

HIGH-YIELD COAL CONVERSION IN A ZINC CHLORIDE/METHANOL MELT UNDER MODERATE CONDITIONS

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INTRODUCTION

Converting coal to soluble material requires cleavage of enough chemical bonds to split the coal into subunits of only moderately high molecular weight. Because coal is inaccessible to conventional solid catalysts, current processing schemes use severe thermal conditions to effect the needed bond scission, with the handicaps of partial fragmentation to gas and partial polymerization of cleaved products.

Hydrogen-donor action involving direct or indirect hydrogenation by solid catalysts has provided minor reductions in the severity of treatment, insufficient to alleviate the wastage of coal and of input hydrogen. To lower the scission temperature adequately requires mobile catalysts which can penetrate thoroughly into the coal. Melts such as zinc chloride are therefore a promising area for study.

Major work on zinc chloride catalysts for hydrogenation and hydrocracking of coal has been carried out by Zielke, Gorin, Struck and coworkers at Consolidation Coal (now Conoco Coal Development Co.)¹. The emphasis there has been on a full boiling-point range of liquid product, from treatment at temperatures between 385 and 425°C and hydrogen pressures of 140 to 200 bars.

In this Laboratory, several potential liquid-phase treating agents have been studied at 225-275°C--that is, at temperatures well below 325°C, which appears to be the initiation temperature for pyrolysis of the coals studied here. Working with Wyodak coal in a ZnCl₂-water melt at 250°C, Holten and coworkers^{2,3} discovered that addition of tetralin increased the pyridine solubility of product to 75%, compared to 25% without tetralin. About 10 wt-% of water is required in the melt, because pure ZnCl₂ melts at 317°C.

We have now found that replacing water in the melt by methanol leads to large increases in pyridine solubility of product from the treatment. In this paper we characterize the effects of temperature, time, hydrogen pressure, reaction stoichiometry, and addition of various inorganic and organic additives. Because oxygen removal from the coal occurs in parallel with solubilization, we conclude that scission of ether-type C-O bonds is the definitive chemical reaction.

EXPERIMENTAL PROCEDURE

The experiments were performed in a 600-ml Hastelloy B stirred Parr autoclave fitted with a 300 ml glass liner. 275 gm of ZnCl₂ (97+% pure from Matheson, Coleman, and Bell) were loaded into the liner with the desired amount of methanol (Mallinkrodt reagent-grade) and heated to about 150°C. At this time, 50 gm of undried Roland seam Wyodak coal (-28 + 100 mesh) and additional solvent (if any) were added to the melt. The autoclave was closed, purged with hydrogen, and pressurized so that it would reach the desired hydrogen pressure at reaction temperature. The contents were heated at approximately 10°C/min with stirring until the desired temperature was reached. After reaction for the desired period, the autoclave was immersed in

a cold-water bath, depressurized, and opened, and the contents were dumped into 2 l. of cold water. The coal was then washed in a Buchner funnel with 6 l. of distilled water at 90°C, and dried to constant weight in a vacuum oven at 110°C under 50 millibars of nitrogen. Some runs were split after water quenching; in these, half of the product was washed with dilute HCl before hot-water rinsing.

Approximately 2 gm of dried product (referred to as melt-treated coal, MTC) were extracted to exhaustion sequentially with benzene and pyridine in an atmospheric soxhlet apparatus. The extracts and residue were dried and weighed to determine solubility of the MTC.

In addition to knowing the total MTC solubility, it was important to determine the amount of methanol or other solvent retained by the MTC. This quantity, the incorporation ratio ($R = \text{gms incorporated organic material/gms coal-derived organic material}$), was determined by a carbon balance on the reaction. By assuming that any solvent retained in the dried MTC is pyridine-soluble, and subtracting it from the total dissolved material, the minimum solubility of the coal-derived material may be calculated. This quantity, the corrected solubility, is an indicator of the true solubilizing effect of a particular run on the coal itself. Based on replicate runs, the standard deviation of the corrected solubility is 6.5% of the reported value.

Additional details on the experimental methods employed are available elsewhere⁴.

RESULTS

Effect of Reaction Conditions on Solubility

Earlier results³ suggested investigation of the ZnCl_2 -methanol system as a coal-liquefaction medium based on high product solubility, low incorporation, and relatively low cost of methanol.

