

ARTIFICIAL SIMULATION OF HYDROCARBON  
GENERATION IN COAL USING HYDROUS PYROLYSIS TECHNIQUES

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INTRODUCTION

Coal, which is usually land plant in origin, occurs in many oil-producing basins. Microscopically, coal consists of various macerals (liptinite, vitrinite, and inertinite). The generative potential of coal reflects the hydrocarbon potential of the composing macerals (Kelly et al., 1985). Although most coals consist of predominantly vitrinite, some contain significant amounts (>20% of total maceral content) of oil-prone liptinite macerals. Work by Brooks and Smith, 1967; Connan, 1974; Durand and Paratte, 1982; Thompson et al., 1985; and MacGregor and McKenzie, 1986 suggests that certain coals can be considered as source rocks for liquid hydrocarbons. Their conclusions are based on the close association of coal with liquid hydrocarbon occurrences and promising source potential supported by various geochemical analyses. However, the liquid hydrocarbon potential of coal cannot easily be evaluated because of its variable maceral composition, its unique occurrence compared to most source rocks, and difficulty in quantifying liquid hydrocarbon expulsion.

The overall objective of this study is to complete hydrous pyrolysis experiments to evaluate the liquid hydrocarbon potential of coal. Specific aspects of this study include: (1) a quantitative assessment of the generative potential of coal, and (2) an evaluation of the composition of liquid hydrocarbons generated from coal at various temperatures.

EXPERIMENTAL

Original (Unheated) Samples

Hydrous pyrolysis experiments were completed using Tertiary lignites from North Dakota and the Far East. Both lignites are thermally immature ( $R_o < 0.35\%$ ) with respect to hydrocarbon generation. The Far East lignite is liptinite-rich (32% of total maceral content), which is supported by elemental analysis ( $H/C=1.0$ ) and Rock-Eval pyrolysis (Hydrogen Index=483 mg HC/g O.C.). Resinite is the most abundant liptinite maceral (13.7%) in the Far East sample. The North Dakota lignite is vitrinite-rich (95% of total maceral content) and

liptinite-poor (3%). Geochemical and microscopic data for the two unheated lignites are listed in Table 1.

### Methods and Procedures

Hydrous pyrolysis was used to evaluate product yields, compositions, and the temperature of liquid hydrocarbon generation from the two lignites. This technique has been suggested as a method that best simulates source rock burial and the natural generation and expulsion of petroleum (Lewan et al., 1979; Lewan, 1983; and Winters et al., 1981). These studies suggest that oil-pyrolysate formed under hydrous pyrolysis conditions closely resembles naturally generated products because of the presence of water at high temperatures and pressures in a closed system. However, other pyrolysis methods (closed system anhydrous) can also simulate petroleum generation. Monthioux et al., 1985 suggests that closed-system pyrolysis of coals more closely simulates natural maturation than open-system pyrolysis techniques.

Hydrous pyrolysis procedures used were similar to those described by Lewan et al., 1979. Both lignites were crushed to 0.5 to 1.0mm chips, sieved to remove fines, and thoroughly homogenized. Individual samples were heated to temperatures ranging between 250 and 360°C for 72 hours in 1-liter stainless steel reactors. Both floating and sorbed (solvent rinsed) pyrolysate, as described by Lewan (1983), were included as expelled product. The pyrolyzed lignite residues were geochemically and microscopically characterized to evaluate changes that occur during artificial maturation.

## RESULTS AND DISCUSSION

### Quantity of Generated Oil-Pyrolysate

A maximum of 48 and 158 mg/g O.C. of oil-pyrolysate is generated from the North Dakota and Far East lignites, respectively (Table 2). Peak generation occurs at 340 and 360°C for the North Dakota and the Far East lignite, respectively (Figure 1). Expelled products consist predominantly of sorbed pyrolysate (Table 2). The differences in oil-pyrolysate yield and temperature of peak generation for the two lignites are probably related to the quantity and type of oil-prone liptinite macerals.

