Class 5

Advanced Coal Characterization Techniques

1

Reading Questions

1. Please summarize the types of data used to formulate proposed coal molecules.
2. For NMR, PyMS, Extraction, and FTIR techniques, discuss the following:
   a. Relative cost of the instrumentation
   b. General types of information available (species considered, range of MW, % of coal observed, etc.)
   c. Limitations/cautions about the data obtained
   d. Rough idea of how the experiments are performed
3. What is the "mobile phase", and what evidence is there for this mobile phase in any of the four techniques from question 1?
4. Please stare at the Py-FIMS data in Figure 4.28 and describe the differences between coals. Don't forget to look at the scales on the y-axes.
5. Please compare the yields of extracts and depolymerization products in Table 4.37 with the spectra obtained on the different fractions in Figs. 4.45-47. What is learned about the structure as a function of coal type from these data, and what fraction of the coal does it represent?
6. Please compare the types of data from the NMR analyses with the types of data obtained from the FTIR analyses. For similar types of data, please compare the numbers obtained from the two techniques. Which do you believe, and why?

2

Techniques

Technique	Cost	Capability
FTIR	$50-100K	Gas, liquids, solid spectra. Limited for heavy hydrocarbons. Capable of trace quantities for specific species.
MS	$75-500K	Gas and light liquids, no solids. Can be combined with GC. Peaks vs MW.
GC	$50-100K	Gas and light liquids. Peaks vs time must be calibrated.
Extraction	$20K	Chemical extraction, must be combined with another technique for analysis.
NMR	$500K+	Solids (^{13}C NMR) or liquids (^{1}H NMR). Spins samples in large supercooled magnet, generates Fourier transform of spectra.
HPLC		High MW liquids

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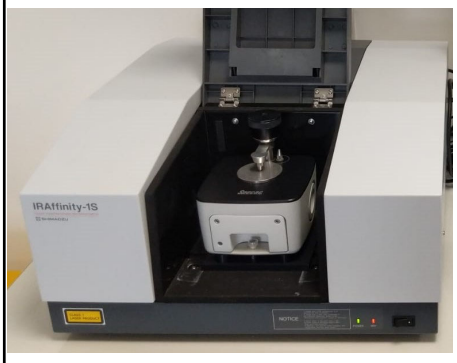
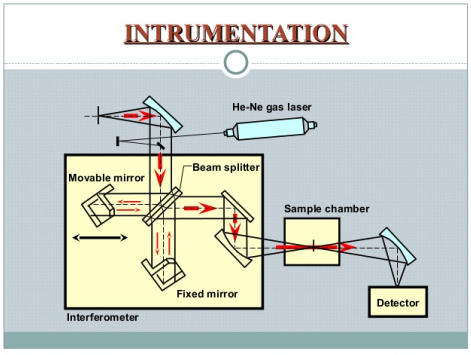
FTIR





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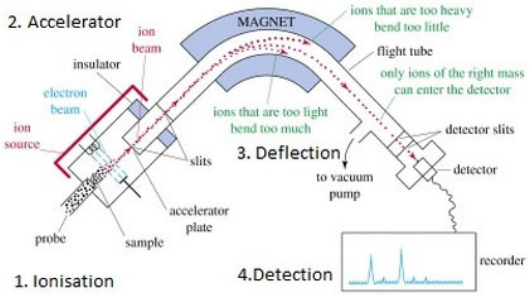
Mass Spectrometer



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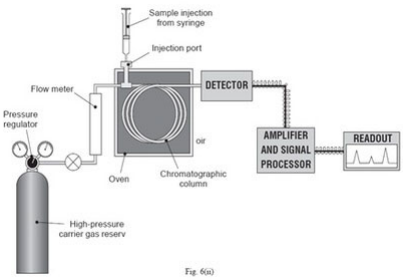
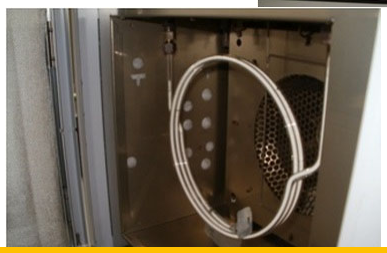
Gas Chromatography

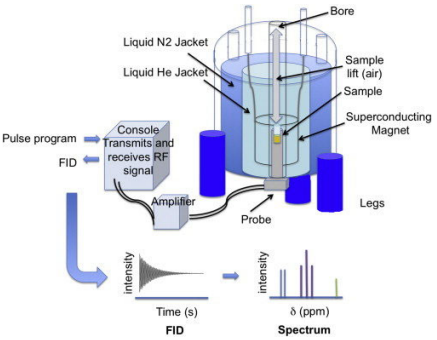




http://chemicalinstrumentation.weebly.com/gc.html

6

Nuclear Magnetic Resonance (NMR) Analysis

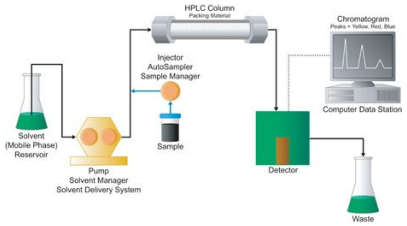


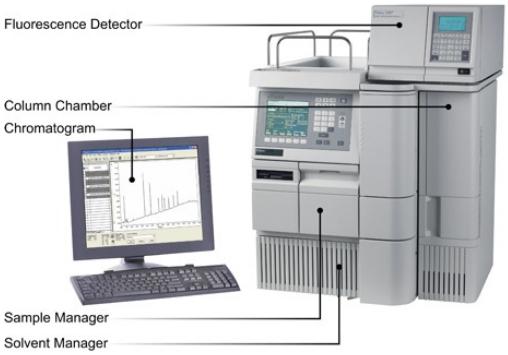
https://nationalmaglab.org/user-facilities/nmr-mri/nmr-instruments/700-mhz

https://www.researchgate.net/figure/Simplified-diagram-of-a-nuclear-magnetic-resonance-spectrometer-At-the-heart-of-the-1H_fig2_266562962

