Characterization of Liquids and Gases Obtained by Hydrogenating Lumps of Texas Lignite

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INTRODUCTION

The increased cost of natural gas and the high cost of fuel oil have increased the importance of Texas lignite as a potential source of chemicals and as a fuel for generating electricity. The lignite resource in Texas has been estimated (1) as 10 billion tons at depths less than 200 feet and 100 billion tons at depths of 200 to 5000 feet. The shallow basin lignite can be recovered by strip mining but the deep basin lignite will probably have to be recovered by *in situ* mining methods. *In situ* liquefaction and comminution have considerable potential for recovering deep basin lignite (2,3,4).

In order to evaluate the potential of underground liquefaction, autoclave experiments have been conducted at pressures of 500 to 5000 psi and temperatures of 650 to 800°F. The charge to the autoclave has been cylinderical cores, 1 1/2 inch in diameter and 3 to 5 inches long, hydrogen, helium and hydrogen donor solvents. In order to gain insight into the reaction mechanisms underlying the conversion process, the liquid and gas products have been analyzed by use of several methods. Generally, coal-derived liquids have been characterized after separating different species by use of solvents with different chemical affinities (5,6). Since the composition of the lignite derived fluids are less complex compared to other coal-derived liquids, an analytical procedure based on boiling points of the components is used.

EXPERIMENTAL

Three Gow-Mac gas chromatographs, Model 69-550, with thermal conductivity detectors were used for simultaneous analysis of gases and liquids. The oven temperatures were manually programmed. Commercially available helium is used as carrier gas. Helium is purified by passing it through molecular seive 5A (3 ft. X 1 1/2" O.D. stainless steel column) and through a high capacity purifier (Supelco Carrier Gas Purifier) to remove the traces of oxygen and water. The gas chromatographs accept only 1/4" columns with a maximum length of 10 ft. Samples were injected directly into the column to avoid the recovery loss in the injection port. The products from lignite liquefaction experiments, which were analysed by gas chromatography can be classified as follows: (a.) gases; (b.) low boiling point liquids (boils below 100°C); (c.) high boiling point liquids (boils above 100°C).

Porapak N was used for identifying methane, carbon dioxide, ethylene, ethane, hydrogen sulfide, propane, water, isobutane and *n*-butane. After an initial 1 min. hold at 25°C, a shotgun temperature program - 25°C to 140°C at a rate of 15 to 20°C per min. - was used to get excellent separations. Molecular Sieve 5A could separate hydrogen, carbon monoxide, oxygen and nitrogen from the gas samples at room temperature. Porapak S also gave a separation similar to Porapak N but did not separate propane and water under identical conditions. The thermal stability of Porapak S (max. temp. 250°C vs. 190°C for Porapak N) favored it as a choice for a few samples.

The low boiling liquids were separated on two Durapak columns. Durapak *n*-octane on poracil C is good for separating aliphatic components while Durapak OPN on poracil C separates the aromatic compounds. The sample is run on both columns simultaneously under identical conditions. A shotgun temperature program from 25 to 150°C gave

fairly good separation of the components.

The high boiling point liquids contain nonvilatile components as well as lignite fragments which may deposit on the columns. The samples were cleaned to get the desired boiling point range by using a fractional sublimator. The sublimator consists of two concentric glass tubes. The outer tube holds the sample and the inner tube contains a coolant, like liquid nitrogen or dry ice-acetone mixture. The space between the tubes is evacuated while the outer tube is heated by a jacket type furnace. The temperature of the furnace is controlled by a Thermolyne proportional temperature controller. The sample temperature is recorded on a strip chart recorder. The sample evaporates and deposits on the outside of the inner tube (liquid nitrogen cold finger). The sample temperature and the degree of vacuum controls the volatility of the fractions deposited.

The clean samples from the sublimator were analysed using five different 8 ft. columns with packings that can withstand column temperatures well above 300°C without appreciable bleeding. The column temperature was programmed from 80°C to 280°C at a rate of 1.5 to 2°C per minute. The same sample was analysed with different columns under identical conditions. A hydrocarbon standard of *n*-alkanes ranging from C_{10} to C_{36} along with pristane and phytane was used to qualitatively identify the boiling point range of the components separated on different columns.

