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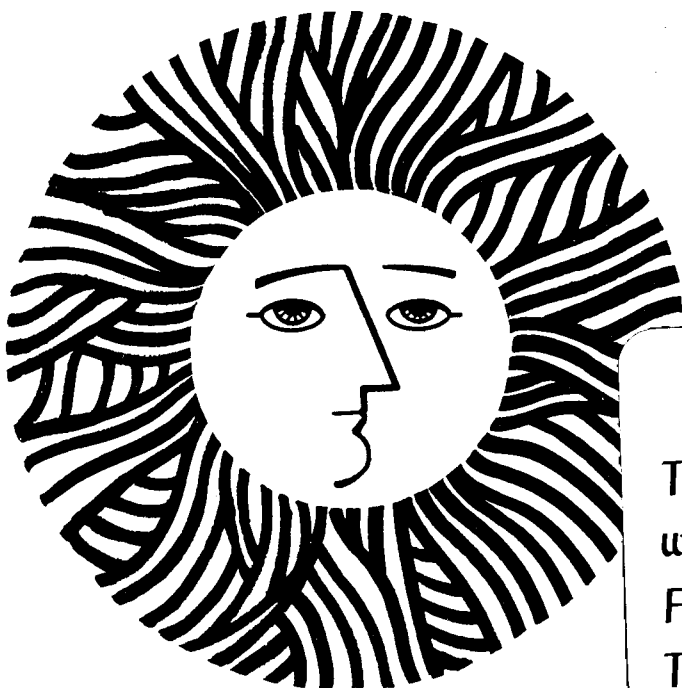
## ENERGY & ENVIRONMENT DIVISION

Submitted to Industrial and Engineering Chemistry  
Process Design and Development

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IN COMBINATION WITH ORGANIC SOLVENTS

Edward A. Grens II, Frank Hershkowitz, Ronald R. Holten,  
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July 1979



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LBL-9411 *e.2*

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COAL LIQUEFACTION CATALYSIS BY ZINC CHLORIDE MELTS  
IN COMBINATION WITH ORGANIC SOLVENTS

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July 1979

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Abstract

High conversions of subbituminous coal to cyclohexane- and pyridine-soluble materials have been achieved at temperatures below the threshold for coal pyrolysis by processing in reaction media composed of a zinc chloride melt mixed with a suitable organic solvent. At 250°C and 35 atm hydrogen, for example, addition of a tetralin phase increased the conversion of Wyodak coal to 68% pyridine solubles, compared to 28% obtained with use of zinc chloride alone. The conversion is accompanied by marked reduction of oxygen content in the treated coal. The hydrogen required is provided partly in the coal itself as well as by hydrogen donors and molecular hydrogen.

Zinc chloride and other Lewis acids have been widely investigated as catalysts for hydrocracking of coal and coal extracts. These catalysts are either used as melts in massive quantities (Zielke et al., 1966, 1979; Struck et al., 1969), or in small amounts impregnated into the coal (Wood and Wiser, 1976). In either case they have been employed at temperatures above the pyrolysis temperature of the coal, that is, above about 325°C. Under these conditions, thermal decomposition of the coal is the initial step in the conversion process, just as it is in most coal liquefaction technology. At lower temperatures where coal pyrolysis does not occur, high conversions of coal to soluble products are not obtained by treatment in zinc chloride melts under hydrogen (Derencsenyi and Vermeulen, 1975).

In the course of investigations, at the Lawrence Berkeley Laboratories, of coal liquefaction with homogeneous catalysts below coal pyrolysis temperature, coal has been treated with zinc chloride melts in combination with organic solvents, at 250 to 300°C. This procedure was found to give much greater conversions of coal to extractible products than did the use of the melt or solvent separately (Holten and Vermeulen, 1977). This result is in contrast to previous work by Conoco Coal Development Company that had shown no significant improvement in conversion of coal to liquids when tetralin was added to zinc chloride processing media operated at 350°C or higher (Goren et al., 1968). The use of organic solvents with zinc chloride melts at lower temperatures has many advantages. These solvents provide hydrogen-donor activity,

improve penetration of the melt into the pore structure of the coal, act as a transport vehicle for hydrogen from the gas phase, and in some cases serve as alkylating agents. In addition, under proper conditions, they can extract reaction products from the coal to leave the coal more accessible, the dissolved products more isolated from catalysis of (undesired) subsequent reactions, and the melt less contaminated with reaction residues.

This paper presents the results of treatment of Wyodak subbituminous coal with "massive" or excess quantities of zinc chloride melts in combination with a number of pure organic solvents. The solvents used include compounds immiscible with the inorganic melt (e.g. tetralin) and compounds soluble in the melt (e.g. methanol). The work was conducted at temperatures below that of coal pyrolysis (in the range 250-300°C) under hydrogen pressures of up to 35 atm. Conversions to pyridine soluble materials in excess of 98% (MAF basis) and to cyclohexane solubles as high as 47% were obtained for 1 hour reaction times. These results indicate the potential for melt/solvent liquefaction processes to give high conversions under mild operating conditions where formation of light hydrocarbon gases and of refractory char is minimized.

