

REVIEW OF DESULFURIZATION AND
DENITROGENATION IN COAL LIQUEFACTION

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INTRODUCTION

With ever increasing demands on fossil fuels as a source of energy and ever decreasing supplies of crude petroleum within the United States, the nation must turn more and more to the use of coal. Yet the people of this country have mandated through their representatives that they do not want the anticipated use of coal to degrade their environment.

The air pollutants of particular concern are nitrogen oxides, sulfur oxides and particulates. Nitrogen oxides are formed from nitrogen in air as well as organic nitrogen in the fuel, and their concentration is primarily a function of combustion parameters. Sulfur oxides and particulates are a function of the chemical composition of the fuel used.

In response to public demand, the Environmental Protection Agency, EPA, has established air quality standards which define maximum allowable concentrations of pollutants in the atmosphere. Individual states have established emission standards for existing sources which meet the EPA's Air Quality Standards while the EPA has established emission standards for new sources. The current Federal Standards for emissions for new fossil fuel fired steam generators larger than 250 million BTU/hr are presented in Table I.

Because nitrogen oxides are so dependent upon furnace operating parameters such as burner configuration, excess air used, air and fuel distribution, etc., it is difficult to predict the level of nitrogen oxides to be expected from a given fuel. On the other hand, reasonable predictions can be made of the expected SO_2 emissions from coal since the only source of SO_2 is the sulfur in the coal. Thus, we would expect that in order to meet the SO_2 emission standard for solid fuels of 1.2 lbs per million BTU's while burning 10,000 BTU/lb coal, the coal must contain 0.6 wt.% sulfur or less. Unfortunately, the sulfur content of coals ranges from 0.2 to over 10 wt.% while the typical coal contains 0.5 to 4 wt.% sulfur.

Sulfur in coal exists in three distinct forms; (a) as organic sulfur, (b) as pyrite or marcasite (two common crystal forms of FeS_2), and (c) as sulfates. The amount of organic sulfur is normally not over 3 wt.%. The sulfates, mainly calcium and iron, rarely exceed a few hundredths percent except in highly weathered or oxidized samples. Because pyrite and marcasite are difficult to distinguish, these forms of sulfur in the coal are called pyrite. Nitrogen in coal exists in organic form, and is generally in the range of 1.0 to 1.5 wt.%. A hypothesized structure which shows possible forms of organic sulfur and organic nitrogen in coal is shown in Figure 1.

COAL LIQUEFACTION

Process Description

One method that is being seriously considered to reduce sulfur and nitrogen contents of coal to acceptable limits is liquefaction in the presence of hydrogen. A conceptual flow diagram of such a process is shown in Figure 2. Coal mixed with a solvent and hydrogen reacts at elevated temperatures and pressure either in the absence or presence of a catalyst to form a mixture of liquid products. If hydrogen consumption is maintained at low levels, 1.5 - 3 wt.% of the coal fed, most of the product is a high boiling, heavy liquid with a heating value in the order of 16,000 BTU/lb. This

product is solid at room temperature and may be used directly as fuel if its sulfur content is less than 0.96 wt.% or further processed to form either gasoline or chemicals. Higher hydrogen consumption in the liquefaction reactor produces lower boiling products with lower levels of sulfur and nitrogen.

Organic sulfur and nitrogen are removed when coal is liquefied mainly by reactions which form H_2S and NH_3 . The ammonia can be recovered by conventional purification methods.

Hydrogen sulfide is normally recovered, concentrated, and then converted to sulfur in the Claus process. The effluent gas from the Claus unit must be further processed in a Claus tail gas cleanup unit to reduce sulfur compounds to an environmentally acceptable level. Hydrogen sulfide produced by gasification of coal or of unliquefied coal to produce hydrogen would normally be processed in that same equipment. Organic nitrogen compounds are converted almost completely to molecular nitrogen in high temperature gasification processes such as the Koppers-Totzek or Texaco.

In the liquefaction process, pyritic sulfur is reduced to FeS_x , where x is about 1.0. FeS_x is then removed mechanically by filtration or by solvent precipitation along with heavy liquid-like product and unconverted coal.

Desulfurization Results

Published data on the desulfurization of coal as a function of hydrogen consumption from the catalytic H-Coal, Gulf CCL, and Synthoil processes are presented for Illinois, Kentucky, Kaiparowits, Pittsburgh, Big Horn, Wyodak, and Middle Kittaning coals in Figure 3 (1,2,3,4,5). Analyses of these coals are presented in Table II. Published data from non-catalytic (SRC) processes are also presented in Figure 3 for Kentucky, Kaiparowits, and Illinois coals(5,6).

