

# A Study of the Origin of Organic Pollutants in Fossil Fuel Production. Part I the Genesis and Origin

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### 中文摘要：

自從1970年能源危機以來，關於各種污染物的分析和鑑別的研究隨之成長起來，其中大部份是有關於無機物的。污染物和周遭生態環境的相互關係也被廣泛的討論。但是有關有機污染物生成和根源的文獻則極少。在此篇論文中，嘗試著以地質化學和石油化學的觀點來討論一般燃料油製程中所產生有機污染物的根源。其中，一些作者以往在油頁岩方面的研究心得也被引用。

### Abstracts:

Since the early 70's and the outbursts of the energy crises, there have been numerous research results pertaining to the analysis and identification of various pollutants, mostly inorganics. The properties of pollutants relating to their transport, retention, and interaction with the ecosystems of the environment have been studied widely. However, rarely can one find any published results dealing with the genesis and the origin of organic pollutants. In this paper, three objectives concerning with the sources of organic pollutants in fossil fuel production from the geochemical and petrochemical standpoints are discussed. The authors' experiences in the investigation of the nature of the nitrogenous pollutants from oil shale processes are also given as examples.

### I. Introduction:

Currently there are no indepth studies on the nature of organic pollutants from fossil fuel related processes. The difficulty is that this type of research

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requires an interdisciplinary approach from geology, biochemistry, microbiology, chemistry, and chemical and environmental engineering. The objectives of the following work are three-fold: (1) to determine where pollutant precursors are formed during the geochemical maturation processes of fossil fuel, (2) to understand the mechanisms of pollutants formation during fossil fuel processing, and (3) to correlate the classes of pollutants with their precursor molecules. This paper will thus provide the basic information needed to reduce treatment of organic pollutants produced from fossil fuels during processing and production.

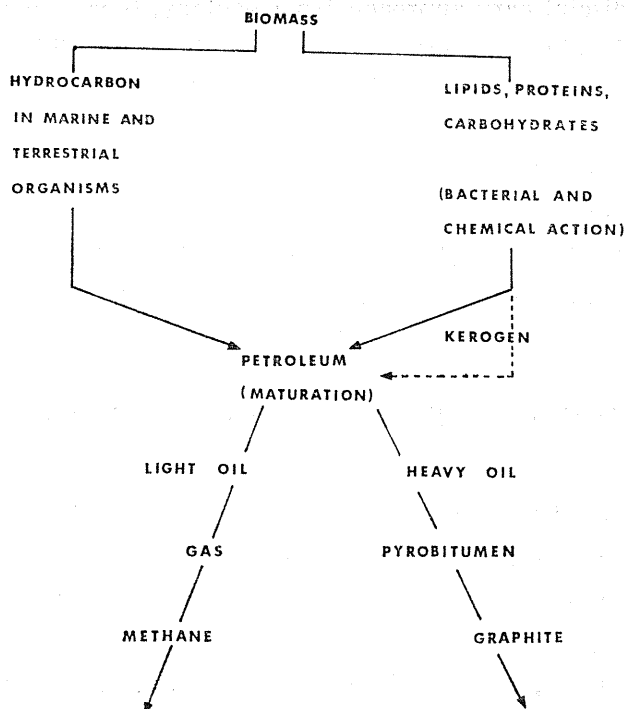
## II. Source Identification of pollutants during Diagenesis, Catagenesis and Metagenesis:

All kinds of fossil fuel originate from the biomass of bacteria, phytoplankton, and zooplankton, as well as higher plants throughout the biosphere. These organics are basically composed of similar chemical constituents, for example, lipid, carbohydrate, protein and lignin (in higher plant). Depending on the deposition environment, most of these biopolymers are transformed by chemical and microbial degradations, with the exception of lipid which may survive in the form of membrane, cuticle, spore, and pollen, etc., in the biological system.

These degraded components may undergo polymerization and condensation to form various types of geopolymers (e. g. humin) which strongly interacts with their host inorganic matrix in sediments. Kerogen is the end product of all crosslinked or grafted geopolymers, whereas there are three major development stages in the geochemical formation of a given fossil fuel:

- Stage 1. Diagenesis,
- Stage 2. Catagenesis,
- and Stage 3. Metagenesis,

In these generalized development stages, oil shale and may be regarded as the end product of stage 1, since they are virtually kerogens. Petroleum, however, is usually considered as at stage 2. Different forms of heavy oil, tar sand, asphalt, asphaltite, asphaltoid, and the extremely different gas and graphite deposits all belong to stage 3. The reason for this is that doing the maturation step (in stage 3), oil disproportionates at one end into simpler molecules, eg., methane, and at the other end, to graphite (Fig. 1) (1). Other intermediate products, including all the known forms of naturally occurring asphalt and bitumen, belong to stage 3.



