

CATALYTIC SYNTHESIS OF CHEMICALS FROM COAL

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While the oil needed for the production of chemicals in the United States is only a small percentage of the total oil consumed, the manufacture and use of chemicals from oil has a tremendous impact on the economy of the country. A recent study by A. D. Little, Inc. (1) showed that the impact of a 15% decline in production of organic chemicals could result via a "multiplier" effect, in a loss of over 1,700,000 jobs and a \$65-70 billion loss in the production value of goods. One need only look around to see how pervasive and ubiquitous chemicals from oil are in our everyday life: our clothes, our automobile's interiors, all sorts of polymers, plastics, drugs and medicinals, tires, tubing (pipelines), building materials -- the list is very long and very important to the economic health and growth of the economy.

Another recent study (2) estimates that by the year 2000, perhaps as much as 42% of the projected U. S. petroleum and natural gas production (23.7 million barrels oil equivalent per day) will be needed to supply the projected U. S. demand for petrochemical feedstocks. Even if this projection is too high, there will still be a very large increase in the demand for petrochemicals. At present, only about 10% of our domestic oil and gas production would be needed to supply petrochemicals. But, the projected growth for petrochemicals is so large, Sherwin and Fuchs estimate that petrochemical demand in the year 2000 will require 10.3 million barrels oil equivalent per day. This is approximately equal to all of our present domestic production of crude oil.

To meet this demand for petrochemicals in the year 2000, it will be necessary to utilize non-conventional hydrocarbon sources, such as coal and shale oil, for the production of petrochemical feedstocks. Coal, which comprises over 80% of the known recoverable fossil fuel reserves in the United States, is the most likely candidate as the "chemical resource material of the future." Figure 1, part of which is from their paper, shows how primary and intermediate organic feedstocks can be produced starting from coal.

This paper is concerned chiefly with the catalytic synthesis of chemicals from coal. While it is not likely that coal or any other new source will be used for chemicals for possibly five or ten years (extensive manufacture of chemicals from coal, except via high-temperature carbonization, will not occur for at least a decade), this paper endeavors to point out the routes to chemicals from coal, emphasizing those that involve the use of catalysts.

The "Structure" of Coal

We have a good idea, after a vast amount of research, of the structures of the myriads of compounds found in crude petroleum. Coals, however, differ more widely in composition than do petroleum crudes. In addition, the physical disadvantages of coal relative to petroleum are that it is solid and has a high ash content, which ranges from a few percent to 20% or more. It will be of help to understand the constitution of coal; in this way, we will know how to process it to chemicals. What is surprising is that coal, in spite of its complexity, often behaves as you would expect an aromatic or hydroaromatic organic compound to behave.

Figure 1. Production of Primary and Intermediate Organic Chemicals From Coal

GASIFICATION: Synthesis gas, $H_2 + CO \rightarrow$ Methanol \rightarrow Ethanol; Acetic Acid; Olefins, Paraffins, Aromatics
 \rightarrow Fischer-Tropsch synthesis of hydrocarbons and oxygenates

\rightarrow Ethylene glycol + other polyols

\rightarrow By-product Tar \rightarrow Benzene, Toluene, Xylenes

LIQUEFACTION: Syncrude \rightarrow Processed to Chemical Feedstocks

Aromatics from Hydrocarbonization

OXIDATION: Benzenepolycarboxylic Acids ("Coal Acids") \rightarrow Phthalic, Isophthalic and Terephthalic Acids

CARBONIZATION: High-temperature carbonization \rightarrow Aromatics, Phenols, Tar Bases

Low-temperature carbonization \rightarrow Aromatics, Phenols, Olefins

ACETYLENE from
Calcium Carbide
or Plasma Arc:

$C_2H_2 \rightarrow$ Chloroethylenes; Vinyl chloride; Vinyl acetate; Acrylonitrile

We know enough technology to be able to obtain chemicals from almost any carbon-containing material, from wood to carbon dioxide, and everything in between. But the nature of the substrate, in this case coal, will strongly influence its treatment to yield chemicals. So let us first look at the "structure" of coal.

