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FOSSIL ENERGY

OXIDATION OF LIGNIN AND CELLULOSE, HUMIFICATION AND COALIFICATION

June 9, 1976

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North Dakota State University
Fargo, North Dakota
and
California University
Irvine, California

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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A. VOLBORTH

North Dakota State University, and University of California, Irvine

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Oxidation of Lignin and Cellulose, Humification and Coalification

A. Volborth

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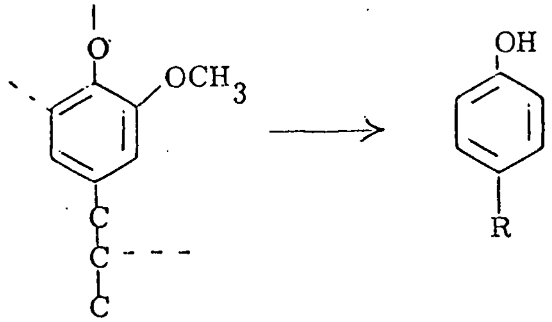
Oxygen plays an important role in the first stages of the decomposition of organic substances derived from plant material. The decomposition and reformulation of such organic matter as cellulose and lignin leads, through humification and a sequence of metamorphic processes, to the formation of coal. Initially, oxidation reactions cause the formation of dark-colored humic acids, later under more anaerobic conditions, pressure and higher temperatures, polymerization occurs as the sediment becomes buried. Under these conditions phenolic compounds are more stable, also during the processes of decomposition phenolic substances are more resistant to microorganisms, and thus seem to accumulate.

A very complex series of reactions results in an organic rock we call coal. This process also consists of a sequence of bacterial decomposition of starches and proteins, fixation of nitrogen derived from peptides, amino acids, and ammonia. Breaking of the cellulose chains by enzymatic action (giving rise to the formation of aliphatic compounds later under reducing conditions), and decomposition of lignin through oxidation of the methoxyl groups, and formation of quinones which later polymerize, all lead to a higher degree of aromatization. The decomposition of lignin is slower than that of cellulose.

Many primary lignin decomposition products have been identified. These are mostly phenolic compounds. Aromatic molecules with side-chains of one or three-carbon atoms are derived from the polymeric lignin . Flaig,[4,13,14] Swain,[10,11] and others[5,6,7] have proposed the following reactions:



lignin

R = —CHO

p-hydroxybenzaldehyde

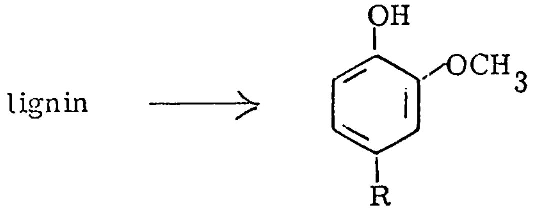
R = —COOH

p-hydroxybenzoic acid

R = —CH=CH—COOH

p-hydroxycinnamic acid

Through cleavage or oxidation reactions the side chain is shortened. Also the following compounds have been identified:



R = —CHO (vanillin)

R = —COOH (vanillic acid)

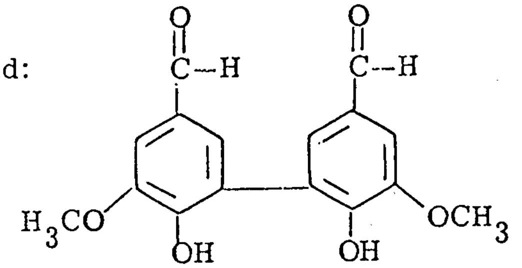
R = —CH=CH-CHO (coniferyl aldehyde)

R = —CH=CH-COOH (ferulic acid)

R = —CHOH-CHOH-CH_2OH (guajacyl-glycerol)