Of primary concern were the effects of temperature, pressure, time, and methanol amount on the solubilizing activity of the melt. Figure 1 presents the effect of hydrogen pressure and temperature on corrected solubility. At 60 min reaction time with 50 gm of methanol, the solubility is roughly linear with hydrogen partial pressure. Even at 225°C there is significant conversion, with 800 psig producing 40% MTC solubility compared to 12% for the raw coal. By 275°C, conversion is rapid with nearly total solubility in one hour at hydrogen pressures as low as 200 psig.

The effect of methanol amount at various hydrogen pressures is shown in Figure 2. At all hydrogen pressures, there is a maximum solubilizing effect near 50 gm methanol (approximately .75/l MeOH/ ZnCl_2 molar). To within experimental error, solubility is linear with hydrogen pressure.

As shown in Figure 3, solubilization proceeds linearly with time at 250°C (800 psig, 50 gm MeOH) with total solubility achieved near 75 minutes. At 275°C, reaction is considerably more rapid, with total conversion possible in less than 30 minutes. Heating alone to 250°C ("zero-time" runs) produces negligible increased solubility, whereas the additional 2-3 minutes between 250 and 275° for heating to 275°C results in almost 40% solubility.

Effect of Reaction Conditions on Incorporation

In addition to solubilizing activity, it is desirable to limit the amount of methanol retained by the MTC. Table 1 shows there is no significant effect of temperature on methanol incorporation at 800 psig, but a rapid rise in incorporation above 250°C at 200 psig hydrogen. There is less incorporation with 25 gm methanol than with 50 gm, and a leveling off of incorporation at higher hydrogen pressures. Also, there is no trend in incorporation with time at 275°C, but a strong increase of incorporation with time at 250°C.

Table 1. Effect of Operating Variables on Incorporation of Methanol and on Corrected H/C Ratios (273 g ZnCl₂, 50 g Wyodak coal)

Methanol (gm)	Hydrogen (psig)	Temp (°C)	Time (min)	Corrected Solubility (Pct. DAF)	Retained MeOH (gm/gm coal organics)	Atomic H/C Ratio	
50	0	250	60	57.3 ¹	.31	.53	
	200			67.4 ¹	.16	.81	
	500			70.3 ¹	.19	.78	
	800			85.0 ¹	.18	.85	
25	200			54.8	.16	.70	
	800			73.6	.05	.96	
50	800	250	0	13.2	.05		
			30	53.7	.16		
			0	35.8	.16		
			30	100.0	.21		
	200	225	60	26.4	.12		
	800			40.0	.11		
	200			275	95.6	.32	
	800				99.1	.17	

¹ Average of replicate runs.

Hydrogen-to-Carbon Ratios

An indicator of the quality of the MTC is the hydrogen to carbon ratio (raw coal H/C = .98). Figure 4 shows the effect of methanol amount and hydrogen pressure on the H/C ratio of the coal derived portion of the MTC. Higher hydrogen pressures result in higher H/C ratios regardless of methanol amount. Higher methanol amounts produce lower H/C ratios at all pressures up to 500 psig. At 800 psig, there is a maximum near 25 gm methanol in the H/C ratio with a sharp drop afterward.

Effect of Additives

Table 2 lists the results of runs in which inorganic additives were used in the ZnCl₂-MeOH melt. Addition of 5 mole % ZnO, a noted poison for ZnCl₂, had little effect on solubility and produced a surprising rise in H/C ratio of the MTC. The addition of 1 gm Zn powder had little effect in solubility but slightly improved the H/C

ratio. 100 psig HCl, while producing total solubility, had little more effect than a dilute HCl wash. The hydrated chlorides of tin and cadmium resulted in reduced yields.

Solvent additives to the melt (Table 3) fall into two categories: extractive and reactive. The extractive solvents (decane, perchloroethane, o-dichlorobenzene, and pyrrolidine) had negligible effect on solubility, possibly due to the preferential wetting of the coal by the solvent and exclusion of the ZnCl₂ melt. Reactive solvents (anthracene oil, indoline, cyclohexanol, and tetralin) all incorporated strongly. Donor solvents, tetralin and indoline, increase corrected solubility, whereas anthracene oil and cyclohexanol have negligible effect.

