Carbon Materials - Fuels

Kaustobiolites

Natural substances

Organic

Kaustobiolites (greek: *kaustum* – fire, furnace, *bios* – life)

rocks with organic origin containing in its structure C,H,N,O:

e.g. peat, lignites, hard coals, anthracite

Nonorganic

Akustobiolites

Kaustobiolites

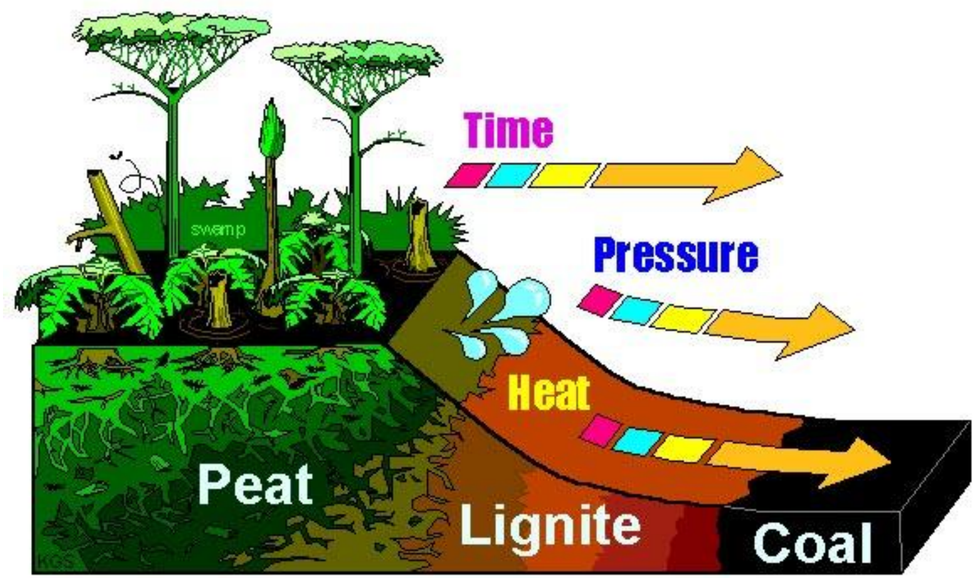
Fossils in order of metamorphism:

- peat
- gytta (muds)
- brown coal (lignite)
- hard coal
    - sub-bituminous
    - bitumonous
- anthracite
- graphit (natural)

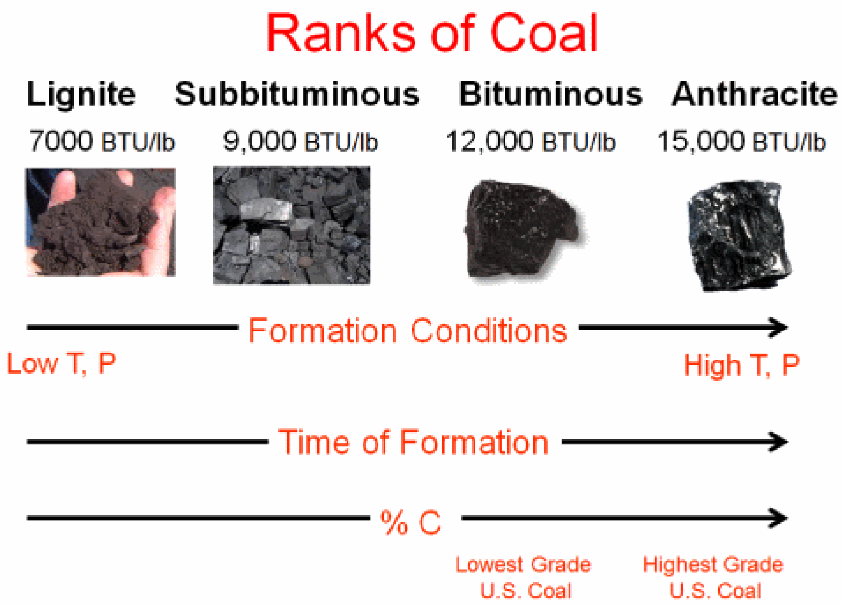
Originated from parts of the plants

- humous – moldered from land plants
- sapropelic – roted from water plants
- liptobiolites – from resins and waxes, hard to deterioration

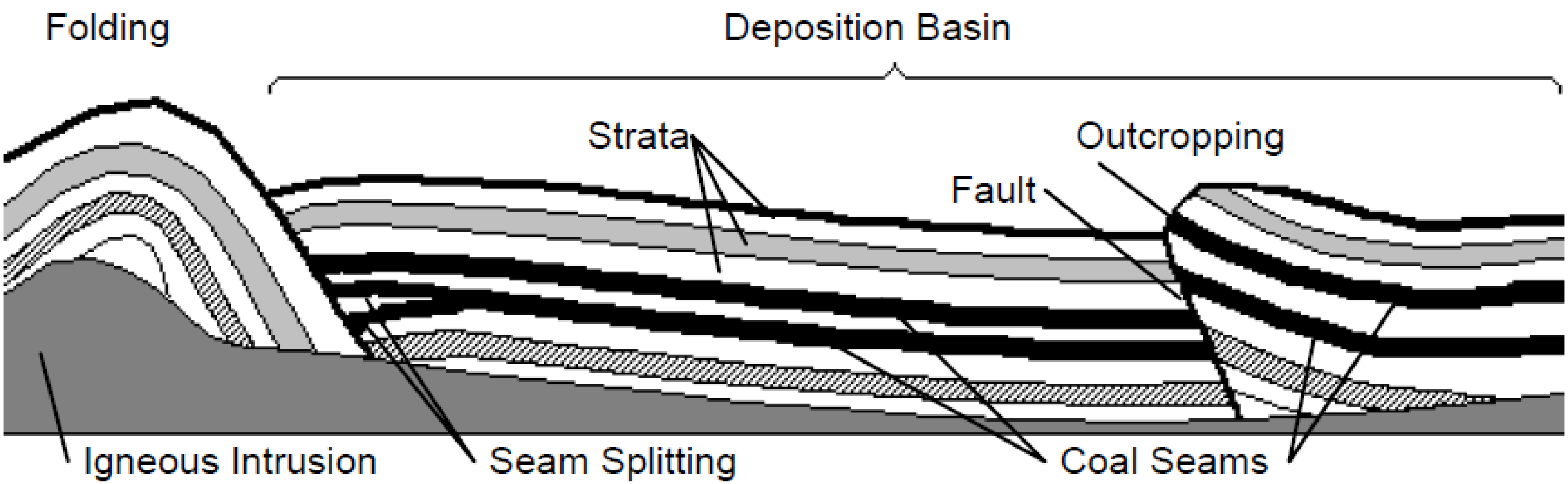
Methamorphism



Source: Modified from Kentucky Geological Survey, University of Kentucky, http://uky.edu/KGS/coal/



Methamorphism



Periods in coal origination

Period one: Carboniferous and Permian

- earliest period of coal formation
- tropical to sub-tropical climate with mild temperature, high humidity and heavy rainfall
    - Coal swamps in the low latitude areas in early Carboniferous period
    - Late Carboniferous, belt of coal swamps formed and extended from the mid-western US through Europe and Africa

Period two: Upper Cretaceous to Miocene

- Cretaceous and Tertiary formation in the western North America, northeastern Russia and Siberia.
- Cretaceous coals were formed in areas where annual rainfall exceeded evaporation

Period three: Quaternary Period

- peat deposits around the world!
- coal bearing formations consist of sedimentary strata

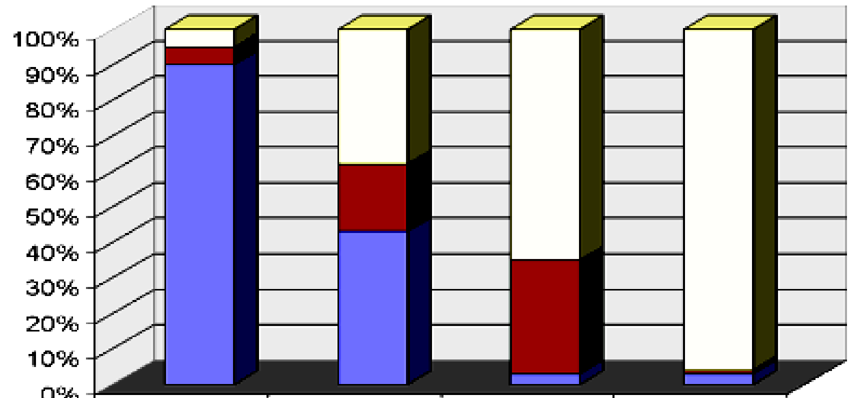
Coal formation

Coal is formed by the physical and chemical alteration of peat

- bacterial decay (biochemical period)
    - aerobic decay – first few inches of peat aerobic bacteria reduce volume by 50%
    - anaerobic decay – anaerobic bacteria still reduce volume of material
- compaction – under pressure of overburden
- heat, pressure and time (geochemical period)

Factors affecting coal formation:

- Transformation of plant debris to peat
- Nature and chemical composition of source plants
- Climate
- Paleogeography
- Depositional environment
- Tectonics
- Time



	peat	lignite	bituminous	anthracite
carbon	5%	38%	65%	96%
volatiles	5%	19%	32%	1%
water	90%	43%	3%	3%

Lithotypes

macroscopically distinguishable component:

- **clarain** - characterized by alternating bright and dull black laminae. The brightest layers are composed chiefly of the maceral vitrinite and the duller layers of the other maceral groups exinite and inertinite
- **durain** - characterized by a hard, granular texture and composed of the maceral groups exinite and inertinite as well as relatively large amounts of inorganic minerals
- **fusain** - commonly found in silvery-black layers only a few millimetres thick and occasionally in thicker lenses. It is extremely soft and crumbles readily into a fine, sootlike powder. Fusain is composed mainly of fusinite (carbonized woody plant tissue) and semifusinite from the maceral inertinite (high carbon, highly reflective) group
- **vitrain** - characterized by a brilliant black, glossy lustre and composed primarily of the maceral group vitrinite, derived from the bark tissue of large plants. Vitrain was probably formed under drier surface conditions than the lithotypes clarain and durain.

Macerals

- In the petrographic approach coal is a composition of macerals with distingtive set of chemical and physical properties
- First time the name of „macerals” was used by Marie Stopes
- Macerals are defined by both their color/reflectance and morphology
- Macerals cannot really be separated
- Macerals are assembled in to the groups

„Macerals are phytogenetic organic substances or optically homogeneous aggregates of phytogenetic substances possessing distinctive chemical and physical properties." William Spackman*

* http://www.cartage.org.lb/en/themes/Sciences/Earthscience/Geology/Coal/MoreaboutCoal/CoalMacerals/CoalMaceral/CoalMaceral.htm

Macerals groups

- 3 major maceral groups:
  - **Liptinite**
  - **Vitrinite**
  - **Inertinite**
- Origine of organic matter:
  - tree tissue and cork - vitrinite, fusinite
  - plant matter different from tree tissue (resines or waxes) – resinite
  - non-identified plant tissues – micrinite
  - spores – sporinite
  - algae – alginite
  - lipids (waxes, oils etc.) – liptinite
  - leaf epithelium - cutinite

ICCP – International Committee for Coal and Organic Petrology: www.iccop.org

Macerals groups

maceral group	defined by level of reflectance
maceral subgroup	defined by degree of destruction
maceral	defined by morphology and/or degree of gelification

Vitrinite group

Lignites

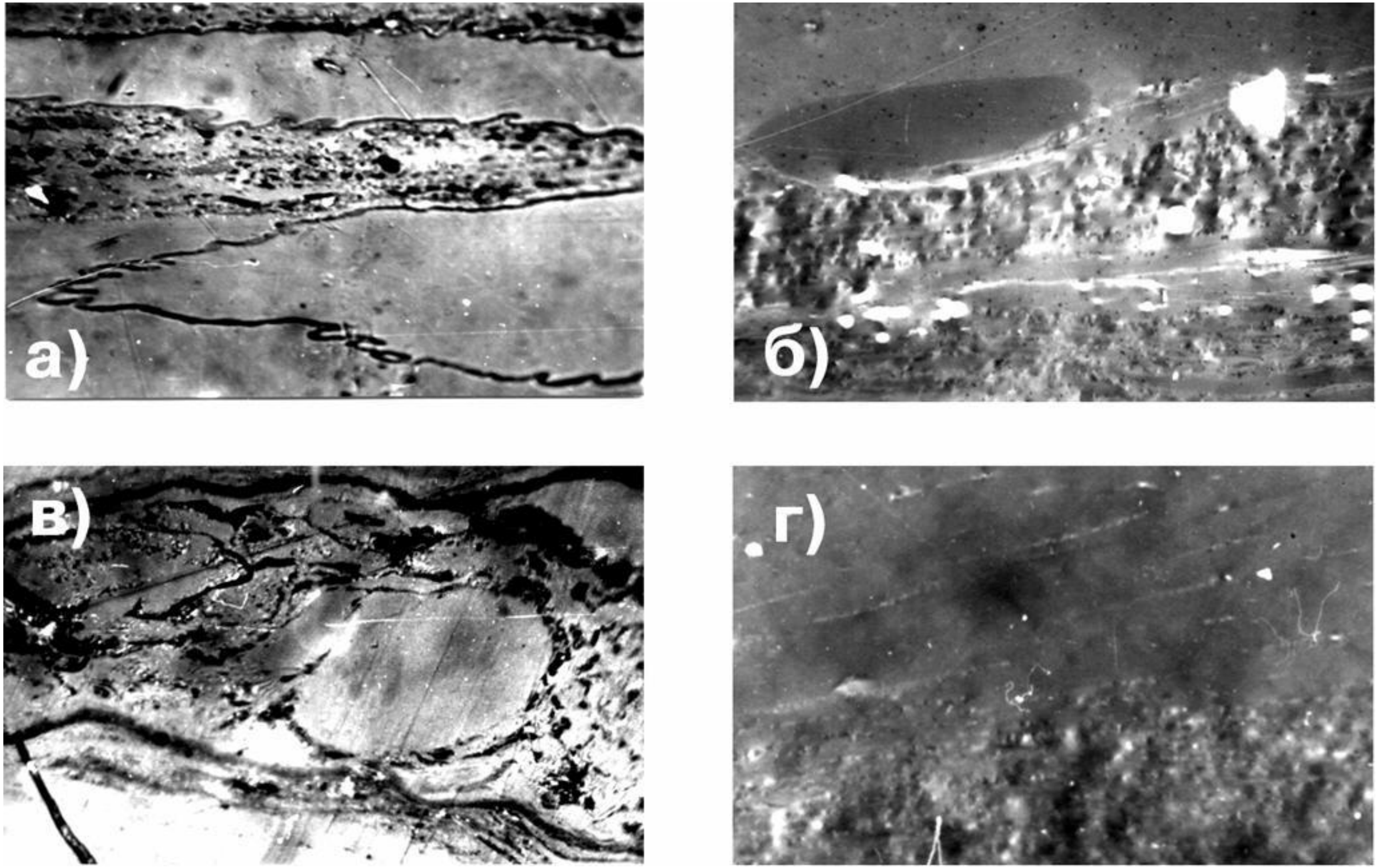
HUMINITE	**Telohuminite** (botanical structure are visible)	**Textinite** (ungelified cell walls)
		Ulminite (cell walls of gelified tissues)
	Detrohuminite (fine humic fragments <10 μm)	**Attrinite** (fine huminitic particles, spongy ungelified amorphous huminitric substances)
		Densinite (fine huminitic particles cemented by dense huminitric substances)
	Gelohuminite (comes from amorphous humic matter)	**Corpohuminite** (cell fillings)
		Gelinite (huminitic structureless or porous substance)

