach used in Chapter III to be about 1. The iron oxide particles had a -325 mesh size and assumed to have an average particle diameter of 30×10^{-4} cm. The density of iron oxide is about 3 gm/cc. Using these values and the measured slope of the straight line portion of the curve in Figure 16, the intrinsic rate parameter K_r' was computed to be about 0.11 cc/gm·s and $\frac{1}{\eta K_r'} \gg \gg \frac{d_p \rho_p}{6K_{ls}}$. The reaction thus appears to be kinetically controlled.

The response of BT conversion to changes in iron oxide loading, w , for the BT-dodecane reaction system was also studied. Two different initial BT concentrations (5 and 10 wt %) were used; both gave essentially the same response as to be expected with first-order kinetics. The results are shown in Figure 17. As for the BT-hexadecane system at low iron oxide loadings, the rate of BT conversion varies linearly with respect to w , with about the same slope. Again, it appears in this range that the reaction is kinetically controlled. This is based on an analysis similar to that performed above. This system exists, however, essentially in a vapor phase and there is a gas-solid mass transfer coefficient, K_{gs} , rather than K_{ls} . Essentially the same type of development used above was employed to show that

$$\frac{1}{\eta K_r'} \gg \gg \frac{d_p \rho_p}{6K_{gs}}$$

It is interesting that at high loading, w greater than about 4 to 5 gm/cc, K decreases with increased loading. As observed for the BT-hexadecane system, normally K would approach a limit with increasing

Table 12. Effect of Additive Preparation on Benzothiophene Conversion

Weight of iron-oxide, g. per 4.5 g. of reactant mixture	Method of preparation	% benzothiophene conversion	Difference in conversion
0.5	1	53.2	-
0.5	2	69.2±2.0	
0.5	3	74.1	4.9
0.5	4	77.2±2.1	-
1.0	2	56.5	
1.0	3	71.0	14.5
1.5	2	35.5	
1.5	3	56.5	21.0

Preparation methods :

- 1 : Iron-oxide used directly as received
- 2 : Dried overnight in a vacuum oven at 100 °C and 25 inches Hg. and then stored in a bottle placed in a vacuum desiccator. The same batch was used subsequently without redrying.
- 3 : Same as 2 but used immediately instead of storing in a desiccator.
- 4 : Dried under air in a furnace at 230 °C for four hours and then handled in a nitrogen atmosphere.

Note : reaction conditions for above experiments are same as described in Table 10

Figure 18: Difference in Benzothiophene Conversion with Iron Oxide Preparation Methods.

Table 13.

Conversion of Dibenzothiophene

Solvent	Initial H ₂ pressure	Final overall pressure	% desulfurization
Tetralin	0	235	62
1-methylnaphthalene	0	0	0
1-methylnaphthalene	250	295	15
Decalin	0	55	8
Decalin	250	275	49

Reference (67)

loading and remain at that limit. The decrease in activity observed here with increased loading is believed to be due to agglomeration of the iron oxide particles. If this indeed occurs, then the gas-solid interfacial area A_{gs} can no longer be approximated by $6w/d_p\rho_p$ (equation 17). That is, the individual particles can not be assumed to be separated from one another.

If agglomeration of the iron oxide particles does occur, then the surface condition of the iron oxide could be very important. The moisture content of the iron oxide powder, or the dryness of the particles, could be important. For such reasons it was felt that the procedure used to prepare the iron oxide powder may not be adequate, for it may accumulate moisture during handling and storage. A comparison was thus made of the two preparation methods described in Table 12. Three different catalyst loadings were used. The difference in BT conversion obtained with the different iron oxide preparation versus iron oxide loading is given in Figure 18. A standard statistical analysis (t test) was done (Appendix C). It was determined with 95% confidence that a significant difference in BT conversion with the different preparations existed. From Figure 18 it is obvious that the difference increases with increasing loading. A loading of 0.5 gms of iron oxide was used throughout this work except for studying the effect of loading on conversion. At this low loading, the difference in conversion with the different preparations is practically within the range of the experimental error (Table 6). However, at higher loadings, a significant difference in BT conversion with the different preparations tested here does exist.

Table 14. Effect of Changes in Hexadecane-Tetralin Compositions on Benzothiophene Conversion

Tetralin concentration $C_T \times 10^4$ g-moles/cc	Mole % tetralin in feed	Experimental % BT conversion	Predicted % BT conversion	% Error
0	0	75.2	80.0	6.0
4.1	25.8	78.0	74.8	- 4.1
12.3	63.6	69.5	65.7	- 5.5
16.3	78.0	63.0	61.9	- 1.8
20.4	90.1	55.6	58.4	4.8

Reaction conditions : 5 minutes, 410 °C, 900 RPM., 1250 psig H_2 at RT., 0.5 g. iron-oxide, 4.5 g. reactant mixture containing 10 wt.% benzothiophene in solvent(s), two steel ball agitators, 15 ml. tubing bomb reactor.

Figure 19: Comparison of the Experimental and Predicted Benzothiophene Conversions in the Presence of Tetralin.

Doyle (67) observed that the direct HDS of thiophene (using molecular hydrogen and an inert diluent) was noticeably slower than the donor desulfurization. Also, Doyle observed the HDS rate of dibenzothiophene to be faster when reacted with tetralin than when reacted with gaseous hydrogen with decalin as a diluent (Table 13). A reaction temperature of 350°C was used for the dibenzothiophene desulfurization, and at this temperature, a significant amount of tetralin decomposition occurs. Some gaseous hydrogen was thus formed during reaction of the dibenzothiophene with tetralin, and some direct hydrogen transfer could have occurred.

Doyle (67), as shown in Table 13, observed dibenzothiophene HDS to occur much slower with 1-methyl-naphthalene than with decalin as the diluent. This was ascribed to the aromatic being more strongly bound to the catalyst surface and inhibiting adsorption of the hydrogen molecules.