Peak generation temperature for the Far East sample is probably influenced by resinite. Lewan (1987) and Hwang and Teerman (1988) document that large amounts of oil-pyrolysate are generated from resinite, with peak generation occurring at, or above 360°C. Based on a hydrous pyrolysis experiment of a representative sample of solvent (methylene chloride)

extracted Far East lignite (to remove soluble resinite), approximately half of the oil-pyrollysate originates from resinite (Table 2).

### Oil-Pyrollysate Composition

Although oil-pyrollysate composition varies with temperature, the pyrollysates generally display a significant amount of n-paraffins and light aromatic and naphthenoaromatic components. Comparison of the Far East and North Dakota oil-pyrollysates at various temperatures are shown in Figures 2 and 3. These oil-pyrollysates are similar to some naturally occurring non-marine oils.

Below 290°C, the Far East oil-pyrollysates are dominated by sesquiterpenoid components, such as cadalene and other alkyl naphthalenes (Figure 2). These (sorbed) oil-pyrollysates consist of soluble resinite rather than a "thermally generated" product. Solvent rinsing the unheated Far East lignite results in a similar quantity of sorbed product. Below 290°C, the North Dakota oil-pyrollysate is dominated by light aromatic and naphthenoaromatic components and contains small amounts of n-paraffins (Figure 3).

Above 290°C, both oil-pyrollysates contain significant amounts of n-paraffins, ranging from  $C_{10}$  to about  $C_{32}$ . Although the odd/even predominance in both oil-pyrollysates decreases with temperature, it is still evident at 360°C. Precursors of n-paraffins consist of cutinite, sporinite, and other liptinite macerals, which contain plant waxes (Brooks and Smith, 1967 and Nip et al., 1988). Liptodetrinite and submicroscopic inclusions of bacterial, algal, and plant lipids in desmocollinite (a vitrinite maceral) probably contribute to the n-paraffins. Differences in the distribution and relative abundance of n-paraffins in the two oil-pyrollysates (Figures 2 and 3) are probably related to variation in their precursors.

In the  $C_6$ - $C_{15}$  range there is also a significant amount of aromatic and naphthenoaromatic products. These originate mainly from vitrinite and resinite. The Far East oil-pyrollysates display significant amounts of  $C_2$ - to  $C_5$ -alkyl naphthalenes, which are similar in distribution to a resinite oil-pyrollysate, described by Hwang and Teerman, 1988. This suggests the importance of resinite as a precursor for the Far East naphthenoaromatic components. Generated products from resinite in the Far East lignite are non-paraffinic consisting of cyclic isoprenoids and their aromatic derivatives.

Phenols also occur in significant amounts in both oil-pyrollysates. These compounds are probably derived from

diagenetically altered lignin precursors in vitrinite and inertinite (Chaffee et al., 1984). However, some liptinite macerals (sporinite) may generate phenolic compounds (Meuzelaar et al., 1984). Resinite does not generate phenolic compounds (Hwang and Teerman, 1988). The presence of phenol and alkylphenols in these oil-pyrollysates indicates a contribution from the lignin precursors. However, the contribution to the total oil-pyrollysate is small relative to that of the wax and resin components. The North Dakota lignite yields relatively larger amounts of phenols compared to the Far East sample. This observation is consistent with the vitrinite-rich maceral composition of the North Dakota lignite.

#### Characterization of Heated Lignites

Atomic H/C and O/C ratios generally decrease with temperature (Table 3). Thermally altered Far East samples plot at the top of the van Krevelen Type III pathway; North Dakota samples plot between the Type III and IV pathways (Figure 4).

Maceral analysis of the Far East samples suggests that hydrocarbon generation from individual liptinite macerals occur at different temperatures. Except for resinite, almost all liptinite macerals have disappeared by 330°C. At 350°C only small amounts of resinite remain. Secondary products consisting of exsudatinite and bitumen smear films still occur at 360°C.

Vitrinite reflectance values increase exponentially with a linear increase in temperature (Figure 5). Differences in the reflectance profiles of the two lignites are probably related to the vitrinite precursor.

#### Generative Potential of Coal

Based on these hydrous pyrolysis results, coals that contain small to moderate amounts of liptinite (<20% total maceral content) cannot generate significant amounts of liquid hydrocarbons. The contribution of desmocollinite to the liquid hydrocarbon potential of coal in a natural system is uncertain.