Table 2. Effect of Inorganic Additives to ZnCl₂-Methanol Melt.
273 gm ZnCl₂; 50 gm MeOH; 50 gm coal; T = 250°C; t = 60 min

Additive (gm)	P _{H₂} (psig)	Corrected Solubility (Pct. daf)	R (gm retained MeOH/gm coal organic)	Corr. Atomic H/C
HCl (100 psig)	500	100.0	0.16	0.84
ZnO (9.0) ³	500	69.2	0.11	1.10
Zn (1.0)	500	73.6	0.15	0.86
CdCl ₂ (38.5) ¹	200	44.3	0.16	0.76
SnCl ₂ (42.1) ²	200	0.0	0.19	0.55
None ³	500	70.3	0.18	0.79
None ³	200	67.3	0.17	0.76

- 1 - 11.4 gm water present with CdCl₂
- 2 - 36.0 gm water present with SnCl₂
- 3 - Average of two replicate runs

Table 3. Effect of Solvent Additives to ZnCl₂-Methanol Melt.
273 gm ZnCl₂; 50 gm MeOH; 50 gm coal; T = 250°C; t = 60 min

Solvent (gm)	P _{H₂} (psig)	Corrected Solubility (Pct. daf)	R (gm retained MeOH/gm coal organic)
n-Decane (50)	250	41.4	0.19
C ₂ Cl ₆ (50)	200	40.5	0.43
o-Cl ₂ -benzene (60)	200	33.5	0.16
Pyrrolidine (10.5)	500	65.6	0.13
Cyclohexanol (10)	200	68.7	0.39
Anthracene Oil (10)	250	73.7	0.77
Tetralin (10)	200	77.4	0.65
Indoline (10)	500	81.5	0.27
Methanol only	500	70.3	0.18

Effect of Wash

Several runs were divided after water quenching of the MTC and 15 ml HCl was added to the cold water wash. Figure 5 shows the increase in benzene and total MTC solubility as a result of the HCl wash. Acid washing produces total pyridine solubility from a 65% soluble water washed MTC. The effect of acid washing on benzene solubility is less marked with a maximum increase of 10-15% at 25% water wash benzene solubility. The maximum benzene solubility with either water or acid wash is 40%.

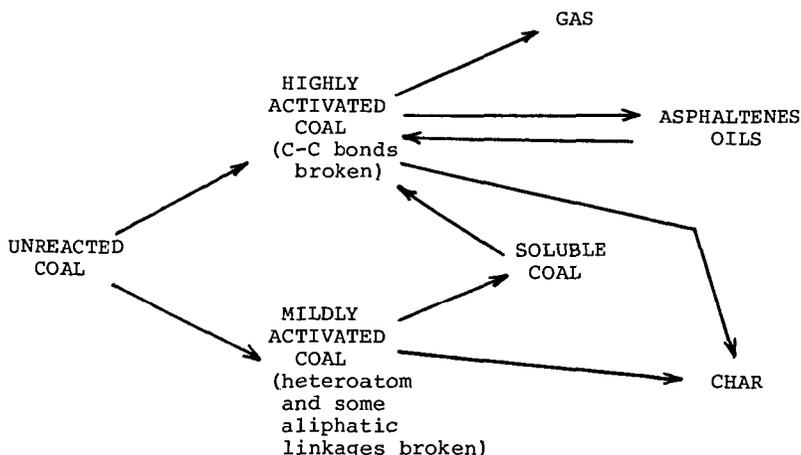
In some runs, a preliminary benzene wash was necessary to make the MTC sufficiently hydrophilic to allow removal of the $ZnCl_2$. The solubilized material from the wash was added to the benzene soxhlet yield for total benzene solubility. As seen in Figure 6, the relationship between benzene solubility and pyridine solubility of the MTC is a function of the type of wash used. Benzene washing produces higher benzene solubility whereas HCl washing produces higher pyridine than water wash.

Oxygen Recovery and Solubility

Earlier work with the $ZnCl_2-H_2O$ system³ had revealed a correlation between the oxygen recovery and the solubility of the MTC. There proved to be a similar relationship in the $ZnCl_2$ -methanol system, as well as a separate relationship for acid-washed runs (Figure 7). Conditions of temperature, hydrogen pressure, reaction time and stoichiometry did not affect the relationship for a particular solvent, whereas additional solvent produced skew points supporting the conclusion that the relationship is solvent dependent. Acid washing produces increased solubility without affecting oxygen removal.

DISCUSSION

The following scheme may be used to explain the conversion of coal to soluble form.



