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ETHYLENE AND AROMATICS BY THE  
CARBONIZATION OF LIGNITE

By

R. S. Montgomery, D. L. Decker, and J. C. Mackey  
The Dow Chemical Company, Midland, Michigan

The work reported in this paper was carried out in an effort to determine the feasibility of manufacturing ethylene and aromatics by the carbonization of lignite. These raw materials are of great importance to the chemical industry and we can look forward to a future of dwindling supplies and increased prices for the crude oil which is now used for their manufacture. Since it was the aim of this research to produce maximum yields of ethylene and aromatics, the carbonization was not carried out in the usual manner. The central idea was to retort the lignite under conditions that will yield a maximum of volatile products and then thermally crack these volatile products under conditions which would produce a maximum yield of ethylene and aromatic hydrocarbons. This entails a low-temperature carbonization of the lignite immediately followed by a high temperature cracking of the volatile products. Preliminary experiments showed that it was very important that the carbonization products be cracked without being first allowed to condense. If the low-temperature tar is allowed to condense, subsequent thermal treatment will produce much greater amounts of residue and smaller amounts of the desired products.

After some preliminary experiments had been made in order to determine approximately the optimum conditions using a sample of Texas Sandow lignite, a series of more carefully planned experiments were made to more precisely determine the effect of the reaction conditions and to compare Texas lignite with North Dakota lignite in this process. All of the carbonization runs were made in a batch-type retort. The temperature of the retort was raised to a maximum of 800° and two cracking temperatures were used, 600° and 800°. Two lengths of cracking zone, 18 inches and 36 inches, were used so that the effect of retention time could be evaluated in addition to the effects of the retorting and cracking temperatures.

Equipment. - The equipment was arranged as indicated in Figure 1. The evolved volatile matter passed from the retort through the cracking zone into the collection train, which consisted of a water-jacketed receiver, spiral condenser, electrostatic precipitator, and another spiral condenser. From there the gas passed through a cotton trap to remove any uncondensed fog and mist, through a dry ice-acetone trap to condense low boiling constituents and finally through a wet-test gas meter used to measure the volume of evolved gas. This train is similar to that used in the Modified Distillation Assay Apparatus described in the Bureau of Mines Report 4954. (1)

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(1) V. F. Parry, W. S. Landers, E. O. Wagner, J. B. Goodman, and G. C. Lammers, Bureau of Mines Report of Investigations 4954, (1953).

FIGURE I

LIGNITE CARBONIZATION APPARATUS

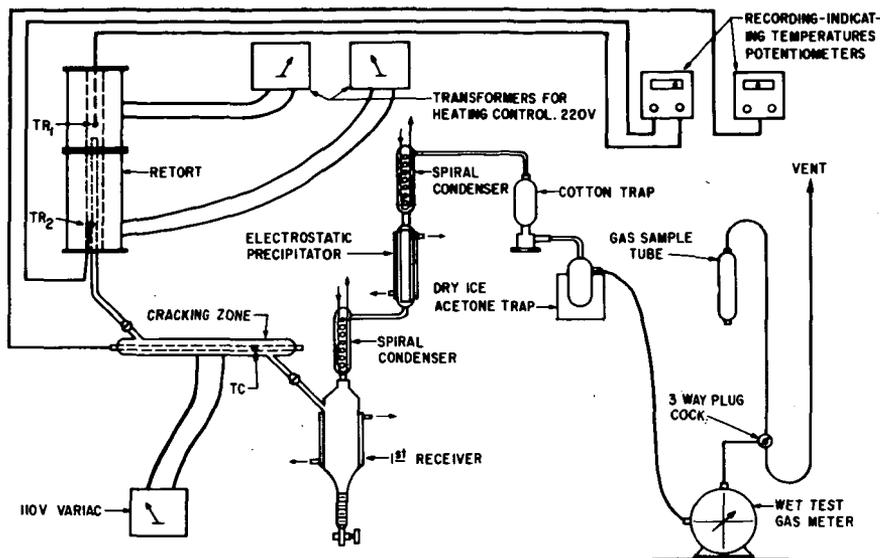
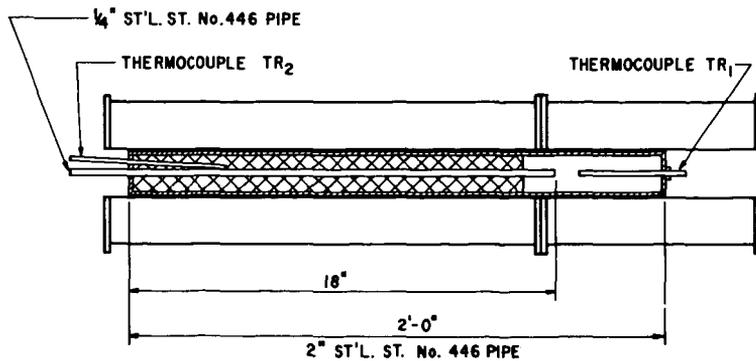