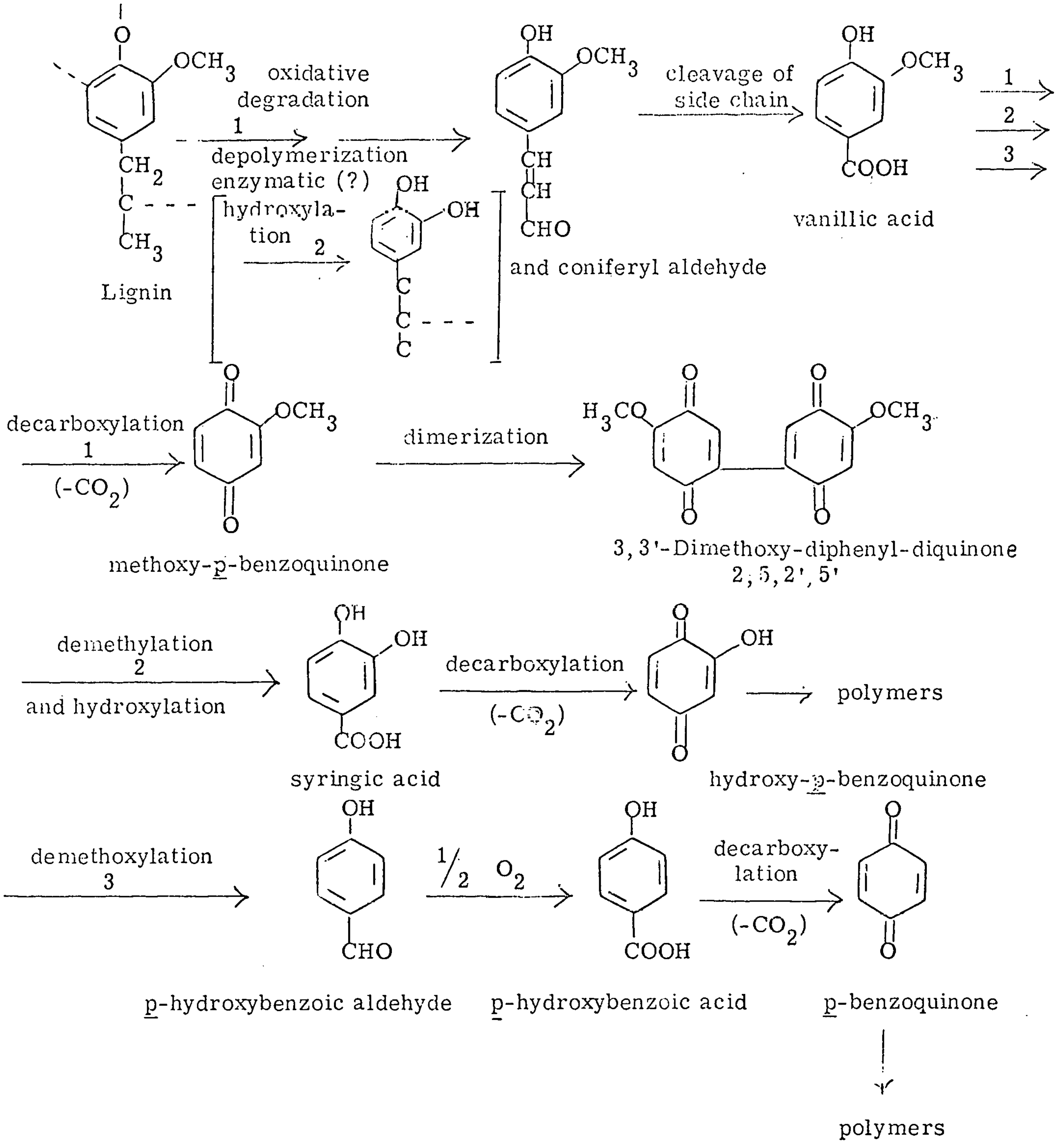
R = —CH_2-CO-COOH (guajacyl-peruvic acid)

and:

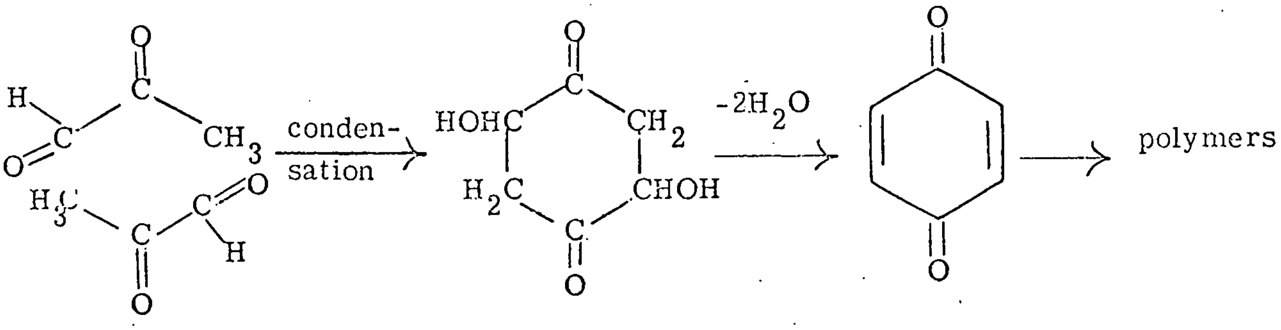


dehydrodivanillin

The oxidation may proceed in the general sequence:[4,5,6,7]



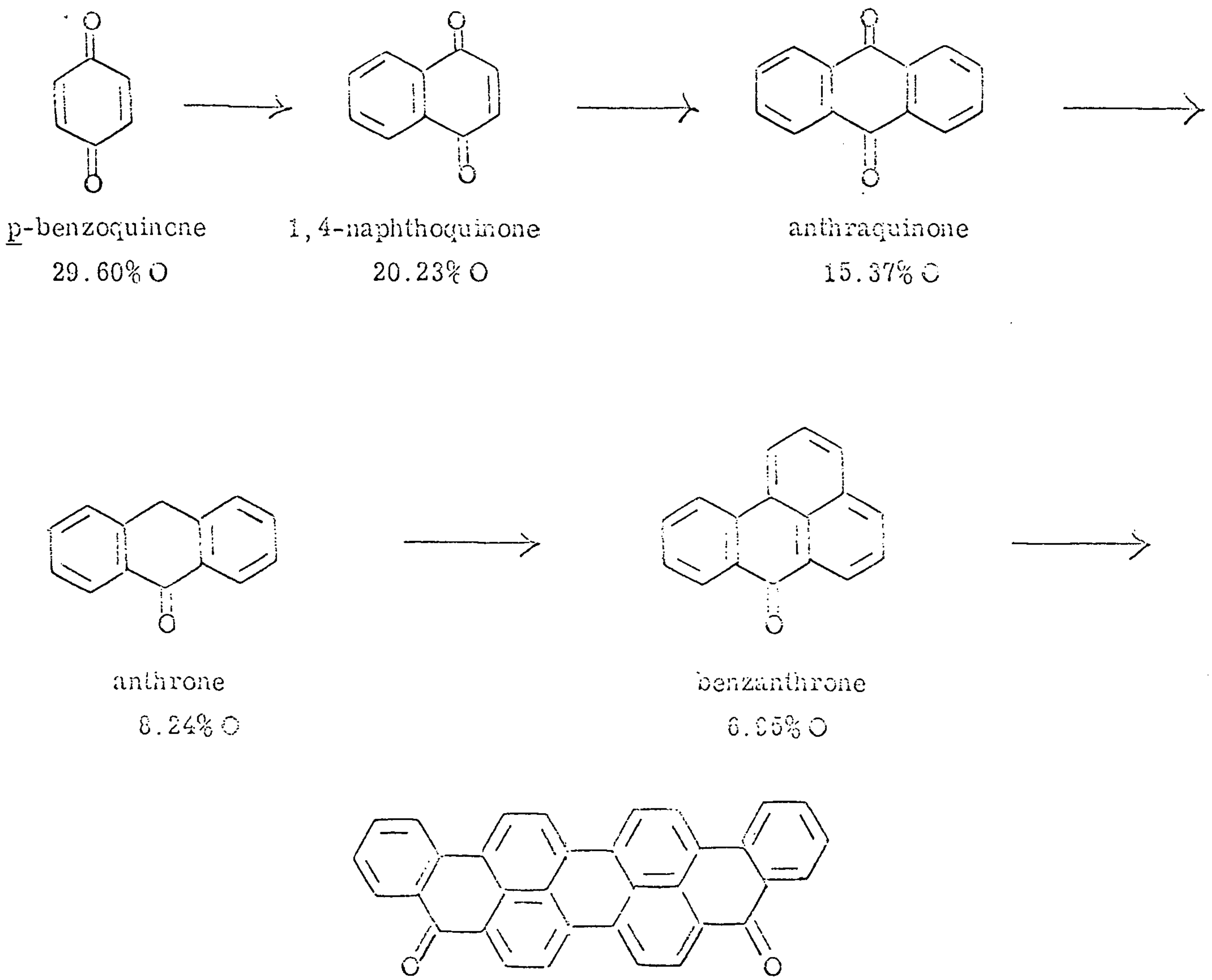
Equally, cellulose, hemicellulose, and other high polymer carbohydrates can decompose through bacterial action to trioses and further to methyl glyoxal which may form quinones by condensation:[11, p. 343]