### Experiments

Materials. The subbituminous coal used in this investigation was supplied by Wyodak Resources Development Corporation from the Roland seam of its mine at Gillette, Wyoming. Its size as received was minus 3/4 inch,

and it subsequently was crushed, milled, and screened until essentially all was in the minus-28, plus-100 mesh fraction. It was then stored under nitrogen until just before use. The properties of this coal are given in Table I.

Zinc chloride in 95+% reagent-grade (the remainder being mostly water) and other inorganic chemicals were supplied by Matheson, Coleman & Bell. Solubility and vapor-pressure data for the zinc chloride/water system are given in Figure 1. The organic solvents used were reagent-grade from Mallinkrodt. Hydrogen gas was of 99.999% ultra-high purity, from Liquid Carbonic. Anthracene oil, a high-boiling fraction of coal tar, was obtained from Coopers Creek Chemical Corp.

Apparatus. Most of the coal treatments were conducted in a 600 ml top-stirred Parr autoclave, fabricated from Hastalloy B and fitted with a 300 ml-capacity borosilicate glass liner. The autoclave was equipped with a 2000 psig pressure gauge and rupture disc. Controlled heating was provided by a 78 watt quartz-fabric-covered mantle, responding to automatic control actuated by an iron-constantan thermocouple which monitored the temperature inside the autoclave.

Procedure. The zinc chloride melts were prepared outside the autoclave to assure complete dissolution before coal addition and to reduce heat-up time. The melt components (usually 273 g  $ZnCl_2$  with 27 g of distilled water or with a miscible organic solvent--sometimes including other additives) were weighed into the glass liner, which was then heated to 170°C under nitrogen. Following this the glass liner was placed in the preheated autoclave, the feed coal (usually 50 g) and organic solvents

added, and the autoclave closed. Heating and stirring (450 rpm) were begun immediately, at a heating rate of approximately 10°C/min. The autoclave was purged with hydrogen to remove air, and at 200°C enough hydrogen was charged so that the hydrogen pressure would be close to the desired value at the run temperature.

Figure 1 was used to determine the water partial pressure, given the composition of  $\text{ZnCl}_2$  melt and the temperature. The partial pressures of organic solvent were determined from their vapor-pressure data, since the organic liquids and the  $\text{ZnCl}_2$  melts were in most cases immiscible. The hydrogen partial pressure was assumed equal to the remainder of the pressure, since  $\text{CO}_2$ ,  $\text{CH}_4$ , and other gases were formed only in very small amounts. Therefore the reported hydrogen pressures are upper limits.

The desired treatment temperature was usually attained within 25 minutes after the autoclave was closed. At this time the pressure was adjusted to the desired level by adding hydrogen or by partial venting. During an experiment the pressure would increase slightly at the start, and then drop somewhat as reaction proceeded. The experiments described here had a duration of 1 hour at experiment temperature, which has been found to give nearly the ultimate conversions.

At the end of the experiment the heating mantle was immediately removed, and the autoclave was immersed in cold water to reduce the temperature (typically to 175°C within 2 minutes, where depressurization was begun, and to 125°C within 5 minutes).

After the autoclave was cooled distilled water was added to the reactor contents, and the resulting mixture was vacuum-filtered in a



6-inch Buchner funnel using filter paper. The solid retained on the filter was washed successively with 2 liters of cold distilled water and 6 liters more of distilled water warmed to 90°C. This material was then combined with any organic phase present in the filtrate and dried to constant weight in a vacuum oven (usually for 12 hours) at 100°C under 0.05 atm of nitrogen. The resulting product material is here referred to as melt-treated coal (MTC).

Analysis and Characterization of Products. The dried MTC was examined for yield of oils, asphaltenes, and preasphaltenes by successive extraction with cyclohexane, toluene (or benzene), and pyridine. These extractions were carried out in a Soxhlet apparatus at atmospheric pressure, using an initial sample of approximately 2 g MTC with 200 cm<sup>3</sup> of extracting solvent; contacting was for 4 hours (24 hours for pyridine), which has been found adequate for complete extraction. The liquid extracts were dried at 100°C under 0.05 atm of nitrogen for 16 hours and weighed to determine gross extract yields.

The MTC and the extracts were analyzed for elemental content, and certain samples were further characterized by vapor-pressure osmometry and gel-permeation chromatography for molecular weight, and proton-NMR spectroscopy for aromatic/aliphatic character of the hydrogen present. In addition, gas samples were collected at the end of some runs and analyzed by gas chromatography. This gas analysis showed very small yields of gaseous products, almost always representing less than 1% of coal carbon with less than 0.1% hydrocarbons, the balance being largely

CO<sub>2</sub>. All yields were evaluated as functions of the carbon present in the coal; they differ slightly from yields on a MAF basis.