Detailed analysis of the lignite derived products were done on GC-MS. The apparatus mainly consists of a Hewlett-Packard 5710A Gas Chromatograph. A 5980A Mass Spectrometer, a 5947A Multi Ion Detector and a 5933A Data System. The gas chromatograph is able to accept packed columns as well as glass capillary columns. A 30 ft. X 1/8" stainless steel column packed with 3% OV 101 on 80/100 mesh Chromosorb W-HP and a 30 M glass capillary coated with OV 101 were used for most of the GC-MS studies. OV 101 is a methylsilicone polymer similar to the SP 2100 used in the Gow-Mac gas chromatographs. The hydrocarbon standard was used to determine the boiling point range of the components as well as the fragmentation pattern of the *n*-alkane series.

The proton nmr spectra of the samples dissolved in $CDCl_3$ were taken on a Varian T-60 nmr spectrometer. JEOL PS-100-PFT was used for scanning C^{13} nmr spectra of samples in $CDCl_3$. Samples used for these studies were not sublimated. The samples, therefore, contained high molecular weight species as well as minute suspended particles.

RESULTS AND DISCUSSION

The gaseous products from different lignite liquefaction experiments were composed of the same components but the composition varied depending on the experimental conditions and the lignite sample cores used. The gaseous components were identified using known standards and simple chemical tests. Figure 1 is a typical gas chromatogram for the gas sample obtained during the hydrogenation of wet Texas lignite. Carbon dioxide is the major component. Hydrogen sulfide is present in an appreciable concentration. Once both carbon dioxide and hydrogen sulfide were removed from the gaseous mixture, the product has a composition comparable to commercial natural gas containing a series of low molecular weight hydrocarbons with methane in large proportion.

Texas lignite is a low grade coal (8000 BTU per pound) with a high oxygen content (up to 30% of dry weight) and about a medium level of sulfur residues (nearly 2% of dry weight). Most of the carbon dioxide represents a major portion of the chemically bound oxygen in lignite which may exist as carboxylic groups. Hydrogen sulfide could be liberated from the sulfhydryl groups (thiols, sulfides, disulfides and chelated sulfur residues) and elemental sulfur (at least a small fraction) in the lignite.

The lignite-derived liquid obtained in this work is less complex than the bituminous coal-derived liquid. The lignite-derived liquid was divided into low boiling liquid and high boiling liquid in order to use two Durapak columns which have an upper temperature limit of about 150°C for the separation of aromatic and aliphatic compounds. As a matter of fact both the low and high boiling point liquids could be separated on any of the five columns used for high boiling liquid but the Durapak columns gave a much better resolution for the low boiling point liquid.

The low-boiling liquid is a clear colorless liquid which turns dark and cloudy on exposure to air at room temperature for a few hours. Figure 2 shows the total ion monitor chromatogram of the liquid using a 30 ft. 1/8" column packed with 3% OV 101 on Chromosorb W-AP. Table 1 summarizes the identification of major components and gives an overview of the general nature of the most common chemical species present in the low-boiling liquid. Aliphatic hydrocarbons, alkylated aromatics, furans and small amounts of thiophenes constitute the bulk of the sample. The mass spectra of these components clearly indicate the substance type, however, in cases where two or more hydrogen atoms have been substituted by alkyl groups, a large number of different patterns is possible. The mass spectra of some of these isomers are quite similar and so the identification has been done by using known standards or using individual boiling point range. All the possible isomers of some alkylated species are identified.

Table 1. Identification of Major Components in the Low Boiling Liquids

Peak No.	Compound	Peak No.	Compound
1	Acetone	19	Ethylbenzene
2	1,1-Dimethylcyclopropane	20	Xylenes
3	C_6H_{12}	21	2,3-Dimethylthiophene
4	Ethylmethylketone	22	C_9H_{20}
5	Hexane	23	2-Methyl 5-propylfuran
6	Methylcyclopentane	24	Cumene
7	1-Methylcyclopentene	25	$C_{10}H_{22}$
8	Pentane-2-one	26	*t*-Butylcyclohexanone
9	Heptene	27	*p*-Ethyltoluene +
10	2,4-Dimethylpentadiene		trimethylthiophene
11	Dimethylcyclopentene	28	Trimethylthiophene
12	Heptene	29	Trimethylthiophene (iso.)
13	C_7H_{12}	30	C_3-Alkylbenzene
14	Toluene	31	*n*-decane
15	2-Isopropylfuran	32	Tetramethylbenzene
16	C_8H_{12}	33	Cyclopropylbenzene
17	Isopropylfuran	34	Tetramethylthiophene
18	1-Ethylcyclohexene	35	C_4-Alkylthiophene
		36	$C_{11}H_{24}$