Au (37), in contrast to Doyle's observations, observed benzo-thiophene HDS to occur at a much slower rate when reacted with tetralin in the presence of iron oxide than when reacted with gaseous hydrogen. The highest BT conversion observed when BT was reacted with tetralin at 410°C was less than 20%. Whereas, with gaseous hydrogen, BT conversion was about 78% with 5 min. of reaction at 410°C. This apparent contrast in observation between Doyle and Au led to the following series of experiments.

BT was reacted with different amounts of tetralin with diluent hexadecane in the presence of gaseous hydrogen. The results are shown in Figure 19. Assuming Langmuir-Hinshelwood kinetics apply to

BT desulfurization,

$$\frac{dC_{BT}}{dt} = \frac{K K_{BT} K_H C_{BT}^m C_H^m}{1 + K_{BT} C_{BT} + K_H C_H + K_T C_T} \quad (20)$$

where C_{BT} , C_H , C_T are the concentrations of BT, hydrogen, and tetralin, respectively; K_{BT} , K_H , K_T are their respective adsorption coefficients; and K is the intrinsic reaction rate constant. Assuming C_H to remain constant and $K_{BT} C_{BT} + K_H C_H \ll 1 + K_T C_T$ as in an earlier development,

$$\frac{dC_{BT}}{dt} \approx - \frac{K_1^* C_{BT}}{1 + K_T C_T} \quad (21)$$

where $K_1^* = K K_{BT} K_H C_H^m$. Integrating,

$$\ln \frac{C_{BT}}{C_{BT0}} = \ln(1-X) = - \frac{K_1^* t}{1 + K_T C_T} \quad (22)$$

Rearranging,

$$\psi \equiv \frac{1}{-\ln(1-X)} = \frac{1}{K_1^* t} + \frac{K_T}{K_1^* t} C_T \quad (23)$$

K_1^* and K_B computed from the ordinate intercept and the slope of the ψ versus C_T data set were 0.3214 and 407.4 respectively. The correlation coefficient of the regression analysis was 0.913.

Summary of Results

From the above studies, the following remarks can be made:

(1) Under the experimental conditions studied here, hydrodesulfurization of benzothiophene appears to be kinetically controlled. That is mass transfer and pore diffusion resistances are insignificant.

(2) HDS of benzothiophene is confirmed to be first order with respect to both benzothiophene and hydrogen concentrations.

(3) Iron-oxide dispersion appears to pose problems. Preparation of this additive plays an important role. Proper drying of iron-oxide is essential for consistent results.

(4) Presence of tetralin appears to retard the benzothiophene hydrodesulfurization rate. It is believed that tetralin adsorbs competitively to benzothiophene on iron-oxide surface. This is probably the reason for reduced reaction rates.

IV. STUDIES OF DELAYED CATALYST CONTACTING IN SINGLE STAGE COAL LIQUEFACTION

Introduction

Catalyst activities for hydrogenation and cracking are very critical for optimum production of oils and gases as well as economics of the liquefaction processes. The exact mechanism of catalyst deactivation is not clearly understood. Some of the factors which cause the deactivation are (i) coking on the catalyst surface and pore structure, (ii) inhibition by compounds which get adsorbed selectively on the active sites and, (iii) pore mouth plugging.

The relative contribution of factors to catalyst deactivation depends on the operating conditions and catalyst type. For example, excessive coking can be avoided by operating at high pressures and low temperatures. Similarly, pore mouth plugging can be reduced by using a macro-micro pore distribution instead of a uniform pore distribution.

In coal liquefaction it is believed that the propensity of the coal-oil reaction slurry for catalyst deactivation decreases with reaction time. Coal contains many precursors of a number of compound-types known to be catalytic inhibitors and coke formers. With reaction some of these types of liquefaction products are converted into products having lower propensity to form coke or to inhibit catalytic activity. Thus, it would seem that there would be a higher rate of

Table 15.

Analysis of Elkhorn #3 Coal Obtained from
Floyd County, Kentucky

<u>Proximate Analysis</u>	<u>Weight %</u>
Moisture	1.81 $\pm$ 0.03
Volatile	37.56 $\pm$ 0.10
Fixed Carbon	46.03
Dry Ash	14.60 $\pm$ 0.02
<u>Ultimate Analysis</u>	
C	69.40
H	4.88
N	1.00
S	1.94
O (by difference)	8.18
<u>Distribution of Sulfur</u>	
Total Sulfur	1.94
Sulfate Sulfur	0.04
Pyrite Sulfur	1.19
Organic Sulfur	0.75

catalyst deactivation during the initial stages of liquefaction as opposed to the latter stages. The stage of liquefaction at which the catalyst is introduced could have a strong influence on deactivation rate.

An extreme case would be a comparison of the deactivation during catalytic reaction of a coal-derived oil as opposed to that during catalytic liquefaction of the coal. Generally, catalyst longevity would be expected to be higher for catalytic reaction of the coal oil. Much lower deactivation rates, e.g., have been reported for the catalyst used in the Exxon Donor Solvent (EDS) Process. In the EDS process, the catalyst is used to hydrotreat only the recycle solvent, a coal-derived oil; whereas, in the H-coal process the catalyst is added to the dissolver and is used to accelerate liquefaction of the coal directly.

It is reasonable then to assume that deactivation depends on the properties of the reaction mixture at the contact time. The objective of this phase of the work was to evaluate the importance that the stage of the liquefaction reaction when the catalyst is introduced (or injected) has on deactivation rate.

Materials Used

Coal: Elkhorn No. 3; -325 mesh; see Table 15 for analysis.

Tetralin: 99% pure, from Aldrich Chemicals.

Cresol: Technical grade; 54% meta, 29% para and 17% phenols from Eastman Kodak Co.

Pentane: 99% pure from Aldrich Chemicals.

Benzene: Nanograde from Fisher Scientific Co.

The 300 cc. autoclave was equipped with a Barber-Colman Model 72 C temperature controller, chromel-alumel thermocouples, an Omega Engineering Model 199 digital readout, and a Fisher 5000 recorder.

Figure 20: Schematic of Autoclave Assembly Used in Coal Liquefaction Experiments

Methylene chloride: Research grade from Fisher Scientific Co.

Naphthalene: Pure crystals from Fisher Scientific Co.

