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Energy Sources of Polycyclic Aromatic Hydrocarbons

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Introduction

The United States consumed an amount of energy (73.7 Quads[†]) equivalent to 13,266 million barrels of petroleum in 1972.[1] Of this, 45% was consumed as crude oil, 19% as coal, and 31% as natural gas. Nuclear power and hydropower constituted most of the remaining 5% of energy resources consumed. Current energy production utilizes essentially the same distribution of resources. Energy consumption in 1985 is estimated[1] to range from 96.97 to 107.30 Quads. In the process, approximately 200 x 10^8 lbs. of particulates and 130 x 10^8 lbs of hydrocarbons are estimated to be emitted into the air and approximately 20,000 tons of nondegradeable organics will be emitted as water pollutants.

The importance of fossil fuels to the nations energy base is apparent by its constituting 95% of current consumption. The emerging preeminence of coal is due to three factors (a) its abundance, (b) dwindling supplies of petroleum and natural gas, and (c) the dependence of society on liquid fuels for transportation. As is illustrated in Table 1, almost three times as much "coal-energy" is available as is energy from natural gas, petroleum, shale oil, and uranium combined. Domestic crude oil and natural gas liquids production is projected to decrease from approximately 11 x 10^6 bbl/day in 1974 to 5 x 10^6 bbl/day in

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[†] 1 Quad = 1 x 10^{15} BTU ≡ 180 million barrels of petroleum ≡ 42 million tons of bituminous coal ≡ 0.98 trillion cubic feet of natural gas ≡ 293 billion kilowatt hours of electricity.

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2020. Natural gas production is estimated to decrease from approximately 23×10^{12} cubic feet per year to 6×10^{12} cubic feet per year in 2020. The equivalent of 1.7 billion barrels of petroleum were imported in 1972 with the current import level approximating one-half of the national annual consumption of oil. While supplies of liquid fuels decline, levels of automobile, bus, truck, and rail transportation are expected to more than double by the year 2000 as compared to 1972 and air transportation is projected to increase by a factor of six.

Combustion is the predominant end-process by which fossil fuels are converted to energy. Combustion, particularly when inefficient, is also the primary technological source[52,109,128] of polycyclic aromatic hydrocarbons (PAHs) released into the environment. The need for liquid fuels to supply the transportation industry and for nonpolluting fuels for heat and power generation provide the incentive to commercialize processes to convert coal to substitute natural gas and oil. These processes represent a potentially massive new source of environmental PAHs.

The relationship between cancer, polycyclic aromatic hydrocarbons, and fossil energy sources is best documented by epidemiological studies of coke oven workers,[96,100,106] gas works operators,[25,26] and an experimental coal liquefaction plant.[130] The association is also indicated by observations[128] of higher incidences of cancer in urban and industrial areas than rural areas and by biological studies[22,145] of energy related materials known to contain high concentrations of PAHs. Results of systematic studies[52,121,122] of airborne PAHs and extensive reviews[109,128] of the subject are available. A large number of papers[17,41,91,95] continue to appear on the PAH composition of airborne particulates. Contamination of the aquatic environment by PAHs has received less attention but has also been excellently reviewed.[4,5,53]

Insuring an adequate supply of energy with minimum impact on the environment and on health is one of the most important, urgent, and challenging goals currently facing science and technology. Polycyclic aromatic hydrocarbon related carcinogenesis is among the most important of possible occupational- and environmental-health impacts of much of the current and projected national energy base. An understanding of the relationship of polycyclic aromatic hydrocarbons (PAHs) to human cancer and a continued surveillance of energy sources for PAH content are necessary to minimize this impact.

