Organic Geochemistry of Fossil Fuels: Probes into Macromolecular Structure

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Since the 1800's geologists have been intrigued by the origin and nature of organic matter in the geologic record. The study of organic matter has spawned the fields of organic geochemistry and fuel science, both of which have become devoted to understanding the chemistry, use, and occurrence of what we today know as fossil fuels. Knowledge of the chemical composition of fossil fuels has been driven by the development of new instrumentation capable of delving into the chemical structure of materials formed millions of years ago from plants remains.

The complexity of fossil organic matter has provided a formidable challenge to the analytical chemist. Simple elemental analyses (C, H, N, O, and S) and poorly resolved (strained spectrometric analyses were the only analytical techniques available to characterize these complex organic substances until gas chromatography and mass spectrometry development in the 1960's. A few years ago, most of what we knew of fossil fuels was obtained from gas chromatographic and mass spectrometric analysis of solvent extractable material, which usually amounts to only 5-10% of most fossil fuels. Most chemical characterization was being done on a very small fraction of the organic matter present. Most of the organic matter in fossil fuels is complex, macromolecular, and insoluble in most organic solvents, which leaves our ability to analyze its composition by chemical, chromatographic and spectroscopic methods.

The advent of two techniques in the 1970's changed perceptions of fossil fuels' composition so dramatically, it is possible to begin constructing chemical models depicting a large fraction of the macromolecular composition of fossil fuels. One technique, nuclear magnetic resonance (NMR), provides spectroscopic information, allowing distribution determinations of principally carbon types. The other, flash pyrolysis combined with gas chromatography-mass spectrometry (py/gc/ms), provides details of the chemical structural units comprising the macromolecular network.

Nuclear magnetic resonance (both 1H and 13C NMR) has been used for more than 30 years, but limited its application until the 1970's to materials soluble in organic solvents. This limited its applicability to fossil fuels. In 1973, Alex Price working in John Wulff's laboratory at MIT demonstrated that the long analysis times required for 13C NMR of powdered solids, rapidly days or weeks could be shortened to minutes by a double resonance experiment where 13C nuclei could be made to exchange their magnetization with or behave like 1H's. This technique, called cross-polarization, was combined with high-speed sample rotation at an angle of 54.7 degrees to the applied magnetic field to produce 13C NMR spectra having peak widths approaching those obtained in solution NMR.

Figure 1 shows 13C NMR spectra of a pure organic compound isolated in solution by conventional NMR and by this solid state 13C NMR technique called cross-polarization with magic-angle spinning (CPMAS). Note the solid's spectrum has broader lines but all peaks except two are separated. The absence of a resonant frequency scale (parts per million of frequency shift relative to a standard) which provides information on the carbon type in a molecule and, therefore, is a structural fingerprint.

Thus, the 13C NMR method provides a quantitative representation. For small molecules, the spectra are simple, but, for macromolecules or complex mixture of macromolecules such as those from fossil fuels, the spectra are complex assemblage of overlapping peaks where only average structural entities are discerned (Figure 2).

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Figure 2. Average structural entities of a humic substance determined through NMR spectroscopy.

is solid. Two solid-state NMR spectrometers exist at Penn State, one operating at a magnetic field of 7 Tesla, in the Department of Chemistry and the other operating at 2.35 Tesla, in the Fuel Science Program. The list spectrometer is used specifically for \( ^{13} \)C NMR studies described below.

The other technique having a major impact on fossil fuels studies, \( \text{py/gc/ms} \), was developed to produce, via pyrolysis (heating in the absence of oxygen), fragment molecules that are volatile enough for \( \text{gc/ms} \) but which provide some details of fossil fuels’ structural units. The pyrolysis temperature, 660/350°C, is enough to obtain products that can be analyzed by \( \text{gc/ms} \) but insufficient for complete pyrolysis to methane, CO\(_2\), H\(_2\)O and other low molecular weight gases that would provide no structural details. The assumption is that pyrolysis clips off volatile molecules that represent the macroscopic network and can be reassessed to depict the original structure.

Figure 3 shows a typical \( \text{py/gc/ms} \) chromatogram. The volatilized pyrolysis products can be analyzed quantitatively by measuring peak areas for the individual peaks which have been chromatographically separated by a fused silica capillary column. The peaks are identified as specific compounds by treating the effluents from gc to a rapidly-scanning mass spectrometer which provides “fingerprint” patterns that are compared with those of pure authentic compounds. Although the gc/ms analysis can be quantitative, we are never sure that the pyrolysis conditions provide a quantitative representation of fossil fuels’ macro-molecular structural components because pyrolysis yields depend on many factors such as mineral matter present and pyrolysis chamber. The pyrolysis technique is used for mostly qualitative purposes. The combined use of solid-state \( ^{13} \)C NMR and \( \text{py/gc/ms} \) provides a valuable protocol for chemical structural elucidation of complex macromolecules. The quantitative distribution of carbon types obtained by NMR can be reconciled with qualitative information regarding molecular structural units.

