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1980 STATUS REVIEW—HYDROLIQUEFACTION OF COAL
WITH SUPPORTED CATALYSTS

By
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1980 STATUS REVIEW -

HYDROLIQUEFACTION OF COAL WITH SUPPORTED CATALYSTS

BY

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1980 Status Review - Hydroliquefaction of Coal with Supported Catalysts

1. Summary

1.1 Catalyst Deactivation Kinetic Models

The objectives of the program have been to determine catalyst deactivation kinetic models and catalyst deactivation modes for supported Co-Mo and Ni-Mo catalysts used primarily in coal liquefaction via the H-COAL process.

Emphasis has been on developing methods to increase catalyst usage by determining how to decrease catalyst replacement rates in the process and how to decrease catalyst poisoning. Future work will also include methods and processes for catalyst regeneration.

1.2 Catalyst Deactivation Data to Substantiate the Pore Mouth Poisoning Model

An important conclusion reached via model analysis⁽⁵⁾ and verified by experiment is that larger diameter (1/16") catalysts resist poisoning deactivation much more than smaller (1/32") catalysts over extended periods (60-110 hours) of time (see Figure 23). This important result (i.e., longer catalyst life) needs to be tested with 1/8" diameter catalysts. If this trend can be verified, it gives a powerful tool for reducing catalyst replacement rate in the H-COAL ebullated bed system by factors of 2 or more (also see Appendix C).

A second conclusion is that poisoning of catalysts occurs by several possible mechanisms or modes. Indirect or direct evidence of all these modes can be presented, though the relative importance of each mechanism has not been established. The modes include (a) poisoning by coking - with gradual increase in C/H ratio (more refractory coke) with time, (b) poisoning by metallization (selective/non-selective adsorption of inorganics such as Ti and Fe on the catalyst), (c) sintering - increase in larger pores/decrease in surface area, and (d) parallel poisoning by "irreversible" nitrogen compound adsorption.

Results presented include descriptions of reactors, chemical analysis of product (via solvent product lumping), analysis of coal, ASTM distillation, sulfur and nitrogen conversion, commercial catalyst testing methods, and a list of experimental run results.

Besides continuation of present investigations, future work will involve regeneration and process simulation of the ebullated bed catalyst replacement rate from CSTR catalyst deactivation studies as well as testing new catalysts.

1.3 Preliminary Results

At least four modes of deactivation have been observed based on preliminary analyses of continuous operations data from the Xytel slurry unit or other experimental work. Run conditions are generally at 440°C, 2000 psig, space velocity of 1.65 gm coal/hr/cm³ catalyst, and with a coal slurry consisting of 25 wt % coal in SRC-II heavy distillate. All catalysts have been presulfided.

1.3.a) The carbon/hydrogen ratio increases as a function of time on stream and as reaction rate decreases (Figure 12). This phenomenon was also confirmed by Amoco.⁽¹⁾ Indications are that catalytically adsorbed hydrocarbons are changing to coke as activity decreases. Total adsorbed material appears to accrue rapidly (1 hr) and does not change perceptibly with time on stream.

1.3.b) As first reported by S. Pollack of the Analytical Chemistry Division in a preliminary examination (two Amocat 1A runs and one American Cyanamid HDS-1442A run),⁽⁶⁾ it appears possible that activity is reduced as the total amount of minerals deposited on the catalyst surface is increased. This result is confounded by simultaneously occurring factors such as coking and sintering.

1.3.c) The percentage of pores larger than 100 Å appears to increase with time on stream, though total porosity decreases. This observation can be due to both small pore clogging and to catalyst sintering. The latter is a real possibility, since MoS₂ can sublime at 450°C.

At least one catalyst was improved in initial activity for pentane soluble product using a controlled sintering procedure. The HDS-1442A catalyst with $60\text{\AA}$ mesopores after sintering at 725°C for 6 hrs. became similar to Amocat 1A ($110\text{\AA}$ mesopores). A higher catalytic activity for coal conversion was observed over the first 20 hours for the modified catalyst, but thereafter its activity was at or below the standard HDS-1442A. The explanation offered is that improved pore size distribution increased internal diffusion rates and thus the initial rate of the overall reaction, but that the accelerated sintering at 725°C caused Mo crystallite growth to increase, resulting in a reduction of active sites as the reaction proceeded.

1.3.d) The finding of Berg and McCandless⁽²⁾ that nitrogen compounds primarily disappear from the liquid by irreversible adsorption on the catalyst substrate rather than by chemical (catalytic) hydrodenitrogenation to NH_3 is another possible explanation for deactivation by parallel poisoning. Sulfide/sulfate interaction with the catalyst or support is also a possibility.

Hydroliquefaction of Coal with Supported Catalysts

A Status Review

2. Introduction

This review of project status will serve to focus on the experimental results obtained to date, on reproducibility, and on those findings which help in understanding the meaning of the data. Solutions to the problems involving catalytic activity, kinetics of coal conversion, modes of catalyst deactivation, and new preparative catalyst techniques could help resolve the deactivation problems and those of product selectivity in the H-COAL process.

While not having solved all of these problems at this time, trends are evident. The results obtained to date will be tied together by a set of investigations involving

catalyst preparation, catalyst testing (batch and continuous), kinetic studies, catalyst surface analysis (on both new and used catalyst systems), and theoretical considerations. An analysis of the preliminary results will be followed by a look at some possible scenarios to explain what is occurring. This will be based both on available data and hypothetical possibilities.

A continuing program of investigation will be described which is mainly based on the interim results reported here.

3. Equipment Description and Use

3.1 Batch Reactor

The batch reactor and conditions were chosen to give a sensitive screening test to measure the initial activity of coal liquefaction catalysts. The test which has evolved incorporates the insights and procedures learned over several years of catalyst screening activity carried out at the Pittsburgh Energy Technology Center (PETC), AMOCO Oil Company, Engelhard Industries, and Harshaw Catalyst Company. The goal was to develop a test sufficiently sensitive to clearly distinguish between catalysts as well as being efficient and reproducible. The conversion obtained during a liquefaction screening test depends on the choice of coal, solvent, and reaction conditions. Illinois #6-Burning Star mine coal is proposed as a standard coal for use in such tests because it has only moderate thermal liquefaction properties and has a large data base from use in previous screening tests. Panasol-AN solvent is a good choice for a slurry solvent because it is a hydrogen donor (once hydrogenated), available in large quantities commercially, has an appropriate boiling range, and is completely aromatic. Because the solvent is originally present in a hydrogen deficient form, the test in part measures the ability of the liquefaction catalyst to hydrogenate the solvent under liquefaction conditions, which may be one of the principle functions of a liquefaction catalyst. Direct hydrogenation of coal liquids also occurs significantly. A 1/1 coal/oil ratio

was used in the test to obtain a product that contains a large fraction of coal-derived liquid, which simplifies product characterization.

The batch test can be run in two modes, a normal heat-up or a rapid injection mode. The standard, normal heat-up autoclave system is shown in Figure 1. The unit consists of a 1-liter magna-drive autoclave equipped with a two-liter hydrogen reservoir. In the normal heat-up mode the coal/catalyst/oil slurry is charged into the autoclave, and the unit pressurized with hydrogen gas to 1000-1100 psi. The unit is then heated to 430°C, which requires approximately 45 minutes. During this time the pressure increases to approximately 2000 psi. The hydrogen reservoir is then connected to the autoclave through a demand regulator which maintains the pressure at 2000 psi. At the end of 30 minutes reaction time at 430°C, the autoclave is isolated from the hydrogen reservoir and quenched to room temperature by means of an internal cooling coil and an external air cooler. The heating and cooling portions of the run are quite reproducible. The time that the reactants are above 350°C is recorded and any runs falling outside the interval of 38-40 minutes are rejected. A summary of the run conditions is given in Table 1.

It is seen that in the normal heat-up mode, the actual reaction period consists of a non-isothermal and an isothermal portion. It is our belief that since the non-isothermal period is quite reproducible, and the time that the slurry is at temperature (other than 430°C) where reaction rates are appreciable is small relative to the overall reaction period, this is a valid screening procedure. Since this viewpoint has been criticized, a mechanism for the rapid injection of coal into hot oil has been included in our test equipment. This unit, shown schematically in Figure 2, was modeled after the unit used by Engelhard in the screening test.

In the rapid injection mode, the oil and catalyst are charged in the autoclave, and the coal charged in an external hopper. The autoclave and hopper are pressured to 500-550 psi with hydrogen. The autoclave is then isolated and heated to 440°C

and held for 30 minutes. During this time the pressure increases to 2000 psi and the Panasol oil is partially hydrogenated.

The hopper is then connected to the two-liter reservoir through the demand regulator, and coal is injected into the autoclave by opening an air-operated ball valve on the injection hopper. Preliminary tests indicate the 99% of the coal in the hopper is charged to the autoclave. The temperature in the autoclave drops to 300°C on injection of the coal, but recovers to 430°C in approximately 3-1/2 minutes. A 2000-

Table 1: AUTOCLAVE SCREENING TEST

A. STANDARD TEST CONDITIONS

150 g TOTAL CHARGE

ILLINOIS #6 BURNING STAR MINE COAL

PANASOL OIL SOLVENT

SOLVENT/COAL RATIO = 1/1

WT. % CATALYST (BASED ON MF COAL) = 3.75%

TEMPERATURE = 430°C

PRESSURE = 2000 PSI

TIME = 30 MIN

B. TIME CRITERIA

$t (T \geq 350^{\circ}\text{C})$

$38 \leq t \leq 40 \text{ MIN}$

Figure 1 - Standard autoclave.

Figure 2 - Rapid injection autoclave.

psi pressure is maintained in the autoclave during this period. Thirty minutes after the autoclave temperature reads 430°C , the autoclave and hopper are isolated from the hydrogen reservoir and quenched to room temperature in the same manner as the normal mode. While the rapid injection autoclave minimizes the uncertainty associated with the heat-up period, preliminary tests indicate that 1-2% of the charged coal adheres to the autoclave lid and does not mix with the catalyst/oil slurry.

Product recovery and analysis is similar whether the test is run in the normal heat-up or rapid injection mode. See Section 4.4 for details of the product analysis procedures.

3.2 Xytel Continuous Slurry Unit

Process Description

The Xytel Coal Liquefaction Unit, shown schematically in Figure 3, is currently being used to evaluate the effectiveness of various supported metal catalysts in liquefying coal. The unit operates continuously using a continuous stirred tank reactor (CSTR). All process control and monitoring is performed by a microcomputer, with operator interaction occurring via a CRT. The unit is capable of operation to pressures and temperatures of 3500 psig and 500°C .

The catalyst to be tested is loaded into an annular basket, which is placed inside the reactor. Rapid agitation causes the reactants to flow through the annular space containing the catalyst. This space is kept relatively small, approximately 10 mm thick, in order to minimize the pressure drop through the catalysts and to permit a more uniform flow pattern. The catalyst is usually activated prior to use by sulfiding, using the hydrogen sulfide portion of the gas delivery section.

Hydrogen is supplied to the unit from either one of two cylinder banks. The gas is compressed to approximately 4500 psig and stored in an accumulator. Gas is drawn from the accumulator and regulated to the desired system pressure and metered through a thermal mass flow meter. A flow control valve controlled by the computer

Figure 3.- Continuous Coal Liquefaction Unit

controls the flow rate of gas around an operator-supplied set point. The fresh gas is either fed to the reactor or is first mixed with recycle gas which has been compressed and metered according to a desired recycle ratio.

The coal-oil slurry to be processed is mixed externally to the desired specifications and then loaded into the slurry feed tank. An agitator and a recycle pump are used to maintain the coal in suspension. The slurry can then be drawn off by either of two high pressure slurry feed pumps and pressurized to system pressure. The outputs of the pumps must be adjusted manually; however, the feed rate is monitored by noting the change in weight of the feed tank over a specified period of time.

The slurry and reactant gas are combined and preheated to a desired temperature. The reactants are then fed to the continuous stirred tank reactor, where they are contacted with catalysts for a specified time. The residence time in the reactor can be adjusted by either changing the slurry feed rate or the reactor holdup. The holdup can be varied by changing the height of an overflow tube which is inserted into the reactor from its base. This overflow tube essentially controls the liquid level in the reactor.

The reaction products leaving the reactor are first separated in the heavy oil separator. The liquid products are depressurized by isolating the secondary separator and then manually throttling the liquid products into the low pressure receiver. When completed, the secondary separator is repressurized with product gas to system pressure and placed back in service. This technique eliminates any fluctuations or upsets in pressure caused by the removal of liquid product and minimizes disturbances in the product gas composition.

Water is injected into the gas stream from the heavy oil separator and then cooled in a heat exchanger. The water and light oils are depressurized using two air operated valves in series. The gas from the light oil separator can either be recycled as discussed previously or depressurized, metered, and vented.

Gases which flash from the liquid products upon depressurization are metered and vented.

As stated earlier, the unit is monitored and controlled by a microcomputer. All process variables to be controlled, such as system pressure and reaction temperature, with the exception of the slurry feed rate, are adjustable through operator interaction via a CRT. Controller settings are also entered via the CRT. Temperatures, pressures, flow rates, etc., are displayed on the CRT for easy access but are also recorded for permanent storage on an analog strip chart recorder. All motors and air-operated devices are activated from the CRT. In cases of emergencies where temperatures and pressures exceed an upper limit or where hydrogen is detected in unit, the computer automatically reverts the system to a fail-safe mode of operation. In particular, the unit is depressurized and purged with nitrogen, all controllers are deactivated, and all motors are deactivated, with the exceptions of the slurry recycle pump, slurry feed tank agitator, and the reactor agitator.

3.3 Procedures for Obtaining Continuous Liquefaction Data

The coal utilized for the work is Illinois #6 Burning Star mine coal obtained from Hydrocarbon Research Inc., which has been wet ground to 60 mesh. The coal was subsequently dried, reground to less than 100 mesh, and uniformly mixed. Particle size larger than 100 mesh usually causes operation difficulties such as plugging, preventing pump checks to seat properly, etc. The ground coal is separated into several small lots, each of which is sufficient to sustain at least a 100 hr. operation. Storage of coal under an inert N_2 atmosphere in bags was established to prevent premature oxidation before use. A sample of the coal from each lot is obtained at the time of use. The following analyses are usually obtained: 1) Ultimate, 2) Proximate, 3) Sulfur forms, 4) Major elements in ash, 5) Heating value, and 6) True specific gravity. Typical results for this particular coal are presented in Table 2.

The vehicle solvents used in the present program are Koppers Creosote oil and SRC-II Heavy Distillate. The former is mainly an anthracene oil of varying composition and solids content. Removal of crystals by decantation is required before use. The latter (SRC-II) is a material of consistent (liquid at room temperature) composition. It has good viscosity characteristics in that it stabilizes coal-oil slurries so that coal-in-oil concentrations can be kept uniform. SRC-II oil is preferred of the two solvents available. Representative samples are obtained from each drum of oil and sent for the following analyses: 1) Ultimate, 2) Solvent, 3) Moisture, 4) Ash, 5) Kinematic Viscosity, 6) Specific Gravity, 7) Heating Value, 8) Vacuum and Simulated Distillation, and 9) Flash and Fire Point. Table 3 presents the analyses of the two solvents, while Figure 4 presents their distillation data.

The coal-oil slurry is made in separate 16 lb. batches and then placed in the unit's feed tank. The slurry consists of 75 wt% oil and 25 wt% coal on a moisture-free basis. The following analyses are obtained for the feed slurry: 1) Ultimate, 2) Moisture, 3) Ash, 4) Solvent, 5) Specific Gravity, and 6) Viscosity.