**Figure 1. Formation of Petroleum Process.**

Fossil fuels of stage 1, namely oil shale and coal, require heat to decompose into bitumen or oil. For a stage 2 fossil fuel, the action of geochemical time of long duration under mild heat already has completed the kerogen decomposition process. In this manner one may conclude that effluents or undesirable by-products formed during this enormously long time have been lost. Therefore, there are fewer pollutants from a stage 2 fossil fuel than from stage 1. On the other hand, when a stage 1 fossil fuel is subjected to heat treatment, release of pollutants is unavoidable. Furthermore, during the diagenesis to catagenesis to metagenesis, chemical reactions take place throughout the whole sequence with simultaneous formation of new species. Among various products of a given stage of geochemical development also exist the pollutant precursors.

In general, pollutants are undesirable by-products or co-products from different stages of fossil fuel production and refining. They may be often grouped as:

- Type A. Phenolics
- Type B. polynuclear Aromatic Hydrocarbons
- Type C. Chlorinated Aromatics
- Type D. Nitrogenous Compounds

- Type E. Monoaromatics
- Type F. Sulfur Compounds
- Type G. Organometallics

The mechanism of formation for each type is not clear at this time and may be very different from each other. A better method for characterizing different organic pollutants is either a source identification or a mechanistic consideration. There are a few essential mechanisms:

- Mechanism 1. Molecules strictly derive from thermal decomposition of fossil fuel,
- Mechanism 2. Molecules generate by the reactants added to fossil fuel, e. g., hydrogen, solvent, nitrogen, oxygen, and catalysts, etc.,
- Mechanism 3. Molecules form by the interaction of simple species from products of Mechanism 2 with the thermally decomposed products. For instance, simple species could be ammonia, hydrogen sulfide, chlorine, etc.,
- Mechanism 4. Molecules are derived from the interaction between two decomposed species (from Mechanism 1) or from species chemically modified (from Mechanism 1 to 3).

The above mechanisms may be represented schematically as:



In equations 1 to 4,  $F_i$ =starting fossil fuel,  $R_i$ =conversion reactants,  $i=1\text{---}n$ . All reactions may be investigated under conditions close to the actual processing or production conditions.

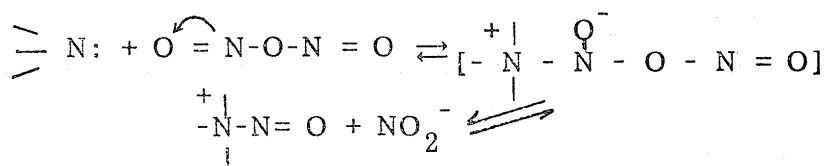
As an illustration of the above equations, species formed may be different even if the same starting fossil fuel is used. For example, in coal conversion, one of the most important factors one has to take into consideration is the conversion conditions, either those common to or those differing in gasification and liquefaction. The nitrogen component inherent to the coal material may form NO or NO<sub>2</sub> during gasification and ammonium during liquefaction. Therefore, at any given instance, the major difference for a given form of pollutant from another originates from the reducing or oxidizing condition. Even under reducing condition, amines or nitrogen-ring compounds may produce ammonium and hydrogen cyanide as long as no solvent is present. In the

presence of solvent remain intact. The extent of nitrogen conversion to ammonium (about 60% of nitrogen for gasification processes) is influenced by the processing temperature, pressure, and the amount of hydrogen present. Cyanide formation may also depend on the presence of solvent, as well as ammonia concentration. Hydrogen cyanide may form from ammonia. Thiocyanate may generate from hydrogen cyanide.

