Degradation of Refractory Organic Pollutants in Tar, Water and Soil Matrices by Ozone or Hydrogen Peroxide with Ultraviolet Light

By Liang-Jiun Uang

Thesis submitted to the faculty of graduate school of
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the degree of Master of Science in Environmental Science
(Toxics Option)

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APPROVE OF THESIS

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ABSTRACT

Title of Thesis: Degradation of Refractory Organic Pollutants in Tar, Water and Soil Matrices by Ozone or Hydrogen Peroxide with Ultraviolet Light

Name: Liang-Jiun Uang

Master of Science in Environmental Science
(Toxics Option)

Thesis directed by: Dr. J.W. Bozzelli

The objective of this research is to develop a method to degrade refractory Tar materials, higher molecular weight 3-5 ring Poly Aromatic Hydrocarbons (PAH's) or degrading these highly refractory PAH structures so that they are amenable to further treatment by biological or chemical methods. The process utilized to achieve this is to treat contaminated soils or tar materials with hydrogen peroxide or ozone plus ultraviolet light. Analysis of 27 specific PAH's was done by gas chromatograph (Flame Ionization Detection) for the reactants and products. The contaminated soil showed significantly lower levels of these PAH's after treatment.

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I. INTRODUCTION

The history of the detection, synthesis, and biological study of polycyclic aromatic hydrocarbons (PAH) is closely related to the establishment of the carcinogenicity of coal tar.(1) These which are referred to as "toxic" are being found more and more frequently in our environment, with the dramatic improvements in analytical methodology which have come about in past 2 decades.

The association of these compounds with causes of cancer has been recognized for more than 200 years.(1) Chemical analytical studies show that PAH's appear in a large number of industrial processes, mainly due to high temperature treatment of coal tar and pitch as well as incomplete combustion or pyrolysis of organic material in general. Furthermore, biological and toxicological studies show that many PAH compounds exhibit carcinogenic effects in experimental animals.(2) Their results combined with wide-spread cancer occurance demonstrate that PAH is one of the largest classes of chemical carcinogens known today.

Coal derived products and thermally cracked petroleum oils and tars are highly aromatic in nature and contain PAH as major components(3,4). They are often composed of discontinuous fractions in discrete boiling point ranges. Many of the PAH are toxic and /or mutagenic in various biological test systems. The ability to effectively and efficiently convert (destroy) these species when they exist as pollutants in environmentally sensitive areas such as soils or water would be of great value. Clearly, knowledge of effective methods to clean or purge these contaminated areas/matrices of systems, such as a wastewater/oil/tar) in their environment will facilitate further development of coal conversion and use.

There are several mechanisms for treating tar/organic matrices at low temperature and where the objective is initiate oxidation or breakdown of the PAH structure.Ozone has been found to be an effective oxidizing agent for rapid decomposition of many organic pollutants in water(5,6). It has an advantage over chlorination and catalytic oxidation, because there is no production of toxic residues such as chloroform, methylene chloride and other halo-methanes (7), which occur in chlorination treatment systems.

An alternative treatment method for organic pollutants in water is chemical oxidation catalyzed by UV light.(8,9) The UV photons enhance the rate of reaction by producing reactive species from the oxidant and/or the pollutant.

Hydrogen peroxide is also an effective oxidant for UV catalyzed reactions and it can be stored for use according to process demand, as it is readily available in concentrated from 30% to 50%. The H_2O_2 is readily mixed with water, and is less sensitive than ozone to scale of operation. The absorption of UV photons by hydrogen peroxide dissociates it into two OH radicals so these can react to form HO_2 + H or add to double bonds of the aromatics as needed to initiate reaction of PAH's. Under suitable operating conditions, the final products are water, carbon dioxide and low molecular weight aliphatic acids, such as acetic and oxalic.(10) Until recently, most studies of the peroxide/UV oxidation (conversion) of contaminants have involved acetates, explosives, organic acids and process water contaminants(10-13).

The objective of this research is to develop a method to initiate degradation of the chemical structure of higher molecular weight (3-5 ring) PAH's in refractory tar materials; and thus making the highly refractory PAH structures more amenable to further treatment, with conversion to CO_2 and H_2O by biological or chemical methods. The process utilized to achieve this is to treat contaminated soils or materials with hydrogen peroxide or ozone plus ultra-violet (UV) light.

It is also possible that complete or near complete conversion of the tar materials to carbon dioxide and water may be achieved by choice of optimal conditions in the process itself.

An alternates result, which would also be considered success, would be to change the nature of the tar materials resulting in a stable suspension, which allows a subsequent treatment process to convert the suspension to nonoffensive materials.

The process to be utilized will be treatment of the samples with ozone or hydrogen peroxide and ultraviolet light. The UV light application is thought to be unique and will yield significant concentrations of the very strong oxidizer OH radical in solutions.

$H_2O_2 + hv \text{ -----------> } 2\ (OH)^{\cdot}$

$\text{ozone} + hv \text{ -----------> } O^{1D} + O_2$

$O^{1D} + H_2O \text{ -----------> } 2\ (OH)$

The combination of ozone and hydrogen peroxide with the UV will also be investigated.

These reactions of ozone or H_2O_2 with refractory tar like materials, will initially be carried out in aqueous media under conditions of :

Acidic --- Nitric Acid, (Conc.)

Basic --- Sodium Hydroxide, (5 M)

Neutral --- pH 5-9 (in water)

The collection of experimental results in this methodical routine will allow the data obtained to serve as a foundation to permit further study of the conversion of combined ozone/UV light and H_2O_2 reaction on tar, soil and water matrices when time and staffing allows. One eventual goal would be to develop a model to describe the overall reaction process and to be optimized by comparison to the experimental data.

In order to accurately evaluate the conversion of soil/liquid and tar samples an analytical procedure will need to be implemented, which will characterize the samples before and after reaction. The characterization will need to show changes in both physical and chemical properties.

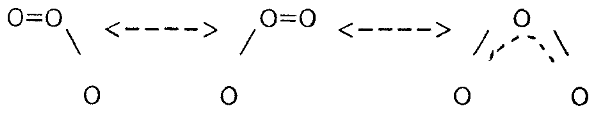
As the initial characterization, we utilized Carbon, Hydrogen and Nitrogen analysis on the dry samples and accurate description of the physical properties and mass. A Gas Chromatographic analysis with Flame Ionization Detection for specific PAH species was implemented to provide a "fingerprint" of the organic PAH'S in the sample i.e. concentrations and types of two, three and four-member ring PAH compounds .

2. THEORY AND PREVIOUS STUDY

2.1 Ozone Properties

Ozone (O_3) is an unstable gas having a pungent characteristic odor. It is produced commercially by passing air or oxygen through an electric discharge. The structure of the ozone molecule is that of an obtuse angle or boomerang. Here a central oxygen atom is attached to two equidistant oxygen atoms at an angle of 116°. Ozone gas is slightly soluble in water, and more so in other liquids. Its solubility increases at low temperatures. In a acidic solution, ozone has an oxidation potential of 2.07 volts and of 1.24 volts in basic solution at 20°C, thereby making it capable of oxidizing many organic and inorganic chemicals. Rosenthal(14) reported that the half-life of ozone in distilled water is about 20 minutes at 20°C. Peleg(15) proposed that the reaction rate of ozone decomposition in an aqueous solution is between first and second order, depending on the pH value and the temperature.

However, agreement seems to have finally been reached that the ozone molecule has an obtuse apex angle and that it should be considered a hybrid of the following structure:



2.2 The Decomposition of Ozone in Water

The decomposition of ozone in an aqueous solution has been thoroughly studied for many years. However, the reaction mechanism and the reaction kinetics of the decomposition of ozone in water are still uncertain. This is because in water solution ozone may react directly with dissolved substance or it may decompose to form secondary oxidants. such as OH and HO_2, which then react with solutes immediately. These separate reaction pathways produce different products, each having a characteristic kinetics and reaction pathways.

Gurol and Singer(16) summarized the literature and suggested that the kinetics of ozone decomposition in an water solution is between first and second order, depending on the pH value and the temperature.

One reaction mechanism, suggested by Weiss(17), showed that the decomposition of ozone in water, at a given pH value, was catalyzed by the hydroxyl ion (OH^-) for the initial reaction. The overall reaction mechanism which he suggested was:

$$O_3 + OH^- \text{---->} O_2 + HO_2\cdot$$

$$O_3 + HO_2\cdot \text{---->} 2O_2 + OH\cdot$$

$$O_3 + OH\cdot \text{---->} O_2 + HO_2\cdot$$

$2HO_2^{\cdot} \text{ ----> } O_3 + H_2O$

$HO_2^{\cdot} + OH^{\cdot} \text{ ----> } O_2 + H_2O$

From this mechanism , Wiess calculated that the kinetics of ozone decomposition was 3/2 order with respect to the O_3 concentration.

Alder and Hill(18), on the basis of their kinetic studies, suggested the following first order reaction mechanism :

$O_3 + H_2O \text{ ----> } HO_3^{+} + OH^{-}$

$HO_3^{+} + OH^{-} \text{ ----> } 2HO_2^{\cdot}$

$O_3 + HO_2^{\cdot} \text{ -----> } HO^{\cdot} + 2O_2$

$HO_2^{\cdot} + OH^{\cdot} \text{ ----> } H_2O + O_2$

Peleg(15) referenced the previous study and proposed the following reaction mechanism for the ozone decomposition in an aqueous solution:

$O_3 + H_2O \text{ ----> } O_2 + 2OH^{\cdot}$

$O_3 + OH^{\cdot} \text{ ----> } O_2 + HO_2^{\cdot}$

$O_3 + HO_2^{\cdot} \text{ ----> } 2O_2 + OH^{\cdot}$

$OH^{\cdot} + OH^{\cdot} \text{ ----> } H_2O_2$

$OH^{\cdot} + HO_2^{\cdot} \text{ ----> } H_2O + O_2$

$OH^{\cdot} + OH^{-} \text{ ----> } O^{-} + H_2O$

$O^{-} + O_2 \text{ ----> } O_3^{-}$

$$HO_2^{\cdot} + HO_2^{\cdot} \text{ ----> } H_2O_2 + O_2$$

Staehelin and Holgne(19) also proposed a completed reaction mechanism for the decomposition of ozone in the pure water and in the presence of organic solutes. Tomiyasu and co-worker(20) presented the kinetics and the reaction mechanism of ozone decomposition in a basic aqueous solution. All of the above mentioned investigators generally agreed that the decomposition of ozone in an aqueous solution can produce hydroxyl radicals and be catalyzed by these hydroxyl radicals. Thus, we can write the overall reaction mechanism of ozone decomposition in an aqueous solution as follows:

$$O_3 + H_2O^{\cdot} \text{ ----> } 2OH^{\cdot} + O_2$$

$$O_3 + OH^{\cdot} \text{ ----> } O_2 + HO_2^{\cdot}$$

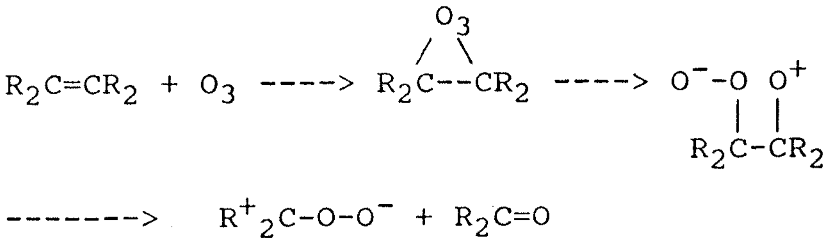
$$O_3 + HO_2^{\cdot} \text{ ----> } 2O_2 + OH^{\cdot}$$

2.3 The Ozone Oxidation of Organic Chemicals

Ozone oxidation can generally be classified into two types: mass transfer controlled and chemical reaction rate controlled, (21) Mass-transfer controlled oxidation with ozone occurs with the reaction is so rapid that the rate is limited only by the speed at which ozone can be added to the solution. Hoigne and his co-workers(22) stated that there are two types of ozonation when the chemical reaction is rate controlling; 1, direct reaction of ozone with the organic compound and 2, the free radical reactions of ozone which involve hydroxyl free radical intermediate.

During ozonation, some of the added ozone may react directly with the solute. However, part of the added ozone decomposes to form hydroxyl free radicals before its reaction with the oxidized solute. Furthermore, at the higher pH values, the ozone decomposes more easily to form hydroxyl radicals(14). Ozone in acidic solution has an oxidation potential of 2.07 volts and of 1.24 volts in a basic solution. However, the oxidation potential of the hydroxyl free radical is 2.8 volts at $H^+ = 1.0$ M and it is 1.7 volts at $H^+ = 1.0$ M for the hydroperoxyl radical. Baxendale(21) sug gested that the OH free radicals in water might be the species responsible for the germicidal activity of the ozonation although Morris(23) stated that there should be no direct relationship between the oxidation potential of a substance and its germicidal activity. Peleg(15) in a review indicated that the reactions of the hydroxyl radical and the ozone were very similar, Where both of the species are known to reduce the organic carbon content of waste water effluents(24,25).

For the direct reaction of ozone with organic compounds, the Criegee reaction mechanism(26) has been given much consideration relative to the nature and fate of active oxygen-containing ozonolysis products. The reaction mechanism is as follows:



$$R_2C{=}CR_2 + O_3 \dashrightarrow \overset{O_3}{R_2C\text{--}CR_2} \dashrightarrow \underset{R_2C-CR_2}{O^{-}\text{-}O\ \ O^{+}}$$

$$\dashrightarrow \quad R^{+}{}_2C\text{-}O\text{-}O^{-} + R_2C{=}O$$

It however, does not explain the initial ozone attack. Bailey(27) proposed a two-step mechanism which was additionally confirmed by other researchers.(27) The first step is the electrophilic attack by a terminal oxygen atom and in the second step the central oxygen atom completes the attack on the other carbon atom.

Ozone oxidation in an aqueous media is dependent on the pH value(28). At a higher pH value, it can increase the formation of hydroxyl free radicals which are more reactive than the ozone molecules.

2.4 Reaction of PAH with Ozone and Free Radicals

Ozone reacts readily with PAH. Studies by Lane and Katz(29) have shown high reactivity of BaP on petri dishes when it is exposed to sub-ppm levels of ozone in air. Irradiation did not seem to significantly affect the reaction rate. They also observed that the reactivity of the PAH varies strongly with their structure. Experiments by Pitts and co-workers(30) have confirmed and extended this work. For the atmospheric reaction of BaP with 0.2 ppm O_3 they found conversion yields (loss) of 50% after 1 hr and 80% after 4 hr.

Reaction of free radicals, such as the hydroxy radical, with aromatic hydrocarbons have been investigated only in a few cases.(31-33) From the study of simple model systems one might expect the formation of hydroxy derivatives of PAH and ring-opening oxidation products.(31) The former could react further, for example, to quinones.

Korfmacher et al.(34) have found that certain PAH are rapidly oxidized in the dark to the corresponding ketones and quinones when adsorbed onto coal fly ash or charcoal. As it has been observed that soot particles contain free radicals,(35,36) the spontaneous oxidation of certain adsorbed PAH might proceed by a radical pathway. Recently, Alfheim et al.(37) studied the thermal transformation of PAH adsorbed on secondary alumina from a dry scrubbing system of an aluminum plant. The amount of extractable PAH decreased rapidly during the thermal treatment of the alumina. No significant amounts of PAH were driven off during heating of the secondary alumina for 30 min to 340°C and PAH was no longer detectable in the extracts after heating. It was suggested that the PAH had been oxidized to polar compounds which were firmly bound to the surface of the alumina.

2.5 Catalytic Ozonation : O_3/UV

The reaction of ozone in combination with ultraviolet radiation (O_3/UV) as a process for the oxidation of refractory and toxic inorganic or organic species was developed in the early 1970's(9). In recent years, this combination has been shown to increase the rate of many ozone oxidations in aqueous solution, especially for those chemicals that do not easily react directly with ozone.

UV radiation at 180 - 400 nm provides 72 - 155 Kcal/mole (38) energy to accelerate the decomposition of ozone and produce other oxidizing free radicals, like OH and HO_2, from ozone as well as the excited state species.

At present, there is no detailed investigation of the O_3/UV reaction mechanism. Prengle and Mauk(38) presented the following steps for the reaction of ozone/UV :

(1) production of highly oxidizing photolytic species from ozone.

(2) Production of free radicals and excited state photolytic species from the parent compound.

(3) Reaction with water species OH and H.

Gary and co-wokers(39) proposed the following simple O_3/UV reaction mechanism:

$$O_3 \xrightarrow{hv} O_2 + O(D')$$

$$O + H_2O \longrightarrow 2HO$$

They also determined the O_3 mass-transfer coefficients between the gas phase and the liquid phase in their reactor at different ozone gas flow rates.

Prengle(40) presented overall reaction mechanism of the O_3/UV photooxidation of species containing sulfur, phosphorus and halogen in an aqueous solution. Molecules are designated as M simplified mechanism includes:

$$O_3 \xrightarrow{hv} O_2^{*} + O$$

$$O + H_2O \longrightarrow 2OH$$

$$O_3 + OH \longrightarrow HO_2 + O_2$$

$$M \xrightarrow{hv} M^{*}$$

$$M^{*} + \{ hv, O, OH, HO_2 \} \longrightarrow R, I, H$$

The overall reaction for a hydrocarbon HC is given as:

$$HC + O_3 \longrightarrow H_2O + CO_2$$

Prengle used trihalomethane as the M species. The overall oxidation rate was enhanced as a result of use of UV radiation.

Although the above listed reactions have different kinds of reaction mechanisms, many investigators(38) believe that they have a common chain mechanism which is initiated by UV photons that decompose ozone into an oxygen molecule and and oxygen radical. The oxygen radical may then react with the water molecule to produce two hydroxyl radicals. Hydroxyl radicals continue to be produced and consumed in a complex radical mechanism. The ozone/UV treatment may also involve the formation of excited organic species which may subsequently react with hydroxyl radicals. Having reviewed the literature on this subject, we suggest the following simple reaction mechanism for the ozone/UV photooxidation of pollutants M species:

$$O_3 + hv \text{ --------> } O_2 + O$$

$$O + HC \text{ -------------> } OH + R\cdot$$

$$OH + O_3 \text{ -----> } O_2 + HO_2$$

$$M + \{ O^*_2, OH, HO_2, O_3 \} \text{ -----> Decompose}$$

Gurol and Vatistas(41) did a comparative study of oxidation of phenolic compounds by UV, O_3, and O_3/UV at different pH values. They obtained the following results:

(1) The ozone molecule is the predominant oxidant in an acidic solution.

(2) In a neutral or basic solution, in the absence or presence of UV radiation, a free radical reaction is the major pathway to the oxidization of phenolic compounds.

(3) The overall removal of the phenols and total organic carbon (TOC) increases with increasing pH value during ozonation, with or without UV radiation.

(4) For a specific pH, the ozone/UV process has the highest removal rate for the phenol and the TOC chemicals, followed by ozone alone, and then UV light alone.

2.6 Hydrogen Peroxide with UV Radiation

While the O_3/UV treatment is undoubtely effective on a wide range of compounds, it still has number of disadvantages. Ozone is an unstable gas and must be provided in a manner which can achieve an adequate mass transfer of ozone into the liquid phase(42). An oxidant which may be as effective as ozone, but is better suited for use in a small treatment system, is hydrogen peroxide plus UV radiation. Malaiyandi and co-workers(43) found that this method could reduce the TOC content of distilled water by about 88%. Hydrogen peroxide, H_2O_2, is a weak acid, colorless and rather unstable liquid and is completely miscible with water.

The chemistry of H_2O_2/UV reaction involves the generation of hydroxyl radicals and other reactive species by the photochemical reaction of UV light on hydrogen peroxide. Hochanadel(44) proposed the following simple mechanism for the H_2O_2/UV reaction :

$$H_2O_2 \xrightarrow{hv} 2OH$$

$$H_2O_2 + OH \longrightarrow H_2O + HO_2$$

$$2HO_2 \longrightarrow H_2O_2 + O_2$$

Under suitable working conditions, H_2O_2/UV can be a very useful source of hydroxyl radicals(45). The decomposition of H_2O_2 has been shown to occur at higher pH values, because it is base catalyzed.