methyl glyoxal

p-benzoquinone

Quinones can thus be formed through condensation of short aliphatic chains derived from cellulose and sugars as well as by cleavage, hydroxylation, demethylation, decarboxylation, and demethoxylation of phenolic compounds with side chains. Starting with benzoquinone through condensation naphthoquinones, anthraquinone, anthrone, benzanthrone, dibenzanthrone, and similar compounds may form. We note that as the condensation proceeds in this direction, the oxygen content is decreased:



p-benzoquinone
29.60% O

1,4-naphthoquinone
20.23% O

anthraquinone
15.37% O

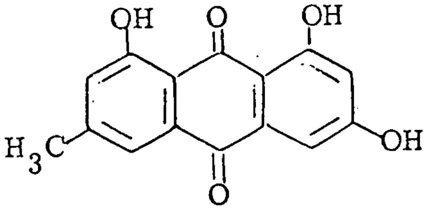
anthrone
8.24% O

benzanthrone
6.95% O

dibenzanthrone
(violanthran)
7.01% O

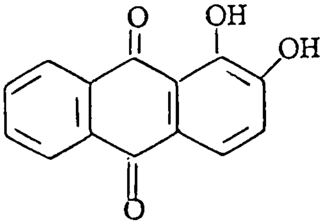
Examples of naturally occurring polycyclic hydroxyquinones that may be produced by polymerization of quinones, according to Steelink, 1966, are:

Emodin, 1,3,8-Trihydroxy-6-methylanthraquinone



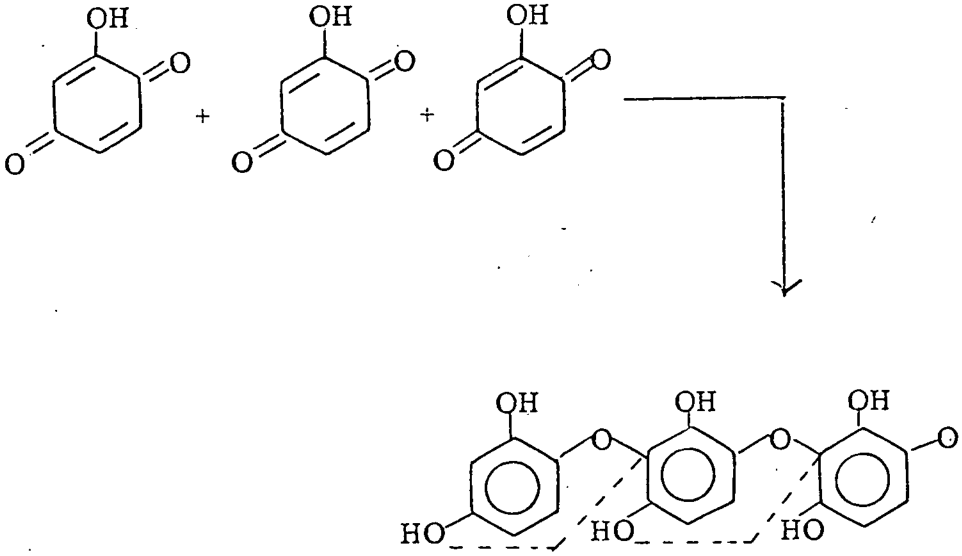
29.6% O

and alizarin, 1,2-Dihydroxyanthraquinone,

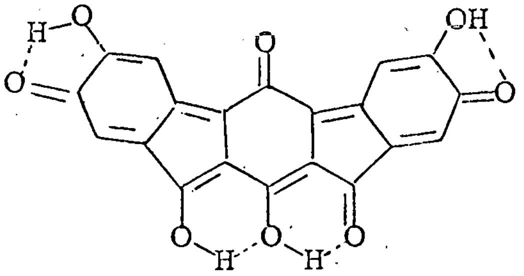


26.64% O

According to Swain,[11] polymerization of hydroxyquinone may proceed as follows:

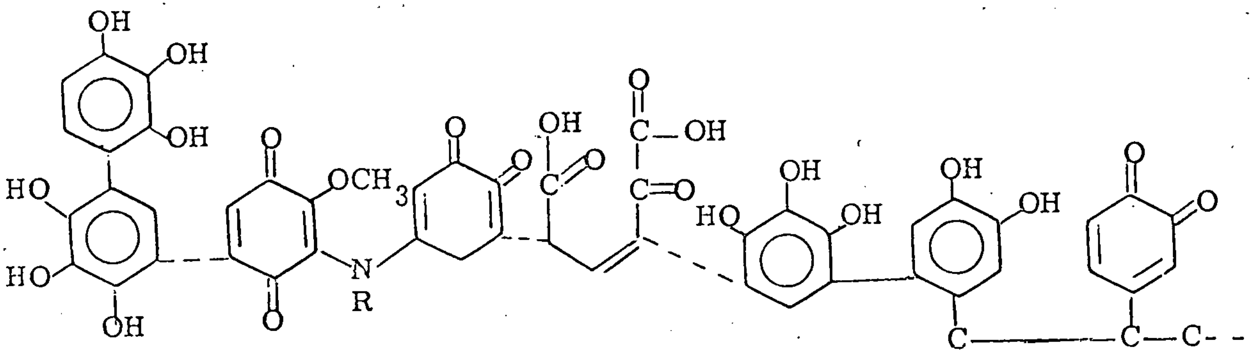


Polymerization also may lead to polycyclic hydroxyquinones and complex heterocyclic molecules. <u>Humic acids</u> are examples of such polymeric matrixes. The structure of these is not yet completely understood. Models of humic acids were worked out by Gillet in 1956:[12]



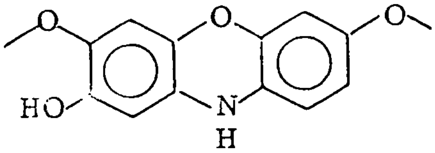
Gillet's humic acid model:
Anthraxylic acid (1956)

and by Flaig in 1960[13,14]:

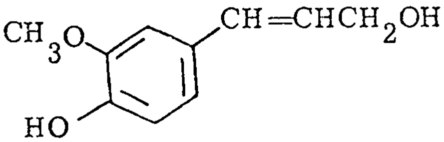


Flaig's humic acid model (1960)

Table 1 is a list of derivatives formed in oxidation studies of lignin and the products of the polymerization of the quinoid compounds and humic acids compared with the composition of bituminous coals. The organic compounds are plotted in the approximate sequence of their formation as delineated above. When compositions plotted in this manner are compared, one notices the role of oxygen in this process. The oxygen content increases slightly during the oxidation of the depolymerized lignin derivative, coniferyl alcohol, then drops with progressing condensation and aromatization. Humic acid compositions indicate that these substances may be intermediate products of oxidation of lignin.



Oxygen is a major constituent of plant material. In general, the content of oxygen decreases during the processes of coalification, however the first stages of decomposition of plant material that lead to humification or formation of the "dark colored" humic substances are triggered by decay organisms, enzymes, and the oxidizing effect of atomospheric oxygen. Gradual oxidation of the sugars derived from the depolymerized cellulose and through enzymatic hydrolysis (rotting) of coniferyl alcohol,



derived from lignin by similar processes, leads to the formation of humic substances; these also contain nitrogen compounds of plant, bacterial, and animal origin, which can form through interaction of carbohydrates with amino acids, resulting as shown by Maillard in mealnoidins.[17] These are dark-colored, amorphous nitrogen-containing substances, similar to humic acids.