High boiling-point liquid was cleaned using a fractional sublimator prior to gas chromatographic analysis. The residue from sublimation was about 20 to 40% of the charge to the sublimator. The sample was sublimated to limit the boiling-point range of the sample so that the column temperature could be set for an upper limit of 280°C. Column bleeding was the major problem in GC-MS studies. Figure 3 shows the chromatogram of a sublimated sample and Table 2 list all the components identified. The same sample was separated on a Dexsil 300 GC column (Figure 4). Comparing the chromatogram of the same sample on five different column helps to resolve some components which may not separate on a particular column under identical conditions. For the GC-MS analysis a 30 ft. x 1/8" stainless steel column packed with 3% OV 101 on 80/100 mesh Chromosorb W-HP gave a better analysis than a 30M glass capillary column coated with OV 101 under similar conditions.

The Dexsil 300 GC column separated components into sharper symmetrical peaks in a shorter time compared to other columns. SP 2250 is the slowest of all. When a sample containing naphthalene and tetrahydronaphthalene is used on five different

columns, SP 2250 gave the best separation while SP 2100 gave no separation. The efficiency of separation in decreasing order can be listed as follows: SP 2250, Dexsil 410 GC, Dexsil 400 GC, Dexsil 300 GC and SP 2100. The bulk of the high-boiling-point liquid sample consists of saturated hydrocarbons mostly *n*-alkanes ranging from C_{10} to C_{36} distributed over the entire boiling point range. The aromatic species were predominantly alkylated phenols, benzenes, indenes, hydrogenated indenes and naphthalenes. Aromatic hydrocarbons containing three or more rings were not detected in the sublimated sample. The *n*-alkanes are not distributed proportionately throughout the series, though not a single member is missing. Unusually large enrichment occures at C_{10}, C_{17} and C_{27}. Mass spectral data of these higher members is not good enough to distinguish between a *n*-alkane and a slightly branched alkane of a higher molecular weight. The peak assigned to *n*-C_{17} alkane may also be assigned to branched alkanes with more than 17 carbon atoms, namely pristane, a branched C_{19} alkane. Pristane is derived from the phytol residues of chlorophyll (7). The hydrogenation products of other diterpene residues in lignite may also contribute to peaks in the range of C_{17} through C_{19}. The branched C_{30} alkanes obtained by the hydrogenation of triterpene type residues may be responsible for the *n*-C_{27} alkane peak enhancement.

Table 2. Identification of Major Components in the High Boiling Liquids

Peak No.	Compound	Peak No.	Compound
1	Phenol	24	Pentamethylindan
2	1-Ethyl-3-methylbenzene plus Decane	25	C_6-Alkylindan
3	*o*-Cresol	26	Trimethylnaphthalene (iso.)
4	*p*-Cresol	27	$C_{16}H_{34}$ plus Trimethylnahthalene (iso.)
5	*n*-Undecane plus methylcresol	28	*n*-Hexadecane
6	*o*-Ethylphenol	29	Diethyl methylnaphthalene
7	2,6-Dimethylphenol	30	$C_{17}H_{36}$ plus Tetramethylnaphthalene
8	*p*-Ethylphenol	31	*n*-Heptadecane
9	*p*-Cymene	32	Alkylated naphthalene
10	$C_{12}H_{26}$ plus 1,3-Dimethylindan	33	$C_{18}H_{38}$
11	*n*-Dodecane plus 2-Methyl-6-ethylphenol	34	*n*-Octadecane
12	3-Methyl-6-ethylphenol	35	$C_{19}H_{40}$
13	$C_{12}H_{16}$	36	$C_{19}H_{40}$
14	3-Methyl-6-ethylphenol	37	$C_{19}H_{40}$
15	$C_{13}H_{28}$ plus 1,6-Dimethylindan	38	*n*-Nonadecane
16	1,2-Dimethylindan	39	*n*-Eicosane
17	*n*-Tridecane	40	*n*-Heneicosane
18	$C_{11}H_{16}$(Methylated benzene)plus $C_{14}H_{30}$	41	*n*-Docosane
19	*n*-Tetradecane	42	*n*-Tricosane
20	Dimethylnaphthalene	43	*n*- Tetracosane
21	2,3-Dimethylnaphthalene	44	*n*-Pentacosane
22	$C_{15}H_{32}$	45	*n*-Hexacosane
23	*n*-Pentadecane	46	*n*-Hepacosane
		47	*n*-Octacosane