Sundstrom and co-workers(45) compared the reaction rates for various halogenated aliphatics with UV, H_2O_2 and H_2O_2/UV at different temperatures. They found the following results:

(1) H_2O_2/UV has the highest efficiency as compared to other methods.

(2) The rate of decomposition is increased when the hydrogen peroxide concentration and the temperature are increased and the rate of decomposition is highly structure dependent.

3.EXPERIMENTAL METHOD

A research scale reactor, 0.5 liter, was utilized in our laboratory. It is operated in a batch mode -- batch inlet of 5 gm of neat tar or 5 grams of tar/soil mixtures where the soil mixture contained approximately 10% tar in a sandy soil, which also included wood chips. The neat tar was cut into chunks approximately 1 cm in diameter before being placed in the reaction flask. These large chunks of tar did not allow the reactants (ozone of H2O2) to access the central part of the lump and thus reaction in this pure tar mode is limited to the exterior surface of the tar lump. Later experients tried to overcome this problem by uniformly coating the tar onto glass bead surfaces. This reaction yielded better results.

The reactor operated with continuous ozone and/or UV light feed and mixing. Usually 5 grams, (± 0.04), of tar or tar/soil mix or tar on uniformly coated glass or sand surfaces was placed in the reactor. Water or solvent was then added with the peroxide or ozone added last. Ozone was added uniformly over the time scale indicted in the listing of experiments and results. Peroxide 50 ml at 30% was added in small aliquots over the initial hour of the experiment to prevent or limit initial reaction runaway -- non was observed.

Hydrogen peroxide, when utilized, is fed directly into the reactor at the initiation of each experiment, e.g. 5 ml/min for 10 min to 1 hour. The ultraviolet light is produced by a 300 Watt Conrad Hanovia Xenon Arc lamp.

Ozone is produced from oxygen by a Welshbach Model T-408 Ozone Generator. The gas stream is bubbled and fed continuously at a flow of 0.1 to 0.5 liter / min through a reactor filled with a 500-ml solution.

3.1 Experimental Equipment

3.1.1 Ozone generation

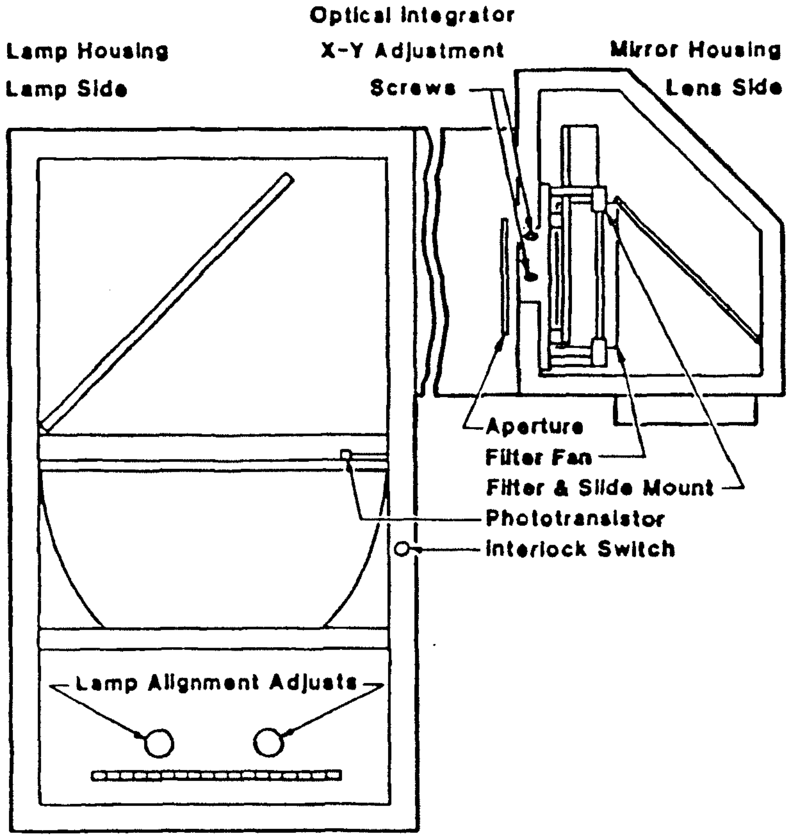
Ozone is produced by an ozone generater, manufactured by the Welsbach Ozone System Corporation, Philadelphia, PA. This generator has a capacity for producing a minimum of 16 grams of pure, dry ozone per hour. It is a corona discharge type apparatus and cooled by water. Ozone made with O_2 or air has a flow rate which is adjustable by a ball valve. The power was set at 110 W and 99.6% pure, dry oxygen or air was used for ozone generation in this experiment. O_2 carrier supplied ozone at 5-6 % total flow and air carrier supplied ozone at 2-3 % of the total flow.

3.1.2 Ultraviolet light source

The ultraviolet light source was purchased from the

ORIEL Corporation, Stratford, Connecticut. It is a XENON SHORT ARC Lamp, high pressure gas lamp. The Arc Lamp Power supply contains a special high voltage ignitor which is employed to start the lamp used with this system. When starting a lamp, this ignitor will produce an RF output voltage pulse train of 20 to 30 KV. ORIEL external blower kit and Exhaust port model 6172 and 6173 are included with 300 W Solar simulator. The ORIEL Solar Simulators produce collimated beams of energy rich in UV and continuous to 2500 nm.

Figure 3-1. The Scheme of Ultraviolet light source.



3.1.3 Gas chromatograph

A Perkin-Elmer Model 3920B gas chromatograph (GC) with a Flame Ionization Detector (FID) has been used to analyze the PAH's in the tar samples and products of tar reaction. A Hewlett-Packard Model 3380A integrator is connected to the GC to measure the retention time and the peak area of the sample.

A 3% SP-2250 on 100/120 Supelcoport, 12' x 1/8" stainless steel column was used in the experiments. Hydrogen gas was used for the FID and nitrogen was served as a carrier gas.

The GC working conditions are as follows:
N_2 pressure : 40 psig, flow rate : 30 ml/min
H_2 pressure : 40 psig, flow rate : 30 ml/min
Detector temp. : 250 °C
Injection temp. : 200 °C
Column temp. : 2 min. at 50 °C, then to 240 °C at 16 °C/min
Column flow rate : 30 ml/min
Sample inject : 1 ul methylene chloride, 0.1 mg each sample
Air flow rate : 300 ml/min
Figures 3-1, 3-2 show the chromatograms of Tar I and Tar II

3.2 Reagents and Chemicals

1. Nitric acid (conc)-----organic residue

Assay (HNO_3) (by acidmetry) : 70.0 %

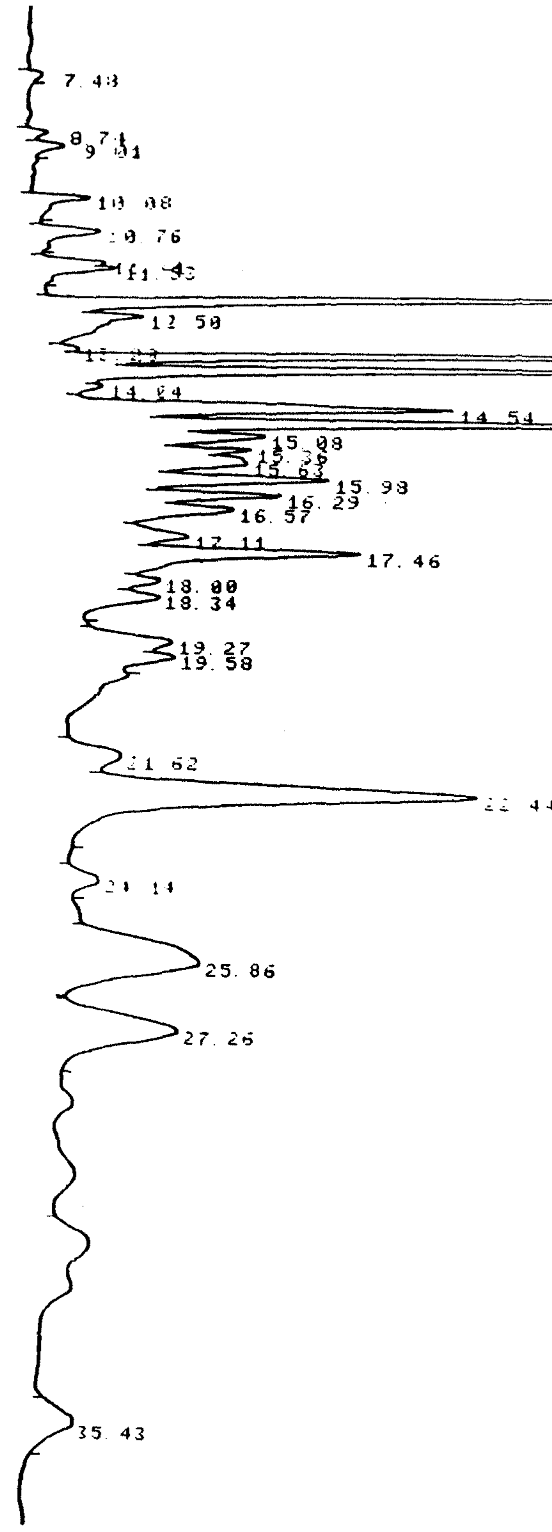
2. Sodium Hydroxide (5M)
3. Ether (organic residue)
4. Hexane (HPLC grade)
5. Methylene chloride (HPLC grade)
6. Methanol (HPLC grade)

The following reagents are used as standard for GC Analysis:

PAH Mixture 610-M (Supelco,Inc.)

1 ml contain : Acenaphthene, 1000 ug/ml
Acenaphthylene, 2000 ug/ml
Anthracene, 100 ug/ml
Benzo(a)pyrene, 100 ug/ml
Benzo(b)fluoranthene, 200 ug/ml
Benzo(ghi)perylene, 200 ug/ml
Benzo(k)fluoranthene, 100 ug/ml
Chrysene, 100 ug/ml
Dibenzo(a,h)anthracene, 200 ug/ml
Fluoranthene, 200 ug/ml
Fluorene, 200 ug/ml
Indeno(1,2,3-cd)pyrene, 100 ug/ml
Naphthalene, 1000 ug/ml
Phenanthrene, 100 ug/ml
Pyrene, 100 ug/ml

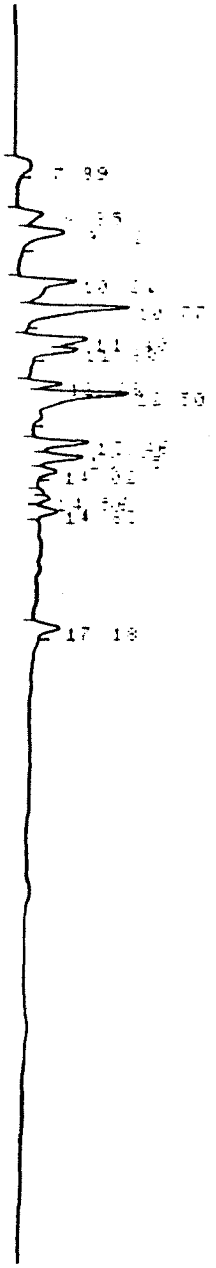
Firure 3-2. Chromatography of Tar I
Col. Temp: 2 min. at 50°C, then to 240°C at 16°C/min.



TAR 1

RT (2)*	
10.08	Methyl indene
10.76	Naphthalene
11.11	Dimethyl indene
11.42	2-methyl-Naphthalene
11.55	Methyl-Naphthalene
11.78	Ehthyl Naphthalene
12.22	Acenaphthylene
12.50	Acenapthene
13.44	Dimethyl Naphthalene
13.74	Methyl ethyl Naphthalene
14.54	Fluorene
14.83	Methyl Fluorene
15.98	Phenanthrene
16.29	Anthracene
16.57	Methyl Phenanthrene
17.11	Dimethyl Phenanthrene
17.46	Fluoranthene
18.00	Pyrene
19.27	Benzo Fluorene
19.58	Trimethyl Phenanthrene
21.62	Benzo (a) Anthracene
22.44	Chrysene
24.14	Methyl benzo Phenanthrene
25.86	Benzo (a) Fluoranthene & Benzo (k) Fluoranthene
27.26	Benzo (a) pyrene
31.50	Indeno pyrene & Dibenzo anthracene
35.43	Benzo perylene

Firure 3-3. Chromatography of Tar II
Col. Temp: 2 min. at 50°C, then to 240°C at 16°C/min.



TAR II

RT (2)*	
10.21	Methyl indene
10.77	Naphthalene
11.40	2-methyl-Naphthalene
11.60	Methyl-Naphthalene
12.28	Acenaphthylene
12.50	Acenapthene
13.46	Dimethyl Naphthalene
13.75	Methyl ethyl Naphthalene
14.56	Fluorene
14.83	Methyl Fluorene
17.18	Dimethyl Phenanthrene

Figure 3-4. The Scheme of Sample Preparation

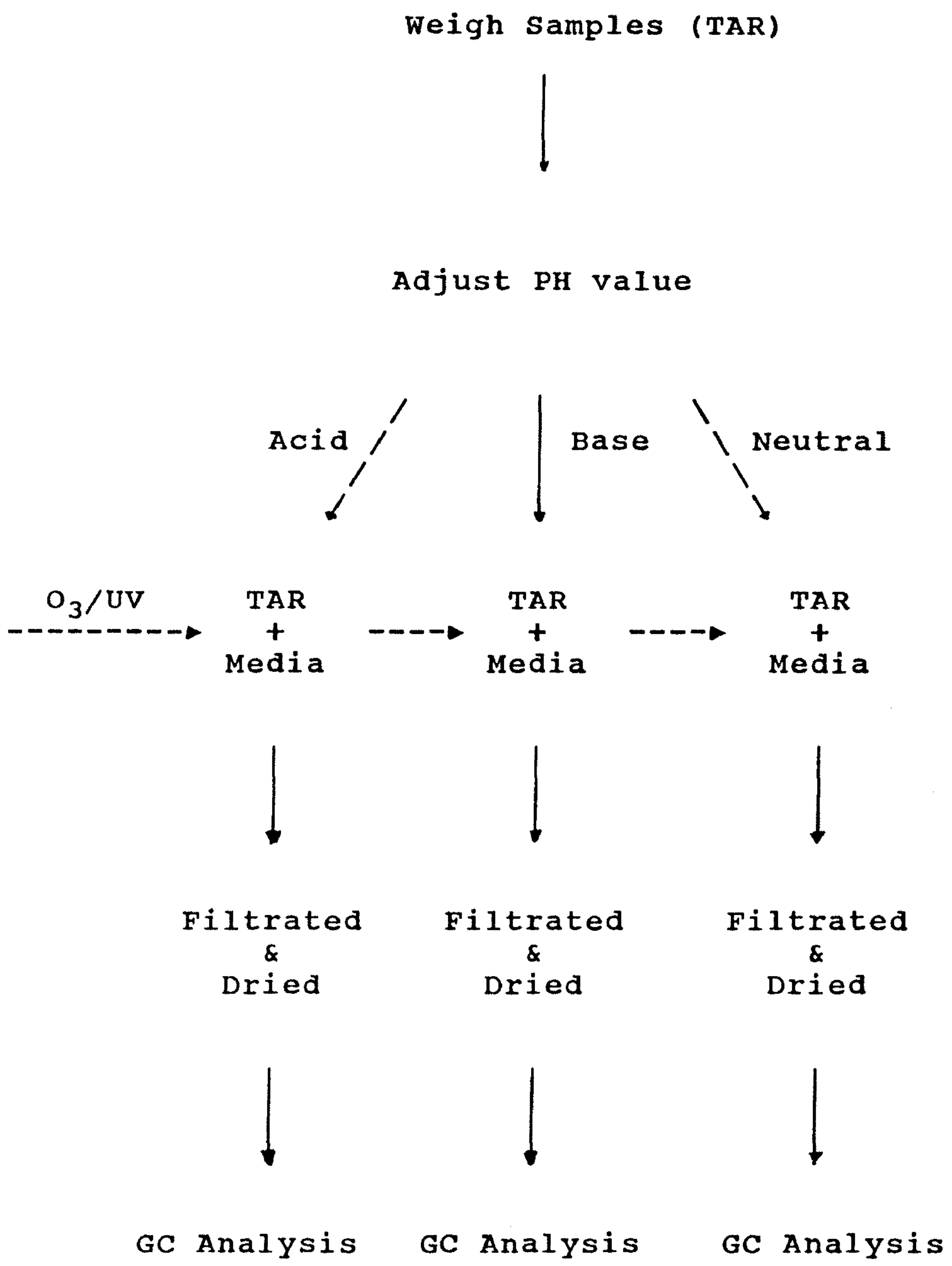


TABLE 3-1

			TREATMENT				
Sample	Media,ml	Tar,gm	hr	Water,ml	H_2O_2,ml	Ozone	UV
TAR							
TAR (2)							
JU1	A (25)	5.0-4.9	15	100	50	N	N
JU2	B (25)	5.0-5.0	15	100	50	N	N
JU3	N (25)	5.0-5.4	15	100	50	N	N
JU4	A (25)	5.0-5.1	15	100	N	Y (O_2)	N
JU5	B (25)	5.0-4.9	15	100	N	Y (O_2)	N
JU6	N (25)	5.0-5.0	15	100	N	Y (O_2)	N
JU7	A (25)	5.0-5.4	15	100	50	Y (O_2)	N
JU8	B (25)	5.0-4.9	15	100	50	Y (O_2)	N
JU9	N (25)	5.0-4.9	15	100	50	Y (O_2)	N
JU10(2)	A (25)	5.0-3.4	15	100	50	N	N
JU11(2)	B (25)	5.0-3.4	15	100	50	N	N
JU12(2)	N (25)	5.0-4.5	15	100	50	N	N
JU13(2)	A (25)	5.0-4.75	15	100	N	Y (O_2)	N
JU14(2)	B (25)	5.0-4.35	15	100	N	Y (O_2)	N
JU15(2)	N (25)	5.0-2.5	15	100	N	Y (O_2)	N
JU16(2)	A (25)	5.0-4.5	15	100	50	Y (O_2)	N
JU17(2)	B (25)	5.0-2.5	15	100	50	Y (O_2)	N
JU18(2)	N (25)	5.0-3.4	15	100	50	Y (O_2)	N
JU19	A (25)	5.0-4.6	15	100	50	N	Y
JU20	B (25)	5.0-4.9	15	100	50	N	Y
JU21	N (25)	5.0-5.0	15	100	50	N	Y
JU22	A (25)	5.0-4.9	24	100	N	Y (O_2)	N
JU23	B (25)	5.0-4.8	24	100	N	Y (O_2)	N
JU24	N (25)	5.0-4.85	24	100	N	Y (O_2)	N

(2)=Tar 2

A=Acid, B=Base. N=Neutral

TABLE 3-2

TREATMENT							
Sample	Media,ml	Tar,gm	hr	Water,ml	H2O2,ml	Ozone	UV
JU25	A (25)	5.0-4.6	15	100	50	N	Y
JU26	B (25)	5.0-4.9	15	100	50	N	Y
JU27	N (25)	5.0-5.0	15	100	50	N	Y
JU28	A (25)	5.0-4.9	36	100	N	Y (AIR)	Y
JU29	B (25)	5.0-4.9	36	100	N	Y (AIR)	Y
JU30	N (25)	5.0-4.9	36	100	N	Y (AIR)	Y
JU31	A (25)	5.0-4.7	72	300	N	Y (AIR)	Y
JU32	B (25)	5.0-5.0	72	300	N	Y (AIR)	Y
JU33	N (25)	5.0-5.0	72	300	N	Y (AIR)	Y
JU34	A (25)	5.0-5.0	1	100	N	Y (AIR)	N
JU35	B (25)	5.0-5.0	1	100	N	Y (AIR)	N
JU36	N (25)	5.0-4.95	1	100	N	Y (AIR)	N
JU37	A (25)	5.0-4.9	3	100	N	Y (AIR)	N
JU38	B (25)	5.0-4.9	3	100	N	Y (AIR)	N
JU39	N (25)	5.0-5.0	3	100	N	Y (AIR)	N
JU40	A (25)	5.0-5.7	3	100	N	Y (AIR)	N
JU41	B (25)	5.0-5.4	3	100	N	Y (AIR)	N
JU42	N (25)	5.0-4.9	3	100	N	Y (AIR)	N
JU43	A (25)	5.0-6.4	24	100	N	Y (AIR)	N
JU44	B (25)	5.0-7.6	24	100	N	Y (AIR)	N
JU45	N (25)	5.0-4.85	24	100	N	Y (AIR)	N
JU46	A (25)	5.0-5.85	3	100	N	N	N
JU47	B (25)	5.0-8.8	3	100	N	N	N
JU48	N (25)	5.0-4.5	3	100	N	N	N

JU34-JU39 using other media ---100 mg Glass bead

JUJU40-JU48 using other media--100 ml Ether + 100 gm Glass bead

GB = Glass beads 100 gm
Diameter = 3mm
With glass bead ether /solvent evaporated before ozone exp.

