

EFFECT OF COAL MINERALS ON REACTION RATES DURING COAL LIQUEFACTION

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Introduction

Coal minerals represent a readily available, abundant, inexpensive source for catalytic agents for use in accelerating liquefaction and hydrodesulfurization reactions in coal conversion processes. Experimental evidence of the catalytic effect of coal minerals on hydrogenation has been reported.¹ In fact, there is a patented coal conversion process in which mineral residue is recycled because of its catalytic activity.² Yet the benefits of coal mineral catalysis has not been well established. The purpose of this paper is to demonstrate that certain coal minerals catalyze the hydrogenation and hydrodesulfurization of creosote oil, a coal-derived solvent used as a start-up solvent in the solvent refined coal (SRC) process; to show that, by accelerating hydrogenation of process solvent such as creosote oil, coal minerals catalysis accelerates indirectly the rate of liquefaction of coal solids; and to provide better insight as to the process advantages and disadvantages of coal mineral catalysis - more specifically, removal of coal minerals prior to hydrogenation/hydrodesulfurization, or recycle of coal mineral residue.

Experimental

Reagents and Materials. Creosote oil (Table 1) used in these experiments was obtained from Southern Services, Inc., and is used as a start-up solvent at the SRC pilot plant located at Wilsonville, Alabama. Southern Services, Inc., obtained the oil, creosote oil 24-CB, from the Allied Chemical Company. The oil has a carbon-to-hydrogen ratio of 1.25 (90.72% C and 6.05% H), a specific gravity of 1.10 at 25°C, and a boiling point range of 175° to 350°C. Kentucky No. 9/14 coal mixture was crushed; and the -170 mesh fraction - having the screen analysis shown in Table 2, and the elemental analysis in Table 3 - was used in the experiments. Table 4 lists specifications of the individual coal minerals studied. Hydrogen and nitrogen gases were the 6000 psi grade supplied by Linde. All coal was dried overnight at 100°C and 25 inches Hg vacuum before use.

Procedures. Basically four different types of experiments were performed: 1) catalyst screening, 2) recycle of mineral residue, 3) hydrogenation and hydrodesulfurization of demineralized coal, 4) hydrogenation and hydrodesulfurization using prehydrogenated solvent.

1. Catalyst Screening. Catalyst or mineral preparation consisted of grinding, followed by screening to the respective size. Depending on the hardness of the catalyst, either a diamond grinder and/or a mortar and pestle was used. For each run: the charge consisted of 15 gms of catalyst, 100 gms of creosote oil, and an initial hydrogen atmosphere of 3000 psig.; reaction was carried out for two hours at 425°C and a stirrer setting of 2000 rpm. A heat-up rate of about 12 to 20°C per minute was used - requiring only about three minutes for heat-up within the zone in which significant reaction occurs³ (above 370°C) and a total heat-up time of about 30-35 minutes. Prior to heat-up 400 psig of hydrogen was charged to the reactor (a 300 cc magnedrive autoclave from Autoclave Engineers, Inc.) and at reaction temperature more hydrogen was added to attain the desired initial hydrogen pressure of 3000 psig. Reaction temperature (425°C) was held constant within ±3°C.

Throughout each run total pressure was recorded periodically (Figure 1); and after exactly two hours of reaction, a gas sample was collected, and the autoclave contents were quenched to below 200°C within five minutes. After allowing the catalyst to settle for one hour, a liquid sample was collected for sulfur analysis.

Between consecutive catalysts screening runs, blank runs, having no catalyst present, were made to eliminate any "memory effect." As shown in Figure 2 about three blank runs were required following a run made with the Co-Mo-Al catalyst, which - having the highest catalytic activity of those agents considered - exerted the strongest memory effect.

2. Recycle of Mineral Residue. The reaction conditions used for all of these runs were 400°C, a stirrer setting of 2000 rpm, and an initial hydrogen pressure of 2000 psig. A 3:1 solvent-to-coal weight ratio (40 gm. of coal, 120 gm. of creosote oil) was used. Two runs were made to establish a base-line for comparison. Once completed, two more runs, each having a charge with a higher concentration of mineral matter, were made: In the first, solid residue from one of the base-line runs was added; and in the second, solid residue from the run with a higher mineral matter concentration was added, increasing further the mineral matter concentration. For each run, total pressure was periodically monitored (Figure 3); and final hydrogen partial pressure was measured. Final cresol soluble yields, y, were also determined (Table 5) where:

$$y = \frac{C - (R - A)}{C(1 - M)} \times 100$$

And C is the charge of moisture free coal; R, the recovered insoluble residue; M, the fraction of mineral matter in dry coal (0.12 for Kentucky No. 9/14 mixture); A, the mass of residue added.

To insure that solid residue was free of solvent prior to its use, after being filtered from the reaction mixture, it was washed with hot cresol and benzene, with clear benzene passing through the filter in the final wash.

