

## 석탄 액화의 화학

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## Chemistry of Coal Liquefaction

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### 요 약

본 논문은 석탄 분자구조에 관한 최근의 견해에 대해서 상술하고 있으며, 석탄 액화시의 반응 메카니즘에 관해서 격렬한 반응과 보다 덜 격렬한 반응조건에 대해서 구분해서 논의하고 있다. 또한 액화된 물질의 Spectrometry와 Chromatography를 통한 분류 및 특성화에 대해서도 상술하고 있다.

### Abstract

Recent view of structure of coal molecule has been discussed. The mechanism of liquefaction and milder degradation of coal has been also discussed. Spectroscopic and chromatographic methods have been mentioned for the separation and characterization of liquefied coals.

## 1. INTRODUCTION

Gradual depletion of conventional liquid fuels have recently prompted the active studies on coal chemistry for the urgency to convert solid to liquid fuels. Structurally coals are composed chiefly of condensed, aromatic rings of high molecular weight. NMR spectra yield

estimates of the distribution of hydrogen atoms between aromatic and nonaromatic structures. About 70% of all carbon atoms are in aromatic rings but only about 23% of the hydrogen atoms are attached to aromatic carbon atoms. These compounds have molecular weights in the order of 10,000.

Oxygen, sulfur and nitrogen are combined in chemically functional groups, such as OH,

**Table 1. Chemical Composition of Some Coals and Petroleum**

|               | Anthracite | Medium<br>Volatile<br>Bit. | High<br>Volatile<br>A Bit. | High<br>Volatile<br>B Bit. | Lignite | Petroleum<br>Crude | Gasoline | Toluene |
|---------------|------------|----------------------------|----------------------------|----------------------------|---------|--------------------|----------|---------|
| C             | 93.7       | 88.4                       | 54.5                       | 80.3                       | 72.7    | 83~87              | 86       | 91.3    |
| H             | 2.4        | 5.0                        | 5.6                        | 5.6                        | 4.2     | 11~14              | 14       | 8.7     |
| O             | 2.4        | 4.1                        | 7.0                        | 11.1                       | 21.3    | —                  | —        | —       |
| N             | 9          | 1.7                        | 1.6                        | 1.9                        | 1.2     | 2                  | —        | —       |
| S             | 6          | 8                          | 1.3                        | 1.2                        | 0.6     | 1.0                | —        | —       |
| atom<br>ratio | 31         | 67                         | 79                         | 82                         | 69      | 1.76               | 1.94     | 1.14    |

Source: Industrial and Engineering Chem. (July 1969).

CO, COOH, NH<sub>2</sub>, CN, S, SH, etc., which occur as integral parts of the original molecules. Main differences between typical analyses of coals and petroleum crudes are shown upper.

As is shown in the *Table 1*, the carbon to hydrogen atomic ratio for bituminous coal is about 1.25 : 1, while in petroleum it is about 6 : 1. The problem is obvious during liquefaction or gasification. One must lower the carbon-to-hydrogen ratio by adding hydrogen or removing carbon as coke or char.

Even prior to Bergius (1913) it was shown that hydrocarbon gases and liquids, tars and the chemicals could be obtained from coal. Early processes employed destructive distillation for the conversion of coal into these useful products. The conversion can be carried out in a number of ways, such as formation and extraction of a slurry with a hydrocarbon solvent (e.g. creosote oil), carbonization (thermalcracking to coal tar), catalytic hydrogenation and hydrogenolysis.

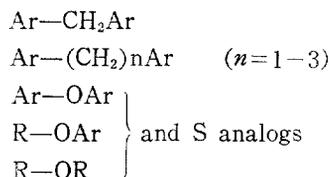
This report reviews coal studies on the coal molecule, its liquefaction and mechanism and methods of analysis and characterization done during the last ten years.

## 2. STRUCTURE OF COAL

The direct study of coals which possess little

solubility in common organic solvents at room temperature provides only qualitative information much of which is of marginal value. Since most coals can be chemically altered and converted to fragments and molecular species amenable to predictive and useful separations, this route provides an indirect approach to deducing major structural and reactivity features of the original coal. The classical view of coal structure<sup>1),2),3)</sup> is a cross linked high polymer with condensed aromatic aggregates that are difficult to cleave and connecting links that are relatively easy to cleave (scissile bonds)<sup>3),6)</sup>.

Listed below are the scissile bonds that appear to be important in the thermolysis of bituminous coal under common operating conditions.



The same types of bonds are probably involved in scissions under strongly acidic conditions, as with phenol plus BF<sub>3</sub>-Etherate.

Contrary to the classic (and current) view that coal is a macromolecule that contains aromatic units of varying degrees of condensation, recently, Chakrabartty and Berkowitz

<sup>7),8),9)</sup> have suggested that the properties of coal, e.g. its proportions of hydrogen and carbon, its ability to produce aromatic compounds, can be explained by assuming that it contains largely non-aromatic 'polyamantane' units of interlocking cyclohexane rings similar to the structure of the adamantane molecule but of greater size. They claimed the rank of the coals has no effect on the reactivity of the coals towards sodium hypochlorite and on the products distributions. No evidence of polynuclear compounds, which should have survived the oxidation was also presented for the 'bridged tricycloalkane configurations.' The result of oxidation of coals with sodium hypochlorite invalidates the significance of the aromaticity of coals.