In general, the data plotted in Figure 3 show that as the total amount of hydrogen consumed increases, the sulfur content of the fuel oil product decreases. A band has been used to indicate the trend of all the catalytic data since this data has been taken over widely different combinations of reactor temperatures and pressures, coal space velocities, catalyst types, catalyst ages and activity levels with resulting wide differences in fuel oil yields. Consequently, no alleged superiority for hydrogen selectivity for sulfur removal of one catalytic system over another can be inferred from this particular collection of data.

Interestingly, the data plotted in Figure 3 show that the amount of hydrogen required to reach a moderate sulfur level of about 0.9 wt.% in large scale non-catalytic reactors corresponds reasonably well with the amount of hydrogen required to reach that same level of sulfur in catalytic systems. However, there may be larger differences in hydrogen consumption requirements between large-scale non-catalytic and catalytic processes at fuel oil product sulfur levels below about 0.5 wt.%. It should also be pointed out that the reactor residence times in non-catalytic systems corresponding to a given hydrogen consumption are much higher than the reactor residence times in catalytic systems at the same hydrogen consumption levels.

As hydrogen consumption will have a large effect on the economics of coal liquefaction processes, it would be advantageous if the process consumed hydrogen only in the formation of H_2S and NH_3 . Material balance calculations show that a hydrogen consumption equivalent to only 0.16 wt.% of the coal is required to convert 2.5 wt.% sulfur in the coal completely to H_2S and a hydrogen consumption equivalent to only 0.11 wt.% of the coal is required to convert 0.5 wt.% nitrogen in coal completely to NH_3 . However, as shown in Figure 3, the amount of hydrogen required to desulfurize coal to products containing sulfur levels of 0.5 - 1.0 wt.% is equivalent to 1.5 to 6.0 wt.% of the coal. A relatively larger amount of hydrogen is required to produce low sulfur fuel oil products from low sulfur subbituminous coals than from bituminous coals because subbituminous coals contain a much larger concentration of oxygen, 15 - 20 wt.%,

than bituminous coals which contain 7 - 12 wt.% oxygen. However, most of the hydrogen consumption shown in Figure 3 goes to the production of gaseous and liquid hydrocarbons with a hydrogen content of about 6 to 12 wt.% from coal with a hydrogen content of about 5 wt.%. Methane, for example, contains 25 wt.% hydrogen.

Although most of the data obtained from both catalytic and non-catalytic coal liquefaction falls within the band shown in Figure 3, a separate line has been drawn through data obtained from a bench scale non-catalytic flow reactor. The observed difference in the results obtained from the bench scale reactor and other reactors is not entirely due to differences in the coal processed. For example, there is a significant difference in the results obtained on the fraction of organic sulfur removed during the processing of a mixture of Kentucky No. 9 and No. 14 coals in the Wilsonville, Alabama six ton per day SRC plant and in the bench scale reactor, as shown below.

DESULFURIZATION RESULTS

	<u>Wilsonville (7)</u>	<u>Bench Scale</u>
Coal Processed	Kentucky No. 9 & No. 14	Kentucky No. 9 & No. 14
T, °F	830	825
P, psig	2400	2500
Space Time, hrs.	0.7	0.7
Fraction of organic sulfur removed, x	0.62	0.82

In order to explain the large observed differences in the fraction of organic sulfur removed in the two different reactor systems, the effect of mixing in the reactor was evaluated. Flow considerations indicated that the Wilsonville reactor may have acted essentially as a backmix reactor while the bench scale reactor may have acted essentially as a perfect plug flow reactor. However, neither a first order nor a second order kinetic rate plot fit the bench scale data.

In similar work, Lessley (8) suggested that the first order cracking rate coefficient in a non-catalytic system is a function of conversion. Applying a simplified form of the Lessley equation to the desulfurization bench scale data, a first order rate coefficient was assumed to have the following dependence on the fraction of organic sulfur removed, x;

$$k = k_0 e^{-ax}$$

where k_0 is an initial rate coefficient
and a is a constant

Assuming a first order reaction mechanism, values of " k_0 " and " a " were obtained which would fit the experimental bench scale data. These results were then used to predict that if the reaction in the bench scale reactor had been carried out in a perfectly backmixed reactor, the fraction of organic sulfur removed under the reaction conditions specified in the preceding table would have been 0.58 rather than 0.62 actually observed. The fact that the Wilsonville reactor only approaches perfect backmixing was confirmed by the existence of a small temperature gradient in the reactor. The results of this analysis, based on limited data, suggest that the flow pattern of the fluid in the reactor may be an important variable.

After pyrite removal, overall reductions of up to 90% of the total sulfur in the original coal are possible. The sulfur levels of the various product fractions generally increase with boiling range. This is shown in Figure 4 for non-catalytic operation and Figure 5 for catalytic operations. Most of the sulfur is contained in the non-distillable ash free residual fraction to which an arbitrary mid-boiling point of 1100 or 1200°F has been assigned depending on the source of the data. These high boiling fractions may contain up to 1.2 wt.% sulfur when obtained from high sulfur bituminous coals.