Table 1. Selected Recoverable Domestic Energy Resources

Resouces	Amount	Equivalent Quads (10^{15} BTU)
Coal	600 billions of tons	12,000
	Indeterminately greater with in-situ utilization	
Natural Gas	750 trillions of cubic feet	775
	1030 Quads with enhanced recovery	
Petroleum	142 billions of barrels	800
	1100 Quads with enhanced recovery	
Shale Oil	200 billions of barrels	1,200
	5800 Quads using low yield shale	
Uranium	3.6 millions of tons U_3O_8	1,800
	130,000 Quads using breeder reactors	

From reference 1

Petroleum

Approximately 73 Quads of energy were consumed[135] in the United States in 1974 with petroleum accounting for 45.8% of the total. Approximately 6 billion barrels of petroleum are required to produce this quantity of energy. Assuming crude oil constituted the entire "petroleum" supply (an overestimate since natural gas liquids are frequently cataloged as "petroleum"), that one barrel contains 140 kg of crude oil, and that the crude oil contains 1.0 wt. % polycyclic aromatic hydrocarbons and 1.0 ppm BaP, the petroleum industry is currently handling 84 million metric tons of PAHs and 840 metric tons of BaP annually. An understanding of the fate of PAHs through the petroleum energy cycle may provide the basis upon which to judge the relative carcinogenic hazard of coal- and shale-conversion processes being developed to supplant dwindling petroleum reserves.

Polycyclic Aromatic Hydrocarbon Content of Crude Oils

There is no conclusive evidence that the extraction and transportation of petroleum crude oils are accompanied by a major polycyclic aromatic hydrocarbon (PAH)-related cancer risk. The PAH content of crude oils is of interest in occupational carcinogenesis primarily through its possible influence on subsequent refining operations and the composition of process streams. PAH content of crudes is of interest in environmental carcinogenesis as it may affect the composition of refinery waste streams and of emissions from the end-use (e.g., combustion) of final products. Estimates[141] that more than 4×10^6 metric tons of crude oils and petroleum products are introduced into the oceans annually further suggest a need to characterize the PAH component of crude petroleum.

More than 7000 crude oils have been analyzed[137] over the years using the "Bureau of Mines Routine Method for Crude Petroleum"[136] which determines physical properties and the weight distribution of distillate fractions. A joint effort of the Bureau of Mines and American Petroleum Institute carried out principally at the Bartlesville and Laramie Energy Research Centers has resulted in a standardized procedure[50] for characterizing "heavy ends" (high boiling distillates) of crude oils. These distillates are enriched in polyaromatic constituents including polycyclic aromatic hydrocarbons. The procedure, involving anion and cation exchange chromatography, ferric chloride treatment and finally combined silica gel and alumina adsorption chromatography provides a weight percentage distribution for acids, bases, neutral nitrogen compounds, saturates, monoaromatics, diaromatics, and polyaromatic/polar compounds. The latter four fractions are further separated by gel permeation chromatography and the subfractions are analyzed directly using nuclear magnetic resonance and mass spectrometry. A weight percentage distribution by compound type (e.g., alkyldinapthenopyrenes, alkyldiphenyldisulfides, etc.) is obtained for approximately 100 "probable type" classifications on analysis of the polyaromatic/polar concentrate.

Data on compound types is difficult to interpret in terms of carcinogenic potency because biological activity is dependent on the specific isomer considered. The weight percentage of the distillate and of the crude oil accounted for by each major fraction provides some insight into the polyaromatic content of the materials and of the matrix in which the polycyclic aromatic hydrocarbons reside in the distillate. These data are summarized in Table 2 for the five crude oils studied[20,28] in detail using the USBM-API procedure.[50] The polyaromatic/polar content of the crudes range from approximately 1-3.5 weight percent (2-6 weight percent if diaromatics are included). Correcting for the reported[28] presence of sulfur and nitrogen compounds in the fractions, an estimate of 1-2 wt. % polycyclic aromatic hydrocarbons (2-4 wt. % if diaromatics are included) seems reasonable. This is in general agreement with our experience of a 3.2 wt. % yield of polycyclic aromatics isolated by solvent extraction and adsorption chromatography from a mixed crude oil for mouse dermal bioassay.[62] The PAH isolate included diaromatics.