FIGURE 2

CROSS SECTION OF RETORT



The retort used for these carbonization runs consisted of a 2 inch 466 stainless steel pipe 24 inches in length. (Figure 2) Extending from the bottom of the retort to within 6 inches of the top was a 1/4 inch stainless steel pipe, used as an exit for all the volatile matter. A 1 inch stainless steel plug fitted with a thermowell (TR<sub>1</sub>) was used at the top of the retort for the introduction of the lignite charge and for the removal of the char. A second thermowell (TR<sub>2</sub>) was provided through the bottom of the retort the innermost point being welded to the 1/4 inch pipe. Heat for the retort was provided by electric furnaces controlled with variacs. The temperatures were measured with thermocouples, and recorded on electronic recorders.

Two cracking zones were fabricated of 31 mm. O. D. "Vycor" brand tubing, so that "L" in Figure 3 was 18 inches and 36 inches respectively. A concentric 9 mm. O. D. "Vycor" tube ran through the entire length of the cracking tube. This arrangement allowed a thermocouple to be placed inside the tube and the cracking temperature (TC) to be recorded for any point in the tube. It was recorded continuously on a single line recording-indicating temperature potentiometer. The thermocouple was placed inside the 9 mm. tube so that the temperature was measured at a point 2/3 of the distance from the entrance of the cracking zone to the exit. The cracking zone was heated with "Nichrome V Alloy" resistance tape wound directly on the tubing and the electric current controlled by means of a variac.

Some difficulty was experienced in the the condensation of the fog and mist during the preliminary experiments. Ice-water condensers proved to be ineffective in most instances so a small electrostatic precipitator was made. It consisted of four parallel 12 inch lengths of 3/4 inch O. D. stainless steel tubing in water-jacketed "Pyrex" brand glass housings. Suspended coaxially in the tubes were No. 31 platinum wires which were connected to a negative D. C. potential of 3 kv. The stainless steel tube was connected to ground.

Lignite Used. - The lignites used in these investigations were samples of Texas and North Dakota lignites. The Texas lignite was obtained from Bastrop County and the North Dakota lignite obtained from the Truax-Traer Coal Company, Minot, North Dakota. The samples were obtained in sealed drums in an "as mined" state and were of 3 inch particle size.

The lignite was dried overnight at 100° in a vacuum oven at 3 to 5 mm. pressure. During this operation the Texas lignite lost 29.3% while the North Dakota lignite lost 31.1 of its weight. The dried lignite was then crushed and the crushed material separated into fractions based on particle size. For the carbonization runs, the fraction was used that passed 3-1/2 mesh screen and remained in 10 mesh screen.