7

High Performance Liquid Chromatography (HPLC)





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Characterization Techniques

- Py-FIMS (Figure 28)
- Extracts/Depolymerization
  - Table 37
  - Figures 45, 46, 47

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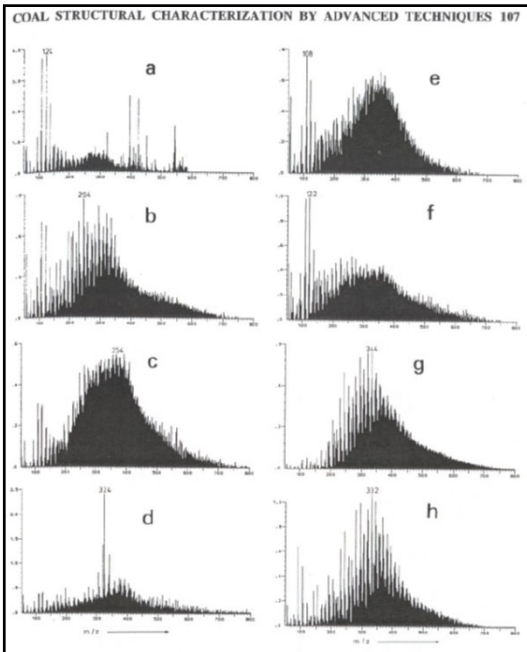

Figure 28. Integrated py-FI mass spectra (50–750°C) of Beulah–Zap (a, $\bar{M}_n$ = 292), Wyodak (b, $\bar{M}_n$ = 338), Illinois #6 (c, $\bar{M}_n$ = 368), Blind Canyon (d, $\bar{M}_n$ = 336), Lewiston–Stockton (e, $\bar{M}_n$ = 327), Pittsburgh (f, $\bar{M}_n$ = 324), Upper Fremont (g, $\bar{M}_n$ = 368), and Pocahontas #3 (h, $\bar{M}_n$ = 359). Heating rate 100 K/m (Simmleit *et al.*, 1992).

Py-FIMS

Simmleit et al., in Advances in Coal Spectroscopy, Plenum, New York, pp. 295-339 (1992)

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Extraction

TABLE 37. Alumina Column Fractionation Yields of Pre-extracts and HT-BCD Products (daf wt. % of coal)

Fraction	Illinois #6		Pocahontas #3		Blind Canyon		Beulah–Zap	
	Pre-extract	HT-BCD	Pre-extract	HT-BCD	Pre-extract	HT-BCD	Pre-extract	HT-BCD
Aliphatic	0.89	2.3	0.05	1.0	3.80	6.4	0.19	2.4
Neutral PAH[a]	2.10	9.2	0.10	7.4	3.97	12.4	0.56	7.2
Polar-1	3.16	2.1	0.49	10.2	3.57	2.6	1.04	23.2
Polar-2	10.65	44.7	0.16	3.4	7.56	34.2	0.41	21.4
Total wt. % of coal[b]	16.8	58.8	0.8	22.0	18.9	55.6	2.2	54.2

[a] PAH = polycyclic aromatic hydrocarbons.
[b] Reported on a dmmf basis.
Source: Carlson *et al.* (1992).

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Extraction

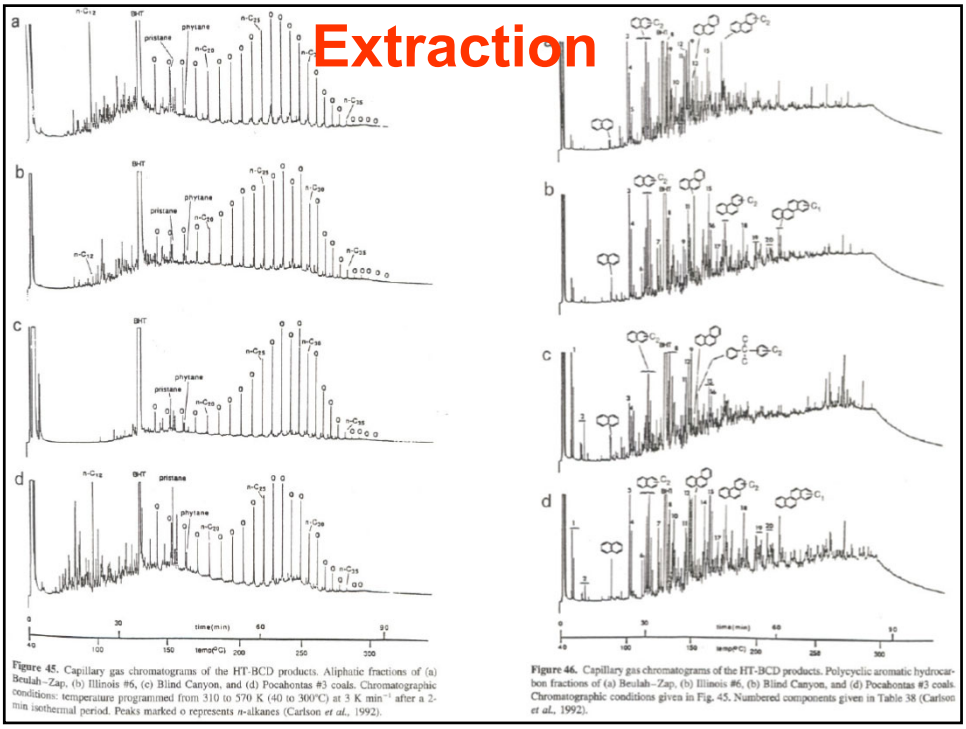

Figure 45. Capillary gas chromatograms of the HT-BCD products. Aliphatic fractions of (a) Beulah–Zap, (b) Illinois #6, (c) Blind Canyon, and (d) Pocahontas #3 coals. Chromatographic conditions: temperature programmed from 310 to 570 K (40 to 300°C) at 3 K min^{-1} after a 2-min isothermal period. Peaks marked o represents *n*-alkanes (Carlson *et al.*, 1992).