There has been a very large effort made over many years to determine the structure of coal. The full weight of the traditional method; elemental analyses, qualitative chemical tests and degradative reactions, plus modern tools of instrumental analysis have been turned loose on coal. An examination of the literature reveals, however, that most of this attack has been aimed only at the constitution of bituminous coals, usually of 81 to 86% carbon on a moisture and ash-free (maf) basis. Very little is known about the structure of subbituminous coals or of lignite, although these constitute the major coal reserves of the United States. It is interesting to note that, while about three-quarters of our coal reserves are west of the Mississippi (mostly lower rank coals, subbituminous and lignite), about 70% of the coal presently used in the United States comes from the higher rank bituminous coals found east of the Mississippi.

Given (3) has developed a structural model which has the elementary composition of a vitrain of a carbon content of 82%. This model is a convenient visualization of certain analytical data. It is useful, especially for discussion purposes, and I would have hoped that the same type of convenient visualization could be done for higher and especially lower ranks of coal. However, I tend not to use the type of model discussed above. Instead, after working with coal for some time, I find myself choosing what amounts to a representative small portion of such a model for chemical guidance. Four ranks of coal are usefully distinguished in this way, with coals of intermediate rank having intermediate structure. I will only mention the fifth rank, anthracite. Anthracite has a large condensed polynuclear structure, usually contains little ash, and has a low oxygen and sulfur content. It makes an excellent fuel and is in great demand for combustion and metallurgical purposes. But it is an expensive coal, and found only in certain areas of the East. Because of its structure, it is not easily processed to chemicals; it can be gasified, but it is almost impossible to convert into a liquid.

The structures shown in Figures 2-5 are not coal models. But they represent, to me at least, a convenient way of cataloging the chemical structures so that the reactions of the various ranks of coals can be understood, at least in a preliminary way. They are useful as an aid to memory and a basis for prediction; they are, in short, frames of reference. The four ranks of coals given in Figures 2-5 are a low-volatile bituminous coal (coal A), a high-volatile A bituminous coal (coal B), a subbituminous coal (coal C) and a lignite (coal D). The analytical data given for each coal are the results of an analysis of an actual coal sample. It is possible to discuss a number of reactions of coal in terms of these representations. The structures help to understand the way the ranks of coal react under different conditions; we can also use some of the reactions to support or attack the validity of these structures. At various points in this paper, I shall refer back to these representations for the different ranks of coal.

Gasification of Coal to Synthesis Gas and Production of Chemicals from Syngas

There are five general routes available to convert coal to chemicals. The first that I wish to discuss is the production of chemicals from synthesis gas -- that is, mixtures of hydrogen and carbon monoxide. These gases are produced by the gasification of coal. After leaving the gasifier, the syngas mixture will be cleaned, catalytically shifted via the water gas shift reaction to the desired hydrogen-to-carbon monoxide ratio, and the carbon dioxide and hydrogen sulfide (and other sulfur compounds) removed to the levels needed for further catalytic reactions.

Pocahontas No. 3 Bed, W. Va. (lvb)

	<u>dry</u>	<u>maf</u>
C	83.8	90.7
H	4.2	4.6
O	2.6	2.8
N	1.2	1.3
S	0.6	0.6
Ash	7.6	-
Volatile Matter	17.3	18.7
Btu per pound		15,660

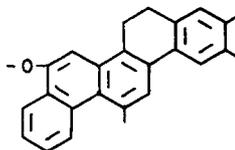


Figure 2 - COAL A
Low-volatile
bituminous

Pittsburgh Bed (hvab)

	<u>dry</u>	<u>maf</u>
C	77.1	84.2
H	5.1	5.6
O	6.4	6.9
N	1.5	1.6
S	1.5	1.7
Ash	8.4	-
Volatile matter	36.5	39.9
Btu per pound		15,040

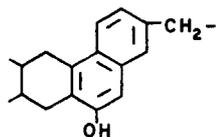


Figure 3 - COAL B
High-volatile A
bituminous

Mammoth Bed, Wyo. (Subbituminous A)

	<u>dry</u>	<u>maf</u>
C	72.9	76.7
H	5.3	5.6
O	14.8	15.5
N	1.2	1.3
S	0.9	0.9
Ash	4.9	-
Volatile Matter	41.5	43.6
Btu per pound		13,490

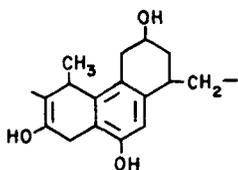


Figure 4.-COAL C
Subbituminous coal

Lignite, Beulah-Zap Bed, N. D.