Hydrogenation and Hydrodesulfurization of Demineralized Coal. Coal was slurred with water and partially demineralized by passing it through a high intensity magnetic separator - reducing its ash content by 64 per cent (as determined by ASTM D-271) and its total sulfur content by 25 per cent as determined by a Leco sulfur analyzer. The partially demineralized coal was then dried overnight under 25 inches Hg vacuum at 100°C; slurred with recycle solvent in a 3:1 solvent-to-

coal proportion; and reacted at 410°C, 1000 psig of initial hydrogen pressure, and a 1000 rpm stirrer setting for reaction times of 15, 30, 60, and 120 minutes. At the end of each reaction, a liquid sample of reaction product was collected; the total sulfur content and cresol soluble yield (Figure 4b) was determined using a Leco sulfur analyzer and Soxhlet extraction, respectively. Assuming, on the basis of prior experimental verification⁴, that the pyritic sulfur content (as determined by ASTM D2492-68) was reduced to the sulfide form (Fe₇S₈)⁸ within fifteen minutes of reaction, the final organic content of each reaction mixture was computed (Figure 4a).

As a basis for comparison, a sample of the feed to the magnetic separator was collected. The coal in the sample was separated from the water by filtering; dried and reacted in the same manner as the demineralized coal. For completeness, coal that had not been exposed to water (as in the slurry feed tank to the magnetic separator) was also dried and reacted (Figure 4).

Hydrogenation and Hydrodesulfurization Using Prehydrogenated Solvent. To improve the hydrogen donor activity of the solvent, it was hydrogenated at 410°C for one hour in the presence of 15 per cent by weight of minus 150 mesh Co-Mo-Al catalyst (Comax-451, Laporte Industries) and an initial hydrogen pressure of 2500 psig. The hydrogenated solvent was then allowed to settle for 24 hours and doubly filtered to remove all the Co-Mo-Al catalysts: emission spectrophometric analysis, and also, outside analysis by Galbraith Laboratories, Inc., showed the Co and Mo content in the resulting hydrogenated solvent to be less than 1ppm and 10ppm, respectively. The hydrogenated solvent has a specific gravity of 1.05 at 25°C and a carbon-to-hydrogen ratio of 1.15 (91.56% C and 6.65% H). Comparative runs were then made in which hydrogenated solvent and untreated solvent were each reacted in a 3:1 solvent-to-coal ratio at 410°C for 15 minutes in the presence of a nitrogen pressure of 2000 psig, and also, in an initial hydrogen pressure of 2000 psig (Table 6).

Results and Discussion

Using total pressure as a rough indicator of reaction rate, from Figure 1 some of the coal minerals definitely appear to provide catalysis for hydrogenation of the creosote oil. The upper and lower curves in Figure 1 represent the extreme behavior present with no catalyst and with a commercial Co-Mo-Al catalyst, respectively. The different mineral matter additives show evidence of catalytic activity, intermediate between these two extremes. Most interestingly, one of the more active catalysts is filter cake residue from the Wilsonville SRC pilot plant. Also, the catalytic activity of -325 mesh pyrite is higher than that of -80 +150 mesh pyrite - demonstrating that not only the composition of the mineral matter, but also its physical state, is of considerable importance in process applications.

Sulfur removal data for each of the catalyst screening runs are presented in Figure 5 and are in general agreement with the catalytic activity sequence evidenced by the total pressure data with two exceptions: Pyrite, despite its pronounced effect on total pressure, appears to be a relatively poor catalyst for hydrodesulfurization. High pressure liquid chromatographic analysis of the creosote oil after hydrogenation reveals that the concentration of dibenzothiophene, an organic sulfur constituent, decreases from 1.271 ± 0.03 to only 0.720 ± 0.09 per cent when pyrite is present; whereas it is reduced to 0.888 ± .05 when no catalyst is present and to only trace amounts (< 0.04%) when Co-Mo-Al is present.⁵ As stated earlier in the experimental section, pyrite is reduced rapidly during

hydrogenation to the sulfide form (Fe_7S_8);^{4,8} some back-reaction by the H_2S generated during reduction of the pyrite may occur, and this reaction may be partly the reason why the presence of pyrite had such a poor effect on hydrodesulfurization of the creosote oil.¹² Secondly, iron, which had a much less effect on total pressure than that of pyrite, is second only to Co-Mo-Al in sulfur removal. However, the role of iron in sulfur removal during hydrogenation is probably more as a reactant than as a catalyst, in that it reacts with any H_2S produced or directly with sulfur in the oil to form sulfides. In fact, gas analysis showed little, or no H_2S to be formed during hydrogenation of the creosote oil in the presence of iron.

An indication of hydrogenation activity is shown in Figure 6 where the final hydrogen partial pressure is presented for each of the catalyst screening runs, as determined from gas analysis and total pressure. Again, the Co-Mo-Al is most effective for hydrogenation; however, iron pyrite and SRC solids residue also indicate relatively high activity. Prather et al.⁵ show, using high pressure liquid chromatography, that the total concentration of the four major constituents in the creosote oil - naphthalene, acenaphthene, phenanthrene, anthracene - decreases the same during hydrogenation in the presence of pyrite as it does in the presence of Co-Mo-Al, and 22 per cent more than it does when no catalyst is present.

The results of experiments showing the effect of recycling filtered mineral matter from successive autoclave runs are shown in Figure 3; again total pressure is assumed to act as a rough indicator of reaction rates. Obviously continued recycle (higher concentrations) of mineral matter residue leads to increased reaction rates, as evidenced also by the resulting higher yields and decreasingly lower final hydrogen partial pressures (Table 5).