Bituminous and Anthracites

VITRINITE	**Telovitrinite** (botanical structure poor visible)	**Telinite** (clearly recognizable cell walls)
		Collotelinite (homogenized vitrinite layers)
	Detrovitrinite (finely fragmented plant remains)	**Vitrodetrinite** (discrete small vitrinic fragments)
		Collodetrinite (mottled vitrinic ground mass)
	Gelovitrinite (colloidal fillings in former voids)	**Corpogelinite** (homogenous, discrete bodies of cell infillings
		Gelinite (homogenous, structureless infillings of cracks and voids)

Indiana Geological Survey: http://igs.indiana.edu/Coal/Macerals.cfm

Vitrinite group



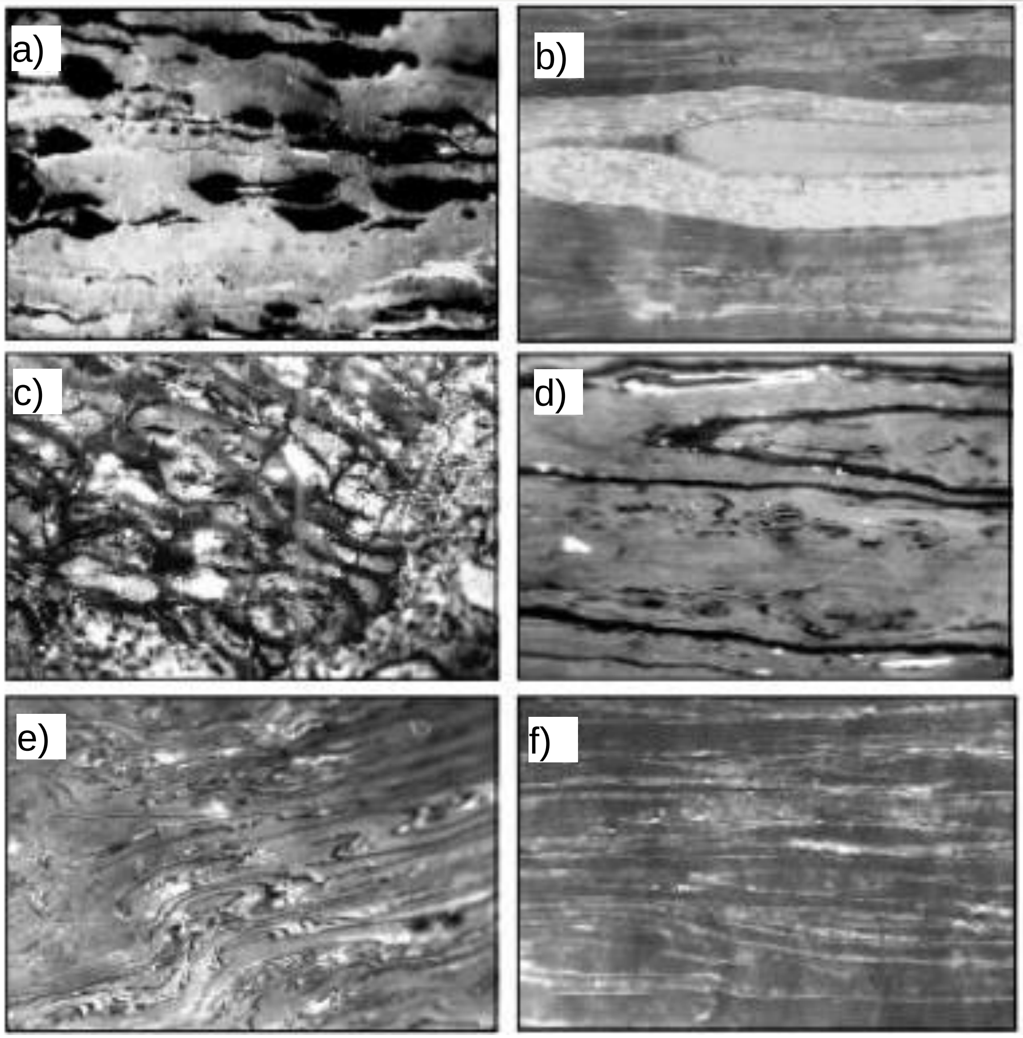
Мала гірнича енциклопедія: В 3-х т. / За ред. В. С. Білецького. — Донецьк: Донбас, 2004. ISBN 966-7804-14-3

Liptinite (Exinite) group

- **Sporinite** – waxy coatings of fossil spores
- **Cutinite** – waxy outer coating of leaves, roots and stems
- **Resinite** – plant resins
- **Alginite** – algae
- **Liptodetrinite** – discreet small liptinite fragments
- **Suberinite** – cork cell walls
- **Chlorophyllinite** – chlorophyl-derived material (not present in above subbituminous coals)
- **Exsudatinite** – secondary maceral filling cracks after oil generation
- **Fluorinite** – semiglobular fluorescing droplets (oil precursors)

Indiana Geological Survey: http://igs.indiana.edu/Coal/Macerals.cfm

Liptinite group



a) Sporinite
b) Liptodentrinite
c) Suberinite
d) Cutinite
e) Suberinite
f) Cutinite

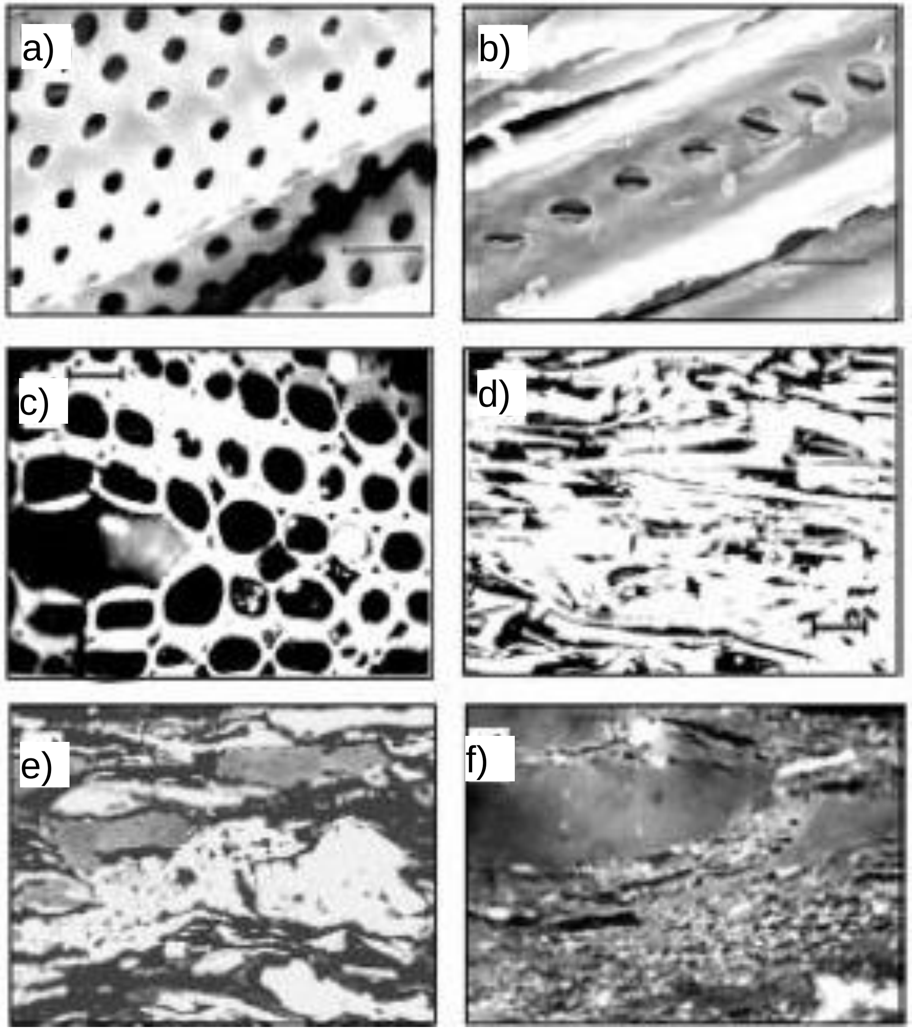
Мала гірнича енциклопедія: В 3-х т. / За ред. В. С. Білецького. — Донецьк: Донбас, 2004. ISBN 966-7804-14-3

Inertinite group

- **Micrinite** – very small rounded grains of high reflectance, orginate from liptinites after coalification
- **Macrinite** – amorphous matrix or discrete, structureless bodies from flocculated humic matrix
- **Fusinite** – highly reflecting, cellular structure from ligno-cellulosic cell walls
- **Semifusinite** – intermediate reflectance, partialy visible cellular structure from stems or leaves (cellulose and lignin)
- **Secretinite** – bodies without plant structure, oxidation product of resins or humic gels
- **Fuginite** – high reflecting fungal spores etc., fungal remains
- **Inertodetrinite** – disrete small inertinite fragments varying in shape

Indiana Geological Survey: http://igs.indiana.edu/Coal/Macerals.cfm

Inertinite group



a) Fusinite
b) Fusinite
c) Fusinite
d) Fusinite (highly gelified)
e) Inertodetrinite
f) Micrinite

Мала гірнича енциклопедія: В 3-х т. / За ред. В. С. Білецького. — Донецьк: Донбас, 2004. ISBN 966-7804-14-3

Macerals in hard coals

Flame coal	Vitrinite, Exinite, Micrinite fraction, Fusinite
Gas-coking coal	Vitrinite, Exinite, Micrinite fraction, Fusinite
Coking coal	Vitrinite, Fusinite
Semi-coking coal	Vitrinite, Fusinite
Anthracite	Vitrinite, Fusinite

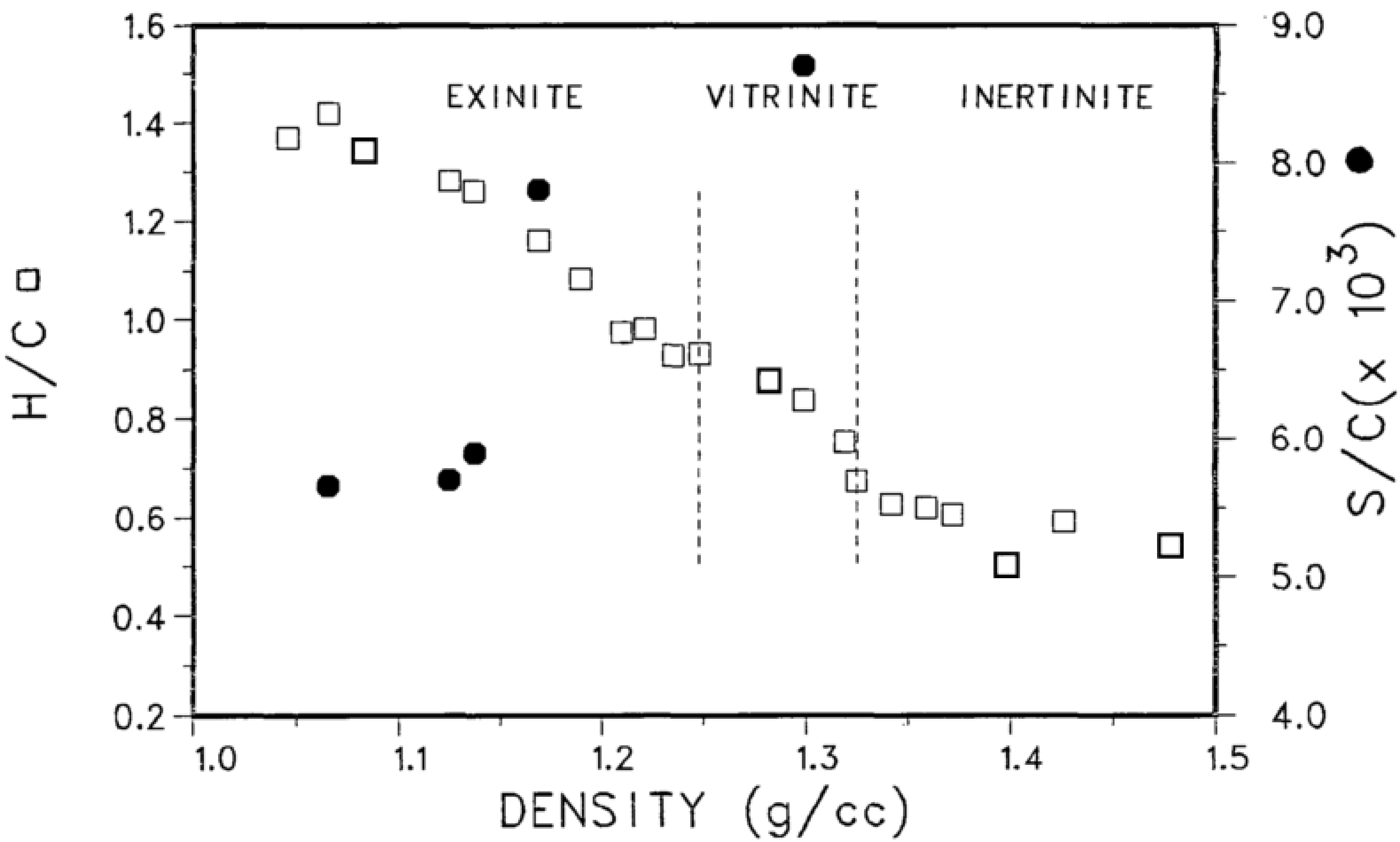
Macerals groups and coking

- Coke production:
  - Vitrinite (V^{daf}>18%) shows high coke-making properties because of plasticability and bulgingability
  - Exinite (V^{daf}>25%) gives the biggest value of liquid and gaseous products, it sinters, gives with vitrinite the biggest dilatation
  - Sporinite, Cutinite and Resinite makes Vitrinite more plastically. Resinite do not produce of coke it self
  - Inertinite group shows the lack of coke-production properties