	<u>dry</u>	<u>maf</u>
C	64.5	72.6
H	4.3	4.9
O	18.0	20.2
N	1.0	1.1
S	1.1	1.2
Ash	11.1	-
Volatile Matter	40.8	45.9
Btu per pound		12,150

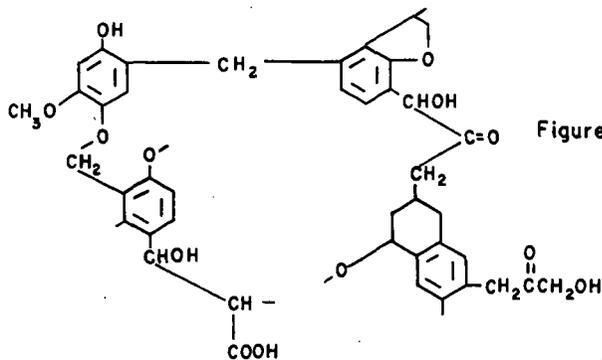


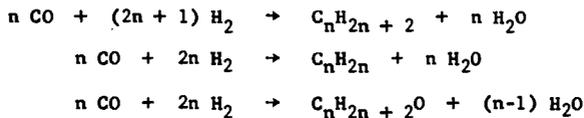
Figure 5.-COAL D
Lignite

One large-scale, commercially proven route to take from here is the production of methanol. The present U. S. production of methanol is about 10,000 tons/day, using almost entirely syngas obtained by the steam reforming of methane over a nickel catalyst. A zinc chromite catalyst is used for methanol synthesis $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$ at pressures near 4000 psi and temperatures near 350°C, or a copper-zinc oxide-on-alumina catalyst is used at lower pressures (800 to 1500 psi) and temperatures near 250°C (4). Given a clean synthesis gas derived from coal, it is anticipated that the large scale production of methanol from coal can be done in this way.

Because of the large production that will be called for as methanol produced from coal becomes necessary as a chemical feedstock, two improvements in methanol catalysts would be desirable. Both are being studied by various investigators. Zinc chromite and (especially) copper-zinc oxide-on-alumina are sensitive to sulfur poisoning. A methanol catalyst more tolerant to sulfur compounds in the feed gas would be very useful with coal-derived synthesis gas.

The methanol synthesis is a highly exothermic reaction. Studies are being made using a three-phase reactor where synthesis gas contacts the catalyst in the presence of an inert liquid which serves to remove the heat of reaction (5). In this way, it is hoped that larger conversions per pass could be obtained than in the conventional gas-solid fixed bed reactor. Also, by varying the liquid in this reactor, it may be possible to produce some useful derivative of methanol from syngas directly.

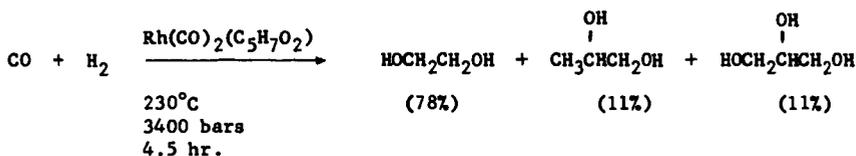
Another source of chemicals from coal-derived synthesis gas is the Fischer-Tropsch (FT) synthesis. This is being carried out in a small-scale commercial plant (5000 barrels/day) at SASOL in South Africa, mainly to produce fuels. In the FT synthesis as done at SASOL, $\text{H}_2 + \text{CO}$ mixtures react over iron catalysts to produce mixtures of hydrocarbons and oxygenates. The reactions are



In the plant at SASOL, two types of reactors are used. One is a fixed bed reactor containing an iron catalyst and operates near 230°C and at pressures near 400 psi. The second is a "Synthol" entrained bed reactor operating at 330°C and 350 psi and uses a different type of iron catalyst specifically designed for this type of operation. As can be seen in Table 1, there is a great deal of difference in the product distribution from the different reactors (6). It is of interest to note that in their planned ten-fold expansion, SASOL intends to use only entrained bed reactors.