Slurry oils produced during the non-catalytic liquefaction of high sulfur bituminous coals and boiling in the range of 450° to 600°F normally contain 0.2 - 0.4 wt.% sulfur. The sulfur content in the slurry oil produced from low sulfur subbituminous coals is normally less than 0.05 wt.%. An interesting, but unexplained anomaly, is indicated for narrow product fractions with a mid-boiling point between 350° and 450°F. These materials have sulfur contents higher than both lighter products and higher boiling products.

Denitrogenation Results

The amount of hydrogen required to obtain fuel oil products with a specific nitrogen content is indicated in Figure 6. There is a differentiation indicated on this figure between catalytic and non-catalytic processing results with higher nitrogen removal obtained catalytically. However, more hydrogen is required to obtain these lower product nitrogen levels. Even in the case of catalytic systems, the nitrogen content of the fuel oil fraction is seldom less than one half the nitrogen content of the feed coal. If higher levels of denitrogenation are required, additional hydrogen processing of the primary products using nitrogen specific catalysts will be necessary.

Figures 7 and 8 show nitrogen content as a function of the average boiling points of product fractions. These results show that there is a steady increase in nitrogen content as average boiling point increases. Surprisingly little difference is evident between the nitrogen contents of particular product fractions from catalytic and non-catalytic systems. However, as the yield of low boiling liquids is much larger from catalytic systems than from non-catalytic systems, the total nitrogen in all products from the catalytic systems is lower than the total nitrogen in all products from the non-catalytic systems.

CONCLUSIONS

Coal liquefaction can provide a low sulfur, environmentally acceptable fuel from high sulfur, environmentally unacceptable coal. However, current coal liquefaction processes require substantial amounts of hydrogen.

There is little difference in the amount of hydrogen consumed to reach a moderate sulfur level of about 0.9 wt.% in the fuel oil products from catalytic processes and in the fuel oil products from large scale SRC processes. There are indications that the hydrogen consumption requirements for desulfurization are significantly affected by the extent of mixing within the reactor.

A significantly larger amount of nitrogen is removed from coal processed in catalytic systems than from coal processed in non-catalytic systems. At the same time, the hydrogen consumptions and yields of low boiling liquids from catalytic systems are substantially larger than the hydrogen consumptions and yields of low boiling liquids from non-catalytic systems.

Finally, analyses of liquefied coal products indicates that the highest nitrogen and sulfur levels are contained in the highest boiling product fractions.

TABLE INEW STATIONARY SOURCE EMISSION STANDARDSFor Fossil Fuel Fired Steam Generators larger than 250×10^6 Btu/Hr.

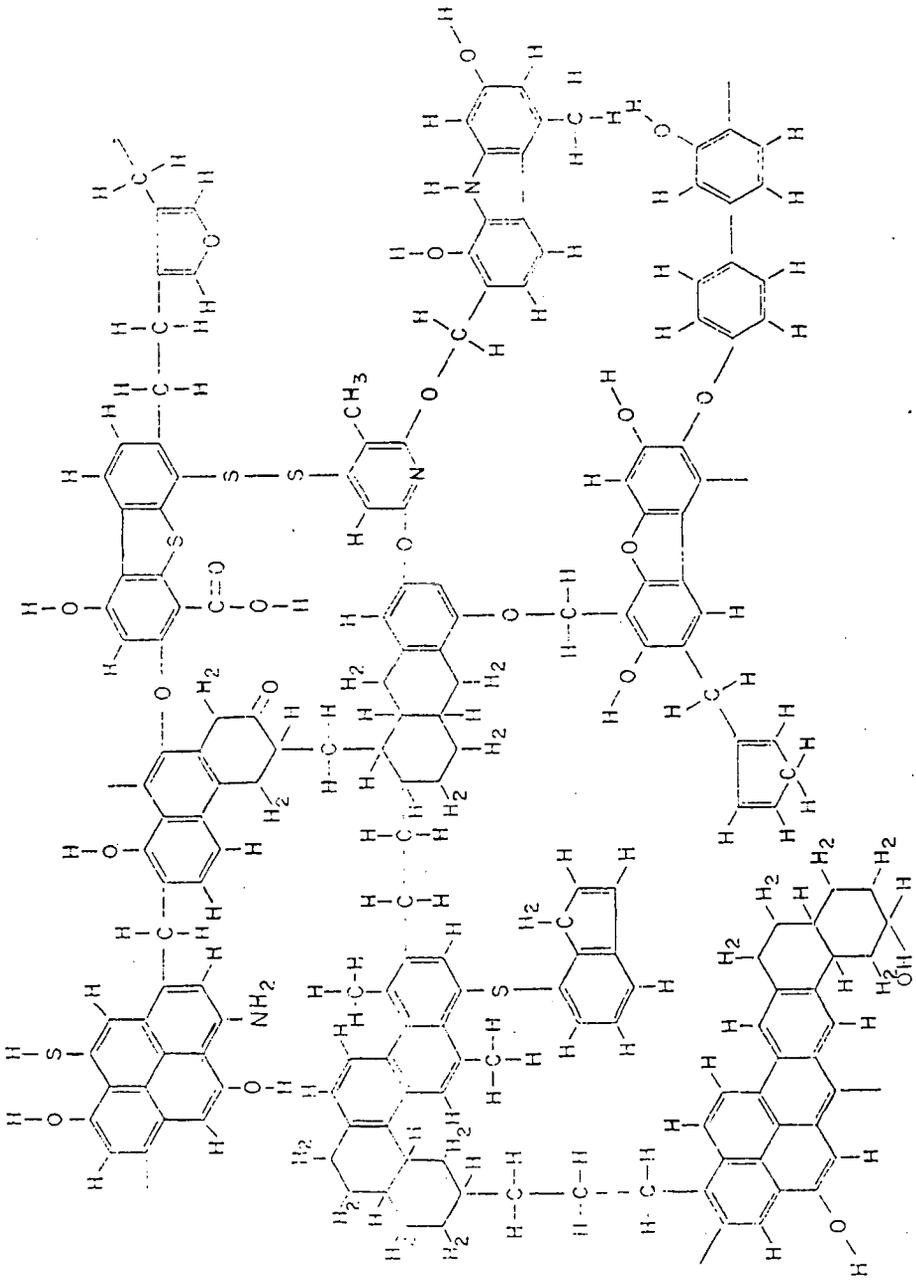
<u>Species</u>	<u>Standard</u>
Particulates	a) $0.1 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) 20% opacity. 40% opacity not more than 2 min/hr. c) Excludes H_2O
SO_2	a) Liquid Fuel: $0.8 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) Solid Fuel: $1.2 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave.
NO_x	a) Gas Fuel: $0.2 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) Liquid: $0.3 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. c) Solid: $0.7 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave.