Macerals - properties

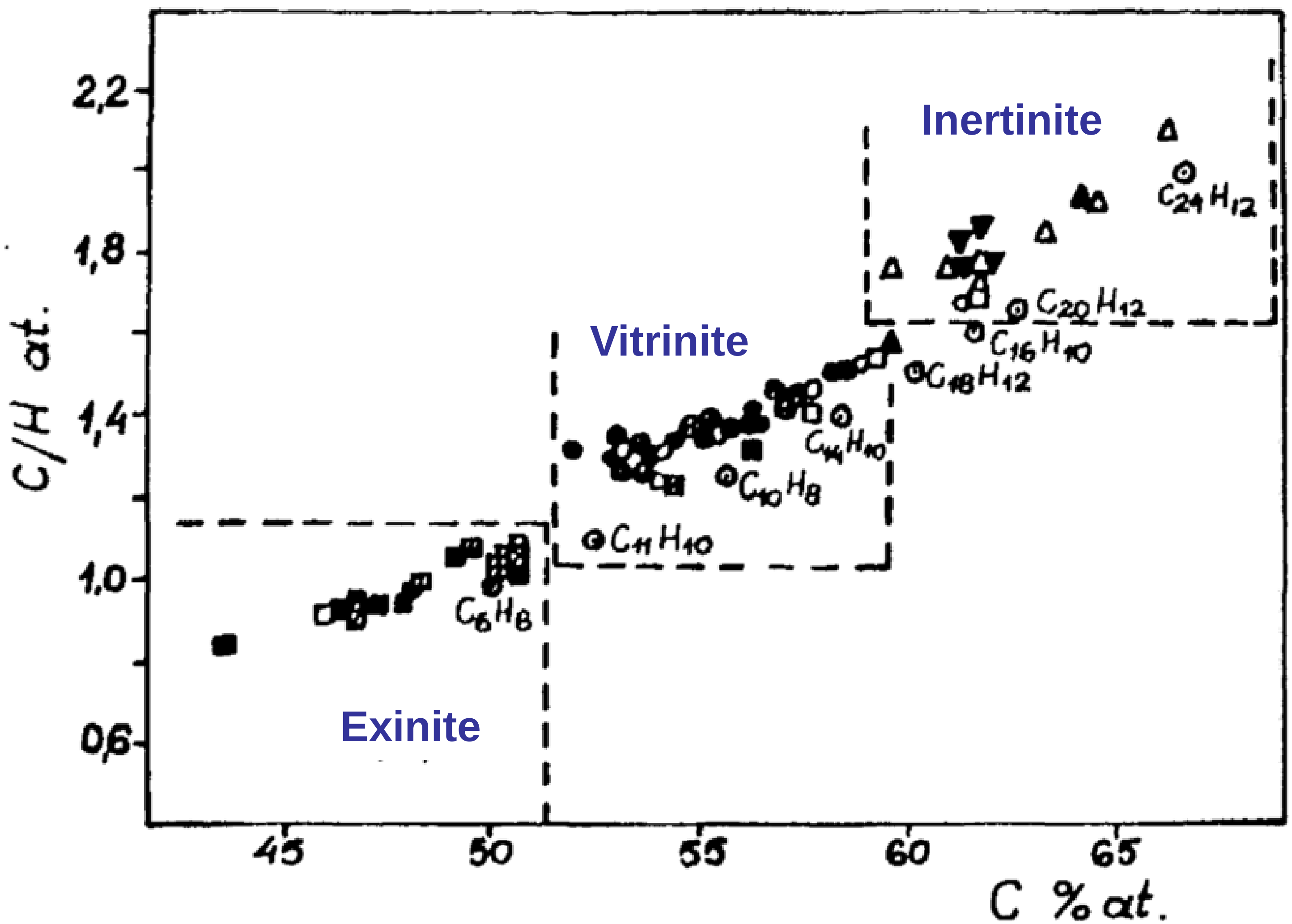
- Floatability of coals is better for gelified elements (Vitrain) than that ones of fibrous structure (Fusain)
- Hardness:
  - Fusinite is the most hard maceral
  - Exinite and Vitrinite hardness is comparable
  - Cleavage decrease the hardness of coal, cleavage is higher in lustrous than in mat coals
- Oxygen reactive groups decrease Vitrinite $\rightarrow$ micrinite $\rightarrow$ exinite $\rightarrow$ fusinite

Macerals - properties



„Separation of Coal Macerals” G.R.Dyrkacz, C.A.A.Bloomquist, L.H.Fuchs, E.P.Horwitz, Argonne National Laboratory„

Macerals - properties

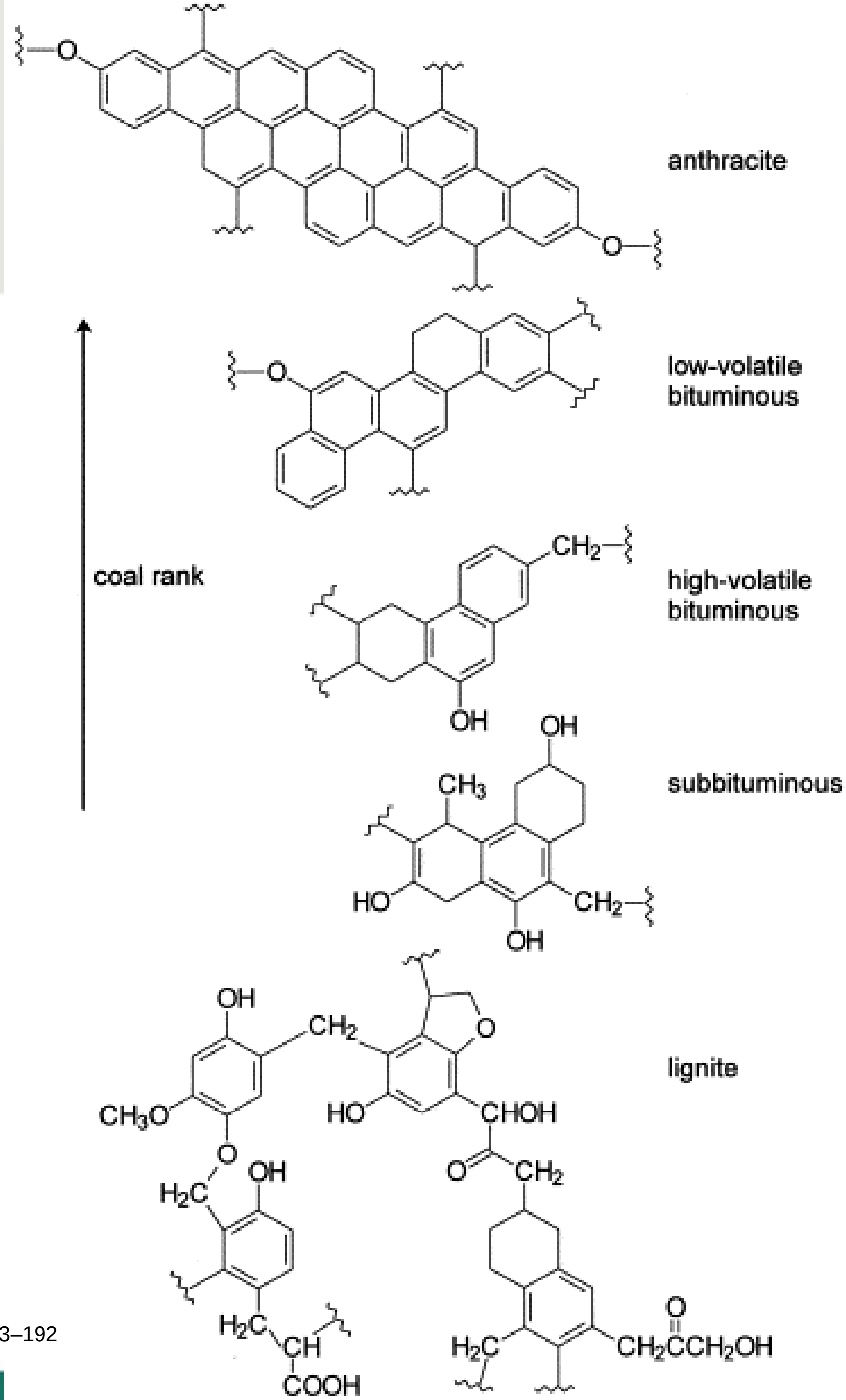


Models of coal structure

- Chemical – explaining chemical properties of coal matter
- Physical – explaining behavior of carbonaceous substance in different natural and technological

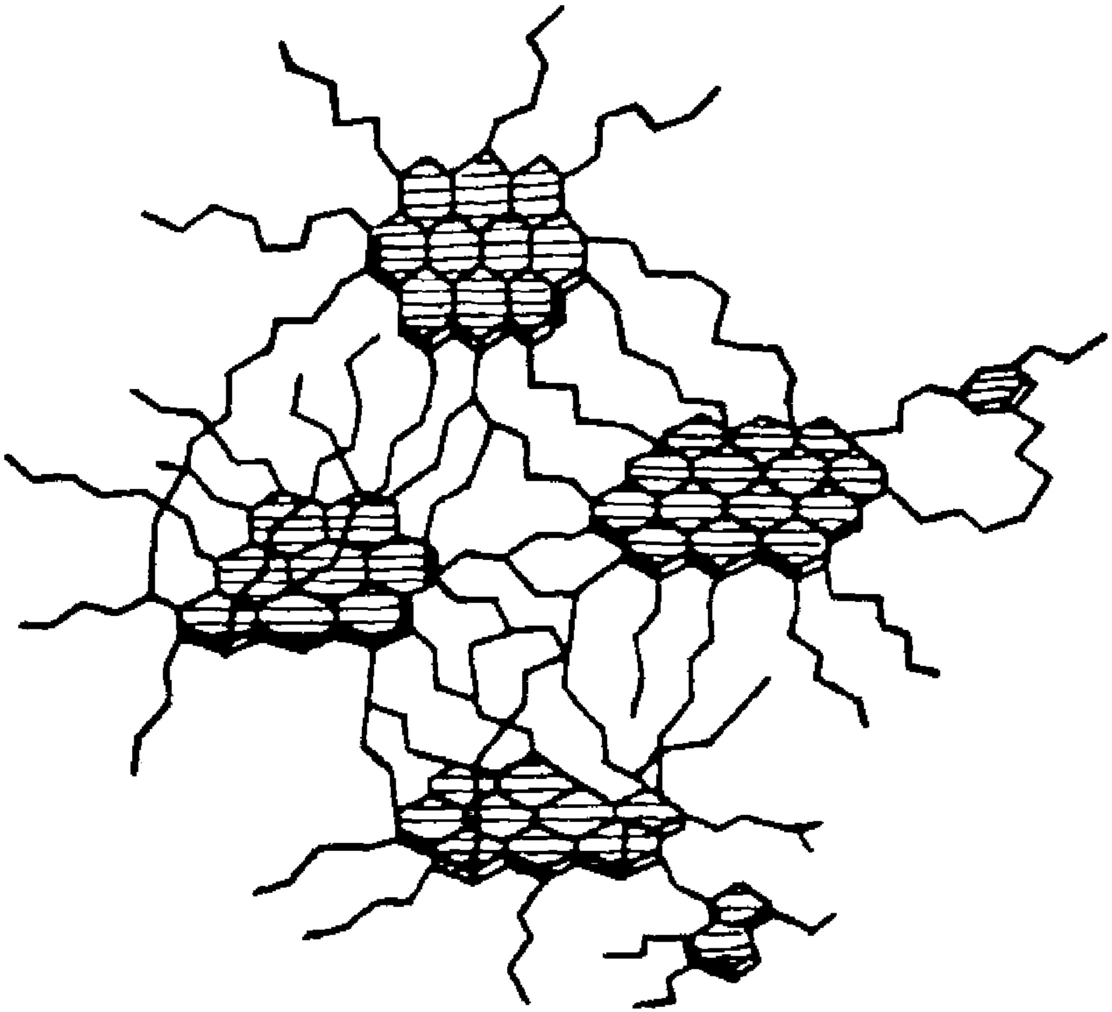
Coal base cell

It is indicated that base cell of call change with degree of coalification (metamorphism)



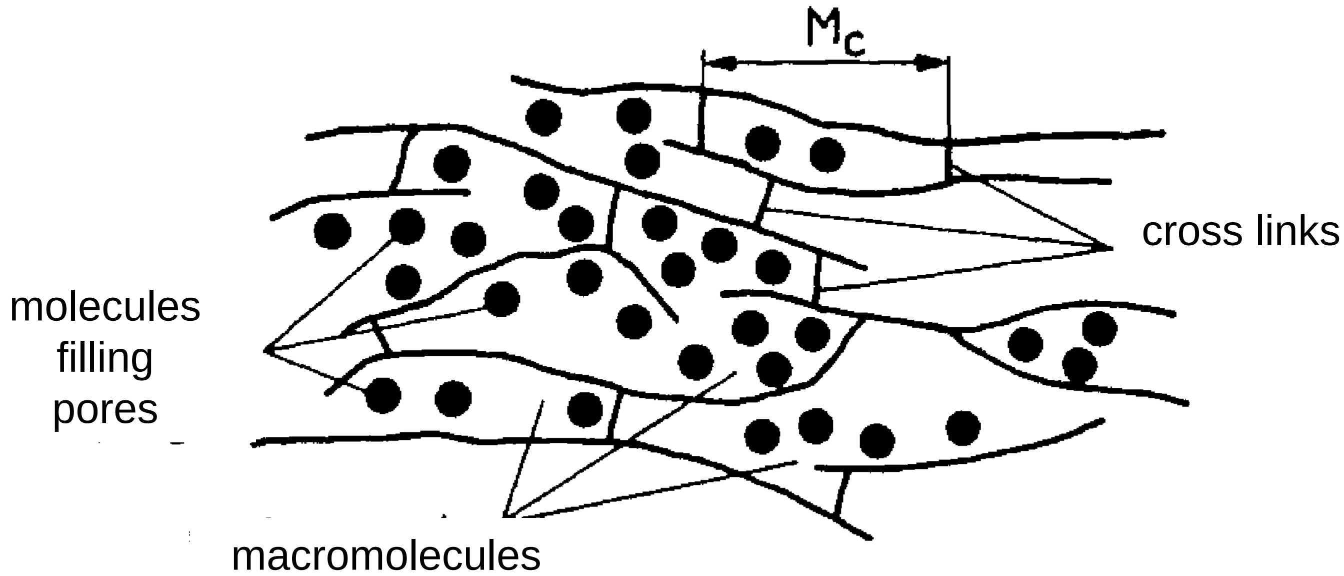
E.Dorrestijn et all., Journal of Analytical and Applied Pyrolysis, Vol. 54, Issues 1–2, March 2000, Pages 153–192