The Hydrogen Index of the unheated Far East lignite (483 mg HC/g O.C.) is similar to some Type II kerogens. However, the quantity of generated product is much less than that from hydrous pyrolysis experiments of Type II kerogens, reported by Lewan (1985) and K. E. Peters (personal communication). The large discrepancy in the quantity of generated pyrollysate between Rock-Eval and hydrous pyrolysis (483 versus 158 mg/g O.C.) can be attributed to the different

methods of measuring pyrolysate quantity and pyrolysis techniques (open- versus closed-system). Caution must be used in directly relating Rock-Eval Hydrogen Index to the source potential of coal.

Although the composition of the North Dakota oil-pyrolysate is similar to some naturally occurring waxy oils, the quantity of generated product is insignificant compared to most source rocks. Both the quantity and composition of an artificially generated product must be considered when evaluating the source potential of coal.

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TABLE 1

CHARACTERIZATION OF UNHEATED FAR EAST AND NORTH DAKOTA  
LIGNITES FOR HYDROUS PYROLYSIS EXPERIMENTS

<u>Total Organic Carbon/Rock-Eval Pyrolysis</u>									
	<u>Wt. % TOC</u>	<u>Mg HC/g rock</u>	<u>Mg HC/g rock</u>	<u>Mg CO<sub>2</sub>/g rock</u>	<u>Tmax °C</u>	<u>S1/S1+S2</u>	<u>S2/S3</u>	<u>Hydrogen Index Mg HC/g O.C.</u>	<u>Oxygen Index Mg CO<sub>2</sub>/g O.C.</u>
Far East	55.01	21.31	265.80	14.06	390	0.07	18.90	483	25
North Dakota	55.29	6.90	67.80	29.02	389	0.09	2.34	123	52

Elemental Analyses and Microscopy

	<u>Far East</u>	<u>North Dakota</u>
Atomic H/C	1.00	0.94
Atomic O/C	0.23	0.35
% Vitrinite Reflectance	0.33	0.29
Maceral Percent		
% Vitrinite (huminites)	65.9	94.9
% Liptinite	31.8	3.0
Exinite	18.1	2.2
Resinite	13.7	0.8
% Inertinite	2.3	2.1

TABLE 2

QUANTITY OF OIL-PYROLYSATE  
 FAR EAST AND NORTH DAKOTA LIGNITES

Temperature °C	Expelled Pyrolysate		Total Expelled Pyrolysate (mg/g TOC) <sup>2</sup>
	Floating (mg/g TOC) <sup>2</sup>	Sorbed (mg/g TOC) <sup>2</sup>	
<u>Far East</u>			
-250	-	68.0	68.0
-270	-	83.5	83.5
-290	-	95.7	95.7
-310	-	97.0	97.0
-330	-	113.5	113.5
-350	68.8	108.1	152.6
-350 <sup>1</sup>	-	87.9 <sup>1</sup>	87.9 <sup>1</sup>
-360	trace	157.6	157.6
<u>North Dakota</u>			
-260	-	11.4	11.4
-270	-	24.0	24.0
-280	-	17.9	17.9
-290	-	7.1	7.1
-310	-	15.8	15.8
-330	-	6.6	6.6
-340	-	46.7	47.7
-350	-	24.1	24.1
-360	-	31.1	31.1

<sup>1</sup> Solvent-extracted lignite

<sup>2</sup> Based on organic carbon value of 64.65 and 63.11 for  
 Far East and North Dakota lignites from elemental analysis