The yields measured for preasphaltenes were corrected for pyridine incorporation on the basis of a nitrogen balance, under the assumption that coal nitrogen distributes uniformly among preasphaltenes and residue. The yields of all extracts were then corrected for incorporation of organic solvents used in the treatment on the basis of an overall carbon balance. In making these corrections it was assumed that the incorporation was the same for all extracts of a given MTC sample, which could lead to some biasing of yields of individual extracts (but not of cumulative yields) when incorporation is high.

### Results and Discussion

The objective of this investigation was to explore the conversions of subbituminous coal that could be obtained by treatment with zinc chloride in combination with organic solvents, while remaining below the pyrolysis temperature of the coal. To this end the effects of the nature of the organic solvent used, the operating temperature, and the hydrogen partial pressure were determined. In addition, the influence of certain inorganic additives, or contaminants, in the zinc chloride melt were qualitatively examined. Although preliminary studies of the effects of the mass ratio of the treatment phases to the coal have been carried out, such experiments are severely constrained by mechanical mixing considerations in the apparatus used here. Only cases where excess zinc chloride melt

(6:1 by weight with respect to coal) was used are discussed here. It had been found that there is no effect from changes in melt/coal ratios so long as they remain above 3:1 (Holten and Vermeulen, 1977).

Since the viscosity of pure zinc chloride melts is excessive for good coal contacting at the moderate temperatures used in this work, about 10% by weight of water was included in the melt for cases where no melt-soluble organic solvent was used. This water was introduced when the melt was prepared, as the moisture present in the (undried) coal was about sufficient to make up for initially vented vapor and for water content of the vapor space in the autoclave. However, additional water was formed from the oxygen content of the coal, and the water content of the melt increased somewhat during an experiment.

Effect of Organic Solvents. Untreated Wyodak coal is about 1% soluble in cyclohexane and 13% (cumulative) in pyridine on a MAF basis. Treatment with zinc chloride in the absence of any organic solvent, at 250°C with 35 atm of hydrogen, increases pyridine solubility moderately (to 28%) but has little effect on cyclohexane solubility, as shown in Table II. Hydrogen pressure is seen to have an important role in this conversion, since there is little increase in yield of solubles in the absence of hydrogen. The effect on the conversions obtained by zinc chloride catalysis has been studied for two general types of organic solvents: those essentially immiscible in the inorganic melt, and those completely soluble in the melt. Very large increases in yields both of oils and of cumulative pyridine solubles (oils plus asphaltenes plus preasphaltenes) have been obtained with appropriate solvents of both types.

Solvents of the immiscible type include tetralin (tetrahydronaphthalene), and other hydrocarbon species. When tetralin is used in combination with the zinc chloride melt, greatly enhanced coal conversion is obtained as shown in Table II, while treatment of coal by tetralin alone has relatively little effect (yield of 16% cumulative pyridine solubles). The molecular H/C ratios for the MTC are lower than that for the coal; however, significant hydrogen is certainly used in water formation from the oxygen in the coal (about 0.3 atom per atom of carbon for the tetralin experiments cited here), and the hydrogen content of this MTC is higher than that obtained for coal treatment for zinc chloride alone. When tetralin is present the influence of hydrogen pressure becomes very slight, in contrast to the situation in the absence of the solvent. This behavior implies a significant hydrogen-donor activity for the tetralin, an activity confirmed by the presence of naphthalene in the reaction products. Tetralin is also incorporated into the extracts to the extent of about 20% by weight (this amounts to about 0.6 tetralin molecule per average molecule of coal extract). The incorporation may be in the form both of solvation effects sufficiently strong to preclude removal by heating at 110°C, and of chemical combination such as by alkylation.

A number of other organic compounds not miscible with  $ZnCl_2$  melt were also examined to determine the effect of different solvent types. These experiments, also described in Table II, all resulted in conversions smaller than those obtained with tetralin under similar conditions. In addition several of these solvents are strongly incorporated into the treated coal, with anthracene oil and dihydroanthracene being retained

to an extreme degree while giving only moderate increases in conversion. Among these solvents anthracene oil, dihydroanthracene, and the tetralin/methyl naphthalene mixture are potential hydrogen donors; the tetralin mixture, with 55% conversion, is less effective than tetralin by itself, and the others gave even lower conversions.

