

## THE EFFECT OF SOLVENT PRETREATMENT ON COAL LIQUEFACTION

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This paper describes research on the chemical and physical phenomena occurring between coal and solvents prior to the onset of the major liquefaction (bond breaking) step. This report is limited to those phenomena that occur readily at temperatures near 200°C and have an effect on the subsequent liquefaction reactions.

A series of microautoclave experiments with Bruceton Coal and W. Kentucky 9/14 Coal, using creosote oil or SRC-II heavy distillate as solvents, showed that small but experimentally significant increases in conversion can be obtained by heating the coal-solvent slurry for one hour at 200°C prior to a short contact time liquefaction test (Table 1). (The presence of hydrogen at 200°C did not appear to be essential for this increase to occur.)

In order to obtain a better understanding of the factors that cause this increase in conversion, and thus propose a means to enhance the effect, several experiments were conducted with coal and model solvent compounds. Quinoline, 1-methylnaphthalene, and blends of these two compounds were chosen as solvent models. The results of these experiments show that these compounds are incorporated into the coal with pretreatment at 200°C, but no incorporation occurs with similar pretreatment at room temperature.

A tetrahydrofuran (THF) soluble-cyclohexane insoluble fraction was isolated from the quinoline treated coal and purified by three successive dissolution and reprecipitation steps in THF and cyclohexane. Nitrogen analysis of the products showed that the original value of 3.3 percent was reduced to 1.9 percent after three reprecipitation steps. Further reprecipitation resulted in no further decrease in the amount of nitrogen present. Comparing these values with the 1.5 percent nitrogen in the original coal shows two-thirds of the original quinoline incorporated into the coal was removed by the dissolution/precipitation steps. This fraction of the initially retained quinoline is considered to be physically incorporated into the pore structure of the crude quinoline-coal adduct. This quinoline is not readily removed by extraction but is removable by dissolution followed by reprecipitation in excess cyclohexane.

The quinoline remaining in the thrice-reprecipitated product is believed to be bound by hydrogen bonds to acidic sites, presumably phenolic. A comparison of the microautoclave liquefaction behavior of this adduct with a corresponding fraction of the coal obtained by analogous treatment of the coal with 1-methylnaphthalene did not show any significant difference. Inasmuch as the 1-

methylnaphthalene treatment of coal at 200°C could not result in acid-base adduct formation it was concluded that the coal quinoline adduct has no significant effect on subsequent liquefaction.

The possibility of a beneficial effect of the physically incorporated solvent was considered. Physical incorporation of the 1-methylnaphthalene as well as quinoline and blends of these compounds occurs readily at 200°C. These physically incorporated solvents are not removable by extraction, apparently because they enter the fine pore structure of the coal when the coal swells and are then locked into the pores when cooling of the coal solvent slurry causes the pore structure to shrink to near its original dimensions.

The beneficial effect of the solvent pretreatment is therefore believed to be a result of a greater extent of solvent aided liquefaction in contrast to the pyrolytic decomposition of some of the coal that reaches liquefaction temperatures before it is contacted by solvent.

Table 1. Effect of Solvent Pretreatment

(1g coal, 5g solvent, 2000 psig, 425°C)

<u>Coal</u>	<u>Solvent</u>	<u>Pretreatment</u>		<u>Run Time</u>	<u>THF Solubles (%)</u>
		<u>Time</u>	<u>Temperature</u>		
Bruceton	Creosote Oil	None	--	15 min.	61.5
Bruceton	Creosote Oil	1 hour	200°C	15 min.	66.7
Bruceton	SRC-II, H.D. <sup>a</sup>	None	--	15 min.	75.6
Bruceton	SRC-II, H.D.	1 hour	200°C	15 min.	78.2
W. KY 9/14	SRC-II, H.D.	None	--	5 min.	85.7
W. KY 9/14	SRC-II, H.D.	1 hour	200°C	5 min.	88.1
W. KY 9/14	SRC-II, H.D.	15 min.	320°C	5 min.	88.2
W. KY 9/14	Creosote Oil	None	--	5 min.	79.5
W. KY 9/14	Creosote Oil	1 hour	200°C	5 min.	81.8

<sup>a</sup>H.D. = Heavy Distillate