Cumene: 97% pure from Aldrich Chemicals.

Hexadecane: Research grade from Pfaltz and Bauer.

Catalyst: Co-Mo-Al (Harshaw 0402T) 1/8 inch pellets, presulfided by the technique described in Chapter III.

Experimental Procedure

For this study a device had to be developed to inject the catalyst into the reaction mixture at the desired time (stage) of reaction. The reactions were made in a SS316 magne-drive autoclave (Autoclave Engr. Inc., Figure 20). A stainless steel basket was attached to the agitator shaft of the autoclave. The basket was designed so as to hold the catalyst as long as the agitation rate was less than 400 rpm. By increasing the agitation rate above 400 rpm., the catalyst could be slung from the basket into the reaction mixture. Therefore, injection of the catalyst was accomplished simply by quickly increasing the agitation rate. Cold runs were made using a plexiglass autoclave to verify that it did indeed work.

The reaction mixture consisted of 30 grams of coal and 60 grams of tetralin. The coal was pretreated by drying it overnight under a 25 in. Hg vacuum, and it was stored in a vacuum desiccator until use. A presulfided Co-Mo catalyst was used in 3 gm. quantities.

Before each run the autoclave was purged with nitrogen gas and tested for leaks. It was then heated at a slow rate of approximately 2 to 3°C per minute to avoid excessive coking and charring. The reaction temperature was controlled within $\pm 5^{\circ}\text{C}$. Upon completion of the

Figure 21: Outline of Analyses Performed on the Products from Coal Liquefaction and the Spent Catalyst

Figure 22: Outline of The Procedure used to Determine Product Distribution

Table 16. Reaction Conditions for Model Compound Experiments
to Rate the Catalyst Activity

Model Reaction	Reaction Conditions
Naphthalene Hydrogenation	5 g. reactant mixture containing 10 wt.% naphthalene in hexadecane, 0.25 g. catalyst, 410 °C, 1250 psig H ₂ at room temperature, 700 RPM., 15 min. reaction time, 15 ml. tubing bomb reactor.
Cumene Hydrocracking	5 g. reactant mixture containing 10 wt.% cumene in hexadecane, 0.5 g. catalyst, 410 °C, 700 RPM., 1250 psig H ₂ at room temperature, 30 minutes, 15 ml. tubing bomb reactor

reaction, the heater was removed, and the autoclave was quenched with cold water. After cooling, product gases were collected in sampling bags, and the liquid product was collected, along with the catalyst pellets and unreacted coal, in beakers for analyses.

Analytical Procedure

Figure 21 and 22 outline the analyses made on the reaction products and the spent catalyst. The catalyst was separated from the liquid sample and repeatedly sonicated with tetrahydrofuran (THF) until the solvent remained almost clear. The spent catalyst was then dried and stored in a vacuum desiccator for further characterization by measuring model compound reactivities and weight loss with oxidation. The reaction products were split into two portions; one was used to determine overall conversion by ash analysis; the other was used to determine the product distribution. A detailed description of each analytical procedure is given below.

Model Compound Study

One way of rating the degree of deactivation of the catalyst is to compare its activity for certain model reactions with that of the fresh catalyst. Since hydrogenation and hydrocracking activities of the catalysts are of critical importance in coal liquefaction, model hydrogenation and hydrocracking reactions were used. Naphthalene hydrogenation was used as a model hydrogenation reaction. The reaction conditions are given in Table 16. The cumene-hydrogen reaction was also used to rate catalyst deactivation. This reaction involves hydrocracking and isomerization as well as hydrogenation. The major

reaction observed was hydrocracking of the cumene to form benzene and propane.

At the reaction temperature (410°C), no reaction was observed to occur in the absence of a catalyst. The reaction conditions used for the cumene-hydrogen reaction are also given in Table 16. The model compound reactions were carried out in a 15 ml. tubing bomb reactor. Experimental and analytical procedures used are identical to those described in Chapter III. Gas chromatography was used to determine the percent conversion of the model reactants.

Coke Burnoff

Coking is one of the major factors causing catalyst deactivation. The amount of coke deposited on the catalyst can be determined by measuring its weight-loss with oxidation under controlled conditions. This was done using the apparatus identical to the one used for catalyst presulfiding.

Empty porcelain boats used to hold the catalyst were predried at 500°C for about 15 minutes. Immediately after predrying, the boats were removed from the furnace and cooled for exactly 2 minutes and kept in a desiccator for 18 minutes. This predrying procedure eliminated variations in weight due to absorption of moisture from the atmosphere. About 0.3 gm of catalyst were added to the boats. The

Oxidation conditions: about 0.3 g of spent catalyst per boat,
24 hrs.; dry air at approximately 150 cc
per minute measured at room temperature.

Figure 23: Effect of Temperature on The Amount of Coke Burned
from The Spent Catalyst

boats were kept in the furnace for one hour at 200°C, one hour at 350°C and 24 hours at 500°C. Throughout heatup of the catalyst air was passed through the furnace at a flow rate of approximately 150 cc per minute as measured at room temperature. This stepwise gradual heatup of the catalyst was used to prevent its sintering. A total oxidation time of 24 hours was found to yield a steady weight-loss. Also, as shown in Figure 23, a maximum reduction in weight was achieved around 500°C. The loss in catalyst weight with oxidation was adjusted to account for that due to oxidation of the sulfided catalyst, and the remainder was assumed to be due to coke burnoff. The amount of weight-loss due to oxidation was determined by oxidizing fresh catalyst.

Coal Conversion

To determine coal conversion, the following method was used:

- (1) About 20 gm of product slurry was collected in a 200 ml beaker.
- (2) In a 500 ml beaker, about 400 ml of technical grade mixed cresol was heated on a hot plate to approximately 170-180°C.
- (3) About 150 ml of the hot cresol was added to the product slurry. The mixture was then heated for about 15 minutes with occasional stirring. This hot solution was then vacuum filtered through a Whatman No. 50 filter paper, which removed 98% of the 2-3 micron particles.
- (4) The filter-cake was washed twice with 100 ml of hot cresol followed by tetrahydrofuran (THF) until the filtrate was clear.