Further evidence that coal minerals catalyze liquefaction reactions are given in Figure 4, in that the rate of conversion for demineralized coal is much slower than that of untreated coal. In addition, soaking of the coal in water, or slurring with water, causes also a significant decrease in the rate of liquefaction. Some of the coal minerals - particularly sulfates - are soluble in water, and thus, are extracted by soaking the coal in water, as evidenced by the 0.12 per cent decrease in total sulfur content of the coal with soaking (Table 7), which is about the same as the per cent sulfur (0.13%) present in the sulfate form in the untreated coal. Yet, since exposure of the coal to water may affect the chemical characteristics of the coal in various ways other than removal of soluble minerals, further experimental study is needed to determine conclusively why slurring coal with water prior to hydrogenation decreases its rate of liquefaction.

Despite the significant effect of demineralization of the coal on its liquefaction behavior, its organic hydrodesulfurization activity remained practically the same (Figure 4a). Assuming that mostly pyrite was removed by the magnetic separator, then no significant difference in the organic hydrodesulfurization activity of the demineralized coal and that of untreated coal should result, and the results given in Figure 4a should be expected; for, as shown in Figure 5, pyrite has relatively little overall catalytic effect on hydrodesulfurization of creosote oil. Depending then on the composition of coal minerals - eg. high pyrite content, etc. - the relative effect of coal mineral catalysis can be significantly greater for liquefaction than for organic hydrodesulfurization. As a result, coal mineral catalysis during hydrogenation/hydrodesulfurization of coal may or may not be

advantageous, depending on process objectives and on composition of the coal minerals. To illustrate: If hydrogenation is limiting, for example, as may be the case in producing a synthetic fuel oil, then catalysis by coal minerals of hydrogenation reactions would be advantageous; and thus, so would recycle of coal minerals. On the other hand, if hydrodesulfurization is limiting and, as usual, minimum hydrogenation is desired, which is often the case in SRC and related processes, removal of coal minerals such as pyrite prior to hydrogenation/hydrodesulfurization would be advantageous; for, to attain the required amount of sulfur removal, more hydrogenation would occur when all the catalytic coal minerals are present than when no pyrite, and similar behaving catalytic coal minerals, is present. That is, in the presence of coal minerals such as pyrite, excess hydrogenation - more than that required to liquefy the coal so that mineral residue can be separated by filtration, etc. - would occur.

For coal particles to dissolve in a carrier solvent, i.e. liquefy, at temperatures of 385 to 450°C, either molecular hydrogen or hydrogen donor species must be available to transfer hydrogen to the coal.⁶ A direct relationship exists between the degree of dissolution and hydrogen transfer: the more hydrogen transferred, the greater the liquefaction.⁷ Coal mineral matter, being solid in form, most likely can not directly catalyze hydrogen transfer to coal solids either from molecular hydrogen dissolved in the carrier solvent or from hydrogen donor species. More reasonably, coal minerals can catalyze transfer of dissolved molecular hydrogen to the solvent - i.e. hydrogenation of the solvent. But, does hydrogenation of the solvent increase its hydrogen donor activity? If indeed it does, then the rate of liquefaction of coal slurried with prehydrogenated solvent should be greater than that of coal slurried with untreated solvent. To verify whether or not this is true, the conversion of coal solids obtained in the prehydrogenated solvent experiments were compared with those obtained with untreated solvent (Table 6). Apparently prehydrogenation of the solvent increases its hydrogen donor activity significantly, for the conversion obtained with the prehydrogenated solvent was 97 and 49 per cent higher than that obtained with untreated solvent in a nitrogen and a hydrogen atmosphere, respectively. Yet, practically the same amount of sulfur removal results when either prehydrogenated or untreated solvent are used. Apparently then, coal minerals serve to catalyze hydrogenation of the solvent, increasing its hydrogen donor activity, and thereby, the rate of hydrogen transfer to the coal, thus the rate of liquefaction.

Supportive evidence that coal minerals serve primarily to catalyze hydrogenation of the donor solvent is provided by Curran *et al.*;⁷ they found that, in a nitrogen atmosphere, "... all attempts to accelerate hydrogen transfer to coal slurried in tetralin with contact type of catalysts of the hydrofining type (cobalt molybdate on alumina) or with cracking catalysts (silica-alumina) were unsuccessful." Whereas, in a hydrogen atmosphere - as shown here and by others¹ - the rate of liquefaction increases directly with increases in the concentration of coal minerals. The rate limiting step in liquefaction furthermore appears to be the transfer of dissolved molecular hydrogen to the donor solvent, with the transfer of hydrogen from the donor solvent to coal solids occurring rapidly.

Conclusions

Certain coal minerals - particularly pyrite - catalyze hydrogenation of coal-derived solvents such as creosote oil and SRC recycle solvent. The rate limiting step in liquefaction of coal is the transfer of hydrogen to donor solvent, and the

rate of liquefaction increases directly with the concentration of coal minerals. Certain coal minerals also catalyze hydrodesulfurization of creosote oil - pyrite having a relatively insignificant effect on total hydrodesulfurization. The physical state, as well as chemical composition, of the coal minerals affect hydrogenation and hydrodesulfurization activity during coal liquefaction. Coal mineral catalysis of hydrogenation and hydrodesulfurization reactions occurring in coal conversion processes may or may not be advantageous, depending on process objectives and on composition of the coal minerals.