Studier *et al.*<sup>10)</sup> studied the fluorination of high-volatile Illinois bituminous coal. Results obtained from the fluorination suggest that coal contains aromatic groups held together by aliphatic chains, rather than the polyamantane groups.

Recently, Carbon-13 NMR spectra of solid coals<sup>11),12)</sup> were reported. The preliminary results also support the classical views that coals are highly aromatic materials and that the aromaticity of coal increases with increasing rank.

In their oxidation studies<sup>7)~9)</sup>, the coals were first nitrated before NaOCl-oxidation. It is the author's opinion that the oxidation may not reflect the real picture of the coals because of the prior nitration.

### 3. REACTION

#### A. Liquefaction

##### i) Mechanism

The three direct general processes for converting coals to liquid fuels are: catalyzed

hydrogenation, staged pyrolysis and solvent refining. Each liquefaction process involves some form of hydrogen transfer though the processes appear not to involve classical catalytic hydrogenation.

Van Krevelen<sup>13)</sup> in 1931 indicated coal pyrolysis involved depolymerization and disproportionation in which free radicals are formed, and Berkowitz<sup>14)</sup> in 1937 amplified this concept in connection with pyrolysis, as did Neavel<sup>15)</sup> in 1975. Hill *et al.*<sup>16)</sup> in 1936 discussed the liquefaction of coal in tetralin (hydrogen donor) in terms of dissolution and stated that the hydrogen transfer reaction will be a second order process since the transfer reaction from tetralin to the coal will not be an abundant process at the temperatures used (350—450°C).

Curran, Struck and Gorin<sup>17),18)</sup> in 1967 were apparently the first investigators to describe the transfer of hydrogen from a slurry vehicle (tetralin) to coal as a free radical reaction involving thermal cleavage of the coal molecules.

Tarrer *et al.*<sup>21)</sup> in 1976 studied the effects of temperature, the presence of H<sub>2</sub> in the gas phase, and solvent hydrogen donor activity on the extent of coal particle breakup. The disintegration of coal is proportional to the increase of temperature, hydrogen pressure and the activity of the hydrogen donor.

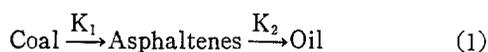
Neavel<sup>22)</sup> in 1976 studied the liquefaction of coal in hydrogen donor and non-donor solvents. While in tetralin (donor-solvent), coal was liquefied to give benzene soluble material, benzene-insolubles were formed in naphthalene (nondonor-solvent).

Based on the studies of coal liquefaction mechanism, the following may be stated. At temperature 350°C and above, the covalent bond of C-C (80 Kcal/mole), C-N (62 Kcal/mole) and C-O (81 Kcal/mole) present in the coal

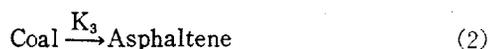
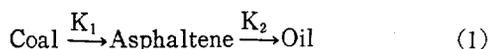
molecules in various forms cleave homolytically to give highly reactive free radicals. At such a high temperature, the radicals thus formed may undergo all kinds of radical reaction paths, competitively; i.e. abstraction of H-atom, fragmentation, addition and recombination. In H-donor solvent, the radicals undergo fragmentation and H-atom abstraction to give smaller molecules soluble in benzene. In non-donor solvent, the radicals undergo fragmentation and addition or recombination reaction which yield large molecules insoluble in benzene.

The mechanism of conversion of coal to oil has now been generally accepted as involving homolytic path way and asphaltenes are considered to be the principal intermediates.

Weller<sup>23)</sup> stated the catalytic conversion of coal involves two consecutive reactions,



Liebenberg and Potgleter<sup>24)</sup> derived another mechanism which includes the following reactions.



More recently Yoshida *et al.*<sup>25)</sup> claimed that the mechanism for catalytic conversion of Hokkaido coals includes reaction (1) and (3). It may be worth noting that according to their experiments  $K_4$  is considerably higher or lower than  $K_1$  and  $K_2$  depending upon coal type.

Sternberg *et al.*<sup>26), 27)</sup> have proposed that pre-asphaltene are the intermediates between coal and asphaltene.

Contrary to this, Schwager and Yen<sup>28)</sup> considered that preasphaltene may arise from reactive coal depolymerization moieties, which are repolymerized into materials more difficult to degrade than the original coal substance.

They<sup>28)</sup> compared atomic C/H ratios of carboid of several coal liquids. In most cases C/H value of carboid is higher than that of original coals. Similar opinion has been advanced by Ruberto *et al.*<sup>29)</sup>

#### ii) Composition of coal-derived liquids

Coal liquids can be separated by solvent fractionation into three crude fractions: pentane (or C—C<sub>6</sub>H<sub>12</sub>)-soluble; pentane-insoluble and benzene-soluble and benzene insoluble. The pentane-soluble may be further separated into a liquid propane-soluble fraction (gas oil), and a liquid propane-insoluble fraction (resin). In Table 2 are shown the product composition of several coal liquids.

The (oil and resin) fraction can be further separated by chromatographic method into: 1) saturates, 2) monoaromatics, 3) di+tri-aromatics, 4) poly-aromatics, which would be discussed in detail in the latter part of this report.