(5) The insoluble filter-cake was collected and dried overnight in a vacuum oven at 110°C and a 25 in. Hg vacuum.

(6) The dried solid was removed from the oven, pulverized, redried for about one hour and then cooled in a desiccator.

(7) About 0.15 gm of this cresol insoluble solids were weighed in a clean porcelain boat, and then it was placed inside a Lindberg tube furnace for ashing for about two hours. The boats were predried using the same procedure described in the previous section. The ashing was carried out in a dried oxygen atmosphere at a flow rate of about 50 ml per minute and 910°C to assure complete combustion.

(8) The boats were removed and weighed. For calculating the percent conversion of coal, an equation derived by making a material balance on ash was used (54).

$$Y = \frac{100(M-F)}{M(1-F)} \quad (24)$$

where Y = percent coal conversion

M = ash fraction in the cresol-insolubles

F = ash fraction in the original dry coal which was found to be 0.146 (Table 15)

In using the above equation, it is assumed that the solids in the product samples analysed have the same composition as those in the remaining product mixture. Excellent duplication of the results was accomplished using this indirect technique based on an ash balance for determining coal conversion.

Product Separation

This involves a conventional solvent extraction postulated by Sternberg (27) for characterizing the product distribution. Figure

22 outlines the separation procedure. About 12 to 15 gm of product slurry were collected in a 150 ml beaker. Since extraction of the oil fraction is difficult, three sonifications and three extractions with about 150 ml of pentane in each, were used. Other solvent extractions were done using only one sonification and three washings. The calculations made as part of this separations analysis are illustrated in Appendix D.

Gas Analysis

Gaseous products were analysed for H_2 , air, CH_4 , CO_2 , C_2H_4 , C_2H_6 , H_2S , C_3H_6 , C_3H_8 , $i-C_4H_{10}$, $n-C_4H_{10}$, and $n-C_5H_{12}$. Hydrogen analyses were done on a Varian Model 920 aerograph using a 15 feet column packed with 75% molecular sieve 13X and 25% molecular sieve 5A. The column was operated isothermally at $100^{\circ}C$ with nitrogen as a carrier gas (40 ml per minute). The other gases were analysed on a Varian Model 1800 aerograph using a 16 feet column packed with 8 feet of Porapak Q, 50-80 mesh and 8 feet of Porapak R, 80-100 mesh. The column temperature was programmed between 40 and $230^{\circ}C$ at approximately $12^{\circ}C$ per minute. Helium was used as a carrier gas (40 ml per minute). Both chromatographs were equipped with thermal conductivity detectors. Calculative procedure for gas analysis is illustrated in Appendix D.

Results and Discussion

As mentioned earlier, coal liquefaction reactions are extremely complex. It is believed that the rate of catalyst deactivation during liquefaction depends on the stage of liquefaction (1), length of

Table 17.

Effect of Reaction Time on Coal Conversion

Reaction time, hours *	% conversion based on cresol-insol- ubles	% Product distribution				Total amt. of gases produced, g-moles
		Oil	Asphaltenes	Preasphaltenes	IOM	
0.0	63.4	25.5	18.0	21.0	35.5	0.1
0.5	74.0	30.0	23.8	20.5	25.7	0.116
1.0	77.6	32.0	28.4	17.5	22.1	0.13
2.0	81.2	29.0	31.0	21.5	18.5	0.148
3.0	82.5	34.0	32.0	16.0	18.0	0.19

* All the experiments had about 3 hrs. heatup time. Reaction time means the time for which the contents were maintained near reaction temperature. Autoclave was quenched with cold water after the reaction time.

Reaction conditions: 425 °C, 425 R^{PM}, 30 g. dry coal, 60 g. tetralin, system purged with N₂

Refer Table 17 for reaction conditions.

Figure 24: Baseline Rate of Coal Conversion

Refer Table 17 for reaction conditions

Figure 2b: Product Distribution for Baseline Coal Conversion

catalyst exposure, and reaction conditions (e.g., temperature, hydrogen partial pressure, and agitation rate). It is impossible to isolate any one of these factors. Here, essentially three types of experiments were performed. A baseline study was done to evaluate, for the selected reaction conditions, the changes in product distribution and the overall conversion based on cresol-insolubles occurring with reaction time.

In the second set of experiments, the catalyst was exposed to different stages of reaction. This was accomplished by using the spinning basket described earlier. These experiments were divided into two types: exploratory and detailed experiments. During the exploratory studies the sensitivity of catalyst deactivation to exposure during the heat up, reaction, and cool down was evaluated. The state of the catalyst was evaluated by testing its activity for model compound hydrogenation and hydrocracking using naphthalene and cumene, respectively. The detailed experiments were more complete in terms of product analysis; i.e., product distribution and overall coal conversion based on cresol-insolubles were evaluated. The amount of coke deposition on the catalyst was measured by burning-off the coke under controlled conditions.

The third set of experiments involved an evaluation of the effect of reaction temperature on liquefaction yield, catalyst deactivation, and coke deposition. The results were intended to supplement those obtained from the former experiments. It was also intended to show whether using this procedure, deactivation would increase with reaction temperature.

Figure 26: Variations in The Reduction of Relative Catalyst Activity With Different Exposures

A baseline study was done by performing non-catalytic coal liquefaction experiments with different reaction times. The results of these experiments are given in Table 17. Figures 24 and 25 show the overall coal conversion based on cresol-insolubles and product distribution, respectively. Gases produced during the reaction were also analysed (Appendix D).

Figure 26 shows the variation in the reduction of relative catalyst activity, for naphthalene hydrogenation and cumene hydrocracking, resulting with different exposures during coal liquefaction. The reduction in relative activity, a_r , is defined as

$$a_r = \frac{a_0 - a}{a_0} \times 100 \quad (25)$$

where a is the amount of model compound conversion with the spent catalyst; a_0 , the fresh catalyst activity in terms of model compound conversions. At the reaction conditions specified in Table 16, a_0 was 70% for naphthalene hydrogenation and 44% for cumene hydrocracking.