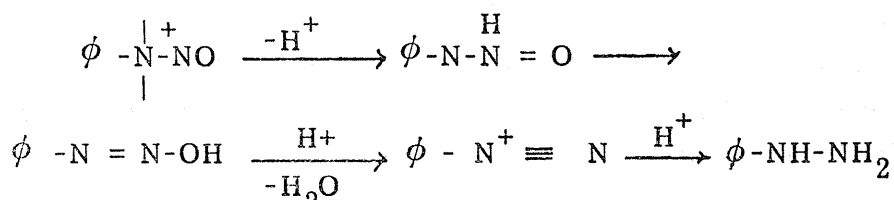
A large number of N-nitrosoamines were formed in the coal wastewater (2). Some phenylhydrazines were also observed. However, the N-nitrosoamine was only found in the gas condensates (3). It is possibly generated by oxidation, e. g., if nitrous acid or dinitrogen trioxide is available.



The presence of nitrous acid has been reported in coal gasification water. On contacting an amine, a N-nitrosoamine is accordingly formed.

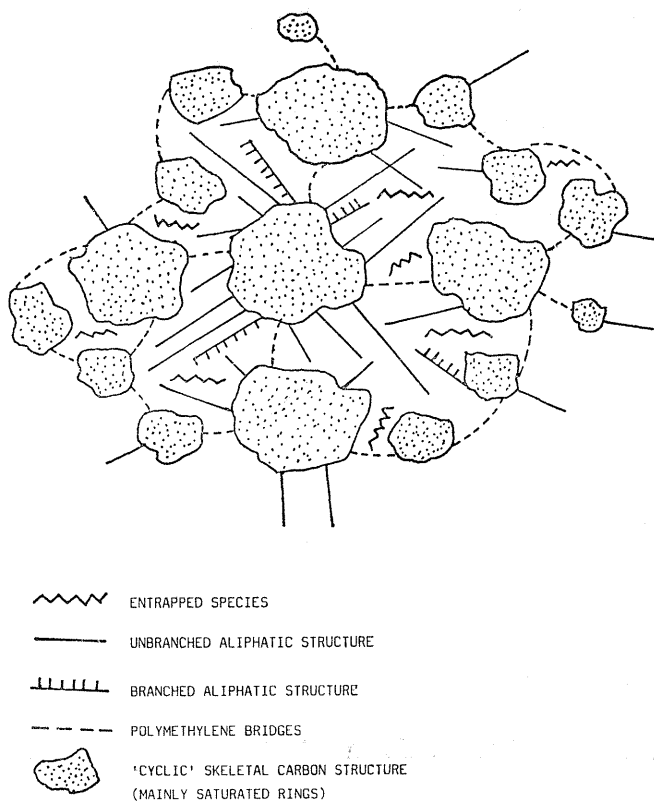


If the amine is secondary or tertiary with two alkyl substituents, then N-nitrosodialkylamine will form. However, if there is a primary amine, a hydrazine is anticipated with diazotic acid and diazonium salt as intermediates under acidic conditions.



This clearly suggests that the chemical composition of coal wastewater from gasification is different from that from liquefaction, since the pollutants contained are different.

When kerogen decomposes, fragments consisting of all the terpenes, i. e., sesquiterpenes, diterpenes, triterpenes and tetraterpenes as well as dipyrroles and tetrapyrroles (porphyrins) are released from the crosslinked bridges (4). The bridges are usually disulfide, ether, ester, heterocyclic, amide, and alkene, etc. in nature. The kerogen structure can be depicted by a 3-dimensional crosslinked gel network, shown in Fig. 2.



**Figure 2. A Hypothetic Structure of kerogen.**

The agents released upon pyrolysis or heat treatment of a macromolecule may lead to possible pollutants. Lignin is a good potential precursor for many of the phenolics, which exist in all fossil fuel waste effluents. Lignin is the main parent biomass from which coal is derived. Lignin commonly contains a lot of monomeric units, consisting of a single ring aromatic with side chains of three carbons and a hydroxyl group. Humic material may contain oxidatively degraded oligomers and dimers of the lignin monomeric unit. Dimers (Fig. 3) are present in coal. Under oxidative conditions, the monomeric unit from lignin may take a number of forms but under reducing conditions, the situation is anticipated to be simpler. No previous studies are available at present. They may be phenolic precursors.

Phenolics containing polyhydroxyl groups probably originate from tannins which are complex derivative of gallic acid and ellagic acid. They are present in fungi and algae as well as in higher plants.