TABLE 3-3

				TREATMENT			
Sample	Media,ml	Tar,gm	hr	Water,ml	H2O2,ml	Ozone	other media
JU49	A (25)	5.0-5.5	16	100	N	N	100 ml Ether + Glass bead
JU50	B (25)	5.0-5.4	16	100	N	N	
JU51	N (25)	5.0-3.6	16	100	N	N	
JU52	A (25)	10.0-11.4	1	100	N	Y (AIR)	100 ml Hexane + Glass bead
JU53	B (25)	10.0-8.2	1	100	N	Y (AIR)	
JU54	N (25)	10.0-8.2	1	100	N	Y (AIR)	
JU55	A (25)	10.0-11.2	3	100	N	Y (AIR)	100 ml Hexane + Glass bead
JU56	B (25)	10.0-11.5	3	100	N	Y (AIR)	
JU57	N (25)	10.0-8.8	3	100	N	Y (AIR)	
JU58	A (25)	10.0-14.8	1	100	N	Y (AIR)	100 ml Hexane + CaCO3
JU59	B (25)	10.0-10.4	1	100	N	Y (AIR)	
JU60	N (25)	10.0-15.4	1	100	N	Y (AIR)	
JU61	A (25)	10.0-30.6	3	100	N	Y (AIR)	100 ml Hexane + CaCO3
JU62	B (25)	10.0-14.1	3	100	N	Y (AIR)	
JU63	N (25)	10.0-15.4	3	100	N	Y (AIR)	
JU64	A (25)	10.0-31.8	1	100	N	N	100 ml Hexane + CaCO3
JU65	B (25)	10.0-11.4	1	100	N	N	
JU66	N (25)	10.0-8.3	1	100	N	N	
JU67	B (25)	*52.7-52.	4	100	N	Y (AIR)	
JU68	A (25)	*51.8-51.	4	100	N	Y (AIR)	
JU69	A (25)	*36.0-35.	4	100	N	Y (AIR)	
JU70	B (25)	*35.5-35.	4	100	N	Y (AIR)	
JU71	B (25)	*49.6-48.	4	100	N	Y (AIR)	
JU72	A (25)	*34.5-34.	4	100	N	Y (AIR)	

* = mass of tar + mass of glass bead

TABLE 3-4

TREATMENT

Sample	Media,ml	Tar,gm	hr	Water,ml	H2O2,ml	Ozone	other media
JU73	--	5.0-3.6	6	--	N	N	100 ml Ether + Glass bead
JU74	B (25)	3.1-3.0	24	100	N	Y	
JU75	A (25)	2.5-2.1	24	100	N	Y	
JU76	--	5.0-3.1	6	--	N	N	200 ml Ether + Glass bead
JU77	B (25)	*50	24	200	N	Y	
JU78	N (25)	*50	24	200	N	Y	
JU79	A (25)	*50	3	200	N	Y	
JU80	--	5.0-3.1	6	--	N	N	100 ml Ether + Glass bead
JU81	A (25)	*30	24	100	N	N	
JU82	B (25)	*30	24	100	N	N	
JU83	--	5.0-4.1	18	--	N	N	
JU84	A (25)	3.9-3.1	24	100	N	Y	100 ml MeOH
JU85	--	5.0-3.6	18	--	N	N	
JU85A	--	#3.6-2.6	24	--	N	N	
JU86	--	5.0-3.8	18	--	N	N	
JU87	--	5.0-3.6	18	--	N	N	
JU88	--	5.0-3.1	18	--	N	N	100 ml MeCl2
JU89	--	5.0-3.5	6	--	N	N	100 ml Ether
JU89A	A (25)	3.0-2.3	24	100	N	Y	
JU90	--	5.0-3.4	6	--	N	N	
JU91	--	5.0-3.1	18	100	N	N	100 ml MeOH

* = mass of tar + mass of glass bead
\# = 85A start with product from 85
\# 73,76,80 evaporate ether only

3.3 Sample Treatment (Reaction)

Tables 3-1 to 3-4 show a summary of the treatment procedure for reaction studies JU 1 through JU 91 on Tar I and Tar II.

A. JU 4-9, 13-18, 22-24, 28-33

5.0 gm TAR 1 (or TAR 2) Weighed to ± 0.05 gm , added to 100 ml H_2O with either 25 ml of HNO_3 (conc) or 25 NaOH (5M), then stirred with magnetic stirrer.

Ozone was added at 560 ml/min per 3 flasks in parallel (186.6 ml/min per 1 flask) using O_2 or air as indicated. O_2 carrier supplied ozone at 5-6% total flow and air carrier supplied ozone at 2-3% of the total flow.

The experiment was run for indicated amount of time. (see Table 3-1 and 3-2)

B. JU 1-3, 7-9, 16-21, 25-27

5.0 gm TAR 1 (or TAR 2) Weighed to ± 0.05 gm , added to 100 ml H_2O with either 25 ml of HNO_3 (conc) or 25 NaOH (5M),Then stirred with magnetic stirrer and 50 ml H_2O_2 was added slowly at a rate of 5 ml 10 minutes. (see Table 3-1 and 3-2)

C. JU 34 -----> JU 39

5.0 gm TAR 1, weighed to ± 0.05 gm, added to 100 ml $H2_O$ with either 25 ml of HNO_3 (conc) or 25 ml NaOH (5M). 100 gm of 3mm glass beads were added for agitation and stirred with magnetic stirrer.

Ozone was added at 560 ml/min per 3 flasks in parallel (186.6 ml/min per 1 flask) using O_2 or air as indicated. O_2 carrier supplied ozone at 5-6% total flow and air carrier supplied ozone at 2-3% of the total flow.

The experiment was run for indicated amount of time. (see Table 3-2)

D. JU 40 -----> JU 51

5.0 gm TAR 1, weighed to ± 0.05 gm, was added to 100 ml Ether and 100 gm glass beads, then stirred with magnetic stirrer till tar was dissolved or uniformly suspended. The solvent was evaporated and after all solvent (ether) was evaporated, the glass bead-tar mix was added to 100 ml $H2_O$ with either 25 ml of HNO_3 (conc) or 25ml NaOH (5M). While stirred with magnetic stirrer.

Ozone was added at 560 ml/min per 3 flasks in parallel (186.6 ml/min per 1 flask) using O_2 or air as indicated. O_2 carrier supplied ozone at 5-6% total flow and air carrier supplied ozone at 2-3% of the total flow.

The experiment was run for indicated amount of time. (see Table 3-2 and 3-3)

E. JU 52 -----> JU 66

10.0 gm TAR 1, weighed to ± 0.05 gm and added to 100 ml hexane and 100 gm glass beads or $CaCO_3$-sand was added with either 25 ml of HNO_3 (conc.) or 25 ml NaOH (5M). Then mixture is stirred with a magnetic stirrer.

Ozone was added at 560 ml/min per 3 flasks in parallel (186.6 ml/min per 1 flask) using O_2 or air as indicated. O_2 carrier supplied ozone at 5-6% total flow and air carrier supplied ozone at 2-3% of the total flow.

The experiment was run for indicated amount of time. (see Table 3-3)

F. JU 67 -----> JU 72

JU 67 was run on the products of JU 43, it was intended to complement the results of this previous run conditions were the same as A, all media are indicated. (see Table 3-3)

JU 68 was run on the products of JU 44, it was intended to complement the results of this previous run conditions were the same as A, all media are indicated. (see Table 3-3)

JU 69 and JU 70 were run on the products of JU 45, it was intended to complement the results of this previous run conditions were the same as A , all media are indicated. (see Table 3-3)

JU 71 was run on the products of JU 46, it was intended to complement the results of this previous run conditions were the same as A, all media are indicated. (see Table 3-3)

JU 72 was run on the products of JU 50, it was intended to complement the results of this previous run conditions were the same as A, all media are indicated. (see Table 3-3)

G. JU 73 -----> JU 82

5.0 gm TAR 1 weighed to ± 0.05 gm , added to 100 ml ether and 100 gm glass beads then stirred with magnetic stirrer till tar was dissolved. After all solvent (ether) was evaporated, the glass bead-tar mix was added to 100 ml $H2_O$ with either 25 ml of HNO_3(conc) or 25ml NaOH (5M). Then stirred with magnetic stirrer.

Ozone was added at 560 ml/min per 3 flasks in parallel (186.6 ml/min per 1 flask) using O_2 or air as indicated. O_2 carrier supplied ozone at 5-6% total flow and air carrier supplied ozone at 2-3% of the total flow.

The experiment was run for indicated amount of time. (see Table 3-4)

H. JU 83 -----> JU 91

(1) 5.0 gm TAR 1 Weighed to ±0.05 gm, added to 100 ml Ether/ MeOH/ $MeCl_2$ (as indicated) then stirred with magnetic stirrer, till tar was dissolved. Filter out particulate.

(2) Treat particulate as previous run conditions as A.

Weighed, then added particulate to 100 ml $H2_O$ with either 25 ml of HNO_3(conc) or 25ml NaOH (5M). Ozone was added at 560 ml/min per 3 flasks in parallel (186.6 ml/min per 1 flask) using O_2 or air as indicated. O_2 carrier supplied ozone at 5-6% total flow and Air carrier supplied Ozone at 2-3% of the total flow.

The experiment was run for indicated amount of time. (see Table 3-4)

Table 4-1

PRODUCTS AFTER TREATMENT

Sample	Odor	Product after treatment	C	H	N
TAR	3	Black tar (oily)6	79.46	4.16	0.63
		(duplicate)	82.04	3.29	1.19
TAR (2)	8	Soil moist looking	16.67	1.90	0.23
JU1	2	Black tar -medium 6	82.56	3.38	0.79
JU2	3	Black tar -medium 6	83.31	3.57	0.71
JU3	4	Black tar -medium 6	83.26	3.54	0.70
JU4	3	Black tar -medium 5	82.54	3.47	0.75
JU5	2	Black tar -medium 6	80.10	3.46	0.67
JU6	3	Black tar -medium 6	81.43	3.52	0.69
JU7	2	Black tar -medium 6	86.27	3.61	0.81
JU8	2	Black tar -medium 6	82.93	3.51	0.69
JU9	2	Black tar -medium 6	85.02	3.66	0.66
JU10(2)	7	Soil like (red brn)8	17.16	1.84	0.36
JU11(2)	7	Soil like (black)9	15.00	1.68	0.77
JU12(2)	7	1 cm lumps soil (black)9	18.65	1.90	0.42
JU13(2)	8	2 cm lumps soil(brn)8	15.60	1.89	1.09
JU14(2)	6	Soil like (brn)8	14.67	1.60	0.39
JU15(2)	6	1cm stone with layer(gray)9	11.12	1.24	0.47
JU16(2)	8	2 cm lumps soil(dark brn)9	16.84	1.79	0.87
JU17(2)	6	Soil --sand like (gray)9	10.27	1.11	0.54
JU18(2)	8	1 cm stone with layer(brn)8	12.42	1.37	0.44
JU19	2	Black tar -medium 6	82.12	3.10	0.98
JU20	2	Black tar -medium 6	86.13	3.50	0.81
JU21	2	Black tar -medium 6	80.18	3.30	0.74
JU22	2	Black tar -medium 6	79.27	3.04	0.87
JU23	3	Black tar -medium 6	80.45	3.28	0.79
JU24	2	Black tar -medium 6	88.96	3.56	0.82

Odor	Hardness scale
	soft (grease)1
1 none	medium 4-7
10 high	hard (stone)10

brn = brown color

TAR (2) = TarII -soil with small amount of tar

Table 4-2

PRODUCTS AFTER TREATMENT

Sample	Odor	Product after treatment	C	H	N
JU25	2	1 cm lumps tar -coal like9	85.64	3.31	1.02
JU26	3	Black tar 6	92.61	3.72	0.81
JU27	3	Black tar 6	78.26	3.08	0.77
JU28	2	2 cm lumps tar -- hard9	84.30	3.47	0.97
JU29	3	Black tar 6	83.40	3.45	0.80
JU30	3	Black tar 6	81.71	3.16	0.88
JU31	2	2 cm lumps tar -coal like9	82.49	3.20	1.47
JU32	3	Black tar 7	87.99	3.46	0.85
JU33	2	Black tar 7	81.34	3.35	0.78
JU34	2	Black tar 7	82.11	3.41	0.74
JU35	2	Black tar 7	84.50	3.42	0.70
JU36	3	Black tar 6	84.22	3.53	0.78
JU37	2	Black tar 6	80.99	3.36	0.83
JU38	2	Black tar 6	81.99	3.39	0.71
JU39	2	Black tar 6	80.58	3.40	0.75
JU40	2	Fine powder (brn)			
JU41	2	Agglomeration with glass bead (dry)			
JU42	3	Agglomeration with glass bead (oily)			
JU43	3	Powder (brn)			
JU44	3	Agglomeration with glass bead (dry)			
JU45	3	1 cm rock with powder(brn)			
JU46	5	1 cm rock with powder(brn)			
JU47	2	Tar coating on glass bead (dry)			
JU48	2	Tar coating on glass bead (oily)			

Odor	Hardness scale
	soft (grease)1
1 none	medium 4-7
10 high	hard (stone)10

brn = brown color

Table 4-3

PRODUCTS AFTER TREATMENT

Sample	Odor	Product after treatment
JU49	3	Fine powder (brn)
JU50	2	Agglomeration with glass bead (dry)
JU51	3	Tar coating on glass bead (oily)
JU52		1 cm lumps tar -- fragile and less oily
JU53		1 cm lumps tar -- fragile and less oily
JU54		1 cm lumps tar -- fragile and less oily
JU55		1 cm lumps tar -- fragile and less oily
JU56		1 cm lumps tar -- fragile and less oily
JU57		1 cm lumps tar -- fragile and less oily
JU58		Rock like -- with CaCO3
JU59		Rock like -- with CaCO3
JU60		Eroded rock like -- with CaCO3
JU61		Rock like -- with CaCO3
JU62		Rock like -- with CaCO3
JU63		Rock like -- with CaCO3
JU64		Rock like -- with CaCO3
JU65		Rock like -- with CaCO3
JU66		Rock like -- with CaCO3
JU67	2	Fine powder (black)
JU68	4	1 cm lumps with powder (black)
JU69	3	Fine powder (brn)
JU70	2	1 cm lumps coal with powder (black)
JU71	2	Sand like (black)
JU72	2	1 cm lumps -- like rice (black)

Odor	Hardness scale
	soft (grease)1
1 none	medium 4-7
10 high	hard (stone)10

brn = brown color

Table 4-4

PRODUCTS AFTER TREATMENT

Sample	Odor	Product after treatment	C	H	N
JU73	2	1 cm lumps (black)			
JU74	2	1 cm lumps (black)			
JU75	2	1 cm lumps (black)			
JU76	2	Agglomeration with glass be	82.26	2.70	0.71
JU77	2	Agglomeration with glass bead (dry)			
JU78	2	Fine powder (brn)			
JU79	2	1 cm rock with powder (black)			
JU80	2	Agglomeration with glass bead (dry)			
JU81	2	Tar coating on glass bead (dry)			
JU82	2	Tar coating on glass bead (dry)			
JU83		Fine powder (black)			
JU84		Fine powder	82.75	3.02	0.92
JU85		Fine powder			
JU85A		Fine powder	78.53	2.42	0.57
JU86		Fine powder	78.23	2.53	0.53
JU87		Fine powder	79.91	2.49	0.51
JU88		Fine powder	86.24	1.11	1.07
JU89		Fine powder	81.67	2.06	0.63
JU89A		Fine powder	73.85	1.24	1.66
JU90		Fine powder	74.78	1.76	0.66
JU91		Fine powder	84.14	3.01	0.49

Odor	Hardness scale
	soft (grease)1
1 none	medium 4-7
10 high	hard (stone)10

brn = brown color

4. RESULTS AND DISCUSSION

4.1 Experimental Results

4.1.1 Results from Visual/Physical & C/ H/ N analysis

The experimental results of Tar I and Tar II reactions using ozone, H_2O_2, ozone + H_2O_2 and H_2O_2 + UV are shown in Tables 4-1 to 4-4. These tables show the observed visual/physical changes and the Carbon, Hydrogen and Nitrogen composition after reaction.

4.1.2 Calculation of concentrations of PAH's

For Standard solution:

Inject X (ug/ml) times Y volume(ml) injected

==> XY (ug) injected

From area, we can obtain $\frac{\text{Area}}{\text{ug}} = \frac{\text{Area}}{\text{per ug}}$

For unknown solution: Use the standard solution peak area and unknown area (U_{area}) to obtain the unknown concentration (in ug injected)

$$U_{area} * \text{ug/area} = \text{ug unknown}$$

The standards (in ug/ml) as listed in Chapter 3.

$$\frac{A_{STD}}{A_S} = \frac{(\ ug/ml\ )_{STD}}{(\ ug/ml\ )_S}$$

$$(ug/ml)_S = \frac{(\ ug/ml)_{STD} * A_S}{A_{STD}}$$

A_{STD} : Area of Standards

A_S : Area of samples

In all cases, 1 micro liter (0.001 ml) of solution containg the standard or the unknown tar was injected into the G.C. (The solvent peak was used as an internal standard.) For example, 5 grams tar sample was treated -- assume no change in final weight (= 5 gram). Place 300 mg (0.3 gram) into 3.0 ml methylene chloride solution. There is equivalent to 0.1 gram tar in 1 ml solvent.

This is 0.1 gram of tar sample. For a sample where we obtained 0.466 ug Pyrene per 1 ul injected yielded 466 ug in 1 ml solution, $(\ ug/ml)_{Py} = 466$ and 1 ml of sample solution from above contain 0.1 gram tar. Therefore:

$$\frac{\text{ug PAH}}{\text{gram tar}}\ \text{Pyrene} = \frac{466\ (ug/ml)}{0.1\ gram/ml} = 4660.$$

======> 4660 ug Pyrene in 1 gram Tar

======> 4.66 mg Pyrene/g Tar

The results mg/g for 9 specific PAH compounds in the tar sample are all listed in Table 4-5 to 4-14

For conversion of tar after reaction:

$$\text{Fraction remaining} = \frac{\text{mg/g Final}}{\text{mg/g Initial}} \Longrightarrow fr = \alpha$$

$$\text{Fraction conversion of Compound} = 1 - \alpha$$

The results for 4 to 5 specific PAH compounds remaining after reaction are shown in Figure 4-1 to 4-19.

4.1.3 Results on specific PAH's conversion

Figure 4-1 to 4-19 show fraction of specific poly aromatic hydrocarbons(PAH's) remaining after reaction (fr). Higher bars indicate more compound remaining or less conversion for that species. Percent conversion (β) is defined as $(1-\alpha)*100$ Thus as in Figure 4-1 for acid media, ozone, 15 hours reaction: 0.78 = fr and $\beta = (1-0.78)*100 = 22$ %.