Polymeric model of coal structure



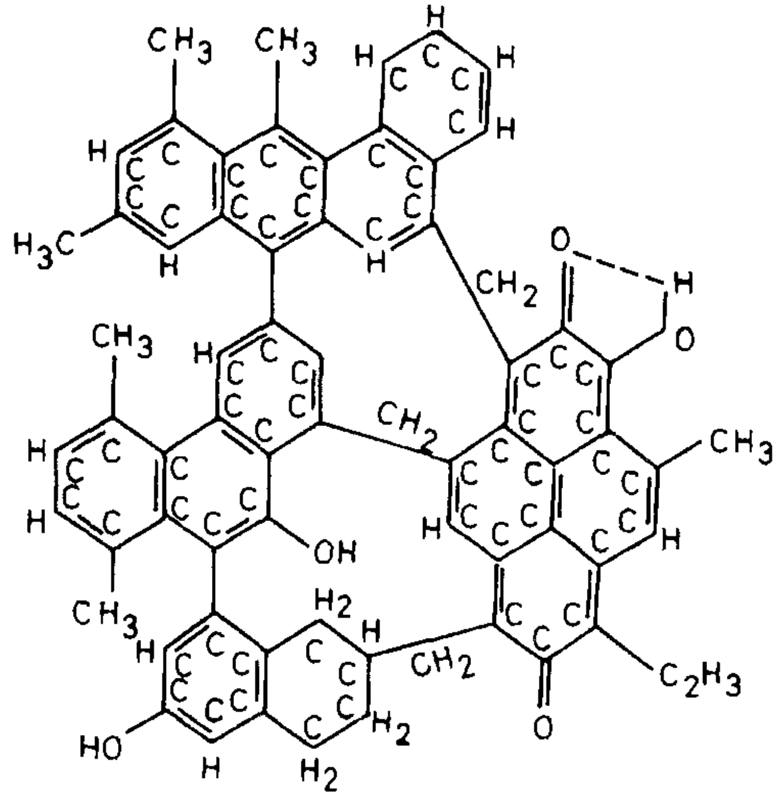
Kasatochkin

Polymeric model of coal structure



Larsen

Polymeric model of coal structure



Dryden

Polymeric model of coal structure

Graphic – statistic method

	$C_{ar/C}$	R_{ar}/R	H_{ar}/H
Fuchs	0.58	0.65	0.72
Gillet	0.76		
Storch	0.78		
Dryden	0.66	0.79	0.85
Huck and Karweil	0.54	0.645	0.76

Polymeric model of coal structure

Graphic – statistic method

- aromaticity:

$$f_{ar} = \frac{C_{ar}}{C}$$

- fraction of aromatic hydrogen:

$$h_{ar} = \frac{H_{ar}}{H}$$

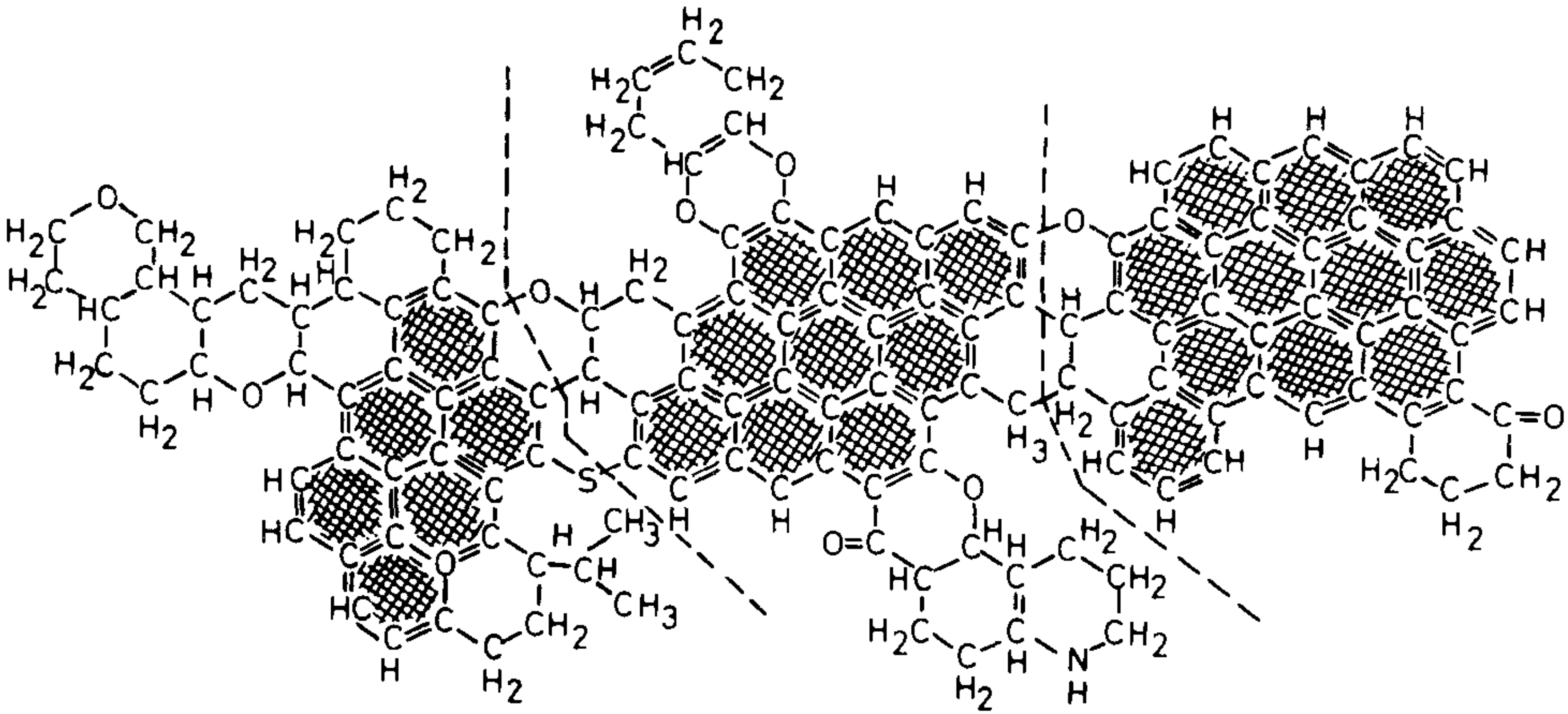
- coefficient of ring condensation:

$$2\frac{R-1}{C} = 2 - f_{ar} - \frac{H}{C}$$

- other factors: H/C, O/C, rings aromaticity R_{ar}/R

van Krevelen

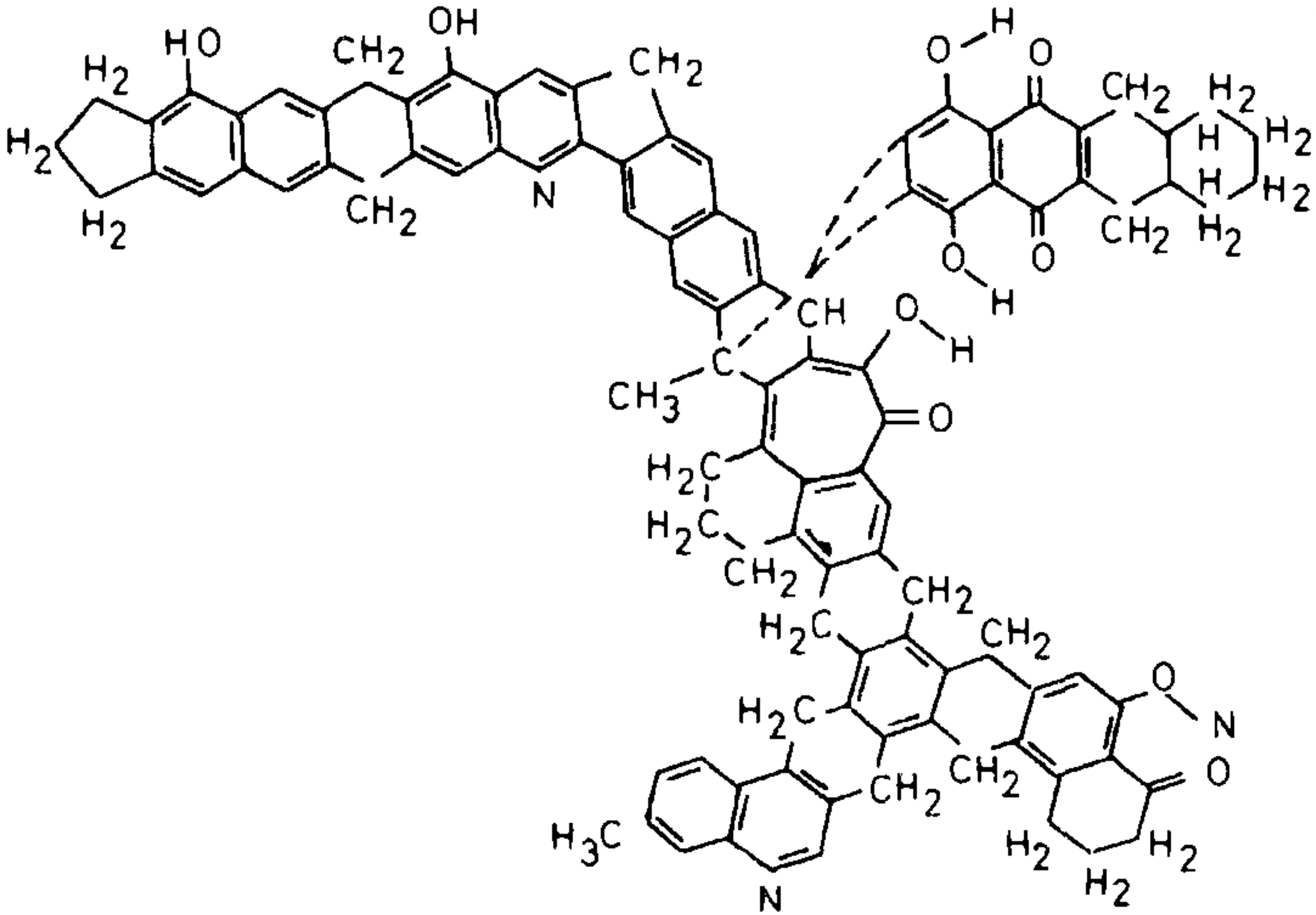
Polymeric model of coal structure



$C_{135} H_{96} O_9 N_9 \; H / C = 0.72$

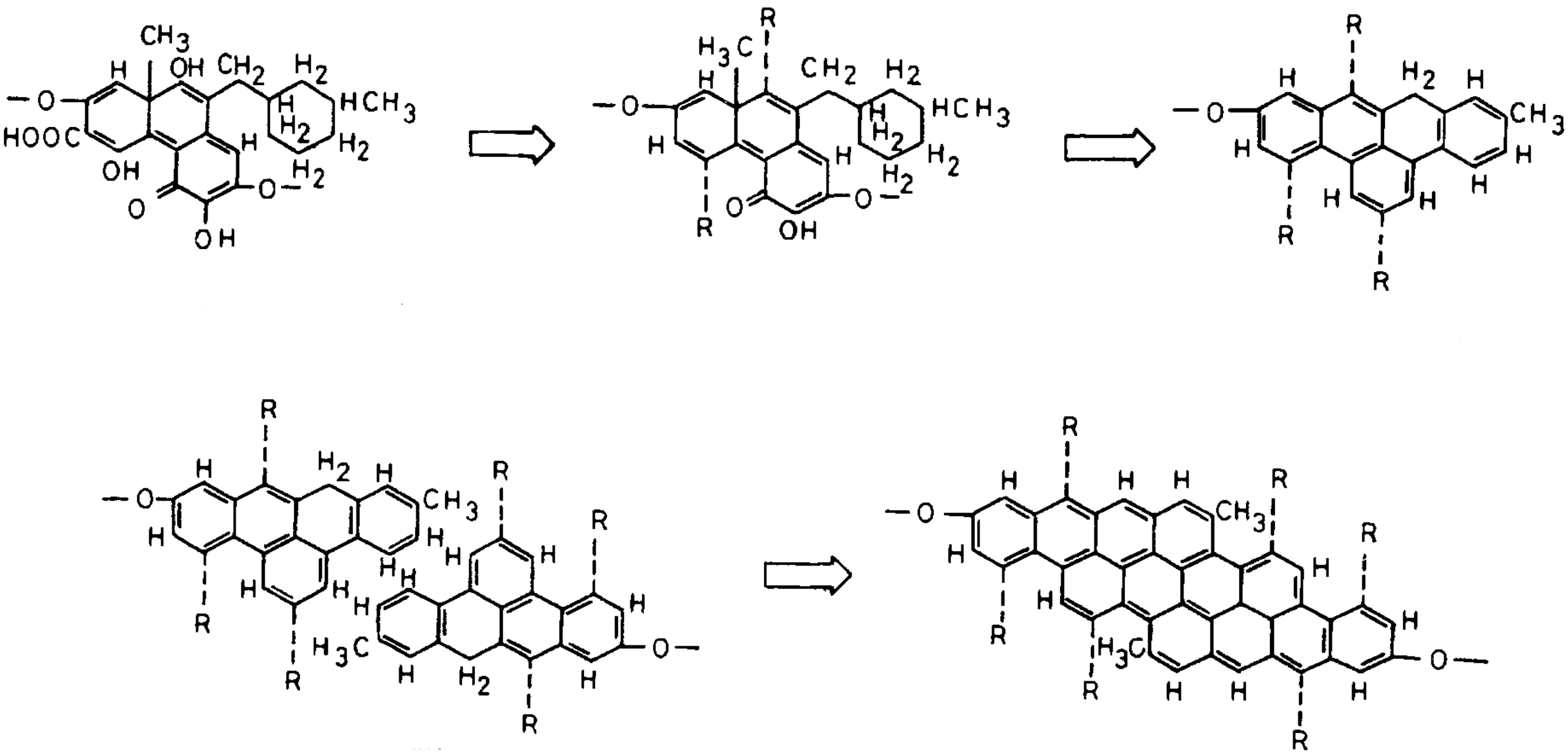
Fuchs, modified by van Krevelen et all.