As shown in Figure 26, a substantial amount of deactivation occurs during heat up and reaction. Nalitham (68) studied the deactivation of a commercial Ni-Mo-Al catalyst (sulfided) during hydrotreatment of solvent refined coal (SRC). Nalitham observed 60% deactivation during the first cycle with 83% deactivation after fourth cycle. Here, with a coal-tetralin slurry, 90% deactivation occurred during the initial exposure.

Nalitham (68) observed that the activity of the spent catalyst depended on the washing procedure. He washed the spent catalyst with

Figure 27: Variations in The Amount of Coke Deposition on The Catalyst with Different Exposures

Refer Tables 16 and 17 for reaction conditions

Figure 28: Catalyst Activity after Coal Runs

Refer Table 17 for reaction conditions

Figure 29: Effect of Reaction Time on The Amount of Coke Deposition on The Catalyst

tetrahydrofuran (THF). THF was also used here to wash the spent catalyst before determining its activity (refer to the analytical steps.)

Since the deactivation with reaction and cool down was so drastic (Figure 26), it was difficult to determine exactly how much deactivation occurred during heat up. During heat up, without catalyst present, 63.4% of the coal was converted to cresol-solubles (Table 17), and 25.5% was converted to oils. The effect of delaying exposure of the catalyst to the reaction mixture until this degree of reaction does not appear to have prevented drastic deactivation from occurring. This is further evidenced by the amount of coke deposition on the catalyst (Figure 27).

Catalytic coal liquefaction experiments were performed for different reaction times. In these experiments, the catalyst was in contact with the slurry from the commencement of heat up. The intention here was to determine an optimum reaction time so that the conversion would not be affected by a limiting reactant situation. That is, to be assured that the reaction was not limited by the amount of tetralin present. After two hours of reaction, all of the tetralin was consumed. As a result, a reaction time of one hour was selected. This reaction time (1 hr) was used in all the subsequent catalytic experiments.

Model compound activities and the amount of coke deposition were evaluated for the spent catalysts from all three catalytic experiments (Figure 28 and 29). It is interesting to note that almost the same degree of deactivation was observed to occur for all three runs. The relative naphthalene hydrogenation activity (a/a_0) of the spent

Figure 30: A Typical Temperature Profile for Autoclave Runs

Table 18.

Effect of Delayed Contacting of Catalyst
on Coal Conversion

Time of injection in heatup and reaction process, hours	% conversion based on cresol-insol- ubles	% product distribution			
		Oil	Asphaltenes	Preasphaltenes	IOM
0.0 (A)	83.2	51.6	22.5	10.4	15.5
2.0 (B)	84.5	57.0	20.5	2.5	20.0
3.0 (C)	84.0	28.0	23.5	23.5	25.0
3.5 (D)	84.0	29.2	24.0	20.5	26.3

Reaction conditions : 425 °C, 425 RPM., 30 g. dry coal, 60 g. tetralin, 3 g. catalyst
(presulfided Harshaw 0402 T Co-Mo-Al, 1/8 inch extrudes), 300 ml.
autoclave reactor, system purged with N₂ .

Refer Table 18 for reaction conditions.

Figure 31: Effect of Delayed Contacting of The Catalyst on Coal Conversion

Refer Tables 16 and 18 for reaction conditions

Figure 32: Effect of Delayed Contacting of The Catalyst on its Activity

catalyst was only 22% after heat up and that after two hours of subsequent reaction was 13%. In other words, the catalyst was very much deactivated after heat up. The relative cumene hydrocracking activity was only 5% after heat up. Both deactivation (Figure 28) and coke deposition (Figure 29) increased with increased reaction time.

Further experiments were performed to evaluate the sensitivity of catalyst deactivation to exposure during different stages of liquefaction. Figure 30 shows a typical temperature profile for heat up and reaction. The alphabetical letters in Figure 30 are used to indicate the time and temperature at which the catalyst was injected in the reacting slurry for the different experiments performed. The results of these experiments are given in Table 18. As shown in Figure 31, the highest oil yield observed resulted when the catalyst was injected at point B. However, the difference in oil yield when catalyst was present throughout the heat up-reaction-quench process (point A, Figure 30) and that when catalyst was injected at point B is only 5 percent which is almost within the experimental error.

The reduction in naphthalene hydrogenation activity varies almost linearly with exposure time (Figure 32). The hydrocracking activity was almost zero for all exposure times. The reaction mixture was quenched using an ice bath for all of the reactions. This quenching is believed to have deactivated the catalyst almost completely. When the reaction mixture was allowed to cool down slowly (Figure 26), the reduction in the relative cumene hydrocracking activity, a_r , was only 45% for the most severe case, i.e., when the catalyst was present throughout heat up, reaction, and cool down.

Figure 33: Coke Deposition as a Function of Injection Time

Table 19.

Effect of Reaction Temperature
on Coal Conversion

Reaction temperature, °C **	% conversion based on cresol-ins- olubles	% product distribution				Total gases produced, g-moles
		Oil	Asphaltenes	Preasphaltenes	IQM	
390	80.1	16.8	22.5	26.0	34.7	0.0778
425	84.0	28.2	23.5	23.5	24.8	0.1630
460	79.7	50.5	21.5	9.8	18.2	0.3303

** 3 hrs. heatup and 1 hr. at reaction temperature followed by quenching with ice & water

Reaction conditions : 425 RPM., 30 g. dry coal, 60 g. tetralin, 3 g. catalyst (presulfided Harshaw 0402 T Co-Mo-Al, 1/8 inch extrudes), 300 ml. autoclave reactor, system purged with N₂, catalyst injected after reaching reaction temp.

Refer Table 19 for reaction conditions

Figure 34: Effect of Reaction Temperature on Coal Conversion

Refer Tables 16 and 19 for reaction conditions

Figure 35: Effect of Reaction Temperature on Catalyst Activity

Figure 36: Coke Deposition as a Function of Reaction Temperature

When evaluating the reduction in the activity of a spent catalyst, the same amount of catalyst was used as that used in evaluating a_0 , its initial activity. The spent catalyst contains some coke, and because the same weight of catalyst was used, the actual amount of catalyst would be lower when evaluating the spent catalyst. In other words, more spent catalyst was not added to compensate for the difference in the weight due to coke. The maximum amount of coke deposition was 11% (Figure 33). An experiment was made in which this additional amount of the spent catalyst was added during the model compound reactions. The differences in model compound conversions were observed to be insignificant.