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TABLE 1
Gas Chromatographic Analysis of Creosote Oil

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

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

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

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

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

Table 4. Description of Coal Minerals Or Catalytic Agents Studied

Species	Classification ^a	Description ^{b,10,11}
Ankerite (Ferriferrous Dolomite)*	Carbonate	An isomorphous mixture of CaMg (CO ₃) ₂ and Ca Fe (CO ₃) ₂ .
Calcite*	Carbonate	A crystalline form (hexagonal scalenohedral class of the hexagonal system) of CaCO ₃ . Often, to a small extent, the Ca is replaced by iron, magnesium, and manganese. Clay, sand, bitumen, and other mechanical impurities may be present.
Oolomite*	Carbonate	A double salt with equal molecular quantities of CaCO ₃ and MgCO ₃ , and not an isomorphous mixture of these two compounds. Usually found in a curved rhombohedral form.
Kaolinite*	Kaolin	A common type of clay; often found in minute pseudo-hexagonal (monoclinic) crystals. Chemically, an acid aluminum silicate, H ₄ Al ₂ Si ₂ O ₉ or 2H ₂ O·Al ₂ O ₃ ·2SiO ₂ (H ₂ O:14%). Iron is often present in small amounts.
Muscovite*	Shale	A lamina type silica substance, having a monoclinic crystal structure; and chemically classified as an acid potassium aluminum orthosilicate, H ₃ KAl ₃ (SiO ₃) ₃ or 2H ₂ O·K ₂ O·3Al ₂ O ₃ ·6SiO ₂ ·(H ₂ O:4.8%). Often, the potassium is partially replaced by sodium, and some varieties contain an excess of silicon over that indicated above.
Pyrite	Sulfide	A cubic structure of FeS ₂ , having, in its crystalline structure, a rock-salt-type of arrangement of Fe ²⁺ and S ²⁻ ions, with iron being octahedrally surrounded by 5 and each S atom having one S and three Fe atoms as neighbors. Uncommonly, Ni, Co, or sometimes both are found substituted for Fe. Obtained from Matheson, Coleman, and Bell (90-95% pure).
Quartz*	Accessory	A crystalline form of SiO ₂ ; a member of the triangular trapezohedral class of the hexagonal system.
Siderite*	Carbonate	A crystalline form of FeCO ₃ , with the brown to gray crystals usually being rhombohedral. Calcium, magnesium, and manganese are usually present in small amounts as replacing elements.
Co-Mo-Al	-	Commercial catalyst from Laporte Industries, Inc., (Comox 451, 1.5 mm Extrudate); surface area = 300 m ² /g; pore volume = 0.66 ml/g. Chemical analysis: 3.7, 12.8, 0.06, 1.4, and 0.03% Co, MoO ₃ , Na ₂ O + K ₂ O, SiO ₂ , and SO ₃ , respectively.
Iron	-	Reagent grade hydrogen reduced iron from Mallinckrodt, Inc.
Reduced Pyrite	-	Solid residue from hydrogenation-of-creosote oil in presence of 15% by weight of Fe ₂ O ₃ at 425°C, stirrer setting of 2000 rpm, and 3000 psig of initial hydrogen pressure.
SRC Residue	-	Obtained from filter cake from Wilsonville SRC pilot plant. Analysis: 55.2% ash content and 13.6% S for -325 mesh material; and, prior to screening, 30% filter aid, 53.6% ash, and 2.9% S.
Coal Ash	-	Obtained by burning Kentucky No. 9/14 mixture (7.2% ash) in a muffle furnace at ~ 1000°C; analysis: 13.7% iron.
Kaolin	-	Obtained from W. H. Curtis and Co.

* Minerals obtained from David New, Minerals and Books, Providence, Utah.

Note: All agents were ground to -325 mesh prior to use, except muscovite which was ground only to -80 mesh because of its lamellar silica structure, and except as indicated.

Table 5. Final Gas Analysis and Conversion for Recycle of Mineral Residue Runs

Run	Total Pressure (PSIA)	Partial Pressure (PSIA)				Conversion Based on Cresol Solubles (MMF)		
		H ₂	H ₂ S	CO ₂	CH ₄	C ₂	C ₃ -C ₅	
Initial	1221	825	36.9	89.5	136.6	48.9	28.7	96.3
Duplicate of Initial	1218	832	36.2	83.4	133.0	47.0	26.5	-
1st Recycle	1089	648	45.3	116.7	173.6	60.5	38.1	100.0
2nd Recycle	1064	607	45.3	113.9	179.4	22.3	33.3	100.6

Table 6. Comparison of Hydrogenation and Hydrodesulfurization Activity of Coal in Prehydrogenated Solvent and That in Untreated Solvent

EFFECT OF PREHYDROGENATION OF OIL

Pretreatment of Solvent	Temperature (°C)	Atmosphere	Reaction Time (min.)	Solvent-to-Coal Ratio	Conversion (Based on Cresol Solubles)	Total Sulfur (%)	Organic Sulfur (%)
None	410	2000psi N ₂	15	3/1	42.13	.904 ± .023	0.34
70 Hydrogenation	410	2000psi N ₂	15	3/1	83.10	.487 ± .030	.39
None	410	2000psi H ₂	15	3/1	61.03	.912 ± .054	.35
Hydrogenation	410	2000psi H ₂	15	3/1	90.70	.506 ± .026	.41