FIGURE 3

CRACKING ZONE

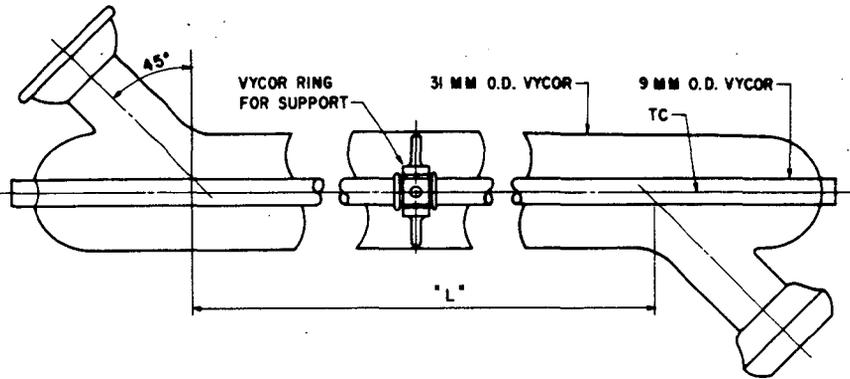


FIGURE 4

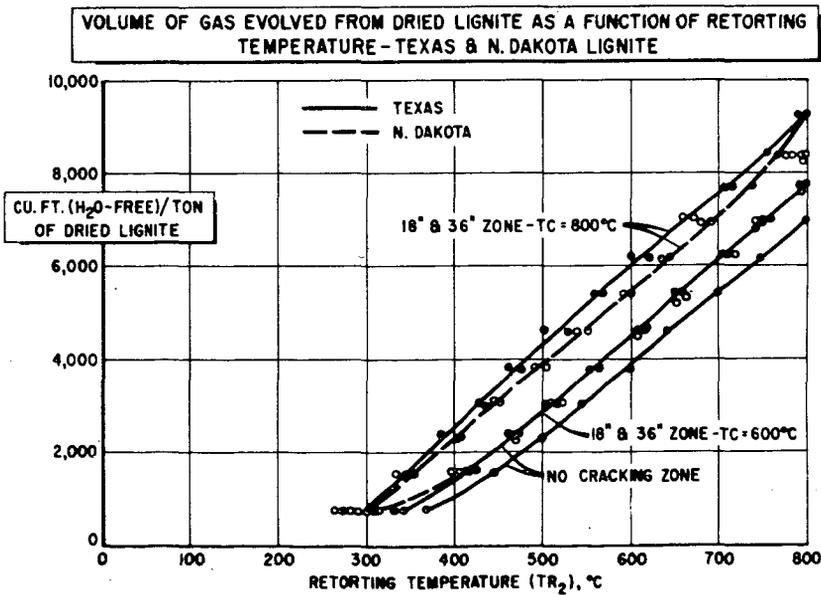


TABLE I  
ANALYSIS OF RAW LIGNITES

<u>Proximate Analysis</u>	<u>Weight Per Cent</u>	
	Texas	North Dakota
Moisture	34.0	35.2
Net Volatile	31.6	45.1
Fixed Carbon	24.7	14.2
Ash	10.6	5.5
	<u>100.9</u>	<u>100.0</u>
 <u>Ultimate Analysis</u>		
Ash	10.6	5.5
Hydrogen	5.2	6.5
Carbon	41.2	40.4
Nitrogen	0.8	0.7
Oxygen	41.5	46.5
Sulfur	0.9	0.5
	<u>100.2</u>	<u>100.1</u>

TABLE II  
ANALYSIS OF DRIED LIGNITES

<u>Proximate Analysis</u>	<u>Weight Per Cent</u>	
	Texas	North Dakota
Moisture	10.0	10.8
Net Volatile	41.5	39.6
Fixed Carbon	36.3	42.3
Ash	12.4	7.3
	<u>100.2</u>	<u>100.0</u>
 <u>Ultimate Analysis</u>		
Ash	12.4	7.3
Hydrogen	5.7	5.1
Carbon	56.8	56.7
Nitrogen	0.9	0.9
Oxygen	23.2	29.4
Sulfur	1.0	0.6
	<u>100.0</u>	<u>100.0</u>

It should be noted that during the drying operation, some volatile, carbon-containing material was removed from the lignite.

#### PROCEDURE

Dried lignite (500 grams) was charged into the retort and the cracking zone temperature brought up to the predetermined level. Ice water was circulated through the condensers and the water jackets. When the cracking zone temperature reached this predetermined point, the temperatures of the retort was slowly and uniformly raised to a maximum of 800°. About 70 minutes was required for TR<sub>2</sub> to increase from 300° to 800°. Electric current to the retort furnaces was controlled manually in such a manner that TR<sub>1</sub> equaled TR<sub>2</sub>. When the retort temperature reached 800°, it was stabilized at this point and maintained there for another hour. After this length of time no further gas evolution was observed. All heat was then turned off, the cold trap was removed from the dry ice-acetone bath and allowed to come to room temperature, and the ice water was removed from the condensers and jackets. Steam was then passed through the condensers and jackets thus forcing any material collected on the condensers and precipitator to run back into the receiver. The volume of water and oil was estimated in the graduated section of the receiver and the contents of the dry ice-acetone trap were poured into the first receiver and the weight of all materials in the first receiver was determined. The cotton trap was weighed to check the efficiency of the electrostatic precipitator and any gain in weight was added to the weight of the water plus heavy oil. For those runs designated "no cracking zone", the cracking zone was eliminated entirely and the retort attached directly to the first receiver.

The contents of the first receiver were steam distilled and the non-aqueous layer of the distillate separated and designated as the "steam distillable oil". The residual oil and tar was designated "heavy oil". Samples of the steam distillable oil were examined by means of infrared and mass spectroscopy and samples of the heavy oil examined by means of infrared spectroscopy. The volume of the gas produced was measured with the wet-test gas meter. Samples of the evolved gas were taken every 12 liters and analyzed for their components by mass spectrometry. The weight of the char was determined by weighing the contents of the retort after the run had been completed.

#### RESULTS

Complete material balances for the runs are given in Table III. Very accurate determinations of the yields of the various gases, the light oils, and char were made but only the total of heavy oil and water was determined in most cases because of the difficulty encountered in separating them. The yields of heavy oil, however, were only of secondary importance since the major emphasis in this work was on the yields of ethylene and benzene.

Analysis of the products obtained in these carbonization runs makes it possible to evaluate the effect of retorting and cracking temperatures and retention times on the yields of the various products. Since all the volatile matter passed through the cracking zone, the volume and composition of the evolved oil and gases were affected by both the retorting and cracking temperatures and retention times. The char, of course, was affected only by the retorting temperature.