Figure 46. Capillary gas chromatograms of the HT-BCD products. Polycyclic aromatic hydrocarbon fractions of (a) Beulah–Zap, (b) Illinois #6, (b) Blind Canyon, and (d) Pocahontas #3 coals. Chromatographic conditions given in Fig. 45. Numbered components given in Table 38 (Carlson *et al.*, 1992).

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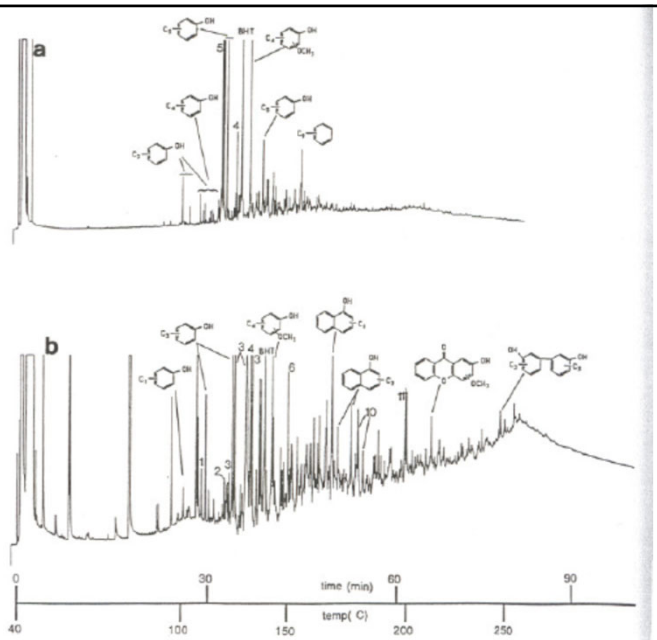

Figure 47. Capillary gas chromatograms of the HT-BCD products. (a) Polar-1 and (b) polar-2 fractions of Beulah–Zap. Chromatographic conditions: 310–520 K (40–250°C) for (a), (b) at 3 K min^{-1} after a 5-min isothermal period. Numbered components given in Table 39.

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NMR Analysis

https://nationalmaglab.org/user-facilities/nmr-mri/nmr-instruments/700-mhz

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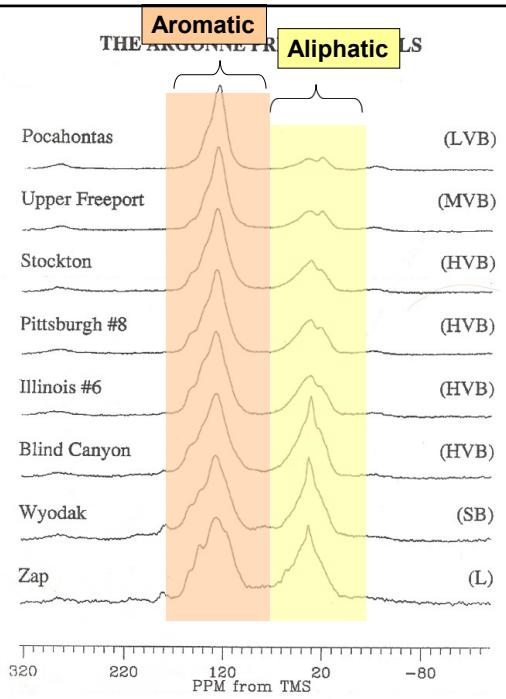

^{13}C NMR Analysis

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Empirical Relationship to Get # of C/Cluster

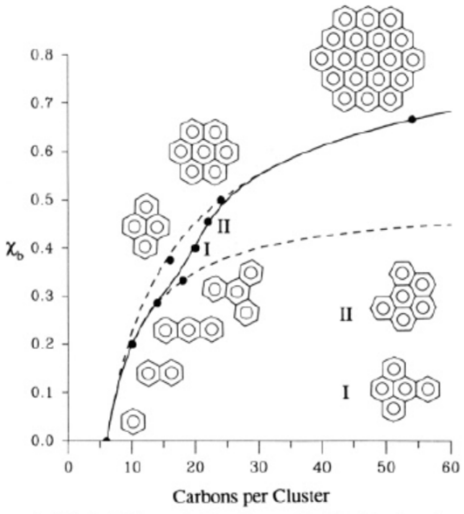

Figure 6. Plot of the mole fraction of bridgehead carbons, χ_b, vs C where C is the number of carbon atoms per aromatic cluster. The solid curve is for the combined model, the upper dashed curve is for the circular catenation model, and the lower dashed curve is for primary catenation model.