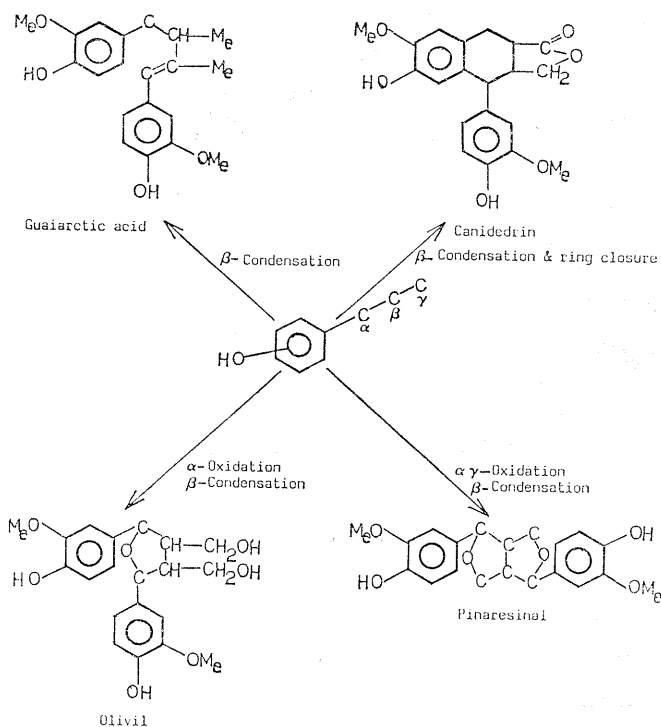
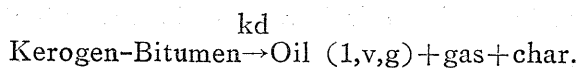


Figure 3. Dimeric Form of Lignin Units in Coals.

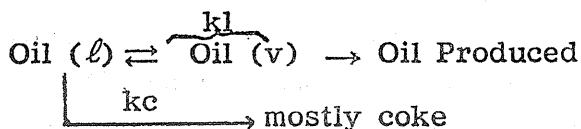
### III. Structure of Precursors Induced by Conditions of production and processing:

A set of chemical equations is sufficient to describe or characterize a particular production or processing method. For example, the LLNL shale oil cracking process (5) involves the following equations:

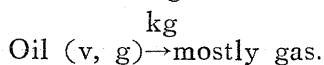
(a) Oil Generation:



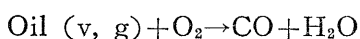
(b) Oil Coking



(c) Oil Cracking

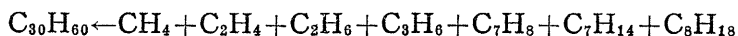


and (d) Oil Combustion

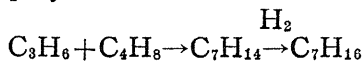


Conventional petroleum refining to gasoline involves one or a combination of multiple reactions. For example,

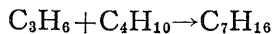
(a) Gas Oil Cracking



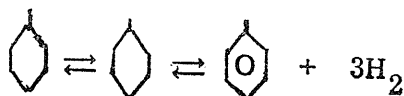
(b) polymerization



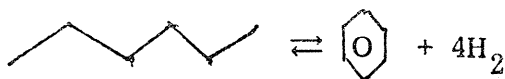
(c) Alkylation



(d) Reforming with Dehydroisomerization



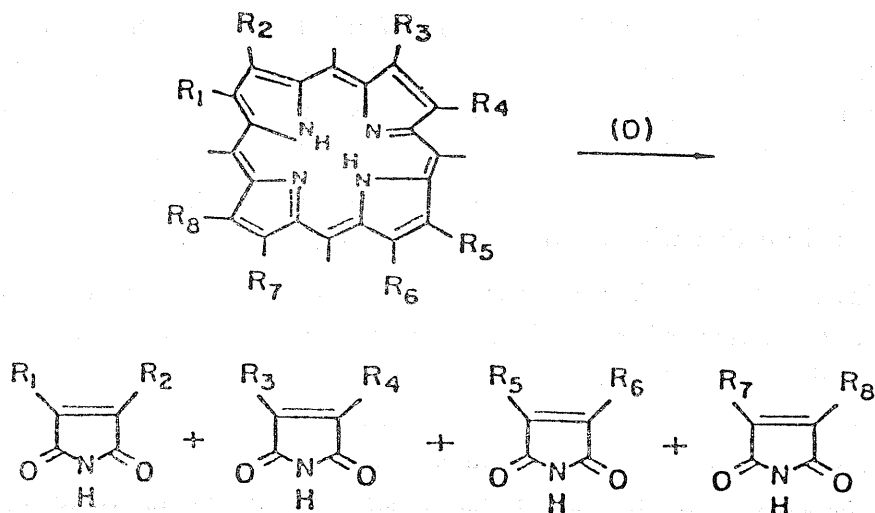
and (e) Reforming with Dehydrocyclization