Table 1

Composition of Some Products of Enzymatic Hydrolysis (rotting, humification) of Lignin Plotted in Approximate Sequence of Their Formation and Their Possible Polymerization Products

		Weight Percent		
		C	H	O
Coniferyl Alcohol	$C_{10}H_{12}O_3$	66.65	6.71	26.64
Vanillin (aldehyde)	$C_8H_8O_3$	63.15	5.30	31.55
Vanillic Acid	$C_8H_8O_4$	57.14	4.80	38.06
Dimethoxybenzoquinone	$C_8H_8O_4$	57.14	4.80	38.06
p-Hydroxybenzoic acid	$C_7H_6O_3$	60.86	4.38	34.75
p-Benzoquinone	$C_6H_4O_2$	66.67	3.73	29.60
Emodin 1,3,8-Trihydroxy-6-methylanthroquinone	$C_{15}H_{10}O_5$	66.67	3.73	29.60
Alizarin 1,2-Dihydroxy-anthraquinone	$C_{14}H_8O_4$	69.98	3.36	26.64
Humic Acids from sub-bituminous coal (7 samples)[4]		69.2	4.5	26.3
Hypericin	$C_{30}H_{16}O_8$	71.43	3.20	25.38
Naphthoquinone	$C_{10}H_6O_2$	75.94	3.82	20.23
Anthraquinone	$C_{14}H_8O_2$	80.76	3.87	15.37
Anthrone	$C_{14}H_{10}O$	86.75	5.19	8.24
Benzanthrone	$C_{17}H_{10}O$	88.67	4.38	6.95
Dibenzanthrone (Violanthrone)	$C_{34}H_{16}O_2$	89.46	3.53	7.01
Low to high rank bituminous coals (Table 2)		79-92	5.5-4.5	14-2

Chitin, $C_8H_{13}NO_5$ (C 47.29%, H 6.45%, O 39.37%, N 6.89%) and glucosamine, $C_6H_{13}NO_5$ (C 40.22%, H 7.31% , O 44.65%, N 7.82%) may be precursors of melanoidins through the Maillard Reaction.[18] Melanoidins are important constituents of the humic acid fractions in soils, peat, and lignite, and probably essential building blocks within the complex humic acid molecules. Analyses of preparations of melanoidin and glucosamine show high carbon, oxygen, and nitrogen contents, similar to that of humic acids (see Table 2).

An interesting aspect of the first stages of the bacterial degradation of carbohydrate chains is the sudden drop in the oxygen content of the fresh organic matter from about 43% in wood and 41% in fresh peat to about 26 to 32 percent in the humic acid concentrates and to 32 to 22 percent in lignitic soft coal and subbituminous coal (see Table 3).

The organic plant matter is mainly a mixture of cellulose (49% O) and lignin (33% O). The composition varies depending on the plant species. Lignin usually amounts to 10 to 35% of the total dry weight, and the cellulose to 20 to 55 weight percent.[48,18,49,50] Sugars, derived from the cellulose, such as glucose and cellobiose, have 51-53% O. The first steps of enzymatic decomposition (oxidation) of cellulose seem therefore to somewhat increase the oxygen content of the rotting plant matter, then lower it abruptly by some 25 percent relative to the original composition. This step must be accompanied by considerable evolution of water and carbon dioxide.

The enzymatic hydrolysis of the lignin proceeds more slowly, but seems to involve a similar sequence, consisting of initial oxygen loss due to degradation of lignin (~ 33 %) to coniferyl alcohol (26.64 % O) or similar compounds. Then an

Table 2

Composition of humic acids, melanoidin and glucosamine*

	C	H	N	O	
Humic Acids:					
From peat	61.78	4.28	1.72	32.22**	Drozdova
From chernozem	57.32	4.25	4.04	34.34**	
From average podzol soil	57.94	5.79	4.86	31.41**	
From humified plant deposits	57.57	6.35	7.64	28.48**	
Melanoidin from glucosamine	52.51	4.99	4.5	38.0	
Melanoidin from glucosamine and glycine	52.8	5.78	8.96	32.46	
Humic acid from straw	53.74	5.19	3.44	37.63	Flaig
Humic acid from chernozem	58.9	3.3	2.5	34.2	
Humic acid from lignitic soft coal, 2 samples	61.2	4.1	~0.6	34.8	
Humic acid from subbituminous coal, 7 samples	69.2	4.5	---	26.3	

* from Manskaya and Drozdova, 1968, pp 42 and 76[18] and humic acids from Flaig, 1966, p. 65[4]

** by difference

Table 3

Composition of Some Carbohydrates, Lignin, Wood, Peat, and Coalification Products