### B. Alkylation, Acylation and Depolymerization of Coals.

Drastic reaction condition of liquefaction makes it impossible to deduce the starting coal

Table 2. Composition of Various Coal Liquids

|                                  | % of  |       |            |                   |
|----------------------------------|-------|-------|------------|-------------------|
|                                  | Oil   | Resin | Asphaltene | Benzene-Insoluble |
| Synth Oil Process <sup>30)</sup> | 61    | 22    | 13         | 3.6               |
| Coed Process <sup>31)</sup>      | 26    | 48    | 15         | 12                |
| SRC by Cat. Inc. <sup>32)</sup>  | 4     | 15    | 45         | 36                |
| Synth Oil Process <sup>33)</sup> | 57~90 |       | 3~25       | 1~9               |

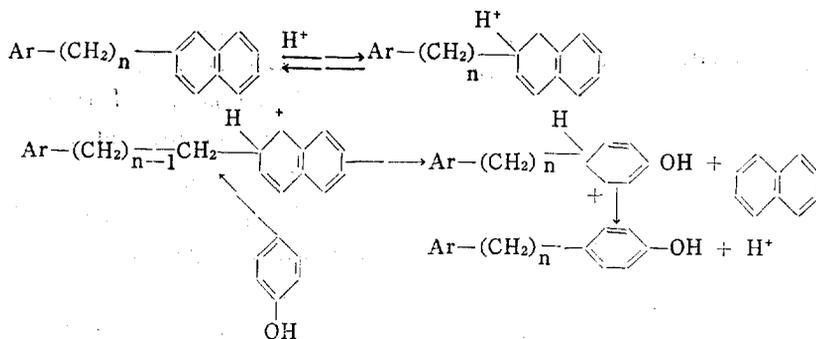


Figure 1.

molecule from the liquefied products. In order to study the structure of coal, milder condition is needed to preserve the original moiety, thereby bisecting only the bridges connecting the condensed aromatic rings. Depolymerized coals give soluble products that would be analyzed using conventional techniques which are not suitable for the unreacted coal. It is this factor which causes much of the interest in the reactions.

#### i) Depolymerization in phenolic solvent

Heredy and Neuworth first reported in 1962 the depolymerization of coal in phenol using Friedel-Crafts catalysts<sup>34</sup>. In subsequent studies<sup>35</sup>, they showed the mechanism of the reaction shown in *Fig. 1*.

In their continuing investigations, Heredy and Neuworth labelled phenol with <sup>14</sup>C so that the amount of phenol present in the product could be measured easily. Using this technique they demonstrated the presence of isopropyl groups in coal<sup>36</sup> as diaryl-methane structures ( $-\text{Ar}-\text{CH}_2-\text{Ar}-$ )<sup>37,38</sup>.

With the production of soluble products from coal, n.m.r. spectra could be obtained and interpreted and this area was also pioneered<sup>39</sup>.

A modification of this technique has been developed by Darlage and co-workers<sup>40</sup>. The coals were first treated with 2 M nitric acid, then reacted with phenol using a  $\text{BF}_3$  catalyst.

This was followed by treatment with acetic anhydride to convert phenolic  $-\text{OH}$  to acetate to enhance solubility. Using this sequence, up to 93% in  $\text{CHCl}_3$ -solubilization of the depolymerized coal was obtained.

Ouchi and coworkers have studied a number of Japanese coals using phenol and p-toluene-sulphonic acid to depolymerize them. They also examined a number of other acid catalysts, none of which was as effective as tosyl acid (p-toluene-sulphonic acid)<sup>41</sup>. In addition to a careful study of the reaction<sup>42</sup>, the molecular weights of the products and dependence of the degree of depolymerization on coal rank have been established<sup>43</sup>. The yields of pyridine-soluble material are quite high and decrease only with high-rank coals. The average molecular weight of the depolymerized coal increases rapidly with coals of higher rank. It is clear that the depolymerization is less effective and gives larger products with coals of higher carbon content.

Ouchi and coworkers isolated the following pure compounds from depolymerized Tempok and Yallourn brown coals<sup>42,44,45</sup>. (see *Figure 2*).

From these results, they suggested that methylene, ethylene and acyl bridges exist between the aromatic nuclei in the coals and from c and d, they tentatively concluded that me-

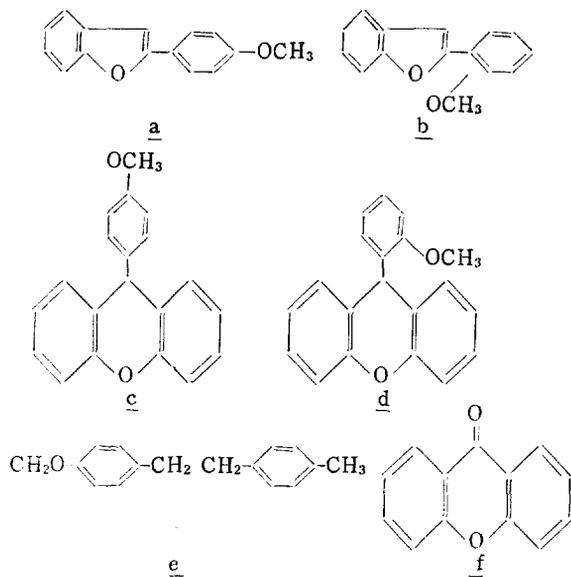
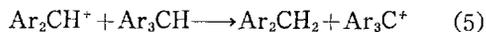


Figure 2

thine carbon must be present in the coals.

Very recently, Grant *et al.*<sup>46),47)</sup> studied acid-catalyzed phenolic depolymerization of lignite using <sup>14</sup>C-labelling.