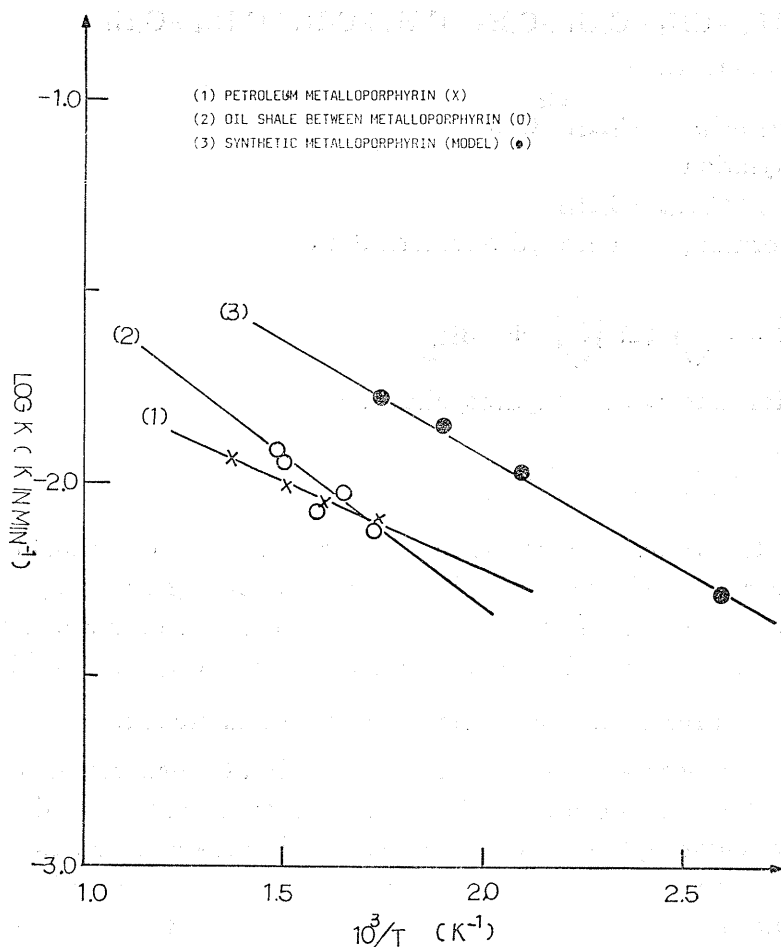
Besides the frequently occurring drastic reactions, one should not ignore the mild reactions which take place during weathing or storage. Chemical alterations of a number of compounds in bitumen are well known. For example, hydrogen disproportion and dehydration may occur at very mild conditions.

#### A. Stability of Precursors Under Heat, Pressure and Redox:

Jackson and Decora (6) employed chlorophyllin (which contains porphyrin) as a model for the precursors of nitrogenous compounds in shale oil. When this reduced chlorophyllin was pyrolyzed, there were similarities between the mononitrogen-containing molecular ions of its polysate and of the shale oil distillate. Both petroporphyrins and the porphyrins from Green River Oil shale bitumen decomposed quite rapidly with an activation energy of ca. 2.1 kcal/mole for petroleum and ca. 3.0 kcal/mole for oil shale (Fig. 4). Porphyrin is known to undergo oxidative degradation to form maleimides.







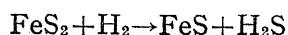
**Figure 4. Arrhenius Plot of Metallic Porphyrin Complex Degradation.**

This will explain the reason why it is extremely easy to isolate porphyrin in raw oil shale bitumen, but it is quite difficult to identify the porphyrins in shale oil. On the other hand, methyl ethyl maleimide has been identified in oil shale retort water, both ETIO and DPEP type of porphyrin yield one maleimide---methyl ethyl maleimide (7). In this instance, the precursor of methyl ethyl maleimide is porphyrin. It is also likely that maleimide is physiologically cative whereas the porphyrin is quite inert.