Approximately 70 cc bulk volume of the catalyst to be evaluated is measured in a 100-ml graduated cylinder. The cylinder must be tapped constantly in order to more closely pack the catalyst. The sample is then weighed. Using a small spatula, the catalyst is slowly placed in the annular portion of the catalyst basket. The basket must also be tapped frequently to permit proper settlement of the catalyst particles. If loaded properly, the catalyst level should be $\frac{3}{4}$ in. to 1 in. below the top of the basket. Glass beads of 3 mm diameter are next loaded into the basket, which is filled to within $\frac{1}{4}$ in. of the top. Glass wool is used to fill the remaining space and to contain the catalyst and glass beads in the basket. The basket is then installed in the CSTR and sealed.

Once this is completed, the unit is pressure tested with nitrogen at 3500 psig, followed by hydrogen at 3500 psig. After all leaks have been sealed and no pressure

loss is observed over a specified period of time, the catalyst is presulfided at the conditions given in Table 15. When this has been completed, the reactor furnace controller, system pressure controller, and feed gas flow controller are set to the desired conditions. Conditions for the catalytic runs are given in Table 16. Once the pressure and flow rate are at their desired set point and the reactor internal temperature has exceeded 390°C , the slurry and water feeds are started. Generally, all conditions are stabilized within a few hours after the start of the slurry feed. Control samples, which are analyzed to obtain THF, Ethyl Acetate, and Pentane conversions, are gathered every ten hours after the start of the slurry feed.

Table 2: Coal Analyses

Proximate (wt%)

Moisture	2.1
Volatile Matter	38.9
Fixed Carbon	47.9
Ash	11.1

Ultimate (wt%, moisture free)

Hydrogen	4.7
Carbon	69.8
Nitrogen	1.2
Sulfur	3.1
Oxygen (by diff.)	9.9
Ash	11.3
H/C Ratio	0.81

Sulfur Forms (wt%, moisture free)

Sulfide	0.03
Pyrite	1.20
Organic	1.81

Major Elements in Ash (wt%)

Silica	46.88
Al_2O_3	19.61
Fe_2O_3	16.01
TiO_2	1.25
CaO	7.69
MgO	0.43
Na_2O	0.56
K_2O	1.85
Sulfides	4.18

Specific Gravity	1.45
Heating Value (Btu/lb)	12453

Table 3: Vehicle Solvent Type and Characterization

Ultimate	<u>KCO</u>	<u>SRC-II</u>
Carbon	91.9	89.6
Hydrogen	5.8	7.4
Nitrogen	0.8	1.0
Sulfur	0.7	0.5
Oxygen (by diff.)	0.8	1.5
Ash	0.0	0.0
H/C mol. ratio	0.757	0.991
Water Content (wt%)	0.3	0.4
Kinematic viscosity (cs @ 140°F)	5.5	16.8
Specific Gravity	1.129	1.089
Heating Value (Btu/lb)	-	17037
Flash Point (°F)	-	335
Fire Point (°F)	-	360
Benzene Insolubles (wt%)	0.1	0.1
Asphaltenes (wt%)	1.6	2.5

Figure 4 - Vacuum distillation of solvents

Three material balance periods, each lasting for a period of five hours, are usually made during a catalytic run. The first usually commences 15 hours into the run, with the remaining two being equally spaced over the remaining time. Two gas samples from both the flash gas and tail gas streams are collected during each material balance period and analyzed using a gas chromatograph. The heavy oil products during a material balance period are collected, and the following analyses are performed: 1) Ultimate, 2) Solvent, 3) Moisture, 4) Ash, 5) Simulated and Vacuum Distillation, 6) Specific Gravity, and 7) Viscosity. All heavy oil products collected during non-material balance periods are stored in 55-gallon drums. After 100 hours or more of continuous operation or after shorter specified time, the unit is shutdown, and the used catalyst is recovered and sent for analysis.

For thermal, noncatalytic runs, a five-hour material balance period is conducted for each set of process conditions. The same types of samples are collected except that the control sample is collected during a material balance period. All product analyses remain the same.

4. Data Accumulation and Analyses

4.1 ASTM Distillation Results Including Comparisons to "Oil Soluble" Product Fractions

The conversion of coal to distillates is an important criterion used by HRI to evaluate catalyst activity. However, other groups have used conversions based on solubility for their measure of activity. Conversion based on solubility in hexane or pentane measures the conversion of coal into an oil fraction and appears to measure the predominate catalytic (non-thermal) component of the liquefaction process. A small study was made to compare the results obtained based on solubility in these commonly used solvents with those obtained by ASTM D1160 distillation results.

The solubility conversion values were determined using the microfiltration technique described in Appendix A. The samples were run in triplicate using 4-5 g samples.

Oils from a continuous thermal run (SC-R3-HO-2) and a catalytic run (SC-R4-HO-2) were used. Because samples from the continuous run tend to ball-up when added to solvents such as pentane or hexane, they were diluted with a weight of toluene equal to the sample weight. This mixture was well mixed and then added to 40 ml of the paraffinic hydrocarbon with stirring. The mixture is then sonicated and filtered, as described in Appendix A. This procedure yields a crystalline precipitate which gives good reproducibility.

Besides hexane and pentane, cyclohexane and isooctane were tried to determine what effect the use of these different common solvents would have on the conversion values and which solvent would give the best correlation with the ASTM results. The results of this study are given in Tables 4 and 5.

Because of its slightly better solvent power, cyclohexane could also be run without the addition of toluene. The results show that with the exception of the cyclohexane/toluene mixture, all the solvents give nearly the same value for conversion of coal to oil fraction. A more important result is that the percent of the solid fraction obtained by the microfiltration method agrees very well with the residue value obtained from the ASTM distillation procedure. Therefore, it appears that a conversion value based on pentane or hexane solubility gives a reliable estimate of the conversion of coal to distillate.

Table 4: Results of Catalytic Run

Sample	SC-R4-HO-1	<u>% Solids</u>	<u>% Conv.</u>
pentane		15.2 $\pm$ 0.2	44.3 $\pm$ 1.0
hexane		14.2 $\pm$ 0.4	48.8 $\pm$ 1.9
cyclohexane		13.1 $\pm$ 0.1	53.7 $\pm$ 0.4
isooctane		15.2 $\pm$ 0.2	44.3 $\pm$ 0.9
cyclohexane*		14.8 $\pm$ 0.3	46.1 $\pm$ 1.2

Distillation Data: 14.6% residue

Table 5: Results of Thermal Run

Sample	SC-R3-HO-2	
	<u>% Solids</u>	<u>% Conv.</u>
pentane	22.7 $\pm$ 0.5	10.2 $\pm$ 2.3
hexane	21.3 $\pm$ 0.5	16.6 $\pm$ 2.5
cyclohexane	19.5 $\pm$ 0.2	25.0 $\pm$ 1.0
isooctane	23.0 $\pm$ 0.4	9.0 $\pm$ 1.7
cyclohexane*	21.3 $\pm$ 0.4	16.7 $\pm$ 1.6

Distillation Data: 20.0% residue

*toluene addition was not used for these determinations

4.2 Product Characterization by Solvent Segregation (THF, EA, Pentane)

At the end of the run, the product recovered amounts to 90-95% of the original charge. Our approach has been to use product work-up and analytical procedures which are as simple and as rapid as possible. Based on this consideration, a variation of the micro-residue test developed by Arrioco for their continuous unit was used as the basis for our product work-up scheme. A flow chart of our scheme is given in Figure 5. The method involved obtaining aliquot samples of the liquefaction product while it is being homogenized in a blender. Using this scheme, we are able to obtain values for conversion of coal to tetrahydrofuran solubles (THF conversion), to ethyl acetate solubles (EA conversion), and to pentane solubles (C_5 conversion). A detailed description of our microfiltration test is given in Appendix A. The method also enables us to make duplicate analyses if necessary. The product not used for the conversion determinations is centrifuged at 10,000 rpm in a Sorvell Model RC-5 Superspeed centrifuge. The viscosity at 60°C of the centrifuged oil is obtained on a Brookfield Model LVJ microviscometer. A sulfur analysis of the centrifuged oil is obtained by the Analytical Chemistry Division using an X-ray fluorescence method. A calibration was obtained using a procedure similar to an ASTM procedure and was based on NBS and LECO sulfur standards. The method has a precision of $\pm 0.03\%$ and an accuracy of $\pm 0.1\%$

Figure 5 - Flow chart for product analysis scheme.

sulfur. A sample of the product oil is also stored under nitrogen in a sealed ampule in case subsequent analyses are required.

The microfiltration determination gives conversions based on solubility of the product in a particular solvent similar to those obtained by using a work-up procedure involving soxhlet extractions. However, since only a 5-10 g sample is involved in the technique, it is a very rapid method. The accuracy of the method depends on getting representative samples of the product slurry for the aliquot samples used in the test. Table 6 gives typical filtration results obtained for multiple determinations made on several products. The data show that representative samples can be obtained and that the method is reproducible. The method gives values which are within several percent of values obtained by traditional solvent analysis methods involving soxhlet extractions. Considering the sensitivity of solvent analysis results to experimental procedures, this rapid technique is considered to be an adequate procedure for determination of conversion values.

The microfiltration data can be used to calculate the conversion of coal into fractions based on solubility properties. In this report we define the following fractions:

Table 6: Typical Filtration Reproducibility Data

<u>Run #</u>	<u>21060</u>	<u>21080</u>	<u>21090</u>	<u>21100</u>
EA CONV. (%)	67.68	49.69	76.29	49.43
S.D.	0.07	0.34	0.28	0.22
# SAMPLES	3	3	3	3
THF CONV. (%)	90.50	81.46	-	72.29
S.D.	0.14	0.49	-	0.42
# SAMPLES	3	3	3	3

<u>Run #</u>	<u>30080</u>	<u>30090</u>
C ₅ CONV. (%)	30.54	16.89
S.D.	0.48	0.13
# SAMPLES	3	3

"Preasphaltene" - fraction soluble in tetrahydrofuran, but insoluble in ethyl acetate.

"Asphaltene" - fraction soluble in ethyl acetate, but insoluble in pentane.

"Oil" - fraction soluble in pentane.

It should be noted that the definitions of preasphaltene and asphaltene fractions are based on solubility properties using ethyl acetate instead of benzene, which is the traditionally used solvent. Ethyl acetate was chosen because its solubility properties are similar to those of benzene, and it does not involve the potential health hazard associated with the use of highly volatile aromatics like benzene. For a number of products the corresponding conversion values based on ethyl acetate and benzene were determined. The results given in Table 7 show that ethyl acetate gives slightly higher conversion values than benzene. However, a good correlation exists between the two sets of data, which enables us to convert our values to a benzene basis if necessary for comparison of our results with those obtained in other laboratories.

The analytical data obtained from the procedures are used to calculate conversion to preasphaltene, asphaltene, and oil; and percent organic sulfur removal. The equation used for making these calculations is given in Table 8.

4.3 Data Reproducibility

Figure 6 illustrates the reproducibility of the data obtained from the Xytel slurry unit, while Figure 7 compares data obtained independently by Amoco with the same test catalyst (American Cyanamid HDS 1442A) at the same experimental conditions.

There are two important differences between Amoco and PETC procedures, one of which has been taken into account on the graph. One difference is that PETC uses ethyl acetate (EA) to measure the product fraction of intermediate quality (asphaltenes plus oils), while Amoco uses benzene (BZ). PETC has developed a correlation for %EA solubles as a function of %BZ solubles ($X_{BZ} = 0.977 X_{EA} - 5.84$). The middle curve of Figure 7 shows the closeness of Amoco and PETC conversion data when this correlation is used.

Table 7: Correlation Between Benzene and Ethyl Acetate Conversion Results

<u>BRU #</u>	<u>BENZENE CONV.</u> (%)	<u>ETHYL ACETATE CONV.</u> (%)
21320	64.9	72.7
21340	42.6	50.4
21350	51.7	57.4
30010	30.9	36.4
30030	53.0	59.4
30040	71.8	78.8
30050	48.5	57.5
30060	43.3	51.3
30070	43.5	50.8

$$\text{BENZENE CONV. (\%)} = 0.9768 (\text{EA CONV.}) - 5.840$$

$$r^2 = 0.9920$$

$$\text{EA CONV. (\%)} = 1.0156 (\text{BENZ CONV.}) + 6.388$$

$$r^2 = 0.9920$$

Table 8: Equation Used for Calculation Evaluation Criteria

A. CONVERSION (BASED ON THF, EA, AND C₅ SOLUBILITY)

$$\% \text{ CONV.} = \frac{AW - (\text{INSOL} - BW)}{AW (1 - C)} \times 100$$

A = WT. FRACTION OF MF COAL IN TOTAL CHARGE

W = SAMPLE WEIGHT USED IN MICROFILTRATION TEST

INSOL = WT. OF INSOL = WT. DRY FILTER CAKE

B = WT. FRACTION OF CATALYST IN TOTAL CHARGE

C = WT. FRACTION OF ASH IN MF COAL

Figure 6 - Reproducibility of coal liquefaction conversion data for HDS-1442A catalyst.

8-19-80 L-17829

Figure 7 - Comparison of PETC's coal liquefaction conversion data with that of Amoco's using HDS-1442A.

8-19-80 L-17830

The second difference is that PETC uses pentane to solubilize the distillable oil fraction in the product, while Amoco uses hexane. No correction was made in this case, since a correlation at all oil concentrations of interest has not been made. In two cases where PETC compared hexane solubility with pentane solubility of the same oil, the hexane solubility was 5% greater. Though no correction has been made for this solvent difference in the oil soluble data (lower curve, Figure 7), one can see that a uniform 5% change to convert all the hexane soluble data to "equivalent pentane soluble" data would put the Amoco data in the center of the PETC "pentane data."

To summarize, the PETC data are both internally consistent and reproducible, and they also match Amoco data as to consistency and magnitude.

4.4 Thermal Liquefaction Run Data

A series of baseline runs have been made in which Illinois #6 Burning Star Mine Coal was reacted in the absence of any added catalyst. The runs, presented in Table 9, covered the expected temperature range of operation when using catalysts (430-440°C). The objectives of the experiments were to determine conversion to THF solubles (preasphaltenes, asphaltenes, and oils), conversion to Ethyl Acetate solubles (asphaltenes plus oils), and conversion to pentane soluble products (distillable oils). Residence times were varied from 27.8 to 64.3 minutes.

Non-catalytic conversions for a typical run (440°C, 45 minutes, 2000 psi, 25 wt% coal in SRC-II Heavy Distillate, reactor holdup 361 cm³) are THF solubles-86.9%, EA solubles-67.6% (BZ solubles-60.2%), and Pentane solubles, 19.4%. The obviously low conversion to pentane soluble product without a catalyst (19.4%) can be compared to a pentane soluble conversion with a fresh catalyst (62%). The large incremental difference indicates that pentane solubility should be the primary effect to measure in order to obtain catalytic effects on the coal product. THF solubility is almost independent of a catalyst presence, while EA (BZ) solubility is slightly catalytic but mostly (> 75%) thermal.