TABLE III

MATERIAL BALANCES ON THE CARBONIZATIONS

(Yields of lbs. per ton of Dried Lignite)

Lignite Cracking Temperature Zone Length	North Dakota						Texas							
	600°		800°		None	600°		800°		None	600°		800°	
	18"	36"	18"	36"		18"	36"	18"	36"		18"	36"	18"	36"
Ethylene	3.6	6.0	7.8	20.0	23.9	5.2	13.6	14.7	39.6	44.2				
Propylene	0.3	2.7	5.4	8.9	1.0	3.6	12.4	13.8	14.4	108.7				
Methane	67.6	67.6	71.5	82.9	89.7	64.4	76.0	82.7	100.1	108.7				
Ethane	7.9	9.6	8.9	6.4	0	8.8	13.2	15.7	9.3	5.9				
Hydrogen	16.3	15.9	15.6	16.8	17.3	12.8	15.2	14.3	16.6	16.9				
Carbon Monoxide	101.7	95.7	102.6	106.7	117.3	79.6	87.2	87.4	109.1	114.1				
Carbon Dioxide	198.6	196.6	198.0	218.9	205.2	155.6	146.0	155.5	149.0	167.0				
Hydrogen Sulfide	2.2	2.2	2.2	3.2	2.5	6.0	7.2	7.2	7.2	7.8				
Total Gases	396.2	396.3	412.0	463.8	456.9	336.0	369.6	391.3	445.2	472.9				
Light Oil	26.1	24.2	22.7	15.4	11.5	52.4	38.1	49.0	17.8	37.8				
Heavy Oil and Water	562	551	519	500	484	408	420	426	435	376				
Char	<u>1032</u>	<u>1028</u>	<u>1024</u>	<u>1028</u>	<u>1028</u>	<u>1096</u>	<u>1092</u>	<u>1096</u>	<u>1096</u>	<u>1096</u>				
TOTAL	2016	2000	1978	2007	1980	1992	1920	1962	1994	1983				

Gas Volume. - The volume of evolved gas is approximately a linear function of the retorting temperature. (Figure 4) When higher cracking temperatures are employed, more gas is obtained due to the conversion of some of the oil to gaseous products. So far as the volume of gases is concerned, there is little difference between Texas and North Dakota lignite.

Gas Composition. - The composition of the gas evolved varies widely as the retort temperature passes through the temperature range from room temperature to 800°C. The effect of the retorting temperature on the instantaneous composition of the gas is quite pronounced, but since a cumulative gas composition would be obtained under the conditions of commercial carbonization, this effect would be much less. The major components of the evolved gas are: ethylene, propylene, methane, ethane, hydrogen, carbon monoxide, carbon dioxide, and hydrogen sulfide. These comprise at least 98% of the gas produced. The effects of the retorting and cracking temperatures on the proportions of each of these gases will be discussed in the order that they are listed above.

Ethylene.- Of all the gaseous products, ethylene is the most valuable. The proportion of this gas shows a maximum at about 400°C. and drops very abruptly when the retort temperature exceeds 500°C. (Figure 5) This latter retort temperature coincides with the point where no further oil is collected in the fore part of the collection train. The retort temperature has a very marked effect of the amount of ethylene obtained although the retention time does not seem to be particularly important. A good deal more ethylene was obtained at a cracking temperature of 800°C. than was obtained at 600°C. Texas and North Dakota lignite behave similarly, but Texas produces almost twice as much ethylene as does North Dakota lignite.

Propylene. - The proportion of propylene in the evolved gas shows a well defined maximum at retort temperatures of approximately 450°C. (Figure 6) The proportion of propylene, contrary to that of ethylene, decreases as the cracking temperature is increased from 600°C. to 800°C. As was the case with ethylene, Texas lignite produces much more propylene than does North Dakota lignite.

Methane. - The production of methane in the evolved gas is a maximum at a retort temperature of approximately 500°C. (Figure 7) More methane is obtained from Texas lignite using a cracking temperature of 800°C. than is obtained with a cracking temperature of 600°C. while the reverse is true with North Dakota lignite. Retention time, however, does not seem very important in this case. Somewhat more of this gas is produced from Texas lignite than is produced from North Dakota lignite.

Ethane. - The maximum evolution of this gas occurs at a retort temperature of about 450°C. and its production is favored by low cracking temperatures. (Figure 8) At the higher cracking temperatures, much of the ethane that is produced in the retort is converted to ethylene. In the case of this gas, too, more is obtained from Texas than from North Dakota lignite.