From Solum et al., Energy & Fuels (1989)

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Chemical Structure Relationships

$$M_{cluster} = \frac{C_{cluster}\, MW_{carbon}}{f_a'\; x_{carbon}}$$

$$m_\delta = \frac{M_{cluster} - C_{cluster}\, MW_{carbon}}{\sigma + 1}$$

σ+1 = coordination number
(avg. number of attachments per cluster)

Attachments = side chains + bridges + loops (not hydrogen)

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Representative NMR data for a Pittsburgh No. 8 coal and chars

Residence Time (ms)	0	43	65	89	128	223
Sampling Distance (mm)	0	40	70	100	150	250
Mass Release (% daf)	0	22	38	47	51	51
Aromatic carbon, $f_a = f_a + f_a^C$	.71	.72	.74	.79	.81	.86
Carbonyl, f_a^C	.04	.05	.04	.05	.03	.02
Aromatic carbon, carbonyl subtracted, f_a'	.67	.67	.70	.74	.78	.84
Protonated aromatic carbon, f_a^H	.27	.29	.27	.34	.33	.32
Non-protonated aromatic C, $f_a^N = f_a^P + f_a^S + f_a^B$	.40	.38	.43	.40	.45	.52
Aromatic carbon with O attachment, f_a^P	.08	.09	.07	.07	.05	.05
Aromatic carbon with alkyl attachment, f_a^S	.17	.19	.16	.19	.18	.22
Aromatic bridgehead and inner carbon, f_a^B	.15	.10	.20	.14	.22	.25
Aliphatic carbon, f_{al}	.29	.28	.26	.21	.19	.14
Aliphatic CH and CH_2, f_{al}^H	.18	.19	.17	.15	.14	.10
Aliphatic CH_3 and non-protonated carbon, f_{al}^*	.11	.09	.09	.06	.05	.04
Aliphatics with oxygen attachment, f_{al}^O	.07	.07	.05	.08	.07	.07
Proton spin-relaxation time, $T_{1\rho}^{Har}$ (ms)	4.0	2.6	2.7	4.4	6.1	8.3
Total carbons per cluster	16	14	19	13	17	18
Aromatic carbons per cluster, C	11	10	14	10	14	15
Aliphatic carbons per cluster	4.8	4.2	5.2	2.8	3.4	2.5
Total attachments per cluster, $\sigma+1$	4.1	4.2	4.6	3.5	4.1	4.8
Bridges and loops per cluster, B_C	2.3	2.8	2.8	2.7	3.2	4.1
Side chains per cluster	1.8	1.4	1.8	0.8	0.9	0.7
Fraction of intact bridges per cluster, p	.56	.68	.61	.77	.78	.85
Average cluster molecular weight	270	230	330	210	280	260
Side chain molecular weight	34	26	35	26	27	17

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Table III. Carbon Structural Distribution of the Argonne Premium Coals[a]

coal	f_a	$f_{a'}$	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
North Dakota (L)	0.61	0.54	0.07	0.26	0.28	0.06	0.13	0.09	0.39	0.25	0.14	0.12
Wyodak (SB)	0.63	0.55	0.08	0.17	0.38	0.08	0.14	0.16	0.37	0.27	0.10	0.10
Blind Canyon (HVB)	0.65	0.64	0.01	0.22	0.42	0.07	0.15	0.20	0.35	0.22	0.13	0.04
Illinois No. 6 (HVB)	0.72	0.72	0.00	0.26	0.46	0.06	0.18	0.22	0.28	0.19	0.09	0.05
Pittsburgh No. 8 (HVB)	0.72	0.72	0.00	0.27	0.45	0.06	0.17	0.22	0.28	0.13	0.15	0.03
Stockton seam (HVB)	0.75	0.75	0.00	0.27	0.48	0.05	0.21	0.22	0.25	0.14	0.11	0.04
Upper Freeport (MVB)	0.81	0.81	0.00	0.28	0.53	0.04	0.20	0.29	0.19	0.09	0.10	0.02
Pocahontas (LVB)	0.86	0.86	0.00	0.33	0.53	0.02	0.17	0.34	0.14	0.08	0.06	0.01
Zap[b] (L)	0.66	0.58	0.08	0.21	0.37	0.08	0.16	0.13	0.34	0.21	0.13	0.10
Rosebud[b] (SB)	0.63	0.53	0.10	0.16	0.37	0.07	0.14	0.16	0.37	0.20	0.17	0.08
Illinois No. 6[b] (HVB)	0.71	0.67	0.04	0.24	0.43	0.09	0.19	0.15	0.29	0.17	0.12	0.03

[a] Fractions of sp^3-hybridized carbon (error estimate): f_a = total carbon ($\approx\pm0.03$); $f_{a'}$ = in an aromatic ring ($\approx\pm0.04$); f_a^C = carbonyl, $\delta > 165$ ppm ($\approx\pm0.02$); f_a^H = protonated and aromatic ($\approx\pm0.03$); f_a^N = nonprotonated and aromatic ($\approx\pm0.03$); f_a^P = phenolic or phenolic ether, δ = 150–165 ppm ($\approx\pm0.02$); f_a^S = alkylated atomatic, δ = 135–150 ppm ($\approx\pm0.03$); f_a^B = aromatic bridgehead ($\approx\pm0.04$). Fraction of sp^3-hybridized carbon (error estimate): f_{al} = total carbon ($\approx\pm0.02$); f_{al}^H = CH or CH_2 ($\approx\pm0.02$); f_{al}^* = CH_3 or nonprotonated ($\approx\pm0.03$); f_{al}^O = bonded to oxygen, δ = 50–90 ppm ($\approx\pm0.02$). [b] An oxidized sample obtained from Advanced Fuel Research.

Table IV. Aromatic Cluster Size of the Argonne Coals from the Combined Model[a]

coal	χ_b	AC/Cl	att/Cl	MW
North Dakota (L)	0.17	9	$3_{.2}$	277
Wyodak (SB)	0.29	14	$5_{.6}$	410
Blind Canyon (HVB)	0.31	15	$5_{.2}$	359
Illinois No. 6 (HVB)	0.31	15	$5_{.0}$	316
Pittsburgh No. 8 (HVB)	0.31	15	$4_{.8}$	294
Stockton seam (HVB)	0.29	14	$4_{.9}$	275
Upper Freeport (MVB)	0.36	18	$5_{.2}$	302
Pocahontas (LVB)	0.40	20	$4_{.3}$	299
Zap[b] (L)	0.22	11	$4_{.5}$	339
Rosebud[b] (SB)	0.30	15	$5_{.8}$	459
Illinois No. 6[b] (HVB)	0.22	11	$4_{.6}$	267

[a] χ_b = mole fraction of bridgehead carbons (error $\approx \pm0.06$). AC/Cl = number of aromatic carbons per cluster (error $\approx \pm3$). att/Cl = number of attachments per cluster. MW = total molecular weight of a cluster. [b] An oxidized sample obtained from Advanced Fuel Research.