Studies on Coal’s Origin and Chemical Composition

Coal is a complex mixture of plant remains which accumulated in past swamps and were transformed by microbial and geothermal activities to a black, sometimes lustrous rock. Inasmuch as a variety of plants growing in the swamp contributed different chemical compounds to the peat and the compounds’ degree of degradation varied from one peat swamp to the next, nearly an infinite compound mixture exists. It was once thought that coal’s chemical composition was an assemblage of similar macromolecules formed by random polymerization of small molecules degraded from plants by microorganisms in the peat. However, petrographic studies added by use of solid-state \( ^{13} \)C NMR and \( \text{py/gc/ms} \) have changed this thinking. Now most investigators believe coal macromolecules were mostly formed from altered biopolymers in plants. The evidence comes from studies showing a direct chemical structural link between biologically recrystallized biopolymers in plants and microscopically recognizable plant remains in coal.

Studies conducted at Penn State’s Fuel Science Program contribute to evidence for a genetic link between coal and modern plant components. By examining modern wood, wood buried in peat swamps, and ancient wood coalified to different ranks with combined NMR and pyrolysis techniques, a detailed understanding is obtained of how wood’s chemical structures evolve to coal structures. Wood transformation to coalified wood, or vitrinite, the major petrographically identifiable component of most U.S. coals, begins at the peat stage. (continued, page 3)

![Buried Wood, Dismal Swamp](image)

Figure 3. A typical pyrolysis gas chromatogram for a buried wood sample from the Dismal Swamp, VA, showing the individual identified compounds formed from flash heating the sample.
stage where cellulose is degraded and removed from the wood while the lignin, an aromatic wood biopolymer, is selectively preserved. Figure 4 shows an SEM photo of coalified wood. Analysis reveals that lignin-derived structural units account for most of its chemistry. The inference is that the cellular remains which are readily observed microscopically are simply remnants of the complex biopolymer lignin, which has undergone only slight chemical alteration during millions of years of burial. Lignin becomes vitrinite’s precursor as it is transformed by a specific series of sequential reactions during coalification to different levels of rank. These reactions can be readily discerned by CP/MAS$^1$ NMR and py/gc/ms. By using lignin biopolymers as templates in molecular and by inducing the observed chemical reactions to these templates, we have generated a specific series of chemical structural models that depict coalified wood at various coalification levels. These studies show that several important chemical transformations of the basic lignin structural framework can be identified as rank increases. The major reactions are depicted in Figure 5. The first reaction is the cleavage of aryl ether bonds in lignin; these include the hydrolysis of methoxyl groups and the cleavage of 6-0-aryl ethers. Both reactions produce a phenolic OH resulting in formatting catechol-like structures (1,2-dihydroxyphenols). The latter reaction leads to the production of a carbonation on the three-carbon sidechain of lignin, and this carbonation is believed to allylate adjacent catechol-like aromatic rings. This reaction is an important step in the overall coalification scheme, because cleavage of the aryl ethers results in small, water-soluble phenols which will be removed from the coal during burial. The allylation reaction preserves the macromolecular integrity of the lignin-derived structures, thereby maintaining the coal’s physical integrity. Subsequent reactions leading to the subbituminous coal rank involve transforming highly crosslinked catechol-like structures to form phenol-like structures by removing one hydroxyl group per aromatic ring. Finally, as the lignin-derived coal structure evolves to bituminous coal, the phenol-like structure is transformed to a structure containing diaryl ethers, benzofurans, alkylbenzenes and alkylarylethanes. The three-dimensional depiction on a computer screen of coal structure evolution depends greatly on the lignin model used. While several two-dimensional lignin models have been published in the recent literature, they have been deficient in three-dimensional space. In an attempt to describe a better three-dimensional model for lignin, Dr. Jean-Leech Fuson, a Visdoc at Hatcher’s group, has proposed that the glyceryl methoxyphenolic ethers comprising the basic building blocks of lignin are linked through the 8-0-4 bonds in a linear chain which assumes a helical configuration when subjected to energy minimization in three-dimensional space. Using this new template for lignin, Fuson and Hatcher, collab-retting with Dr. Gary Carbon of Sandia National Laboratory, are constructing a rank series of three-dimensional coal structural models to depict lignin coalification to form subbituminous and bituminous coals.
that of other petrographic microscopic techniques. An advantage that NMR imaging has over petrographic methods is the ability to view internal structure with minimum sample preparation and without preparing a petrographic specimen. Also, the sample can be examined in three dimensions with 2D projections along all orientations. Information is gathered simultaneously and is simply recalled from computer memory. Figure 7 shows 2D "slices" through the coal sample along the cross-section and along a longitudinal section. The cross-sectional view shows individual vessel elements and annual rings and the longitudinal section represents a slice across a row of vessel elements in an annual ring. The bright areas represent coal-rich in hydrogen, in this case the hydrogen in water within the pore space. The microscopic components in coal contain sufficient differences in water content to yield microscopically identifiable contrast with a level of spatial resolution approaching 20 μm.