As shown by the data in Table 1, the choice of catalyst and operating conditions profoundly affects the product distribution in the FT synthesis. As a further example of this, in preliminary work at the Pittsburgh Energy Research Center of ERDA using an iron-on-silica-alumina catalyst, almost all of the hydrocarbons formed from syngas at 320°C were in the C_1 to C_4 range, primarily paraffins (7).

Ethylene glycol is another chemical which can be obtained by reacting equimolar amounts of carbon monoxide and hydrogen in the presence of rhodium dicarbonyl-acetylacetonate (8).



The polyols comprise 64% of the oxygenated products; the balance consists of methanol, water, and methyl formate. There is some evidence (9) that the pressure needed for this reaction can be lowered to at least 400 atmospheres, which would be a considerable improvement.

TABLE 1. Product distribution at SASOL from fixed bed and Synthol Fischer-Tropsch synthesis on iron catalysts

	Fixed bed reactor		Synthol reactor	
	Wt pct total	Wt pct olefins	Wt pct total	Wt pct olefins
Temperature, °C	220-240		320-340	
Pressure, bars	26		22	
H ₂ /CO ratio in feed gas	1.7:1		3:1	
Primary products	Wt pct total	Wt pct olefins	Wt pct total	Wt pct olefins
C ₁	7.8	--	13.1	--
C ₂	3.2	23	10.2	43
C ₃	6.1	64	16.2	79
C ₄	4.9	51	13.2	76
C ₅ -C ₁₁	24.8	50	33.4	70 ^a
C ₁₂ -C ₂₀	14.7	40	5.1	60 ^a
> C ₂₀	36.2	~ 15	--	--
Alcohols, ketones .	2.3	--	7.8	--
Acids	--	--	1.0	--

^a - These fractions also contain appreciable amounts of aromatic compounds.

Mobil Research and Development Corporation under contract from ERDA is developing a catalytic process for converting methanol to gasoline. This will be a two-step process, in which methanol is first catalytically dehydrated to dimethyl ether. In the second step, over a zeolite catalyst, dimethyl ether is converted to hydrocarbons. Most of these hydrocarbons are in the C₅+ range and the mixture contains appreciable quantities of aromatics. At present, the process is being optimized for gasoline production, but could conceivably be used as a means of producing chemical feedstocks starting with coal-derived methanol.

The reaction of methanol with carbon monoxide to form acetic acid is homogeneously catalyzed by either cobaltous iodide or an iodide-promoted rhodium carbonyl complex. The latter catalyst is more efficient since it allows the reaction to proceed at low pressures (200 psig), a temperature of 175°C, and a very high selectivity of methanol to acetic acid of 99% (10). The authors of this review paper state that "As coal replaces natural gas and petroleum as a source of petrochemical raw materials, the most important building block is expected to be synthesis gas... the methanol carbonylation route to acetic acid should enjoy an enviable raw material position in the transition from natural gas and petroleum to coal as a petrochemical raw material base."

The chemistry of this reaction has been studied in detail, and the reaction is believed to occur via the following steps. Methanol and hydrogen iodide react reversibly to form methyl iodide



which then reacts with the metal carbonyl, probably through oxidative addition, to form a methyl carbonyl complex



where M = Co or Rh and L is a ligand other than CO. The next step is the CO "insertion reaction"



This last complex then reacts with water to form CH_3COOH , HI, and regenerates the original complex, $\text{M}(\text{CO})_x\text{L}_y$.

The homologation of methanol to ethanol using synthesis gas and $\text{Co}_2(\text{CO})_8$ as the catalyst was first reported in 1951 (11).