From Solum et al., Energy & Fuels (1989)

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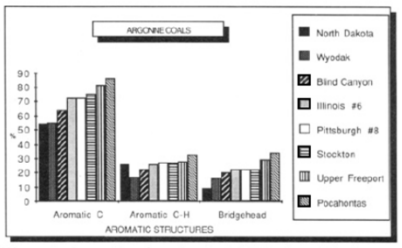

Figure 2. Aromatic carbon structural distribution of the Argonne coals.

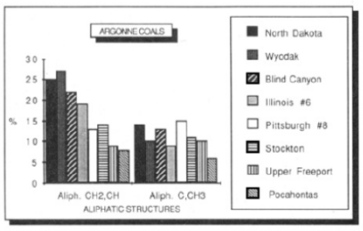

Figure 4. Carbon distribution of the aliphatic region of the Argonne coals.

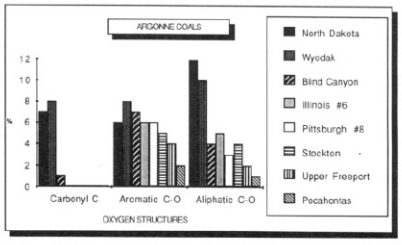

Figure 3. Structural distribution of carbons associated with oxygen in the Argonne coals.

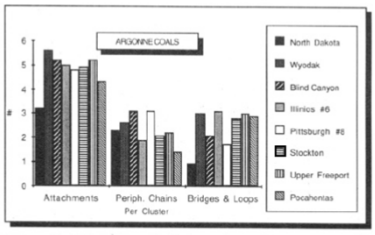

Figure 8. Distribution of attachments on an average aromatic cluster in the Argonne coals as determined from the combined catenation model and the structural parameters.

From Solum et al., Energy & Fuels (1989)

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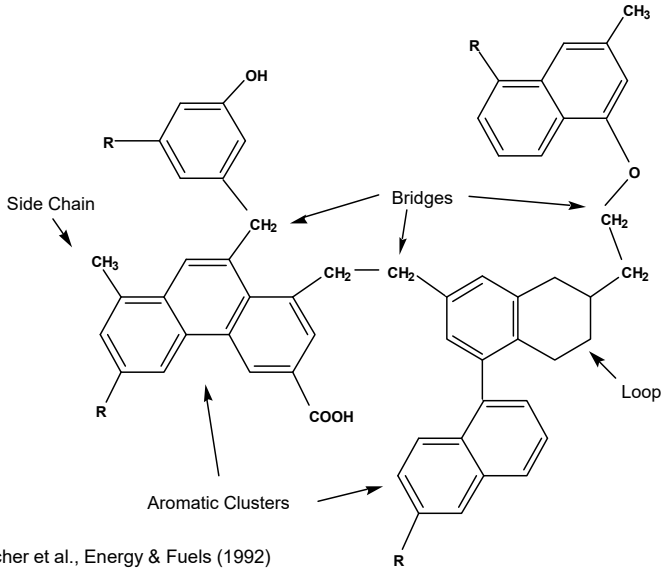
Representative chemical structures identified in ^{13}C NMR analyses of coals



from Fletcher et al., Energy & Fuels (1992)

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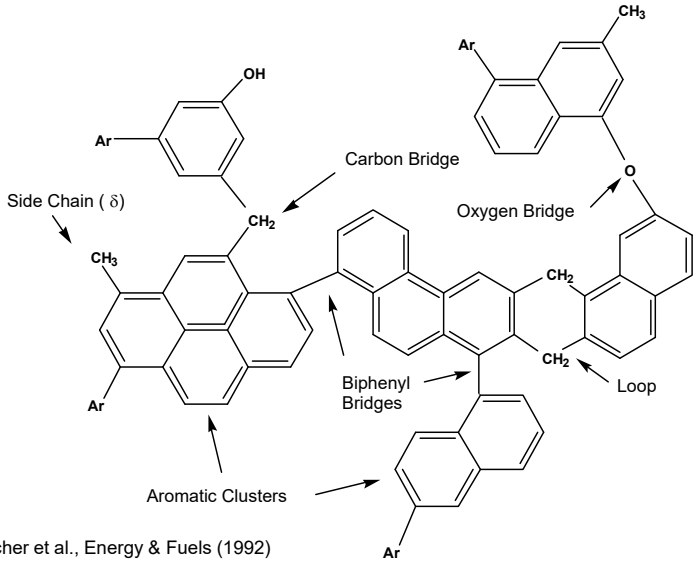
Representative chemical structures identified in ^{13}C NMR analyses of coal chars



from Fletcher et al., Energy & Fuels (1992)

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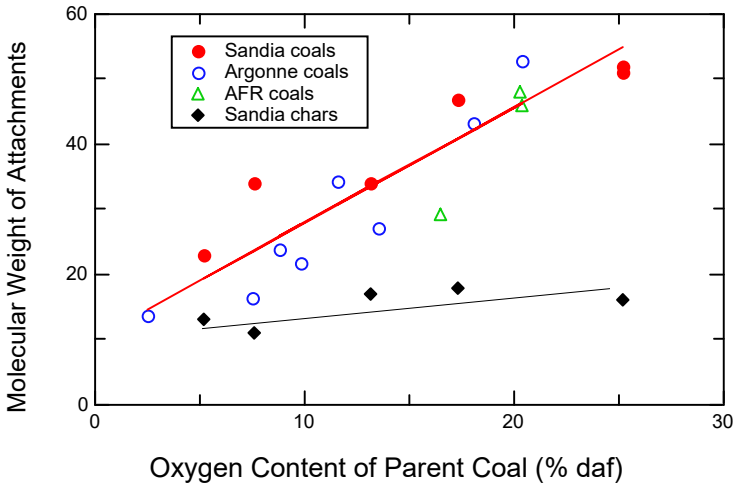
MW of Attachments vs. Rank



from Fletcher et al., Energy & Fuels (1992)

