

COAL LIQUEFACTION CATALYSIS

USING IRON PYRITE AND HYDROGEN SULFIDE

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ABSTRACT

An unreactive hvC bituminous coal has been hydrogenated in a batch stirred reactor using pyrite, hydrogen sulfide, and pyrite + hydrogen sulfide as catalysts. The data indicate that both H_2S and pyrite exhibit catalytic effects for coal conversion.

INTRODUCTION

Direct hydrogenation processes for coal liquefaction are generally hampered by two processing problems: slow formation of distillate oils at "mild" conditions and poor hydrogen utilization efficiency due to formation of light hydrocarbon gases ($C_1 - C_4$). Unfortunately, raising the temperature to increase the rate of oil formation causes the rate of light hydrocarbon formation to greatly accelerate, leading to even poorer hydrogen efficiency and hence increased processing costs. To overcome these problems, catalysts may be used which are selective for hydrogenation, and accelerate the rate so that lower temperatures may be employed. It is well known that the reactivity of certain coals liquefied by the I.G. Farben process during the 1930's in Germany was enhanced by addition of iron and/or sulfur to the feed slurry (1). In the early 1970's, Wright and Severson (2) reported that minerals present in bituminous coal mineral matter served as hydrogenation catalysts. Additionally, Na, K, and Fe were found to catalyze CO-steam lignite liquefaction. Subsequent to these discoveries, research on disposable catalyst liquefaction of coal was initiated in order to identify the active catalytic species in coal mineral matter. Mukherjee and Chowdhury (3) found increasing conversion with increasing mineral content, and identified iron pyrite as the active catalyst. They also indicated a synergistic effect between pyrite and organic sulfur. Extensive research by Guin et al. (4, 5, 6, 7) and Tarrer et al. (8) on the catalytic activity of coal minerals clearly established the role of pyrite as that of a hydrogenation catalyst, and further identified other catalytic agents present in coal mineral matter. Hamrin (9) investigated HDS of model compounds with coal minerals as catalysts. Granoff et al. (10), in batch autoclave studies of mineral matter catalysis demonstrated the effect of pyrite on product distribution, and illustrated the magnitude of the observed catalytic effect on net oils formation. More recently, Mössbauer analysis of liquefaction residues by Montano et al. (11, 12, 13) has led to a greater understanding of the behavior of iron/sulfur species at liquefaction conditions. Attar and Martin (14) have speculated that an iron sulfide intermediate (between $FeS_{1.09}$ and FeS_2) is the active pyrite-derived catalyst.

This paper presents the results of batch autoclave hydrogenation experiments where H_2S , pyrite, and H_2S + pyrite were used as liquefaction

catalysts. Products were analyzed for oils, asphaltenes, and preasphaltenes, and the effect of H_2S , pyrite, and H_2S + pyrite additives on the rate of coal liquefaction as well as production distribution was determined.

EXPERIMENTAL

A hvC bituminous coal from the Wadge seam of the Energy Fuels Mine near Yampa, Colorado (Rocky Mountain coal province) was hydrogenated in a 300-cc stirred batch reactor. The coal employed was similar to standard sample PSOC-233, and was chosen due to its low inherent pyrite and total sulfur content, and relatively poor thermal liquefaction reactivity. An analysis of the coal sample is presented in Table 1. Ash analysis showed 47% and 33% SiO_2 and Al_2O_3 respectively, and 3.3% total iron as Fe_2O_3 . Titanium as TiO_2 was 1.05% of the ash; no other potential catalysts were indicated in the ash analysis. Pyrite was separated from a Kentucky bituminous coal from the Colonial Mine near Madisonville, Ky. by first grinding the parent coal then separating pyrite from coal on a shaker table. The pyrite was analyzed by x-ray diffraction and Mössbauer spectroscopy and found to be a mixture of pyrite and marcasite, with marcasite comprising about 38% of the mixture.