Table 7. Ash and Total Sulfur Content of Kentucky No. 9/14 Coal and That After Slurrying
 With Water and After Demineralization

	Ash Content (%) (ASTM D-271)	Total Sulfur Content (%)	Conversion* After Two Hours of Reaction
Original Coal	7.16	2.55	87.8
Coal From Slurry Feed Tank	6.28	2.43	77.38
Demineralized Coal	2.55	1.90	67.23

*Refer to Figure 4

Reaction Conditions

Temperature: 425°C
 H₂ Pressure: 3000 psig @ 425°C
 Agitation Rate: 2000 rpm
 Autoclave: 300 cc
 Charge: 100 g Creosote Oil/15 g catalyst

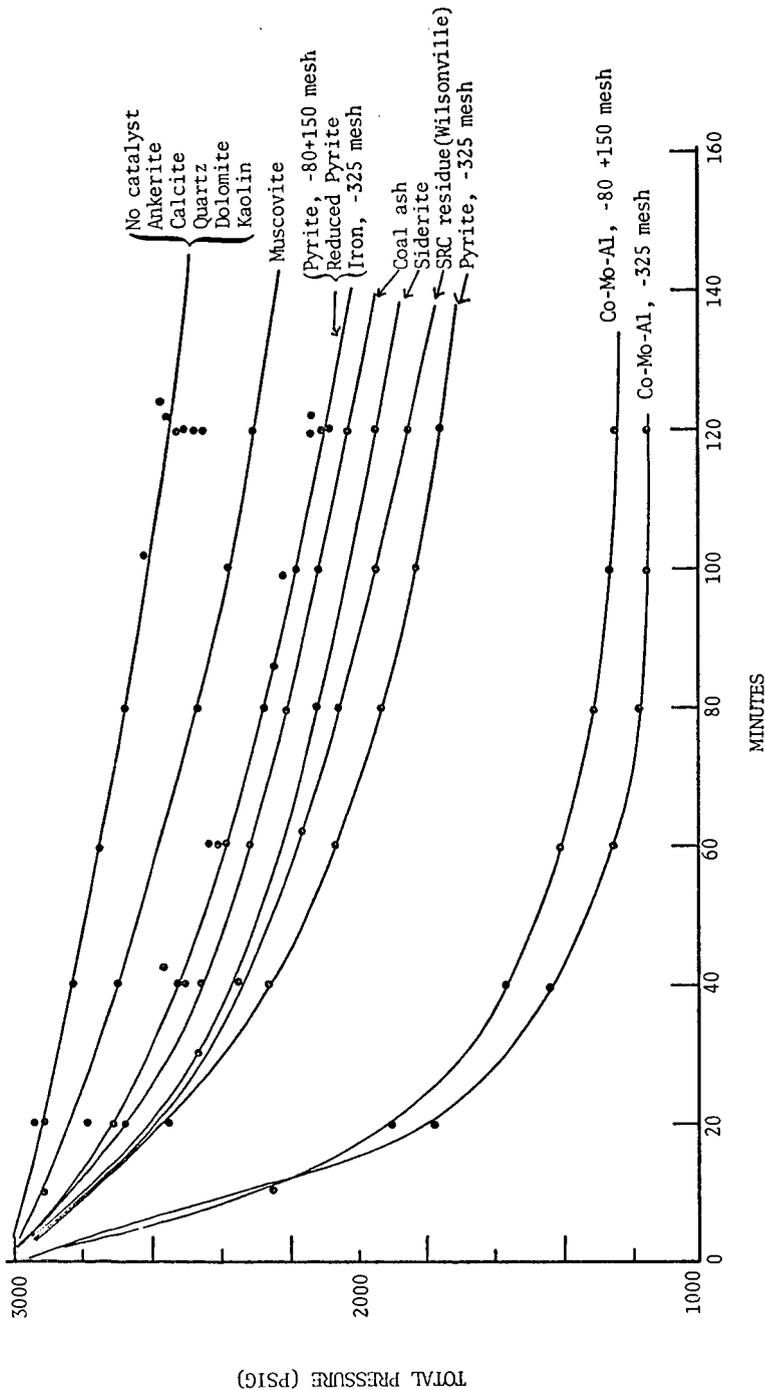


Figure 1. Catalytic effect of coal mineral matter as indicated by total pressure.