Figure 4-1 to 4-4 show the conversion of Tar I by ozone reaction on the specific PAH's ---Naphthalene, Acenapthene, Fluorene and Chrysene with and without glass beads to

CONVERSION OF TAR

Naphthalene

(TAR I)

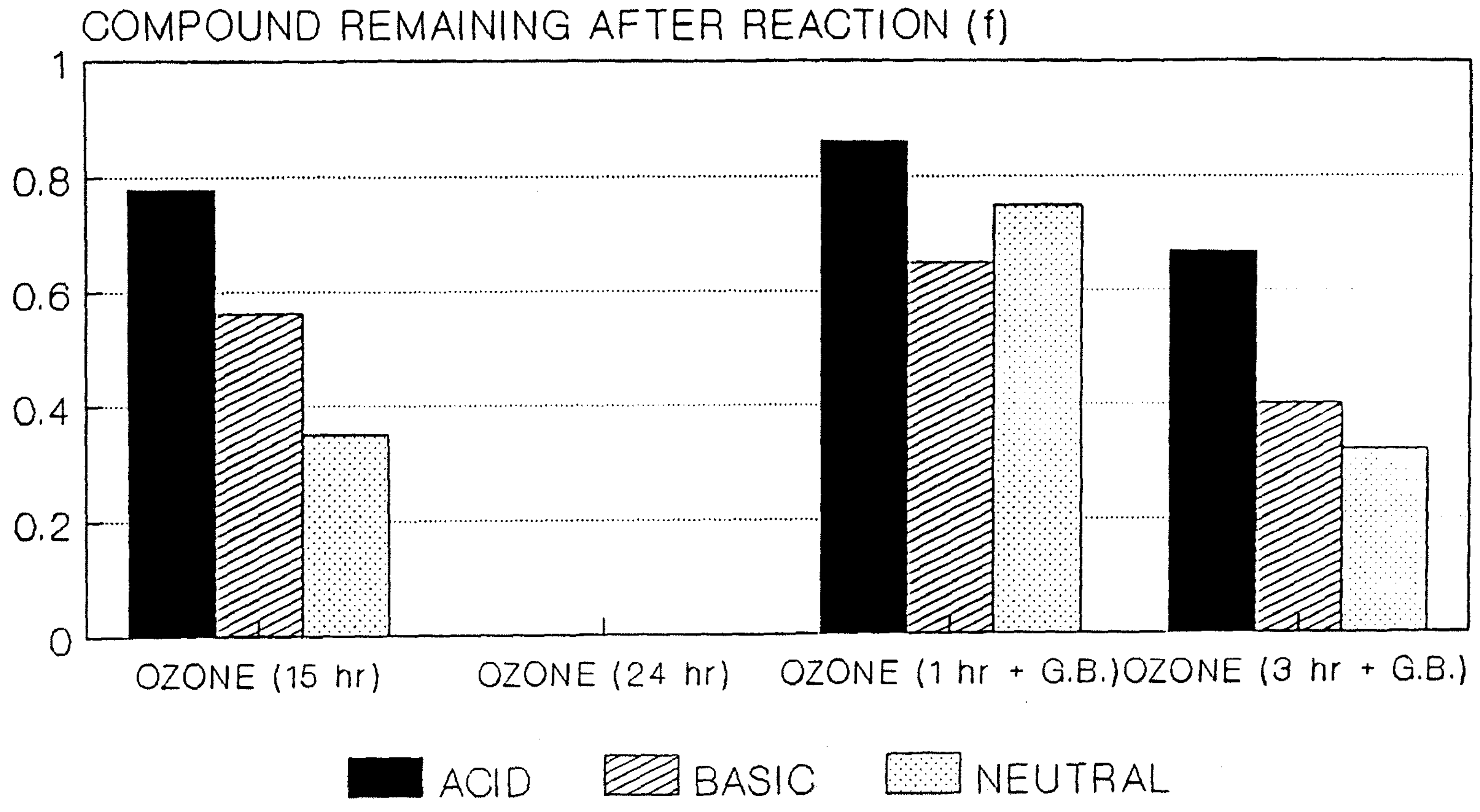


Figure 4-1

G.B. : GLASS BEAD

CONVERSION OF TAR

Acenapthene

(TAR I)

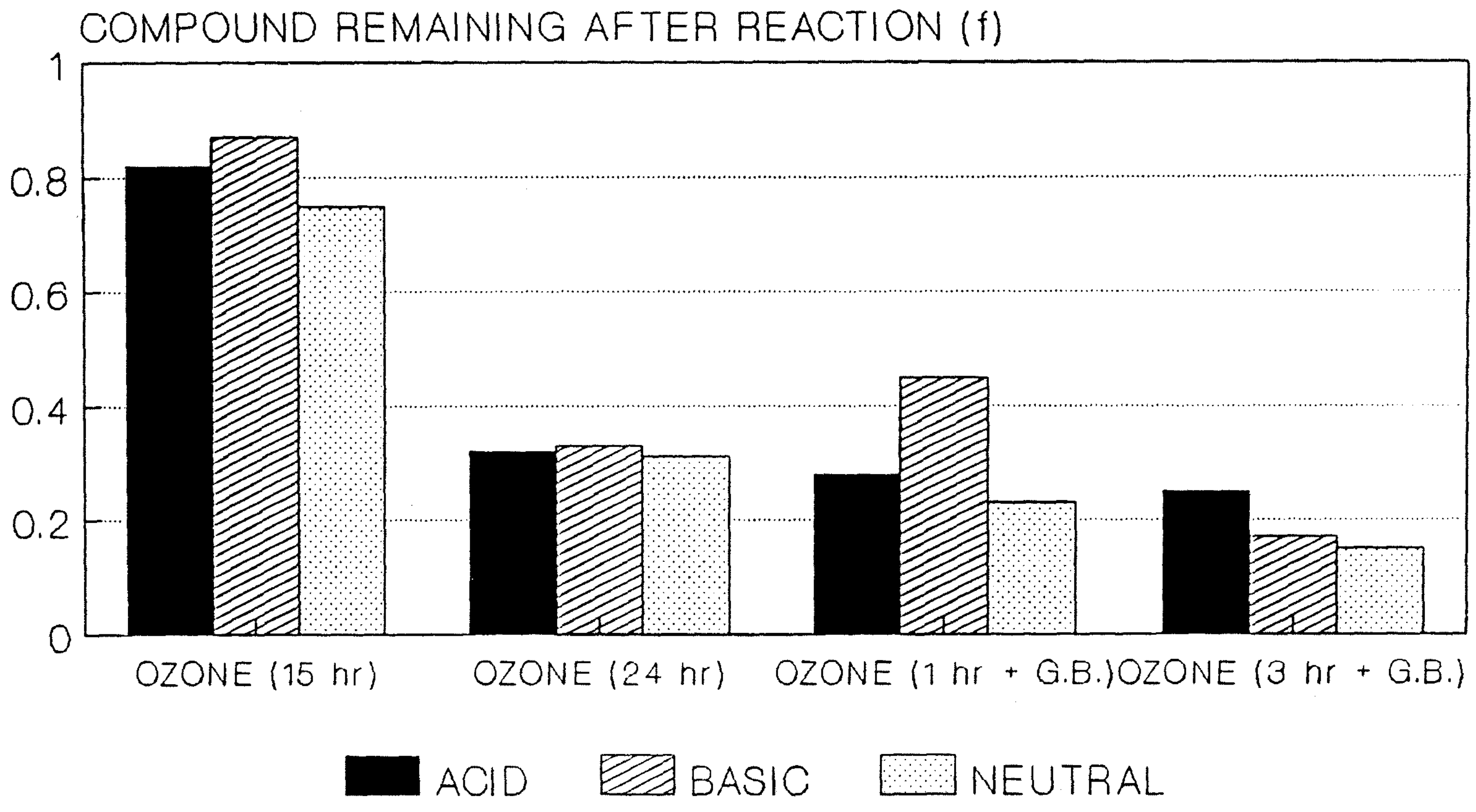


Figure 4-2

G.B. : GLASS BEAD

CONVERSION OF TAR
Fluorene
(TAR I)

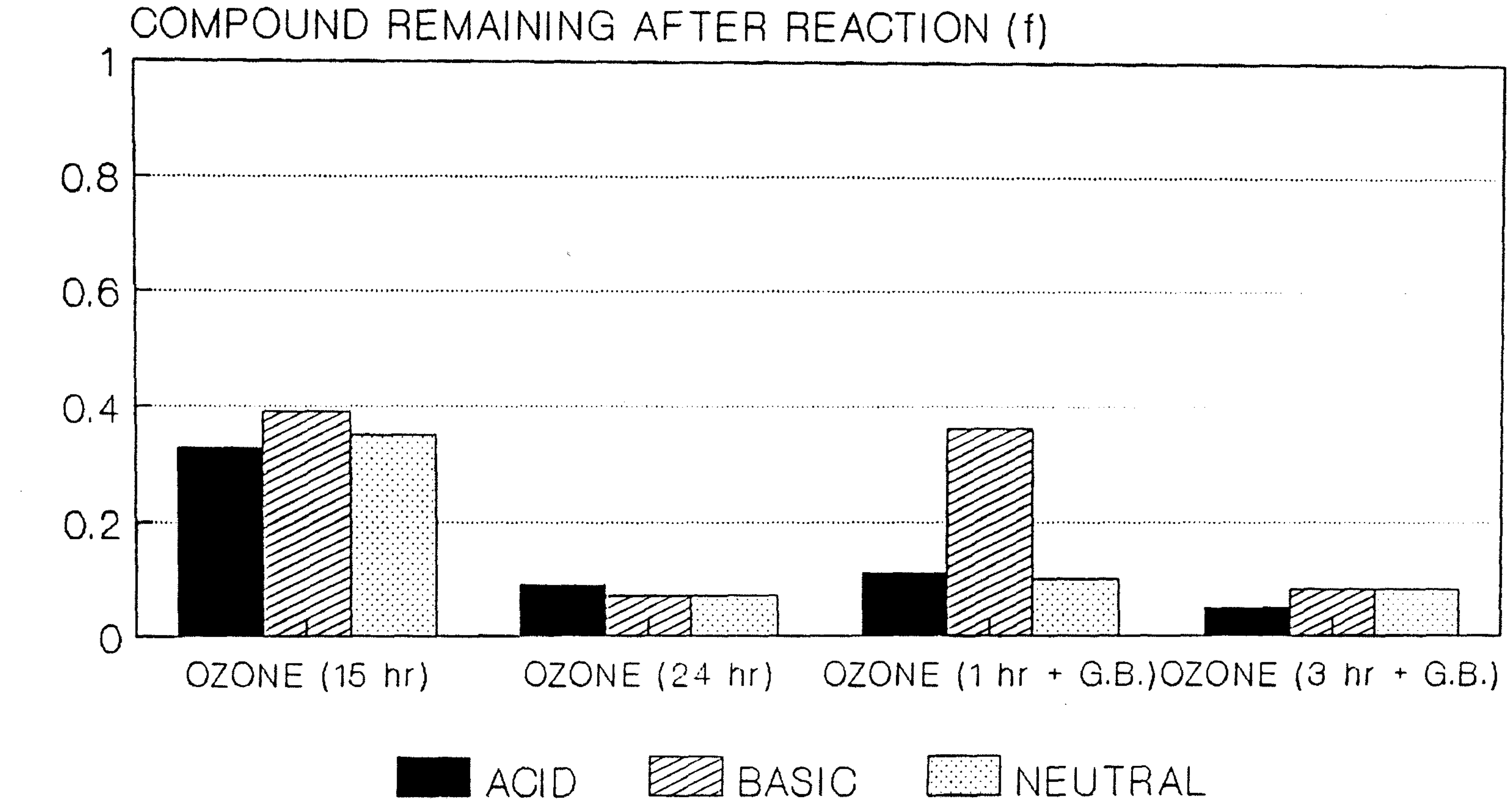


Figure 4-3

G.B. : GLASS BEAD

CONVERSION OF TAR
Chrysene
(TAR I)

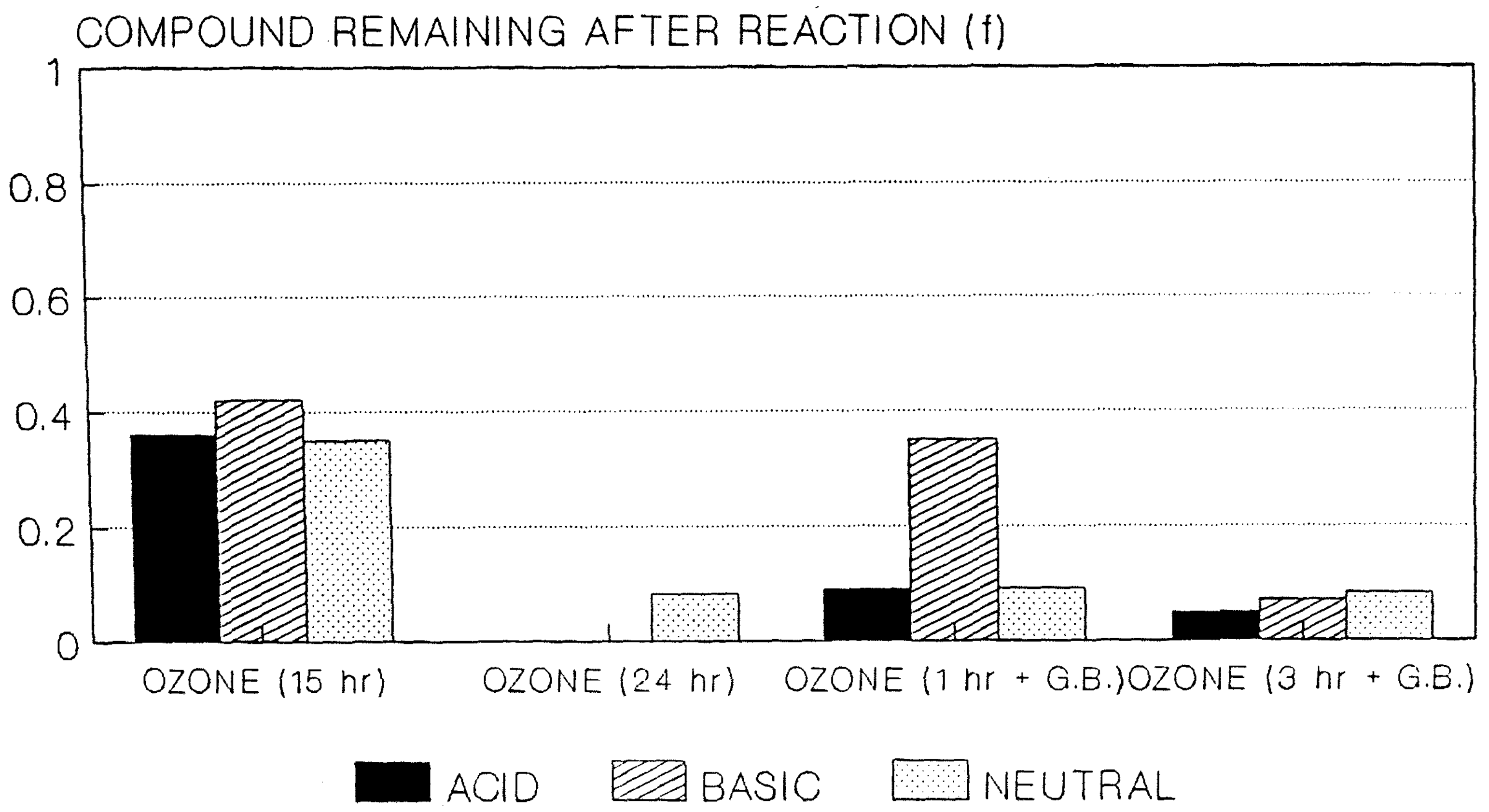


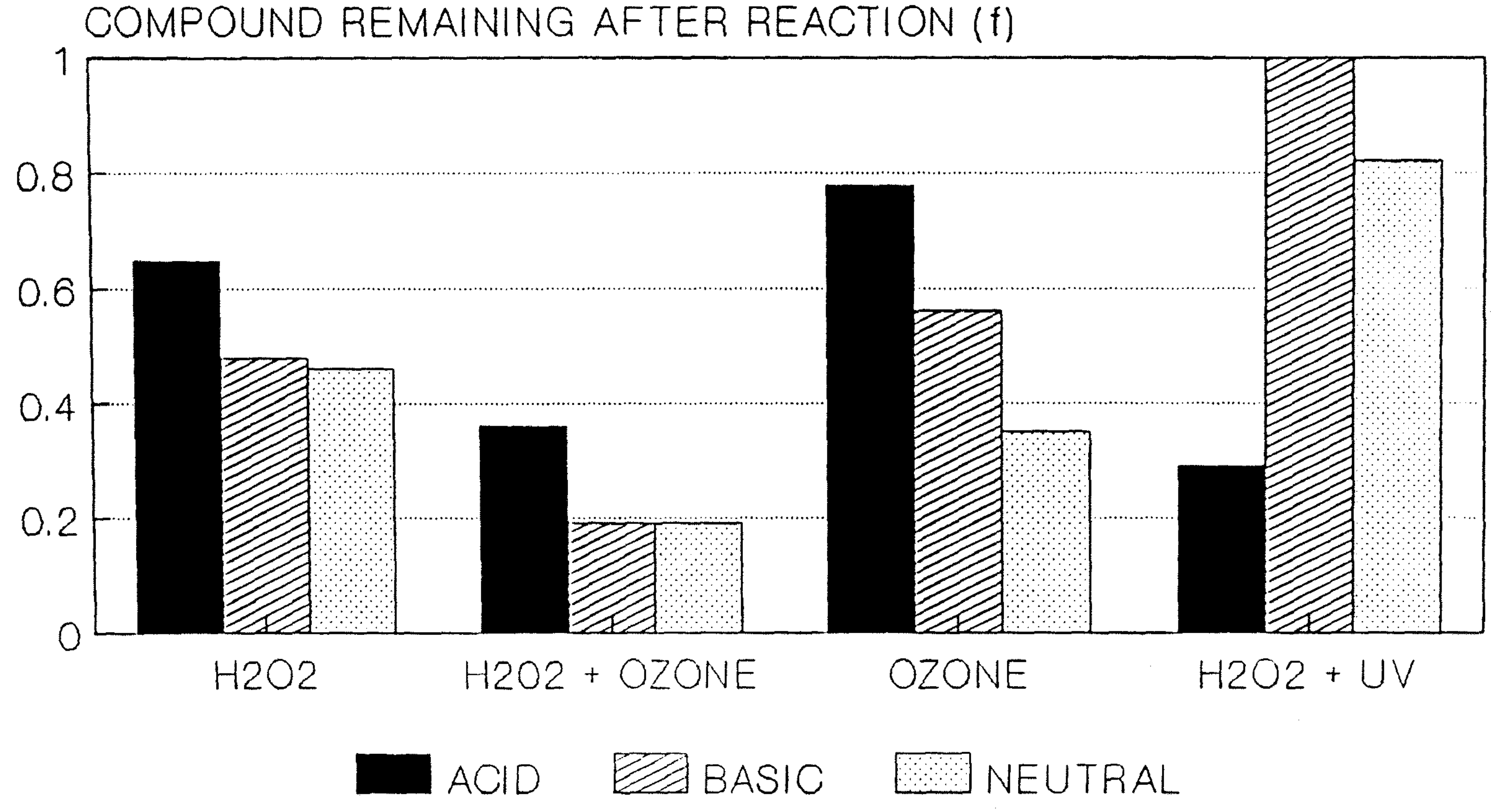
Figure 4-4

G.B. : GLASS BEAD

CONVERSION OF TAR

Naphthalene

(TAR I)



REACTION TIME : 15 hr

Figure 4-5

CONVERSION OF TAR

Acenapthene

(TAR I)