Table 9: Thermal Run Data Using Illinois #6 Burning Star Coal

Run No.	SC-R2-1	SC-R2-2	SC-R2-3	SC-R2-9	SC-R3-1	SC-R3-2	SC-R3-3	SC-R3-4	SC-R3-5	SC-R8-1	SC-R8-3
Solvent	KCO	KCO	KCO	KCO	FSN-10	FSN-10	FSN-10	FSN-10	FSN-10	FSN-10	FSN-10
Temperature °C	440	440	440	440	430	430	430	430	440	440	440
Pressure psig	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
Slurry Conc. (wt%)	25	25	25	25	25	25	25	25	25	25	25
Slurry Feed Rate (g/hr)	886	633	578	392	620	823	481	391	802	557	837
Hydrogen Feed Rate (SCFH)	12	12	12	12	10	10	10	10	10	10	10
Reactor Hold- up (cm ³)	349	349	349	349	361	361	361	361	361	367	367
Residence Time (min.)	27.8	38.6	47.5	62.7	40.5	30.5	52.2	64.3	31.3	45.0	30.0
Conversion											
THF	93.0	90.7	92.8	92.6	87.6	86.1	87.7	88.8	88.3	86.9	87.2
Ethyl Acetate	74.7	73.2	75.9	74.2	68.1	66.2	72.7	73.5	71.7	67.6	65.8
Benzene	67.1	65.7	68.3	66.7	60.7	68.8	65.2	66.0	64.2	60.2	58.4
Pentane	25.9	35.8	44.4	40.7	17.0	15.2	21.1	21.9	25.3	19.4	14.3
Hexane	-	-	-	-	-	-	-	-	-	24.6	-

Run #SC-R8-1 was selected as being a primary baseline coal conversion point for "no - catalyst." Catalyst rate data on catalytic runs, including rates of catalyst deactivation, can be determined by subtracting the pentane soluble conversion at reaction conditions from the pentane values of run SC-R8-1.

4.5 Heteroatom Removal

Heteroatom removal of the catalysts tested in the Xytel unit ranges from moderate to good for sulfur removal and remains poor under all conditions tested for nitrogen removal. These data are presented in Table 10.

For the case of unsulfided catalyst both sulfur and nitrogen removal is lower by as much as a factor of two compared to that of sulfided catalysts. There is no significant trend as to whether S and N removal decrease as the catalyst ages, but small decreases in activity are indicated. XP-1, which showed higher initial liquefaction conversion than 1442A, also showed somewhat higher initial HDS and HDN activity.

The disposition of the heteroatoms is not known at this time. It is assumed that since these catalysts are well known for HDS activity, sulfur heteroatoms are removed via decomposition to H_2S gas. The nitrogen heteroatoms, however, may be "removed" from the liquid product either by HDN reaction to NH_3 or by irreversible adsorption of basic nitrogen compounds on the catalyst.

The irreversible adsorption would be a form of irreversible catalyst poisoning occurring in parallel with the liquefaction reaction itself and would help account for a shrinking core of active catalyst as a function of time. The latter has been modeled successfully⁽⁵⁾ and actually predicts the trend in the data of Figure 23, where particle diameter effects are characterized.

Table 10: Percent Heteroatom Removal from Catalytic Experiments

	<u>Time, hr</u>	<u>S</u>	<u>N</u>	<u>Catalyst</u>
SC-R4-1	4	50	9.1	HDS-1442A*
-2	28	45.5	9.1	
-3	60	30.0	0.0	
-4	75.5	36.4	9.1	
-5	98	36.4	0.0	
SC-R5-1	13	66.7	18.2	HDS-1442A
-2	49	63.6	18.2	
-3	95	66.7	18.2	
SC-R6-1	13	72.7	27.3	XP-1
-2	49	66.7	18.2	
SC-R7-1	15	54.5	18.2	HDS-1442A
-2	61	57.1	9.1	
SC-R11-1	15	75.0	18.2	Amocat 1A
SC-R12-1	18.5	72.7	10.0	HDS-1442B
-2	59.5	36.4	0.0	

*The catalyst used in this run was not presulfided prior to operation.

5. Catalyst Preparation

5.1 Preparation of Bimodal Supports and Catalysts

Several methods were developed to prepare catalyst having bimodal pore size distributions. Two general approaches were tried. The first was to prepare bimodal alumina supports having the desired pore size distribution and to prepare Co-Mo catalysts from the supports using the impregnation-to-incipient-wetness technique. These supports were prepared by extrusion techniques, and most of the work was directed along this approach. The second approach was to prepare the Co-Mo catalyst directly by coextrusion of suitable catalyst precursors.

The supports or catalysts were prepared by the extrusion of γ -Alumina precursors, chiefly boehmites. Two commercial boehmite powders were tried, Conoco's Catapal SB and Kaiser's SA Medium. The Catapal SB is a high purity boehmite ($SA = 240 \text{ m}^2/\text{g}$) which has excellent extrusion characteristics and converts to a medium density ($PV = 0.45 \text{ cc/g}$), high surface ($190 \text{ m}^2/\text{g}$) $\gamma\text{-Al}_2\text{O}_3$ on calcination. The Kaiser SA Medium is a much lighter boehmite ($SA = 350 \text{ m}^2/\text{g}$) containing small amounts of Nordstrandite or Gibbsite. On calcination it produces a low density ($PV = 0.93 \text{ cc/g}$), high surface area ($270 \text{ m}^2/\text{g}$) $\gamma\text{-Al}_2\text{O}_3$. Its extrusion characteristics are not as good as Catapal SB. These materials were mixed in a 300-ml tongue rheometer/laboratory mixer and extruded using a hydraulic extrusion press.

Extrusion of well peptized batches of Catapal SB and SA Medium produced supports that show very narrow monomodal pore distributions having an average pore diameter of $55\text{\AA}$ and $75\text{\AA}$, respectively. The consistency of the extrusion mixtures was found to depend on the solids content of the mixture, the pH of the solution used to peptize the boehmite, and the degree of mixing. However, none of these factors has any appreciable effect on the size distribution of pores in the mesopore range. It is therefore necessary to both modify the extrusion batch and sinter the final extrudates to obtain the preferred structure having mesopores in the $80\text{-}200\text{\AA}$ range and macropores in the $1000\text{-}4000\text{\AA}$ range.

Several methods were tried to introduce a bimodal pore size distribution into the extrudates. They were

1. Partial peptization of the extrusion batch
2. Addition of $\gamma\text{-Al}_2\text{O}_3$ to the boehmite
3. Incorporation of combustible fibers into the extrusion batch

Addition of $\gamma\text{-Al}_2\text{O}_3$ into the boehmite extrusion batch produced a bimodal structure, but the resulting extrudates have poor strength characteristics. Therefore, this method was abandoned. The other two techniques yielded extrudates with good strength characteristics and were examined in some detail.

For incompletely peptized batches, a bimodal pore size distribution is obtained consisting of mesopores in a range characteristic of the starting boehmite powder and very large macropores consisting of the remaining void spaces between the unpeptized boehmite particles. The macropores tend to be quite large for extrudates prepared from Catapal SB. However, Kasier SA medium gives better results. For this boehmite, the addition of 10% butyl alcohol to the extrusion batch interferes in some way with the peptization process and produces bimodal supports with macropores in the 2000-4000 Å range. The work on this method is preliminary and needs to be expanded.

A preferred method for producing bimodal supports involves the incorporation of a combustible fiber into a well peptized extrusion batch. A typical pore size distribution for extrudates prepared by this method is shown in Figure 8. Since the development of the macroporosity is primarily controlled by the amount and type of cellulose fiber added to the extrusion batch and depends only slightly on mixing effects, the method is easily controlled and gives good reproducibility. It was found that the total pore volume and average pore diameter of the macropores increase as the amount of fiber addition to the batch is increased. The nature of the cellulose fiber is also quite important. With fibers composed of non-dispersible cellulose, the macropores produced by this method are the same size as the cellulose fibers or larger due to

Figure 8 - Pore size distribution for extrudates produced by addition of microcrystalline cellulose filler to completely peptized extrusion batch.

aggregation of the fibers into bundles of higher loadings. For a microcrystalline cellulose fiber, such as Avicel, the resulting pores are smaller than the diameter of the starting fibers due to dispersion of the fibers into small fibrils during the mixing process.

Figure 9 shows the effect of addition of Avicel on the pore volume and the average pore diameter (APD) of supports prepared by this method. Table 11 shows the wide range of bimodal supports which can be produced by this technique.

Coextrusion of ammonium heptamolybdate (AHM) and boehmite mixtures should give very uniform molybdena/alumina catalysts upon calcination. Preliminary experiments show that both monodispersed and bimodal catalysts can be prepared by coextrusion. However, the addition of a soluble molybdenum salt has a large effect on the peptization process. If the molybdenum salt is dissolved in the acetic acid solution used to peptize the batch prior to the addition of the solution to the Catapal SB powder, the batch does not peptize to any significant degree. This results in very weak extrudates. However, extrudates of good strength can be prepared by adding the acetic acid solution to a mixture of Catapal SB and molybdenum salt. Apparently the acid solution is imbibed by the porous boehmite aggregates before any appreciable amount of molybdenum salt dissolves into the solution. This allows the batch to peptize before the molybdenum anion can interfere. A series of bimodal molybdena/alumina catalysts were prepared by this technique. Also the presence of molybdena in the catalysts promotes the sintering of the catalysts so that lower temperatures are required to obtain the desired 120 Å average pore diameter. It is not known if the molybdenum-alumina interaction that promotes the sintering at lower temperatures is beneficial or detrimental to the ultimate catalyst performance.

A paper was written reporting on these results and describing the techniques useful for preparing bimodal supports. It is in the process of being submitted for publication.

Figure 9 - Pore volume and apparent pore diameter characteristics; Catapal /Avicel supports calcined at 1000° C/ 3 hr

Table 11: Comparison of Supports Prepared Using Different Cellulose Fibers^a

Sample #	30490C	30491C	30530C	30550C	31681	31671	31661
Type fiber	Avicel	Avicel	Avicel	Avicel	Fisher	Fisher	Fisher
wt% Fiber	10	20	30	40	5	10	15
Pore Vol. (cc/g)	0.401	0.486	0.636	0.770	0.427	0.453	0.491
APD ($\text{\AA}$) Mesopores	104	108	117	129	103	103	103
APD' ($\text{\AA}$) Macropores	-	184	795	1287	2500	4000	9000
SA (m^2/g)	148	153	137	123	141	141	141
Pellet Density (g/cc)	1.47	1.27	1.08	0.99	1.40	1.34	1.28

^aExtrusion batch contained 55 wt% ALOOH, 5 vol% acetic acid as peptizing agent, mixed to energy input of 10,000 meter-g-min for batches containing Avicel and 40,000 meter-g-min for batches containing Fisher filter pulp, 1/16" extrudates-calcined 1000^o C/3 hr.

5.2 Sintering and Steaming Techniques

The pore structure produced in gamma-alumina supports and catalysts, obtained from boehmite precursors, comes from the gel-like pore structure present in the original boehmite or boehmite/salt mixtures. Commercially available boehmites do not produce catalysts with mesopores in the desired 80-200Å range. Therefore, the extrudates were sintered or steamed to produce the desired average pore size.

The thermal sintering was carried out in a box furnace, which was purged with one liter/min of dry air. A temperature of 900°C is required to produce an average pore diameter of 100Å in extrudates prepared from Catapal SB. At this temperature the extrudates are converted into a mixture of delta and/or theta-alumina. A similar pore structure is produced in Kaiser SA extrudates by a 800°C/2 hr. treatment. This milder treatment produces gamma-alumina in these supports. Since molybdena promotes the sintering of alumina, an even milder thermal treatment is required for the molybdena/alumina catalysts. For such catalysts prepared from Catapal SB, a thermal treatment at 725°C/4.5 hr. produces the desired pore structure. At this milder condition, the supports remains as gamma-alumina, and the molybdena is present as an interaction species.

It is well known that water vapor promotes the sintering of many oxides. Steaming extrudates of Catapal SB at 770°C for 7 hours produces the same pore size distribution obtained by thermal sintering at 900°C/3 hrs. Also, the lower temperature prevents the conversion of gamma-alumina into delta- and/or theta-alumina. The extrudates are steamed in a tube furnace which is purged with air at the rate of 200 cc/min. A peristaltic pump feeds 0.81 cc/min of distilled water to the furnace to produce a steam/air mixture containing 73% steam.

5.3 Controlled Sintering Techniques

The pore structure of Mo/Al₂O₃ or Co-Mo/Al₂O₃ can be changed by controlled sintering. Such treatments tend to eliminate micropores and to increase the average

pore diameter of mesopores, and have little effect on the total volume of pores above 50Å provided the treatment is not too severe. Preliminary experiments on Amocat 1A, Amocat 1B, Engelhard 11015-25-1, and American Cyanamid's 1442A showed that treatment at 725°C/3 hr. increased the average pore diameter to 165Å, 150Å, 190Å, and 92Å, respectively. At temperatures between 750-800°C, the extrudates lose strength, and $\text{Al}_2(\text{MoO}_4)_3$ is detected in their XRD patterns.

This controlled sintering technique was used to convert American Cyanamid 1442A into a catalyst (XP-1) having a pore size distribution equivalent to Amocat 1A. A treatment of 725°C/6 hr. is required. The screening test results presented in Table 12 show that this treatment produces a significant improvement in the initial activity of the catalyst, even though the BET surface area is decreased from 274m²/g to 175m²/g in the sulfided catalyst. The improvement in activity is due to the opening up of the pore structure of the catalyst. Attempts to determine the effect of controlled sintering on the surface chemistry of the catalyst using the techniques of LR, XRD, ISS, and ESCA have only yielded inconclusive results to date.

The catalyst was subsequently tested in the continuous (Xytel) slurry unit. Under these test conditions, the significant improvement in activity was lost after 20 hours, and the catalyst was at best no better than standard 1442A. (See Figure 10).

5.4 PETC Catalyst Properties

Table 13 presents the physical and chemical properties of several catalysts which have been developed in PETC's laboratory. A comparison with Amoco's catalyst Amocat 1A is also presented for convenience.

5.5 Commercial Catalyst Properties

The properties for the commercial Amocat 1A catalyst were supplied by Amoco and are presented in Table 14.

Table 12: Autoclave Screening Test Results with Panasol Oil¹

Catalyst	Thermal	Harshaw 0402T	Am. Cyd. 1442A	Am. Cyd. 1422A-S (XP-1)
# Runs	3	2	1	2
% Conv.				
THF	67.9 $\pm$ 1.1	85.6 $\pm$ 0.9	88.4	92.6 $\pm$ 2.8
E.A.	47.1 $\pm$ 0.8	67.0 $\pm$ 2.5	69.1	83.6 $\pm$ 3.0
Pentane	22.4 $\pm$ 0.6	32.1 $\pm$ 0.4	35.1	42.2 $\pm$ 0.4
Selectivity				
% 'Preasph.'	29.0 $\pm$ 0.5	23.4 $\pm$ 1.0	21.4	11.4 $\pm$ 1.1
% 'Asph.'	38.4 $\pm$ 1.2	38.5 $\pm$ 1.4	38.9	42.6 $\pm$ 2.1
% Oil	32.7 $\pm$ 1.5	38.1 $\pm$ 0.4	39.5	46.0 $\pm$ 1.1

¹76 g coal, 76 g oil, 3.75 wt% catalyst, heated to 430°C - 2000 psi with 30 min. hold.