Pyrolysis Microscopy
Pyrolysis/gas normally requires small quantities of sample (e.g., 0.1-10 mg). Though tedious, coal components can be hand-picked in sufficient amounts for studies. Coal component pyrolysis in situ would be a preferable means of examining coal components with minimum processing. A laser beam with enough energy is pyrolyze organic matter was developed for such studies by F. Vostola, Provost Emeritus of Penn State’s Fuel Science Department, in the 1960s. This pulsed ruby laser has been mounted on a microscope and collimated through the microscope to a focal point within a pyrolysis chamber housing coal samples.
BREAKING THROUGH THE GLASS CEILING

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Science and engineering presently provide intellectually stimulating and challenging careers, as they have in the past. What is new is that in recent years women have found increasing opportunities to participate in these discoveries. Recent events in the political arena show that women are finally breaking through the glass ceiling and are being appointed to top science and engineering leadership positions. This can only be looked upon as an encouragement to decision makers in academia and the private sector who will follow suit and appoint more women to positions for which they are qualified and ready to take up responsibilities.

These recent breakthroughs have come after a steady growth in women's participation in the stimulating enterprise of science and engineering careers. Women comprised 43.8% of 1991's doctoral recipients in science and engineering disciplines. However, because of their under-representation in the past, women represent only 17.2% of the doctoral science and engineering work force. A variety of factors, stemming from early childhood experiences, and continuing through pre-college, undergraduate and graduate school experiences, a multitude of micro-insults and discouragements, have kept the pipeline of women into science and engineering, degrees at a level significantly lower than that of men. Efforts have been made by various interventions to increase the flow of women in the science and engineering pipeline through targeted scholarships and counseling. These interventions were especially prevalent in engineering during the 1975-85 period and were very successful in increasing the flow of women into engineering during that ten year period.

However, as the intervention programs were enacted, the number of women engineering students declined, in part because of the difficulties many women engineers experienced in the work force subsequent to graduation. Personal studies show that the attrition rate for women on the job is approximately two-and-a-half times as high in industrial employment as for men. While family responsibilities account for some of the differential attrition rates, the attrition rates for married women without children and for single women are also much higher than for their male counterparts.

Studies of the pipeline model have been conducted in fields such as law and business, where women have been in the pipeline in sufficient numbers for a long enough period to have reached senior positions. These studies show that for the lower tier to have reached senior positions, there would be expected by the pipeline model. Women in science and engineering have also faced glass ceilings and other obstacles to advancement, particularly in industry and government.

Recently, a major step has been taken to increase the opportunities for women in science and engineering — the appointment of a number of top women science and engineering professionals to key positions in the federal government. Some recent examples in the Clinton administration include: Anita Jones (computer science), appointed Director of Defense Research and Engineering of the Department of Defense; Janet Chappell (deskilling), appointed Director of the National Institutes for Standards and Technology of the Department of Commerce; Martha Koeps (physicist), appointed Director of the Office of Energy Research of the Department of Energy; and Sheila Widnall (aeronautical engineering), appointed as Secretary of the Air Force.

These appointments have come at a time when women are also making major strides forward in the election process in Congressional and Senate races. Of course, the appointment of Ruth Bader Ginsberg to the Supreme Court also follows this trend. In Japan, women now comprise 10% of the Diet Seats and three of the cabinet positions. These all are encouraging signs toward increasing opportunities for women in the profession. If 1992 was the year of the women, then perhaps we can look forward to the 1990s being the decade of the women, propelling us into a new century without glass ceilings.

Figure 7. NMR microscopic image of coalified wood shaving, top, a series of cross sections, and right, longitudinal sections.

The laser beam can be focused onto a pyrolysis coal sample to induce pyrolysis. Volatile pyrolysis products are swept into the gas chromatograph/mass spectrometer for identification. The nature of py/ gc /ms provides information on the macromolecular chemistry of the coal's surface to a depth of 2-30 µm. The coal's individual components can be seen and characterized by laser pyrolysis/gc /ms.

This petrologic laser pyrolysis system is still developmental; however, examining several coal samples indicates that it has great promise for characterizing microscopic entities in coal which are on the order of 10-50 µm diameter. Components like cell inclinations, pollen grains, algal spores, and other microscopic bodies in coal can be examined individually. Of course, the laser technique is not limited to coal but can be used to study organic remains in sediments and other materials, both natural and synthetic.

SUMMARY

Organic geochemistry benefits from developing more sophisticated methods for analyzing complex macromolecular organic matter. Developing solid-state 13C

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Organic Geochemistry, continued

NMR and pyrolysis/gc/ms has made a tremendous impact. Many hypotheses about macromolecular organic matter are being revised as new techniques are applied. Characterizing the complex chemical structures in coal and humic substances is a goal that has been sought many years and now we have tools that make it possible. No doubt developments and refinements to these techniques are forthcoming. The development of NMR and py/gc/ms has also had a major impact in fields that overlap with or extend into organic geochemistry. Continued interaction among these fields will be synergistic.

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