TABLE 3

ELEMENTAL ANALYSES AND VITRINITE REFLECTANCE  
DATA FOR RESIDUAL (HEATED) FAR EAST AND  
NORTH DAKOTA LIGNITE SAMPLES

<u>Temp. °C</u>	<u>Atomic H/C</u>	<u>Atomic O/C</u>	<u>% Ro</u>
<u>Far East</u>			
Original	1.00	0.23	0.33
250	1.01	0.15	0.57
270	1.05	0.13	-
290	0.97	0.12	0.72
310	0.92	0.10	-
330	0.91	0.07	1.01
350	0.72	0.06	1.34
<u>North Dakota</u>			
Original	0.94	0.35	0.29
260	0.77	0.25	0.60
270	0.78	0.22	0.70
280	0.71	0.20	0.77
290	0.68	0.20	0.80
310	0.66	0.13	1.08
330	0.68	0.10	1.28
340	0.64	0.10	1.40
350	0.61	0.09	1.45
360	0.60	0.08	1.58

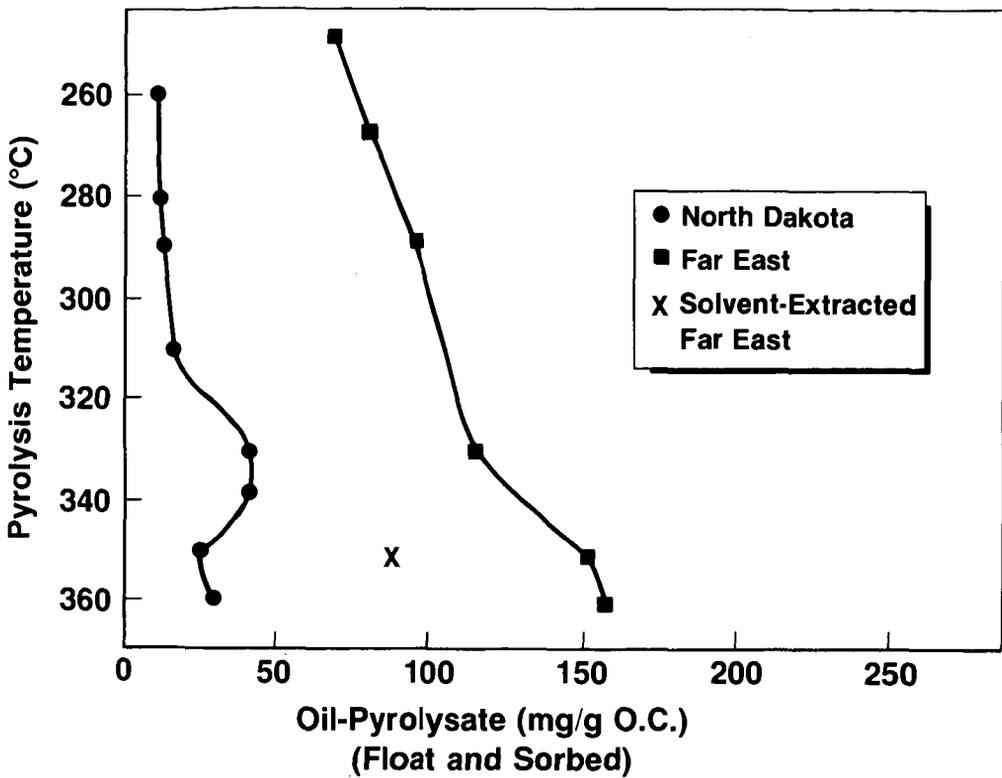
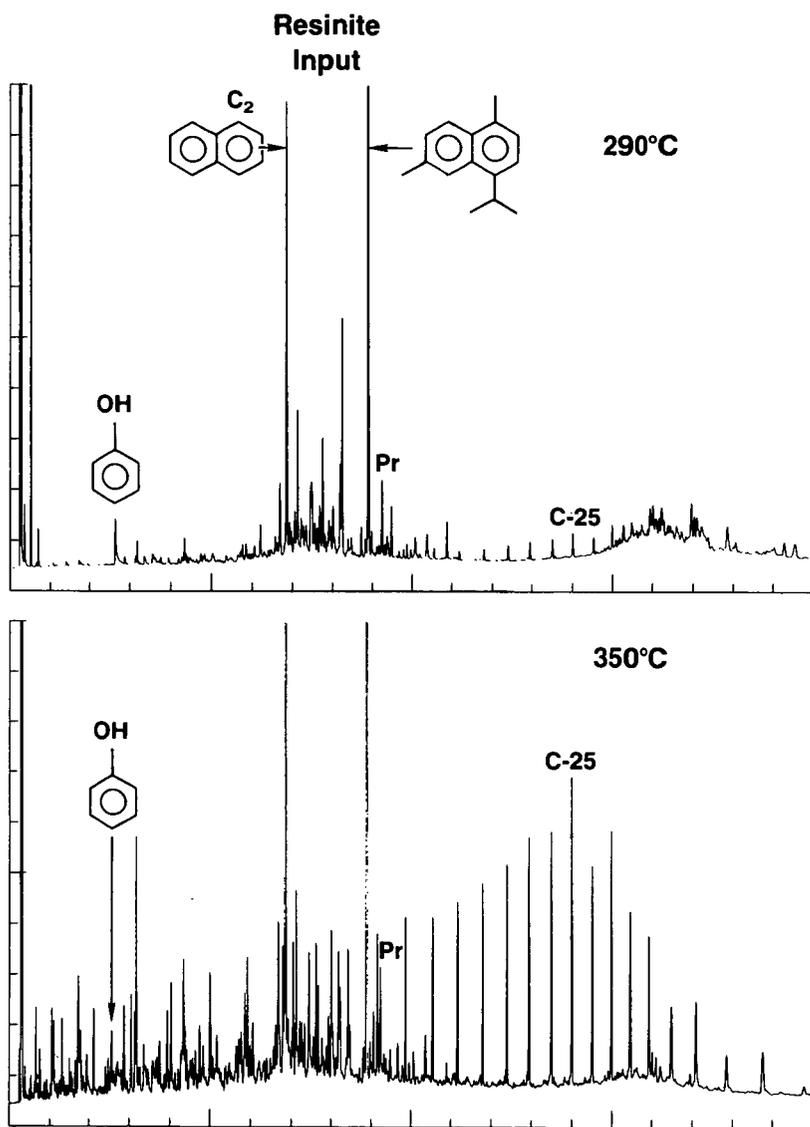