FIGURE 5

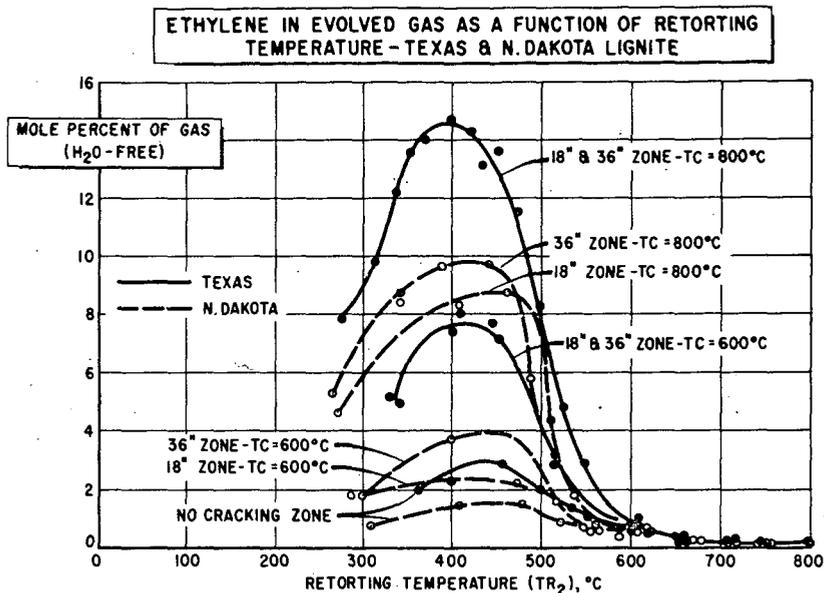
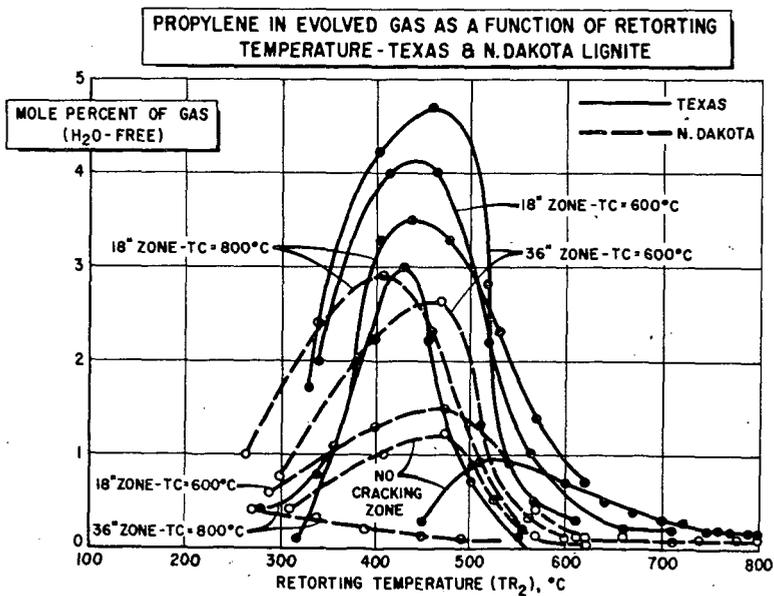


FIGURE 6





Hydrogen. - The evolution of this gas is different from that of the hydrocarbon gases in that it continues to increase with retort temperature to the highest retort temperatures investigated. (Figure 9) Below a retort temperature of 500°C., its production is favored by high cracking temperatures and the longer retention time, conditions which would be expected to favor the conversion of saturated to unsaturated hydrocarbons. The production of this gas was almost identical from both lignites.

Carbon Monoxide. - As the retort temperature is increased the proportion of carbon monoxide in the evolved gas shows a minimum at 540° and a well defined maximum at 670°C. at all cracking temperatures and retention times. (Figure 10) The production of this gas is almost completely insensitive to the cracking conditions. Texas and North Dakota lignites behave very similarly although slightly more carbon monoxide is obtained from North Dakota lignite at retort temperatures below 600°C.

Carbon Dioxide. - Less of this gas is evolved as the retort temperature is raised until essentially none is evolved at retort temperatures in excess of 730°C. (Figure 11) The proportion of carbon dioxide in the evolved gases below a retort temperature of 550°C. is lower at the higher cracking temperatures although this is due entirely to the greater amount of total gas produced under these conditions. More carbon dioxide is obtained from North Dakota lignite than is obtained from Texas lignite.

Hydrogen Sulfide. - Only rather small amounts of this gas are obtained and almost all of it below a retort temperature of 600°C. (Figure 12) While the proportion of this gas in the evolved gas is affected by the cracking conditions in the case of the Texas lignite, it is not in the case of the North Dakota lignite. Approximately twice as much hydrogen sulfide is also obtained from the Texas lignite.

Liquid Products. - Since the liquid products were determined only at the end of the run, little can be said about the effect of retorting temperature on their amount and composition but it was noticed that all the evolution of oil occurred between retort temperatures of 250°C. and 550°C. The effect of cracking temperature and retention time, however, was determined.

Light Oil. - Less light oil is obtained at the higher cracking temperatures. (Figure 13) The retention time had little effect on the amount produced from North Dakota lignite but significantly more was produced from Texas lignite at the longer retention time. At the longer retention time, approximately twice as much light oil was produced from Texas lignite than was produced from North Dakota lignite.