Methylene-methine and ethylene-bridged aromatic products were identified, which showed a close similarity to products from the depolymerization of brown coals<sup>44),45)</sup> and lignites. However, reactions of model triarylmethane compound under depolymerization conditions (BF<sub>3</sub>-phenol or *p*-toluene sulphonic acid-phenol) demonstrated the facile conversion of triarylmethane structures to diarylmethane structures.



Consequently, the *simple interpretation*<sup>37),38),44),45)</sup> of diarylmethane products as having derived from diarylmethane functional groups in coal is no longer valid.

Bailey and Darlage<sup>48)</sup> studied the depolymerization of coal in the presence of Friedel-Crafts catalysts in a variety of phenolic and non-phenolic solvents.

Only the phenolic solvents were found to be

useful in this reaction.

### ii) Friedel-Craft Alkylation

The alkylation of coal occurs quite readily and a number of different systems have been studied. Kröger and coworkers<sup>49),50),51)</sup> studied the alkylation of coals using (AlCl<sub>3</sub> and isopropyl chloride) or olefins (ethylene or propylene) by heating.

The alkylations enhanced the solubilization of coal, which might be cited as an evidence for some structure disruption of the coal. It is interesting to note the report that AlCl<sub>3</sub> accelerates graphite formation from aromatics.<sup>52)</sup>

Larsen and Kuemmerle<sup>53)</sup> examined the reaction of several coals with *iso*-butylene catalyzed by sulfuric acid. All coals alkylate readily, but none of them shows any softening or melting before decomposition. This might mean that the crosslinking reaction (internal alkylation) dominates the structure-breaking external alkylation.

Denson and Burkhouse (the results in reference 53) have alkylated coal with ethylene, propylene and isobutylene using anhydrous HF. The products show softening as well as extractability with THF.

Hodek<sup>54)</sup> reported the improved extractability on their study of alkylation of coal with C<sub>3-18</sub> alkyl chlorides and AlCl<sub>3</sub> or with 1-hexadecene and HF-BF<sub>3</sub>.

Recently Aczel *et al.*<sup>55)</sup> reported the alkylation of bituminous coal using AlCl<sub>3</sub> or ZnCl<sub>2</sub> under very mild conditions (temp. 0–5°C). The alkylated products have both higher H/C ratio and solubility in benzene and pyridine.

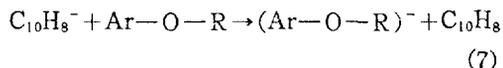
### iii) Reductive Alkylation

Sternberg and coworkers<sup>56),57)</sup> investigated the alkylation via coal anion, which formed by the treatment of coal with potassium in THF. The alkylated products showed decent solubility in pyridine and benzene.

When coal is treated with naphthalene anion, electrons are transferred to aromatic hydrocarbons (Equation 6).



and to aryl ethers (Equation 7)



The intermediate aryl ether anion is unstable and decomposes in the presence of excess naphthalene anion. It may be the rupture of this ether linkage present in the coal molecules, which gives the solubility of the coals.

#### iv) Friedel-Crafts Acylation

Hodek and Kölling<sup>53)</sup> studied the acylation of bituminous coals with aliphatic acyl chlorides using Friedel-Crafts catalysts. The acylated coal shows good extractability, which may be due to depolymerization of the coal structure during acylation.

## 4. SPECTROMETRY

### A. I.R. Spectrometry

The application of I.R. spectra to the study of coal may provide valuable information on the structure of coals. Cannon and Sutherland<sup>59)</sup> were the first introducing the I.R. spectroscopy to the coal study. They obtained the I.R. spectra of coal and coal pyridin-extract.

Brown<sup>60)</sup> extended his examination of raw coals to carbonized coals, to investigate the changes of the group contents and basic structure as a function of heating temperature.

From the examination of C(sp<sup>2</sup>)-H, C(sp<sup>3</sup>)-H, O-H IR stretching and H/C ratio, they reported the most marked changes of the coal structure are caused by heating to between 400~550°C and the process continued at higher temp. with the loss of aromatic hydrogen and some graphitization ensues.

Durie and Sternhell<sup>61)</sup> reported the use of

the potassium halide disk technique in a quantitative infra-red absorption (optical density) investigation of acetylated coals and chars.

Czuchjowski<sup>62)</sup> has also used carbonized coals in his studies of absorption bands of the hydroxyl and carbonyl groups.

Shih *et al.*<sup>63)</sup> studied the I.R. spectra of heated coals. They correlated the optical density of certain groups (e.g. aromatic or aliphatic CH) with fa (aromaticity) or carbon content.

From the results based on those correlations, they reported the high-temperature heating causes certain changes in the aromatic cluster structure of coal. The analyses of optical densities of different groups was shown to explain the change of the aromatic structures.

Employing transmission infra-red method through the use of efficient and extensive grinding, Friedel *et al.* have obtained the IR spectra of activated carbons,<sup>64)</sup> coals, carbon blacks and some chars,<sup>65)</sup> which were difficult to obtain.

They assign the 1600 cm<sup>-1</sup> band in coals arising from the graphitic structures (non-crystalline).