Solvents miscible with zinc chloride serve to replace water in the melt. They can increase the access of the melt to the interior of the coal, and serve as alkylating agents or other reactants. The effects of those investigated in this work are given in Table III. Methanol gives high conversions at 250°C, and, not being a hydrogen donor, shows a moderate effect of hydrogen pressure on conversion. It serves as an alkylating agent and thus incorporates significantly into the MTC; the solvent retention observed corresponds to about two methanol molecules per average molecule of coal extract. Ethanol and isopropanol also act as alkylating agents in the presence of acid catalysts, are effective in promoting coal decomposition, and incorporate strongly into products. On the other hand, the presence of tertiary butanol, which is not expected to be an effective alkylating agent, actually reduces the conversion from that obtained with zinc chloride alone. When high conversions are obtained, the molecular H/C ratio of the MTC is increased significantly above that in the original coal (and that in MTC obtained with melt-immiscible solvents); this result is attributable to the incorporation of hydrogen-rich groups through alkylation.

Acetone is about as effective as methanol in promoting conversion of the coal, but incorporates in the products to a much greater extent (about

four molecules per average molecule of extract). The hydrogen atoms alpha to the carbonyl group in ketones or aldehydes are known to be quite reactive, so this result is not surprising. The use of acetic acid reduces the conversion given by the zinc chloride treatment; along with other organic acids, it appears to interfere with the catalytic activity of the melt.

Effect of Temperature. The conversion of Wyodak coal by zinc chloride in combination with tetralin increases considerably with temperature in the range 250-300°C as shown in Table IV. The temperature dependence is, however, relatively much less than that found for treatment of the coal with zinc chloride melt alone. Thus, apparently, decomposition mechanisms of lower activation energy are involved when tetralin is present. Table IV also reveals the much larger yield of oils, and the fraction of total extract that is cyclohexane-soluble, where tetralin is present. This result is especially significant, since conversion of preasphaltenes to oils often constitutes the most difficult aspect of a coal-liquefaction process.

Effect of Inorganic Additives. The action of zinc chloride melts can potentially be modified by the presence of inorganic additives or contaminants. The effects of addition of moderate amounts of alkali and alkaline earth salts are given in Table V. Sodium and potassium chlorides form binary combinations (and a ternary) with  $ZnCl_2$ , reducing the melting point of the system. They also reduce the mutual solubility of melt with organics, such as the liquid product from higher-temperature liquefaction

by  $\text{ZnCl}_2$  and hydrogen (Zielke et al., 1966). From a thermodynamic standpoint, they increase the concentration of polychlorozinc anions, and thus reduce the concentration of zinc cation which potentially is an active catalyst. Addition of 14% of KCl and 11% of NaCl, relative to  $\text{ZnCl}_2$ , completely eliminates the catalytic activity shown by  $\text{ZnCl}_2$  alone. The use of KBr and NaI as additives gives a similar degradation of the catalytic activity of the melt, although Scarrah has found that the presence of iodide and bromide increased conversions obtained with zinc chloride treatment (1973).

Calcium in coal mineral tends to enter a zinc chloride melt, partly by simple dissolution and partly by ion exchange with zinc. Therefore it is important to examine the effect of calcium salts on the catalytic activity of the melt. Addition of 9%  $\text{CaCl}_2$  to the  $\text{ZnCl}_2$  gives no significant change in conversions obtained with Wyodak coal.

#### Properties of Reaction Products

The products of combined zinc chloride/organic solvent treatments are mainly oils (cyclohexane-solubles) with low oxygen content and H/C ratios above that of the coal, and preasphaltenes (pyridine-solubles) with moderately high oxygen contents and H/C ratios below that of the coal. Relatively small amounts of asphaltenes are formed. The analysis of products for treatment with zinc chloride/tetralin at 250°C with 35 atm of  $\text{H}_2$  is given in Table VI.

Molecular Weights of Extracts. The number-average molecular weights of cumulative pyridine extracts are in the range of 300 to 500 for all experiments, as determined by vapor-pressure osmometry in pyridine. The molecular-weight distributions for the individual extracts, as determined by gel permeation chromatography, ranges from less than 200 to about 1000 for oils, 200 to perhaps 10000 for asphaltenes, and up to apparently colloidal materials (complete exclusion) for preasphaltenes. These are shown in Figure 2 for the case described in Table VI. Since the ordinate in this figure represents UV absorption (313 nm), the curves are not quantitative representations of distributions of molecular weight but only show the relative ranges involved.

Oxygen Removal. With the high oxygen-content subbituminous coal used in this work (19.0% MAF O) the decrease of oxygen in the coal treated with zinc chloride/tetralin and other mixtures is notable. As shown in Figure 3, this decrease is roughly proportional to the extent of conversion of the coal to pyridine-soluble material, with use of solvents either immiscible or miscible with the zinc chloride melt. These results strongly indicate that oxygen-containing linkages in the coal structure are selectively attacked under reaction conditions, and are responsible for a considerable part of the coal decomposition. This possibility, for other coal-treatment methods, was long ago suggested by Fischer and Eisner (1937) and others, and was proposed as an approach to coal processing by Mayo (1977). Similar reductions in oxygen content have been described by several investigators (Weller et al., 1951; Whitehurst et al., 1977), and most recently by Szladow and Given (1978).



