HIGH-PRESSURE CATALYTIC MICROREACTOR FOR HYDROPROCESSING
OF COAL-DERIVED LIQUIDS

BY

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ABSTRACT

A high-pressure liquid-phase microreactor was developed to determine the kinetics and reaction networks of catalytic hydrodesulfurization and hydrodenitrogenation of polynuclear aromatic compounds found in coal-derived liquids. This reactor permits the use of small quantities of reactants and catalyst. Studies associated with this reactor have been planned for model compounds, many of which are not available commercially, and synthesis is required. Also many of the compounds will have boiling points that make the standard fixed-bed gas-phase microreactor impractical. This reactor design is expected to be useful generally and is not limited to hydroprocessing.

The microreactor was designed to operate entirely in the liquid phase. The hydrogen required for the hydrogenation reactions is dissolved into the liquid phase before entering the reactor. A high total pressure is kept on the system, and no gas phase is ever permitted. This avoids the modeling problems encountered with trickle bed reactors. Further, the system was designed to allow either the pulse or steady-state mode of operation. The specific design criteria were: hydrogen saturation pressure 0-61 atm, total pressure 0-272 atm, reactor temperatures up to 450°C and space velocities between 1 and 10 (1/hr).

The equipment has been operated at 21 atm hydrogen pressure and 104 atm total pressure over a range of temperatures and flow rates. A four day test was conducted at steady-state conditions. The results indicate a significant break-in period for fresh catalyst.

I INTRODUCTION

Research needs: catalytic hydrodesulfurization of coal

The current sources of oil and natural gas are rapidly being depleted, and the potentially unlimited sources of power from controlled fusion and solar radiation require processes still not developed. There is a clear need for sources to bridge the gap until the technologies of fusion and solar energy can be applied economically. Therefore, the main thrust in the development of new energy technology is focused on coal with related efforts on petroleum residua and oil shale.

Coal has been used for years in homes and electric power plants but oil has been preferred, since liquids are easier to handle than solids and since coal contains more pollutants than most oils. To produce better fuels from coal a number of industrial and governmental groups are developing processes for coal liquefaction. Examples of such processes are the Solvent Refined Coal Process, the Consol Synthetic Fuels Process and the ERDA Synthoil Process.¹ These processes also have the objective of removing sources of pollution such as sulfur-and nitrogen-containing compounds. The progress in technology of hydrodesulfurization of various fossil fuels is summarized in Table 1. This table shows, that coal hydroprocessing will require an increase in severity over residuum hydroprocessing, and the increase

TABLE 1

Processing Conditions in Catalytic Hydrodesulfurization¹

Processing Conditions \ Feedstock	Petroleum Distillate	Petroleum Residuum	Coal
Temperature, F°	575-750	650-800	750-850
Pressure range, psi	500-1000	800-2500	2,000-4,000
LHSV	2-10	0.2-1	undetermined
H ₂ recycle rate, SCF/bbl	300-1,500	2,000-10,000	25,000-100,000 (uncertain)
Catalyst Life, Yr.	10	1/2-1	undetermined

NOTES: Petroleum processing conditions have been inferred from many literature sources; coal processing conditions reflect the pilot scale studies of the Bureau of Mines in development of the Synthoil process.

may be similar to the difference between conditions for processing petroleum distillates and residua.¹

In the Synthoil process for liquefaction and hydroprocessing of coal, thiophenic compounds are formed, and a number of these have been identified (specifically, Table 2).² A large number of related compounds is to be expected when one considers the structure of coal as the generally accepted lamellae of condensed rings. Organic sulfur occurs randomly throughout the coal, particularly within the ring structures. Processing of coal with hydrogen donor solvents breaks down these large structures into the smaller, identifiable ones.

In processes undergoing development, hydrogenation and liquefaction are accomplished by contacting coal with a coal-derived solvent in the presence of hydrogen. Further hydroprocessing of the liquid produced is performed in the presence of a catalyst such as sulfided $\text{CoO}/\text{MoO}_3/\gamma\text{Al}_2\text{O}_3$. The entire process can be carried out in one or two steps, and only the second step clearly involves catalysis.^{3,4} Studies of these processes are usually carried out in pilot-plant reactors. Coal introduced into the plant undergoes liquefaction and hydroprocessing reactions, and the products are usually analyzed with regard to molecular weight, viscosity, sulfur content, etc. Operating parameters such as temperature, LHSV, and hydrogen partial pressure are typically varied in processing studies. Because of the limitations of such experiments, very little has been reported in the way of kinetics or mechanisms of the specific reactions that occur.