There has been much disagreement in the case of the 1600 cm<sup>-1</sup> band, the most intense band in coal spectra. After the initial work of Cannon and Sutherland,<sup>59)</sup> the 1600 cm<sup>-1</sup> band was usually assigned to aromatic structures, thought to be mainly 1-, 2-, and 3-ring compounds. Brown<sup>60)</sup> and Friedel<sup>66)</sup> independently proposed that the band be assigned to conjugated, chelated carbonyl structures.

With this assignment, spectroscopists have nearly gone full circle in two decades from assigning the 1600 cm<sup>-1</sup> band to aromatic structures, then to conjugated chelated carbonyls and lastly, to graphite structures.

### B. NMR Spectrometry

By the 1960's, high resolution proton NMR

techniques have been widely used on coal studies.<sup>67)~75)</sup>

Based on the  $^1\text{H}$  NMR coupled with elemental analysis and M.W. determination,  $H_a$ ,  $H_b$  and  $H_c$  values can be easily determined.  $f_a$  ( $C_{ar.}/C_{tot.}$ ) values also can be obtained from Brown-Ladner equation.<sup>68)</sup>

$$f_a = [(C/H) - H_{ali}/(H_{ali}/C_{ali})]/(C/H) \quad (6)$$

The drawback of the Brown-Ladner equation is to assume the ratios of aliphatic hydrogen/carbon arbitrary. The aliphatic groups in coal molecules are mostly methylene bridges and methyl groups.

Despite the greater potential than  $^1\text{H}$  NMR, the early application of  $^{13}\text{C}$  NMR to coal research has been severely restricted due to the poor spectral resolution and sensitivity.

In their pioneering work,<sup>76)~78)</sup> Friedel and Retcofsky discussed the method of obtaining  $f_a$  values from  $^{13}\text{C}$  NMR.

From the  $^{13}\text{C}$  NMR Spectra of a synthetic blend liquid using proton decoupled and CAT technique, they determined the  $f_a$  value, which was in good agreement with the known value. The advent of new technique of pulse Fourier transform (PFT) NMR spectroscopy<sup>79), 80)</sup> combined with proton-decoupled technique opened a new road to the study of coal-derived liquids by  $^{13}\text{C}$  NMR.

In 1975, Bartle *et al.*<sup>81)</sup> determined the value of  $f_a$  and  $C_{ar.}$  by this method for a novel, supercritical-fluid extract of coal.<sup>82)</sup> The values are in reasonable agreement with those determined by  $^1\text{H}$  NMR method.<sup>83), 84)</sup>

Dorn<sup>85)</sup> employed a combined  $^1\text{H}$  and  $^{13}\text{C}$  PFT method in a model study of phenanthrene.

The values  $H/C$ , wt. % of carbon and hydrogen were determined, indicating the possibility of application of this method to other coal-derived liquids with reasonable level of accuracy and precision.

Retcofsky *et al.*<sup>86)</sup> determined the  $f_a$  value of various coal-derived liquids by PFT  $^{13}\text{C}$  method and compared with those obtained by Brown-Ladner equation.<sup>68)</sup> Generally the agreement between two values is quite good.

As an extension of study of his previous one,<sup>85)</sup> Dorn *et al.*<sup>87)</sup> separated a SRC product by molecular size (GPC) into fractions.

With the supplement of elemental analysis and M.W. data,  $^1\text{H}$  and  $^{13}\text{C}$  PFT method gives molecular parameters for the accurate chemical characterization.

Recently, Cantor<sup>88)</sup> calculated several average molecular structure parameters for anthracene and coal liquid based upon the data of  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

Gavalas *et al.*<sup>89)</sup> has developed a technique, "Computer-Assisted Molecular Structure Construction (CAMSC)"; for the structural elucidation of coal-derived compounds. It utilizes elemental analysis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and M.W. data to determine the allowable combinations of functional groups constituting the structure. CAMSC is applied to four cases of experimental data from the literature, the results of which compare well with those obtained by other methods.

While the quantitative study of high-resolution  $^{13}\text{C}$  spectra of coal-derived liquids has progressed,  $^{13}\text{C}$  studies of solid coals have been limited to the broadline variety<sup>90), 91)</sup> which permit only qualitative data concerning coal structure.

In the qualitative studies,<sup>91)</sup> coals were compared with those diamond and graphite and found to be best rationalized in terms of increasing carbon aromaticity with increasing coal rank leading finally to the formation of graphite-like structure.

Recently two papers<sup>92), 93)</sup> have been published on the possibility of quantitative study

of coal solids by  $^{13}\text{C}$  NMR using new techniques such as cross-polarization<sup>94)</sup> and magic-angle<sup>95), 96)</sup> spinning.

The combination of magic-angle sample spinning and H dipolar decoupling (with cross polarization) may constitute a promising approach for (CP)  $^{13}\text{C}$  NMR studies of fossil fuels. Gross structural information, e.g. aromatic/aliphatic carbon ratio carbon ratios can be readily accessible. However, additional experiments will be necessary to place limits upon the uncertainties due to differences in the CP efficiencies, or to correct for them and to explore modifications of the basic experiment to provide more detailed spectral information.

### C. Mass Spectrometry

Mass spectrometry is one of the most promising tools for the characterization of very complex mixtures. In the 1950's high resolution<sup>97), 98)</sup> and in the mid-1970's ultra-high resolution<sup>99)</sup> mass spectrometers became available and have been used in the characterization of petroleum and, more recently, coal liquids.

Very recently, field ionization mass spectrometry<sup>100)</sup> had been used for the analysis of coal liquids.