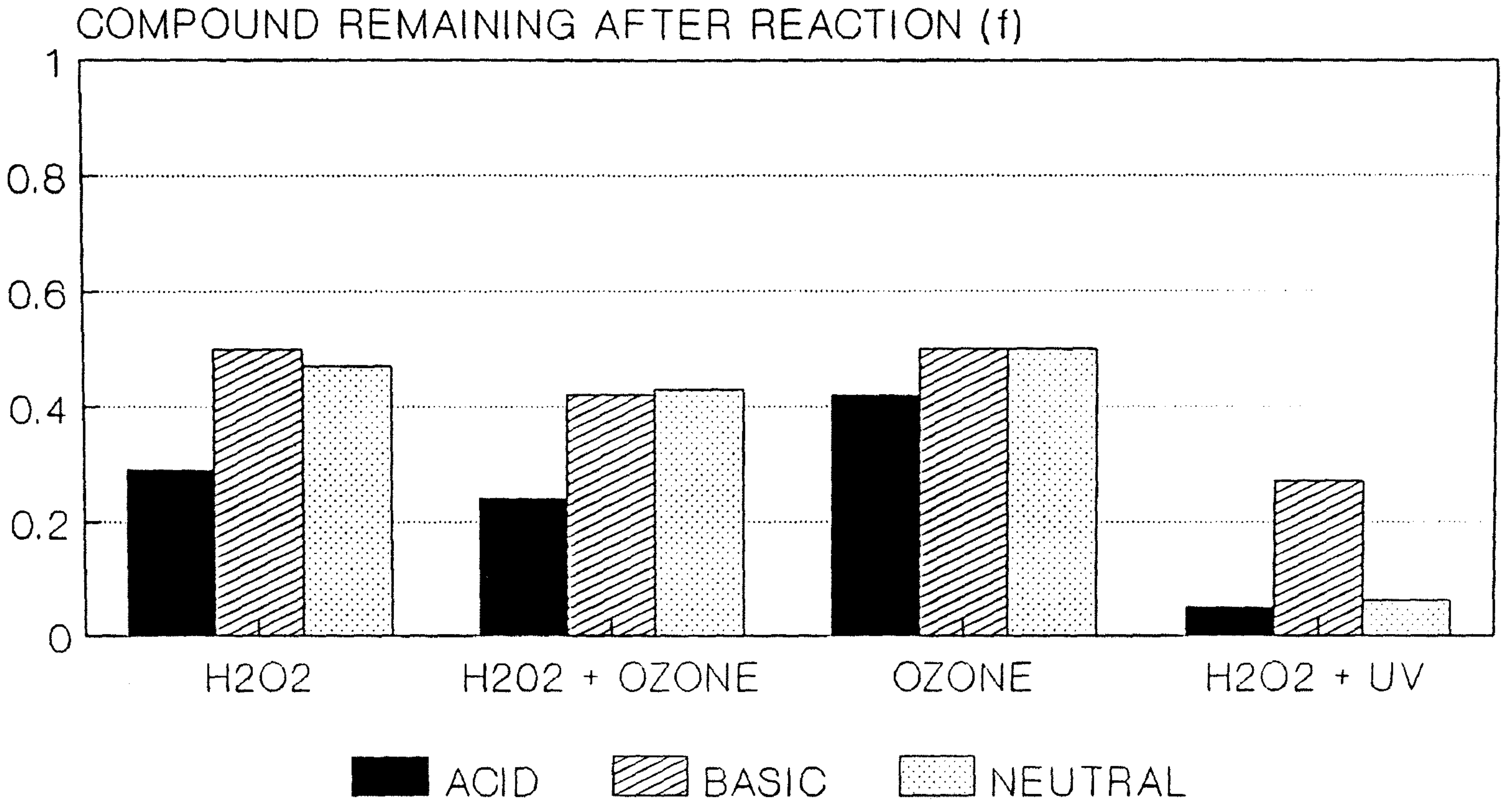


Figure 4-6

REACTION TIME : 15 hr

CONVERSION OF TAR

Fluorene

(TAR I)

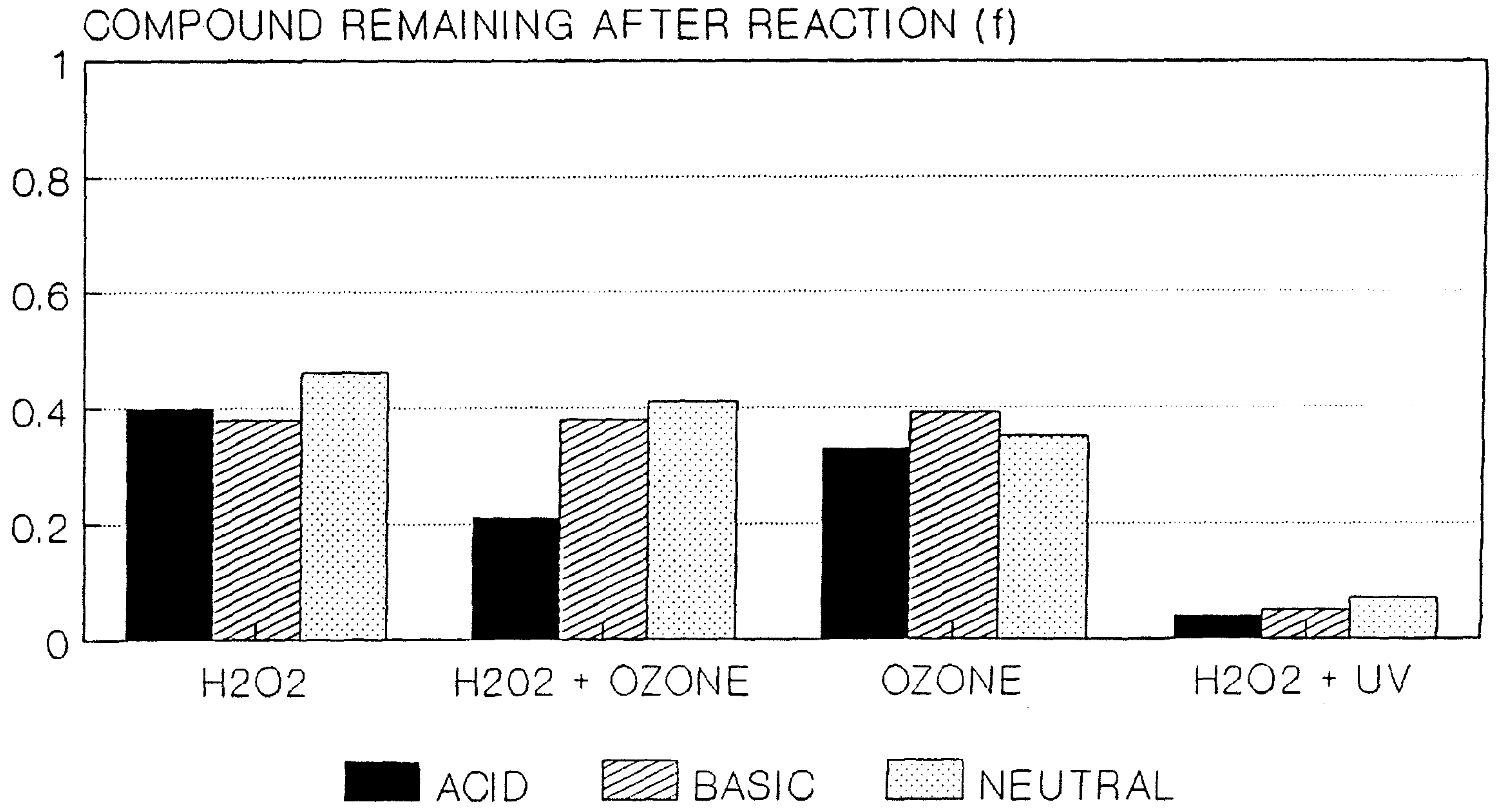


Figure 4-7

REACTION TIME : 15 hr

CONVERSION OF TAR

Chrysene

(TAR I)

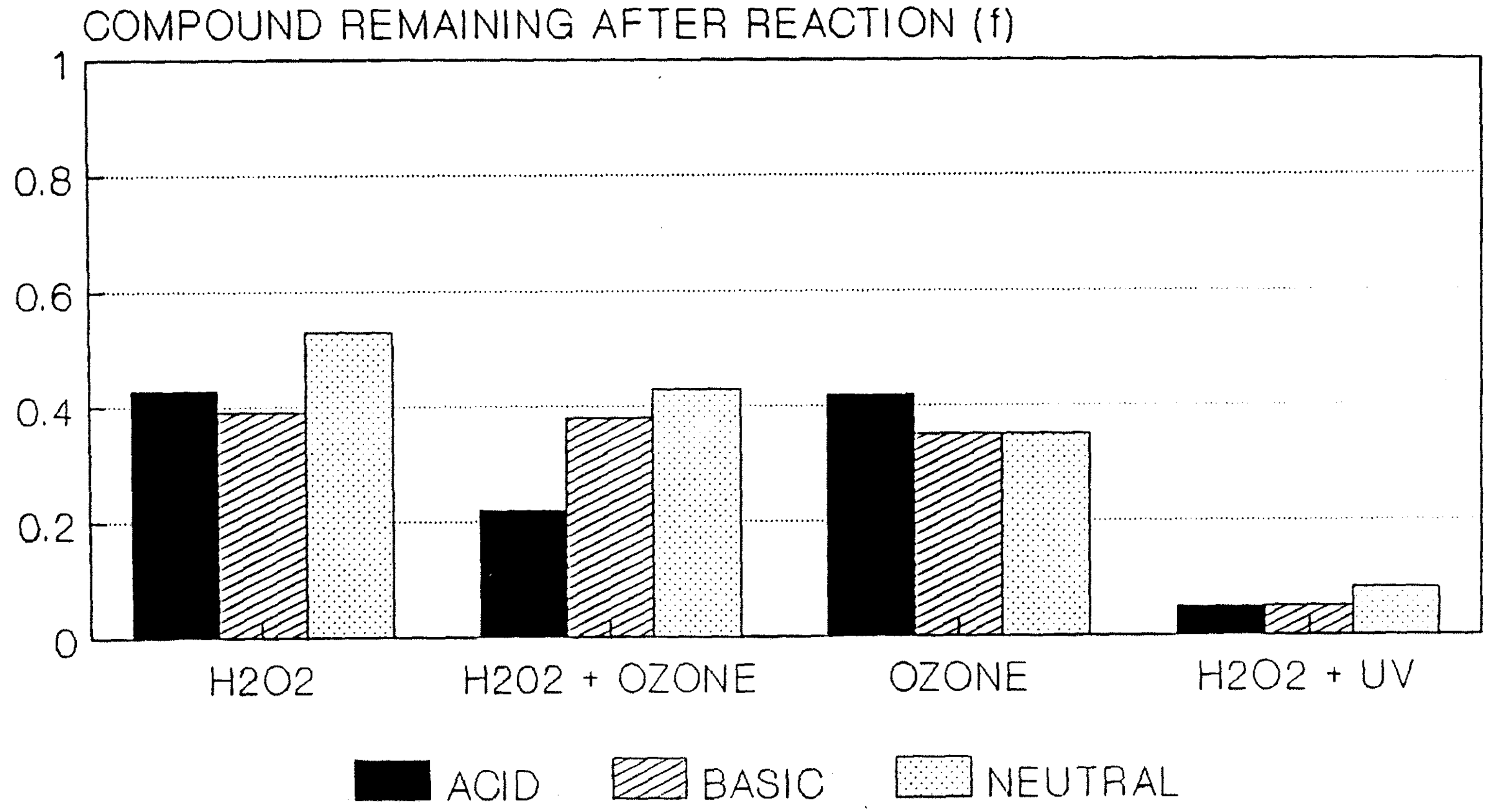


Figure 4-8

REACTION TIME : 15 hr

CONVERSION OF TAR
Pyrene
(TAR I)

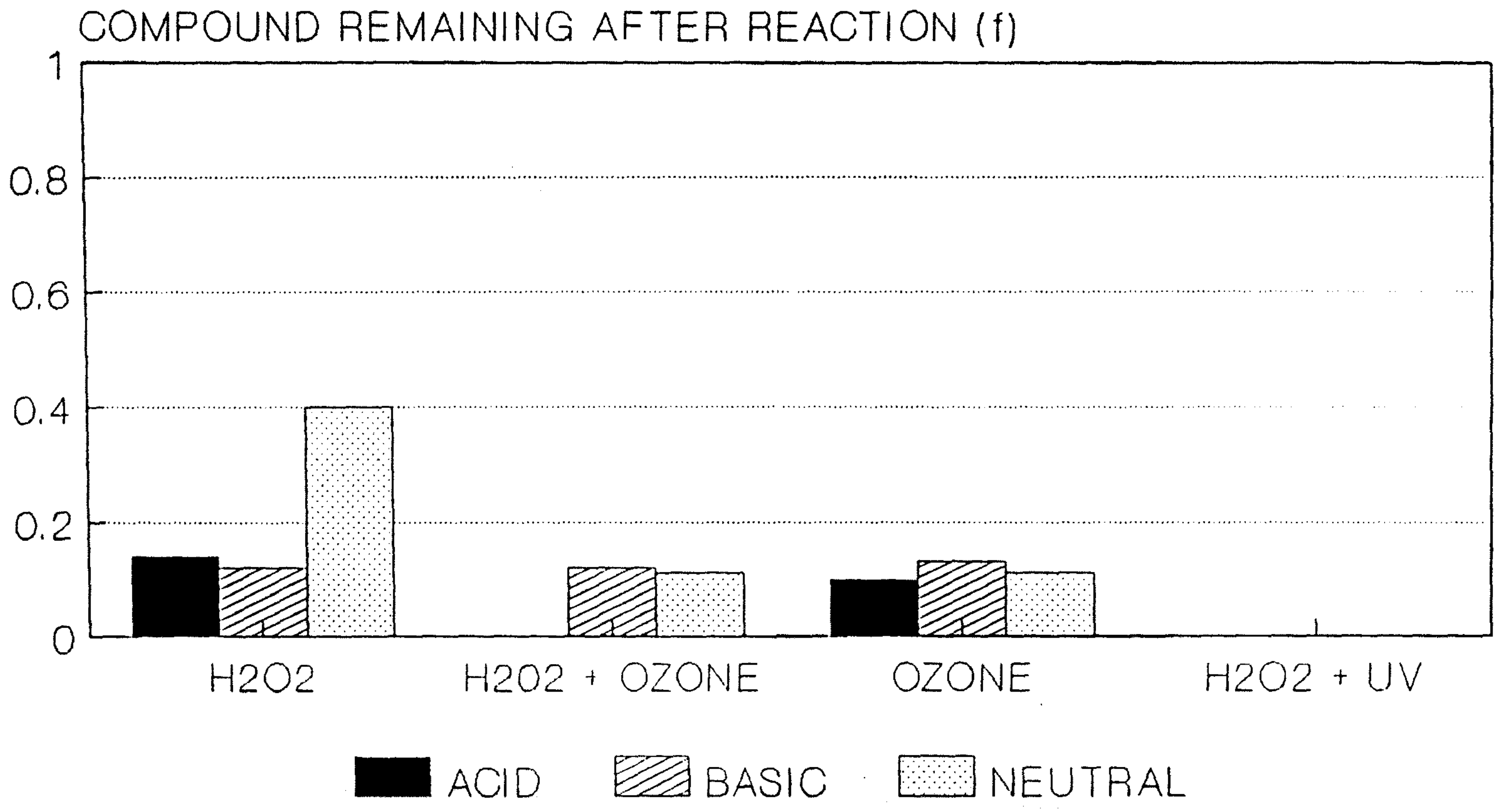


Figure 4-9

REACTION TIME : 15 hr

CONVERSION OF TAR

Naphthalene

(TAR I)

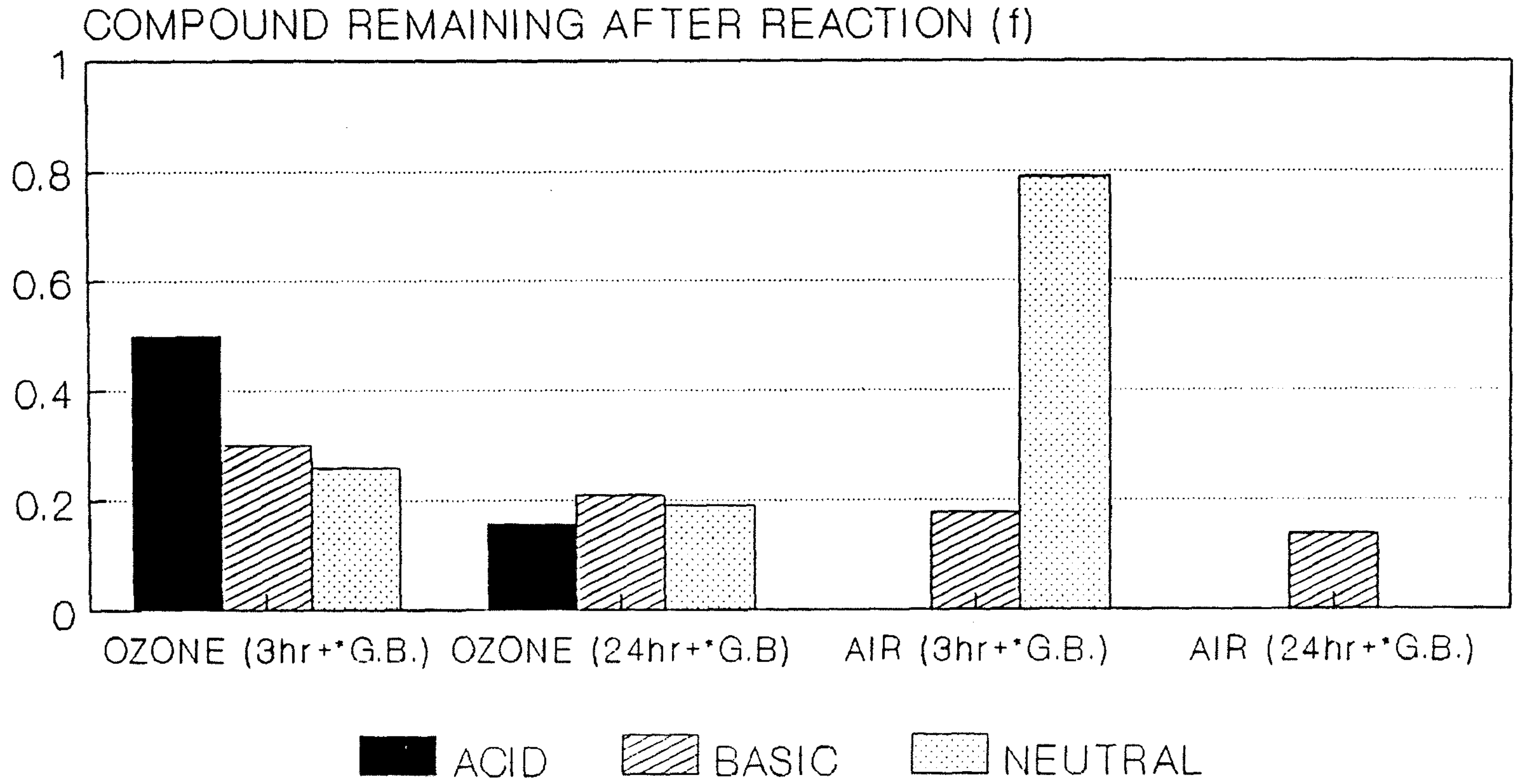


Figure 4-10

G.B. : GLASS BEAD
* Be treated with Ether

CONVERSION OF TAR

Acenapthene

(TAR I)