The first step in conversion is activation. This activation may be weak (by using low temperatures and less active catalysts) cleaving only weaker heteroatom bonds or strong (by using higher temperatures and active catalysts such as HCl) cleaving weaker as well as stronger C-C bonds. (Weak bonds include ether and thioether as well as aliphatic linkages with suitably substituted neighboring aromatic centers^{5,6}.) Keys to the mild activation are penetration of the catalyst into the coal, sufficient catalyst activity toward weak bond cleavage and resistance to poisoning. Massive amounts of molten ZnCl₂ provide the proper activation and the correct choice of solvent allows for proper contacting.

Scanning electron micrographs of methanol-treatment MTC show that methanol addition causes massive physical change in the coal particles, presumably enhancing phase contact and removing product during reaction so as to expose unreacted coal⁷.

The cleaved weaker bonds must now be properly "capped" to prevent polymerization to char. Several mechanisms are available for such capping. First, hydroaromatic structures in the coal may exchange hydrogen with the reacted fragments, as noted by Whitehurst et al.⁸ This type of donation may result in a net lowering of H/C ratio of the product as hydrogen is lost forming water upon oxygen removal. Two sources of external hydrogen are also available: from donor solvents and gas-phase hydrogen. The contribution of gas-phase hydrogen is normally small but there is promise for enhancement of this effect through the use of additives with hydrogenation activity still being investigated. Finally, capping may occur without hydrogen, by means of alkylation. Methanol may be important in this step, as its presence may prevent crosslinking subsequent to ZnCl₂ attack.

Conversion of soluble coal to asphaltenes and oils will require further activation of the coal with C-C bond cleavage and further heteroatom removal. Higher temperatures and/or more active catalysts will likely be required with sufficient hydrogen donors and hydrogenation catalysts to reduce char formation. Preliminary investigations on this further conversion are currently under way in our labs. The soluble coal should facilitate contacting, allowing a greater choice of catalysts for upgrading.

CONCLUSIONS

Some preliminary work was done with other solvents which were miscible with the ZnCl₂. We have discovered that replacing water with methanol as a liquefying agent for the ZnCl₂ results in large increases in pyridine solubility of the treated coal. There are several explanations for this effect: improved contacting between the coal and the melt; higher activity of the ZnCl₂ in a methanol media; methylation of cleaved bonds resulting in reduced char formation; extraction of the reaction products, leaving the coal more accessible.

Solubility is linear with hydrogen pressure and time, at constant temperature and methanol charge. There is a strong effect of temperature leading to complete solubility at 275°C in less than 30 minutes. Incorporation is best limited by lower methanol amounts and higher hydrogen pressures.

Extractive solvents reduce solubility; donor solvents increase solubility, but involve incorporation. A relation between benzene and pyridine solubility is dependent on wash conditions. Finally, oxygen recovery and corrected solubility are related, the relationship varying with the solvent used.

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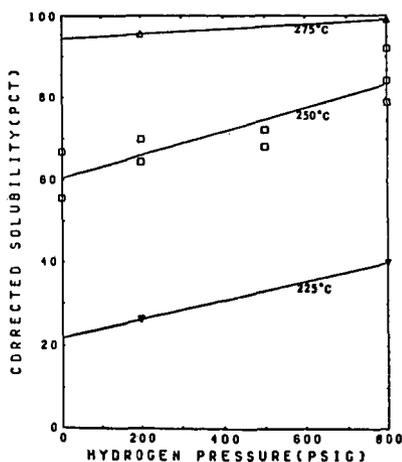


Figure 1.
Effect of Hydrogen Pressure and Temperature on Corrected Solubility. 273 gm $ZnCl_2$; 50 gm coal; 50 gm MeOH; 60 min.

Figure 2.
Effect of Methanol Charge and Hydrogen Pressure on Corrected Solubility.
273 gm $ZnCl_2$; 50 gm coal;
250°C; 60 min.