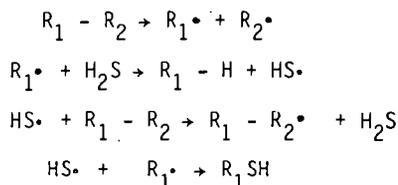
Hydrogenation experiments were carried out in a 300-cc stirred batch autoclave, modified to permit rapid injection of coal into a preheated pressurized reactor. Experiments were carried out at $380^\circ C$, in a 10/1 excess of tetralin as the vehicle, 200 psig total pressure (\approx hydrogen partial pressure). Two different reaction times were employed, 10 and 60 minutes, to test for rate effects due to the additives employed. Runs where pyrite was employed as the additive were made by injecting a coal/pyrite mixture (10% pyrite by weight) into the reactor. At the end of a run, the reactor was quenched by rapid forced-convection cooling.

Reaction product gases were analyzed for hydrocarbons through C_5 , CO, CO_2 , H_2 , and H_2S and the liquid products were analyzed by selective solvent fractionation (SSF) to separate oils, asphaltenes, preasphaltenes, and insoluble organic matter (IOM). Inorganics in the liquefaction residue were analyzed by Mössbauer spectroscopy to determine pyrite/pyrrhotite, and yields of all products were calculated based on a 100% workup of the product slurry.

RESULTS AND DISCUSSION

Data for coal hydrogenation in the presence of added H_2S , pyrite, and H_2S + pyrite are shown in Figures 1-4 along with baseline data for hydrogenation without the use of additives. What is perhaps most striking about these data is the influence of added H_2S in the absence of added pyrite. The percentages of H_2S refer to the mole % H_2S in the gas atmosphere prior to heating and reaction (cold composition). A 56% increase in overall conversion is indicated at the 10 minute residence time (2, 5, and 10% H_2S level), with a 21% increase found at 60 minutes when gaseous H_2S alone (5 and 10% level) is added to the reaction gas atmosphere. The predominant influence on product distribution is in the preasphaltene fraction, especially at the short residence time. Clearly, H_2S is acting as a catalyst for coal conversion at these conditions.

Concentrations above 2% H₂S in the initial gas phase mixture do not seem to appreciably increase the conversion at 10 minutes, but a substantial effect is present with increasing H₂S concentration at 60 minutes. The function of H₂S in this case may be as either a homogeneous or heterogeneous catalyst. Rebick (15) has reported a catalytic effect of H₂S on n-hexadecane pyrolysis, and attributed the noted effect to catalysis of hydrogen transfer. Since the early stages of coal liquefaction are thought to proceed via free radical chemistry, a similar effect may be operative here. Free radicals formed rapidly by initial pyrolysis of the coal matrix could interact with H₂S in the following manner:



where R₁ - R₂ = coal macromolecule. Similar reactions could be written for radical R₂[•]. This mechanism also predicts that sulfur could become incorporated in the lower molecular weight products of reaction (R₁SH). Preliminary analysis of SSF samples have shown a very small increase in total sulfur in the oil, asphaltene, and preasphaltene fractions, and a very large (factor of 2 to 3) increase in total sulfur in the THF-insolubles (IOM plus mineral matter).

An incremental enhancement in reactivity over the H₂S alone data is seen with 10% added pyrite and H₂S at 2, 5, and 10% initial H₂S fraction. The increase in conversion noted here is reflected most strongly in both the preasphaltene and oil fractions, especially at long residence times. The combination of added pyrite and H₂S gave the highest overall oil yield. The data at 10 minutes with pyrite and H₂S show the importance of iron-sulfur stoichiometry in maintaining the catalytically active iron sulfide species in the reactor. The data clearly show a strong synergistic effect between gaseous H₂S and pyrite/pyrrhotite in the reaction mass. Apparently, for this low sulfur coal, additional sulfur is needed to obtain and maintain the most active iron sulfide catalyst. A 25% increase in conversion (at 60 minutes) is seen when 2% H₂S is added with 10% pyrite, in comparison with 10% pyrite and no added H₂S. No additional benefit is derived by increasing the H₂S level above 2% for the combined catalyst system. Mössbauer spectroscopy was used to follow the iron sulfide stoichiometry in the liquefaction residues. Results of these analyses are shown in Table 2. Obviously, the final pyrite/pyrrhotite mixture present in the liquefaction residue is a very strong function of both residence time and H₂S partial pressure. However, very little variation in the stoichiometry of the pyrrhotite was observed with a change in H₂S partial pressure. Although the data in Table 2 are presented as pyrite/pyrrhotite fractions, the Mössbauer spectra indicate that the non-magnetic phase (reported as pyrite) is not comprised of pure pyrite (FeS₂). The iron/sulfur stoichiometry of this non-magnetic phase cannot be determined with the precision of the magnetic phase. Such measurements should allow the

active catalytic species to be identified, as it is clear from the data that the non-magnetic phase is the phase in which the catalytically active iron sulfide is being formed.