TABLE 2: Structural Formulas of the Organic Sulfur Compounds Found in Coal Derived Liquids²

<u>Molecular Formula</u>	<u>Name of Compound</u>
C_5H_6S	Methylthiophene
C_8H_6S	Benzothiophene
$C_8H_{10}S$	Tetrahydrobenzothiophene
C_9H_8S	Methylbenzothiophene
$C_{10}H_{10}S$	Dimethylbenzothiophene
$C_{11}H_{10}S$	Benzylthiophene
$C_{12}H_8S$	Dibenzothiophene
$C_{13}H_{10}S$	Methyldibenzothiophene
$C_{14}H_8S$	Benzo(def)dibenzothiophene
$C_{16}H_{10}S$	Naphthobenzothiophene
$C_{17}H_{12}S$	Methylnaphthobenzothiophene
$C_{20}H_{12}S$	Dinaphthothiophene
$C_{21}H_{14}S$	Methyldinaphthothiophene

This thesis describes equipment to be used in a project having the broad objective of determining the kinetics and mechanisms of catalytic reactions of hydrogen with sulfur- and nitrogen-containing compounds found in coal-derived liquids. This study has been planned for individual compounds such as dibenzothiophene, and related compounds, such as methyl-substituted dibenzothiophene. Since many of the pertinent compounds are not available commercially, synthesis is required, and therefore the research plans call for the use of only small amounts of the reactants. Therefore, small-scale equipment is required for the reaction studies, and the primary objective of the research described here was the construction of a high-pressure catalytic microreactor. This thesis is confined to the design, construction and preliminary testing of such a microreactor.

Laboratory scale catalytic reactors

The first research task was the choice of a reactor type. Anderson⁵ has given a concise description of different types of the commonly used small-scale experimental reactors used in studies of heterogeneous catalysis:

1. Fixed-bed reactors

These reactors contain a stationary catalyst in a tube, through which the reactants flow. This reactor may be operated in either the single-pass or recycle modes, and it may be operated with either steady-state or pulse flow of reactants.

2. Stirred (slurry) reactors

A vessel contains the reactants and catalyst, which are well mixed. Either batch or steady-state flow operation is commonly applied.

3. Spinning basket (Carberry) reactor

In this reactor, the catalyst is held in a basket attached to the stirrer, which is rotated rapidly through the reactants. This system is used to obtain rapid heat and mass transfer.

Fixed bed microreactors are most advantageously used when the reactants are confined entirely to a gas or a liquid phase. With compounds of high molecular weight, such as dibenzothiophene, operation with gas-phase reactants is impractical. Therefore, the fixed-bed microreactor would be a good choice for this research, only if liquid-phase reactants could be used. This restriction could be met if sufficient hydrogen could be dissolved in the reactant feed stream.

The stirred reactors, including the Carberry reactor, are often used for catalytic reactions when both gas and liquid phases are present. Mass transfer effects involving dissolution of the gas can pose problems, however, and the fluid flow patterns in such a reactor operated at high pressure are difficult to predict.

Therefore, the choice was made to use reactants entirely in the liquid phase and to use a fixed bed reactor. The following design requirements were then recognized:

1. A method of saturating the liquid reactant with hydrogen

at various pressures was needed.

2. The design required that the hydrogen stay in solution until it had passed through the reactor.
3. Operation over a range of temperatures, pressures, and space velocities was needed, specifically, 0-61 atm hydrogen partial pressure; 136-272 atm total pressure; temperatures up to 450°C and space velocities between 1 and 10 (1/hr).

The following thesis describes the details of the design and construction of a high-pressure, fixed-bed catalytic microreactor meeting these design criteria for the study of hydrodesulfurization and hydrodenitrogenation of compounds found in coal-derived liquids.

II EQUIPMENT DESIGN

Figure 1 shows a flow diagram of the high-pressure liquid-phase microreactor designed for this project. In general, the hydrogen for the hydrogenation reaction must first be dissolved into the carrier oil and any reactants used. The liquid is pumped through the reactor at the desired flow rate and reaction temperature. The reaction products are collected in the sample loop and analyzed later in a gas chromatograph.