FIGURE 10- Comparison of presintered and as-is coal hydroliquefaction catalysts

Table 13: Characteristics of Amocat 1A and PETC Catalysts

ID	Metal Content	Thermal Treatment	Form	Pellet Density (g/cc)
Am. Cyd. 1442A	3 CoO-15 MoO ₃	Sulfided 260°C/4hr	-80+140 mesh	1.02
"	"	Sulfided 350°C/4hr	"	1.01
"	"	Sulfided 450°C/4hr	"	1.00
RET 30990	15 MoO ₃	Sulfided 350°C/4hr	100 mesh	N.A.
30992	2 CoO-15 MoO ₃	"	"	"
30993	3 CoO-15 MoO ₃	"	"	"
30994	4 CoO-15 MoO ₃	"	"	"
30997	7 CoO-15 MoO ₃	"	"	"
30998	8 CoO-15 MoO ₃	"	"	"
21500	19 MoO ₃	500°C/16hr	325 mesh	"
21260	"	1000°C/3hr	"	"
21270	"	900°C/3hr	"	"
21280	"	800°C/3hr	"	"
31060	3 CoO-15 MoO ₃	600°C/3hr	1/16" extrudate	0.96
31061	"	700°C/3hr	"	1.11
31062	"	725°C/3hr	"	0.96
31063	"	750°C/3hr	"	0.95
31064	"	800°C/3hr	"	1.11
31065 (XPI)	"	725°C/3hr	"	0.95
31800	"	1000°C/6hr	"	1.23
31820	"	900°C/3hr	"	1.21
40050	"	Standard 700°C/7hr	"	1.15
31201	15 MoO ₃	Coextruded 725°C/3hr	"	0.99
31202	"	Coextruded 725°C/6hr	"	1.02
31241	"	Coextruded 725°C/6hr	"	1.30
Amocat 1A	3 CoO-15 MoO ₃	Sulfided 350°C/4hr	"	1.07

1. Pore volume and average pore diameter from mercury porosimeter measurement except for those given in parenthesis, which were obtained from N₂ gas absorption data.
2. NA means that characterization does not apply to sample.

Pore Vol. (cc/g)	BET SA (m ² /g)		APD (Å)		PV 1000A (%)
	Oxidic	Sulfide	Mesopores	Macropores	
0.671	287	274	58	3400	23.5
0.612	"	"	"	"	24.8
0.688	"	"	"	"	23.5
(0.656)	185	-	(142)	NA	NA
(0.630)	175	-	(144)	NA	NA
(0.636)	179	-	(142)	NA	NA
(0.631)	181	-	(139)	NA	NA
(0.567)	160	-	(142)	NA	NA
(0.550)	157	-	(140)	NA	NA
-	-	-	-	NA	NA
(0.283)	-	81	(140)	NA	NA
(0.305)	-	105	(116)	NA	NA
(0.318)	-	131	(97)	NA	NA
0.736	287	274	58	3400	22.1
0.750	262	233	76	3500	22.8
0.758	205	222	92	3400	22.0
0.741	114	108	165	3600	24.0
0.630	56	-	320	3600	28.7
0.793	190	175	100	3500	24.5
0.544	81	70	152	1400	31.8
0.562	121	-	115	1050	23.5
0.617	110	-	126	2000	35.2
0.711	162	-	100	740	6.3
0.726	116	-	140	1000	19.0
0.506	110	-	140	12000	21.3
0.657	201	171	120	3800	17.2

Table 14: Amocat 1A Specifications on
Grace 120B Alumina Support

Chemical Composition

MoO ₃ , wt% on dry basis	16.0 ± 0.9
CoO, wt% on dry basis	3.0 ± 0.25
Na ₂ O, wt% on dry basis	0.04
S, wt% on dry basis	0.15
CaO, wt% on dry basis	0.01
Loss on Ignition, 1000°F - 2 hr, wt%	3.0

Physical Properties

Shape Nominal 1/16" diameter extrudates
Nominal L/D of 2.5

Average diameter, inches	0.062 ± 0.005
Average length, inches	0.14 minimum
Average size crush strength, lb/mm	1.5 minimum
Bulk density, g/cc	0.63 ± 0.05

Surface Properties

BET surface area, m ² /g	170 minimum
Average micropore diameter, Å (determined by N ₂ sorption)	120 ± 10
Minimum micropore diameter, Å (determined by N ₂ sorption)	40
Total pore volume, cm ³ /g (determined by N ₂ sorption and Hg porosimetry)	0.75 ± 0.05
% Pore volume in macropores (determined by N ₂ sorption and Hg porosimetry)	18 ± 5

6. Commercial Catalyst Testing/Analysis

Some of the "commercial" catalysts from outside PETC, notably American Cyanamid 1442A, 1442B, and Amoco's Amocat 1A, are pretreated (sulfided), tested under reaction conditions, aged at various times, and analyzed for coke deposition kinetics, coke composition changes, hydrothermal sintering effects, and other poisoning phenomena (metallization and irreversible adsorption of components). Pore size distribution of aged and virgin catalysts are also compared.

Finally, the diameter effect is analyzed using a model which considers the effects of parallel poisoning and a shrinking core of active catalyst to correctly predict the faster aging rate of smaller diameter catalysts compared to larger ones.

6.1 Experimental Testing Conditions

Table 15 lists the presulfiding conditions for the catalysts tested in the Xytel continuous slurry unit. These conditions were used on all experiments except the initial 1442A test run.

Table 16 compares testing conditions of catalysts at PETC with those at Amoco. The closeness of these parameters was proposed so that catalysts can be compared on an equivalent basis in both units. Thus, improved catalysts found in one laboratory can be verified by the other.

Table 17 is a listing of all the runs completed at the time of this report. Note that on-stream times vary from 1 hour to 117 hours, with many appropriately spaced times. This enables parameters causing catalyst deactivation to be measured as a function of time. Both overall deactivation rates and rates of change of such variables as coke formation, C/H rates of the coke, metal deposition rates, surface area loss, pore size distribution changes, and other factors can be separately measured. The contribution of the individual effect can then be estimated from this approach.

Table 15: Catalyst Presulfiding Conditions

H ₂ S/H ₂ (mole %)	10
Temperature (°C)	350
Pressure (psig)	60
Flow Rate (SLM)	1.0-1.3
Total Time (hrs.)	2

Table 16: Summary of Catalytic Run Conditions

	<u>PETC</u>	<u>AMOCO</u>
Temperature (°C)	440	440
Pressure (psig)	2000	2000
Slurry Concentration (wt% mf.)	25	25
Slurry Feed Rate (g/Hr)	465-475	413
Hydrogen Feed Rate (SCFH)	10	8
Reactor Holdup (cm ³)	306-310	310
Residence Time (min.)	45	45
LHSV (g-coal/hr/cm ³ cat)	1.6-1.7	1.72
Agitation (rpm)	1700-2000	1500

Note: Amoco's reported residence time assumes the specific gravity of the reacting mixture to be one whereas PETC's residence time is based on the specific gravity of the feed slurry.

6.2 Tested Catalysts

Table 17 below presents a listing of the catalysts evaluated and their total exposure to the coal slurry.

Table 17: Catalysts Employed in Aging Studies

<u>Run No.</u>	<u>Catalyst</u>	<u>Total Hrs on Slurry</u>
SC-R4 ⁽¹⁾	HDS-1442A	107
SC-R5	HDS-1442A	117
SC-R6	XP-1	77
SC-R7	HDS-1442A	103
SC-R8	Amocat 1A	1

<u>Run No.</u>	<u>Catalyst</u>	<u>Total Hrs on Slurry</u>
SC-R9	Amocat 1A	6.5
SC-R10	Amocat 1A	18
SC-R11	Amocat 1A	48
SC-R12	HDS-1442B	60
SCR-2A	HDS-1442A	2

(1) Catalyst was not presulfided prior to use. Reaction temperature and residence time were 430°C and 30 minutes, respectively.

6.3 Carbonization Effects

Figure 11 is a composite curve showing coking rates on two very similar catalysts as a function of on-stream time. The curves are very typical of coking-rate studies reported by Bischoff et al.⁸ for other types of systems.

The "coke" appears to fill the pores rapidly because the pore volume is reduced from 0.66 cc/g at zero hours to 0.37 cc/g at only 7 hours on stream. Thereafter, it levels off so that even at 107 hours the pore volume is still 0.34 cc/g. However, the nature of the coke (as characterized by H/C ratio) does not remain the same. Nor does the rate of coke formation (after 20 hrs) keep up with the rate of catalytic deactivation for liquefaction.

There is no obvious correspondence between coking rate and catalyst deactivation. The coking rate is initially extremely fast (even after only 1 hour on stream). After around 10 to 20 hours, it appears to have stopped at 20 to 30 wt% coke on the catalyst.

The quality and refractoriness of the coke does appear to change with time. It remains to be seen exactly how this relates to deactivation rate.

A general trend (for a given catalyst) of slow increases in carbon-hydrogen ratio with time on reaction slurry has been observed.

It is possible that lower hydrogen content would indicate a greater refractoriness and possible reluctance of the coke to react off the catalyst. The higher C/H ratio at low times for Amocat 1A is perhaps more a reflection of operating problems than of catalyst effects (Figure 12). The short runs of 6 and 18 hours were due to reactor plugging, which generally results in loss of pressure, a phenomenon that creates excessive

Figure 11 - Changes in the pore volume of Amocat 1A and I442A at different levels of deactivation (via carbonization)

coking due to desolubilization of hydrogen from the reaction mixture. While this effect does occur under normal operation conditions (Figure 11, Catalyst 1442A), the carbon levels and C/H ratio are not as high as with those runs in which process upsets occur (Figure 12, Amocat 1A).

Additional data will be obtained to monitor the effect of this phenomenon on extent of deactivation:

6.4 The Effects of Metallization on Catalyst Activity

The deposition of unwanted metallic or metal oxide foulants on liquefaction catalysts is a known mechanism for deactivating coal liquefaction catalysts. PETC's Analytical Chemistry Division has been doing extensive investigations on this phenomenon for some time. The data presented here were developed primarily by the A.C. Division.⁽⁶⁾

By plotting catalyst activity remaining (% hexane soluble) versus amount of metal deposition, one can obtain reasonable straight line correlations as shown in Figure 13 either with % titanium or % titanium plus iron. One can also get a reasonably straight line by plotting $\%(\text{Ti} + \text{Fe})$ in the catalyst versus time on stream as shown in Figure 14.

The total deactivation (% hexane initially about 75% to a final level of 45%) can be estimated since % hexane solubility with no catalyst is known (15% hexane solubility). The actual total reduction in activity may be "guesstimated" at being on the order of 50%.

Two separate determinations indicate that the contribution to activity loss due to metallization may be on the order of only 5 to 25%.

(a) A regeneration (Amoco, HRI) of an aged catalyst, followed by retesting, shows initial regenerated activity to be 92% of the original.

(b) Calculations of the surface coverage, which estimate active component blockage, can be made with certain assumptions as to the disposition of the metal poisons:

Figure 12- Comparison of the C/H atomic ratio of various spent catalysts which have been aged to different degrees.

9-23-80 L-17869

Figure 13- Catalyst deactivation by metals.

9-23-80 L-17870

Figure 14-Metallization effects.

10-7-80 L-17888

The average fresh catalyst is $180 \text{ m}^2/\text{g}$ catalyst or $180 \times 10^{20} \text{ \AA}^2/\text{g}$. The wt. of Ti + Fe is 5% or $0.05\text{g}/\text{g}$ catalyst or 0.001 mol Ti . This is $0.001 \times 6.02 \times 10^{23} = 6.02 \times 10^{20}$ atoms of titanium, which is estimated to have an atomic radius of $1.4 \text{ \AA}$ (area of $6.15 \text{ \AA}^2$). The total Ti area is then $6.15 \text{ \AA}^2/\text{atom} \times 6.02 \times 10^{20}$ atoms or $37 \times 10^{20} \text{ \AA}^2$. Assuming Mo is 80% dispersed on the Al_2O_3 ($180 \times 10^{20} \text{ \AA}^2/\text{g}$), we have a $144 \times 10^{20} \text{ \AA}^2/\text{g}$ Mo area. Assuming all the Ti adsorbs selectively onto the Mo in a unimolecular fashion (probably not so), then only 26% of the Mo surface is poisoned by metallics when 5% (Ti + Fe) is observed to be on the catalyst.

While the above calculations are crude, the assumptions are conservative with respect to assuming maximum poisoning efficiency.

6.4.2 Further Characterization of Metal Fouling of Coal Conversion Catalysts

The investigation of catalyst aging rate as affected by metals deposition has been further characterized.

Conversion data from the strictly catalytic reaction mode (pentane solubles) elicits the fact that the diameter effect can be critical (Figure 15). Conversion using $1/32$ inch catalyst deactivates fast, crossing over to a lower value conversion than the $1/16$ " catalyst at 30 hr on-stream time.

The crossover point between the $1/16$ " and the $1/8$ " catalyst is less apparent, but extrapolation of existing data indicates it will occur at 160 hours.

Examination of metal deposition amounts on $1/32$, $1/16$, and $1/8$ " catalysts after 90 hours confirms that metallization is partly a function of the mass transfer surface available where fouling effects can occur. The data also qualitatively predict that the differences in rate of activity loss between the $1/32$ " catalyst and the $1/16$ " catalyst will be greater than that between the $1/16$ " and $1/8$ " catalysts if fouling is important (Fig. 16).

FIGURE 15- Comparison of a 1/32 in. (HDS 1442B) and A 1/16 in. (HDS-1442A) Catalyst with HDS 2 (1/8 in. diameter)

Figure 16 - Metal accumulation at 90 hours for three catalyst diameters.

L-81419

Figure 17 is a plot of various metal accumulations on our tested catalysts vs time. Differentiating this curve to obtain instantaneous metal adsorption rates leads us to Fig. 18, which indicates two separate deactivation mechanisms are operable -- a fast initial rate when all the pores fill, followed by a slower rate when diffusion through an initial layer of metal foulant occurs.

From Figure 17, one can also infer the results of Figure 16, and the additional observation that catalyst XP-1, which had its pore diameter increased and its surface area lowered, has a greater susceptibility to metal fouling than unsintered catalyst (see also Figure 10).

6.5 Irreversible Adsorption as a Poisoning Effect

The used PETC test catalysts have not been completely characterized with respect to irreversible basic nitrogen compound adsorption on the catalytic supports. The analyses are in progress; however, some will be included.

The primary rationale for looking for this type of poisoning lies in the evidence supplied through the catalyst testing of Berg and McCandless⁽²⁾ who recently reported this phenomenon. They tested the rather acidic TCC cracking catalysts for nitrogen removal at reaction conditions of 425°C, 1000 psi, 1.0 liquid hourly space velocity using SRC-II liquid (1.17%N) as the reactant. Coke laydown appeared rather rapidly (4 hr) in the two catalysts tests. This is to be expected from our experience as well. The unusual result occurred when the whereabouts of the removed nitrogen was traced. In run #35, 77% of the N was removed from SRC-II. Of this removed material, 88% was found in the coke laydown, with 12% having been hydrodenitrogenated to NH_3 . This material was diluted (2:1) with tetralin before testing.

In run #36 in which the SRC-II was reacted undiluted, a total of 65% of the N was removed. Of this amount, 78% stayed on the coked catalyst, while only 22% hydrodenitrogenated to NH_3 in the off-gases. Both catalysts were <50% deactivated after 2 hours. Though the active (Co, Mo, Ni, and W) HDN metals were absent from these catalysts, they also appear to coke and lose activity rapidly (<4hr). This leads

Figure 17 - Metal accumulation on supported-metal catalysts as a function of time.

L-81426

Figure 18.- Instantaneous rate of metal accumulation for 1/16 inch diameter catalysts.

L-81420

one to suppose that the selective-adsorption-of-N-compounds phenomenon may be more general than suspected heretofore. The low (1000 psi) pressure used by these researchers may tend to accentuate this characteristic.

As a result of this evidence, our aged deactivated catalysts have been analyzed for %N adsorbed thereon as a function of time on stream. Results now available, Table 18, indicate that our catalysts are not coated significantly by irreversibly adsorbed N-compounds.