Polymeric model of coal structure



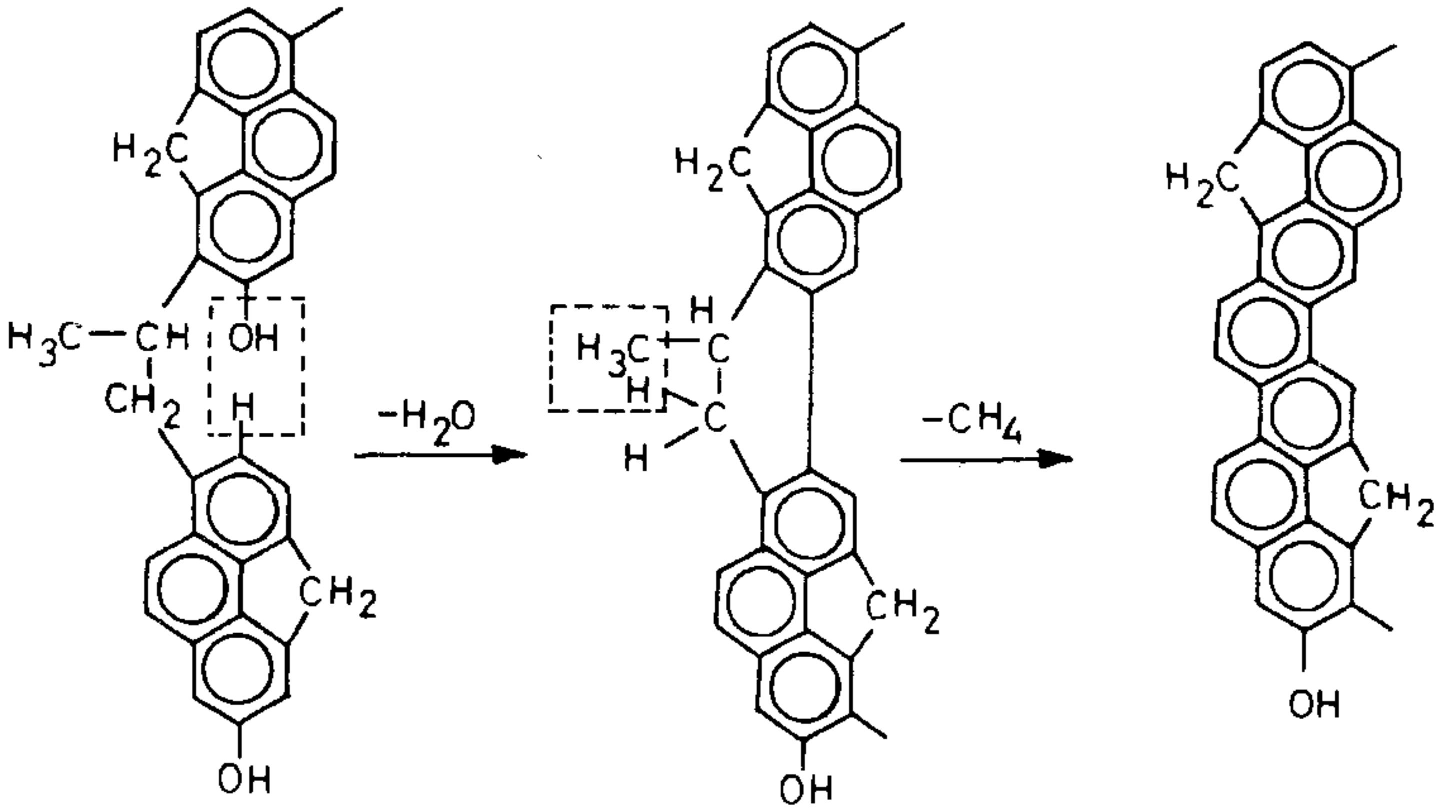
Given

Polymeric model of coal structure



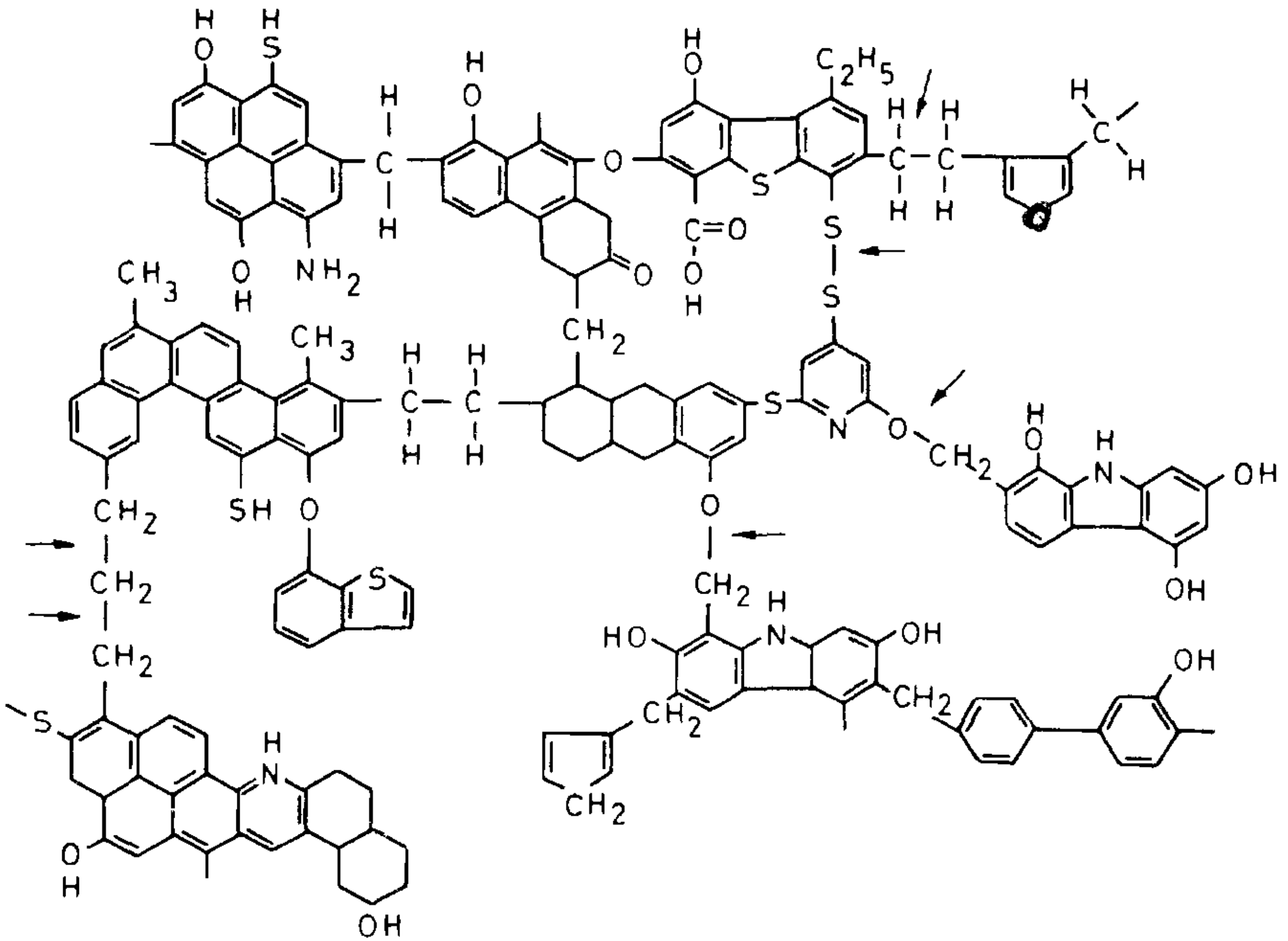
Mazumdar et all.