The organization of the equipment can be divided into five major sections. These are the reactor, the pulse forming network, the sample collection network, the carrier oil saturator, and the flow control system. Each of these sections is discussed in detail in the following pages. A description of the safety precautions is also included. A list of the parts used in construction is included in the appendix.

Reactor

The limiting factor in designing the reactor was the availability of small amounts of synthetically produced compounds. For this reason, the catalyst bed was designed to be only 0.32 cm inner diameter and 3.8 cm long. If the void fraction is assumed to be 0.4, the internal volume is 0.12 cc. Ideally, the liquid would be

Figure 1: Schematic flow diagram of Liquid-phase Catalytic Microreactor

well dispersed across the catalyst bed and no channeling would occur. Also, the liquid should be at the reaction temperature the entire time it is in the catalyst bed. For these reasons, quartz chips were to be present for 2.85 cm above the catalyst to enhance the flow characteristics and to act as a preheater. Also, 0.95 cm of quartz chips were to be below the bed to prevent channeling in that end of the reactor. Rules of thumb indicate that the reactor bed should be 100 times longer and 10 times larger in diameter than the diameter of catalyst particles used.⁶ These dimensions should eliminate heat and mass transfer effects in the fluid phase. Commercial catalyst pellets and quartz chips were ground to a nominal diameter of $400\mu\text{m}$ to accommodate these criteria.

The reactor is a commercially available nipple with high pressure fittings on the ends. Sintered stainless steel filters have been placed on the ends to contain the catalyst.

The oven to heat the catalyst consists of a stainless steel cylinder with hexagonal plates on the ends which fit over the high pressure fittings of the reactor. A hole was drilled in the side of the oven to accommodate a thermocouple that is used to monitor the temperature at the outer wall of the reactor. Heat is supplied by a twelve foot length of beaded ceramic nichrome wire that was cut in half, and each half coiled around the oven. One half is attached to a variac. The variac is adjusted by trial and error to a setting that results in a temperature that is close to but below the one desired. The other half is attached to a proportional temperature controller

with a platinum resistance thermal detector. The detector is located between the heater and the oven so that temperature changes are detected quickly. The controller is used only for trimming the temperature. The entire system is insulated by several layers of asbestos tape held in place by standard hose clamps. This heating system controls oscillations to within $\pm 0.4^{\circ}\text{C}$ of the set point.

Pulse forming network

One of the main difficulties of pulse operation is determining how large to make the pulse. There is little difference between very large pulses and steady-state flow. Steady-state flow is certainly the easiest mode to design and operate. However, it uses considerable quantities of reactants that are in short supply. On the other hand, if very small pulses are used, the catalyst surface may not be representative of steady-state operating conditions, and the kinetics and mechanisms of reactions may be obscured.⁷ In this system, a factor of four reactor volumes for the size of the pulse was chosen as a compromise between an attempt to approximate steady-state flow and the need to use as little of the compounds as possible. The reactor dimensions from the previous section determine that the catalyst bed has a volume of about 0.12 cc. Thus, the pulse forming loop, S1, has a volume of 0.5 cc.

A 25 cc hydrogen saturator was designed for the pulse formation (Fig. 2,3). It is essentially a cylinder with inner dimensions 3.2 cm dia. x 3.2 cm high, and thick enough to withstand the 900 atm maximum hydrogen saturation pressure. There is an O-ring seal on the

Figure 2: Top of 25 cc Sparger

Figure 3: Base of 25 cc Sparger

top to prevent leaks. Mixing is to be provided by a magnet driven by a magnetic stirrer beneath the saturator. The design is such that this can be replaced by a motor driven paddle if necessary.

A small glass observation window was included in the network to allow the operator to tell when the pulse loop was full (Fig. 4). The window was a piece of 6-7 mm o.d. x $\frac{3}{4}$ - $1\frac{1}{4}$ mm i.d. glass tubing. There were O-ring seals on the ends to prevent leaks. A bracket was placed around the O-ring fittings so that they cannot be forced axially off of the tubing. Also, a cylindrical piece of plexiglass was fitted around the outside of the O-ring fittings and was held in place by set screws. The plexiglass prevented torque from being transmitted to the glass tubing, and it was designed to contain any glass that may shatter during use. A vent through V9 was provided to clear the window between runs.