Table 18: Catalytically Adsorbed Nitrogen

<u>Run or Source</u>	<u>Catalyst</u>	<u>Time on Stream (Hr)</u>	<u>Adsorbed wt % Nitrogen Found</u>
SRC-2A	1442A	2	0.5%
SRC-4	1442A	107	0.3%
Amoco	Amocat 1A	144	0.2%
Amoco	1442A	167	0.4%

6.6 Sintering Effects

Only short term data are available on sintering of Amocat 1A catalyst. Though no general conclusions can be reached, it appears tentatively that the sulfiding step which occurs at 350°C results in a 15% reduction in fresh catalyst surface area. Reacting the catalyst for only a short time, 6-18 hours, results in a further reduction in BET surface area, perhaps another 15% (Figure 19); a leveling off in surface reduction may be taking place (if data on XP-1 and 1442A are indications) as time on stream increases. However, irrefutable data are not yet available. The loss of area is not due to sintering only. Plugging of pores by carbon is the major cause of area loss. Regenerated samples (after C burnoff) would normally have only a slight loss of surface area.

Sintering effects shown in Figure 20 are also seen in the observation that a larger percentage of total pore volume is due to pores larger than 100Å at increased times in use.

Figure 19 - Changes in the surface area of Amocat 1A at different levels of deactivation.

9-23-80 L-17872

Figure 20- Percentage of total pore volume due to pores larger than 100°A of Amocat 1A at different levels of conversion

The sintering may be due to MoS_2 crystal growth, hydrothermal support sintering, or other factors to be determined. The effect will be studied further by examining the effect of stabilized supports on sintering of aged catalysts.

6.7 Pore Size Distribution Effects

The pore size distribution in a bimodal catalyst can be examined qualitatively and to some degree quantitatively when aged and fresh catalysts are compared. In Table 19, two catalysts are compared as to aging effects.

Table 19: Comparison of Aging Effects on Two Catalysts

Comparison		
<u>Catalyst</u>	<u>1442A</u>	<u>XP-1</u>
History	Virgin from manufacturer	Presintered at controlled rate 6 hr/725°C
Macropore Size (fresh)	3500 Å	3500 Å
Macropore Size (aged)	3500 Å	3200 Å
Micropores (fresh)	50 Å	110 Å
Micropores (aged)	55 Å	60 Å
Time on Slurry	107 hr.	77 hr.
Virgin SA	321 m ² /g	182 m ² /g
Aged SA	128 m ² /g	139 m ² /g
P. V. Fresh	0.671 cc/g	0.755 cc/g
P. V. Aged	0.346 cc/g	0.329 cc/g
% Porosity Lost	48.4%	56.4%

It appears that around 50% of the total pore volume is lost during aging, as shown in Figure 21. The micropores only are reduced by about 70%, while the macropores lose about half their pore volume.

Figure 21- Pore volume determination of fresh and aged American Cyanamid 1442A catalyst.

In the case of the larger 110Å micropores (XP-1), a partial filling occurs, which leaves predominantly 60Å pores after aging. This is shown in Figure 22. In the case of the smaller 60Å micropores (1442A), the pores are wholly blocked, and no shift in micropore size occurs with age. The 100Å micropore catalyst had higher initial activity, but it decayed quickly (20 hrs); the final pore size distributions of the two catalysts were similar, as were their final activities.

6.8 The Diameter Effect

The diameter effect is detailed in the paper entitled "The Use of Fundamental Concepts In Catalyst Aging to Increase Catalyst Utilization During Coal Liquefaction, Steam Reforming, and Other Carbon-Forming Reactions" (included in Appendix C).

A major conclusion from this analytical treatment (Appendix C) when seen from the viewpoint of catalyst utilization is that larger diameter catalysts will tend to reduce the relative rate of poisoning. Under certain conditions, including those in which the H-COAL process may be run, this allows one to increase dramatically the mass of feed processed per unit mass of catalyst before catalyst deactivation proceeds too far (Figure 23).

The model when applied to coal hydroliquefaction enables one to lower catalyst usage significantly in an ebullated bed process. The model should also hold in other catalytic processes in which catalyst poisoning occurs, such as steam reforming, methanation, and auto exhaust.

Data from Figure 23 show that the results predicted by the model hold. The 1/16" catalyst (with lower initial activity than the 1/32" catalyst) ends up having longer life at a relatively higher activity over the long run. The effect of even larger 1/8" diameter catalysts will be examined as a next step.

The working out of two separate rate phenomena as a function of diameter--
(1) overall reaction rate with internal (intraparticle) diffusion is inversely proportional to catalyst diameter ($\eta < 0.5$), while (2) poisoning rate is inversely proportional to

Figure 22-Pore volume determination of fresh and aged XP-1 catalyst.

9-23-80 L-17875

Figure 23-Comparison of HDS-1442B with HDS-1442A catalyst (diameter effect).

8-12-80 L-17822

the square of the catalyst diameter (pore mouth (shrinking core) poisoning model)-- when considered together add up to the simple conclusion that catalyst replacement rate, CRR, is inversely proportional to the catalyst radius, with a complex correction factor ($K\alpha_i$) accounting for reactant/product diffusion through already deactivated pores.

$$\frac{CRR_1}{CRR_2} = \frac{R_2}{R_1} \frac{K\alpha_2}{K\alpha_1} \quad (1)$$

Values for $K\alpha_i$ as a function of the catalyst radius, effectiveness factor, and fraction of catalyst deactivated are related to fraction of initial activity remaining. The basis for comparing different diameter catalysts of differing η 's with each other for differing degrees of catalyst deactivation is spelled out.

An important observation is that a reversal may take place in the importance of the catalyst diameter effect on reaction rate, depending on whether or not a catalyst is removed from the system after being slightly deactivated or extensively deactivated.

The paper defines efficacy ratio (E_p) as the ratio of the amount of reactant converted per unit weight of catalyst (the inverse of catalyst replacement rate). A comparison of catalyst efficacy, the efficiency of utilization before the catalyst becomes poisoned to an arbitrary amount, is given in Table 20.

Table 20: Comparison of Catalyst Efficiency for 1/16" and 3/16" Catalysts

<u>Fraction of Catalytic Activity Remaining (F)</u>	<u>Fraction of Catalyst Poisoned Before Catalyst Removal</u>	<u>Efficacy Ratio, E_p (3/16" Catalyst vs 1/16" Catalyst)</u>
0.75	0.25	0.86
0.50	0.50	1.36
0.33	0.67	2.28
0.20	0.80	2.85
0.10	0.90	2.87

The reversal in this case comes between an F of 0.75 and 0.50. Since catalysts are not in general removed in the H-COAL process until thoroughly deactivated, the efficacy ratio predicted experimentally would be expected to approach 3.0 as a limit. That is, the 3/16" catalyst would process three times as much coal as the 1/16", provided the initial conversions are reasonable in both cases. For further details, see Appendix C.

7. Future Work

7.1 Reproducibility and Extension of the Diameter Effect on Catalyst Deactivation

A major finding over the last several years of catalyst development both in industry and government laboratories is that even the most improved catalyst to date (Amocat 1A) has only about 20-30% more activity for conversion of coal to hexane (pentane) soluble fractions than the standard American Cyanamid 1442A catalyst over 140 hours of testing.

On the other hand, we have experimentally determined (Figure 23) that the total yield from coal of hexane solubles or pentane solubles can be potentially doubled over the life of the catalyst simply by increasing the catalyst diameter from 1/32" to 1/16" due to the shrinking pore poisoning mechanism which appears to operate in our system at reaction conditions. This amounts to having an equivalent catalyst which retains 100% more activity for conversion than the smaller catalyst. We would like to reproduce this data both with Amocat catalysts (now being undertaken at Amoco due to our recommendation) and with 1/8" catalysts at our laboratory to see if further increases in catalyst life result. If the latter does in fact occur at a high enough initial conversion rate,⁽⁵⁾ then our recommendation will be to have the H-COAL catalyst made in 1/8" extrudates rather than 1/16" extrudates. This will also have a favorable hydrodynamic effect on the process in terms of minimization of catalyst carryover and "bunching" at the reactor top. Accordingly, the diameter effect on aging kinetics has a top priority for study in FY 81.

7.2 Catalyst Regeneration Techniques

The need for catalyst regeneration becomes obvious when up to 1.5 lb catalyst (\$6.00 to \$7.50) per ton of coal is required in supported catalyst (H-COAL) processes. The catalyst cost alone is equivalent to \$2 to \$3 per bbl oil recovered and is expected to be inflationary, especially since both Mo and Co may be in short supply. The availability of sufficient Mo and Co may be even more of a problem than the cost. The regeneration problem is not a trivial one, since the types of poisons and foulants may not respond to a simple or uniform treatment. Example of such treatments are given below:

- (a) Hydrocarbon adsorption or coke may respond to a controlled burnoff in which sintering is minimized.
- (b) Steaming before burning off may remove some of the materials at a lower temperature.
- (c) Selective solvent treatment (pyridine, THF, DMSO) could possibly result in a low temperature removal of "irreversibly adsorbed" nitrogen compounds.
- (d) Selective acid treatment could result in selective removal of some of the inorganic metal foulants (Fe, Ti).
- (e) High temperature hydrogenation (600°C) could result in increasing the H/C ratio of the adsorbed coke, making it more removable.
- (f) Use of Cl_2 to remove Fe and Ti as FeCl_3 and TiCl_4 vapor might be considered, though AlCl_3 might also be removed non-selectively.

These and other techniques will be considered and if found plausible, they will be experimentally tested. Retesting of the "cleaned" catalyst for initial activity will be carried out in a batch reactor. If the activity on regeneration is greater than or equal to 90% of the virgin catalyst, then a continuous run to test its long term stability upon regeneration will be considered.

7.3 Testing New Catalysts and Supports

7.3.1 Stabilized Support Catalysts

There are several means of stabilizing supports against thermal or hydrothermal sintering and against reacting with the active metal components (in this case Co and Mo).

(a) The support of choice, which is often gamma Al_2O_3 , can be reacted with certain inorganic single or mixed salts as described in Ger. Offen. 2,905,292, issued to Engelhard Minerals and Chemicals Corp., August 23, 1979. The salts are decomposed and the composite calcined at sufficiently high temperatures so that the added components form mixed oxide compounds, usually perovskites (ABO_3) or scheelites (ABO_4), with the surface Al_2O_3 or with themselves. For example, $\text{La}(\text{NO}_3)_3$ added to Al_2O_3 in the correct mole ratio upon decomposition and calcination forms LaAlO_3 , a thermally and hydrothermally stable compound that waterproofs the catalyst. This hydrophobicity will stabilize the support against sintering by steam or heat or against reactive interaction with active metal additives (Mo or Co) which otherwise might react with surface Al_2O_3 to form spinels or other aluminates.

(b) Current methods for obtaining alumina having mesopores in the 100-200 Å range involve thermal sintering of the supports in dry air or steam. Steaming reduces the sintering temperatures necessary to obtain a given pore size but also accelerates the transformation of the desirable gamma and/or eta aluminas to alpha alumina. Both methods cause a large reduction in the surface area during the thermal treatment. Another method for producing thermally (and hydrothermally) stable aluminas has been described by Spoor & Fisher (SNAM Method - South Africa Patent #746,596 and #746,597). The method involves treating gamma Al_2O_3 with non-aqueous silane ether for three hours at 190°C in a nitrogen atmosphere and then calcining in air at 500°C to remove residual organic matter. The product is then calcined at 1000°C for four hours to obtain the desired pore range. Several samples of calcined boehmite (Kaiser S. A. medium) were stabilized by this method. The results (see Table 21) show that alumina with mesopores in the 100-200 Å range can be prepared by this method without the large loss of surface area observed during simple thermal sintering. Note that only untreated Al_2O_3 destabilized under calcination conditions and was thermally converted to theta and/or alpha Al_2O_3 . However, the silane-treated samples will

contain an appreciable amount of SiO_2 , which may influence their ultimate activity. Activity tests will be made on molybdenum-containing catalysts prepared from these supports.

(c) Still another method of stabilizing Co/Mo catalysts against the effects of steam has been first reported by Amoco.⁽¹⁾

Table 21: Results Obtained for Aluminas Treated by SNAM Method¹

Sample #	1000A ²	1000B ³	1000C ⁴
SA (m ² /g)	222	196	109
P.V. (cc/g)			
20-80	0.175	0.167	0.041
80-200	0.421	0.312	0.109
200-600	0.349	0.266	0.661
TOTAL	0.927	0.745	0.811
APD (Å)	120	97	290
XRD Results			
Major Phase	Eta-Al ₂ O ₃	Eta-Al ₂ O ₃	Theta-Al ₂ O ₃
Minor Phase	-	-	Alpha-Al ₂ O ₃ , Iota-Al ₂ O ₃

1. All samples were calcined at 1000°C for four hours.
2. Sample A was treated with silane ether and autoclaved in nitrogen for three hours at 190°C.
3. Sample B was treated with silane ether and heated in dry air at 190°C.
4. Sample C was untreated Al₂O₃ (but heated).

Amoco finds that certain rare earth stabilizers appear to have a more desirable effect when impregnated onto a Co-Mo/ Al_2O_3 catalyst rather than incorporated into the support itself. Impregnating the stabilizer onto the finished support does not interfere with the desired pore-size distribution of the original catalyst, while it appears to enhance the effect of the efficiency of the promoter on activity maintenance after steaming.

The following example was given using praseodymium:

<u>Case A</u>	<u>Fresh Activity</u>	<u>Activity After Steaming</u>
Pr in Al_2O_3 sol, followed by gelling and incorporation of Co/Mo.	56.8% conv.	51.5%
<u>Case B</u>		
Impregnating Pr into Co/Mo bimodal Al_2O_3	60.5%	58.9%

The results may however be an artifact of the catalyst preparation (Case A), since with proper preparation, the decomposition and calcining of $\text{Pr}/\text{Al}_2\text{O}_3$ would be carried out so as to have a stabilized bimodal system (Pr reaction with Al_2O_3 to form PrAlO_3) before the Co-Mo is added.

7.3.2 Catalysts on Novel Supports

The term "novel" supports is usually meant to imply that the support used for the active ingredients (in this case Co and Mo) will be other than the conventional support, i.e., Al_2O_3 . Such supports which have been suggested include high surface area TiO_2 (from DeGussa), SiO_2 , ZrO_2 , rare earths (CeO_2 , La_2O_3), and even carbon.

The supports may very well result in different catalytic activity, as the substrate may interact (or fail to interact) with Co and/or Mo in significantly different ways than Al_2O_3 , which interacts to form molybdenum aluminate and CoAl_2O_4 spinel.

Certain supports (carbon) may be eliminated on the grounds that they cannot be regenerated in air. ZrO_2 or CeO_2 may be considered to have too low a surface area for catalytic purposes.

TiO_2 may be of special interest because of its recent fame as a generator of strong metal support interactions (SMSI). Notably, because in reducing atmospheres, TiO_2 becomes Ti_4O_7 and may tie up the MoS_2 (Mo is considered to be more active in its lower +4 valence state rather than +5 or +6).

The most promise of a support of this type may lie in its incorporation as part of a mixed (double support) composite with Mo on Al_2O_3 combined with Co or Ni on the novel support. The rationale for a mixed bifunctional support will be described in 7.3.3.

7.3.3 Catalysts on Mixed Supports

The rationale for mixed supports comes from the theories of dual or polyfunctional catalysis together with the observation that support metal interaction and metal-metal interactions may result in antagonistic as well as possible synergistic effects. As an example, one might consider Co_9S_8 as a spacer between MoS_2 molecules being a synergistic effect which slows down Mo sintering. On the otherhand, the XRD analyses of catalyst samples show CoMoO_4 to be a presumably inactive scheelite compound when the single catalyst support is prepared, and this should result in an antagonistic effect, reducing both Co and Mo effectiveness. To avoid this phenomenon, a mixed catalyst extrudate can be constructed that could result in positive effects.

The degree of closeness of two active ingredients in a dual functional catalyst may not be as critical as one might suppose. In any event it can actually be calculated for some catalyst systems and in general is allowed to be 50 to 300 microns without becoming a limiting resistance in the overall reacting scheme.