Polymeric model of coal structure



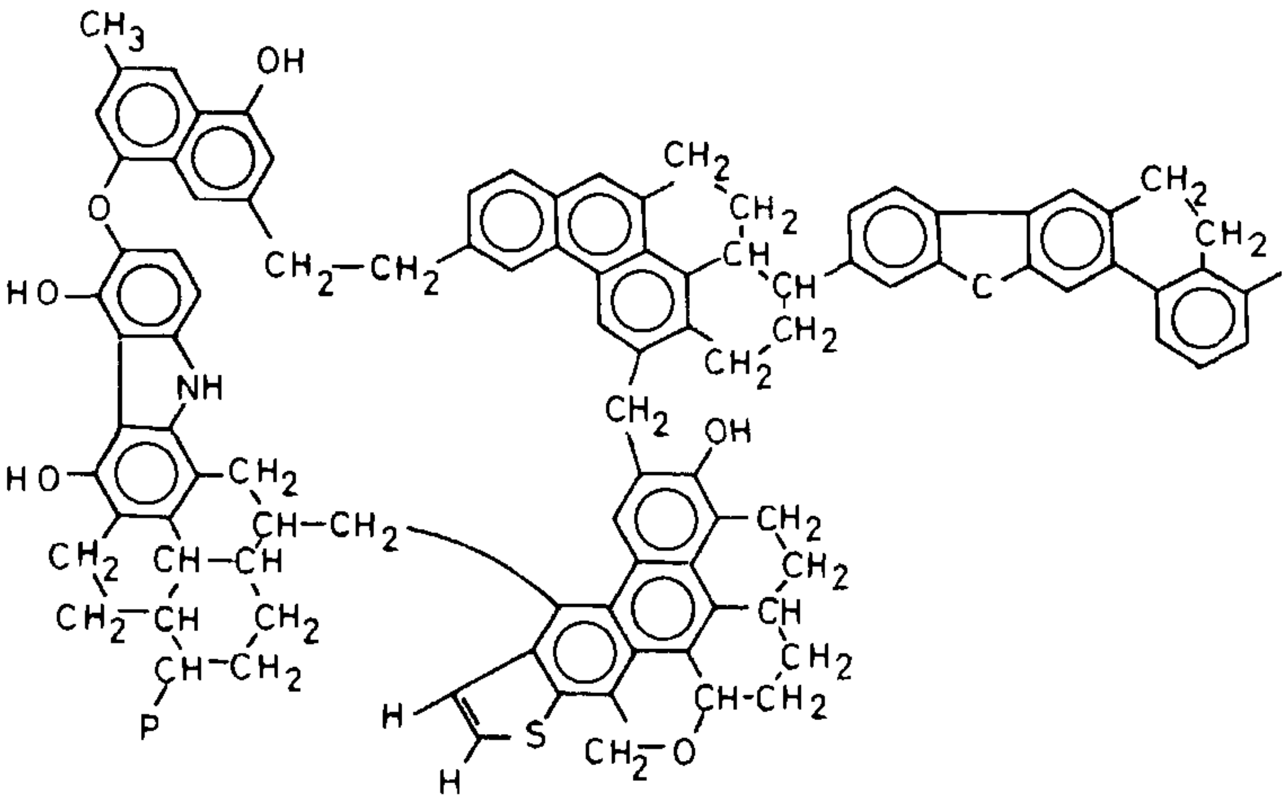
van Krevelen

Polymeric model of coal structure



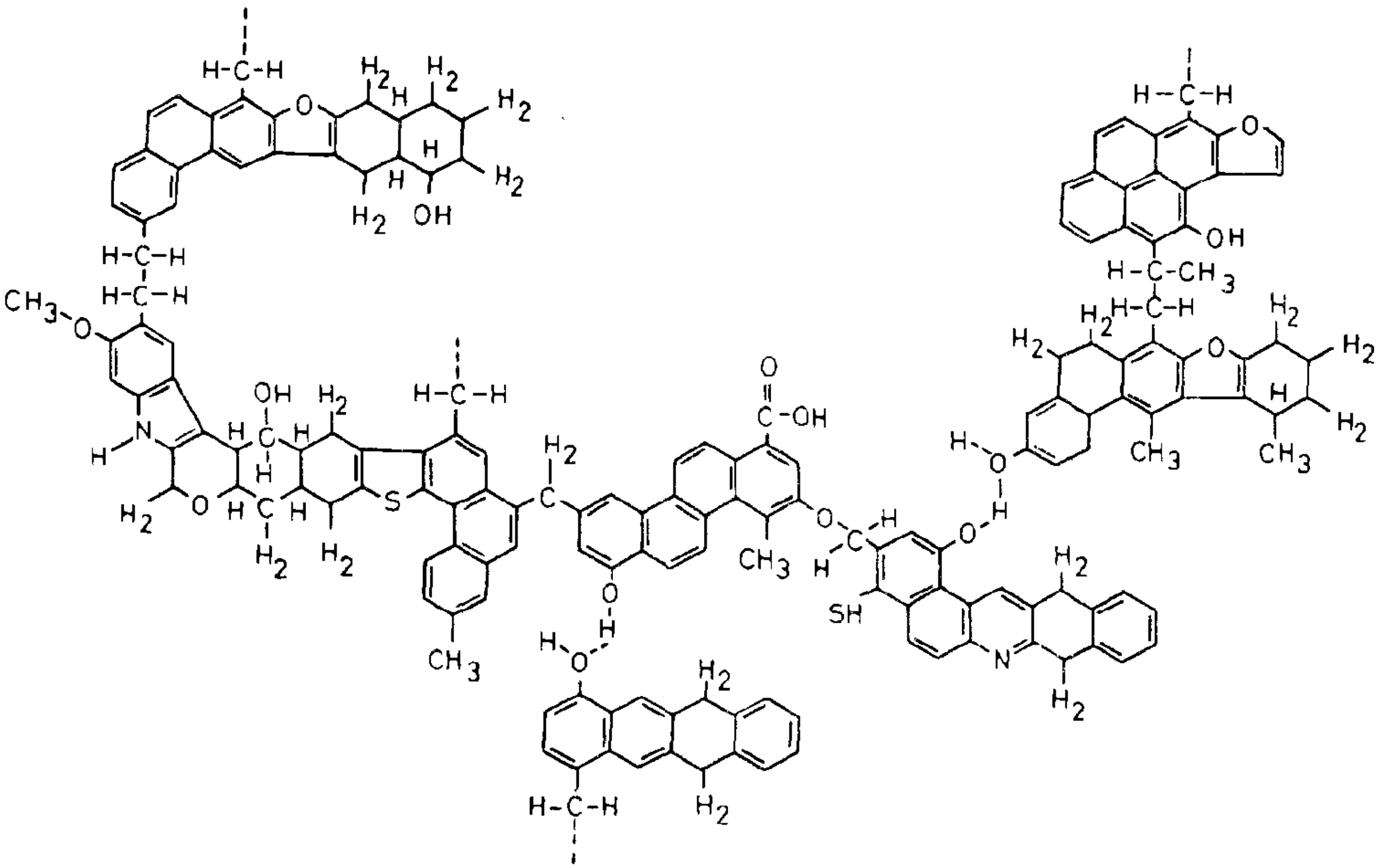
Wiser

Polymeric model of coal structure



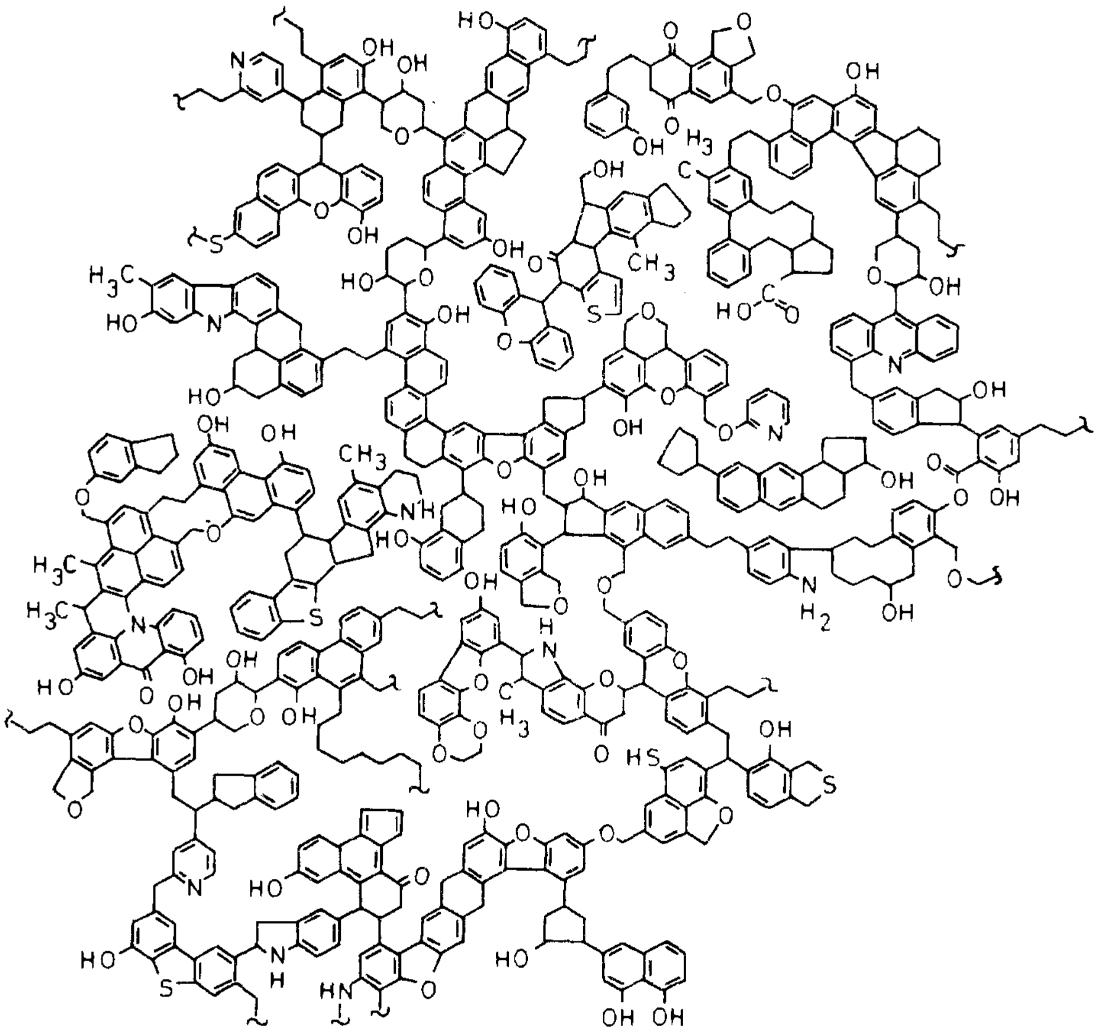
Heredy and Wender

Polymeric model of coal structure



Solomon

Polymeric model of coal structure

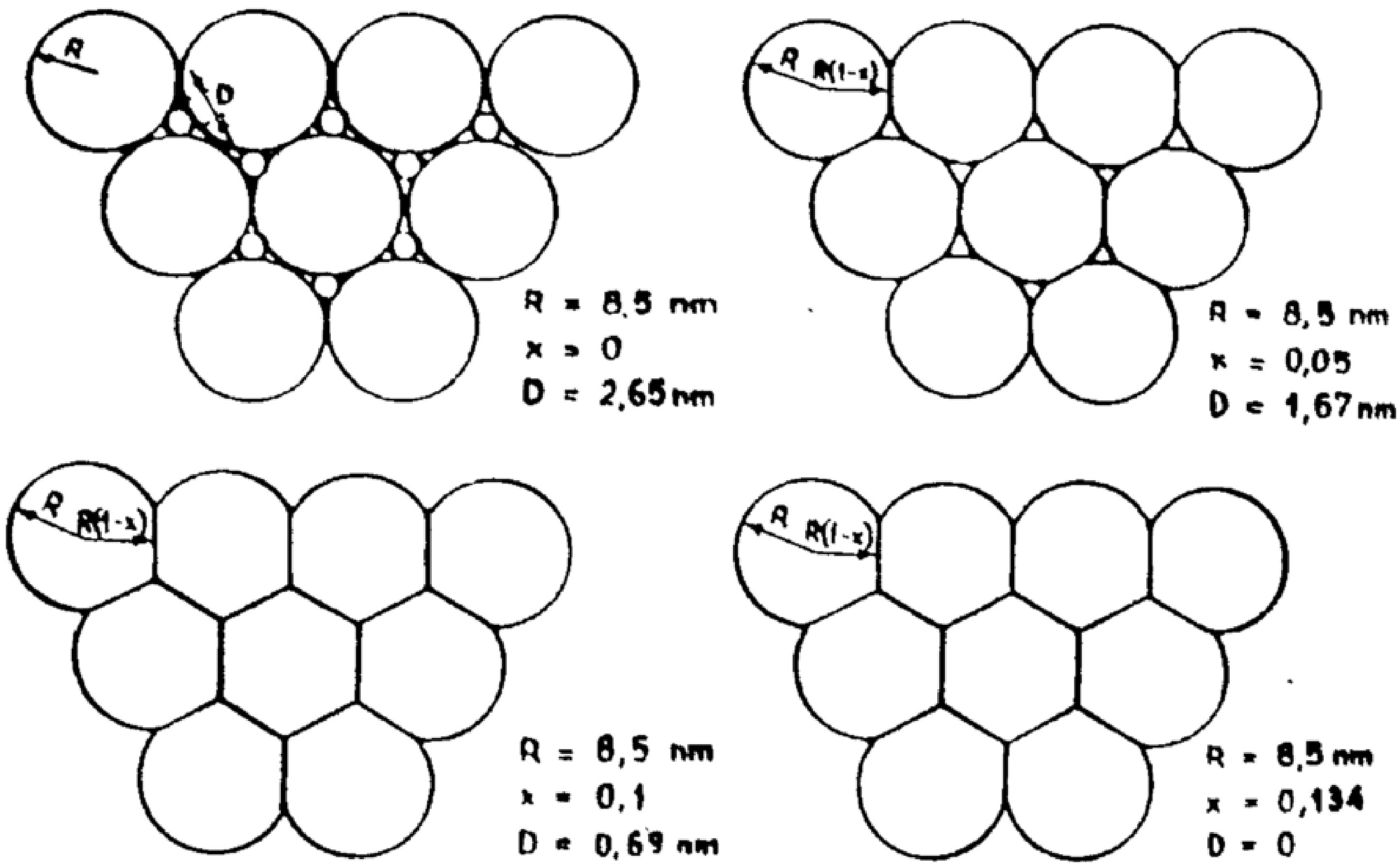


Shinn

Polymeric model of coal structure

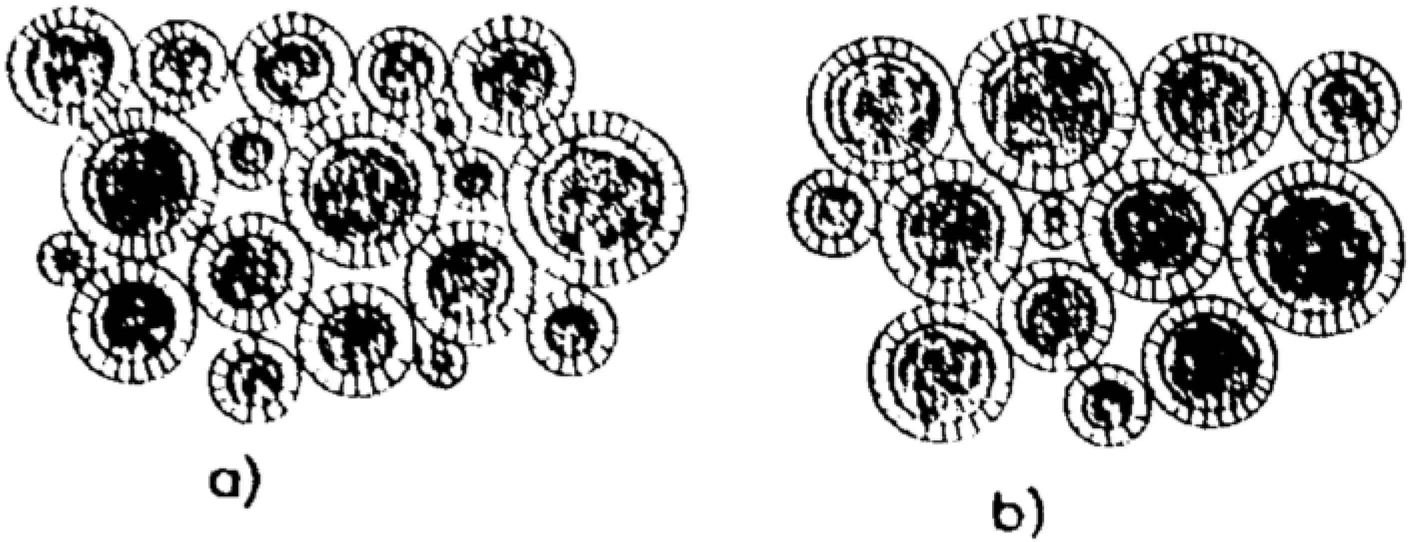
- Cosky and Spiro – 3D modelling
- Marzec, Milewska-Duda – copolymeric model of coal structure
  - macromolecular phase
    - arene domains
    - crosslinked chains
  - molecular phase
    - non-crosslinked chains
  - mineral admixtures
  - pore structure (sub-micro-pores)

Coloidal model of coal structure



Bangham

Coloidal model of coal structure

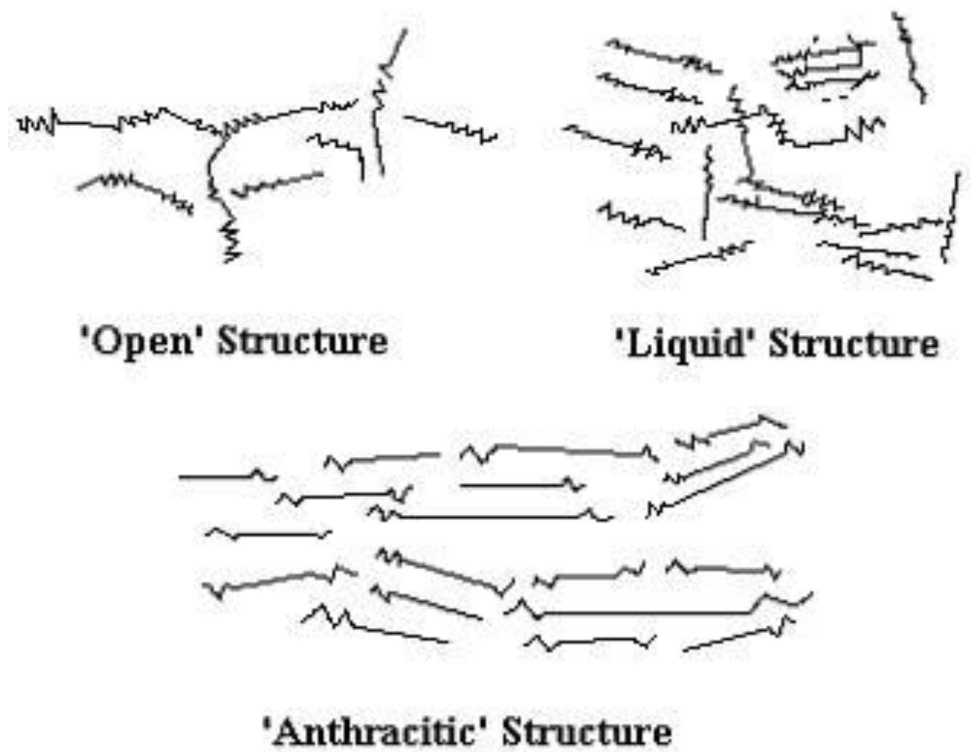


Kreulen

Lamelar - turbostratic model of Coal

Riley

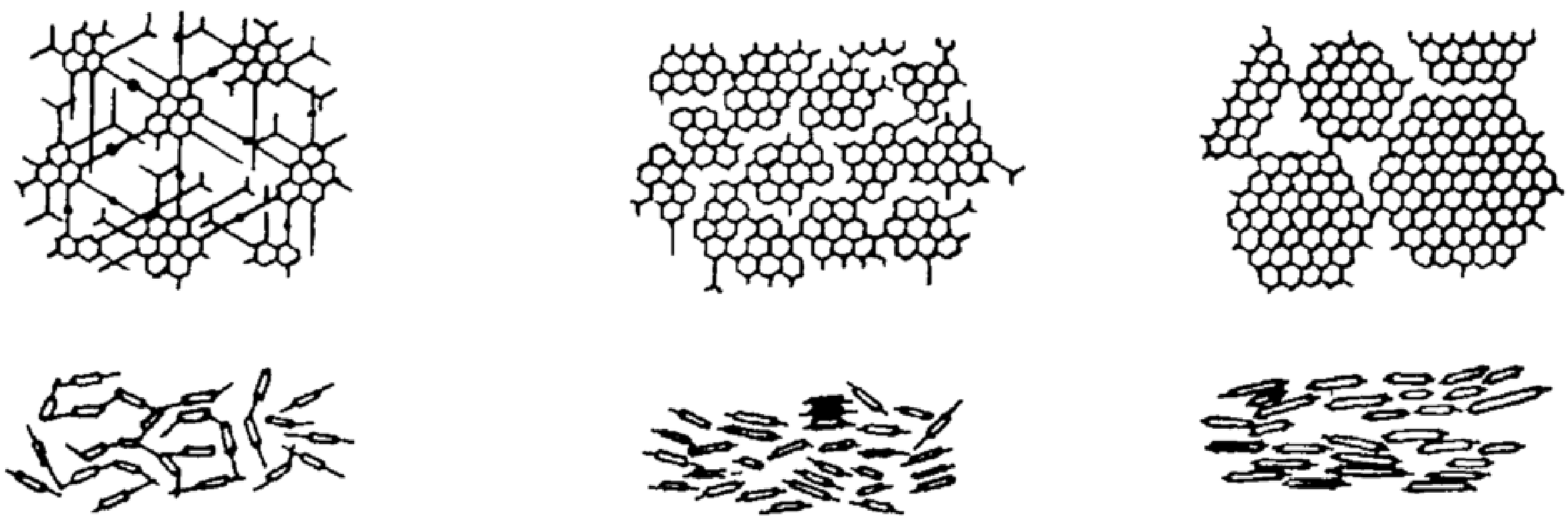
Lamelar - turbostratic model of Coal



Hirsch, P.B. Royal Society London A London, 1954, 226, 143.