The dead volume, DV1, was designed to contain hydrogen at a pressure at least as great as the saturation pressure. The pulse is to be forced into the loop by pressure from the hydrogen cylinder. Note carefully that this design assures that degassing of the pulse does not take place during filling of the loop. Also, since the liquid pulse is forced to the reactor by liquid flowing from the Ruska pump, the loop is always filled with liquid so gas pockets that could disrupt flow are not formed.

If the saturator were to be filled to 40 per cent, there should still be enough hydrogen volume above the reactants to permit

Figure 4: Observation Window for Pulse Loop

good mixing. Even if an amount of sample equal to the pulse is wasted on each run, this would still yield ten runs before refilling the saturator. Only 20 mg of reactant would be needed for these 10 runs.

Sampling loop

The sampling loop is of essentially the same design as the pulse loop. Obviously, no sparger or glass window is necessary. There are removable syringe attachments to the tubing leading from valves V13 and V15. Thus, air pressure can be applied at V15 to force a sample out through V13. Then liquid can be pushed back up V13 to refill the sample loop. The purpose of this is to prevent gas bubbles from forming in the sample loop.

There are two interchangeable sample loops for this system. The larger one, about 1.5 cc, is for the pulse mode and the smaller one, about 0.3 cc, is for continuous flow. The larger loop has more volume than the pulse to ensure that all of the pulse will be captured. Thus, although the positioning of the pulse can be estimated by careful timing, the excess volume of the loop will allow for errors. This method is used because a high pressure detector which can indicate the exact position of the pulse has not been developed. A non-reactive compound of known concentration is dissolved with the reactant as an internal standard. This will permit calculation of the amount of pulse collected. Hence, kinetic information will be available even if some of the sample is missed. The advantage of having a second, smaller loop for steady-state flow is that it will take less time for reacted liquid to replace the unreacted liquid in the loop.

There is no concern about catching a particular part of a continuous flow operation.

Carrier oil saturator

The purpose of the carrier oil saturator is to mix hydrogen with the carrier oil. The hydrogen gas flows through a Deoxo catalyst and then a molecular sieve to remove all the oxygen and water from the gas. This then flows into a 300 cc sparger which is filled with about 250 cc of carrier oil and mixed thoroughly. The only modification made here was that the 0-340 atm pressure gauge supplied with the autoclave was replaced with a less expensive 0-68 atm gauge. The larger gauge was put on the Ruska pump that will be operated at the higher pressure. Again, note that the liquid will be prevented from degassing. This was done by maintaining at least saturation pressure in the Ruska pump. The pump is driven manually in reverse. Excess pressure is supplied from the hydrogen cylinder to force liquid into the pump.

Flow control system

The flow control equipment is the most expensive part of the system. This expense occurs both because of the very low flow rates and the precision of the flow required for wide ranges of operating pressure.

Since the reactor volume is 0.12 cc, a flow rate of 0.12 cc per hour gives a residence time of one hour, and a flow rate of 1.2 cc per hour gives a residence time of six minutes. These very low

flow rates are difficult to maintain consistently -- 0.12 cc is only about three drops. A specially designed positive displacement pump was obtained to yield these flow rates. The pump provides a range in residence times of 1.2 to 0.1 hours.

This pump can maintain the desired flow rate against any pressure up to 545. atm. However, ordinary back-pressure regulators and metering valves are not expected to control the pressure very well at these low flow rates. The pressure drop through even very small constrictions will be minimal. In fact, the metering valve, MV, has been of no use except as a convenient on-off valve. To obtain the pressures required, a second pump has been included at the end of the system with its own 0-340 atm gauge. This diaphragm pump provides the back pressure needed to carry out high pressure studies. The pump is coupled with a 500 cc dead volume, DV3, to be pressurized with hydrogen by the pump. This dead volume will minimize the change in pressure that would result if the system were running and entirely liquid filled. The small amount of liquid collected in the dead volume can be vented periodically through valve V17.