TABLE 2

COAL PROPERTIES

	-----Bituminous-----						-----Subbituminous-----		
	Kentucky #4	Illinois #9,11, 12,13	Pittsburgh #6	Pittsburgh #8	Middle #8	Middle Kittaning	Kaiparowits	Big Horn	Wyodak
<u>Proximate Analysis</u>									
<u>Wt. %</u>									
Ash	8.5	17.2	11.6	8.3	8.3	9.7	6.3	4.4	7.3
Volatile Mater	39.2	37.8	42.0	34.1	42.8	40.3	43.9	42.5	46.4
Fixed Carbon	52.3	45.0	46.4	57.6	48.9	50.0	49.8	53.1	46.3
<u>Ultimate Analysis</u>									
<u>Wt. %</u>									
Hydrogen	5.1	4.8	4.8	5.1	5.1	5.3	5.1	4.6	4.8
Carbon	73.0	60.7	70.2	76.8	73.9	72.8	72.5	69.4	66.0
Nitrogen	1.3	1.2	1.4	1.6	1.2	1.3	1.0	1.2	1.1
Oxygen	9.0	11.3	9.3	6.7	7.5	7.5	14.7	19.9	20.4
Sulfur	3.1	5.5	3.2	1.5	4.0	3.1	0.4	0.5	0.4
Ash	8.5	16.5	11.1	8.3	8.3	10.0	6.3	4.4	7.3
<u>Forms of Sulfur</u>									
<u>Wt. %</u>									
Sulfate	0.26	0.47		[.66	0.00	0.01	0.02		[.14
Pyritic	1.42	3.08			2.1	1.32	0.00		
Organic	1.35	1.95		.83	1.9	1.77	0.38		.40