P. B. Weisz⁽⁹⁾ has shown that in a polystep reaction (such as coal liquefaction - cracking - hydrodesulfurization - hydrogenation), a reactant may be catalyzed by two separate catalysts, and the overall rate (dN/dt) of reaction $A \rightarrow B \rightarrow C$ is

$$dN/dt \leq \frac{(B_{eq}) D_{eff}}{R^2} \quad (2)$$

The value of B_{eq} is the equilibrium concentration or, in practice, the steady state concentration of the intermediate B in a series where B is eventually converted to product. In general $A \rightarrow B$ is catalyzed by one catalyst and $B \rightarrow C$ by a second separate catalyst.

In the case of coal hydroliquefaction, the system might be analyzed as follows:

The actual intrinsic size range of Co particulates and Mo particulates which must be squeezed together by extruding micron sized particulates into a cohesive mixed base catalyst is calculated rather easily.

For a reaction dN/dt must fall within 10^{-7} to 10^{-5} mol/sec/cc catalyst volume. If not, either the conversion is not sufficient to get a desired amount of product in a finite catalyst bed or the rate is so fast that the exotherm destroys the (selective) product. Diffusion in porous materials of high surface area is $\sim 10^{-3}$ cm²/sec. The intermediate material B in lowest concentrations in the liquid will probably be H₂ even at 2000 psig. Via Henry's law one can show 0.002 mole fraction H₂ in H₂O and probably 0.01 mole fraction H₂ in oil. Even at the high conversion (smallest radius) substitution into the equation 2,

$$R \text{ particulate} = \frac{(H_2) D_{eff}}{(dN/dt)} = \frac{0.002 \times 10^{-3}}{10^{-5}} \quad (3)$$

which gives values of $R > 0.4$ cm for this reaction as being the maximum radius for a segregated particle of one catalyst component to be separated from the cocatalyst component.

Thus it would be quite satisfactory for 100 to 1000 micron particles of Co on support #1 to be combined in a composite with a 100 to 1000 micron particles of Mo on support #2.

Amoco has done a preliminary run from which they have some results. Batch runs show that Co and Ni can be separated from MoO_3 without affecting liquefaction activity. This observation permits one to modify each catalyst component support independently to produce an "optimal" catalyst.

As one example, Amoco mixed Co-Na/ Al_2O_3 and Mo/ Al_2O_3 and found this mixed catalyst to be 4% more active than HDS 1442A, a cosupported Co-Mo catalyst.

PETC will examine this phenomenon using supports of many types, especially those mentioned in Section 7.3.2.

7.4 Catalyst Replacement Rate Simulation of Ebullated Beds from CSTR Data

The computer modeling of an ebullated bed using catalyst activity decay rate data generated either by Amoco or PETC will enable us to simulate catalyst replacement rates of different catalysts, assuming a baseline of 1.5 lb catalyst/ton of coal for American Cyanamid 1442A and an average pentane solubles of 45 to 50% as a desired output from the process.

Modeling will be based on the assumption that (a) the ebullated bed is a backmixed reactor, (b) the ebullated bed is a plug flow reactor, (c) the ebullated bed has a residence time distribution equivalent to the result obtained by Bickel and Thomas⁽³⁾ using radioactive modeling of catalyst residence time in the HRI 100 lb/day pilot unit at Trenton.

This will enable us to identify the best overall catalyst from among the high initial activity - low activity maintenance catalysts and the lower initial activity - high activity maintenance catalysts.

This valuable test will be of assistance in recommending catalysts for the 500 TPD unit in Catlettsburg, KY.

8. Conclusions

8.1 Deactivation Dynamics

Experimental confirmation that parallel poisoning of catalysts occurs via a "shrinking core" model seems to be at hand. Comparison of a 1/16" with a 1/32" diameter catalyst shows the predictable (via the model) result that the 1/32" catalyst is the better catalyst only at the start of reaction and that a crossover occurs after ~ 50 hr. on stream after which the 1/16" diameter catalyst is more active. This is due to a slower poisoning effect which is calculated to occur with larger diameter catalysts. A paper by Polinski, et al.⁽⁵⁾ explains this phenomenon. Advantage may be taken of this result to allow lower catalyst replacement rates in the H-COAL process, perhaps by a factor of two or more.

8.2 Modes of Sintering

A scenario can be proposed which includes the various deactivation modes. To quote from the Catalyst Handbook,^(4,7) "The catalyst consists of a mixture of CoO and MoO₃ supported on high surface area Al₂O₃. There is some speculation concerning the active phases formed from this mixture responsible for the catalyst activity.

Fresh unsulfided catalyst consists of Al₂O₃, CoAl₂O₄, CoO, MoO₃, CoMoO₄, and a complex Co/Mo oxide." More recent analyses indicate Mo interaction with Al₂O₃ has a more important effect than CoO, MoO₃, and CoMoO₄.⁽⁶⁾

"The catalyst, charged in the oxide state, is sulfided. Under desulfurization conditions (after H₂S treatment), the catalyst consists of Al₂O₃ and CoAl₂O₄ (both inactive), Co₉S₈ (slightly active), MoS₂ (active), plus some unsulfided MoO₂ and MoOS.

The "active" catalyst has been described as MoS_2 promoted with nonreducible cobalt. The function of the CoO is to minimize MoS_2 sintering by keeping MoS_2 crystallites apart and to enhance activity by increasing effective surface area of the MoS_2 phase."

Taking this as a reasonable description of the catalyst, the catalyst poisoning can occur by means of carbonaceous or heteroatomic adsorption (N, S, O atoms) on catalyst sites, which on desorption and cracking leave behind hard-to-desorb deposits with low H/C ratios. The adsorption takes place almost at once, but the active carbon slowly gives way to the more refractory low H/C ratio variety with time. This may be accomplished either by replacement or surface cracking reaction whereby the intermediate product will neither react nor desorb quickly, or as an alternative, an increase in irreversible adsorption of basic nitrogen-heteroatoms (as shown by Berg and McCandless) takes place. The latter does not hydrodenitrogenate but instead deactivates an acidic site.

Concurrent with this mode of deactivation is that of inorganic constituent deposition. The accumulation of TiO_2 and $\text{Fe}_{(1-x)}\text{S}$ (pyrrhotite) deposits as pore blocking agents and surface coating components will tend to block the outermost catalyst surfaces (via the shrinking core model).⁽⁵⁾ This deposition appears slower than the carbonization, and it may not be as severe, as reactivation of catalysts via carbon (O, N, S) burn-off regenerates most of the initial catalyst activity. Nevertheless, this deactivation mode is important and is perhaps the hardest to reverse.

Sintering effects are least known and least studied due to difficulties in surface analysis of coked catalysts. Analysis of carefully burned-off coked catalysts is one way to approach the problem, but deactivation during burn-off is an artifact interfering with a true analysis. There are, however, methods of catalyst surface stabilization which can slow this effect, possibly by minimizing deactivation during regeneration.

The formation of CoAl_2O_4 , an inactive spinel, was noted by Richardson.⁽⁷⁾

As more CoAl_2O_4 forms, the effectiveness of Co as a dispersive aid to MoS_2 decreases. Means of stabilizing the support Al_2O_3 against formation of CoAl_2O_4 are readily available. Ger. Offen. 2,905,292 (to Engelhard Minerals and Chemicals Corp.) shows that addition of certain refractory metal salts and subsequent deposition to oxides forms perovskite-like compounds with Al_2O_3 (such as LaAlO_3) which maintain a high surface area while rendering the Al_2O_3 unreactive for spinel formation and simultaneously making it hydrophobic. The latter property would minimize catalyst sintering due to steam (formed from coal oxygen heteroatoms and hydrogen) at reaction conditions as well as keep the Co in the non-spinel form.

The use of a non Al_2O_3 support (such as TiO_2), provided surface area was sufficient, might be another approach to optimizing support-metal/metal sulfide interactions.

8.3 Program Emphasis for the Future

The study of catalyst aging kinetics has proved to be very important to upholding catalyst activity maintenance, and this avenue will continue to be explored in FY 81. The aging effects and their magnitude will be examined more closely. Catalyst preparation on stabilized and mixed support materials will be emphasized. Simulation of catalyst replacement rates will be a useful new addition to the program.

Finally, a much greater emphasis on catalyst regeneration and catalyst behavior after regeneration will be given.

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Appendix A

Microfiltration Test for Determining Coal Conversions

Description

This method is designed to determine the insoluble solids portion of a coal liquefaction product. The solids content will vary qualitatively and quantitatively depending on the solvent used.

Summary

A representative sample of the coal liquid is dissolved (and/or dispersed) in the designated solvent. The solution is poured into a Millipore filter apparatus that is prefitted with a 10 mm teflon filter. The vial that contained the sample is washed with solvent, and the solvent is added to the Millipore filter apparatus, which is then sealed. 400 ml of the same solvent is added to the large reservoir above the filtration unit, and the filtration apparatus is pressurized to 40 psig (dry nitrogen). After liquid stops flowing out of the filtration apparatus, the filter cake is removed, dried, and weighed. The dried residue should be a friable powder containing no tarry material.

Precision

Standard deviation = ± 0.50 (tetrahydrofuran)
 ± 0.50 (ethyl acetate)
 ± 0.50 (pentane)

Calculations

$$\% \text{ Conv.} = \frac{AW - I}{AW(I-C)} \times 100 \quad (A-1)$$

A - wt. fraction of MF coal in feed charge to reactor

W - sample weight used in microfiltration determination

I - weight of insol (based on solvent used) minus weight of dry filter cake

C - wt. fractions of ash in MF coal.

Equipment Needed

1. Solvent
 - Tetrahydrofuran (Fisher Histological Grade)
 - Ethyl Acetate (Fisher Certified Pesticide Grade)
 - N-Pentane (Fisher Certified Pesticide Grade)
2. Waring Blender (Model 31 BL 42)
3. Eberbach #9590 Semi-Micro Container Assembly
4. Eberbach Teflon gasket kit for blender assembly #8762
5. Millipore 47-mm stainless steel filtration cell, 190 ml (#XX40-047-00)
6. Millipore 47-mm teflon Mitex filters, 10-mm pores (LCWP 047-00)
7. Millipore Teflon cap O-ring (XX40-047-19)
8. Millipore Teflon sealing O-ring (XX40-047-16)
9. Whitey 1000-ml stainless steel sampling cylinder (304-HDF4-1000)
10. Bottles, 22-ml
11. Aluminum weighing pan
12. 1000-ml flask
13. Small ultrasonic bath (American Beauty #069-S-30)

Procedure:

1. The coal liquefaction product is added to the blender containing solvent, and blender speed is gradually increased to maximum over a 1-minute period.
2. Samples of 5-6 grams are pipetted out of the operating blender into 22-ml preweighed vials. The preweighed sample bottles are then weighed again to determine the exact weight of the aliquot. Prepare six samples.
3. Partially assemble Millipore apparatus by placing a preweighed 10-mm filter and preweighed teflon sealing O-ring into the cell. Place a piece of teflon tubing between the outlet of the filtering apparatus and the 1000-ml glass flask.

4. The samples (in the sample vials) are diluted with either tetrahydrofuran, ethyl acetate, or pentane. Each sample is stirred with a glass rod, and the vial is put into the ultrasonic bath for approximately 3 minutes.
5. Pour the contents of the sample vial (obtained from Step 4) into the filtration cell and wash out the sample bottle with the particular solvent being used. The cell is then filled with solvent.
6. Assemble the Millipore apparatus as shown in the attached diagram.
7. Close Valve V_1 . Add 400 ml of solvent to the large reservoir. The filtration apparatus is then connected to a dry low pressure nitrogen source (40 psig).
8. Close valve 3 and open 1 and 2. Leave 40 lbs. pressure on the cell until the solvent has passed through. There will be a pressure surge when all of the solvent has passed through the filter and nitrogen begins passing through the filter cake. Allow the nitrogen to pass through the cake for 3 minutes.
9. Close valve 2 and open valve 3 to vent the apparatus. Discard liquid collected in filter flask.
10. The filter cell is disassembled, and the teflon sealing O-ring, filter paper, and residue are put into the preweighed weighing pan. Inspect the filter cell and scrape any residue on the walls into the weighing pan.
11. The residues (one from each of the three solvents) are dried in a vacuum oven at 100°C for one hour.
12. Remove pan from oven, cool, and weigh. Reject any determination which does not give a friable filter cake or shows evidence of a tarry residue.
13. Repeat Steps 4 thru 12 for each of the solvents: tetrahydrofuran, ethyl acetate, and pentane.

Example:

Samples of liquefaction product from a run having a feedstock consisting of 25 wt% Illinois #6 - Burning Star mine coal in creosote oil are collected. The coal

contains 10.1% ash on a moisture-free basis. The following data were obtained from the filtration determinations:

<u>Solvent</u>	<u>Tetrahydrofuran</u>	<u>Ethyl Acetate</u>	<u>Pentane</u>
weight of sample	5.643 g	5.878 g	5.784 g
weight of sample	0.238 g	0.469 g	1.004 g

$$\text{THF conv.} = \frac{(5.643)(0.2500) - .238}{(5.643)(0.2500)(1-0.101)} \times 100 = 92.5\%$$

$$\text{EA conv.} = \frac{(5.878)(0.25) - 0.469}{(5.878)(0.25)(1-0.101)} \times 100 = 75.7\%$$

$$\text{C}_5 \text{ conv.} = \frac{(5.784)(0.2500) - 1.004}{(5.784)(0.2500)(1-0.101)} \times 100 = 34.0\%$$

Figure A-1- Microfiltration unit

Appendix B

Method for Calculating Percentage Organic Sulfur Removal

Since we are really interested in the ability of the catalyst to affect sulfur removal, a method is needed to calculate the percent sulfur removal. However, the sulfur is present as both organic sulfur associated with organic compounds and inorganic sulfur associated with insoluble mineral matter. Because of the solid separation step, only organic sulfur will remain in the centrifuged liquid product (CLP). By making certain assumptions, the percent organic sulfur in the CLP that would have been present if no organic sulfur removal occurred can be calculated as a function of coal conversion. These assumptions are the following:

1. All unreacted coal and mineral matter are removed in centrifugation step.
2. CLP contains no dissolved H_2S .
3. One can neglect the small weight change due to addition of H_2 to liquid and loss of light hydrocarbon and acid gases.
4. All inorganic sulfur will be excluded from centrifuged liquid product.
5. The ratio of inorganic to organic sulfur in each fraction of liquified coal is not a function of conversion; that is, the last fraction of coal liquified has the same organic/inorganic sulfur content as the first fraction.
6. No organic sulfur heteroatoms are removed by the conversion and separation process.