To be able to collect as much data as possible in a short time, the time required to obtain one datum point should be kept to a minimum. For this reason, dead volume in the system should be as small as possible. 0.159 cm ($\frac{1}{16}$ in.) o.d. x 0.015 cm (0.006 in.) i.d. tubing was used in all the transfer lines. Unfortunately, these lines plugged too readily and had to be replaced by 0.159 cm ($\frac{1}{16}$ in.) o.d. x 0.076 cm (0.030 in.) i.d. lines.

Safety

The weakest tubing is chosen to withstand at least 402 atm. The valves and fittings are guaranteed to be able to withstand the pressure of the tubing. The reactor, which is the only part of the system to be at high temperature, was rated for 4080 atm at 70°F. This unit should be safe up to 3075 atm at 450°C. The only glass in the system is the observation window in the pulse loop. It is designed to hold 68 atm and will only be used up to 61 atm. This glass will be replaced each 100 operating hours. In addition, the sight glass is shielded. The entire system, except the Ruska pump and gas cylinders, is enclosed behind a 1.07 m (3.5 ft.) high x 1.37 m (4.5 ft.) long x 0.61 m (2. ft.) deep x 0.318 cm ($\frac{1}{8}$ in.) thick steel barricade on wheels. The valves are mounted so that only the valve stems protrude from the barricade. This arrangement permits complete external control. Also, all the pressure gauges can be read from outside the barricade. There is a rupture disc, RD, in the flow system between the pump and the reactor designed to vent at 340 atm. Plastic hoses that can be attached to the vent lines have been placed on the system. These carry the hydrogen gas to exhaust fans in the roof of the building. Finally, the system was hydrostatically tested, with first liquid and then gas, above the operating pressure before experimental operation was attempted.

III OPERATING PROCEDURE

Preparation for a run

After the system had been pressure tested, the lines were flushed with acetone and then normal-hexadecane to remove any compounds that may have remained. Hexadecane was used because it was to be the solvent for the first set of experiments. Then, the lines were flushed with hydrogen to remove any oxygen that would be present from exposure to the atmosphere. During this time, the plunger of the Ruska pump was fully inserted into the cylinder. This minimized the amount of undesired material that could have been trapped within it.

Hydrogen saturation

The initial reactant charge was introduced in the following way. First, all the valves in the system were closed. The autoclave was filled with the reactants to a level about two inches from the top. This required about 250 cc of liquid. The autoclave was sealed, and the water that acts as packing coolant was turned on. The hydrogen cylinder was opened with the regulator off, and valves V1 and V18 were opened. The hydrogen pressure was increased until flow could be heard from the outlet of the hose that went from the vent to the fan in the roof of the building. Hydrogen was allowed to flow for about 15 minutes. Then, valve V18 was closed and the hydrogen pressure was

adjusted to the desired saturation level. Valve V1 was closed, and the autoclave stirrer was turned on and allowed to run for about five minutes. Then, the hydrogen was allowed to vent through V18. This mixing procedure was repeated several times. Finally, the autoclave was brought up to pressure and allowed to run for half an hour without venting. The purposes of these procedures were to saturate the carrier with hydrogen and to remove any other gases that may have dissolved in the oil while it was exposed to the atmosphere.

Charging the reactants

During this time, the diaphragm pump was turned on, and the dead volume, DV3, was filled with hydrogen to a pressure slightly above saturation pressure. Then valves V16, MV, V10, V11, V12, and V7 were opened. The pressure was maintained above saturation pressure. Then, all the valves just opened were closed again, the lines having been pressurized with hydrogen. The autoclave was turned off and pressurized above the pressure in DV3. Valve V19 was opened, and liquid was allowed to flow into the Ruska pump. To eliminate any gas in the pump, the joint at the top of the cylinder that leads to the pressure gauge was loosened until liquid, rather than gas, was flowing out of it. The joint was immediately retightened. The pump was driven manually in reverse until the gauge indicated that it had been filled with 100 cc of liquid. A careful watch was kept on the pressure gauge to make sure that filling did not occur so rapidly as to drop below saturation pressure. Valve V19 was closed in preparation for filling the lines.

The lines were filled by manually raising the pressure in the Ruska pump well above saturation pressure. Then valve V7 was opened and liquid was allowed to fill the lines. This procedure was repeated for valves V10, MV, and V16. Then, valve V10 was closed and the space between V11 and V12 was filled similarly. Now, except for bringing the system up to operating pressure, and filling the volume between V13 and V14, as described in the sample collection procedure, the system is ready for operation.