Products obtained after oxidation are different from those obtained under reduction. Oxidation of the substrate precursor usually leads to peroxide, epoxide, aldehyde, ketones, and many other oxygencontaining compounds, terminated with carbon dioxide. In contrast, the reaction products in highly reducing conditions are quite unstable, and tend to be highly active. Often, under a reductive environment, circumstances may be conducive to organom-

etallic formation e. g.,

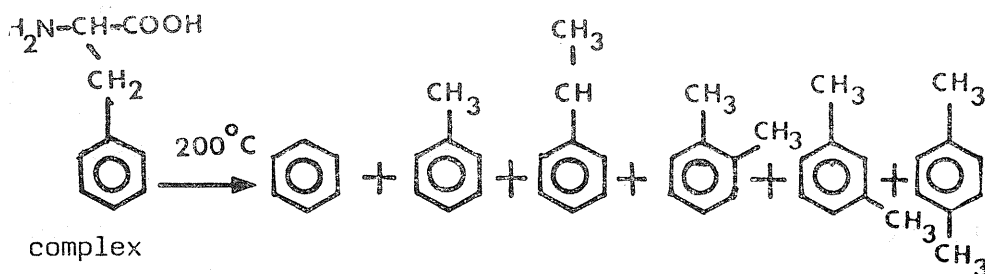
- a. ligands (electron donors such as N, S, O) can be exchanged by other organometallics or form new complexes with free metals
- b. presence of H at high pressures and high temperatures may induce the formation of hydrides
- c. high CO pressure employed may yield metal carbonyls
- d.  $\pi$ -systems present may lead to the formation of arene carbonyl organometallics
- e. reaction of anions bound to metal may leave metals in a relatively reactive stage, e. g.,



## B. Catalysis and Intermediates Regulated Reactions:

Industrial catalysis used for refining is summarized by Heinemann (8) to include the following: catalytic cracking, acid catalysis, Zeolite catalysis, dual function catalysis, hydrogenation catalysis, catalytic dehydrogenation, catalytic dealkylation, etc. For coal conversions, regardless of whether this process is gasification, or indirect or direct liquefaction, the use of catalysts is essential. In some refining schemes, the inherent minerals in the process can serve as an internal autocatalyst, such as the Aurobon process using the vanadium and sulfur in heavy oil for hydrodesulfurization. The effective species is  $\text{VSx}$ . The pyrrhotite ( $\text{FeSx}$ ) in coal liquids also exhibits a catalytic effect.

It is known that mica-type layer silicates such as smectite, can exchange their cations with organic compounds. In this manner a number of organic molecular structures are modified. For example a simple amine, e. g., phenylalanine can give a number of aromatics in the presence of clay, as demonstrated experimentally by Almon and John (9).



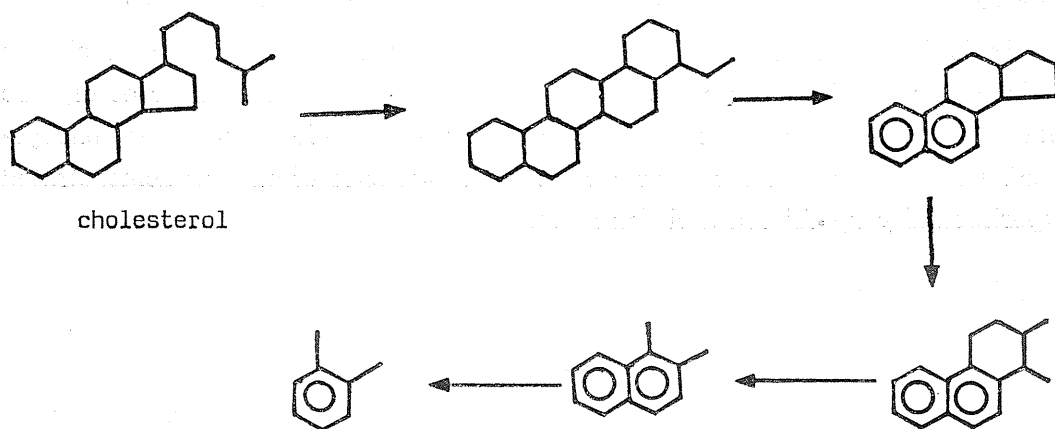
Ionic chloride was detected in many coal wastewaters. Chloride as well as bromide and fluoride have been detected in coals, e. g., 21 coals in the U. S.

contain 0.01–0.46% by weight chlorine (10). So far there have been no chlorine-containing organics isolated from coal decomposed products. Yet recently chlorine-containing aromatics have been identified in two coal wastewaters (2).