In the present report, we will review the recent development of high resolution low voltage (HRLV) and field ionization (FII) mass spectrometric techniques on the analysis of coal-derived liquids. Both techniques utilize the gentle ionization method and show only molecular ions and no fragmental ions thereby simplifying the spectra.

#### 1) High Resolution Low Voltage (HRLV) Mass Spectrometry

Low voltage method has been developed in late 1950's by the workers<sup>101), 102)</sup> at Exxon Research & Engineering Co., Baytown, Texas. With the low voltage (-10 eV) only unsat-

urates, olefins and aromatics can be ionized without fragmentation

With the advent of high resolution technique, HRLV<sup>103)~105)</sup> has been successfully applied for the quantitative characterization of aromatic fractions of high boiling petroleum, in terms of molecular composition.

With the aid of computer, HRLV-MS analysis<sup>106), 107)</sup> of coal liquids can provide very detailed quantitative information on the complex mixtures, e.g. compound type, molecular weights, weight %, carbon number distribution and other molecular parameters, etc.

The disadvantage of HRLV-MS is that it is limited to double bond compounds-olefins, aromatics and polar molecules. Because of the low voltage employed, the sensitivity is low and reproducibility is poor.

#### ii) Field Ionization (FI) Mass Spectrometry

FI-MS is a relatively new technique which has been extensively studied by Beckey<sup>100)</sup> and coworkers on a wide variety of organic compounds. This technique seems to have great potential value for the study of complex mixtures of petroleum or coal-derived liquids. This method is particularly useful for the saturate fractions to which HRLV-MS is not applicable.

Mead<sup>108)</sup> analyzed heavy petroleum fractions by this method. Homologue series (e.g.  $\text{C}_n\text{H}_{2n}$ ,  $\text{C}_n\text{H}_{2n-2}$ , ...), their relative wt. % and average carbon numbers were determined and compared reasonably well with that of other workers.

Pyska *et al.*<sup>109)</sup> studied the adsorption phenomena on emitters and the effects on the sensitivity coefficients of paraffins in field ionization in the presence and absence of aromatic hydrocarbons. Scheppele *et al.*<sup>110)</sup> studied the FI sensitivity for heptane relative benzene as a function of both ion-source temperature and binary-mixture composition.

Ryska *et al.*<sup>111)</sup> also studied the dependence of sensitivity of paraffins on molecular weight and structure.

The previous studies<sup>108)~111)</sup> of FI-MS mentioned might point the sensitivities of the paraffins are influenced by i) the presence of aromatics, ii) ion source temperature, iii) molecular weights of the paraffins,

Scheppele *et al.*<sup>112)</sup> determined the sensitivities of 60 aromatic compounds relative to ethylbenzene, which are ingeneral typical of those encountered in coal-derived liquids. The sensitivities are within the limits of experimental precision independent of sample composition. The variations in the FI relative cross sections with change in molecular structure are not as large as those for EI by low voltage but the trends are similar. Three synthetic blends were also analyzed by GC-FID, FI-MS and LVEI-MS assuming unit relative sensitivities. The results by FI-MS are in better agreement with the known distribution than those similarly obtained by LV-EI method.

Very recently, Anbar and coworkers<sup>113)</sup> studied various coal-liquefaction products using a highly efficient and sturdy FI-MS. The products have been analyzed and their molecular-weights profiles were determined by the integrating multiscan technique.

The coal derived liquids can be meaniigfully characterized in several ways,

1) extraction by a number of solvents, 2) gross average molecular weight by VPO, 3) gross molecular weight profiles by GRC, 4) separation by HPLC. However, the detailed molecular weight profiles of the crude mixtures by HRLV- or FI-MS are still more informative than any other data obtained by other methods.

#### D. Miscellaneous

Gas chromatography, GC-MS, EPR, U.V.,

ion-exchange and liquid chromatography have been used for the separation and characterization of coal liquids, which we hope to discuss in a later paper.

## 5. MEANINGFUL SEPARATION OF COAL-DERIVED LIQUIDS

The detailed characterization of coal-derived liquids is a prime requirement for the development of a coal liquefaction technology as well as for its utilization. Data on the composition of these products are vital for the evaluation of process variables, product quality control environmental studies and so on.

The experience in the analysis of petroleum cruds has shown that in order to obtain meaningful results, it is necessary to separate a sample into a certain number of well-defined fractions and to analyze these fractions in detail. Conclusions as to the composition of the original sample are then arrived at by combining the results of the analyses on each fraction in a manner consistent with the steps performed to obtain them. This same approach can be used for the synthetic liquid fuels.

Yen and coworkers<sup>114)</sup> have separated the coal liquids by solvent fractionation into five crude fractions according to the *Figure 3*.

Representative coal liquid samples produced via the three direct coal liquefaction processes (Synthoil, FMC-Coed, Cat. Inc. SRC) were separated into five fractions and each fraction has been characterized by elemental analysis, color indices, and semiquantitative metal analysis.

From the results of the fractions being the fun of the aromatic pi-system, it might be assumed that the increase in going from oil, to resin to asphaltene to carbene reflects an increase in the size of respective  $\pi$ -systems.