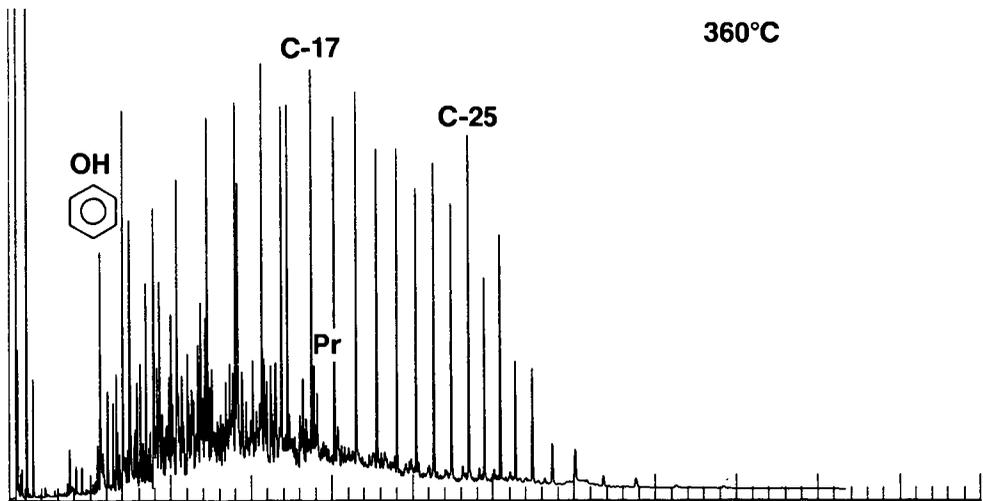
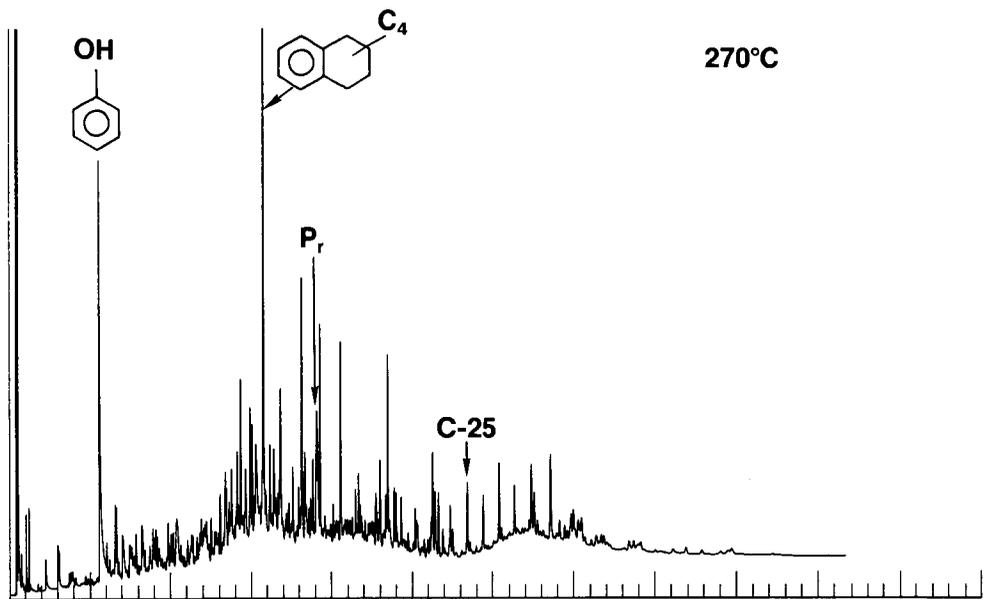
Figure 1