Both arsenic and selenium are present in shale oil and retort water. Manahan et al. (11) have spiked both organic and inorganic forms of selenium and arsenic in coal for coal pyrolysis studies (heated up to 1000°C). The results show a striking difference in volatilities between the inorganically and organically bound selenium and arsenic. Inorganic selenium spiked into coal was 81% volatile, whereas organic selenium was only 21% volatile. The corresponding values for arsenic were 48.4% and 7.5%, respectively. In line with the work of Filby (12), it is plausible that the inorganic forms of the elements are readily converted to volatile hydrides, whereas the organically bound elements are trapped by char and residue and retained with the coke. The mechanism and pathways of these reactions have not been thoroughly investigated.

#### C. Fate of Pollutants in Different Unit Operations:

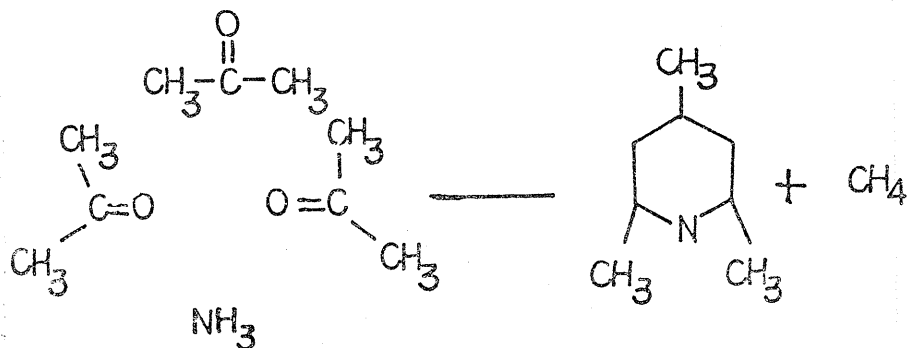
Engineering operations for refining syncrude usually are not one-step simple operations. For staged pyrolysis of coal there are different units of pyrolysis chambers; at least at three different temperature levels. Indeed, the average value of aromaticity increases. Even for petroleum, the gradual aromatization is observed under heat soaking:



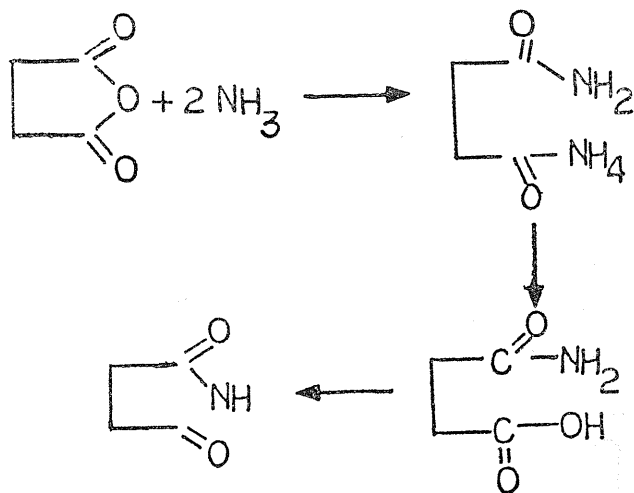
In SRC II, the preheater and dissolver may be at different conditions. (Fig. 5). The dissolver is under much stronger reducing conditions. In the presence of ammonia, other nitrogen species can be formed at elevated temperatures. Ammonia is known to react readily with oxygen-containing



aliphatics to form pyridines and picolines. For instance, paraaldehyde and ammonia in an autoclave at 200-250°C will form aldehyde collidine and 2-picoline; acetone and ammonia will form syn-collidine and methane.



There are a number of oxy-bearing functional compounds isolated in coal wastewater, including dicarboxylic acids (3). Amides or related species may be found.



#### IV. Conclusion:

The genesis and origin of organic pollutants obviously are dynamic. The formation and elimination hinges largely on the process variables. In order to be able to control their concentrations under a given set of conditions for a given process, characterization of the fundamental genesis of organic pollutants is issential.

Tentatively, it is concluded that there are multiple factors which influence the formation of the organic pollutants. For example, the origin of chlorine-containing aromatics present in coal wastewater is totally unknown. It is

hypothesized that inorganic chloride is converted to chlorine gas under process conditions, which then acts on aromatics to produce chlorinated aromatic hydrocarbons. However, it requires experimental verification.

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