The high boiling liquid is composed of species with a very wide range of boiling points. Starting with phenol (181°C) at the low end and *n*-$C_{36}H_{74}$ (497°C) at the upper end. A careful examination of Table 2 reveals that fractional distillation or sublimation can be effectively used to separate the high boiling liquid into separate fractions enriched with phenols (180-230°C), aromatic hydrocarbons (230-300°C) and alkanes (300-500°C). Similarly the low boiling liquids can also be fractionated into

enriched samples. The minor components of the high and low boiling liquids are concentrated in these fractions and can be identified by use of GC and GC-MS.

The proton nmr spectra show the distribution of chemically bound hydrogen among the aromatic rings, aliphatic chains and other carbon atoms with varying chemical shifts due to different functional groups. The spectra give only a very qualitative picture about the chemical nature of the numerous components present in the lignite derived products. An approximate estimation of the aromatic and the aliphatic moieties in the sample could be attempted with reasonable success.

Due to the high resolution power of the C^{13} nmr spectroscopy a cumulative estimation of a sample containing many components may result in the disappearance of a large number of C^{13} absorptions in the noise. The sample spectra will show few nmr absorption peaks representing carbon centers with nearly identical chemical shifts. Each narrow peak is formed by summing up the nmr absorptions of C^{13} carbons from similar but different compounds. The C^{13} nmr spectra of a non sublimated high-boiling liquid derived from hydrogenated lignite has about ten major absorption peaks. These peaks are listed in Table 3. Three peaks are in the aromatic region (110-130 ppm) and seven in the aliphatic region (10-40 ppm). The peak at 14.19 ppm could be due to terminal methyl groups of saturated long chain hydrocarbons. The intense absorption at 29.91 ppm is due to methylene groups in the middle regions of one or more long chain saturated dydrocarbon compounds. Relatively very large area of the peak at 14.19 ppm suggests that n-alkanes are the bulk species in the lignite derived fluids. The C^{13} nmr studies also show that most of the GC peaks of alkanes are due to straight chain rather than branched hydrocarbons.

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Table 3. C^{13} NMR Data of Products from Hydrogenated Lignite

Peak No.	Chemical Shift ppm	Peak Height(rel)	Peak Area(rel)
1	14.19	7.16	22.17
2	19.77	6.62	27.30
3	22.84	11.07	38.04
4	29.53	20.94	65.52
5	29.91	122.68	603.50
6	32.10	11.77	42.25
7	37.64	5.72	25.24
8	115.54	6.22	10.52
9	128.37	8.95	57.72
10	129.57	7.67	22.30

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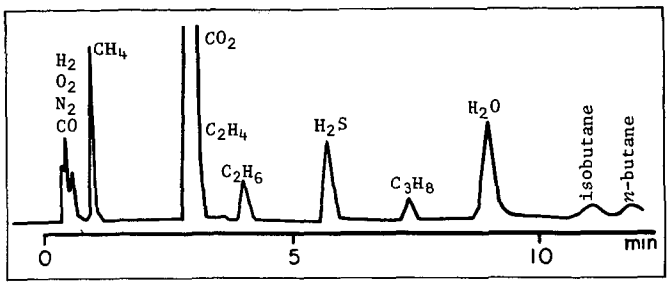

Fig. 1. Gas chromatogram of Texas lignite derived gas. Conditions: stainless steel column, 5ft x 1/4" O.D. packed with 80/100 Porapak N; carrier gas (helium) flow rate: 60 ml/min; temperature program: 25C (1 min.), 25-140°C at 15-20°/min.