Figure 33 shows the variation in coke deposition for the different experiments. The increase in coke deposition when the catalyst was injected at point D over that when it was injected at point C was unexpected. The evaluation was duplicated. The exposure time when the catalyst was injected at point D as opposed to point C was 30 minutes shorter. However, the amount of coke deposition was about 3% higher.

To evaluate the effect of temperature on catalyst deactivation, experiments were performed at three different reaction temperatures. Here, the catalyst was injected upon attaining the reaction temperature. The results are shown in Table 19. As shown in Figure 36, the overall coal conversions based on cresol-insolubles were only marginally different; however, the amounts of oil and gases produced increased as reaction temperature was increased. Also as expected, the model compound reactivities (Figure 35) decreased as reaction temperature was increased and the amount of coke deposited increased (Fig 36).

Summary of Results

Drastic catalyst deactivation (reductions to 20% or less of the initial activity) was observed for most of the experiments made. No distinct advantages of delaying contact of the catalyst to some advanced stage of liquefaction were observed.

VI. RECOMMENDATIONS

(1) At agitation rates lower than those used in this work, mass transfer would be more significant. More work is needed to study the importance of solvent properties at such conditions, but with catalytic systems (e.g. homogeneous catalysts or heterogeneous catalysts with modified reactor system) for which catalyst dispersion is not a problem.

(2) Competitive adsorption of various compounds needs detailed investigation. Development of a reliable and efficient analytical method (e.g. ultra-violet spectroscopy) to quantify the adsorption is essential. This may lead to a better understanding of catalyst deactivation in coal liquefaction processes.

(3) A sophisticated and flexible system for contacting catalyst with the reacting slurry needs to be developed in order to study various catalytic effects and deactivation in coal liquefaction.

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APPENDIX A

ESTIMATION OF LIQUID-SOLID
MASS TRANSFER RESISTANCE

Since there is no direct experimental way to check for liquid-solid mass transfer resistance in a 3 phase system (40), theoretical estimation and comparison with experimental reaction rate is essential to identify the controlling regime. To estimate liquid-solid mass transport and pore diffusion resistances, knowledge of diffusivities of different components is required. Though very few diffusivity data, are available in literature, diffusion coefficients can be empirically estimated to reliable extent.

Estimation of Diffusivities

Diffusivities in liquids are estimated only for order of magnitude since no reliable correlations are available which take into account the effects of concentration and activity. Fairly reliable correlations are Scheibel correlation and Reddy-Doraiswamy correlation (57). The latter is given by

$$D_{AB} = \frac{K M_B^{1/2} T}{\mu_B (V_A V_B)^{1/3}} \quad (26)$$

where,

M_B = Molecular wt. of Solvent B

μ_B = Viscosity of solvent, cP

V_A, V_B = Molal volume at normal boiling temperature, $\text{cm}^3/\text{g-mol}$

$K = 10 \times 10^{-8}$ for $V_B/V_A \leq 1.5$

$= 8.5 \times 10^{-8}$ for $V_A/V_B \geq 1.5$

V can be best estimated by Tyn and Calus method (57),

Table 20. Calculated Diffusivities of Solutes in Solvents for
Certain Reaction Systems Encountered in this Work

Solute (A)	Solvent (B)	Diffusivity, D_{AB} , at 410 °C, cm ² /sec **
Hydrogen	Hexadecane	9.2×10^{-4}
Hydrogen	Tetralin	6.9×10^{-4}
Hydrogen	Dodecane	8.6×10^{-3}
Hydrogen	Benzene	7.1×10^{-3}
Hydrogen	Cyclohexane	1×10^{-3}
Naphthalene	Hexadecane	4.2×10^{-4}
Naphthalene	Benzene	3.8×10^{-3}
Naphthalene	Cyclohexane	1×10^{-3}
Benzothiophene	Hexadecane	4.3×10^{-4}
Benzothiophene	Dodecane	4×10^{-3}
Benzothiophene	Tetralin	3.8×10^{-4}

** Diffusivities in supercritical conditions are assumed to be
an order of magnitude higher than those in liquids.

$$V = 0.285 V_C^{1.048} \quad (27)$$

where V_C is critical volume. Estimation of liquid viscosity at high temperature is accomplished by Letsou and Steil method (57).

For $0.76 \leq T_r \leq 0.98$,

$$(\mu_L \xi)^{(0)} = 0.015174 - 0.02135 T_r + 0.0075 T_r^2 \quad (28)$$

and

$$(\mu_L \xi)^{(1)} = 0.042552 - 0.07674 T_r + 0.0340 T_r^2 \quad (29)$$

where μ_L is in centipoise, and

$$\xi = \frac{T_C^{1/6}}{M^{1/2} P_C^{2/3}} \quad (30)$$

where T_C is in °kelvins and P_C is in atmospheres. Also,

$$(\mu_L \xi) = (\mu_L \xi)^{(0)} + \omega (\mu_L \xi)^{(1)} \quad (31)$$

where ω is the accentric factor. Table 20 shows estimated diffusivities of some solute-solvent systems encountered in this work.