Subsequent rechargings of the pump have not been necessary yet, but the procedure is as follows. The piston is to be fully inserted into the cylinder manually to remove all of the previous reactants. The new reactants are to be saturated with hydrogen as before. V7 is closed and V19 opened to fill the Ruska pump to a volume of about 25 cc. V19 is closed and V7 opened and all of this liquid is to be forced through the system to flush out unwanted compounds. Then, V7 is closed and V19 opened and the Ruska pump filled to a volume of 100 cc. V19 is closed and V7 opened, and the system should be ready for operation.

Sample collection procedure

Samples were collected in the following way. Valves V11 and V12 were closed and valve V10 was opened. A sample collection bottle was placed under the vent at V13. Then, V13, V14 and V15 were opened. An empty 10cc syringe was connected to the vent at V15, and air was used to force the sample out of S2.

A second syringe was filled to 5 cc with pure carrier solvent; perhaps less could be used. This was attached at V13, and the solvent was forced to fill the sample loop past V14. Then, V13 was closed; the syringe removed, and V14 and V15 were closed. There are now no gas spaces in the sample loop. V10 was closed and V12 and V11 were reopened. The system is now ready for continued operation.

Operation of the reactor

The system was brought up to the desired operating pressure by turning on the diaphragm pump. After this the liquid flow rate was selected, and the Ruska pump was turned on. The reaction temperature was chosen, and the controller was set accordingly. After the temperature had become constant, the system was allowed to run until ten reactor volumes had been displaced and a sample was collected. Ten reactor volumes were used to assure that the sample loop was filled with products that went through the reactor at steady-state.

Injecting a pulse

Pulse operation of this system has not yet been attempted, but the intended procedure is as follows. Hydrogen saturation is to be carried out as before, except that the 25 cc sparger, rather than the 300 cc sparger, is used. The mixing device is a magnetic stirrer rather than a motor driven paddle. Also, venting is to occur through V9 rather than V18.

To fill the pulse loop, V5 and V6 are closed and, if operat-

ing, V7 opened. Then V3 is closed, and the pressure in the sparger is to be brought above saturation pressure. Do not exceed 68 atm, or the observation window may shatter. Valves V4 and V8 are to be opened, and the appearance of fluid in W is to be looked for. If fluid has not appeared in a reasonable time, it probably means that the pressure in DV1 has become equal to the driving pressure. V4 and V8 are to be closed and V3 opened. The hydrogen is to be vented through V9 until the pressure gauge, P3, reads saturation pressure. The procedures in this paragraph are to be repeated until the pulse loop, S1, is full. Then V4 and V8 are to be closed, and the excess hydrogen and liquid are to be vented through V9.

For operation in the pulse mode, valve V7 is to be closed and valves V5 and V6 are to be opened. This injects the pulse into the flow stream. Careful timing must be used to catch the pulse in the sample loop, S2. This is essentially a trial and error procedure that will become routine with experience.

IV RESULTS

Upon completion of the microreactor construction, the equipment was tested to demonstrate system operability in the steady-state mode. For this demonstration the hydrodesulfurization reaction of dibenzothiophene was selected. The reaction products that were anticipated were biphenyl and hydrogen sulfide. Other possible products include: tetralin, indane and a series of cyclohexylbenzenes.^{8,9}

Normal hexadecane was chosen as the carrier solvent. Dibenzothiophene was the reactant, and dodecane was the internal standard (a list of the grades and suppliers of the materials can be found in the appendix). The appropriate GC column and temperature programming conditions necessary to separate normal-hexadecane, normal-dodecane, dibenzothiophene, and biphenyl were found by trial and error for this test (Table 3). The table lists the most up to date set of GC conditions, and not necessarily those used on any particular set of experiments.

The reactant mixture was made by taking a bottle containing about 200 g of normal-hexadecane and adding one half gram each of dibenzothiophene and normal-dodecane. The concentrations were verified by use of the gas chromatograph.