In the present work, the cases where 80% of the oxygen is removed would yield, in the absence of multiple cross-linking, coal fragments of molecular weight of only about 100 if all oxygen were in ether-type linkages. Of course, much of the oxygen removed is phenolic and other non-bridge oxygen: but if 30-40% is from linkages (within the range mentioned by Szladow and Given), then the conversion of coal to products of about the molecular weight obtained (approximately 400 by vapor-pressure osmometry) could result from just this type of decomposition. Recent model compound studies in this Laboratory by Mobley and Bell (1979) have shown that dibenzyl ether reacts almost quantitatively at 250°C in the presence of  $ZnCl_2$ , to eliminate water and incorporate benzene to form diphenyl methane. Such reactions are possible in the  $ZnCl_2$ -catalyzed conversion of coal, and may be responsible for part of the oxygen removal and solvent incorporation observed.

Hydrogen Transfer. The results of the treatment of coal with zinc chloride alone, in the absence of hydrogen, as presented in Table II suggest that some hydrogen is lost from the coal, even though almost no conversion occurs. This would be caused by minor evolution of methane or other low-molecular-weight aliphatic hydrocarbon, and by water formation.

In the absence of added organic solvents, the extent of conversion with  $ZnCl_2$  treatment is seen to increase significantly with rising hydrogen pressure. However, no significant addition of hydrogen to the products is found. Rather the products have, in total, a lower H/C ratio than the coal, although this ratio is somewhat elevated in the oils produced. When solvents are present, the hydrogen content of melt-treated

product is increased; but solvent incorporation, rather than addition of molecular hydrogen, is primarily responsible. Proton NMR analysis indicates that the hydrogen in the oils obtained from zinc chloride/tetralin treated coal (e.g. 250°C, 35 atm H<sub>2</sub>) is about 70% aliphatic, giving a Brown-Ladner carbon aromaticity of about 60% (Brown and Ladner, 1960).

With zinc chloride catalyst, at higher temperature and pressure, reaction of molecular hydrogen with coal is a clear-cut effect (Zielke et al., 1966). Under the reaction conditions investigated here, three additional mechanisms are evident: hydrogen transfer to oxygen from within the coal, hydrogen transfer from added hydrogen-donor compounds, and incorporation (e.g. by alkylation) of some of the added organic solvent into the treated product.

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This work was supported by the Basic Energy Sciences Division of the  
U.S. Department of Energy under contract No. W-7405-ENG-48.

Table I. Analysis of Roland Seam Coal - Wyodak Mine

	<u>Proximate Analysis</u>		<u>Ultimate Analysis</u>	
	<u>As Received</u>	<u>Dry Basis</u>	<u>Dry Basis</u>	<u>MAF Basis</u>
Moisture	23.6%	-	-	-
Ash	11.4	14.9%	14.9%	-
Volatile	34.5	45.2	-	-
Fixed Carbon	30.5	39.8	-	-
Elemental:				
C			61.9	72.7%
H			5.10	5.99
N			.80	.94
Cl			.00	.00
S			1.14	1.34
O (by difference)			16.2	19.0

Molecular H/C ratio: 0.99

Initial pyrolysis temperature: 325-330°C

Table II. Effects of Organic Solvents Immiscible with the Zinc Chloride Melt.  
(50g Wyodak Coal + 273g  $ZnCl_2$  + 27g  $H_2O$  at 250°C for 1 hour.)

Organic Solvent	$H_2$ pressure atm	Cumulative % Soluble <sup>a</sup>		Molal H/C ratio of MTC	Solvent incorporation g/g MTC (MAF)
		cyclohexane	pyridine		
(Untreated coal )	-	1	13	0.99	-
None	0		16	0.90	-
None	15		21	0.86	-
None	35	2	28	0.89	-
Tetralin - 50g	0		65	0.94	
Tetralin - 50g	35	31	68	0.93	0.21
Anthracene oil - 50g	35		33	0.88	1.7
Dihydroanthracene - 50g	35		41	0.86	2.0
Methyl naphthalene - 50g + tetralin - 10g	35		55	0.96	0.37
Mesitol - 50g	35		39	0.91	0.11
p-Xylene - 50g	35		15	0.89	0.16

<sup>a</sup> Percent of C in original coal, corrected for solvent incorporation.

Table III. Effects of Organic Solvents Miscible with the Zinc Chloride Melt.  
(50g Wyodak Coal + 273g  $ZnCl_2$  + 50g solvent at 250°C for 1 hour.)

Organic solvent	H <sub>2</sub> pressure atm	% Soluble <sup>a</sup> in pyridine	Molal H/C ratio of MTC	Solvent incorporation g/g MTC (MAF)
Methanol	15	65	1.10	0.18
Methanol	35	72	1.12	0.17
Ethanol	15	>98	1.12	0.39
i-Propanol	35	71		0.45
t-Butanol	15	12	1.04	0.34
Acetone	15	66	0.95	0.68
Acetic acid	15	11		0.15

<sup>a</sup> Percent of C in original coal, corrected for solvent incorporation.