Estimation of Liquid-Solid Mass Transfer coefficients

Two correlations are illustrated. For a system of suspended solid particles and surrounding liquid, most reliable correlation is by Brian and Hales (40):

$$\left(\frac{k_{1s} d_p}{D_A} \right)^2 = 16 + 4.84 \left(\frac{g d_p^3 (\rho_a - \rho_l)}{18 \mu D_A} \right)^{2/3} \quad (32)$$

The rate of reaction, if it were controlled by liquid-solid mass transfer of component A, would be

$$\tilde{r}_A = \frac{6 k_{1s} W C_{A,g}^*}{d_p \rho_p} \quad (33)$$

For conservative estimates, $(\rho_a - \rho_l)$ can be taken as 3.0 g./cc. Also, for -325 mesh particles, average catalyst particle diameter would be about 30 microns. With $g = 981 \text{ cm/sec}^2$, diffusivity as estimated in the previous section, and viscosity as estimated by equation 31, for hydrogen (A)-benzothiophene (B)-hexadecane system we get,

$$\left(\frac{k_{1s} \times 30 \times 10^{-4}}{9.2 \times 10^{-4}} \right)^2 = 16 + 4.84 \left(\frac{981 \times 30^3 \times 10^{-12} \times 3}{18 \times .054543 \times 10^{-2} \times 9.2 \times 10^{-4}} \right)^{2/3}$$

Thus, $k_{1s} = 1.39 \text{ cm/sec}$, and

$$\tilde{r}_A = \frac{6 \times 1.39 \times 0.5 \times 1.129 \times 10^{-4}}{30 \times 10^{-4} \times 3} = 0.05231 \text{ g-moles/sec}$$

Disagreement with experimental rate of 0.00009 g-moles/sec indicates that liquid-solid mass transfer of hydrogen is not controlling. Same was observed for benzothiophene. For all the three phase systems encountered in this work, liquid-solid mass transfer

was estimated to be not controlling.

The more appropriate correlation for the vertically shaken tubing bomb system is given by Lemcoff and Jameson (64):

$$Sh = 2 + 0.434 Re^{0.85} H^{-0.045} Sc^{1/3} \quad (34)$$

$$Sh = k_1 d_p/D, Re = n A d_p/\nu, H = A/R, \text{ and } Sc = \nu/D$$

where,

n = cycles per second

A = amplitude, cm stroke length/2

ν = kinematic viscosity cm^2/sec

R = catalyst particle radius, cm

D = diffusivity, cm^2/sec

For hydrogen-naphthalene-hexadecane system,

$$Re = \frac{800 \times 1.9 \times 30 \times 10^{-4} \times 0.568}{60 \times 0.54543 \times 10^{-2}} = 79.15$$

$$H = \frac{1.9}{15 \times 10^{-4}} = 1266.67$$

$$Sc = \frac{0.054543 \times 10^{-2}}{0.568 \times 9.2 \times 10^{-4}} = 1.044$$

This gives $Sh = 15.12$ and hence $k_{1s} = 4.64$, cm/sec , which is higher than that predicted by previous correlation. This is expected because of vigorous mixing in the tubing bomb reactors compared to stirred tank reactors.

APPENDIX B

ILLUSTRATIVE MATERIAL BALANCE ON
BENZOTHIOPHENE REACTION SYSTEM

Table 21. A Typical GC Analysis output from CDS-111.

Blank Sample

PK #	TIME	AREA	AREA %
1P	6.73	3823	.04
2P	8.53	3096	.04
3P	8.87	830	.01
4P	10.55	8033190	91.22 ①
5T	10.98	24756	.28
6T	13.30	6700	.08
7P	14.04	733498	8.33 ②
TOTAL		8806891	100.00

Peak Identification

1 : Dodecane

2 : Benzothiophene

3 : Ethylbenzene

4 : Dihydrobenzo-
thiophene

Product Sample

PK #	TIME	AREA	AREA %
1P	.55	14631	.17
2P	.61	17402	.20
3P	.74	21680	.25
4P	1.02	23888	.27
5P	1.33	1665	.02
6P	1.60	21755	.25
7P	1.83	4120	.05
8P	2.17	4301	.05
9P	2.67	24665	.28
10P	3.07	2173	.02
11P	3.24	1319	.01
12P	3.48	548399	6.21 ③
13T	4.39	20861	.24
14T	4.96	827	.01
15T	6.73	6886	.08
16T	8.49	1980	.02
17P	10.53	7020342	88.87 ①-
18T	10.93	17916	.20
19T	11.39	696	.01
20T	13.28	7976	.09
21P	13.87	232900	2.84 ②-
22P	15.97	22856	.26 ④-
23P	17.20	1188	.01
TOTAL		8826424	100.01

Table 22.

An Illustrative Mass Balance on Benzothiophene
Reaction System

Compound	m	X	Y	Moles in	Moles out
benzothiophene	1.2170	0.091377	0.1112058	0.0033611	-
		0.029773	0.0362341	-	0.0010951
dihydro- benzothiophene	1.2170	0.0	0.0	0.0	-
		0.002932	0.0035685	-	0.0001063
ethylbenzene	0.8383	0.0	0.0	0.0	-
		0.070035	0.0587103	-	0.0022432
			Total	0.0033611	0.0034446
			% error	2.42	

In order to evaluate the material balance for the benzothiophene-dodecane reaction system, gas chromatographic responses were obtained for benzothiophene and the desulfurization product, ethylbenzene. The response curves were linear thus,

$$Y = m X + c \quad (35)$$

where,

Y = weight ratio of the specie and the standard,

X = GC peak area ratio of the specie and the std.,

m = slope of the Y versus X plot,

and c = ordinate intercept of the Y versus X plot.

Here, dodecane was used as an internal standard. From the analysis of standard solutions, values of m and c were evaluated to be :

$$m_{BT} = 1.2170, m_{EB} = 0.8383, c_{BT} = c_{EB} = 0.0$$

Tables 21 and 22 summarize the calculative procedure.

Basically, two assumptions were made here to simplify the calculations. (i) Dodecane was assumed to remain unchanged during the reaction, and (ii) dihydrobenzothiophene was assumed to have same chromatographic response factor as benzothiophene.

APPENDIX C

STATISTICAL ANALYSIS (t TEST) FOR COMPARING THE ADDITIVE
PREPARATION METHODS FOR BENZOTHIOPHENE REACTION SYSTEM

Table 23.