Figure 1 A REPRESENTATION OF BITUMINOUS COAL STRUCTURE



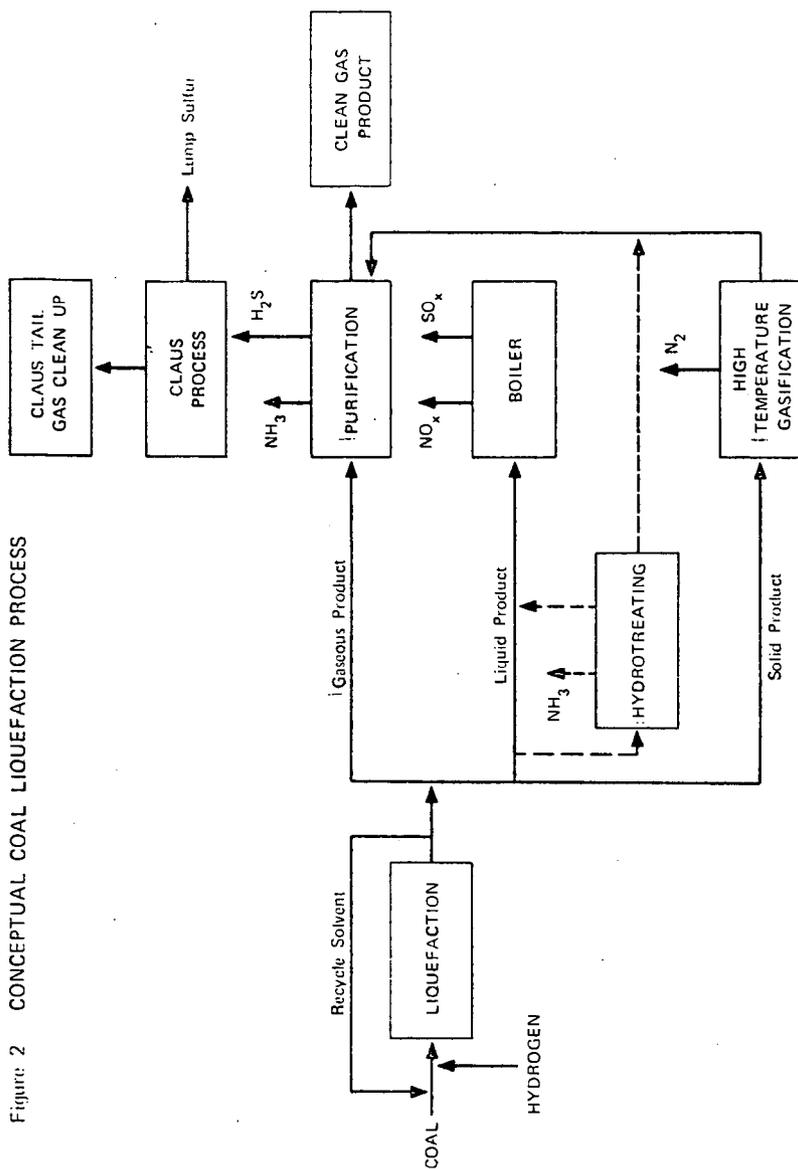


Figure 3 HYDROGEN REQUIRED TO PRODUCE LOW SULFUR FUEL OIL