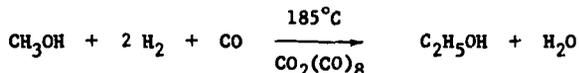


Table 2 gives reaction conditions and products formed in a batch autoclave experiment where 76% of the starting methanol had reacted. Work at the Pittsburgh Energy Research Center of ERDA is under way to improve the yields of this reaction (12). Gas chromatographic analysis of the reaction mixture shows that it can contain as many as 25 compounds. This indicates the need to find catalysts or conditions to make the reaction more selective; however, ethanol is the major constituent of the product, and would thus be a source of ethylene, based on coal-derived methanol as the raw material.

Chemical Refining of Coal Liquefaction Products

"Syncrude" obtained by the catalytic liquefaction (and hydrodesulfurization) of coal will also serve as a source of raw materials for the chemical industry. A review of coal liquefaction processes that can now be seriously considered as providing a supply of petrochemical feedstocks has been recently prepared (13). The processes can be divided into the following categories:

- Hydroliquefaction -- Solvent Refined Coal (SRC)
- Catalytic hydroliquefaction -- H-Coal, SYNTHOIL Process
- Pyrolysis -- COED
- Extraction (and hydrotreating) -- Cresap type plant
- Indirect -- Fischer-Tropsch (SASOL)

Products from these processes are broken down by boiling range (much in the way that petroleum fuels are considered) and, within each boiling range, hydrocarbon type analyses are given; light constituents are identified. One very important point that is mentioned is that coal liquids differ in their aromatic, naphthene and cycloparaffin content from similar petroleum fractions.

TABLE 2. Products from reaction of methanol with $H_2 + CO$ at $185^\circ C$ and 4000 psi using $Co_2(CO)_8$ as the catalyst

	<u>Yields as percent of converted methanol</u>
Methyl formate	2.0
Methyl acetate	9.0
Ethyl alcohol	38.8
Ethyl acetate	6.3
Propyl alcohol	4.7
Propyl acetate	0.1
Butyl alcohol	0.9
Methane	<u>8.5</u>
Total	70.3
Water	90.8

Several specific petrochemicals which could be produced from these coal derived liquids are:

- Olefins, via steam cracking;
- BTX and naphthalene, recovered directly and via hydrocracking of heavy oils and extraction;
- Phenols, recovered directly; and
- Aromatic amines and N-bases, recovered directly.

O'Hara et al. present one possible scenario based on (economic) incentives to produce alternate petrochemical feedstocks from coal leading to the construction of a number of plants. This scenario requires facilities to process 100,000 tons per day (TPD) of coal in 1985, 270,000 TPD in 1990 and 570,000 TPD in 1995. They also present a conceptual scheme depicting a combination of process steps which include coking, hydrocracking, hydrodesulfurization, catalytic naphtha reforming, aromatics extraction, extraction and fractionation, and gas recovery and fractionation.

Table 3, taken from their paper, lists the potential for production of petrochemical feedstocks from coal, based on their assumptions in their studies. This estimate gives a potential supply of ethylene feedstock ranging from 20% in 1985 to 115% in 1995 of that used in 1974. Similarly, for naphtha feedstock, the range is from 82% (1985) to 470% (1995). Benzene production via coal liquefaction processes could range from 9% to 50% of 1974 volume. The authors summarize by stating that a significant portion of our petrochemical needs can be produced from coal liquefaction processes and that the potential should be further evaluated, and the economics should be studied in detail.

Chemicals by Oxidation of Coal to Benzenepolycarboxylic Acids and Their Selective Decarboxylation to Phthalic Acids

When coal is carefully oxidized, a mixture consisting largely of aromatic acids is produced. Two methods of oxidation have shown most promise, controlled air oxidation in the presence of alkali (14) and oxidation by nitric acid (15); the first method uses inexpensive oxidizing agents and is preferred. The oxidations were originally carried out to obtain structural information by examination of the fragments produced by oxidative cleavage of the large coal molecules.