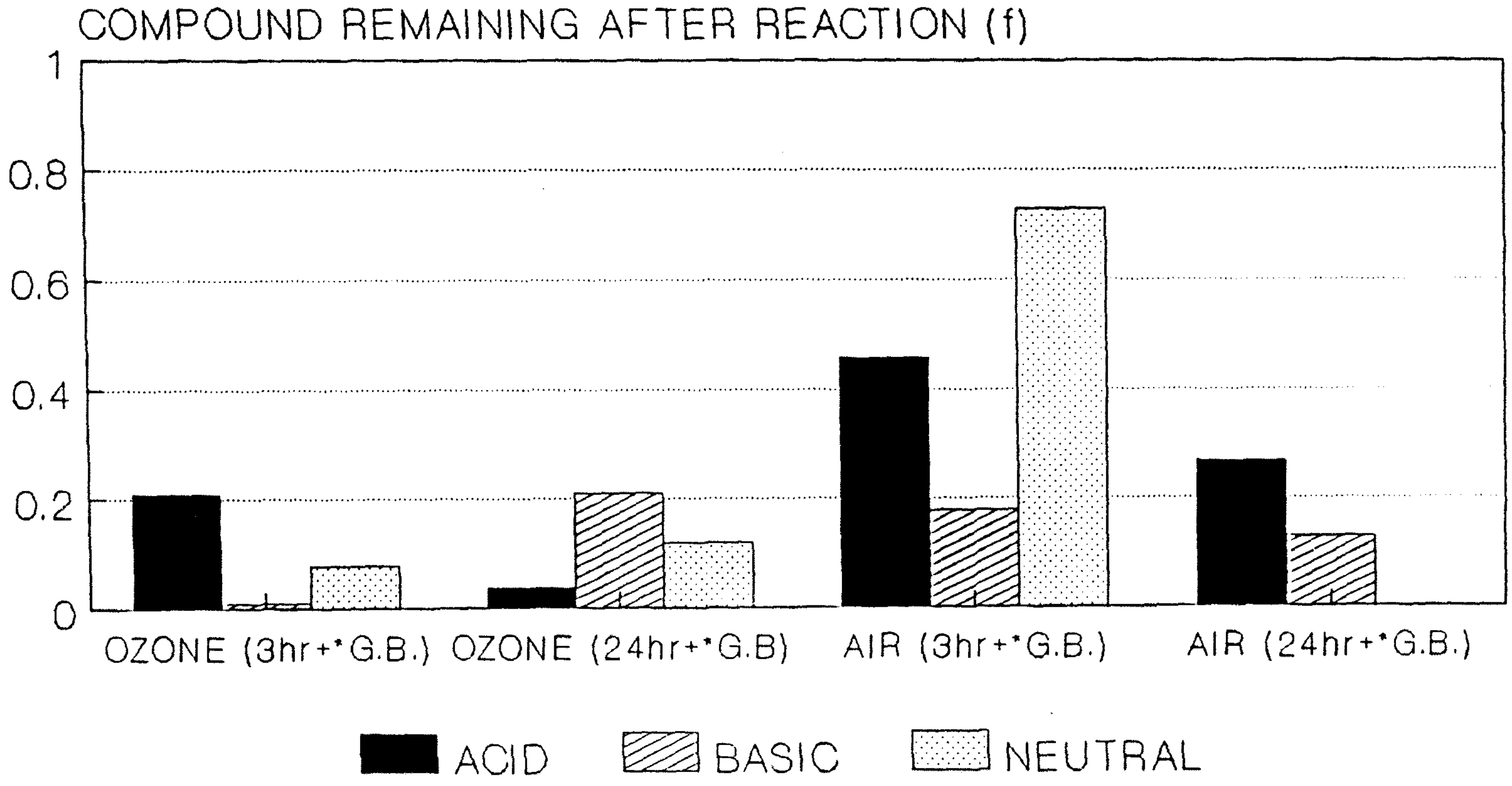


Figure 4-11

G.B. : GLASS BEAD
* Be treated with Ether

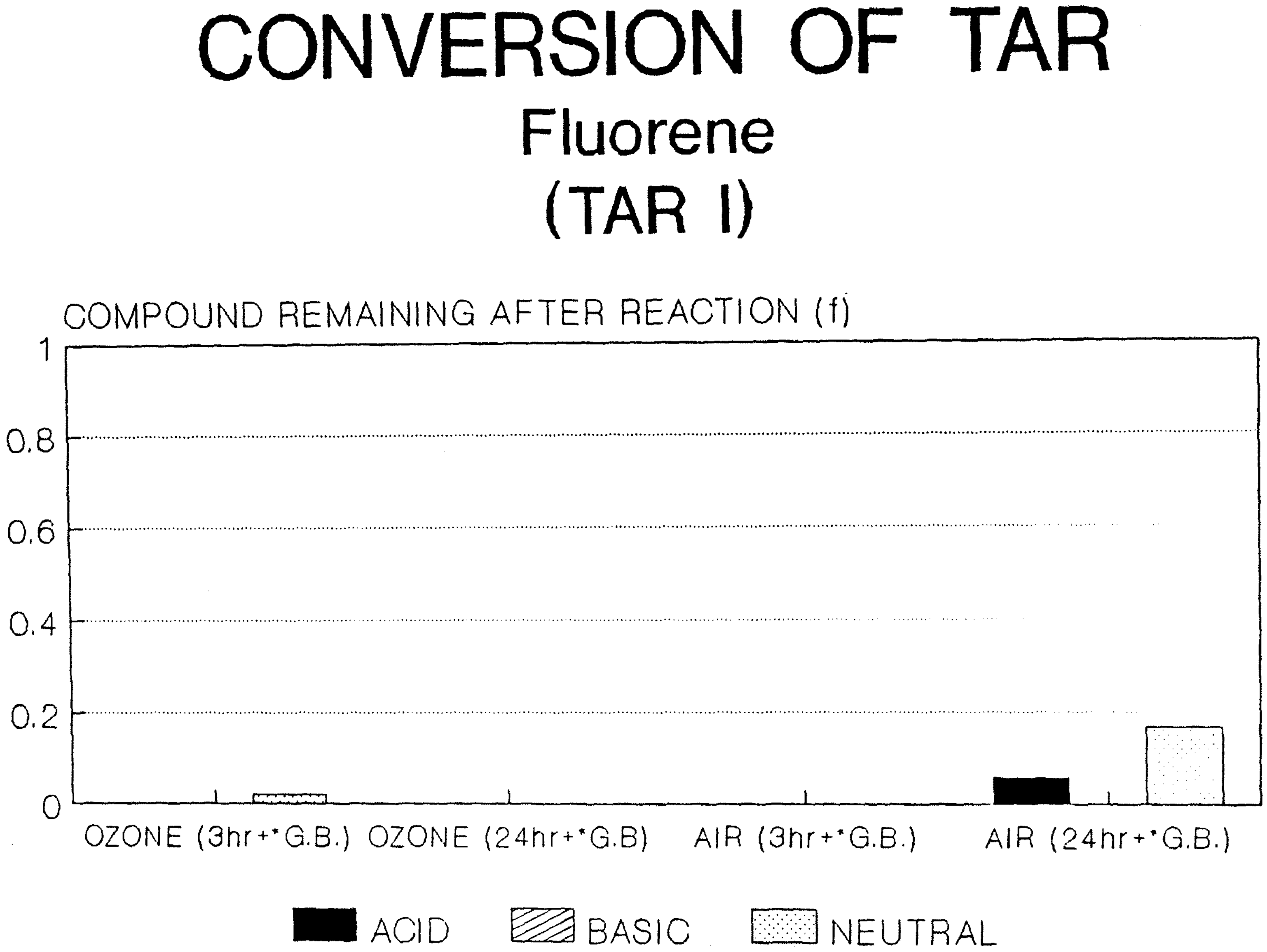


Figure 4-12

G.B. : GLASS BEAD
* Be treated with Ether

CONVERSION OF TAR
Chrysene
(TAR I)

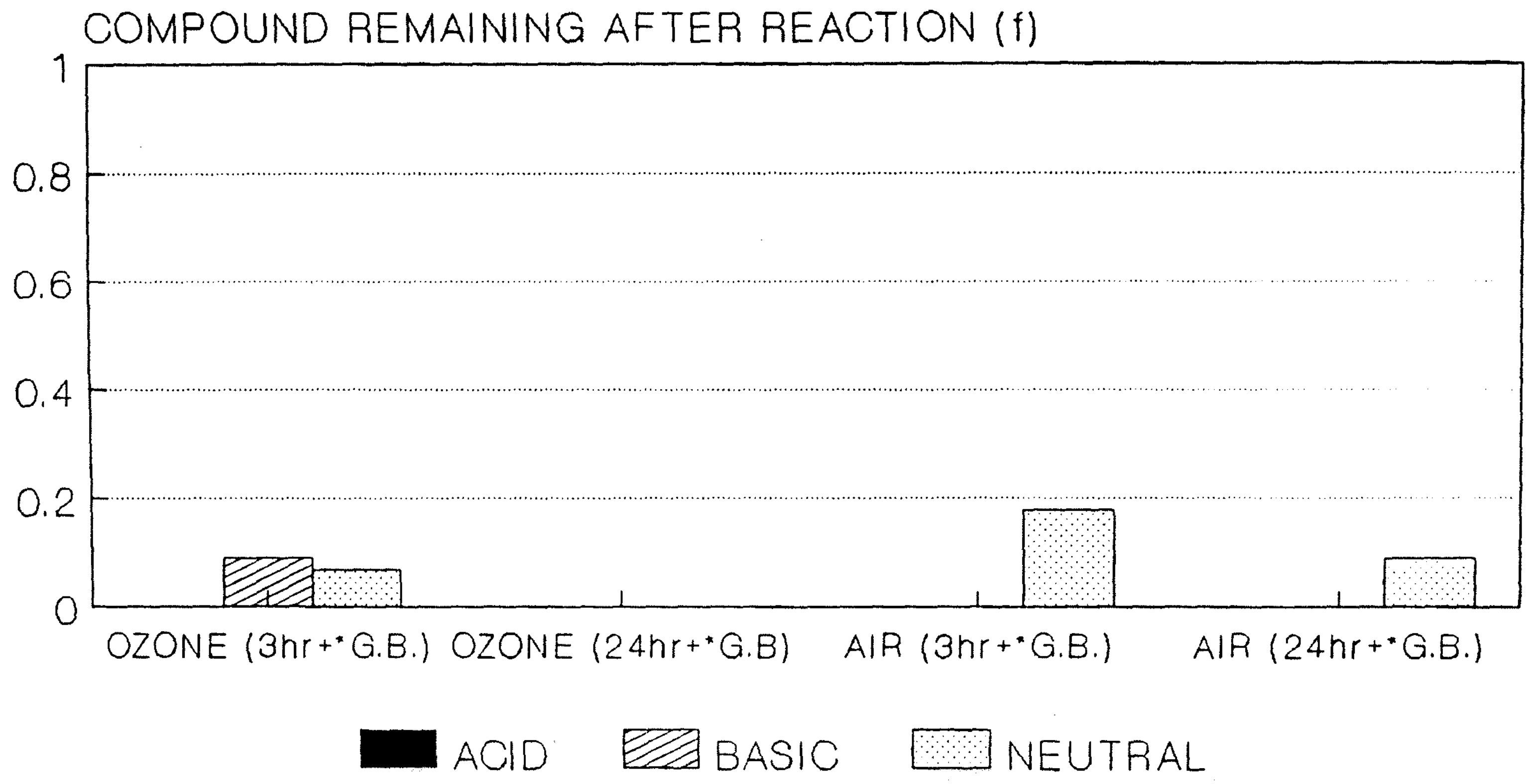


Figure 4-13

G.B. : GLASS BEAD
* Be treated with Ether

CONVERSION OF TAR

Naphthalene

(TAR II)

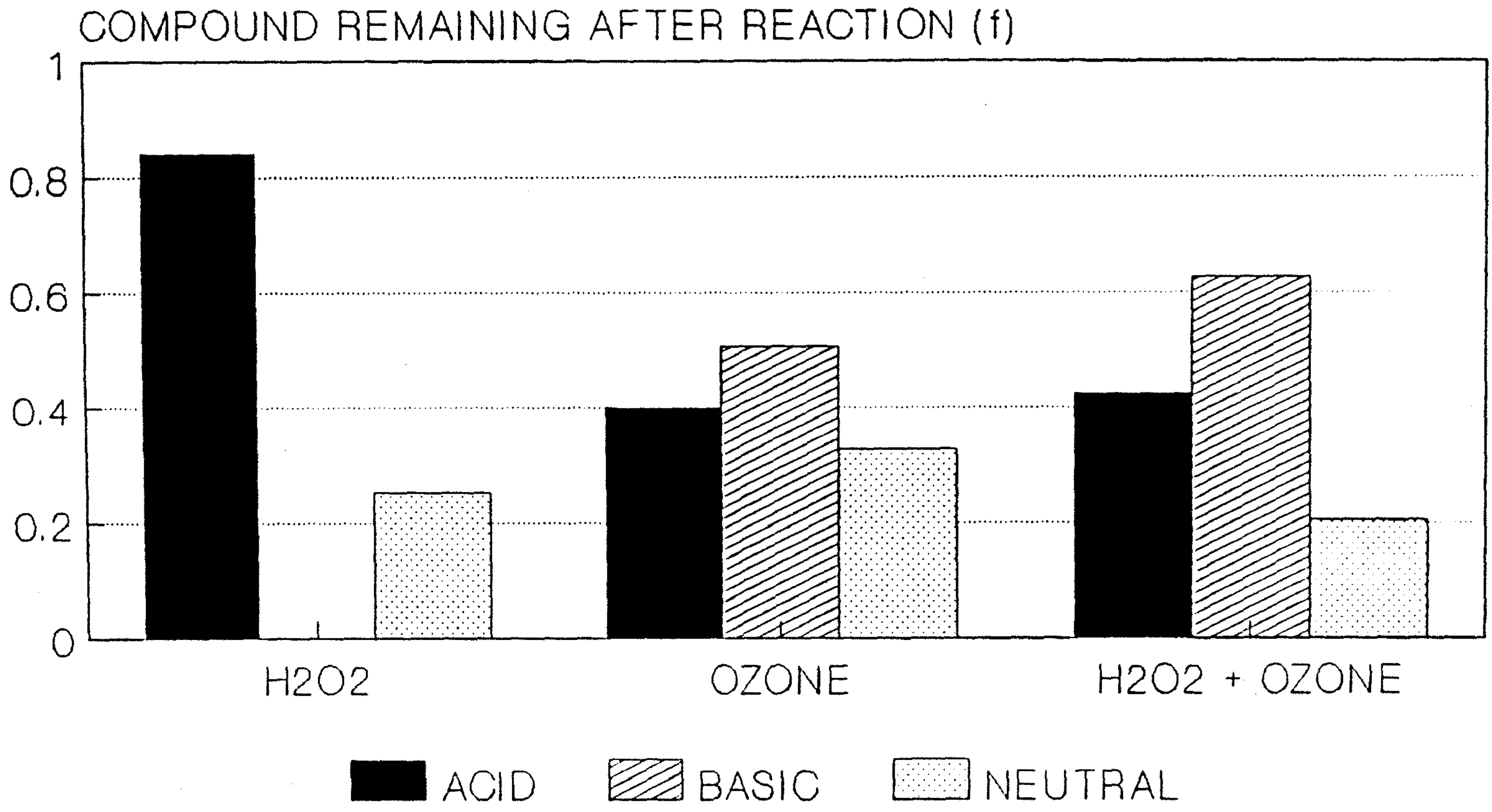


Figure 4-14

REACTION TIME : 15hr

CONVERSION OF TAR

Acenapthene

(TAR II)

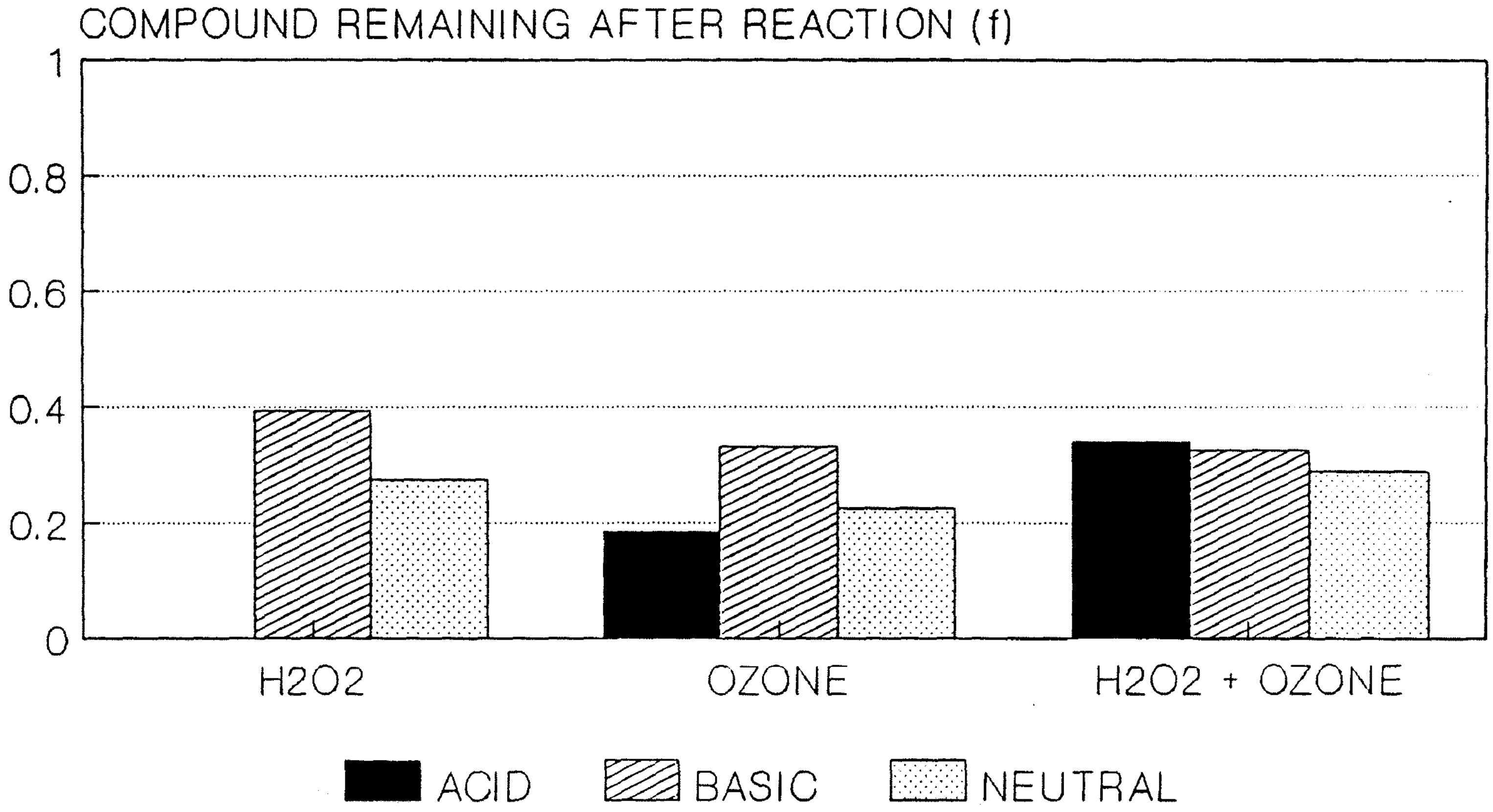


Figure 4-15

REACTION TIME : 15hr

CONVERSION OF TAR

Naphthalene

(TAR I)