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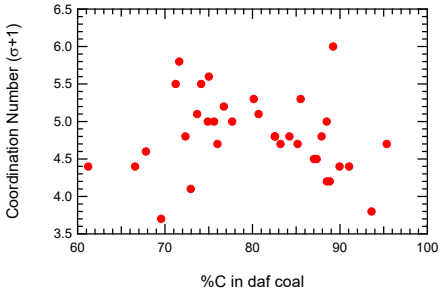
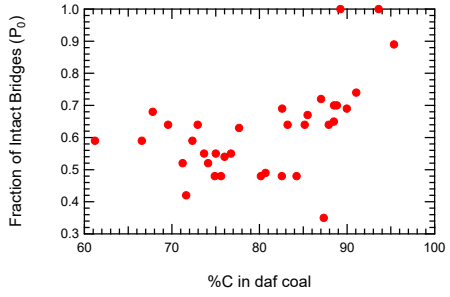
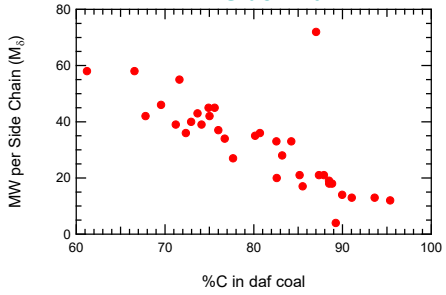
Attachments / Cluster



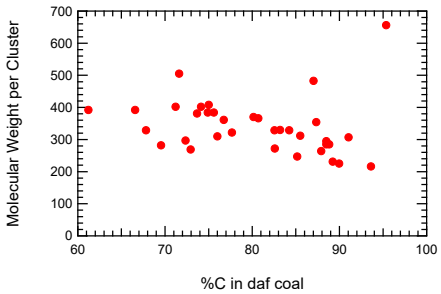
Fraction of Attachments that are Bridges (p_0)



MW / Side Chain



MW / Cluster



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FTIR

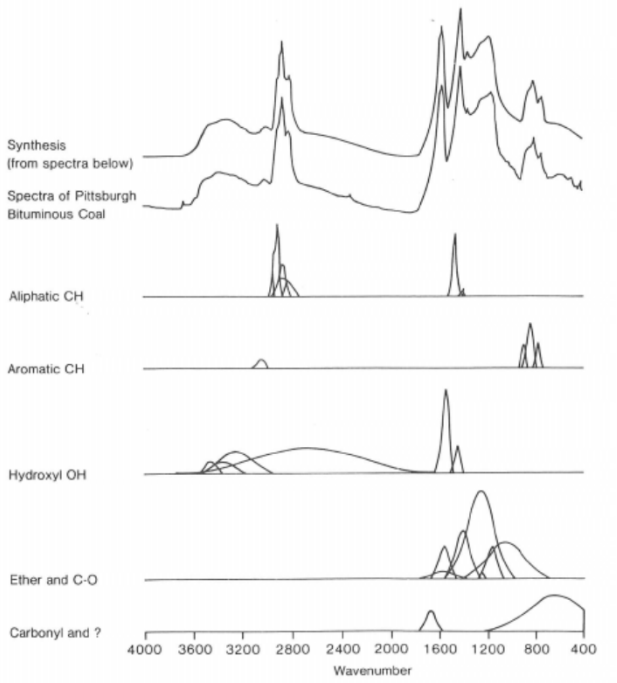

Figure 2.5. Synthesis of infrared spectrum. (Figure used with permission from Solomon, 1980.)

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FTIR Data

TABLE 40. FTIR Functional Group Analysis on the Argonne Premium Coals (wt. % dmmf)[a]

Coals	Hydrogen[b]					Aromatic hydrogen[c]			Carbon	Carbonyl[d]	Oxygen	
	H_{al}	H_{OH}	H_{ar}	H_{total}	H_{ar}/H_{total}	1 Adj	2 Adj	3 or more	C_{al}	Units (Abs. × cm^{-1})	O_{OH}	O_{ether}
1. Upper Freeport (mvb)	3.43	0.11	2.08	5.62	0.37	0.66	0.71	0.71	22.87	0.63	1.75	0.75
2. Wyodak (subC)	3.03	0.33	1.73	5.09	0.34	0.52	0.78	0.43	20.20	23.86	5.25	5.0
3. Illinois #6 (hvCb)	3.41	0.23	2.07	5.71	0.36	0.69	0.78	0.60	22.73	4.48	3.75	2.25
4. Pittsburgh (hvAb)	3.60	0.16	2.07	5.83	0.36	0.67	0.80	0.60	24.00	0.86	2.5	1.88
5. Pocahontas #3 (lvb)	1.97	0.06	2.19	4.22	0.52	0.60	0.73	0.86	13.93	1.92	1.0	1.25
6. Blind Canyon (hvBb)	4.79	0.16	1.90	6.85	0.28	0.51	0.80	0.58	31.93	8.70	2.5	4.0
7. Lewiston–Stockton (mvb)	3.48	0.23	2.12	5.83	0.36	0.67	0.67	0.79	23.20	3.59	3.75	1.75
8. Beulah–Zap (ligA)	2.02	0.34	1.58	3.94	0.40	0.46	0.74	0.37	13.47	24.67	5.5	5.0

[a] Except carbonyl: relative peak area.
[b] H_{al} = wt. % hydrogen as aliphatic hydrogen, H_{OH} = wt. % hydrogen as hydroxyl hydrogen, H_{ar} = wt. % hydrogen attached to aromatic groups, C_{al} = wt. % carbon in aliphatic groups, O_{OH} = wt. % oxygen in hydroxyl groups, and O_{ether} = wt. % oxygen in ether groups.
[c] 1 Adj = one adjacent hydrogen which is attached to an aromatic carbon; 2 Adj = two adjacent hydrogens attached to an aromatic carbon.
[d] Peak height at 1700 cm^{-1} (arbitrary units).
Source: Solomon *et al.* (1987b, 1990c).