Table IV. Effect of Temperature on Conversion.  
(50g Wyodak Coal + 273g ZnCl<sub>2</sub> + 27g H<sub>2</sub>O with 35 atm H<sub>2</sub> for 1 hour.)

Organic solvent	Temperature °C	Cumulative % Soluble <sup>a</sup>		
		cyclohexane	toluene	pyridine
None	250	2	6	28
None	300	9	19	51
Tetralin - 50g	250	31	41	68
Tetralin - 50g	300	47	59	82

<sup>a</sup> Percent of C in original coal, corrected for solvent incorporation.



Table V. Effect of Inorganic Additives  
(50g Wyodak Coal + 273g  $ZnCl_2$  + 25g  $H_2O$  at 250°C for 1 hour)

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Additive to $ZnCl_2$ melt	$H_2$ pressure atm	% Soluble in pyridine	Molal H/C ratio of MTC
None	0	16	0.90
None	35	28	0.89
$CaCl_2$ (25g)	35	26	0.85
KCl (38g) + NaCl (30g)	35	11	0.96
KBr (45g) + NaI (57g)	35	13	0.90

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Table VI. Analysis of MTC and Extracts  
(50g Wyodak Coal + 273g ZnCl<sub>2</sub> + 25g H<sub>2</sub>O + 50g Tetralin at 250°C with 35 atm H<sub>2</sub> for 1 hour.)

	Product fraction				
	Total MTC	Oils	Asphaltenes	Preasphaltenes <sup>b</sup>	Residue
Yield as % of coal C	97.7 <sup>a</sup>	31.4	9.3	26.8	30.2
Elemental Analysis (% MF)					
C	67.1	91.0	84.7	74.0	53.5
H	5.22	7.93	7.77	5.66	3.70
N	0.80	0.05	0.34	1.16	1.89
O + S	11.3	1.02	7.19	19.2	11.4
Ash	15.6	0	0	0	29.5
Molal H/C ratio	0.93	1.05	1.10	0.92	0.81

<sup>a</sup>Total MTC differs from coal charged because of gas formed and other carbon losses.

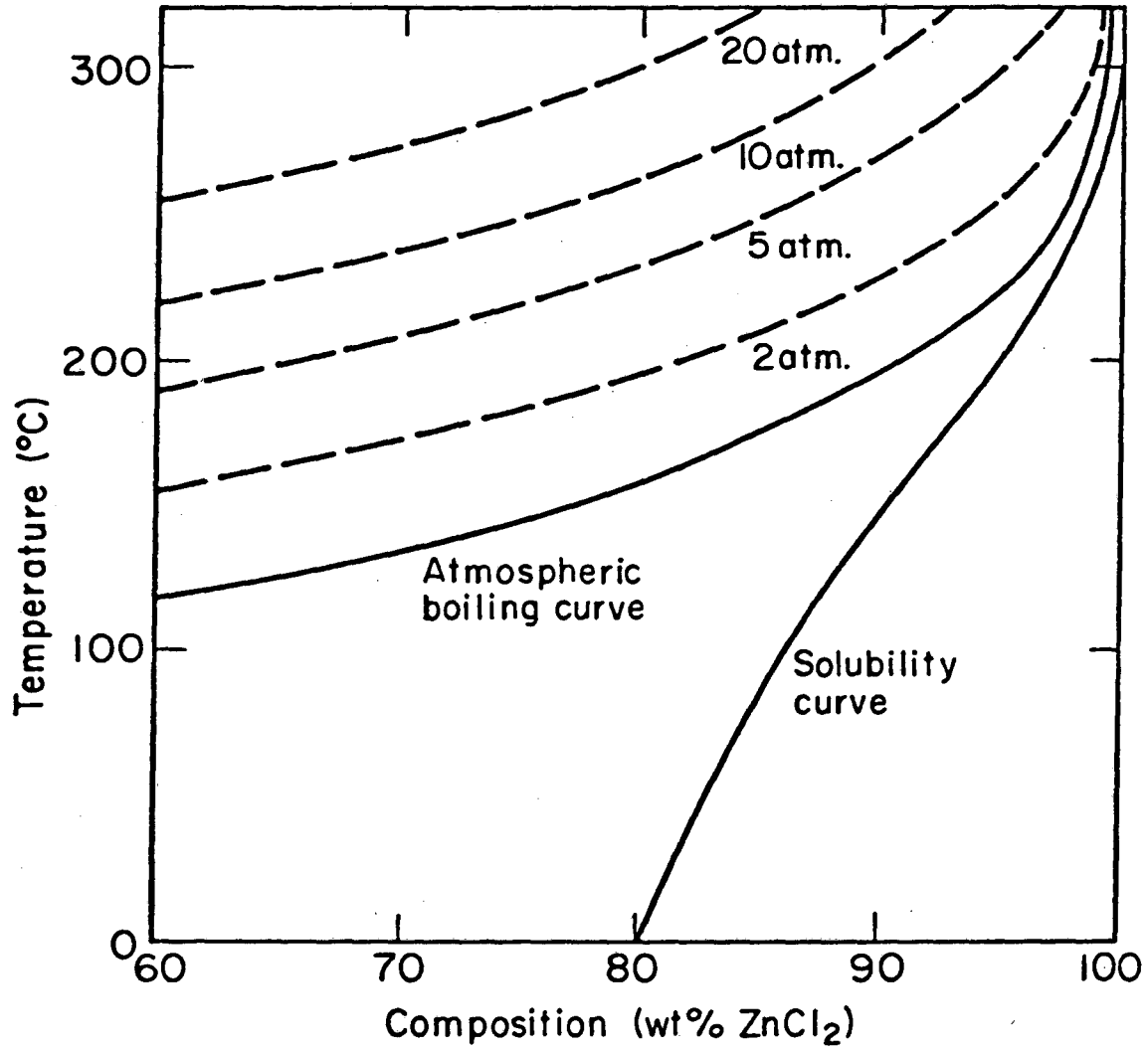
<sup>b</sup>Corrected for pyridine incorporation.