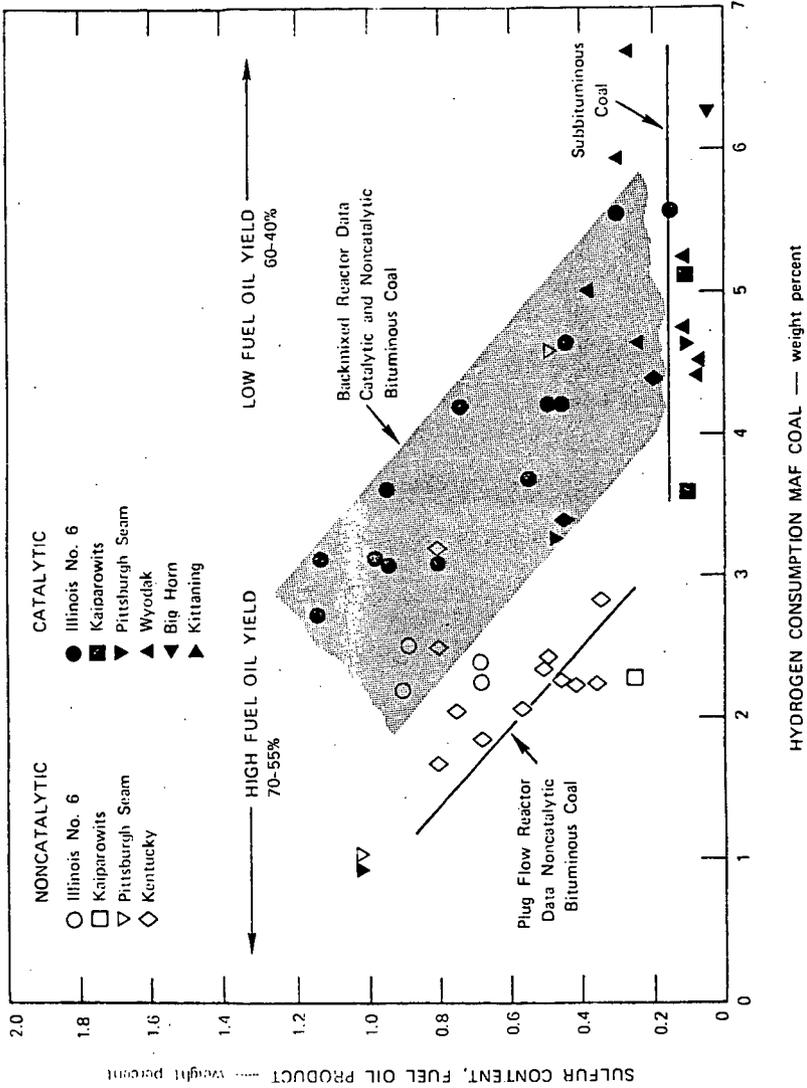


Figure 4 SULFUR CONTENT OF COAL LIQUIDS FROM NONCATALYTIC OPERATIONS

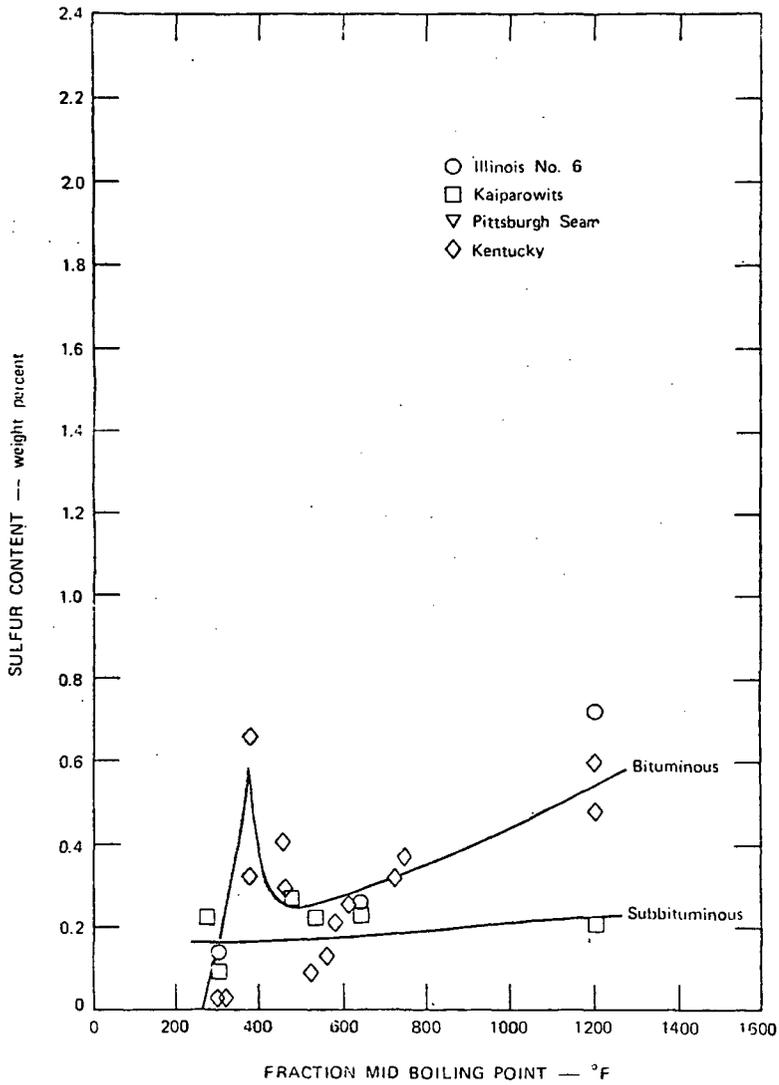
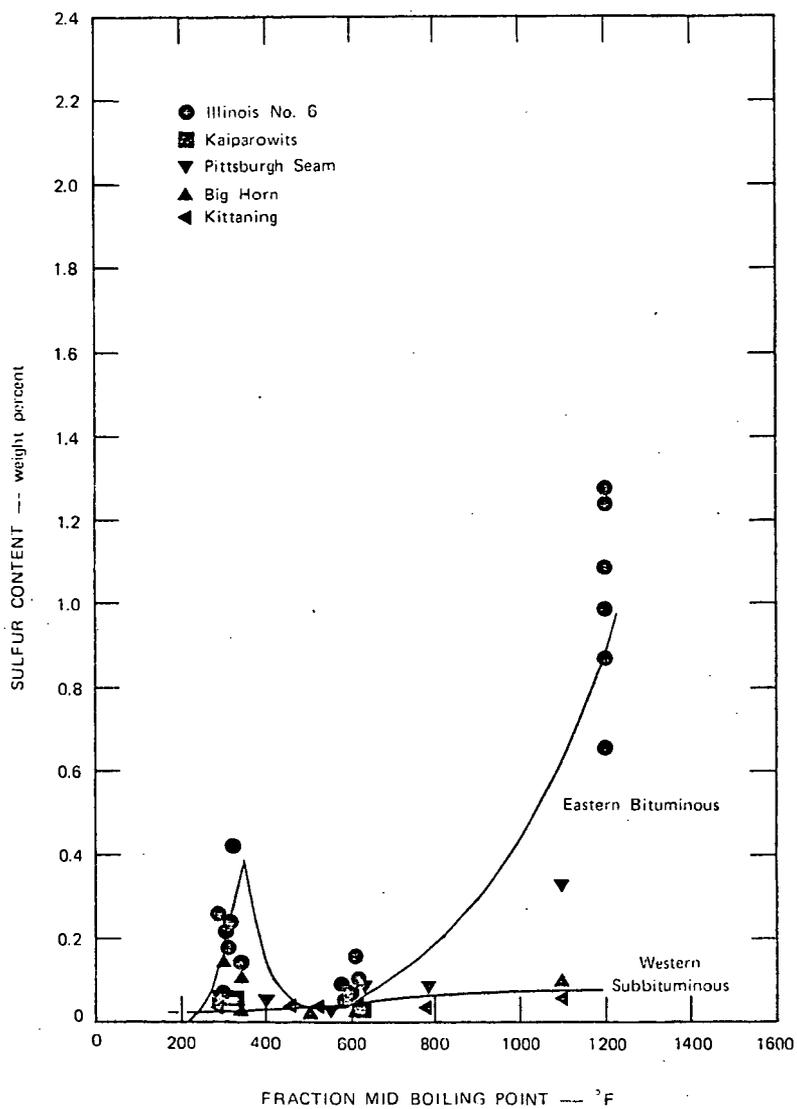