Norris and Hill analyzed[108] three base-stock oils (partially refined crudes) for the presence of ten specific PAHs by isolating the constituents using extraction, column chromatography and thin layer chromatography followed by ultraviolet spectrometric measurement. None of the compounds could be detected in one of the oils. Results for the other oils are summarized in Table 3.

The finding[108] of 8 to 10 times as much benzo(e)pyrene (BeP) as BaP illustrates the need for additional characterization at the isomeric level and the ease with which carcinogenic potency can be overestimated by results of analyses capable only of "class" resolution. The results summarized in Table 3 and the fact that a third oil examined by the investigators produced negative results for all the individual constituents sought also illustrates the high degree of variability in PAH content between crude oils. This is not suggested by the USBM-API 60 procedure which indicates a variability in total polyaromatic and diaromatic content no greater than a factor of three across the five crudes studied to date. The total weight of PAHs found in sample "C" accounts for only 1.7 mg/kg of the 10 g/kg of PAHs which would be expected if the oil contained 1% polycyclic aromatic hydrocarbons. The great majority of PAHs constituting these oils remain unidentified.

Values of 0.04, 1.3, and 1.6 ppm BaP have been reported by Graf and Winters[42] for crude oils from the Persian Gulf, Libya, and Venezuala, respectively. Analyses of crude oils in our laboratory using multiple extraction, multiple chromatographic purification, gas chromatographic and fluorescence measurement with carbon-14 BaP to determine recoveries have produced results ranging from 1 to 4 ppm BaP. Multicomponent gas chromatographic analysis of PAH-enriched fractions reveal the presence of a wide variety of other PAHs at concentrations 1000 times that of BaP as is illustrated by the data in Tables 9 and 10.

Petroleum Processing and Products

Crude oil must be processed into useable products. Each oil refinery is practically unique in terms of its crude oil capacity and variety of products produced, but all rely on distillation for the primary separation. Depending on the sophistication of the refinery, the distillates are further upgraded by purification, catalytic cracking, hydrotreating, and other processes to produce a variety of products. The products may be processed further to produce, for example, chemicals from the olefins or petroleum pitch from the refinery stock by other industries. PAHs are generally found to concentrate in the higher boiling point distillates and solid residues as would be expected.

Oil refineries constitute a major energy-related source of both aquatic[93,117,140] and airborne[109,140] PAHs. Reid[117] reports that 1000 gallons of water are required to process each barrel of crude oil suggesting that some water contamination is inevitable. Lebowitz[93] has identified PAHs as likely contaminants of several aqueous streams of the refining operation. Refining and petrochemical plant waste oils have been estimated[141] to contribute 195,402 metric tons to the annual source of crude oils and petroleum products introduced into the ocean. Fugative emissions are suggested[93] as the primary source of hazardous constituents from petroleum refining.

The single most important source of airborne PAHs from petroleum refining is catalytic cracking.[52,109,128] Approximately 6 tons of BaP are released annually as a result of combusting the coke on the catalyst surface to regenerate the catalyst. The nature of airborne emissions are further defined in a study of a

Table 2. Composition of the 370°-535°C Distillates of Crude Oil*

	Wt. % of Crude Oil (of Distillate)				
	Gach Saran Iran	Swan Hills Canada	Wilmington California	Recluse Wyoming	Prudhoe Bay Alaska
Acids	0.34 (1.7)	0.33 (1.8)	1.38 (5.6)	0.25 (1.3)	0.61 (2.8)
Bases	0.42 (2.1)	0.40 (2.2)	1.67 (6.8)	0.21 (1.1)	0.53 (2.4)
Neutral Nitrogen Compounds	0.23 (1.2)	0.08 (0.4)	1.04 (4.2)	0.17 (0.9)	0.19 (0.9)
Saturates	9.54 (48.5)	12.10 (65.9)	9.12 (36.9)	10.16 (54.7)	10.45 (48.3)
Monoaromatics	3.31 (16.8)	2.30 (12.5)	4.15 (16.8)	2.09 (11.2)	3.67 (17.0)
Diaromatics	2.30 (11.7)	1.15 (6.3)	3.05 (12.4)	0.94 (5.0)	2.58 (11.9)
Polyaromatics-Polar	3.54 (18.0)	1.99 (10.8)	4.28 (17.3)	1.14 (6.1)	3.59 (16.6)
Whole Distillate	19.67 (100)	18.35 (100)	24.69 (100)	18.58 (100)	21.63 (100)