26

FTIR Data on Argonne Premium Coals

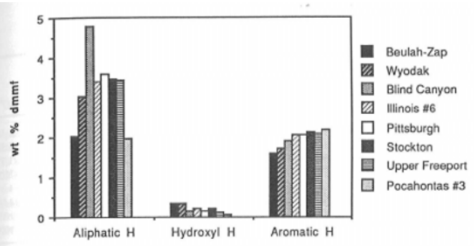

Figure 48. Distribution of hydrogen functional group structures of FTIR.

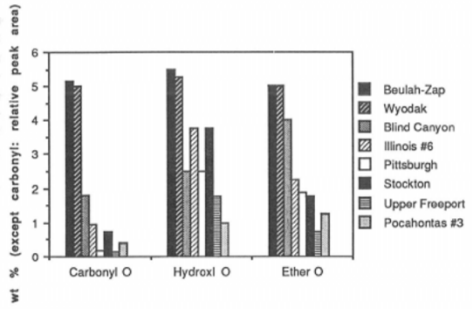

Figure 49. Distribution of oxygen functional group structures by FTIR.

27

Baxter, Fletcher, Ottesen

Energy & Fuels 1988, 2, 423–430

Spectral Emittance Measurements of Coal Particles[†,‡]

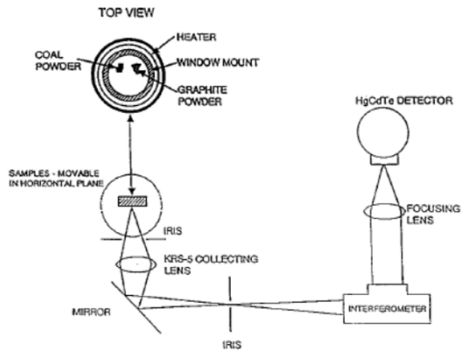

Figure 1. Schematic diagram of experimental apparatus used to determine spectral emittance of particles.

28

Typical Coal Spectra

Energy & Fuels 1988, 2, 423–430

Spectral Emittance Measurements of Coal Particles[†,‡]

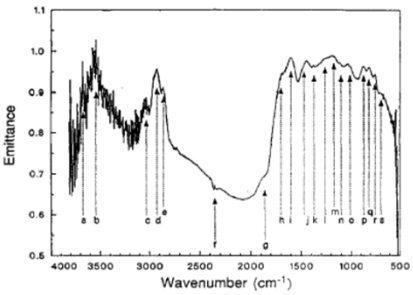

Figure 2. Spectral emittance of a 40-μm hvA bituminous coal (PSOC 1451) at 171 °C. Chemical functional groups responsible for the emission peaks are labeled. See Table I.

Table I. Identification of Chemical Functional Groups Responsible for Spectral Peaks Found in Coal Samples[a]

wavenumber, cm^{-1}	alphabetic code(s)	chemical functional groups
3700–3300	a, b	–OH and –NH stretching
3030	c	aromatic C–H stretching
2940	d	aliphatic C–H stretching
2925–2860	e	aliphatic $C–H_i$ stretching
2370	f	atmospheric CO_2 interference
1865	g	unknown
1700	h	C=O stretching
1600	i	"coal" peak (probable aromatic ring structures)
1500–1400	j	aromatic C=C stretching aliphatic $–CH_3$ asymmetric deformation aliphatic $–CH_2$ scissor deformation
1370	k	$–CH_3$ symmetric deformation, cyclic $–CH_2$
1250–1020	l–o	phenolic and alcoholic C–O stretching aromatic and aliphatic C–O–C stretching Si–O
850–750	p–r	polycyclic aromatic skeleton
700	s	aromatic $–CH_3$

[a] Compare with Figure 2. Most assignments were adopted from Berkowitz[10] or van Krevelen.[11]

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Bituminous Coal vs Char Spectra (Pitt 8)

Energy & Fuels 1988, 2, 423–430

Spectral Emittance Measurements of Coal Particles[†,‡]

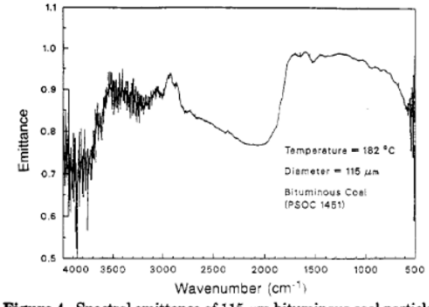

Figure 4. Spectral emittance of 115-μm bituminous coal particles (PSOC 1451) at 182 °C. Compare with Figure 2.

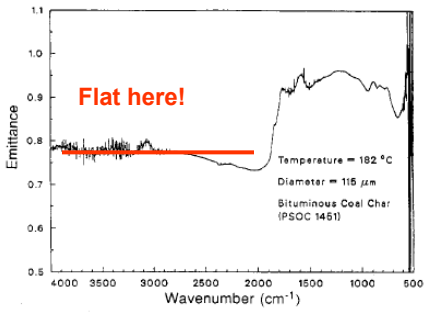

Figure 7. Emittance spectra of originally 115-μm bituminous coal particles (PSOC 1451) after 50% mass loss by devolatilization. The particle temperature during the emittance measurement was 182 °C.