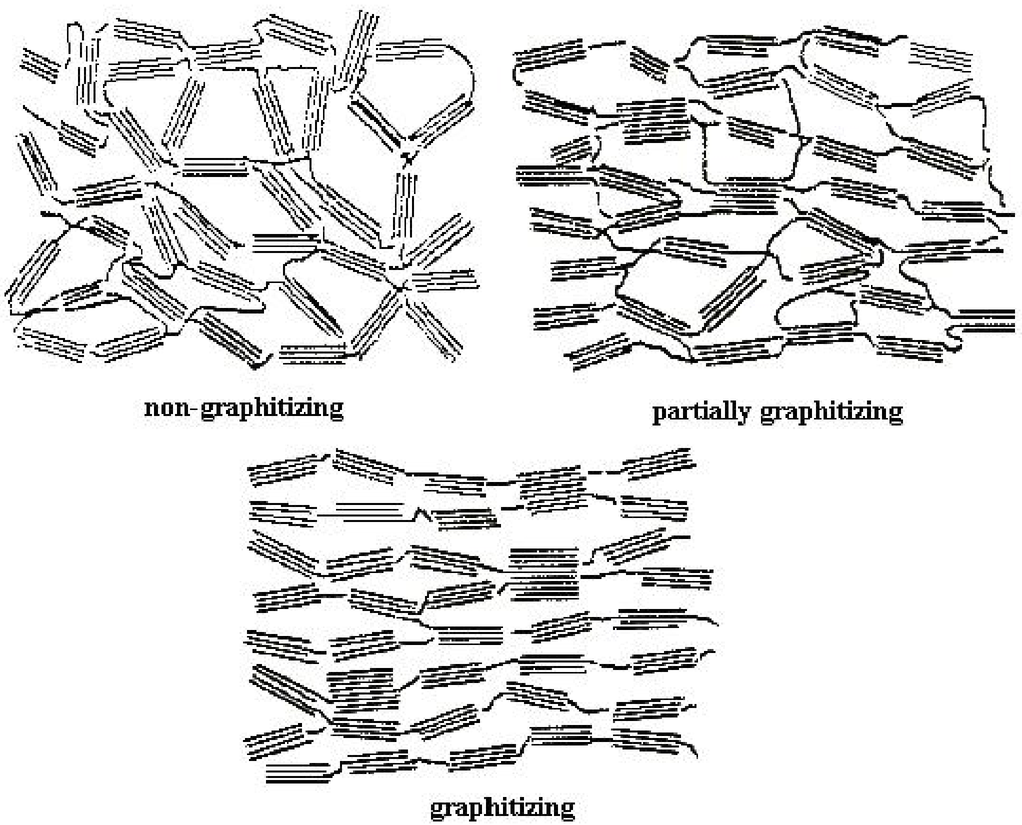
Lamelar model of Vitrain

V^{daf}~35% V^{daf}~22% V^{daf}~5%



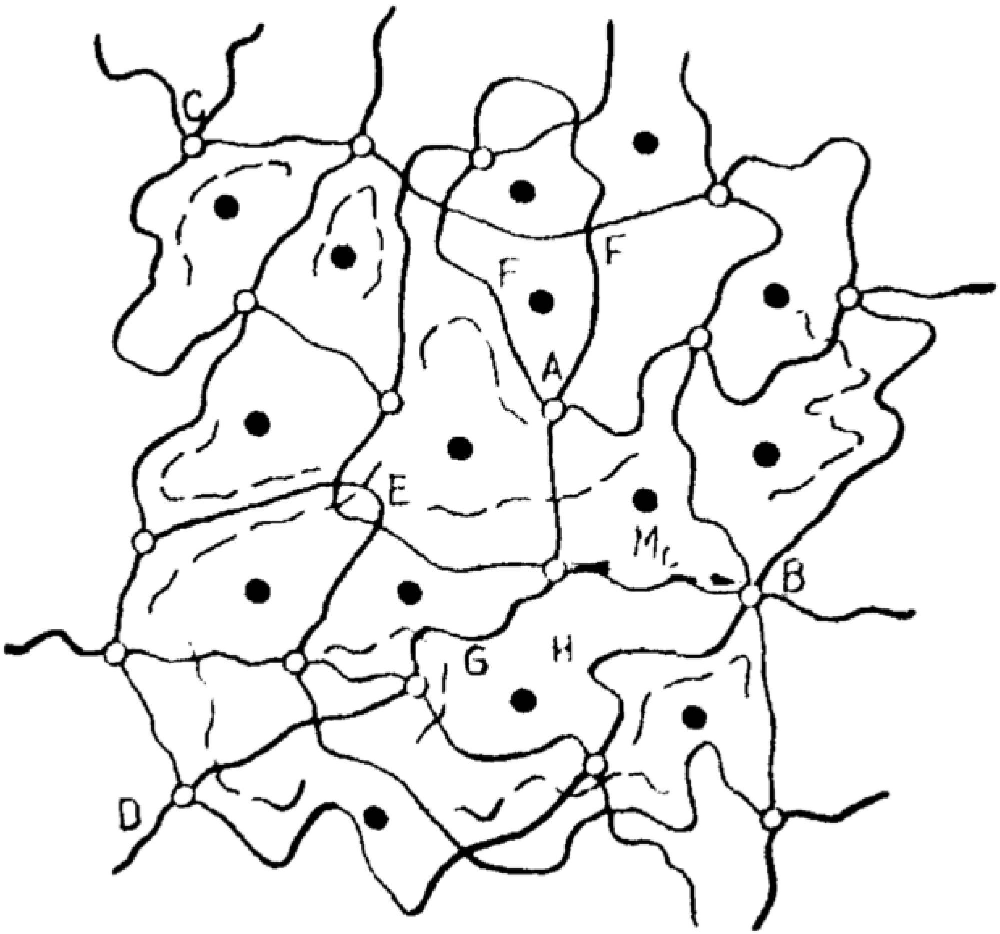
Teichemüllers

Model of Coal structure by Franklin



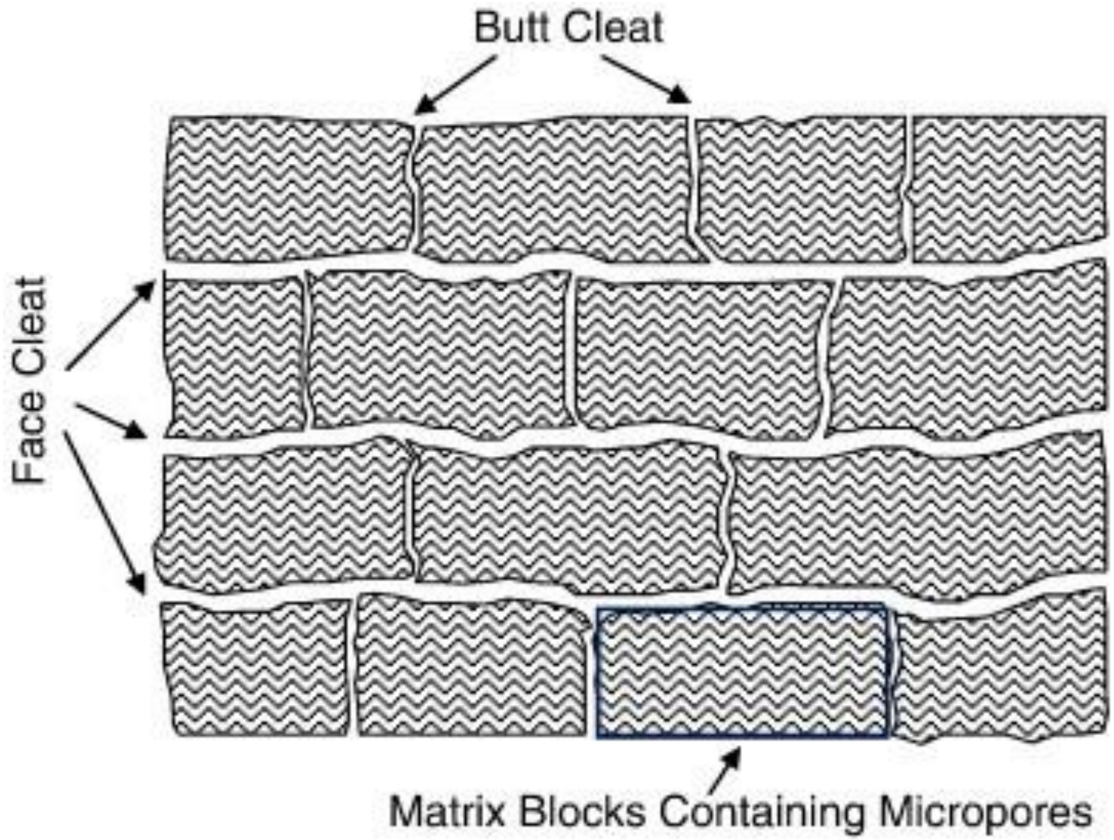
Franklin, R.E. Royal Society London A London, 1951, 209, 196.

Simplified model of coal



Lucht and Peppas

Permeability of coal bed



Zhejun Pan, Luke D. Connell, International Journal of Coal Geology, Volume 92, 1 March 2012, Pages 1–44

Coal Classification

There are a number ways to classify coals.

One way is to ***Rank*** the coal. It indicates the degree or extent of maturation.

It is a qualitative measure of carbon content.

Thus lignites and sub-bituminous are low rank coals

While bituminous and anthracite are high rank coals.

Rank is not synonymous with grade which implies quality.

Low rank coals may not be suitable for some applications as the higher ranked ones

Although they may be superior to them in other applications

Rank of Coal - assumption

With increasing Rank, the following characteristics are noticed:

1. Age of coal is increased. This increases with increase in depth of deposit.
2. A progressive loss of oxygen, hydrogen and in some cases sulfur, with a corresponding increase in carbon.
3. A progressive decrease in equilibrium moisture content.
4. A progressive loss of volatile matter.
5. Generally, a progressive increase in calorific value.
6. In some cases, a progressive increase of ash content.

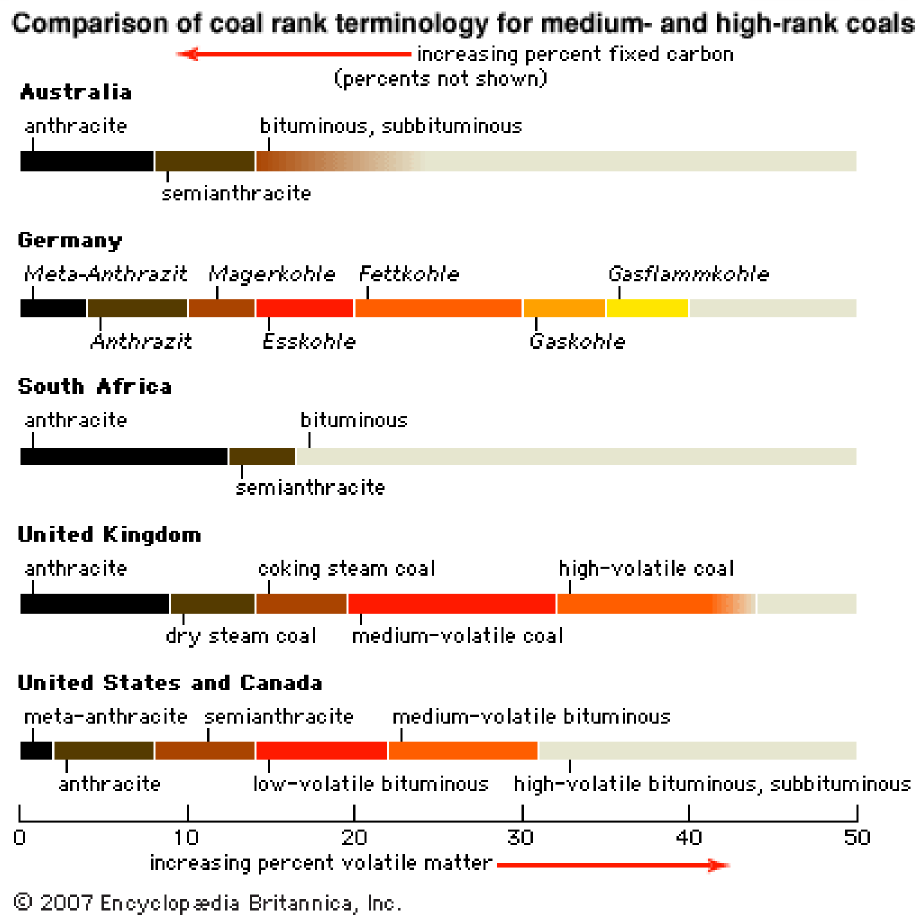
Coal types - terminology

Coal classification by ICCP

Name	Volatiles %	C Carbon %	H Hydrogen %	O Oxygen %	S Sulfur %	Heat content kJ/kg
Lignite	45-65	60-75	6.0-5.8	34-17	0.5-3	<28470
Flame coal	40-45	75-82	6.0-5.8	>9.8	~1	<32870
Gas flame coal	35-40	82-85	5.8-5.6	9.8-7.3	~1	<33910
Gas coal	28-35	85-87.5	5.6-5.0	7.3-4.5	~1	<34960
Fat coal	19-28	87.5-89.5	5.0-4.5	4.5-3.2	~1	<35380
Forge coal	14-19	89.5-90.5	4.5-4.0	3.2-2.8	~1	<35380
Non baking coal	10-14	90.5-91.5	4.0-3.75	2.8-3.5	~1	35380
Anthracite	7-12	>91.5	<3.75	<2.5	~1	<35300

by ICCP

Coal types - occurence



http://www.britannica.com/EBchecked/media/95181/Comparison-of-coal-rank-terminologies-by-country

Proximate Analysis of some typical Lignites

Class and group	Fixed Carbon, %	Volatile Matter, %	Age in million years	Calorific Value kJ/kg
Lignite A	58-64	36-42	1	36050
Lignite B	51-57	42-49	To	35000
Lignite C	41-51	49-59	40	-do-

Proximate Analysis of some typical sub-bituminous coals

Class and group	Fixed Carbon, %	Volatile Matter, %	Age in million years	Calorific Value kJ/kg
Sub-bituminous A	69-72	28-31	40	36050
Sub-bituminous B	64-69	31-36	To	35000
Sub-bituminous C	<64	>36	100	-do-

Proximate Analysis of some typical bituminous coals

Class and group	Fixed Carbon, %	Volatile Matter, %	Age in million years	Calorific Value kJ/kg
Low volatile	78-86	14-22	100	36520
Medium volatile	69-78	22-31	To	-do-
High volatile: A,B,C	<69	>31	180	-do-

Proximate Analysis of some typical anthracite coals

Class and group	Fixed Carbon %	Volatile Matter %	Age in million years	Cal. value kJ/kg
Meta-anthracite	>98	<2	180	35820
Anthracite	92-98	2-8	- (300)	40700
Semi-anthracite	86-92	6-14	250	36750