The above hypothetical process can be assumed to calculate the percent sulfur for centrifuged liquid products as a function of conversion level. Such a process does not truly exist, since organic sulfur is removed during the thermal reactions and/or catalytic reactions due to indigenous "mineral matter" catalysis during thermal liquefaction runs. The calculations given in Table B-1 show that for 100% conversion,

our standard test mixture contains 1.69% total sulfur (1.01% present as organic sulfur and 0.68% as inorganic sulfur). The sulfur content of the centrifuged liquid product obtained for the above hypothetical process as a function of conversion level is given in Table B-2 for a reaction slurry having a 1/1 solvent/coal ratio. The percent organic sulfur removal effected during a run is then given by

$$\% \text{ Organic Sulfur Removal} = \frac{\% \text{ Sulfur in CLP} - \% \text{ Sulfur (calc)}}{\% \text{ Sulfur (Calc)}} \times 100$$

Table B-1: Calculation of Sulfur Content in Liquefaction Product

	Illinois #6	Panasol	Raw Product	CLP
H	4.7	7.9	6.30	6.68
C	70.8	92.1	81.41	86.41
N	1.3	-	0.65	0.69
O	9.7	-	4.85	5.15
S _o	2.02	-	1.01	1.07
S ₁	1.37	-	0.68	-
Ash	10.2	-	5.10	-
H/C	0.802	1.022	0.922	0.922

- ASSUMPTIONS:
1. No addition of hydrogen during reaction
 2. Neglect gas make
 3. Hydrogen sulfide is not retained in CLP
 4. All mineral matter is removed in centrifugation step

Table B-2: Maximum Possible Sulfur Contents for Centrifuged
Liquid Product Obtained from Autoclave Screening Runs as a
Function of Percent Coal Conversion

<u>% Conversion</u>	<u>% Sulfur</u>
100	1.07
90	1.01
80	0.95
70	0.87
60	0.79
50	0.70
40	0.60
30	0.48
20	0.34
10	0.19
0	0

C-1

APPENDIX C

**THE USE OF FUNDAMENTAL CONCEPTS IN CATALYST AGING TO INCREASE CATALYST
UTILIZATION DURING COAL LIQUEFACTION, STEAM REFORMING,
AND OTHER CARBON-FORMING REACTIONS**

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ABSTRACT

A theoretical treatment of catalyst aging based on the shrinking core model is presented. An analogy between pore mouth poisoning and carbon burnoff from a sphere is invoked but modified by a factor which accounts for an additional resistance to the diffusion of reactants through clogged pores. The results indicate that larger diameter catalysts tend to reduce the rate of poisoning, and under certain conditions, a dramatic increase in the amount of feed processed per unit mass of catalyst can be realized. The maximum catalyst diameter recommended for practical applications varies with the extent of deactivation. Experimental data for reactions involving a synthesized coal gasification product with different diameter catalysts are presented to illustrate the validity of the model. Preliminary experimental data also indicate that the model's predictions are applicable to catalytic coal liquefaction.

INTRODUCTION

Catalyst deactivation is a serious problem in many catalytic reactions, especially catalytic coal conversion processes. Feedstocks which contain undesirable components such as carbon-forming precursors and metals or metallic oxides, or form undesirable intermediate reactions products, can adsorb on the catalyst surface and cause a rapid decline in catalyst activity. When this occurs, the life of the catalyst is reduced substantially, and therefore the catalyst must be replaced more often. As a result, the economics of the catalytic process become less favorable.

Several methods can be employed to enhance catalyst utilization in processes where rapid catalyst deactivation is likely. The first approach is to formulate inexpensive disposable catalysts, which would be prepared as a finely divided powder. These catalysts essentially expose their entire surface area for reaction in order to obtain maximum effectiveness from its active components. However, these catalysts would be expected to poison quickly. A second approach is to develop highly selective, regenerable catalysts which have a long on-stream life and can be recovered, regenerated, and reused in the process. In either approach, the development of a high efficacy catalyst (where efficacy is defined as mass of feed converted/unit mass of catalyst) can minimize catalyst costs.

The physical properties of the catalyst will play a very important role in determining the efficacy of the catalyst. Both porosity and pore size distribution have been cited frequently as important parameters affecting chemical reactions and catalyst life. Often in catalysis, intraparticle diffusion is the rate-limiting step in a chemical reaction. Under this condition, the rate of reaction increases with decreasing catalyst diameter and is immediately discernible to the experimenter. However, the catalyst diameter can also be seen to have an opposite influence on the rate of poisoning. This has been more or less ignored except for some excellent theoretical work by Masamune and Smith (1966) and Lee and Butt (1973) which predicts the kind of results reported in

this work. This neglect is due to the fact that although the reaction rate increases with decreasing diameter, the rate of poisoning also increases but is less obvious except through the use of extensive catalyst aging studies.

In most cases, one is left with the option of optimizing the rate of reaction or catalyst life, but one cannot optimize both simultaneously. It is by careful examination that an economic balance can be achieved which recognizes that the trade-off between high rates of reaction and long catalyst life does not necessarily lie with smaller and smaller diameter catalysts unless disposable catalysts are utilized.

Hegedus and Summers (1977) have presented a theoretical development of catalyst poisoning with consideration to the poisoning reactions where interparticle mass transfer to the catalyst surface is the rate limiting step. Two opposing criteria pertaining to catalyst life and activity that must be satisfied simultaneously were presented. They further concluded that a deeper penetration of active metal (equivalent to a lower effectiveness factor) resulted in higher catalyst efficacy (moles of hydrocarbon converted/mass of catalyst) before poisoning becomes detrimental. Much of this work was done with thin layers (39 to 103 micrometers) of catalyst components in a bulk mass transfer controlled regime.

Masamune and Smith (1966) have mathematically analyzed the poisoning of monofunctional pelleted catalysts. These authors concluded that (1) catalysts with relatively large intraparticle diffusion resistance lost activity at a slow rate even though their initial activity is low; (2) a catalyst with high diffusion resistance will be more stable than one with low resistance but a high initial activity; and (3) it is possible that optimum reactor design could require a catalyst with significant diffusion resistance. In another study, Lee and Butt (1973) theoretically analyzed parallel and series fouling, and the activity and selectivity of bifunctional catalysts. They concluded "In poisoning (including multifunctional systems), there is an optimum level of diffusional resistance for extending the total life of the catalyst; small transport

limitations, while leading to higher initial activity, allow more rapid poisoning and result in shorter useful life. The degree of diffusional resistance for maximum productivity and that for maximum life are not generally the same and some compromise is necessary in individual cases."

The following discussion is limited to the region of catalyst sizes commonly formulated for coal hydroliquefaction and reforming of gasification products (i.e., 90% 1:1 CO/H₂ and 10% mono and polycyclic aromatics). In these reactions, intraparticle diffusion rather than interparticle mass transfer tends to be the controlling mechanism.

THE MECHANISM OF CATALYST AGING

The catalyst efficacy concept used in the present development is defined as the mass of reactant processed per unit mass of catalyst and is described mathematically by

$$E = \int_0^L \frac{1}{w_c} r dt = \int_0^L \eta k_d C^n dt \quad (1)$$

where nth order kinetics are assumed.

An expression for the catalyst life L can be obtained by invoking the analogy between carbon burnoff from a spherical particle and deactivation by pore mouth poisoning (Weisz and Goodwin, 1963; Satterfield, 1970). This analogy is illustrated below. For carbon burnoff, the rate is given by

$$\frac{1}{2} [1 - Y^{2/3}] - \frac{1}{3} (1 - Y) = \frac{D_{eff} C_s t v}{R^2 C_c} \quad (2)$$

-carbon burnoff

whereas the rate of catalyst poisoning by the pore mouth mechanism is

$$\frac{1}{2} [1 - (1 - \alpha)^{2/3}] - \frac{1}{3} \alpha = \frac{D_{eff} C_{pc} t v}{R^2 C_{PFS}} \quad (3)$$

-poisoned pores

Solving equation (3) for t and combining all constant terms, the following expression for the catalyst life in terms of α , the fraction of catalyst poisoned, can be obtained:

$$t = L = \frac{R^2}{2D_{\text{eff}}} K_0 \left\{ \frac{1}{2} [1 - (1-\alpha)^{2/3}] - \frac{2}{3}\alpha \right\} \quad (4)$$

Basing the effective diffusivity on the Stokes-Einstein equation (Satterfield, 1970), the catalyst life is expressed for liquid as

$$L = \left(\frac{V_B^{1/3} \mu \tau}{1.05 \times 10^{-9} T \theta} \right) \left(\frac{K_0 R^2}{2} \right) \left\{ \frac{1}{2} [1 - (1-\alpha)^{2/3}] - \frac{2}{3}\alpha \right\} \quad (5)$$

Equation (5), however, will not be used further in this development since catalysts with varying porosities will not be compared. At present, the technique discussed will be limited to catalysts with similar chemical and physical characteristics but with different particle diameters. Gaseous systems can be treated analogously.

Expressing the deactivation rate constant, k_d , in equation (1) as

$$k_d = k_0 (1-\alpha) \quad (6)$$

and performing a change of variables by using equation (4) so that the integral in equation (1) is in terms of α rather than t , one obtains the following expression for the catalyst efficacy:

$$E = \int_0^{\alpha} \frac{1}{3} \eta k R K_0 C^n (1-\alpha) \left[(1-\alpha)^{-1/3} - 1 \right] d\alpha \quad (7)$$

Integrating the above equation (assuming η is not a function of α) and evaluating it between the limits specified, one obtains

$$E = \frac{1}{30} \eta K R^2 k_0 C^n \left[5(1-\alpha)^2 - 6(1-\alpha)^{5/3} + 1 \right] \quad (8)$$

The catalyst replacement rate, CRR, which is the inverse of the efficacy (i.e., $CRR = 1/E$), can be used for comparing two catalysts as shown below:

$$\frac{(CRR)_1}{(CRR)_2} = \frac{E_2}{E_1} = \frac{\left[\eta_2 R_2^2 \left[5(1-\alpha_2)^2 - 6(1-\alpha_2)^{5/3} + 1 \right] \right]}{\left[\eta_1 R_1^2 \left[5(1-\alpha_1)^2 - 6(1-\alpha_1)^{5/3} + 1 \right] \right]} \quad (9)$$

For a spherical catalyst and a first order reaction, the effectiveness factor (Smith, 1970) is given by

$$\eta = \frac{1}{\phi_s} \left[\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right] \quad (10)$$

For values of $\phi_s \geq 5$ and using the mathematical definition of the Thiele modulus, equation (10) reduces to

$$\eta \approx \frac{1}{\phi_s} = \frac{1}{R} \sqrt{\frac{D_{eff}}{k}} \quad (11)$$

Comparing the effectiveness factors of the same catalyst with differing diameters, one obtains

$$\frac{\eta_1}{\eta_2} = \frac{1/R_1}{1/R_2} = \frac{R_2}{R_1} \quad (12)$$

Substituting the above into equation (9) yields

$$\frac{(CRR)_1}{(CRR)_2} = \frac{E_2}{E_1} = \frac{R_2 K_{a_2}}{R_1 K_{a_1}} \quad (13)$$

where

$$K_{\alpha_1} = 5(1 - \alpha_1)^2 - 6(1 - \alpha_1)^{5/3} + 1 \quad (13)$$

From the above development, based on the assumptions presented, it can be seen that the greater the catalyst radius, the lower the catalyst replacement rate. A similar development can also be performed for other types of geometry.

For the first order isothermal reaction, Wheeler (1951) mathematically analyzed the pore mouth progressive poisoning of cylindrical catalysts pores (Hill, 1977). His results showed that the fraction of initial catalyst activity, F , remaining in pore after poisoning (i.e., observed reaction rate in the poisoned pore divided by the rate in a clean pore) is given by

$$F = \frac{\tanh (1 - \alpha) \phi_L}{\tanh \phi_L} \left\{ \frac{1}{1 + \alpha \phi_L \tanh (1 - \alpha) / \phi_L} \right\} \quad (14)$$

For values of the pore diameter much smaller than the catalyst radius, $\phi_L = \phi_s$. Substituting Equation (11) for ϕ_s , one obtains

$$F = \frac{\tanh (1 - \alpha) / \eta}{\tanh (1 / \eta)} \left\{ \frac{1}{1 + \frac{\alpha}{\eta} \tanh (1 - \alpha) / \eta} \right\} \quad (15)$$

Figure 1 presents a plot of the fraction of activity remaining, F , versus the fraction of catalyst poisoned, α , for various values of the effectiveness factor and is similar to that given by Satterfield (1970). Only when the effectiveness factor is equal to one does F equal $1 - \alpha$. For the realistic case in which $\eta \neq 1.0$, an expression can be developed utilizing an efficiency factor for the actual catalyst surface utilization. When comparing two catalysts of different diameters ($\eta_1 \neq \eta_2$) on the basis of efficiency of surface utilization, it must be done at equal fractions of activity remaining ($F_1 = F_2$). Because the effectiveness factors of the two catalysts are different but the fractions of remaining activity are equal, it follows from equation 15 that the fraction of internal surface of each catalyst poisoned will be different (i.e., $\alpha_1 \neq \alpha_2$). Equation

(3) is the rate expression for the fraction of catalyst poisoned and is the correction or efficiency factor which must be used in the pore mouth poisoning model. This efficiency factor is defined as the ratio of K_{α_i} for the catalyst with $\eta \neq 1$ to K_{α_0} for the same catalyst with $\eta = 1$.

Table 1 presents a relative comparison of the efficiencies of surface utilization and the efficacies for various catalyst radii for activity losses of 25% ($F = 0.75$), 67% ($F = 0.33$), 80% ($F = 0.20$), and 90% ($F = 0.10$). In this table, the values of the relative radius, R , are assumed to be proportional to $1/\eta$. The results indicate that a higher catalyst efficacy can be obtained if a less active, larger diameter catalyst is used. Catalysts with $\eta = 1$ result in higher reaction rates but unfortunately may be poisoned relatively faster than less efficient catalysts with $\eta < 1$. Experiments with various catalyst diameters can be performed to test this hypothesis.

In assuming that the relative values of the radii are inversely proportional to the values of η , a conservative estimate has been made. Actual values of η versus catalyst diameter have been obtained experimentally by Allen et al. (1972). The relative radii calculated from these data are compared in Table 2 with those which would have been used in the present study, given their effectiveness factors. As can be seen, the assumed values of R_R are lower than those from actual data and therefore the values of catalyst surface utilization and efficacy are conservative. Table 3 shows a relative comparison of the efficacies and the efficiency of surface utilization using the η versus R data obtained experimentally by Allen et al. (1972). The values of α for the smallest diameter catalyst (i.e., the catalyst with the largest effectiveness factor) have been assumed to be equal to those for a catalyst with $\eta = 1$. Comparing these results with those in Table 1, one can see that the diameter effect is even greater than for the conservative assumption used to derive Table 1.

Figure 2 presents a plot of the catalysts efficacies in Table 3 versus the effectiveness factor at various levels of deactivation. As shown, for a given level of deactivation,

there is an optimum effectiveness factor, hence catalyst diameter, which maximizes the efficacy of a particular catalyst. This maximum also occurs at various effectiveness factors for each value of F .

Therefore, one must be careful as to the extent to which the catalyst is allowed to deactivate in the reactor. The larger catalyst pellet may not result in increased efficacy if the catalyst is removed while the fraction of initial activity remaining is still high. A larger catalyst particle will also result in lower reaction rates demanding reactors of increases size to maintain a specified throughput. However, as in many cases, if the catalyst is changed when F is small ($0.01 < F < 0.5$), then significant improvements in catalyst usage are obtainable.

APPLICATIONS

Ebullating Bed Reactors

For ebullating bed reactors in which fresh catalyst is continually added and aged catalyst continually removed, the values of α are considered constants and equal to the value of the removed (deactivated) catalyst. This is analogous to a CSTR wherein the catalyst can be treated as one of the reactants with an exit "concentration" of F_{exit} corresponding to the particular α_{exit} of the removed catalyst.

From particle to particle, the value of α is not constant, since the age of each particle in the reactor is determined by a residence time distribution (RTD) for a backmixed reactor. At steady state, the distribution of the α values of the removed catalyst does not vary with time. If the reactor is operating in a CSTR mode where catalyst is continually added and removed, the diameter effect will be a strong function of the fraction of catalyst activity remaining after removal of used catalyst, this fraction of remaining activity being dependent on the catalyst replacement rate.