FIGURE CAPTIONS

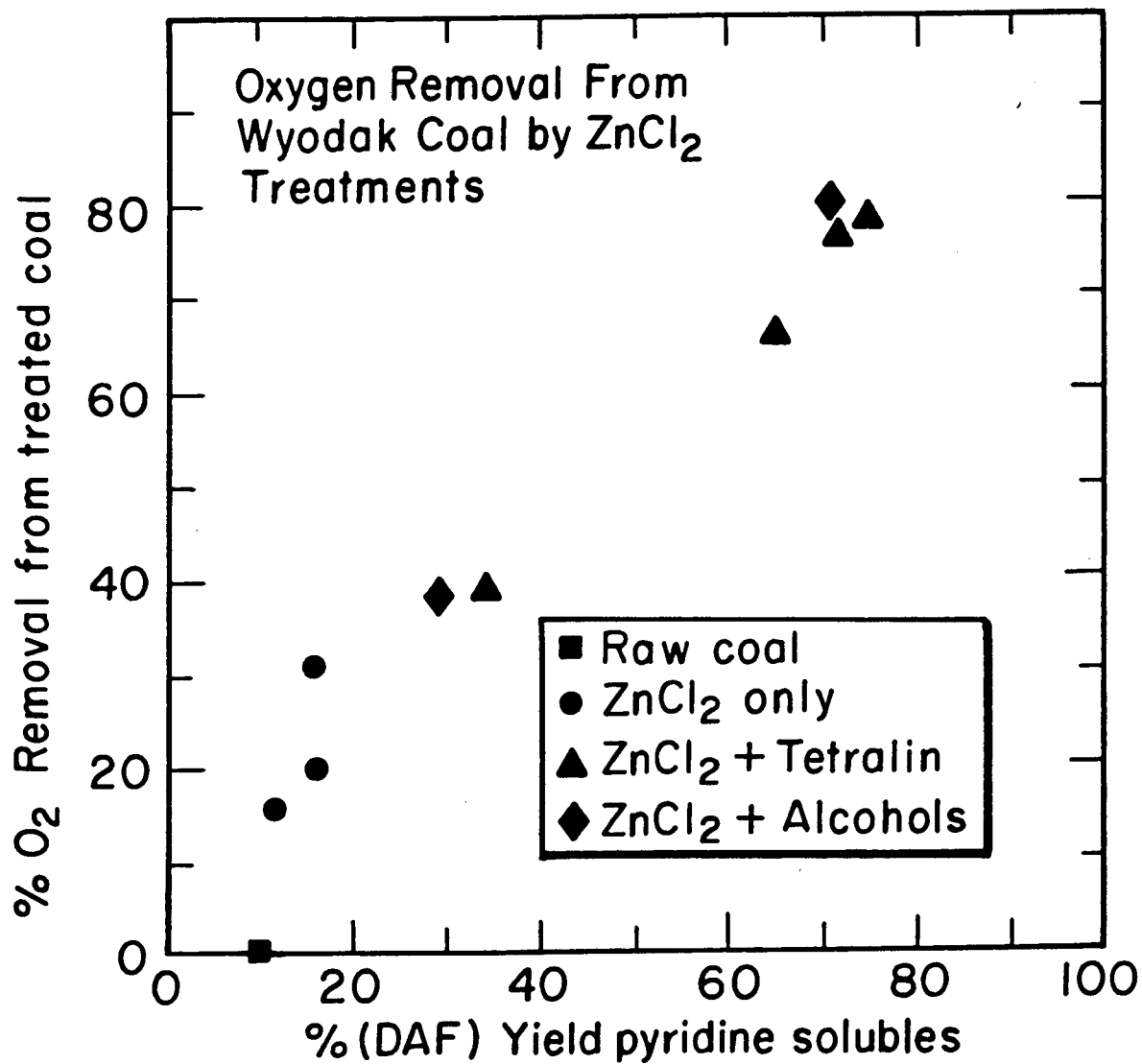
Figure 1. Solubility and boiling temperatures for the zinc chloride/water system (Holten and Vermeulen, 1977).