Table 3: Gas Chromatograph Conditions for Separation of normal-dodecane, biphenyl, normal-hexadecane, and dibenzothiophene

Gas Chromatograph: Perkin Elmer 3920B

Detector: Flame Ionization

Column 6 ft. 1/8" ss

Packing: SP 2100 D B

Flowrate setting: 30

Pressure: He 00 psig

H₂ 20 psig

Air 50 psig

Temperature Program: Isothermal 150°C

Sample Size 0.3 microliter

A $\text{CoO}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ was put into the reactor, and the catalyst surface was sulfided by passing a gas stream containing 10% H_2S in H_2 across the catalyst at 40 cc/min at 400°C for approximately an hour.¹⁰ Then, while the reactor was cooling, hydrogen was passed across the catalyst.

The reactants were loaded into the system as described in chapter III. For run #2 hydrogen pressure was 21 atm. The total system pressure was 104 atm. The flow rate was set at 1.2 cc/hr. The temperature, as measured by the thermocouple, was $428 \pm 7^\circ\text{C}$. This temperature oscillation occurred on only the first few runs and was due to inadequate design of the temperature control system. This apparatus has been modified and the temperature can now be held to within 0.4°C of the set point.

About 80% of the dibenzothiophene reacted. Comparing the elution time of the reaction products with the elution time of biphenyl in the calibration studies shows that biphenyl was indeed a major reaction product. Table 4 and Figure 5 are presented for run #A-6-3, conducted at 353°C .

Additional preliminary results show that the break-in of the catalyst is significant over several days of operation (Figure 6). These experiments in Figure 6 were done with a flow rate of 1.2 cc/hr, 19 atm hydrogen pressure and 350°C . The total pressure increased from 93 to 117 atm due to liquid filling the dead volume. The graph shows that catalyst activity decreased by more than 50%

Table 4: Chromatographic Retention Times of Reactants and Products

sample \ compound	1	2	4
calibration	1.36	2.72	12.79
unreacted feed	1.37	NA	12.79
test run #A-6-3	1.38	2.75	12.88

times in minutes

1 normal - dodecane

2 biphenyl

4 dibenzothiophene

Figure 5: Gas Chromatographic Analysis of Reactants and Products;
1-C₁₂, 2-BPh, 3-C₁₆, 4-DBT.

Figure 6: $\text{CoO}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst break-in period for 4-day run at 350°C and 1.2 cc/hr.

over four days of operation.

On a mole percent conversion basis, the amount of dibenzothiophene reacted is larger than the biphenyl observed. This indicates either that other reaction products are formed or that some of the biphenyl formed reacted further. Analysis of the samples showed that a number of undetermined compounds in addition to biphenyl were present; these were probably cracking products of the carrier oil. However, identification of these has not been completed. Use of the sulfur-specific detector indicated that there were no sulfur-containing compounds other than dibenzothiophene present.

A series of experiments was conducted to determine the response of the reactor to changes in flow rate. Figure 7 shows the results of this test. The plot of conversion versus reciprocal flow rate for a differential reactor should yield a straight line. However, the temperature at which this study was made, 353°C , resulted in conversion levels that were above the level where a straight line would be expected to exist. Experiments with higher flow rates and smaller catalyst loadings are now underway to verify differential reactor operation. These data indicate that it should be easily achievable.

Figure 7: Disappearance of Dibenzothiophene vs. Reciprocal Flow Rate at 353°C.

V RECOMMENDATIONS

Equipment improvements

1. A rapid traverse gear should be included as part of the positive displacement pump in addition to the transmission gears required to control the flow rate within the desired operating range. The rapid traverse gear would eliminate the need for manual operation of the pump, which is difficult at high pressures. The gear would be advantageous during pressure testing of the equipment and during the initial filling of the system or while flushing the transfer lines with new solvents or reactants.

2. A valve and vent just upstream of the 25 cc sparger would be useful to assure the removal of oxygen and nitrogen from the system during hydrogen saturation of the reactants to be used during pulse operation.

3. A second temperature controller with a limit point shut-off and an independent sensor should be hooked in series with the present controller. This would prevent temperature run-away in the event the proportional controller malfunctioned.

4. Replace all valves used in the system which are not easy to operate. A tight valve, or one that is difficult to reach, is of

little value in an emergency situation.

5. The volume of tubing leading from the sample loop to the vents should be made as small as possible to avoid dilution of the sample with carrier fluid present in the vent lines.

Experimental

1. Experiments should be conducted to determine how large the pulse loop should be. The length of the current loop is merely a guess, and may cause either waste of reactants or provide false information due to chromatographic separation along the catalyst bed.