It is also possible that the influence of added H_2S was to sulfide non-pyritic iron in the idigenous coal mineral matter. Ash and sulfur forms analysis on the parent coal indicated that about one half of the total iron was present as iron pyrite (including marcasite), with the remainder of the iron being present in a non-sulfided state. Hydrogen sulfide in the reaction gas atmosphere would quickly sulfide any non-pyritic iron, and thus generate additional quantities of the active catalyst. This hypothesis would explain the enhanced conversion found with H_2S only added, as well as the large increase in total sulfur found in the THF -insolubles. Unfortunately, the small sample size of this fraction precludes analysis for forms of sulfur. Such information could aid in elucidating whether a homogeneous or heterogeneous catalytic effect is operative at these conditions.

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Table 1
Analysis of Coal

Penn State Reference No.: PSQC-233

Seam: Wadge

Mine: Energy Fuels

State: Colorado

Rank: hvCb

Ultimate Analysis (wt%, as received)

C = 69.0

H = 5.3

N = 1.7

S = 0.5

O = 17.8

ash = 5.6

Sulfur Forms (wt%)

Pyritic - .05

Sulfitic - nil

Organic - .45

Proximate analysis (wt%, as received)

Moisture = 5.8

Ash = 5.6

Volatile Matter = 36.9

Fixed Carbon = 51.6

Maceral Distribution (vol%, DMMF)

Vitrinite - 88.8

Inertinite - 6.5

Liptinite - 4.7

TABLE 2
Mössbauer Results

Residence Time*	H ₂ S Content(%)	Non-Magnetic Phase (Pyrite Fraction)	Magnetic Phase (Pyrrhotite Fraction)	Pyrrhotite X-value (Fe _x S)
10	0	29	71	.892
10	2	26	74	.894
10	5	30	70	.891
10	10	41	59	.885
60	0	25	75	.891
60	2	16	84	.899
60	5	24	76	.891
60	10	27	73	.886

* all runs with 10% added pyrite

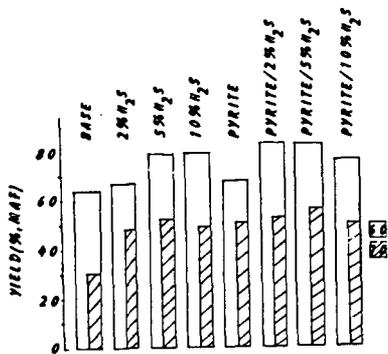


FIGURE 1
CONVERSION TO THF-SOLUBLES

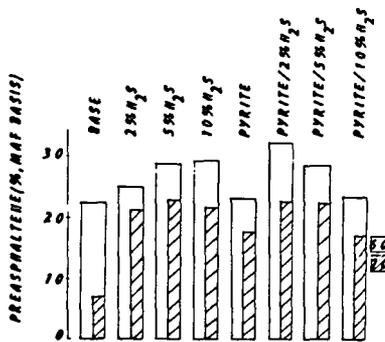


FIGURE 2
PREASPHALTENE YIELD

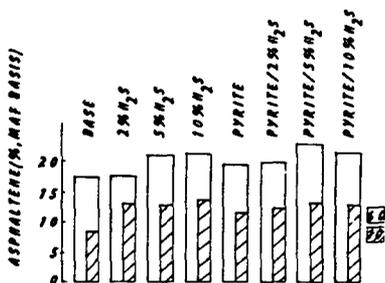


FIGURE 3
ASPHALTENE YIELD

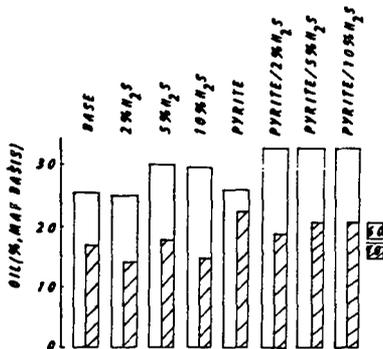


FIGURE 4
OIL YIELD