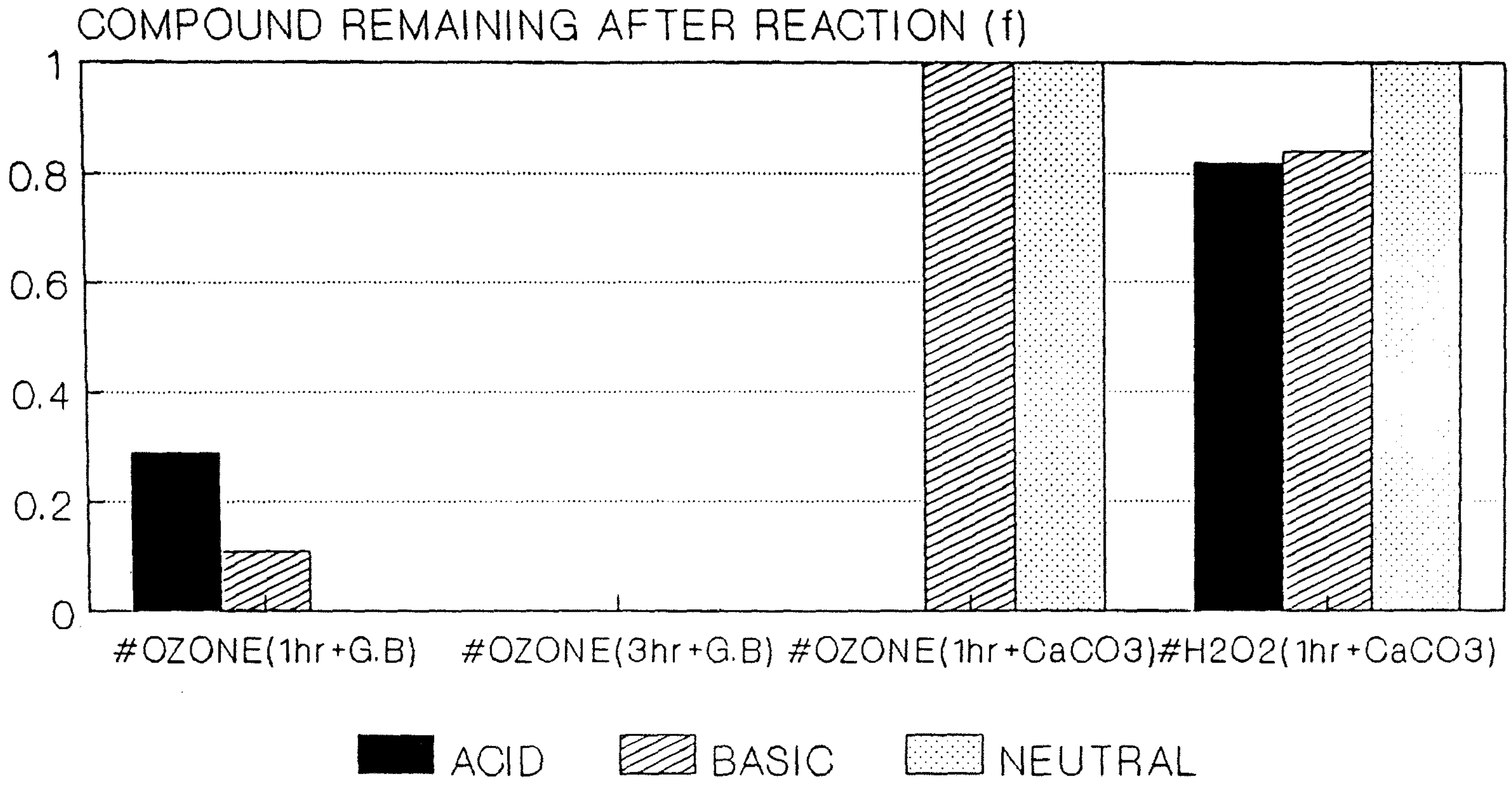


Figure 4-16

G.B. : GLASS BEAD
=reaction with Hexane

CONVERSION OF TAR
Acenapthene
(TAR I)

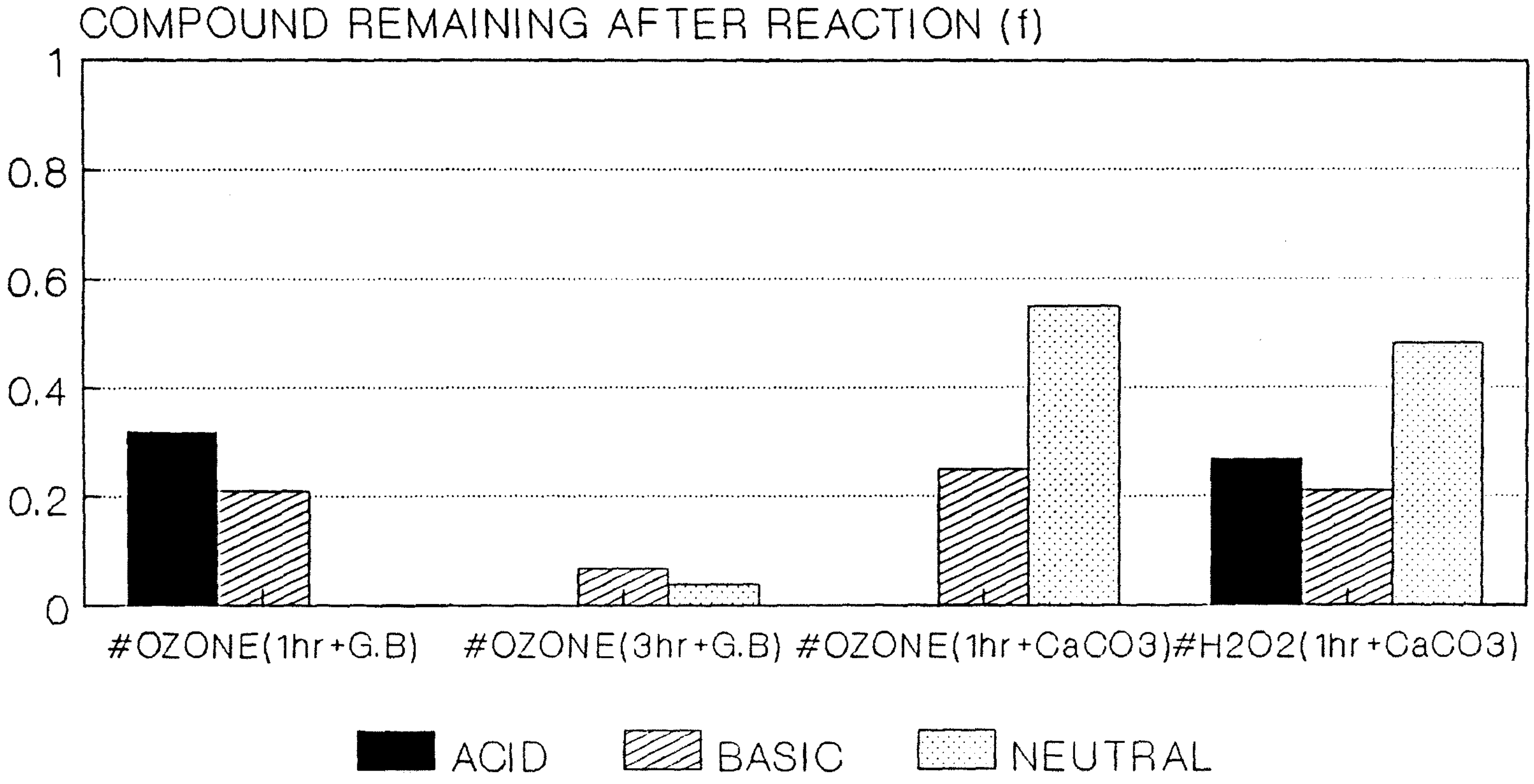


Figure 4-17

G.B. : GLASS BEAD
=reaction with Hexane

CONVERSION OF TAR

Fluorene

(TAR I)

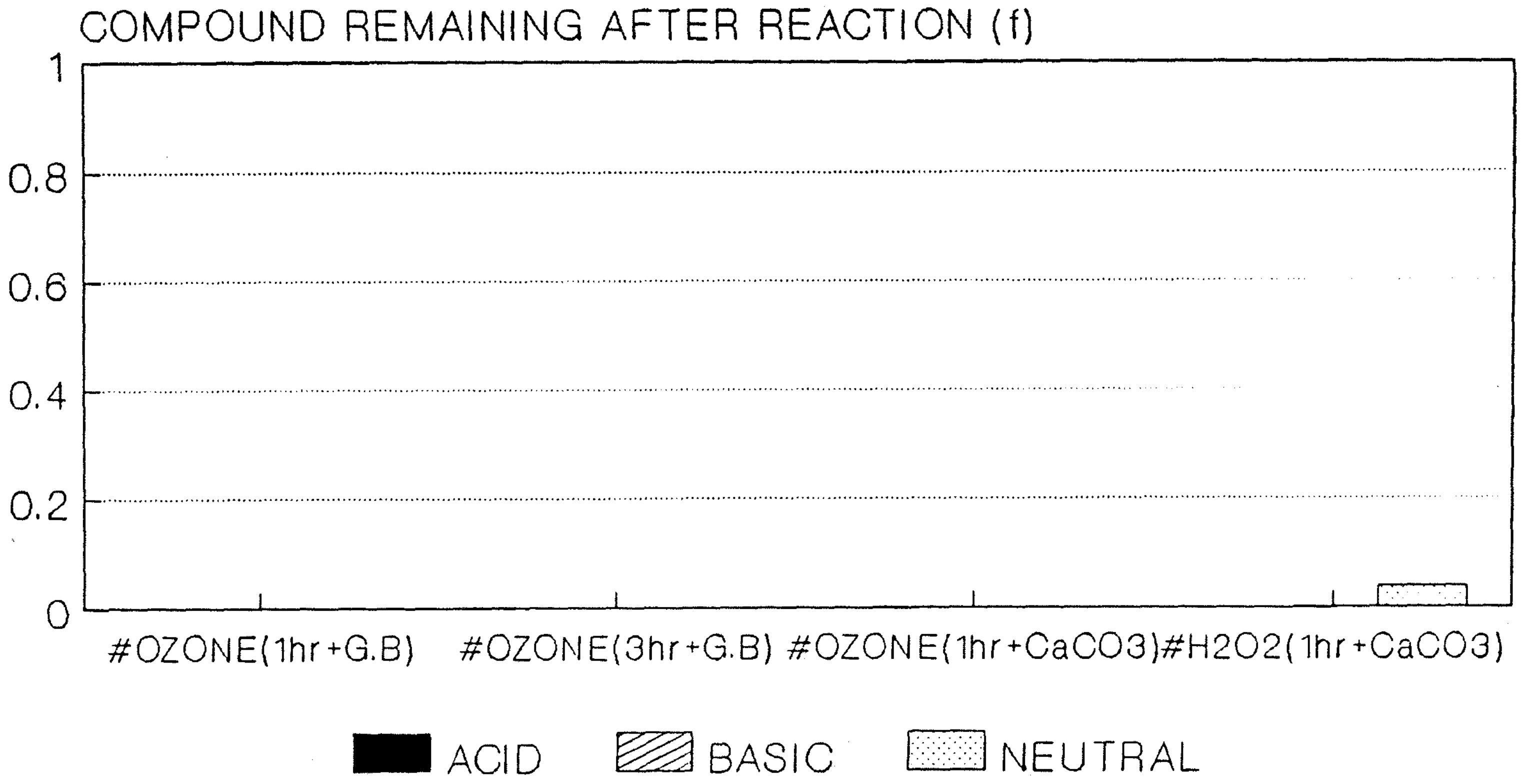


Figure 4-18

G.B. : GLASS BEAD
=reaction with Hexane

CONVERSION OF TAR

Chrysene

(TAR I)

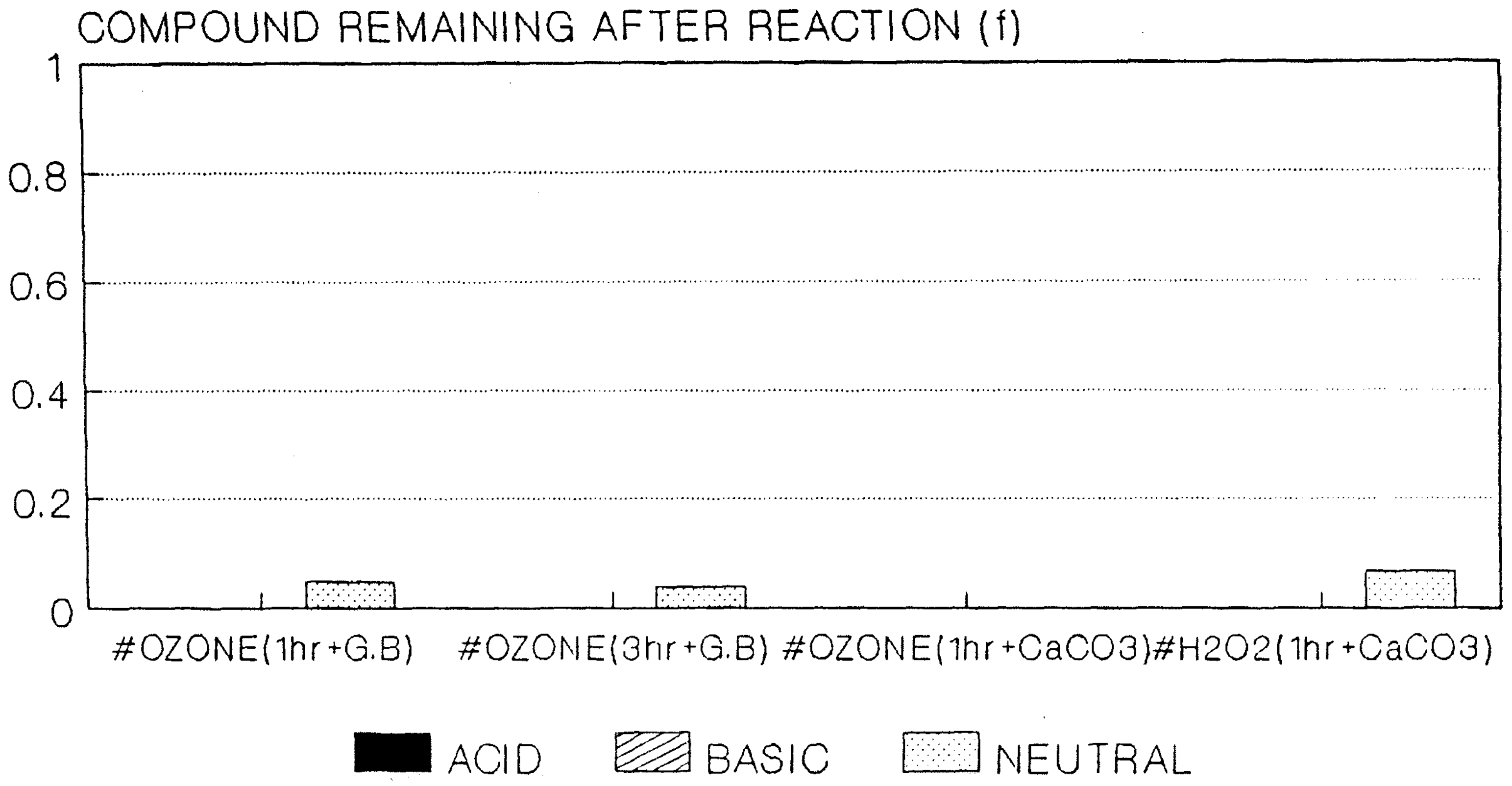


Figure 4-19

G.B. : GLASS BEAD
=reaction with Hexane

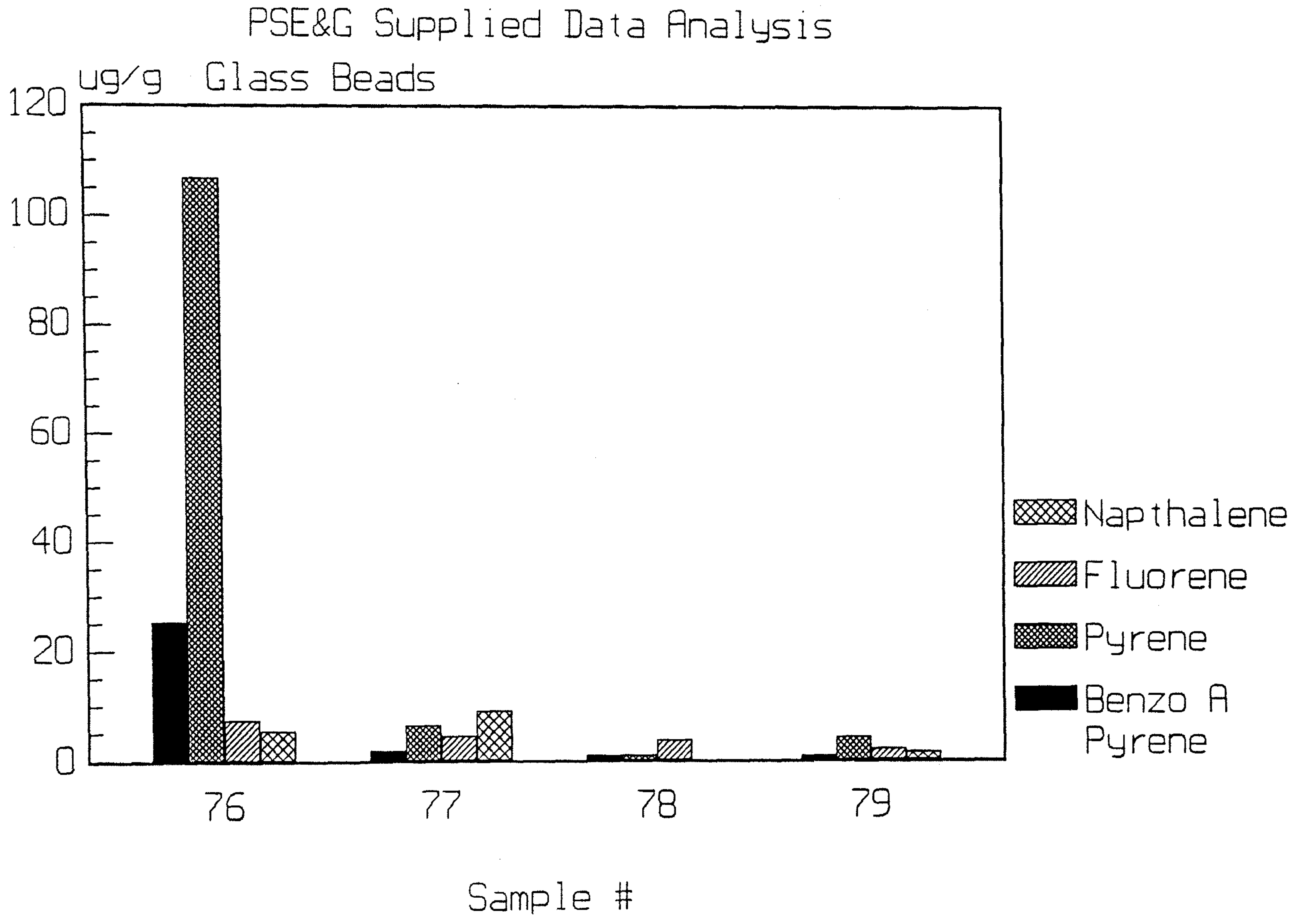

PSE&G Supplied Data Analysis
ug/g Glass Beads
120
100
80
60
40
20
0
76
77
78
79
Sample #
▨ Napthalene
▨ Fluorene
▨ Pyrene
■ Benzo A Pyrene

Figure 4-20

increaseor the surface area.

Figure 4-5 to 4-9 show the conversion of Tar I, in ozone alone, in H_2O_2 alone, in H_2O_2 + ozone and in H_2O_2 + UV on specific PAH's --Naphthalene, Acenapthene, Fluorene, Chrysene and Pyrene.

Figure 4-10 to 4-13 show the conversion from ozone reaction on Tar I coated on glass beads via ether solution for specific PAH's --Naphthalene, Acenapthene, Fluorene and Chrysene.

Figure 4-14 tO 4-15 show the conversion of Tar II in H_2O_2 and ozone reactions or H_2O_2 + ozone on specific PAH's -- Naphthalene and Acenapthene.

Figure 4-16 to 4-19 show the conversion of Tar I in ozone reaction on specific PAH's --Naphthalene, Acenapthene, Fluorene and Chrysene where the Tar was dissolved in hexane solution and either glass beads or carbonate-sand was added for mixing (agitation). Ozone was added to the hexane/Tar solution.

Figure 4-20 show the results of samples JU 77, JU 78 and JU 79, which were a second processing on the product of JU 76.

4.1.4 Level of specific PAH's found in Tar I

Table 4-5 to 4-14 show mg/gram of specific PAH's in the initial pure tar --Tar I and in the products of reaction for samples JU 1- JU 72 using GC analysis obtained at NJIT.

4.2 Discussion

(1) Carbon / Hydrogen / Nitrogen Analysis

Analysis on fraction Carbon, Hydrogen and Nitrogen composition show no statistically significant trends for products of Tar I reaction with ozone or H_2O_2. The data in Table 4-1 shows the variation obtained for the different Tar I reactions. We feel that this lack of positive trend is a combination of low experimental sensitivity on the small mass of sample we supplied for analysis and the small decrease in carbon and hydrogen in tar via our reaction. While significant reaction has occurred as illustrated in Figure 1 to Figure 8, most of these reactions served only to partially oxidize the PAH's in the tar, not to completely convert them to CO_2 and H_2O. There is a begining of a significant trend in carbon reduction for samples Ju83-Ju90, but more results are needed to further verify this data.