Figure 5 SULFUR CONTENT OF COAL LIQUIDS FROM CATALYTIC OPERATIONS



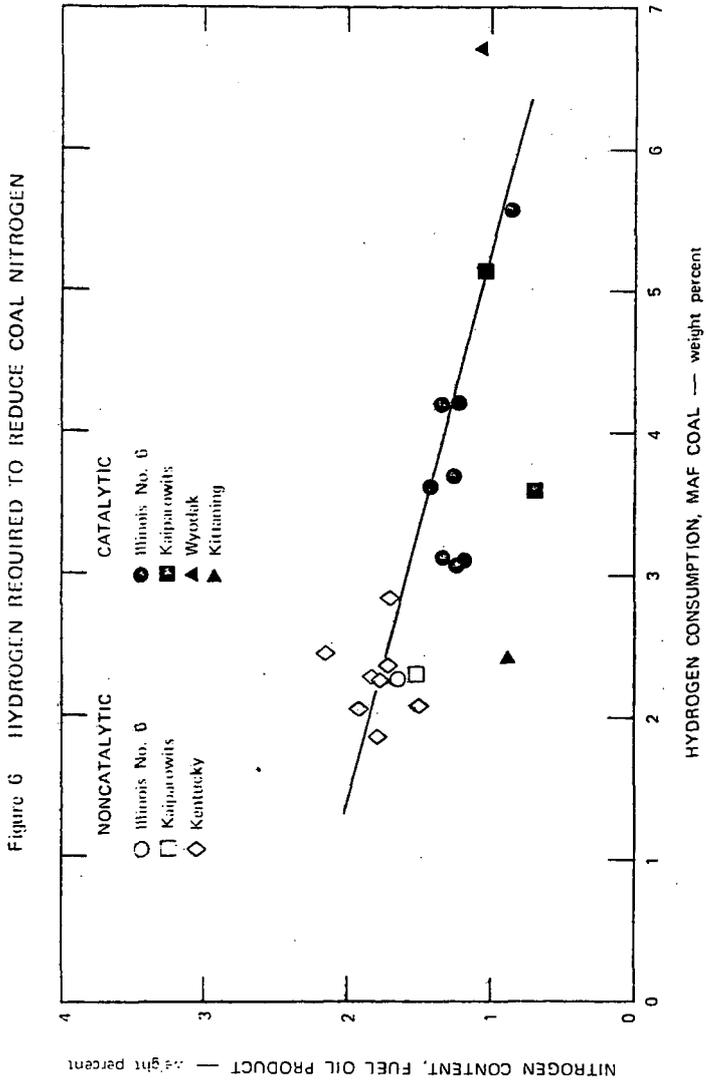


Figure 7 NITROGEN CONTENT OF COAL LIQUIDS FROM NONCATALYTIC OPERATIONS