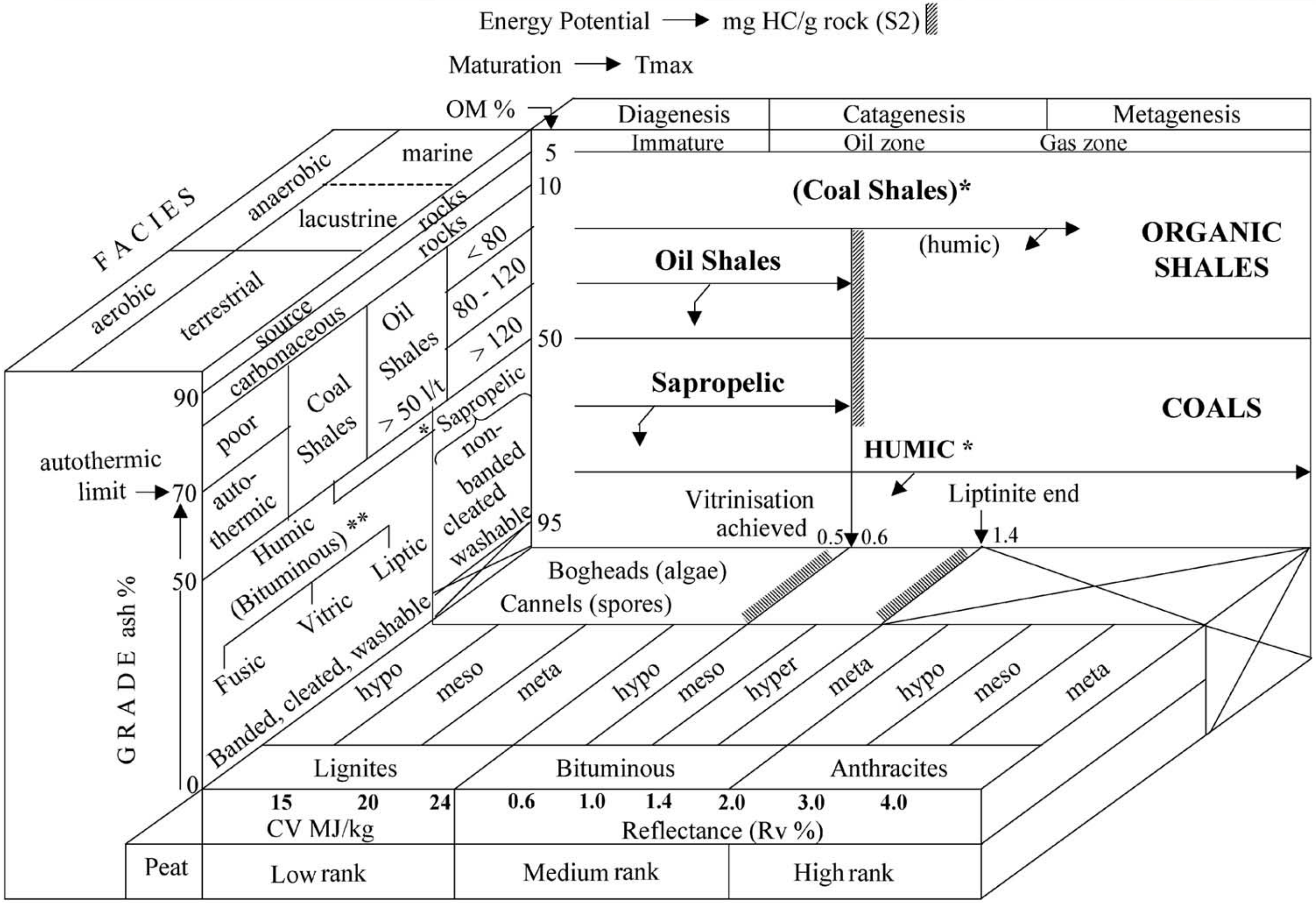
Problematic classification

The border between lignites and hard (stone) coals is unprecisely stated

IEA	BROWN COAL (Lignite + Subbituminous)	
USA	LIGNITE + SUBBITUMINOUS (B + A) (C + B + A)	
Former USSR	BROWN COAL (1 + 2 + 3)	
China	BROWN COAL (1+ 2)	
Australia	BROWN + SUBBITUMINOUS SOFTCOAL	
Germany	BROWN COALS (soft + matt + bright)	
UN / ECE	LIGNITE (ortho+meta) + SUBBITUMINOUS or/and LOW RANK C + B + A	
Alpern and Lemos de Sousa (1991)	LIGNITE hypo + meso + meta	
OTHER SOLUTIONS (N°2 IS THE PROPOSED ONE)	1	LOW RANK COAL 1 + 2 + 3 or A + B + C
	2	***PEAT INCLUDED*** **moisture>OM** | **OM>moisture** **PEAT** | **Hypolignite** | **Mesolignite Metalignite*** **LIGNITE** ± BROWN BLACK (reddish) *only partly equivalent to Subbituminous

Boris Alpern a, M.J. Lemos de Sousa, International Journal of Coal Geology 50 (2002) 3– 41

Problematic classification, cont...



NB: * Coal Shales and Humic coals lines correspond in terms of coalification to the left part of the chart.
** Petrographic composition, banding and cleating are mainly restricted to Bituminous coals.

Coal classification – parameters and factors

Name	unit	symbol
Volatile matter content	%	V
Roga Index	-	RI
Dillatation	%	b
Free swelling index	-	FSI
Gross calorific value	kJ/kg	GCV
Net calofific value	kJ/kg	NCV
Ash content	%	A
Total sulphur content	%	S_t
Total moisture content	%	W_t

index:
af – ash free
d – dry
ex – external
h - hygroscopic

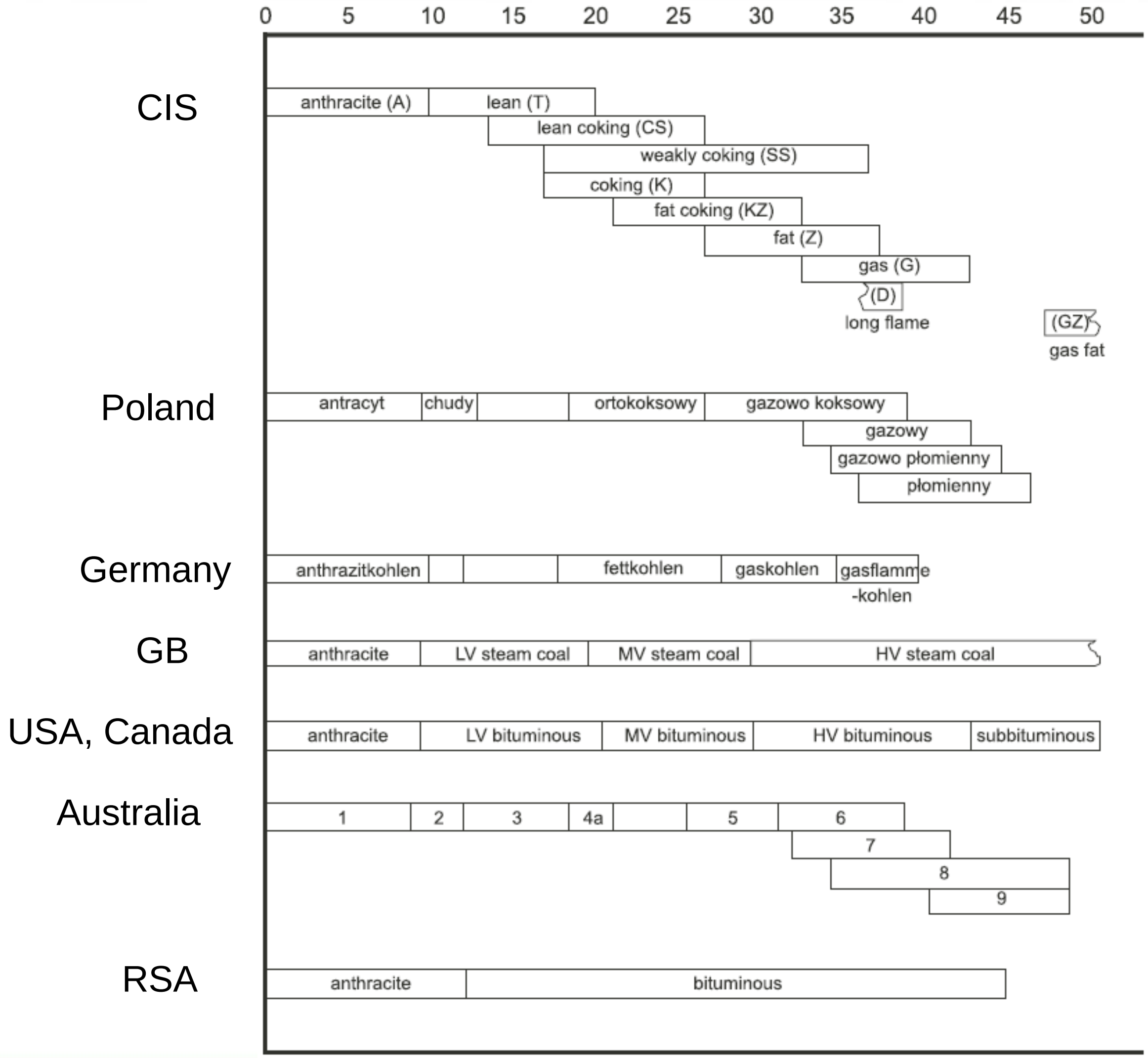
AR – as received
AD – air-dried

$$S_o^{daf} \qquad W_{AR}^{ex}$$

Coal types - international

Coal Types and Peat: UNECE	USA (ASTM)	Germany (DIN)	DIN group	Total Water Content (%)	Energy Content a.f.* (kJ/kg)	Volatiles d.a.f.** (%)	Vitrinite Reflection in oil (%)
Peat	Peat	Torf					
				75	6,700		
Ortho-Lignite	Lignite	Weichbraunkohle					
				35	16,500		0.3
Meta-Lignite	Lignite / Sub-bituminous Coal	Mattbraunkohle	Hartkohle				
				25	19,000		0.45
Sub-bituminous Coal	Sub-bituminous Coal	Glanzbraunkohle	Hartkohle				
				10	25,000	45	0.65
Bituminous Coal	Sub-bituminous Coal / High Volatile Bituminous Coal	Flammkohle	Hartkohle, Steinkohle				
						40	0.75
Bituminous Coal	High Volatile Bituminous Coal	Gasflammkohle	Hartkohle, Steinkohle				
						35	1.0
Bituminous Coal	High Volatile Bituminous Coal / Medium Volatile Bituminous Coal	Gaskohle	Hartkohle, Steinkohle				
						28	1.2
Bituminous Coal	Medium Volatile Bituminous Coal / Low Volatile Bituminous Coal	Fettkohle	Hartkohle, Steinkohle	Hard Coking Coal	36,000		
						19	1.6
Bituminous Coal	Low Volatile Bituminous Coal	Eßkohle	Hartkohle, Steinkohle				
						14	1.9
Anthracite	Semi-Anthracite	Magerkohle	Hartkohle, Steinkohle				
				3	36,000	10	2.2
Anthracite	Anthracite	Anthrazit	Hartkohle				

Coal types - international



Coal types - Poland

<table>
<tr><td colspan="2" rowspan="2">Coal type</td><td colspan="5">Classification parameters</td></tr>
<tr><td>V</td><td>RI</td><td>GCV</td><td>b</td><td>FSI</td></tr>
<tr><td>Name</td><td>Symbol</td><td>%</td><td></td><td>kJ/kg</td><td>%</td><td></td></tr>
<tr><td rowspan="2">Flame</td><td>31.1</td><td rowspan="2">>28</td><td rowspan="2"><5</td><td>≤31,000</td><td rowspan="5">N.A.</td><td rowspan="8">N.A.</td></tr>
<tr><td>31.2</td><td>>31,000</td></tr>
<tr><td rowspan="2">Flame-Gas</td><td>32.1</td><td rowspan="2">>28</td><td>5÷20</td><td rowspan="8">N.A.</td></tr>
<tr><td>32.2</td><td>20÷40</td></tr>
<tr><td>Gas</td><td>33</td><td>>28</td><td>40÷55</td></tr>
<tr><td rowspan="2">Gas-Coke</td><td>34.1</td><td rowspan="2">>28</td><td rowspan="2">>55</td><td><0</td></tr>
<tr><td>34.2</td><td>~ 0</td></tr>
<tr><td rowspan="3">Ortho-coking</td><td>35.1</td><td>26÷31</td><td rowspan="3">>45</td><td>>30</td></tr>
<tr><td>35.2A</td><td rowspan="2">20÷26</td><td>>0</td><td>>7.5</td></tr>
<tr><td>35.2B</td><td></td><td><7.5</td></tr>
</table>

Coal types - Poland

Coal type		Classification parameters				
		V	RI	GCV	b	FSI
Name	Symbol	%		kJ/kg		
Meta-coking	36	14÷20	>45	N.A.	0	N.A.
Semi-coking	37.1	20÷28	≥5		N.A.	
	37.2	14÷20				
Lean	38	14÷28	<5			
Anthracite coal	41	10÷14	N.A.			
Anthracite	42	3÷10				
Metaantracite	43	<3				

Economical Classification by IEA

Classification used by IEA for production and trade statistics

Brown coal; <23.9	Lignite	<17.4
	Subbituminous	17.4–23.9
Hard coal; >23.9; *R*>0.6	Coking coal	
	Steam coal	all non-coking coals +recovered slurries, middlings +subbituminous (only in 22 countries)

Values in MJ/kg; *R*=reflectivity.
Remark: In this chart, brown coals include lignite and subbituminous coals, but subbituminous are also comprised in steam (hard) coal!

Production (Mtce)			Trade (Mtce)			
	1980	1998	1980		1998	
			Import	Export	Import	Export
Hard coal	955	1102.39	195.14	154.48		
Coking	259.41	211.22	117.79	115.29		
Steam	695.59	891.17	77.35	39.19		
Brown coal/lignite	180.57	166.57	1.51	0.14		
Peat	2.53	2.15	–	–	–	0.01
			CP[a] 19.7	18.66	15	6.75
Total	1138.09	1271.10	216.34	173.29	314.90	270.32

International classification of hard coals

GROUPS determined by caking properties			CODE NUMBER										SUB-GROUPS determined by coking properties		
Group number	Alternative group parameter: Swelling number	Alternative group parameter: Roga index	*The first figure of the code number indicates the class of coal determined by volatile matter content up to 33% V.M and by calorific parameter above 33% V.M.* *The second figure indicates the group of coal determined by caking properties.* *The third figures indicates the sub-group, determined by coking properties.*										Sub-group number	Alternative sub-group parameters: Dilatometer	Alternative sub-group parameters: Gray-King
3	**>4**	**>45**					435	535	635				**5**	>140	**>G8**
						334	434	534	634				**4**	>50-140	**G5-G8**
						333	433	533	633	733			**3**	>0-50	**G1-G4**
						332a / 332b	432	532	632	732	832		**2**	≤ 0	**E-G**
2	**2½-4**	**>20-45**				323	423	523	623	723	823		**3**	>0-50	**G1-G4**
						322	422	522	622	722	822		**2**	≤ 0	**E-G**
						321	421	521	621	721	821		**1**	Contraction only	**B-D**
1	**1-2**	**>5-20**			212	312	412	512	612	712	812		**2**	≤ 0	**E-G**
					211	311	411	511	611	711	811		**1**	Contraction only	**B-D**
0	**0-½**	**0-5**		100 A / B	200	300	400	500	600	700	800	900	**0**	Non-softening	**A**
Class Number			**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	As an indication, the following classes have approximate volatile matter content of: Class 6 .... 33 - 41% Class 7 .... 22 - 44% Class 8 .... 35 - 50% Class 9 .... 42 - 50%		
Class parameter	Volatile matter (d.a.f)		0-3	>3-10 (>3-6.5 / 6.5-10)	>10-14	>14-20	>20-28	>28-33	>33	>33	>33	>33			
	Calorific parameter [a]		-	-	-	-	-	-	>7750	>7200 - 7750	>6100 - 7200	>5700 - 6100			
CLASSES Determined by volatile matter up to 33% V.M and by calorific parameter above 33% V.M -															