RUN

- Co-Mo-Al Catalysis
- ◇ First Blank
- Second Blank
- △ Third Blank
- X Fourth Blank

Reaction Conditions

Temperature: 425°C
H₂ Pressure: 3000psig@ 425°C
Agitation Rate: 2000 rpm
Autoclave : 300cc

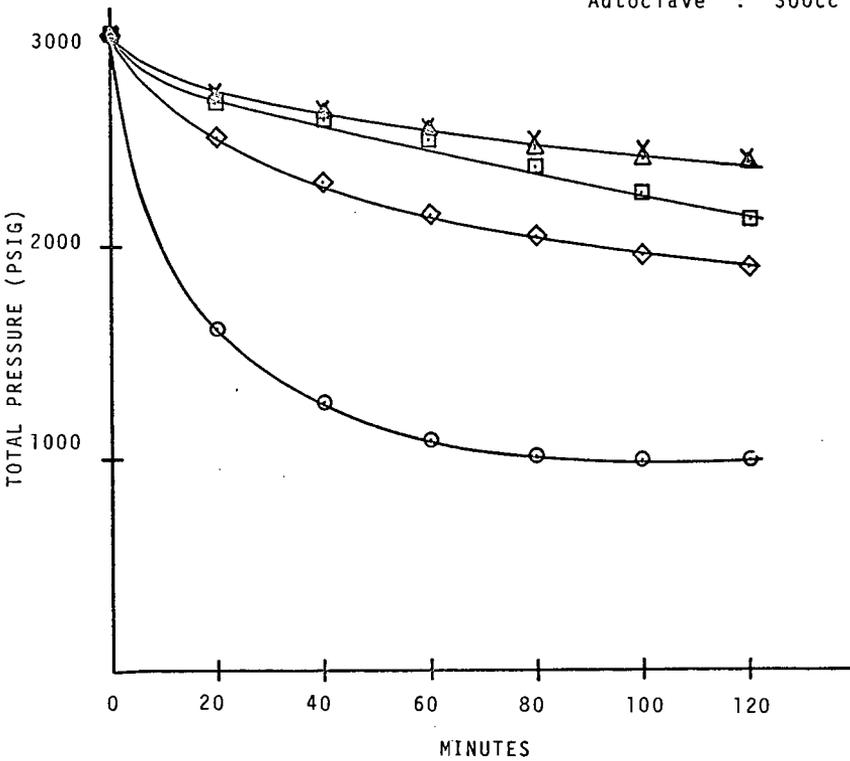


Figure 2. Determination of number of blank runs required to eliminate memory effect.