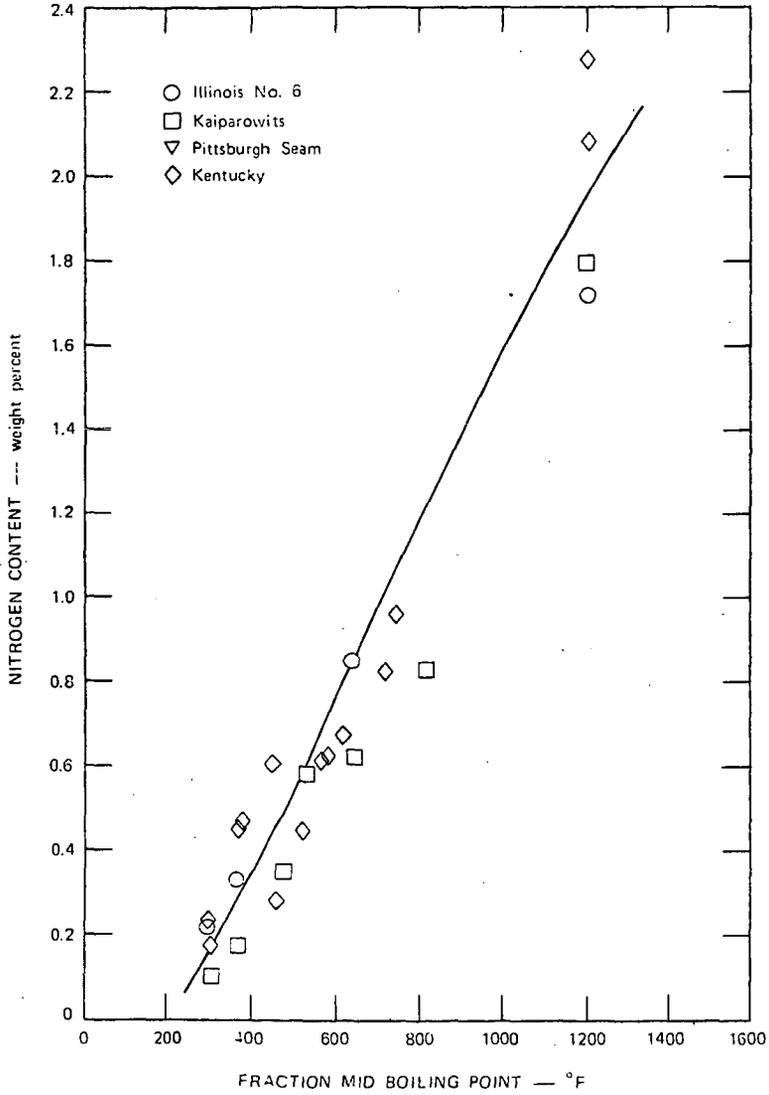
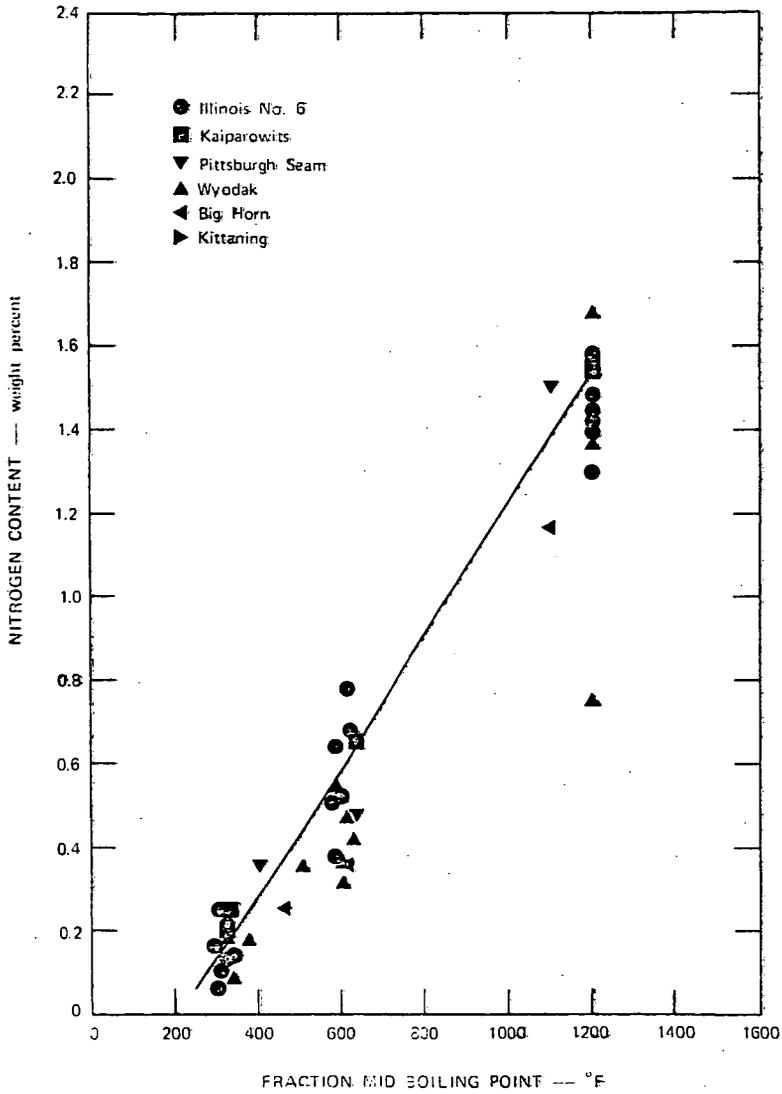


Figure 8 NITROGEN CONTENT OF COAL LIQUIDS FROM CATALYTIC OPERATIONS



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