Effect of Additive Preparation Method
on Benzothiophene Conversion

Iron-Oxide loading, W, grams	% Benzothiophene conversion preparation method 2	preparation method 3	Difference d
0.5	69.2	74.1	4.9
1.0	56.5	71.0	14.5
1.5	35.5	56.5	21.0

Refer Table 12, Chapter IV, for details of the preparation methods

A statistical analysis (t test) was made for comparing the effect of two different preparation methods of iron-oxide on benzothiophene conversion. From the data of conversion versus iron-oxide loading, differences in conversion were calculated between the two preparation methods. Mean and standard deviation of the difference were evaluated. Probability of the mean difference was estimated using the t distribution tables.

Table 23 shows the data of benzothiophene conversion with two different preparation methods of iron-oxide, at three levels of iron-oxide loading. The mean difference, $\bar{d}$, and the standard deviation of the difference, s_d , were evaluated to be 13.5 and 8.1, respectively. Fixing a 95 % level of confidence,

$$P [\bar{d} - \mu_d \geq t_{0.95}^{(2)} s_d / \sqrt{n}] = 0.05 \quad (36)$$

where n is the sample size and t is the tail area (from the t distribution tables). Here, $n = 3$ and $t_{0.95}^{(2)} = 2.92$. Making a null hypothesis, i.e., $\mu_d = 0$, we get;

$$\bar{d} - 0 \approx \frac{2.92 \times 8.1}{\sqrt{3}} \approx 13.7$$

Hence, it can be said, with 95 % confidence, that a difference in benzothiophene conversion does exist with the two iron-oxide preparation methods considered here.

APPENDIX D

CALCULATIVE PROCEDURES FOR COAL LIQUEFACTION
PRODUCT ANALYSES

Table 24.

Calculation of Product Distribution

Product	Fractional weight	Adjusted weight	Recalculated percentages
oil	0.8291	0.1624	57.0
asphaltenes	0.0590	0.0590	20.7
preasphaltenes	0.0076	0.0076	2.7
residue(IOM)	0.1043	0.0558	19.6

Calculation of Product Distribution

Product distribution was evaluated from the results of solvent extraction analysis. After evaporating the solvents, weights of various fractions were calculated. Since the oil fraction contains volatile components,

$$\text{wt. of oils} = \text{original sample} - \text{IOM} - \text{preasphaltenes} - \text{asphaltenes} \quad (37)$$

Also, almost all the tetralin and naphthalene were observed to be extracted by pentane and thus encountered in the oil fraction. Thus, since approximately 2/3 of the initial charge was tetralin, 0.6667 was subtracted from fractional weight of the oil fraction. Also, since 14.6 % was the ash content of the coal, for 1/3 of the initial charge, 0.0485 was subtracted from IOM fractional weight to get moisture and ash free (maf) results. Typical calculations are as follows: let

$$\text{weight of sample} = 18.6121 \text{ g.}$$

$$\text{weight of IOM} = 1.9428 \text{ g.}$$

$$\text{wt. of preasphaltenes} = 0.1411 \text{ g.}$$

$$\text{wt. of asphaltenes} = 1.0975 \text{ g.}$$

This gives 15.4307 g. for the oil fraction according to equation 37.

The calculation steps that follow are given in Table 24.

Calculations for Gas Analysis

After an instrumental gas analysis, peak areas of the standards and product gases were fed to the computer to calculate composition

Table 25.

A Typical Computer Gas Analysis

DSAG-30
 METHANE PEAK AREA FOR STANDARDS
 H2 DETERMINATION 242.50
 CO DETERMINATION 1.00
 PROGRAMMED COLUMN 7400.00

COMPONENT	AREA	MOLE%	AIR FREE BASIS	NORMALIZED BASIS	NORMALIZED AIR FREE BA
H2	215.000	23.350	31.366	24.251	33.014
AIR	2400.00	25.557	---	26.543	---
CH4	1400.00	17.469	23.466	18.143	24.699
CC	0.0	0.0	0.0	0.0	0.0
CC2	2000.000	18.743	25.177	19.466	26.500
C2H4	80.000	0.698	0.938	0.725	0.987
C2H6	585.000	4.780	6.420	4.964	6.758
H2S	90.000	2.503	3.362	2.599	3.538
C3H6	150.000	0.724	0.972	0.752	1.024
C3H8	230.000	1.524	2.047	1.582	2.154
I-C4H10	30.000	0.172	0.231	0.179	0.243
N-C4H10	60.000	0.344	0.462	0.357	0.486
C5H12	60.000	0.423	0.568	0.439	0.597
	SUM	96.285	SUM	95.010	
	ERROR	-3.715	ERROR	-4.990	
				SUM	100.000

Figure 37: Total Gas Production as a Function of Reaction Time

Figure 38: Total H₂ and CO₂ Production as a Function of Reaction Time

Figure 39: Total CH₄ and H₂S Production as a Function of Reaction Time

Refer Table 19 for reaction conditions.

Figure 40: Total Gas Production as a Function of Reaction Temperature

of the gases produced. Since volume and pressure were known, absolute quantity of each gas can be calculated as follows:

volume of autoclave = 300 cc.

volume of agitator and shaft = 15 cc.

average volume of slurry or liquid products = 100 cc.

volume of tubing and pressure guage = 50 cc.

Hence, average volume of gases can be taken as 235 cc. Assuming that ideal-gas law applies, moles of N_2 present initially can be obtained. The same is true for calculating the total quantity of gases after the reaction. Once the total amount of gases produced is known, individual quantities of various gases can be calculated from the knowledge of mole %. To illustrate the calculations, consider the case of non-catalytic reaction for 30 minutes.

$$P_i = 15 \text{ psig} = 2.02 \text{ atm.}, T_i = 293 \text{ }^\circ\text{K}$$

$$P_f = 14.6 \text{ atm.}, T_f = 308 \text{ }^\circ\text{K}$$

Hence,

$$n_i = \frac{2.02 \times 235}{82.06 \times 293} = 0.0198 \text{ g-moles}$$

and

$$n_f = \frac{14.6 \times 235}{82.06 \times 308} = 0.1358 \text{ g-moles}$$

Hence, $n_t = n_f - n_i = 0.116 \text{ g-moles}$

Table 25 shows a typical computer analysis of gases. Figures 37, 38, 39, and 40 show various plots of gas amounts for certain sets of experiments performed.