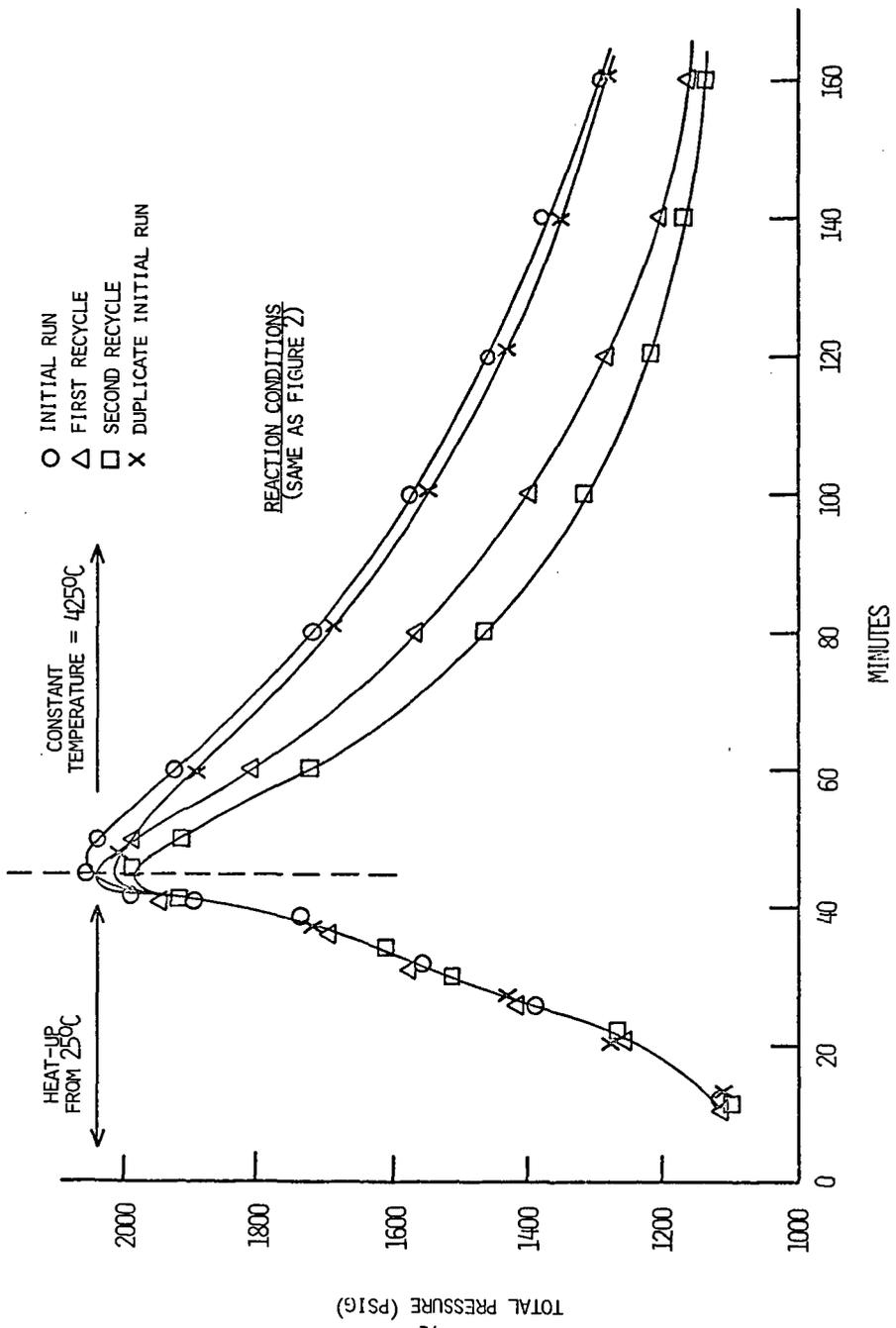
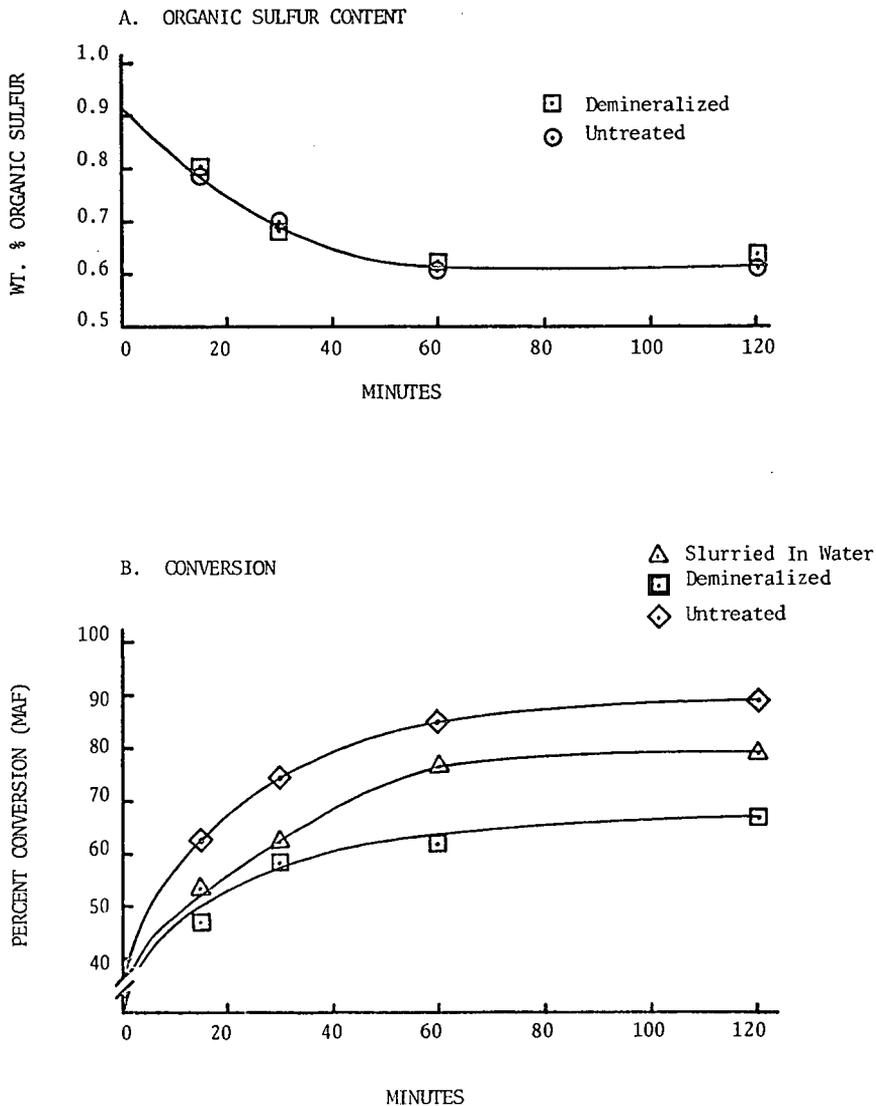


FIGURE 3. EFFECT OF RECYCLING MINERAL MATTER RESIDUE AS INDICATED BY TOTAL PRESSURE

FIGURE 4. EFFECT OF DEMINERALIZING COAL FEED AND SLURRYING COAL FEED WITH WATER ON CONVERSION

Temperature Reaction Conditions: 410°C
 H₂ Pressure: 2000 psig @ 410°C
 Agitation Rate: 1000 rpm
 Autoclave: 300 cc