TABLE 3. Examples of potential for production of petrochemical feedstocks from coal

Feedstock	1985		1990		1995	
	Millions of pounds per year	Percent of 1974 consumption	Millions of pounds per year	Percent of 1974 consumption	Millions of pounds per year	Percent of 1974 consumption
Ethane	2400	15	6500	40	13,700	90
Propane + LPG	3100	20	8300	55	17,600	115
Naphtha (Raffinate)	4500	80	12,100	220	25,500	470
Benzene	1000	9	2800	25	6000	50
Toluene	2800	40	7600	110	16,000	235
Xylenes	2100	45	5600	125	11,900	265

All aromatic compounds from toluene on up, on chemical oxidation, eventually yield benzenecarboxylic acids, which are then stable to further oxidation. Thus, toluene yields benzoic acid, p-xylene yields terephthalic acid, tetralin or naphthalene yield phthalic acid and anthracene yields pyromellitic acid.

Oxidative work has been used to show that coal has an essentially benzenoid structure. In going from coal structures D to A (Figures 2-5), the aromatic nature of the coal shows progressive development during natural maturing. It is not surprising that the ultimate yield of benzenepolycarboxylic acids (BPCA) is a function of the molecular structure of the coal. Coal A, a low-volatile bituminous coal with its highly aromatic structure containing some hydroaromatic linkages, would probably give the best yield of BPCA. Anthracite, with even more condensed polynuclear aromatic rings, would oxidize with greater difficulty to give a larger yield of mellitic acid (benzenhexacarboxylic acid). Coal B should oxidize at a greater rate than coal A with perhaps a lower yield of BPCA; aromatic rings containing phenolic groups tend to oxidize to quinones and then cleave. Coals C and D are more highly oxygenated, should oxidize rapidly but should not give acids with many carboxylic acid groups. See Table 4.

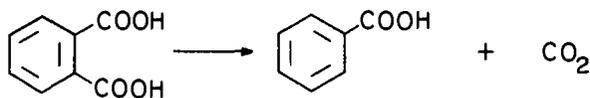
TABLE 4. Distribution of benzenepolycarboxylic acids from oxidation of coals with air and alkali

Percent carbon in coal, maf	Acids, percent			
	Tri	Tetra	Penta	Hexa
84	3	9	5	5
88	6	12	8	7
91	4	9	8	8
92	4	11	10	12
94.5	1	5	7	17

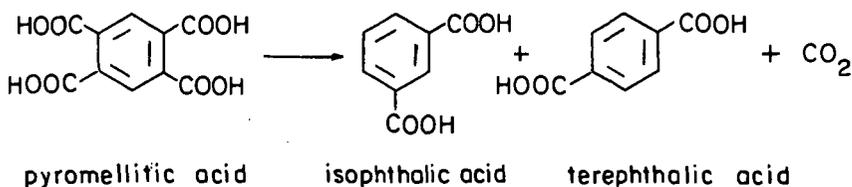
The product from the oxidation of coal with air and alkali was interesting enough for a large chemical company to do bench-scale work on oxidizing coal to coal acids (16). The product of this controlled air oxidation of a 90% carbon coal (coal A) consisted of a mixture of benzenepolycarboxylic acids (about 50% by weight of the coal) and other higher molecular weight, oxygenated materials of unknown structure. Potential uses were found for the whole mixture, but the crude product could not compete against the relatively pure compounds or mixtures usually demanded by our present sophisticated chemical industry. The possibility of using the benzenecarboxylic acids, once they had been separated from the rest of this material, has not been adequately investigated.

Though commercialization did not occur, interest in coal acids has remained high, and workers in laboratories scattered around the world have published on this topic in recent years (15-23). Analyses indicate that these coal acid mixtures may contain up to 95% benzenepolycarboxylic acid (BPCA), ranging all the way from phthalic acid to mellitic acid. Conversion of this complex mixture to a simple mixture with but few separable components would make oxidation of coal and its derivatives a promising route to valuable chemicals. This second step, the conversion of coal acids to a mixture rich in isophthalic and terephthalic acids, is feasible as a result of a catalytic reaction discovered at the U. S. Bureau of Mines (24).

Initially, it was found that when phthalic anhydride or phthalic acid was heated to 200°C in the presence of $\text{Co}_2(\text{CO})_8$ and under pressure of synthesis gas ($\text{H}_2 + \text{CO}$), it was converted quantitatively to benzoic acid.