The components of the steam distillable oil obtained at the lower cracking temperatures were mainly saturated aliphatic hydrocarbons, while at the higher cracking temperatures, the components were benzene, toluene, naphthalene, aliphatic substituted naphthalenes, mixed alkyl benzenes, and some phenolics and polynuclear aromatic hydrocarbons of the lower molecular weights. (Table IV)

FIGURE 9

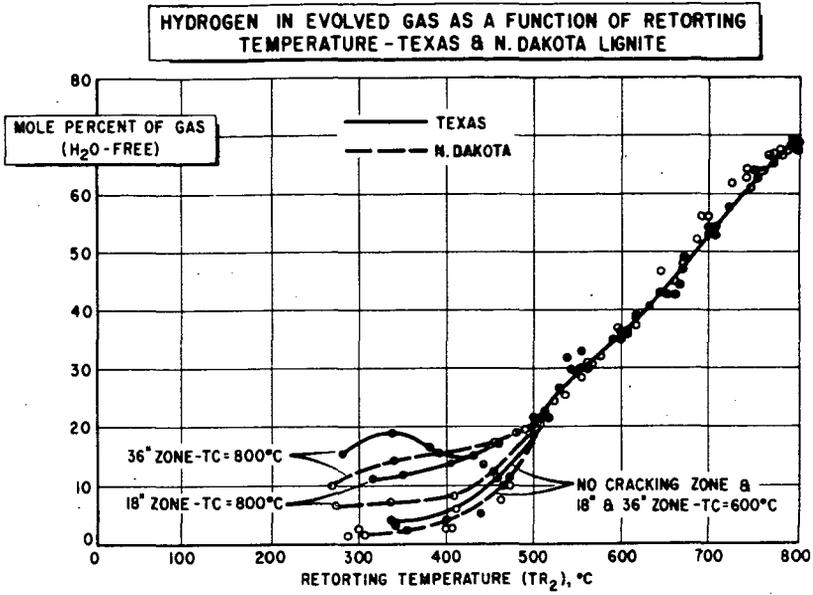


FIGURE 10

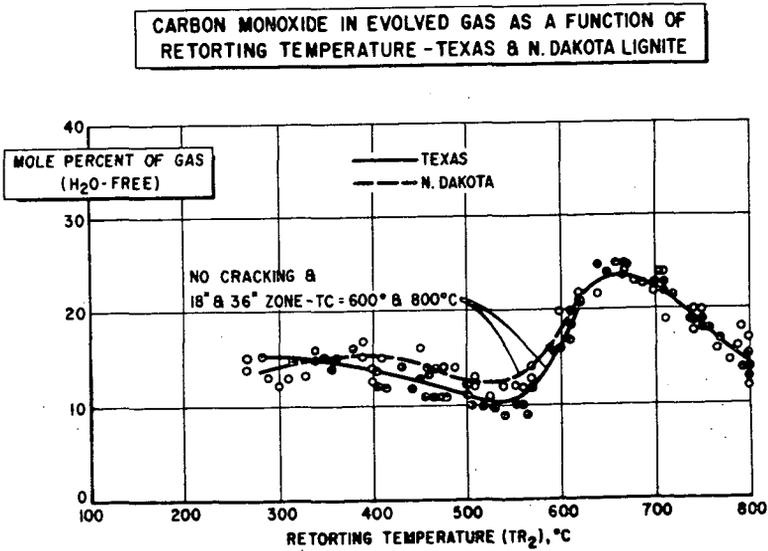


FIGURE 11

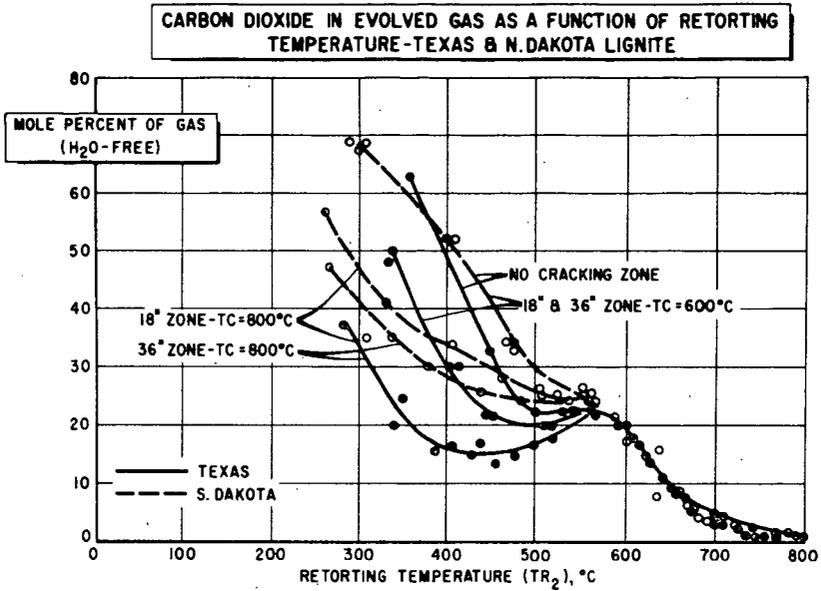


FIGURE 12

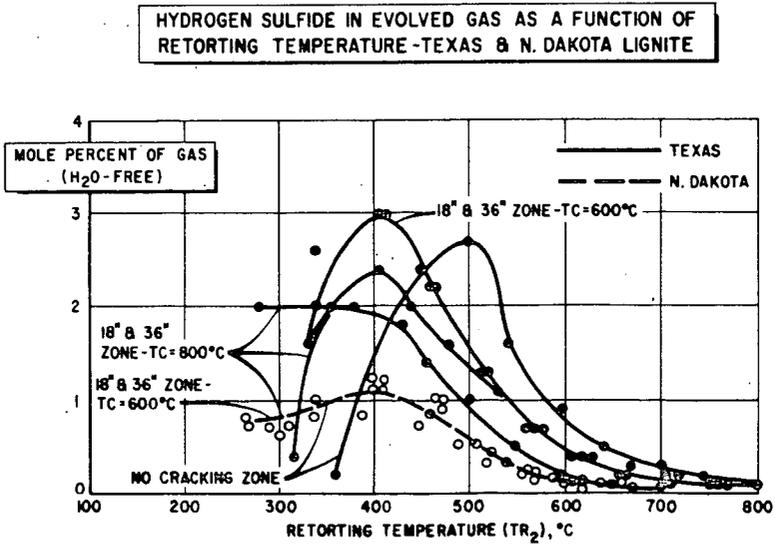


FIGURE 13

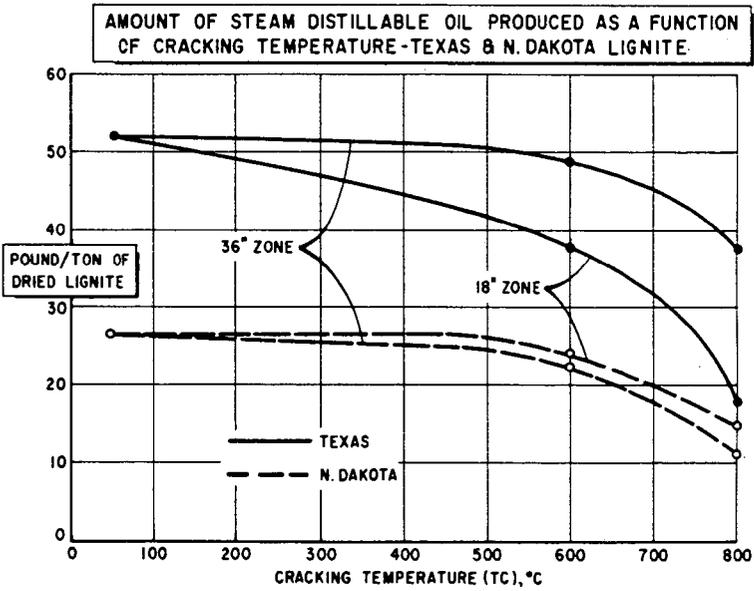


TABLE IV  
EFFECT OF CRACKING CONDITIONS ON THE COMPOSITION  
AND YIELDS OF LIGHT OIL  
(Yields in lbs. per Ton of Dried Lignite)

Lignite	North Dakota						Texas					
	Cracking Temperature	600°			800°			None	600°		800°	
		18"	36"	36"	18"	36"	36"		18"	36"	18"	36"