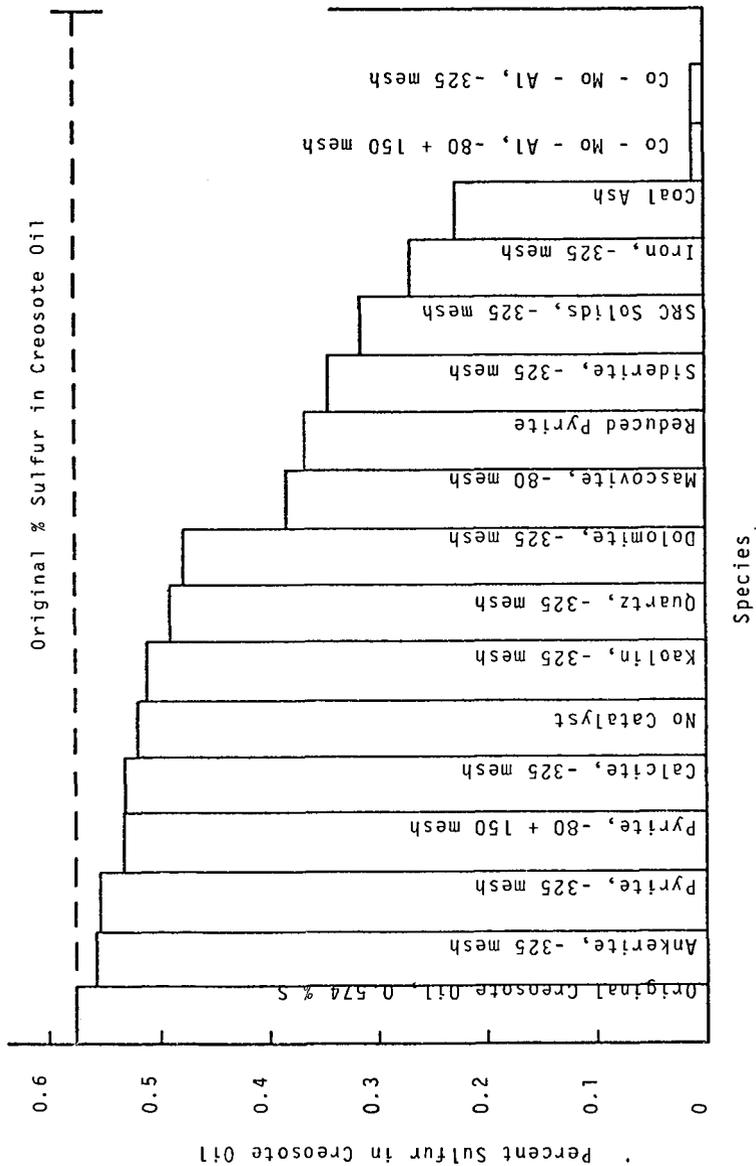


Figure 5. COMPARISON OF DESULFURIZATION ACTIVITY OF CATALYST Species.

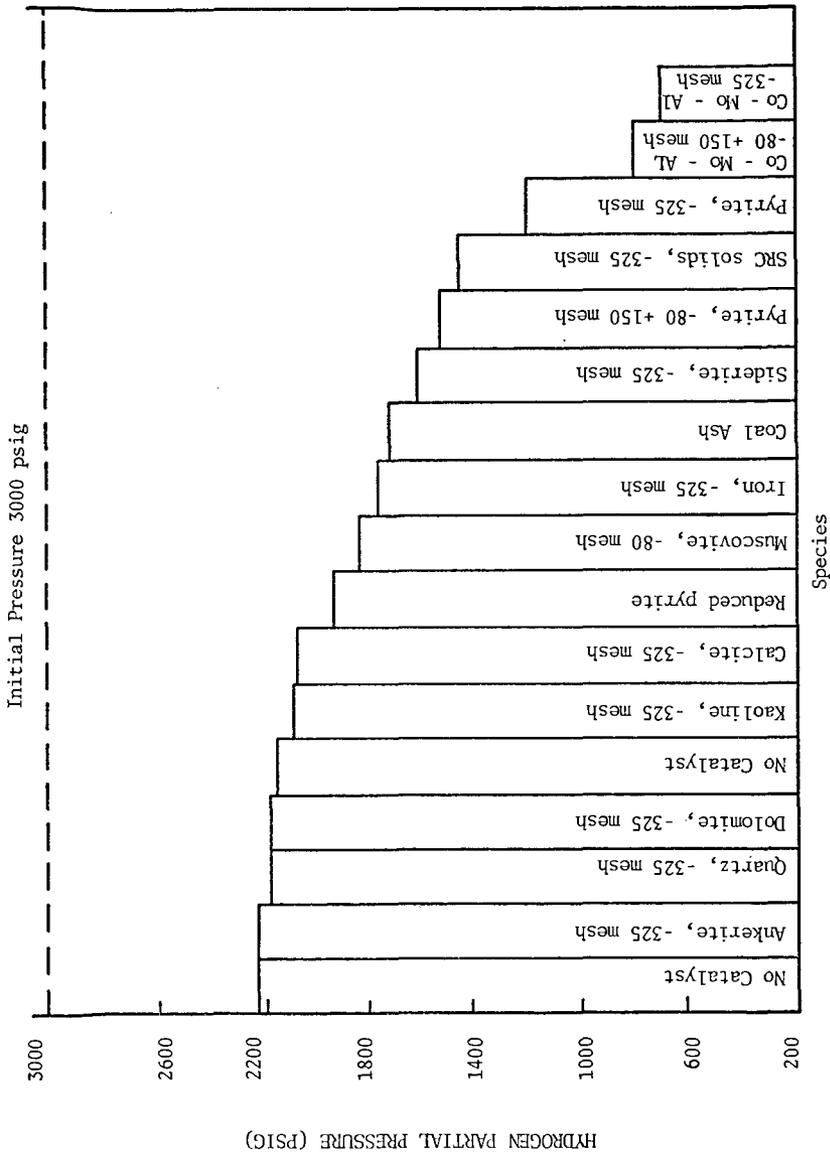


Figure 6. COMPARISON OF HYDROGENATION ACTIVITY OF CATALYST