Oil-Pyrollysate from Hydrous Pyrolysis Experiments of Far East and North Dakota Lignites

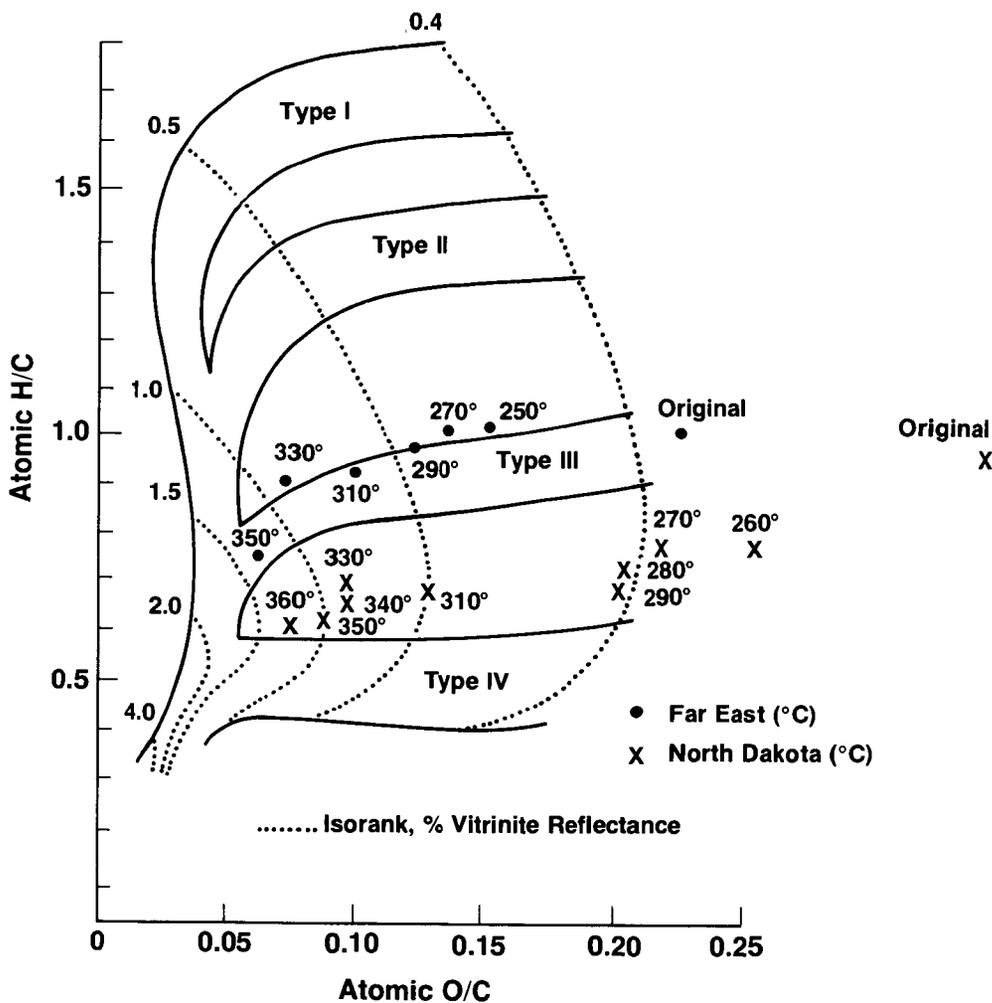


**Figure 2**  
**Comparison of Far East Lignite Oil-Pyrolsates, 290° and 350°C**

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**Figure 3**  
**Comparison of North Dakota Oil-Pyrolysates, 270° and 