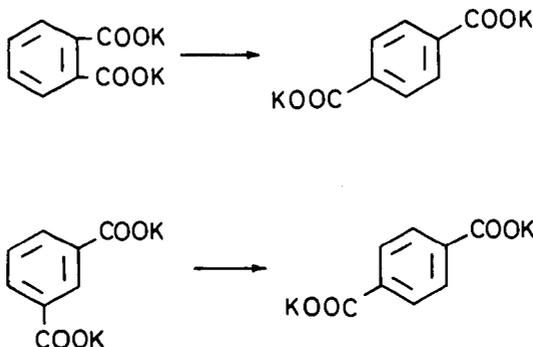
This contrasts with other decarboxylation procedures which yield only benzene from phthalic anhydride or acid. Further experiments established that benzenepoly-carboxylic acids, up to mellitic acid, could all be selectively decarboxylated by this same method to yield principally iso- and terephthalic acids, as shown for pyromellitic acid.



The decarboxylation occurs whenever there are two carboxyl groups on adjacent aromatic carbon atoms.

This decarboxylation provides a way of converting the previously mentioned mixture of aromatic polycarboxylic acids into a simple mixture containing large and recoverable amounts of isophthalic and terephthalic acids (17), both of which have expanding markets at the present time. The present source of these acids is the xylene fraction obtained by dehydrocyclization of petroleum feedstocks. Demands for low-lead, high-octane gasoline may result in shortages of xylenes. This factor, coupled with the shortage of domestic petroleum, may encourage the move to coal-based chemicals. Improved catalysts, formed by substituting tertiary alkylphosphine ligands for one or two of the carbon monoxides in $\text{Co}_2(\text{CO})_8$, have been found for the decarboxylation. These catalysts are more stable and more easily recoverable than is the unsubstituted catalyst (17). The decarboxylation has been carried out in the laboratory on several mixtures of coal acids obtained by alkaline oxidation of a low-volatile bituminous coal (coal A). Conversions of the BPCA to isophthalic and terephthalic acids have been high.

Another approach to the production of terephthalic acid from the BPCA is the Henkel Reaction, in which the dry potassium salts of the acids are heated to about 400°C in the presence of zinc or cadmium catalysts under 10 or more atmospheres of CO_2 .



Yields approaching 95% have been obtained on a large scale. The process has been used on an industrial scale in Japan to produce terephthalic acid.

It is obvious that the oxidation of coal to BPCA is noncatalytic. But the two processes for obtaining individual compounds from the complex mixture involve intriguing catalytic reactions which merit further study. A review of the production of chemicals by oxidation of coal has been recently published (25).

Chemicals from the Carbonization of Coal

The traditional route to chemicals from coal, and the one first used, is to extract and purify the chemicals contained in the tars obtained by the coking of coal. The process is usually called coal carbonization and is carried out at temperatures of about 900-1000°C. Almost any coal heated to these temperatures will give the same products and we can consider coal carbonization to essentially be noncatalytic, although coal contains over 70 elements, with Na, K, Ca, Cl, Si, Fe and Ti present in significant amounts. Carbonization has been and still is an important source of chemicals since almost 90 million tons of coal were transformed into coke in 1974. (It is the second most important use of coal.) The most important chemicals obtained from coking processes are aromatic compounds (benzene, toluene, xylenes, naphthalene, phenanthrene, anthracene, etc.), phenols, and tar bases.

While coke is ordinarily obtained by carbonizing coal at 900-1000°C (high-temperature carbonization), low-temperature carbonization, ordinarily carried out at around 500°C, yields more tar and is a possible source of aromatic chemicals and olefins. Low-temperature carbonization was practiced in Europe and in this country some years ago but is not important today. The inorganic compounds in coal present may have some catalytic effect in low-temperature carbonization.

Of the many publications on carbonization products, review articles by Karr (26), Weiler (27), and Muder (28) are particularly worthwhile.