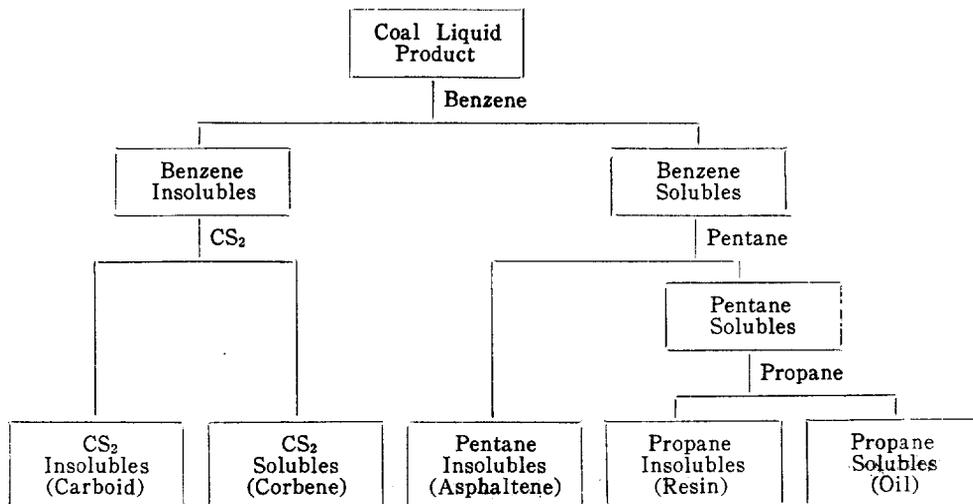


Figure 3. Solvent Fractionation Scheme for Coal Liquid Product

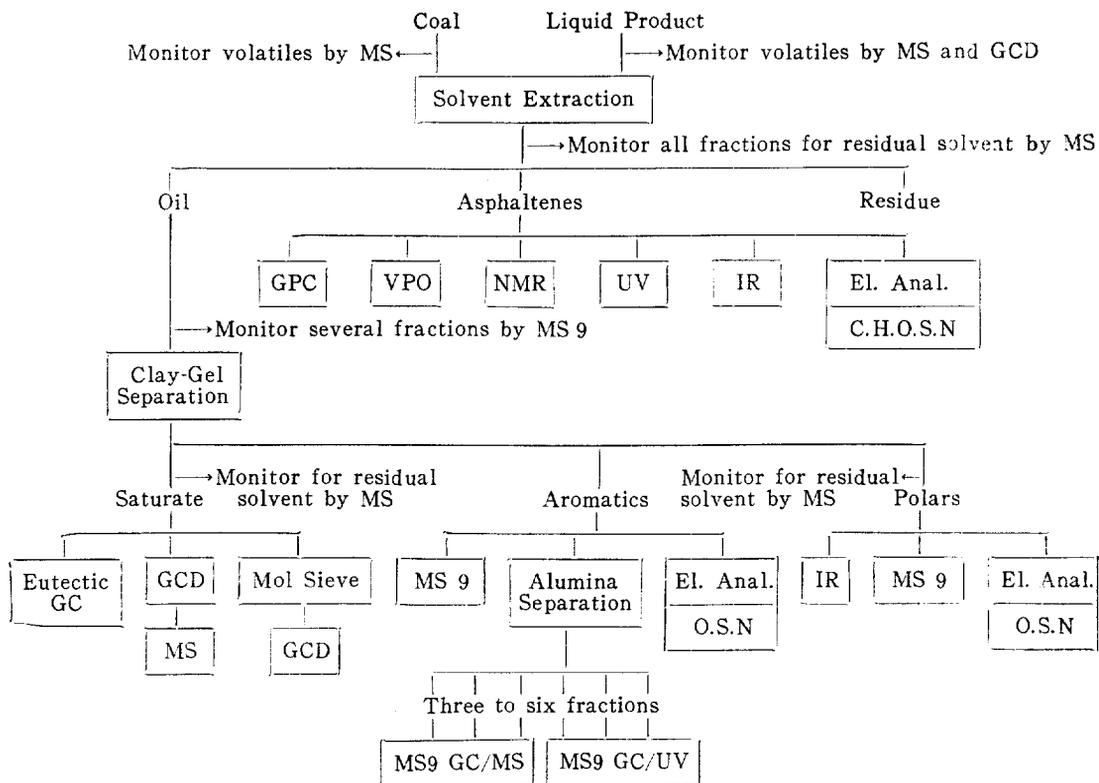


Figure 4. Analytical Scheme

Carbon aromaticities determined by X-ray diffraction were also found to increase in going from asphaltene to carboid, which is consistent with the color indices results.

They have further separated asphaltenes into two major fractions by elution from silica gel with benzene and ethylether. The three fractions were then characterized by color in-

dices, elemental analysis and molecular weight. Asphaltene had been previously separated by Sternberg *et al.*<sup>115)</sup> into acidic component.

Yen *et al.*<sup>116)</sup> claimed the words "acid" and "base" do not adequately classify or clarify the coal-derived asphaltene and suggested different classification of acceptor( $\pi$ -deficient) and donor( $\pi$ -abundant) since their association and the nature of charge transfer is well known in asphaltene.

Aczel and coworkers<sup>117)</sup> analyzed coal liquid of synthoil products according to the *Figure 4*.

The overall composition of one SYNTHOIL feed and three products were characterized by solvent extraction, clay-gel percolation and mass spectral analyses.

The cyclohexane soluble oil content ranges from 57 to 90% and the asphaltenes range from 3 to 25% in all products.

The oil fractions of the products contain saturated compounds but consist mostly of aromatic and polar aromatic components.