2. Rather precise tests will have to be run to determine the volume of liquid required to force the reactants from the pulse loop to the sample loop.

3. Hydrogen solubility data are required. The kinetics of HDS reactions may depend on the concentration of hydrogen in solution in the carrier oil.

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APPENDIX

Parts List

1. Fittings

A. Swagelok

3 1/16 NPT x 1/16 Sw	male connector
1 1/16 NPT x 1/8 Sw	male connector
4 1/8 NPT x 1/8 Sw	male connector
2 1/4 NPT x 1/4 stud	male adapter
4 1/8 NPT x 1/8 Sw	female connector
1 1/8 NPT x 1/4 Sw	female connector
1 1/4 NPT x 1/4 Sw	female connector
2 1/8 Sw x 1/8 Sw	union
2 1/16 Sw x 1/8 Sw	reducing union
6 1/8 Sw x 1/4 Sw	reducing union
4 1/4 Sw x 1/2 Sw	reducing union
3 1/16 Sw	union tee
7 1/8" Sw	union tee
4 1/16 Sw x 1/8 stud	reducer

B. High Pressure Equipment Company

3 1/8 tube x 1/4	high pressure adapter
2 1/16 tube x 3/8	high pressure adapter

C. Cajon

2 1/8"	male tee
1 1/16"	female tee
1 1/4" O-ring x 1/8 NPT	female connector
1 1/4" O-ring x 1/8 Sw	reducing union
2 1/8" plugs	

2. Pressure Gauge

A. Matheson

1 gas regulator 0-4000 psi cylinder, 0-2000 psi delivery
2 0-1000 psi pressure gauges

B. High Pressure Equipment Company

1 0-5000 psi pressure gauge

3. ValvesA. High Pressure Equipment Company

10 1/8" two way straight valves

5 1/16" two way straight valves

1 1/8" metering valve

B. Whitney

2 1/8" severe service union bonnet valves

4. Reactor

1 1/8" ID x 3/8 OD x 3" long H.P. ends nipple

1 oven - cylinder with hexagonal plates to cover high pressure fittings and hole to admit sensor (Chemical Engineering Shop)

5. Tubing

1/8" OD x .069 ID, 1/4" OD x .180 ID, 1/16" OD x .006 ID stainless steel

6-7 mm OD x 3/4 - 1 1/4 ID type one glass tubing

6. Temperature ControlA. Electron Marketing Associates (RFL Distribution)

1 Model 71/115 proportional temperature controller

1 Direct reading dial assembly 0-500°C

1 RTD platinum sensor

B. Scientific Glass Company

1 12 ft. length beaded ceramic heating wire

7. Spargers

1 25 cc (Chemical Engineering Shop) with 1 Magne-Matic magnetic stirrer (Scientific Glass Company)

1 300 cc - SPV-1 autoclave without heater (High Pressure Equipment Company)

8. Pumps

1 Ruska Model 2252 positive displacement pump 0.1-1.2cc/hr
 1 Aminco Model 46-4025 diaphragm pump

9. Cart (barricade)

1/8" plate steel, 1" x 1/4 angle iron, 4" wheels for construction
 of 4 1/2' wide x 3 1/2' high x 2' deep barricade

10. Miscellaneous

2 inline removable filters (Nupro) with 2 u size filters
 1 rupture disc assembly with 5000 psi discs (high Pressure Equipment Company)

11. Chemicals

A. Aldrich

Normal-Dodecane 99% pure
 Dibenzothiophene 95% pure

B. Columbia Organic Chemical Co.

Normal-Hexadecane ASTM grade

C. Cyanamid

CoO/MoO₃/γ-Al₂O₃ catalyst
 Aero-R HDS-16A
 MTG-S-0731

D. Eastman Organic Chemicals

Biphenyl purity uncertain

HIGH-PRESSURE CATALYTIC MICROREACTOR FOR HYDROPROCESSING
OF COAL-DERIVED LIQUIDS

BY

Kenneth Frank Eliezer

An abstract of a thesis submitted to the Faculty of the
University of Delaware in partial fulfillment of the requirements
for the degree of Master of Chemical Engineering

June, 1976

Approved: _____

Dr. B.C. Gates
Professor in charge of thesis