Acetylene from Coal

Acetylene can be made from coal via calcium carbide or in a plasma arc (29), both of which are noncatalytic processes. The chemistry of acetylene and the routes to various chemicals that can be made from acetylene (vinyl chloride, chloroethylenes, vinyl acetate, acrylonitrile, acrylates, etc.) are well known.

References

- (1) United States Petrochemical Industry: Impact Analysis, Arthur D. Little, Inc., November 1973, 15 pages.
- (2) M. B. Sherwin and W. Fuchs, Paper presented at the 79 National AIChE Meeting, Houston, Texas, March 16-20, 1975.
- (3) P. H. Given, Fuel, 39 147 (1960).
- (4) C. L. Thomas, Catalytic Processes and Proven Catalysts, Academic Press, New York, 1970, Chapter 14.
- (5) D. Blum and M. B. Sherwin, Paper presented at Division of Fuel Chemistry, 170th National Meeting American Chemical Society, Chicago, Illinois, August 1975.
- (6) C. D. Frohning and B. Cornils, Hydrocarbon Processing, 53 (11) 143-146 (November 1974).
- (7) R. A. Diffenbach, Pittsburgh Energy Research Center, ERDA, unpublished data.
- (8) W. E. Walker and R. L. Pruett, Belgian Patent 793,086 to Union Carbide.
- (9) A. M. Brownstein in Chem. Eng. News, March 31, 1975, pages 10-11.
- (10) R. P. Lowry and A. Aguilo, Hydrocarbon Processing, 53 (11) 103-113 (November 1974).
- (11) I. Wender, R. A. Friedel, and M. Orchin, Science, 113 206-207 (1951).
- (12) I. Wender, S. J. Metlin, and B. D. Blaustein, Pittsburgh Energy Research Center, ERDA, unpublished data.
- (13) J. B. O'Hara, N. E. Jentz, and J. E. Papso, Paper presented at the 79th AIChE National Meeting, Houston, Texas, March 1975.
- (14) R. C. Smith, R. C. Tomarelli, and H. C. Howard, J. Am. Chem. Soc., 61, 2398 (1939).
- (15) A. Benning, Brennstoff-Chemie, 36 38 (1965).
- (16) W. L. Archer, R. S. Montgomery, K. B. Bozer, and J. G. Louch, Ind. Eng. Chem., 52 849 (1960).
- (17) S. Friedman, S. R. Harris, and I. Wender, Ind. Eng. Chem. Prod. Res. Dev., 9 347 (1970).

- (18) J. E. Germain and F. Valadon, Bull. Soc. Chem. Fr. 1960, 11.
- (19) Aranda V. Gomez and Beltran F. Gomez, Combustibles, 22, 147 (1962).
- (20) Y. Kamiya, Fuel, 40 149 (1961).
- (21) J. Biner and A. Wieloposki, Koks-Smola-Gaz., 14 159 (1969).
- (22) C. Caneva and S. Fumasoni, Il Calore, 1966, 3.
- (23) E. I. Rukin, Khim. Tverd. Topl. 1969, 70.
- (24) S. Friedman, M. L. Kaufman, and I. Wender, Ann. N. Y. Acad. Sci., 145, 141 (1967).
- (25) A. E. Bearse, J. L. Cox, and M. Hillman, Production of Chemicals by Oxidation of Coal. Battelle Energy Program Report, March 31, 1975, 45 pages.
- (26) C. Karr, Jr., Low-Temperature Tar. Chapter 13 in Chemistry of Coal Utilization - Supplementary Volume, H. H. Lowry, editor, Wiley, New York, 1963.
- (27) J. F. Weiler, High-Temperature Tar. Chapter 14 in Chemistry of Coal Utilization - Supplementary Volume, H. H. Lowry, editor, Wiley, New York, 1963.
- (28) R. Muder, Light-Oil and Other Products of Coal Carbonization. Chapter 15 in Chemistry of Coal Utilization - Supplementary Volume, H. H. Lowry, editor, Wiley, New York, 1963.
- (29) R. Gannon and V. Krukonis, Final Report, Arc-Coal Process Development, Contract 14-01-0001-493, April 19, 1972, Office of Coal Research, Washington, D. C.