Dooley and Thompson<sup>118)</sup> at Bartlesville Energy Research Centre characterized coal derived liquids from SYNTHOIL and COED processes by means of distillation, elution, chromatography, acid base extractions and gel permeation chromatography, followed by instrumental analyses such as M.S. and N.M.R. spectrometry. These are shown in *Figure 5*.

Retcofsky *et al.*<sup>119)</sup> separated SYNTHOIL products into four fractions by silica gel col-

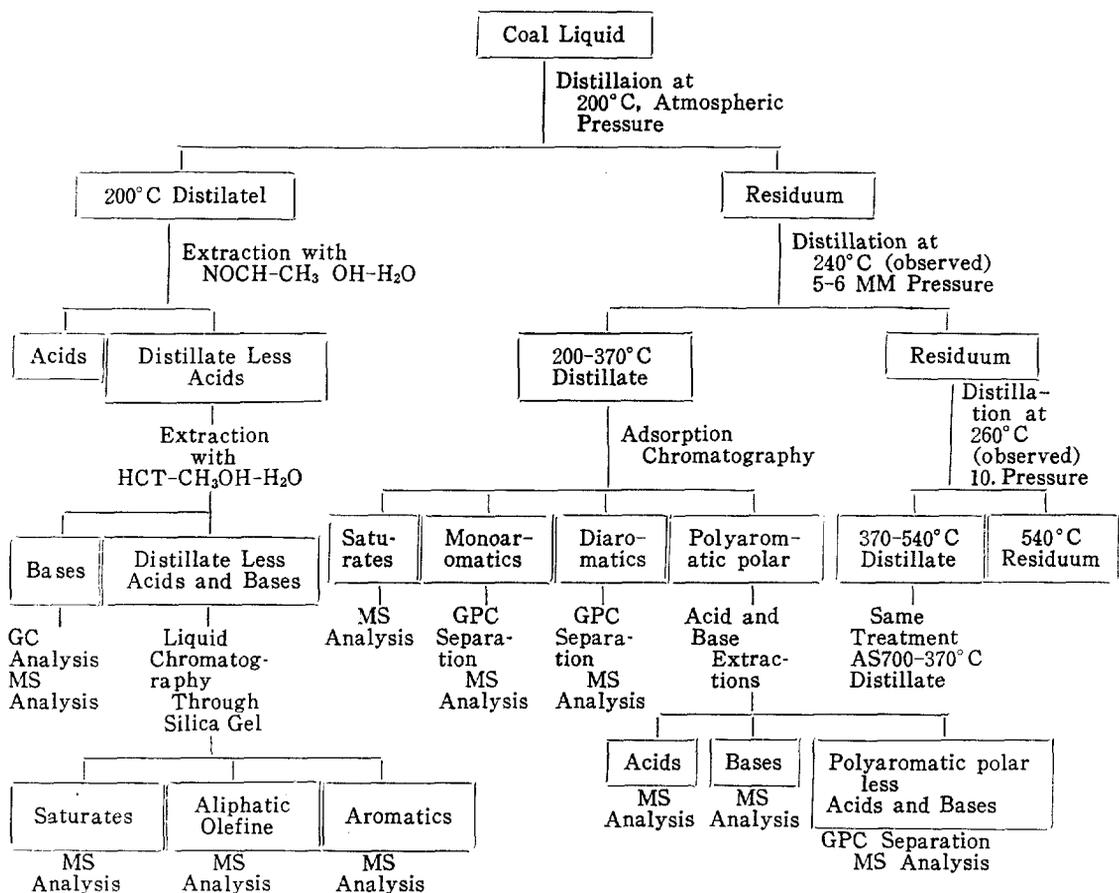


Figure 5. Analytical Scheme

umn chromatography. All fractions were chromatographed by TLC and thin-layer electrophoresis (TLE) on silica gel, alumina and cellulose plate. The fractions were further characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR which showed the increasing aromaticity from 1st to 4th fractions. Fraction 4 closely resembles asphaltene material by its NMR, IR and U.V. spectra, which was further separated into acidic components. The hydrogen bonding study of the coal-derived asphaltene acidic and basic components indicates that a hydrogen-bonded complex does exist in the SYNTHOIL product.

Farcasiu<sup>120)</sup> studied the separation of SRC coal liquids by sequential elution with specific solvents on silica gel columns with special emphasis to achieve a fractionation based primarily on the different chemical functionality.

The coal liquids were separated into 10 fractions, and each was further characterized by elemental analysis, M. W. -determination,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

The relative retention factors  $R_f$  for the fractions and model compounds were determined and compared.

Schiller *et al.*<sup>121)</sup> have developed a simple chromatographic method to fractionate coal derived liquids. The liquids were eluted from the neutral alumina with series of solvents of solvents to give five principal compound types; saturated H.C., aromatic H.C. and benzofurans, nitrogen compounds and hydroxyl compounds. The four fractions except for the saturates were further characterized by HRLV-MS.

## 6. CONCLUSION

The structure of coal is now generally considered to be the condensed polyaromatics

connected by methylene, oxygen or sulfur bridges. However, further work is required for the more accurate structure. The condition of coal liquefaction requires drastic condition of high pressure and temperature. It is the task of contemporary fuel chemists to find a proper catalytic system by which coal would be liquefied under milder condition, thereby minimizing the energy needed for the liquefaction.

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