*Abstracted from references 20, 28.

Table 3. Individual Polycyclic Aromatic Hydrocarbons in Base Stock Oils

Compound	Oil		Compound		
	"B"	"C"		"B"	"C"
	ppb			ppb	
Benz(a)anthracene	- -	-	Pyrene	19	-
Benzo(a)pyrene	29	106	Triphenylene	5	-
Benzo(e)pyrene	370	831	Chrysene	1	-
Benzo(ghi)perylene	48	-	Fluoranthene	3	-
Coronene	28	61	Perylene	-	666

From Reference 108.

Russian petroleum refinery. Kireeva[84] reports air concentrations of 258 μg/100 m^3 for BaP and 61.5 μg/100 m^3 for 1,12-benzperylene in the vicinity of process stages dealing with high-boiling products (fuel oil, tar, cracking residues). Air concentrations of these PAHs were lowest in the first stages of the refining and at stages involving lower boiling distillates. Especially high concentrations, 3659 μg/100 m^3 and 996 μg/m^3 for BaP and 1,12-benzperylene respectively, were found in the vicinity of the coking equipment. The authors report evidence for at least 15 other PAHs in the coking environment and identified anthracene, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, and 1,2,3,4-dibenzanthracene.

The concentrations of several PAHs as determined by Norris and Hill[108] in common petroleum products are summarized in Table 4. Results for the BaP content of gasolines are in good agreement with concentrations of 0.48 and 0.21 μg/gm reported[140] for nationwide composite premium and regular gasolines, respectively. Concentrations of BaP in gasolines ranged to 3.1 μg/gm in the study. Graf and Winter[42] report finding 0.03 ppm BaP in a diesel fuel, fuel oil, and unused motor oil.

The high concentration of BaP in gasolines compared to higher boiling distillate products may be due to upgrading steps in processing. Gasoline "B" (Table 4), containing catalytically reformed product, is found to contain ten times more BaP and most other PAHs than do the other gasolines. While initial distillation undoubtedly produces a gasoline fraction depleted in BaP and PAHs relative to the starting material, upgrading steps result in gasolines containing approximately the same concentrations of these constituents as is found in petroleum crudes. The range of concentrations of PAHs in gasolines is sufficiently large to overlap concentrations found in kerosene, diesel fuels, and No. 2 heating oil.

Data (Table 4) on motor oils[108] represent an interesting case of the end use of a petroleum product enriching its PAH content. Graf and Winter[42] report a 200-fold increase in BaP content of a motor oil, from 0.03 μg/gm to almost 6 μg/gm after only 1400 miles of use. It has been estimated[117] that 350,000,000 gallons of used motor oils are discarded (much into municipal sewer systems) annually. A worse-case calculation (assuming a concentration approximately 6 ppm BaP) suggests that up to 8 metric tons of BaP is released into the environment annually as waste motor oil. The total PAHs released by this route would be expected to be many times higher. The complexity of the PAH content of motor oils is well illustrated by the capillary column gas chromatographic profiles reported by Lee et al.[94]

Petroleum pitch is an example of a petroleum product heavily enriched in PAH content. Methylphenanthrenes, pyrene, methylpyrenes, chrysene, benz(a)anthracene, methylchrysenes, dimethylchrysenes, benzo(a)pyrene, and benzo(e)pyrene constitute[43] almost 2.5 wt. % of one pitch studied. The petroleum pitch volatiles from the same materials were composed of almost 5.5 wt. % of these PAHs. The pitch contained 0.2 wt. % BaP and the volatiles 0.4 wt. % BaP.