There are fewer results for reactions with Tar II, but for the longer time reactions there is a trend to lower carbon (about 20 % reduction) especially in the base and neutral reaction media (about 30 % reduction). Again these results need to be further verified. It must also be noted that the Tar II material is more variable in nature than the pure tar of tar I samples.

(2) Ozone Reaction

Figures 4-1 to 4-4 show the results of ozone reaction on specific PAH's -- Naphthalene, Acenapthene, Fluorene and Chrysene.

Figures 4-1 to 4-4 show the general trend that reaction at longer times yields higher conversion. It is difficult to see any statistical trends in acid vs base vs neutral or surface area effects here.

(3) Reaction in H_2O_2/ Ozone/ $H_2O_2 + O_3$/ H_2O_2 + UV

Figures 4-5 to 4-9 show the results of reaction with ozone alone, H_2O_2 alone, H_2O_2 + ozone, or H_2O_2 + UV on Tar I for the specific PAH's --Naphthalene, Acenapthene, Fluorene, Chrysene and Pyrene.

All figures show reaction at 15 hours.

With the one exception of Naphthalene, H_2O_2 + UV reaction showed the highest conversion. Naphthalene was alone the only compound that did not show conversion consistently higher than 50 %. Pyrene, on the other hand, showed the highest conversion for all conditions.

(4) Ozone Reaction be Treated with Ether

Figures 4-10 to 4-13 show the results of ozone reaction on specific PAH's ---Naphthalene, Acenapthene, Fluorene and Chrysene with glass beads.

For ozone reaction with glass beads, neutral solution showed the best results on naphthalene and acenapthene.

Reaction in acid solution yielded conversion of only 50 % for Naphthalene and 20 % for Acenapthene after 3 hour.

Reaction in basic solution showed more conversion than acid but less than in neutral solution. For ozone reaction with glass beads on Fluorene and Chrysene, acid solution showed the best results with neither fluorene or chrysene detected after 3 hours of reaction. Reaction in basic solution also had good results after 24 hours on these two compounds.

(5) Reaction in H_2O_2/ Ozone /H_2O_2 + Ozone

Figures 4-14 tO 4-15 show the results of H_2O_2 alone, ozone alone or both H_2O_2 + ozone on specific PAH's -- Naphthalene and Acenapthene.

For naphthalene, neutral reaction showed the best results in the 3 reactions above. Basic solution showed more conversion than acid but less than neutral solution. For acenapthene, acid solution showed the best result in all 3 reactions while neutral solution is the second one.

(6) Ozone Reaction in Hexane solution

Figure 4-16 to 4-19 show the results of ozone reaction on specific PAH's --Naphthalene, Acenapthene, Fluorene and Chrysene with the tar dissolved in hexane solution (ozone reacted with the hexane/Tar mix) plus either glass beads or carbonate-sand to help in mixing (agitation).

For reactions with glass beads, the neutral solution showed the best results with none of the above 4 compounds detected after 1 hour of reaction. Reaction in acid solution yielded conversion of only 70 % for Naphthalene and acenapthene after 1 hour. Reaction in basic solution showed more conversion than acid but less than in neutral solution.

For ozone reactions with carbonate-sand --acid media showed the best results and neutral the least conversion. No compounds were detected after 1 hour reaction for the acid reaction. H_2O_2 reaction in carbonate-sand did not show the same high conversion in acid solution, with similar conversion to that of acid also observed for the neutral and the basic reactions. Higher conversion for Naphthalene and

Acenapthene compounds was observed after longer times; while Fluorene and Chrysene showed nearly 100 % conversion for all media in 1 hour time.

(7) Retreated Reaction After Products

The samples of JU 77, JU 78 and JU 79 were reacted a second time using the product of JU 76. The data are shown in Figure 4-20. The samples treated twice yield much better results.

The levels of fluorene are reduced from 110 ug/g glass beads to less than 10 for all conditions of JU 77-79 and Benz-a-Pyrene was reduced from 25 to less than 3 for all reactions. Benz-a-Pyrene was converted best with base and neutral reactions conditions, but the 1 % poorer acid yield may result from lack of analytical accuracy.

(8) Level of specific PAH's Found in Tar I

Table 4-5 to 4-14 show concentrations mg/gram of specific PAH's in the untreated pure Tar --Tar I and in the products of reaction for samples JU 1- JU 72 using GC analysis obtained at NJIT. These tables can be used to examine the conversion of the specific compounds for the ozone and H_2O_2 reaction where -- indicates no detectable concentration in the product extract.

TABLE 4-5

Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 1	JU 2	JU 3	JU 4	JU 5	JU 6
Naphthalene	6.41	4.15	3.10	2.92	5.03	3.62	2.27
Acenaphthylen	67.86	19.81	33.65	32.23	28.63	33.62	33.76
Acenaphthene	22.01	8.97	11.49	10.01	12.45	11.97	10.09
Fluorene	40.40	7.80	9.42	10.79	9.07	10.01	8.70
Phenanthrene	1.12	0.13	0.14	0.18	0.14	0.16	0.13
Anthracene	1.39	0.16	0.18	0.22	0.18	0.20	0.16
Fluoranthene	19.46	3.12	3.36	4.96	3.39	3.66	3.13
Pyrene	4.66	--	0.34	1.10	0.33	0.38	0.30
Chrysene	51.62	11.09	12.21	15.88	12.57	13.70	11.07

TABLE 4-6

Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 7	JU 8	JU 9	JU 19	JU 20	JU 21
Naphthalene	6.41	2.28	1.21	1.23	8.01	16.66	24.99
Acenaphthylen	67.86	16.43	28.60	29.36	3.86	6.58	10.80
Acenaphthene	22.01	4.10	7.10	7.67	5.97	12.33	14.09
Fluorene	40.40	5.71	9.47	10.32	1.59	2.16	2.88
Phenanthrene	1.12	0.09	0.15	0.17	0.03	0.04	0.05
Anthracene	1.39	0.11	0.18	0.21	--	0.03	0.05
Fluoranthene	19.46	1.73	3.44	3.73	--	--	1.04
Pyrene	4.66	--	0.33	0.33	--	--	--
Chrysene	51.62	7.62	12.26	13.91	2.24	2.85	4.05

-- = nondetectable

TABLE 4-7

Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 22	JU 23	JU 24	JU 25	JU 26	JU 27
Naphthalene	6.41	10.50	6.21	7.52	1.84	7.30	5.29
Acenaphthylen	67.86	8.41	8.61	9.27	3.17	4.26	4.05
Acenaphthene	22.01	7.70	5.38	6.51	--	5.99	11.20
Fluorene	40.40	3.29	2.56	2.82	1.56	1.54	1.77
Phenanthrene	1.12	0.05	0.04	0.05	0.03	0.03	0.04
Anthracene	1.39	0.05	0.04	0.05	--	--	0.03
Fluoranthene	19.46	1.16	0.51	1.06	--	--	0.77
Pyrene	4.66	--	--	--	--	--	--
Chrysene	51.62	4.76	3.39	4.16	2.70	2.42	3.41

TABLE 4-8

Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 28	JU 29	JU 30	JU 31	JU 32	JU 33
Naphthalene	6.41	2.23	4.97	9.11	9.49	10.18	8.46
Acenaphthylen	67.86	9.87	10.09	13.64	3.28	7.92	6.09
Acenaphthene	22.01	3.91	5.92	6.91	7.60	7.43	6.57
Fluorene	40.40	2.68	4.44	3.63	1.22	2.48	2.01
Phenanthrene	1.12	0.04	0.06	0.05	--	0.04	0.03
Anthracene	1.39	0.04	0.05	0.05	--	0.04	0.03
Fluoranthene	19.46	0.52	1.17	1.03	--	0.86	0.74
Pyrene	4.66	--	--	--	--	--	--
Chrysene	51.62	3.26	4.68	4.21	1.45	3.50	2.98

-- = nondetectable

TABLE 4-9
Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 34	JU 35	JU 36	JU 37	JU 38	JU 39
Naphthalene	6.41	5.49	4.19	4.81	4.32	2.57	2.07
Acenaphthylen	67.86	8.12	39.21	29.31	16.02	13.39	14.08
Acenaphthene	22.01	6.02	10.06	5.17	5.19	3.33	3.31
Fluorene	40.40	2.07	14.60	4.25	4.08	2.95	3.39
Phenanthrene	1.12	0.03	0.35	0.06	0.05	0.04	0.05
Anthracene	1.39	0.03	0.40	0.05	0.05	0.04	0.05
Fluoranthene	19.46	0.63	5.34	1.20	1.11	0.62	0.75
Pyrene	4.66	--	0.52	--	--	--	--
Chrysene	51.62	2.64	18.31	4.89	4.47	3.38	4.17

TABLE 4-10
Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 40	JU 41	JU 42	JU 43	JU 44	JU 45
Naphthalene	6.41	3.21	1.90	1.65	1.03	1.36	1.21
Acenaphthylen	67.86	--	0.40	7.45	--	--	--
Acenaphthene	22.01	4.53	2.08	1.66	0.87	4.62	2.59
Fluorene	40.40	--	--	0.84	--	--	--
Phenanthrene	1.12	--	--	0.04	0.11	0.03	--
Anthracene	1.39	--	--	0.03	--	--	--
Fluoranthene	19.46	--	--	0.30	--	--	--
Pyrene	4.66	--	--	--	--	--	--
Chrysene	51.62	--	4.52	3.58	--	--	--

-- = nondetectable

TABLE 4-11
Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 46	JU 47	JU 48	JU 49	JU 50	JU 51
Naphthalene	6.41	--	1.14	--	--	0.92	5.09
Acenaphthylen	67.86	5.40	--	10.08	--	--	--
Acenaphthene	22.01	10.12	2.29	--	5.94	2.78	15.98
Fluorene	40.40	--	--	--	2.57	--	7.04
Phenanthrene	1.12	0.06	--	0.03	0.06	--	0.13
Anthracene	1.39	--	--	0.04	--	--	--
Fluoranthene	19.46	--	--	1.12	--	--	--
Pyrene	4.66	--	--	--	--	--	--
Chrysene	51.62	--	--	9.06	--	--	4.84

TABLE 4-12
Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 52	JU 53	JU 54	JU 55	JU 56	JU 57
Naphthalene	6.41	1.87	0.68	--	--	--	--
Acenaphthylen	67.86	--	--	0.57	--	1.80	--
Acenaphthene	22.01	6.96	4.58	--	--	1.46	0.85
Fluorene	40.40	--	--	--	--	--	--
Phenanthrene	1.12	0.16	0.06	0.03	--	0.05	0.02
Anthracene	1.39	--	--	--	--	--	--
Fluoranthene	19.46	--	--	--	--	--	--
Pyrene	4.66	--	--	--	--	--	--
Chrysene	51.62	--	--	2.59	--	--	2.07

-- = nondetectable

TABLE 4-13
Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 58	JU 59	JU 60	JU 64	JU 65	JU 66
Naphthalene	6.41	--	7.99	20.41	5.28	5.38	9.58
Acenaphthylen	67.86	1.31	--	--	--	--	--
Acenaphthene	22.01	1.43	5.60	12.10	5.96	4.62	10.56
Fluorene	40.40	--	--	--	--	--	1.49
Phenanthrene	1.12	0.10	--	0.02	0.06	--	0.03
Anthracene	1.39	--	--	--	--	--	0.03
Fluoranthene	19.46	--	--	--	--	--	--
Pyrene	4.66	--	--	--	--	--	--
Chrysene	51.62	--	--	--	--	--	3.61

TABLE 4-14
Levels of Specific PAH (mg/g) in TAR I and Products after Reaction

Compounds	TAR I	JU 67	JU 68	JU 69	JU 70	JU 71	JU 72
Naphthalene	6.41	8.50	6.00	6.08	6.08	4.49	15.89
Acenaphthylen	67.86	--	--	--	--	--	--
Acenaphthene	22.01	7.54	5.78	5.00	9.20	4.50	16.03
Fluorene	40.40	--	--	--	1.13	--	--
Phenanthrene	1.12	--	--	--	--	--	0.04
Anthracene	1.39	--	--	--	--	--	--
Fluoranthene	19.46	--	--	--	--	0.60	--
Pyrene	4.66	--	--	--	--	--	--
Chrysene	51.62	--	--	--	--	--	--

-- = nondetectable

A significant increase in conversion for all media can be observed in reaction numbers higher than JU 40. This is because in these samples the tar was uniformly dispersed onto surfaces of glass beads so that the ozone/ H_2O_2 and other oxidizing species could more readily attack it. (As opposed to 1 cm pure tar lumps in the earlier reaction numbers). It also served to increase the surface area of tar, i.e. increased the effective concentration of PAH's in the tar for reaction.

$$\text{Reaction rate} = -\,d\,[\text{PAH}]/d\tau = k\,[\text{oxidant}]\,[\text{PAH}]$$

where [ ] = concentration

Therefore, higher concentrations will increase reaction rates.

(9) Level of Specific PAH's Found in Tar II

Our analysis using 0.3 gram of Tar II material showed significant variations due to the highly nonuniform nature of these samples. We are continuing to try and obtain consistent reaction from these samples using GC analysis.

These reactions are on pure (essentially 100 %) tar material and the analysis reports mg PAH/gram of Tar remaining. We note that the analysis performed by Cambridge Analytical (PSE&G. supplied data) is ug PAH per gram tar + glass beads. Where the weight of glass beads is 100 gram. Thus the PSE&G supplied data showed be muitiplied by 21 (=105/5) to correspond to our data.

5. CONCLUSION

A number of varied oxidative treatments on two types of refractory organic tar samples were experimentally performed and shown to be effective in reducing the poly aromatic hydrocarbon content of the samples. The two types of samples treated were pure tar samples and a sand/soil matrix which contained about 10 percent tar plus wood and moisture.

Several treatment processes in the project showed significant changes in the physical properties of the pure Tar - Tar I material and results are even more dramatic for Tar II, which consisted of a sandy soil matrix with approximately 10% tar plus some wood and moisture in it. Specific analysis on extracts of these samples showed significantly lower levels (10% or less - of the initial) of polynuclear aromatic hydrocarbons, PNA's or PAH's, initially present. Analysis of the specific level of PNA's remaining after treatment needs to be further evaluated and quantified to determine if the treatment is sufficient to be utilized as a cleaning or site recovery technique. Included in this further evaluation is the need to analyze the effluent or solvents used in the process for contamination.

Treatment with ozone and hydrogen peroxide under acid, base and neutral condition effectively degraded the tar samples to some extent, but no one set of parameters degraded masses of pure tar to complete mineralization -- $H_2O + CO_2$. This is clearly because there is no significant access for these oxidizers or products from their decomposition to the tar other than on surfaces. For these treatments to be further tested where the goal is complete mineralization, the tar will need to be dispersed into sub millimeter size particulate or into very thin layers on other surfaces e.g. sand, rocks or stones.

The treatment of small percent samples of tar in soils, Tar II, appeared much more satisfying with visual / physical analysis of the sand - soil after treatment showing a much cleaner appearing soil with a few lumps of tar or tar-like material, which had hardened somewhat, i.e. experienced some degradation as well. Results from chemical analysis further indicate that the extracts of the tar show significantly less, in some cases on the order of only 1%, of the 1 - 4 member ring PAH's originally present. Many results (See Table 4-5 to 4-14) showed no detectable benz-a-pyrene remaining.

Physical mass reduction was often very significant, but this is not necessarily representative because there were often non-tar organic materials, such as wood chips, in the soil, which were completely mineralized by the processes.

OZONE VERSUS HYDROGEN PEROXIDE

Ozone appeared to work as well as hydrogen peroxide. It is possible that the similar reactivity of the ozone reagent results from a constant, steady state level of ozone in the reaction system, while the hydrogen peroxide, which is admitted to the reactor in an initial 5 to 30 minute period, decomposes or evaporates over a short initial period of time. The peroxide would then not be present as an oxidizing agent for the entire reaction time. It is also possible that ozone also generates the OH radicals or that the OH from the H_2O_2 is degraded in some other manner and therefore not fully applied to PNA destruction.

ACID VERSUS BASE VERSUS NEUTRAL

Acid or mildly buffered acid solution should function the best because in basic solution CO_2 produced would stay in solution and be converted to carbonate neutralizing the base.

Acid and base treatment each had significant effects on the pure tar materials, base however seemed to convert the tar into more colored product indicative of salt formation. This we presume is the respective salt of the organic acids made in the oxidation process, e.g. sodium Benzoate would be formed from benzoic acid.

Base on a statistical average, base reaction seemed to do less conversion of one specific PNA - benz-a-pyrene (BaP) than either acid or neutral reactions. It is noted that treatment with base usually decreased the levels of BaP, but this decrease was somewhat less than for the acid treatments. There were a number of experiments where no BaP was observed at the limits of our detection.

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APPENDIX

Table A-1.

Nomenclature, Structure, Formulas and Molecular Weights of Relevant Polynuclear Aromatic Hydrocarbons

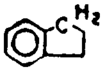
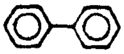
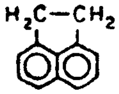
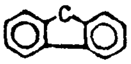
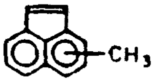
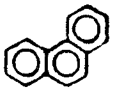
Molecular Weight	Name	Formula	Structure
116	Indene	C_9H_8	
128	Naphthalene	$C_{10}H_8$	
142	Methylnaphthalene	$C_{11}H_{10}$	
152	Biphenylene	$C_{12}H_8$	
152	Acenaphthylene	$C_{12}H_8$	
154	Biphenyl	$C_{12}H_{10}$	
154	Acenaphthene	$C_{12}H_{10}$	
166	Fluorene	$C_{13}H_{10}$	
166	Methylacenaphthylene	$C_{13}H_{10}$	
168	Methylbiphenyl	$C_{13}H_{12}$	
176	Cyclopent(f,g)acenaphthylene	$C_{14}H_8$	
178	Phenanthrene + anthracene	$C_{14}H_{10}$	 

Table A-1.(continued)

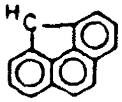
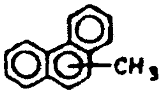
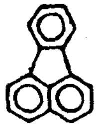
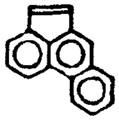
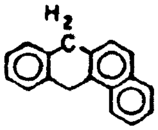
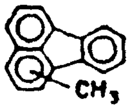
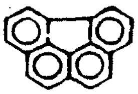
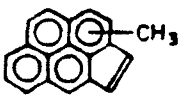
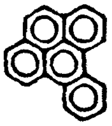
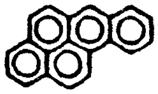
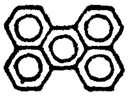
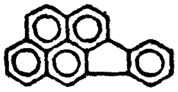
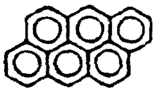
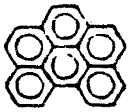
Molecular Weight	Name	Formula	Structure
190	4H-cyclopenta(def)phenanthrene	$C_{15}H_{10}$	
192	Methylphenanthrene	$C_{15}H_{12}$	
202	Fluoranthene	$C_{16}H_{10}$	
202	Benzacenaphthylene	$C_{16}H_{10}$	
202	Pyrene	$C_{16}H_{10}$	
204	2-phenylnaphthalene	$C_{16}H_{12}$	
216	Benzofluorene	$C_{17}H_{12}$	
216	Methylfluoranthene + methylpyrene	$C_{17}H_{12}$	 
226	Benzo(ghi)fluoranthene	$C_{18}H_{10}$	
226	Cyclopenta(cd)pyrene	$C_{18}H_{10}$	
240	Methylcyclopenta(cd)pyrene	$C_{19}H_{12}$	

Table A-1.(continued)

Molecular Weight	Name	Formula	Structure
252	Benzofluoranthene	$C_{20}H_{12}$	
252	Benzo(e)pyrene + benzo(a)pyrene	$C_{20}H_{12}$	 
252	Perylene	$C_{20}H_{12}$	
276	Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	
276	Benzo(ghi)perylene + anthanthrene	$C_{22}H_{12}$	 
300	Coronene	$C_{24}H_{12}$