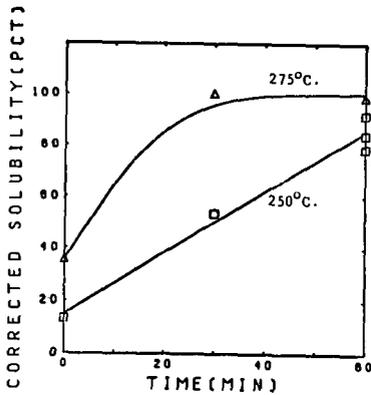
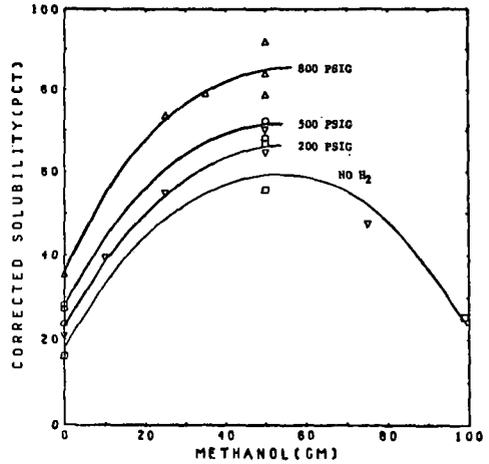
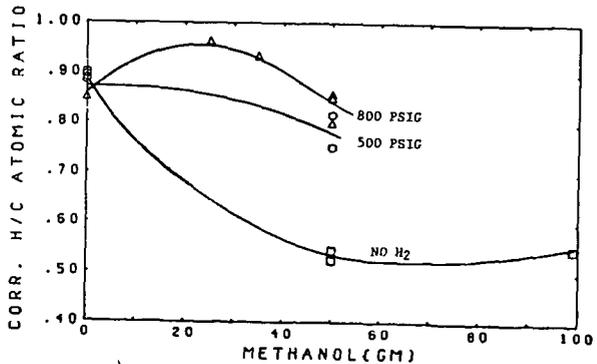


Figure 3.
Effect of Run Time on Corrected Solubility at 250° and 275°C.
273 gm $ZnCl_2$; 50 gm coal;
50 gm MeOH; H₂, 800 psig.

Figure 4.
Effect of Methanol Charge and Hydrogen Pressure on Atomic H/C Ratio.
273 gm $ZnCl_2$; 50 gm coal;
250°C; 60 min.



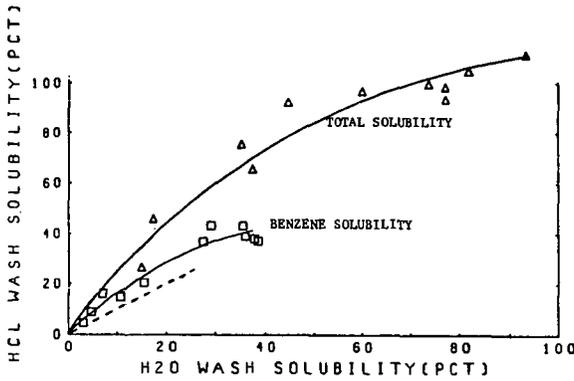


Figure 5.
Effect of Acid Wash
on Solubilities.
273 gm $ZnCl_2$;
50 gm coal.

Figure 6.
Relations Between
Benzene and Total
Solubility.
273 gm $ZnCl_2$;
50 gm coal.

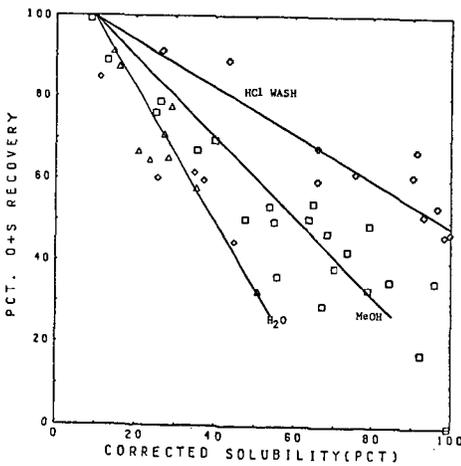
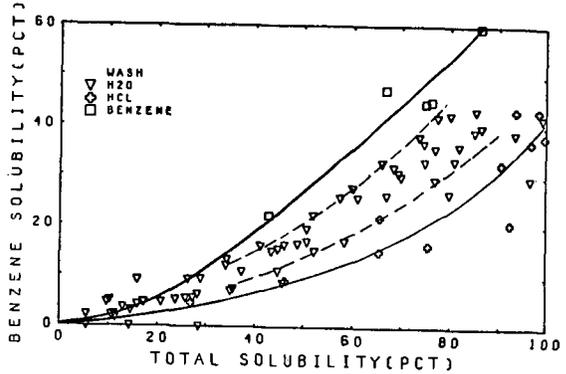


Figure 7.
Oxygen and Sulfur
Recovery in Product
vs Total Solubility.
273 gm $ZnCl_2$; 50 gm coal.