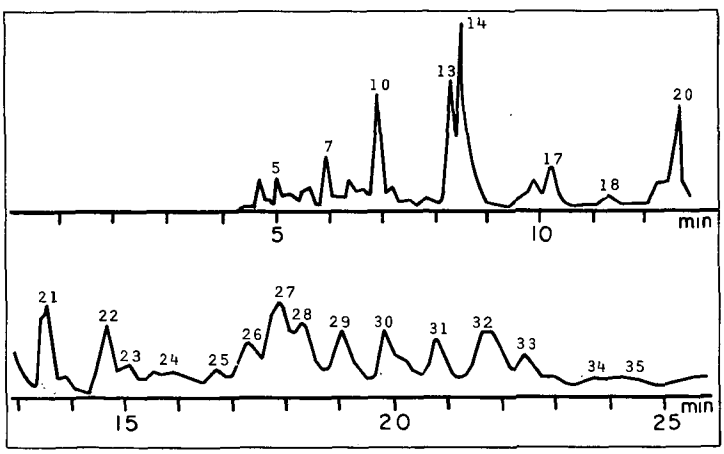

Fig. 2. Total ion current monitor chromatogram of low boiling liquid. Conditions: stainless steel column, 30ft x 1/8" O.D. packed with 3% OV 101 on 80/100 Chromosorb W-HP; carrier gas (helium flow rate: 20 ml/min; temperature program: 75-200°C at 2°/min. For identification of peaks see Table 1.

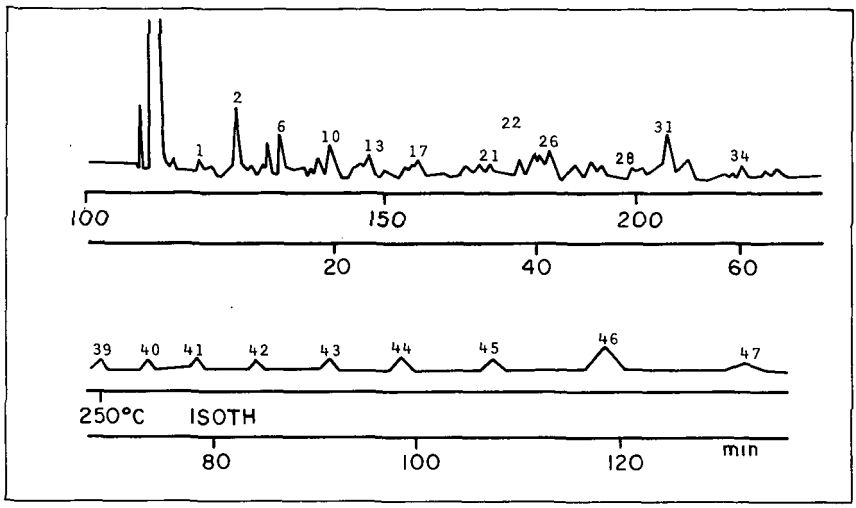

Fig. 3. Gas chromatogram of high boiling liquid. Conditions: stainless steel, 8ft x 1/4" O.D. packed with 10% SP 2100 on 100/120 supelcoport; carrier gas (helium) flow rate: 60 ml/min; temperature program: 100-250°C at 2/min. For identification of peaks see Table 2.

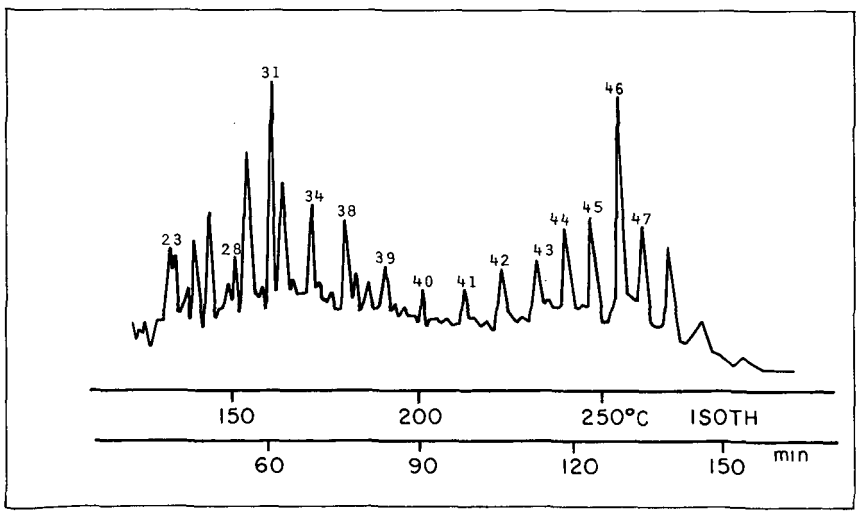

Fig. 4. High boiling liquid separated on a 3% Dexsil column. Column size and conditions are similar to those of Figure 3. For identification of peaks see Table 2.