For a CSTR operation in which the catalyst is not removed and replenished continually, the values of α will not be those of the exiting catalyst but will be a mean

value averaged over the period in which the initial catalyst activity, F_0 , deteriorates to the final catalyst activity, F_n , just before the catalyst is replaced. The mean values $\bar{\alpha}$, can be calculated via a numerical integration for given values of η and fraction of initial activity remaining, F_n . In the range of interest, the former, α , depends on diameter, while the latter, F_n , is generally dependent on the experimenter's program. Numerical integration is obtained by applying equation (16)

$$\bar{\alpha} = \frac{1}{F_0 - F_n} \sum_{i=1}^n \left\{ \left[\frac{\alpha(F_{i+1}) + \alpha(F_i)}{2} \right] (F_i - F_{i+1}) \right\} \quad (16)$$

Various incremental $\alpha(F_i)$ values are assumed, the F_i 's calculated, and the indicated summation performed to calculate $\bar{\alpha}$. The function, $F(\alpha, \eta)$ is that of equation (15). Tabulated values of F_n for selected η 's and α 's are presented in Table 4, for a fresh catalyst with an initial activity of one. These results are also graphically displayed in Figure 3. Similar graphs can also be constructed for regenerated catalysts, which possess only a portion of the activity of the fresh catalysts. Figure 4 is such a graph for a regenerated catalyst with 90% of its original activity.

In catalytic coal liquefaction processes such as the H-COAL process, the catalyst loses 50% of its original activity in less than 100 hours, yet it remains in the reactor on the average of about 1200 hours. Under these conditions, the catalyst can be assumed to be completely deactivated, and the diameter effect illustrated in Figure 2 can be fully utilized. To illustrate this effect even further, Table 5 presents the efficacy ratio of a 1/8 in. catalyst to a 1/16 in. catalyst and a 3/16 in. catalyst to a 1/16 in. catalyst at various levels of deactivation. As shown, the larger catalysts are better in all cases except that in which the catalyst is removed with 75% of its activity still remaining. The value of E_R also approaches a maximum of R_2/R_1 as the fraction of activity remaining tends to zero.

Preliminary aging data have recently been obtained in a continuous coal liquefaction unit to test the validity of the theory in catalytic coal liquefaction. American Cyanamid HDS-1442A (1/16 in.) and HDS-1442B (1/32 in.) catalysts were evaluated. The data indicate that although the initial activity of the smaller diameter catalyst was higher (as expected), it deactivated much more rapidly than did the larger catalyst. After approximately 50 hours on stream, the activity of the larger diameter catalyst was higher and remained that way throughout the remainder of the test, which lasted approximately 100 hours. The ratio of the activities of the larger to the smaller diameter catalyst actually increased continuously with time on stream. Further details will be the subject of a future publication, following additional evaluations with other catalysts.

Packed Bed Reactors

For a packed bed reactor with reaction occurring at constant space velocity, SV, as the reaction zone progresses through the bed, all of the catalytic material upstream of the reaction zone can be considered poisoned, $F \approx 0$, while that downstream of the reaction zone has catalyst activity $F \approx 1$. Considering the case of nearly complete poisoning (i.e., $\alpha \geq 0.8$), the catalyst efficacy is given by equation (13) with $K_{\alpha_2} \approx K_{\alpha_1}$. Therefore,

$$E_2/E_1 \approx \frac{R_2}{R_1} \quad (17)$$

For a packed bed reactor, the efficacy is indirectly related to the time it takes the reaction zone to progress a specified length of the reactor. Thus for a constant flow operation with constant conversion and first order kinetics, the efficacy is directly proportional to the time it takes the reaction zone to traverse a specified length of the reactor.

Experimental data for a catalytic reaction occurring in a packed bed reactor have been obtained to verify the model presented. A synthetic coal gasification product

consisting of 90% CO/H₂ (1:1 mole ratio) and 10% mono and polycyclic aromatics was reacted over 1/8 in. and 1/16 in. diameter steam reforming catalysts. The aromatic components were added to accelerate carbonization poisoning. The space velocity was held constant at 10,000 hr⁻¹. The times for the reaction zone to traverse 50% of the catalyst bed are presented in Table 6. As shown, the experimental results appear to approximate the theoretical predictions. Realistically, however, the catalyst upstream of the reaction zone may not be completely deactivated (i.e., $F \neq 0$); instead it may still have some remaining activity (i.e., say $F \approx 0.1$). In this case the agreement between the experimental results and the theoretical predictions would be improved.

CONCLUSIONS

As shown, depending upon the extent of catalyst deactivation allowed, larger diameter catalysts may result in longer catalyst life. Commercial steam reforming catalysts, for example, have been empirically shown to be optimum when $\eta \approx 0.1$ (i.e., diameter = 5/8 in.). The model has also been shown to be applicable in ebullating bed, CSTR, and fixed bed reactors. Improvements in catalytic life will affect processes such as the H-COAL coal liquefaction process, steam reforming processes, and other processes for reforming coal gasifier effluents.

To illustrate how the results of the proposed model can affect process economics, consider a commercial size H-COAL process with a capacity of 50,000 tons of coal/day. Under present conditions, one pound of catalyst is required per ton of coal liquefied; therefore, 50,000 lbs. of catalyst is deactivated each day. Assuming a 300 day operating year and estimating catalyst costs in 1985 to be \$4.50 to \$6.00/lb., a 50% improvement in catalyst life can result in a savings of \$34 to \$45 million/yr/plant. Partly offsetting this saving will be the added capital cost of larger reactors, but catalyst costs are inflationary while capital, once spent, is not. Additional consideration in the analyses must also be given to the fact that current molybdenum supplies may not be available to maintain an estimated ten such plants plus the requirements of the steel industry, unless catalyst recovery and regeneration is possible.

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NOMENCLATURE

C_c	Initial concentration of carbon-free surface sites
C_s	Bulk concentration of carbon formers in the liquid or gas
C_{PFS}	Initial concentration of poison-free surface sites/g catalyst
C_{pc}	Concentration of poison precursor in coal
C	Reactant concentration
CRR	Catalyst replacement rate
D_{eff}	Effective diffusivity
E	Efficacy of catalyst use (amount of reactant converted per unit weight of catalyst)
E_R	Ratio of efficacies for two catalyst sizes and also = $R_R (K\alpha/K\alpha_o)$
F, F_i, F_n	Fraction of catalyst activity
F_o	Initial catalyst activity
k_o	Kinetic rate constant for fresh catalyst
k_d	Kinetic rate constant for deactivated catalyst
K	Constant equal to $\frac{K_o}{D_{eff}}$
K_o	Constant equal to $\frac{C_{PFS}}{vC_{pc}}$
$K\alpha_i$	Defined by equation (13)
$K\alpha_o$	The value of $K\alpha_i$ at $\eta = 1.0$
L	Catalyst life
n	Reaction order
r	Reaction rate
R	Catalyst radius
R_R	Relative radius, normalized to the catalyst which has $\eta = 1$
S_V	Space Velocity

t	Time
T	Temperature
V_B	Molecular volume
W_c	Catalyst weight
Y	Fraction of initial carbon remaining after time t (during burn-off)

Subscripts

L	Cylindrical Pore
s	Sphere

Greek Letters

α α_i	Fraction of catalyst poisoned
η	Effectiveness factor
θ	Catalyst porosity
μ	Viscosity
ν	Stoichiometer coefficient
τ	Catalyst tortuosity
ϕ	Thiele Modulus

TABLE 1. Relative comparison of efficacies for various catalyst radii assuming $R \propto 1/\eta$.

$F = 0.75$					
η	R_R	α	$K\alpha$	$K\alpha/K\alpha_0$	E_R
1.0	1.0	0.250	0.0978	1.0	1.0
0.70	1.429	0.192	0.0586	0.5993	0.857
0.50	2.0	0.156	0.0391	0.3994	0.799
0.35	2.857	0.115	0.0214	0.2193	0.627
0.25	4.0	0.083	0.0113	0.1151	0.461
0.20	5.0	0.067	0.0074	0.0753	0.377
0.10	10.0	0.033	0.0018	0.0184	0.184
$F = 0.33$					
1.0	1.0	0.670	0.5989	1.0	1.0
0.70	1.428	0.687	0.6241	1.0419	1.488
0.50	2.0	0.677	0.6093	1.0173	2.035
0.35	2.857	0.618	0.5229	0.8731	2.494
0.25	4.0	0.492	0.3498	0.5840	2.336
0.20	5.0	0.399	0.2379	0.3972	1.986
0.10	10.0	0.200	0.0635	0.1060	1.060
$F = 0.20$					
1.0	1.0	8.0	0.7896	1.0	1.0
0.70	1.428	0.838	0.8424	1.0668	1.523
0.50	2.0	0.852	0.8611	1.0905	2.181
0.35	2.857	0.857	0.8676	1.0988	3.139
0.25	4.0	0.829	0.8329	1.0548	4.219
0.20	5.0	0.760	0.7319	0.9269	4.634
0.10	10.0	0.400	0.2390	0.3027	3.027
$F = 0.10$					
1.0	1.0	0.90	0.9207	1.0	1.0
0.70	1.428	0.929	0.9522	1.0341	1.477
0.50	2.0	0.941	0.9638	1.0467	2.093
0.35	2.857	0.952	0.9735	1.0573	3.021
0.25	4.0	0.959	0.9792	1.0635	4.254
0.20	5.0	0.961	0.9985	1.0844	5.422

Table 2. Comparison of η versus R obtained experimentally with those assumed in the present study.

η	<u>Actual diameter</u>	<u>Relative radius (experimental)</u>	<u>Relative radius, $R^{(1)}$ (assuming $R \propto 1/\eta$)</u>
0.954	0.0175	1.0	1.0
0.884	0.0395	2.26	1.13
0.699	0.0671	3.83	1.43
0.394	0.125	7.14	2.54
0.279	0.1875	10.7	3.58
0.216	0.25	14.3	4.63

(1) Relative radius is calculated relative to the catalyst with the largest effectiveness factor.

Table 3. Relative comparison of efficacies for various catalyst radii

F = 0.75						
η	Actual diameter	R_R	α	$K\alpha$	$K\alpha/K\alpha_0$	E_R
0.954	0.175	1.0	0.25	0.0978	1.0	1.0
0.884	0.0395	2.26	0.211	0.0705	0.7201	1.627
0.699	0.0671	3.83	0.192	0.0586	0.5993	2.295
0.394	0.125	7.14	0.128	0.0265	0.2708	1.934
0.279	0.1875	10.71	0.0930	0.0141	0.1442	1.544
0.216	0.25	14.29	0.072	0.0085	0.0869	1.241
F = 0.5						
0.954	0.0175	1.0	0.500	0.3601	1.0	1.0
0.884	0.0395	2.26	0.487	0.3434	0.9535	2.155
0.699	0.0671	3.83	0.472	0.3244	0.9008	3.450
0.394	0.125	7.14	0.370	0.2066	0.5737	4.096
0.279	0.1875	10.71	0.276	0.1183	0.3286	3.520
0.216	0.25	14.29	0.216	0.0737	0.2047	2.926
F = 0.33						
0.954	0.0175	1.0	0.67	0.5990	1.0	1.0
0.884	0.0395	2.26	0.685	0.6211	1.0370	2.344
0.699	0.0671	3.83	0.687	0.6241	1.0419	3.991
0.394	0.125	7.14	0.646	0.5637	0.9411	6.719
0.279	0.1875	10.71	0.538	0.4106	0.6855	7.342
0.216	0.25	14.29	0.430	0.2734	0.4564	6.522
F = 0.2						
0.954	0.0175	1.0	0.80	0.7896	1.0	1.0
0.884	0.0395	2.26	0.829	0.8301	1.0513	2.376
0.699	0.0671	3.83	0.839	0.8437	1.0685	4.092
0.394	0.125	7.14	0.858	0.8689	1.1004	7.857
0.279	0.1875	10.71	0.845	0.8518	1.0787	11.553
0.216	0.25	14.29	0.791	0.7768	0.9837	14.058
F = 0.1						
0.954	0.0175	1.0	0.90	0.9207	1.0	1.0
0.884	0.0395	2.26	0.921	0.9439	1.0252	2.317
0.699	0.0671	3.83	0.929	0.9522	1.0341	3.961
0.394	0.125	7.14	0.949	0.9709	1.0545	7.529
0.279	0.1875	10.71	0.957	0.9776	1.0617	11.371
0.216	0.25	14.29	0.961	0.9807	1.0651	15.221

Table 4. Values of F_n , α , and η for a fresh catalyst with initial activity of one

$\frac{\eta}{1.0}$	$\frac{F_n}{1.0}$	$\frac{\alpha}{0.00}$	$\frac{\eta}{0.3}$	$\frac{F_n}{1.0}$	$\frac{\alpha}{0.00}$
1.0	1.0	0.00	0.3	1.0	0.00
1.0	0.70	0.15	0.3	0.750	0.045
1.0	0.5	0.25	0.3	0.500	0.116
1.0	0.25	0.375	0.3	0.300	0.210
1.0	0.1	0.45	0.3	0.207	0.273
1.0	0.0	0.5	0.3	0.055	0.378
0.5	1.0	0.00	0.2	1.0	0.00
0.5	0.960	0.010	0.2	0.769	0.028
0.5	0.791	0.065	0.2	0.50	0.078
0.5	0.699	0.90	0.2	0.254	0.167
0.5	0.55	0.151	0.2	0.150	0.231
0.5	0.462	0.195	0.2	0.067	0.302
0.5	0.370	0.246	0.1	1.0	0.00
0.5	0.304	0.287	0.1	0.714	0.018
0.5	0.211	0.345	0.1	0.50	0.039
0.5	0.101	0.412	0.1	0.250	0.085
0.5	0.038	0.448	0.1	0.10	0.156

Table 5. Comparison of catalyst efficacy for 1/16 in. and 3/16 in. catalysts.

<u>Fraction of Catalytic Activity Remaining</u>	<u>Efficacy Ratio, E_R</u>	
	<u>1/8 in. vs 1/16 in.</u>	<u>3/16 in. vs. in.</u>
0.75	0.84	0.67
0.50	1.19	1.02
0.33	1.68	1.84
0.20	1.92	2.82
0.10	1.90	2.87

(1) Efficacy data obtained from Table 3 using values obtained for catalyst diameters of 0.0671 in., 0.125 in., and 0.1875 in.

Table 6. Results from packed bed reactor studies.

<u>Catalyst Diameter</u>	<u>Average Catalyst Life (hr.)</u>	<u>No. of Runs</u>	η <u>(estimated from Table 2)</u>	<u>Efficacy (assuming $F = 0$)</u>	
				<u>Theoretical</u>	<u>Experimental</u>
1/16 in.	767 $\pm$ 120	3	0.699	2	1.72
1/8 in.	1320 $\pm$ 80	2	0.394		

TITLES OF FIGURES

- Figure 1: Fraction of Catalyst Activity Remaining as a Function of the Fraction of Catalyst Poisoned and the Effectiveness Factor.
- Figure 2: Final Activity as a Function of the Average Fraction of Catalyst Poisoned at Various Effectiveness Factors for a Fresh Catalyst with Initial Activity of One.
- Figure 3: Final Activity as a Function of the Average Fraction of Catalyst Poisoned at Various Effectiveness Factors for a Regenerated Catalyst with 90% of Initial Activity.
- Figure 4: Final Activity as a Function of the Average Fraction of Catalyst Poisoned at Various Effectiveness Factors for a Regenerated Catalyst with 80% of Initial Activity.

Figure 1.—Fraction of catalyst activity remaining as a function of the fraction of catalyst poisoned and the effectiveness factor.

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Figure 2.- Comparison of efficacies at various catalyst effectiveness factors and extents of deactivation.

Figure 3.-Final activity as a function of the average fraction of catalyst poisoned at various effectiveness factors for a fresh catalyst with initial activity of one.

Figure 4.-Final activity as a function of the average fraction of catalyst poisoned at various effectiveness factors for a regenerated catalyst with 90 % of initial activity.

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