360°C**



**Figure 4**  
**Atomic H/C and O/C Ratios of Far East and North Dakota Lignites from Hydrus Pyrolysis Experiments**

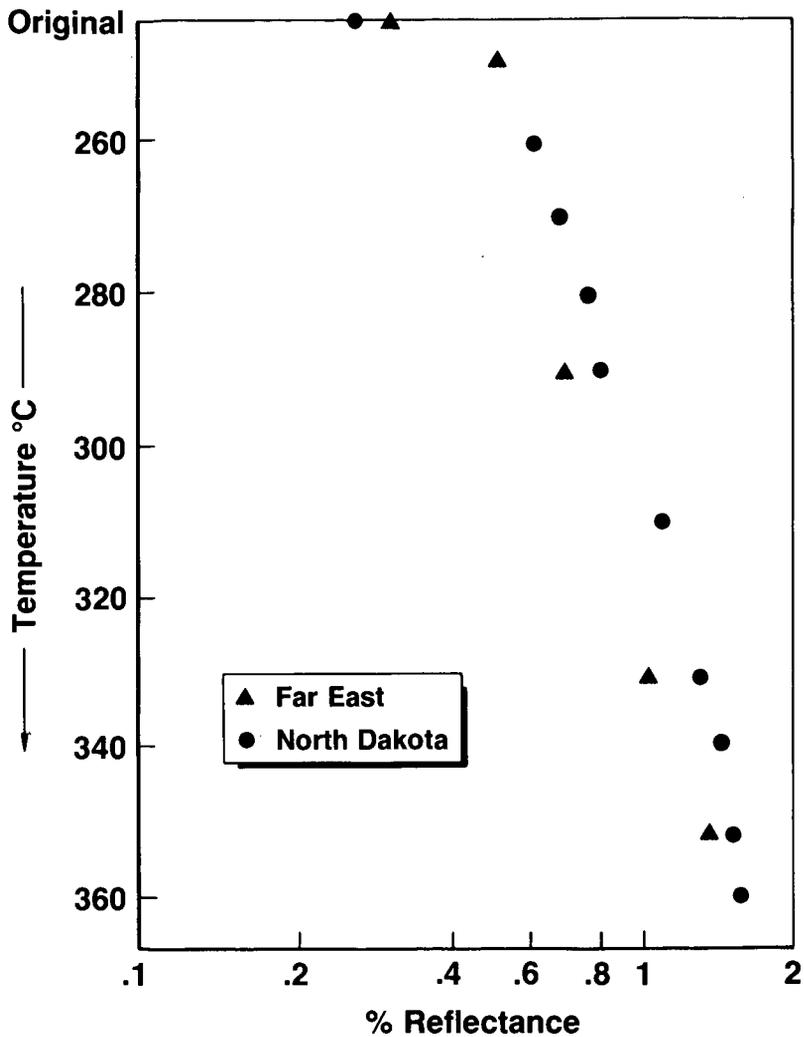


Figure 5

Vitrinite Reflectance for Far East and North Dakota Lignites Versus Hydrous Pyrolysis Temperature

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