Benzene	0	0	0.2	0.2	0.2	0.6	0.5	0.4	1.0	0.2	6.0	
Toluene	0	0.2	0.7	0.9	0.7	0.7	1.0	1.1	1.5	1.2	4.9	
Xylene and/or ethylbenzene	1.0	1.0	1.4	1.2	0.3	0.3	1.6	2.3	2.0	1.4	2.3	
Mass 120 (C <sub>3</sub> benzene)*	1.0	1.0	0.9	0.6	0.1	1.0	1.0	1.5	1.5	0.4	0.4	
Mass 134 (C <sub>4</sub> benzene)	1.0	0.7	0.7	0.3	0.3	0.3	1.0	0.8	1.0	0.4	1.1	
Styrene	0.1	0.07	0.2	0.6	0.6	0.6	0.2	0.4	0.5	0.9	1.9	
Naphthalene	0.3	0.2	0.2	0.6	1.4	1.4	0.5	0.8	0.5	1.1	3.0	
Methylnaphthalene	0.3	0.2	0.2	0.5	0.2	0.2	0.2	0.4	0.5	0.5	1.1	
Indene	0.3	0.2	0.2	0.8	0.6	0.6	0.2	0.8	0.5	1.2	1.9	
Mass 118	0.3	0.2	0.5	0.9	0.3	0.3	0.5	1.1	0.5	1.1	0.7	
Other components	21.7	20.3	17.5	8.9	6.3	6.3	45.6	28.6	39.6	9.4	14.4	
TOTAL	26.0	24.1	22.7	15.5	11.4	11.4	52.3	38.2	49.1	17.8	37.7	

\*This notation designates a benzene ring substituted with three saturated carbons, i.e. methyl ethyl benzene, propyl benzene, and/or mesitylene.