Message:
Chars have lost functional groups, emissivity becomes more gray.

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FTIR Data

TABLE 40. FTIR Functional Group Analysis on the Argonne Premium Coals (wt. % dmmf)[a]

Coals	Hydrogen[b] H_{al}	H_{OH}	H_{ar}	H_{total}	H_{ar}/H_{total}	Aromatic hydrogen[c] 1 Adj	2 Adj	3 or more	Carbon C_{al}		Carbonyl[d] Units (Abs. × cm^{-1})		Oxygen O_{OH}	O_{ether}
1. Upper Freeport (mvb)	3.43	0.11	2.08	5.62	0.37	0.66	0.71	0.71	22.8	19	0.63	0	1.75	0.75
2. Wyodak (subC)	3.03	0.33	1.73	5.09	0.34	0.52	0.78	0.43	20.2	45	23.86	8	5.25	5.0
3. Illinois #6 (hvCb)	3.41	0.23	2.07	5.71	0.36	0.69	0.78	0.60	22.7	18	4.48	0	3.75	2.25
4. Pittsburgh (hvAb)	3.60	0.16	2.07	5.83	0.36	0.67	0.80	0.60	24.0	30	0.86	1	2.5	1.88
5. Pocahontas #3 (lvb)	1.97	0.06	2.19	4.22	0.52	0.60	0.73	0.86	13.9	14	1.92	0	1.0	1.25
6. Blind Canyon (hvBb)	4.79	0.16	1.90	6.85	0.28	0.51	0.80	0.58	31.9	39	8.70	2	2.5	4.0
7. Lewiston–Stockton (mvb)	3.48	0.23	2.12	5.83	0.36	0.67	0.67	0.79	23.2	25	3.59	0	3.75	1.75
8. Beulah–Zap (ligA)	2.02	0.34	1.58	3.94	0.40	0.46	0.74	0.37	13.4	45	24.67	10	5.5	5.0

[a] Except carbonyl: relative peak area.
[b] H_{al} = wt. % hydrogen as aliphatic hydrogen, H_{OH} = wt. % hydrogen as hydroxyl hydrogen, H_{ar} = wt. % hydrogen attached to aromatic groups, C_{al} = wt. % carbon in aliphatic groups, O_{OH} = wt. % oxygen in hydroxyl groups, and O_{ether} = wt. % oxygen in ether groups.
[c] 1 Adj = one adjacent hydrogen which is attached to an aromatic carbon; 2 Adj = two adjacent hydrogens attached to an aromatic carbon.
[d] Peak height at 1700 cm^{-1} (arbitrary units).
Source: Solomon *et al.* (1987b, 1990e).

NMR Data

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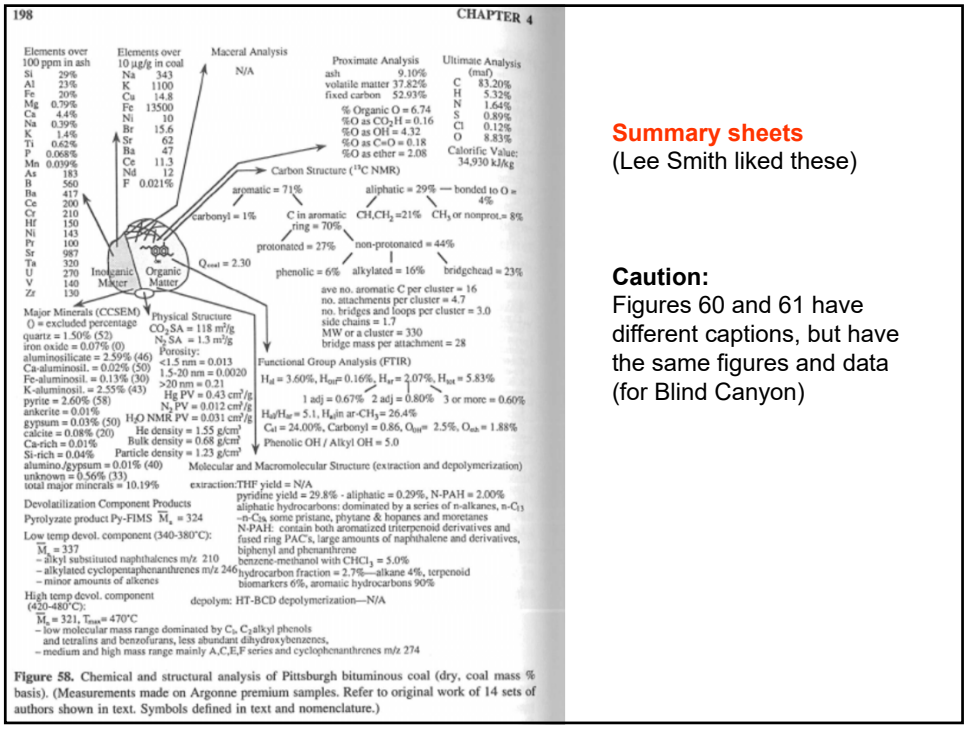

Figure 58. Chemical and structural analysis of Pittsburgh bituminous coal (dry, coal mass % basis). (Measurements made on Argonne premium samples. Refer to original work of 14 sets of authors shown in text. Symbols defined in text and nomenclature.)

Summary sheets
(Lee Smith liked these)

Caution:
Figures 60 and 61 have different captions, but have the same figures and data (for Blind Canyon)

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Summary

Analytical Instruments

- NMR
- FTIR
- XPS
- MS
- GC
- HPLC

Destructive Methods

- Extraction
  - Solvents
  - HT-BCD
- Pyrolysis
- Mild oxidation (RuO)

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Concluding Remarks

- Why did we focus so much in the class on coal chemical structure, when this is a coal *combustion* class?

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