Figure 2. Oxygen removal from Wyodak coal as a function of conversion by zinc chloride treatment at 250 and 300°C.

Figure 3. Gel permeation chromatograms of products from treatment of Wyodak coal with zinc chloride and tetralin at 250°C and 35 atm H<sub>2</sub> for 1 hour. Conducted with pyridine carrier using 100 A + 500 A + 1000 A micro Styragel columns and 313 nm UV detector at flow of 1 cm<sup>3</sup>/min.

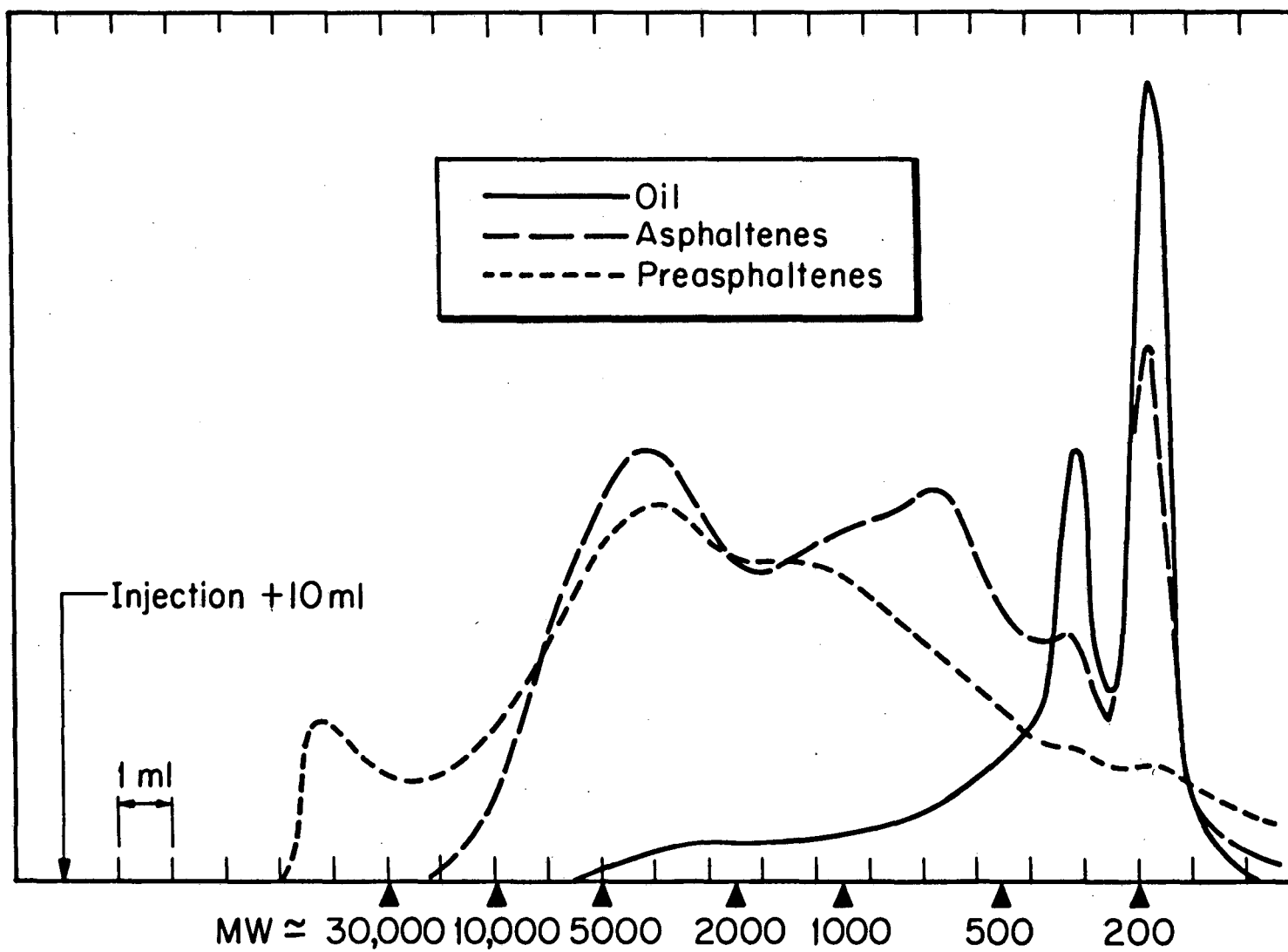


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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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