	Weight Percent			
	C	H	O	N
Glucose $C_6H_{12}O_6$	40.00	6.72	53.29	
Sucrose $C_{12}H_{22}O_{11}$	42.10	6.48	51.42	
Cellobiose $C_{12}H_{22}O_{11}$	42.10	6.48	51.42	
Cellulose $(C_6H_{10}O_5)_n$	44.45	6.22	49.34	
Wood[16]	49.65	6.23	43.20	0.92
Peat[11] *	51.13 → 58.48	6.05 → 5.64	40.99 → 33.54	1.83 → 2.34
Bjorkman Lignin[4] (fresh straw)	60.68	5.79	33.11	0.4
Lignitic soft coal 2 samples[4]	63.2	4.5	32.3	1.
Subbituminous coal, 10 samples[4]	73.2	5.3	21.5	0.8
Low rank bituminous coal[11]	79	5.45	14	1.55
Bituminous coal, 5 samples[4]	84.3	5.3	10.4	0.8
Medium rank bituminous coal[11]	85-88	5-5.2	7-5	1 - 1.75
High rank bituminous coal[11]	91.7	4.5	2.2	1.6
Semianthracite coal[11]	92.3	4.2	2.0	1.5
Anthracite[11]	93-97	3.7-0.6	1.9-1.8	1.4-0.6

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* German peats, variation in composition with increasing maturity, from Swain, p. 339, 1970[11].

increase is noted due to oxidation (hydroxylation) to vanillin (31.55% O) and vanillic acid (38.06% O), and through decarboxylation to dimethoxybenzoquinone (38.06 % O). Further oxidation (decarboxylation) reduces the oxygen content due to the evolution of carbon dioxide, thus p-hydroxybenzoic acid (34.75 %O) is formed and p-benzoquinone (29.60% O). Aromatization of the quinones leads to a further drop in oxygen content, e.g., Emodin (29.60% O, hydroxyanthraquinone found in nature[5]), and alizarin (26.64% O), see Table 1. It may be of interest to note that humic acids extracted by Flaig[4] from subbituminous coals seem to have a nearly identical composition (Table 1), and little or no nitrogen. It also should be noted that the natural oxidative degradation of chitin (39.37% O) to glucosamine (44.65% O) to melanoidins (31-35% O)[18] seems to show a pattern of an initial increase, then an abrupt drop of the oxygen content by some 20% relative, followed by a more prolonged and gradual removal of oxygen from the system, similar to the degradation of cellulose and lignin. If these processes of enzymatic decomposition of organic matter do occur simultaneously, the bulk oxygen content variations in the decaying matter may serve as a good indicator of the respective stages of humification and coalification and thus of the rank of coal. This is shown in Table 3, which is a compilation of analyses of lignite to anthracite taken from numerous sources. In this table comparison is made with compositions of wood, fresh lignin, and some carbohydrates to emphasize the whole spectrum of oxygen depletion during the coalification processes.

In summary, the humification process may be considered as the first step in coalification of plant matter. It starts by rapid decomposition of the cellulose and by enzymatic degradation of the lignin of the rotting plant substance to form C_6-C_3 or C_6-C_1 compounds. These lose methoxyl groups and carboxyl groups and can form hydroquinones which may polymerize and combine, forming humic acids.[5,10,11,12,13,14] Degradation may proceed also to aliphatic compounds which again serve as energy supply for the microorganisms. Most of the reactions seem to lead to benzoquinones which dimerize and polymerize further, causing an increase in aromatization with age (see Table 1), and under more anaerobic conditions later during coalification. During the later stages of the process of humification when conditions become anaerobic, melanoidin and glucosamin compounds form and nitrogen fixation occurs when decomposing nitrogen compounds, such as protein-derived α-amino acids react with the dimerized and polymerized aromatics. This explains the presence of about 1 to 3.5 percent nitrogen in humic acid concentrates,[4] lignin, lignite, subbituminous and bituminous coal (see Table 3). The fixation of nitrogen also results in further reduction of carbon in humic substance during the later stages of humification. Further coalification of buried humified strata of decomposed organic material causes reduction as the methoxyl and oxygen group content decreases, and CO and CO_2 gases and H_2O evolve and gradual dehydration occurs. This process leads to lignite, subbituminous coal, bituminous coal, coal and finally anthracite. Increasing pressure, temperature, and time are obviously critical factors in the formation of coal[8,9] (see Table 3).

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