Heavy Oil. - As expected, the amount of heavy oil obtained decreases as the cracking conditions become more severe due to the conversion of some of this material to light oils and volatile hydrocarbon gases. The infrared spectra indicates that the heavy oil obtained using the lower cracking temperatures was composed of saturated aliphatic hydrocarbons of high molecular weights with little of the aromatic hydrocarbons present. Heavy oils obtained using higher cracking temperatures, however, were primarily polynuclear aromatic hydrocarbons of the higher molecular weights with some phenolic components present.

Char. - Retorting, of course, converts part of the lignite into volatile products so that less char is obtained as the retorting temperature is raised. The char, however, has a significantly greater calorific value than did the original dried lignite.

TABLE V  
YIELDS OF CHAR OBTAINED FROM TEXAS AND NORTH DAKOTA LIGNITES

	Retorting Temperature	
	550°C.	800°C.
Texas Lignite	1220	1100
North Dakota Lignite	1160	1020

- Yields in lbs. per ton of dried lignite.

TABLE VI  
CHAR ANALYSES

	Texas Lignite	
	550°C.	800°C.
<u>Proximate Analysis</u>		
Moisture	0.0	0.0
Net Volatile	11.4	3.6
Fixed Carbon	68.7	72.2
Ash	20.0	23.7
	<u>100.1%</u>	<u>100.0%</u>
<u>Ultimate Analysis</u>		
Ash	20.0	23.7
Hydrogen	2.7	0.9
Carbon	72.3	73.3
Nitrogen	1.3	0.9
Oxygen	2.8	0.2
Sulfur	0.9	0.9
	<u>100.0%</u>	<u>99.9%</u>
Calorific Value	12,035 BTU/lb.	11,443 BTU/lb.

TABLE VI (Cont'd)

North Dakota Lignite

Proximate Analysis

Moisture	0.0	0.0
Net Volatile	14.8	4.0
Fixed Carbon	72.8	82.3
Ash	12.4	13.8
	<u>100.0%</u>	<u>100.1%</u>

Ultimate Analysis

Ash	12.4	13.8
Hydrogen	2.9	1.3
Carbon	78.0	73.4
Nitrogen	1.3	0.9
Oxygen	4.9	0.2
Sulfur	0.5	0.5
	<u>100.0%</u>	<u>100.1%</u>

<u>Calorific Value</u>	12,571 BTU/lb.	12,608 BTU/lb.
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CONCLUSION

Ethylene and aromatics have been obtained by means of a low-temperature carbonization of lignite immediately followed by a thermal cracking of the volatile products. Texas Sandow lignite was found to be much superior to North Dakota lignite in this process and produced almost twice as much ethylene and about ten times as much benzene. Of the conditions evaluated, the best results were obtained when using retorting temperatures only up to 550°C., a cracking temperature of 800°C., and a cracking zone length of thirty-six inches. This was the longest cracking zone length investigated and its use resulted in an "average" retention time of about 1.5 seconds. Of course, these "optimum" conditions would probably be altered somewhat with a large commercial unit. An estimate, however, can be made of the performance of a large unit on a basis of the experimental results reported here. This estimate is given in Table VII.

TABLE VII

YIELDS OBTAINED FROM TEXAS SANDOW LIGNITE

Conditions: Retort temperature - up to 550°C.  
Cracking zone - 36 inches, 800°C.

Yields in lbs. per ton of Dried Lignite

GASES

Ethylene	40.0
Propylene	7.6
Methane	70.5
Ethane	4.9
Hydrogen	5.6
Carbon Monoxide	56.1
Carbon Dioxide	-126.0
Hydrogen Sulfide	7.2
TOTAL	318

LIQUIDS

Benzene	6.0
Toluene	4.9
Xylene and/or ethylbenzene	2.3
Mass 120 (C <sub>3</sub> benzene)	0.4
Mass 134 (C <sub>4</sub> benzene)	1.1
Styrene	1.9
Naphthalene	3.0
Methylnaphthalene	1.1
Indene	0.7
Mass 118	0.7
Other Components	14.4
TOTAL LIGHT OIL	37.7
TOTAL HEAVY OIL	~44

CHAR

Weight	1,220
Calorific Value	12,035 BTU/lb.