Additional information about the PAH content of petroleum products, process streams, and process effluents is particularly important to the development of coal conversion technologies. Concerns about the carcinogenic impact of these processes, largely due to documented occupational exposure hazards and high concentrations of PAHs inherent to the processes, are destined to slow the commercialization of these needed technologies. Industrial hygiene[32] and environmental control methodologies which have proven effective in minimizing the hazards of exposure to petroleum related PAHs can only be translated to coal conversion processing if the relative quantities of PAHs in the materials and the carcinogenicity of these materials are known.

Table 4. Some Polycyclic Aromatic Hydrocarbons in Petroleum Products

	Gasolines µg/ml (ppm)				Kerosene µg/gm	Diesel Fuel (ppm)	No. 2 Heating Oils µg/g (ppm)				Motor Oils µg/ml (ppm)	
	A	B	C	D			A	B	C	D	New	Used
Anthracene	-	-	-	-	0.04	2.9	4.2	1.0	6.7	2.4	-	-
Phenanthrene	-	-	-	-	ND	ND	ND	ND	ND	ND	-	-
Methylanthracene	-	-	-	-	<0.01	9.3	6.6	20.7	15.2	20.7	-	-
Benz(a)anthracene	1.0	11.5	ND	0.54	<0.01	0.13	0.03	0.03	0.06	0.02	ND	2.2
Pyrene	2.0	10.6	0.15	5.1	0.16	0.37	ND	3.0	0.58	0.45	1.3	11.6
Fluoranthene	1.8	20.8	0.06	3.2	0.09	0.57	0.47	3.2	ND	3.6	-	-
Chrysene	0.57	4.9	ND	0.54	ND	0.45	0.50	0.51	0.37	0.81	-	-
Triphenylene	-	-	-	-	ND	3.3	ND	0.76	0.23	1.2	-	-
Benzo(a)pyrene	0.46	6.2	0.03	0.55	<0.01	0.07	0.04	0.01	0.05	0.01	ND	2.4
Benzo(e)pyrene	0.37	2.0	0.03	0.85	<0.01	0.18	0.02	0.02	0.02	<0.01	0.67	2.7
Benzo(ghi)pyrene	0.83	6.4	0.04	1.40	<0.01	0.03	0.07	0.02	0.01	0.01	0.28	1.8
Coronene	0.22	0.53	0.01	0.34	-	-	-	-	-	-	ND	0.57

From reference 108.

Combustion of Petroleum Products

Approximately one-half of the petroleum presently consumed in the United States is consumed in the form of gasoline. An additional quantity of petroleum is also consumed for transportation as diesel fuel. Annual consumptions of gasoline and diesel fuel in 1968 were estimated[109] as 80.6 x 10^9 and 5 x 10^9 gallons per year, respectively. Higher-boiling distillates of petroleum crudes are consumed to produce process - or space-heat and for electric power generation. Combustion is clearly the predominant end-use of petroleum as an energy source.

Combustion processes are among the most intensively studied energy-related sources of environmental PAHs. Concern about air pollution in the late 1950's prompted a study of the polycyclic aromatic hydrocarbon content of 28 rural and 103 urban atmospheres by Sawicki et al[121,122] which found BaP present in all of the urban areas sampled. Concentrations ranged from 0.1 to 61 ng/m^3 with a geometric mean of 6.6 for the urban areas and from 0.01 to 1.9 ng/m^3 with a mean of 0.4 for the non-urban areas. Continuing studies have produced extensive tabulations[123,124] of the BaP content of air and of natural and man made materials. Systematic investigations of the polycyclic aromatic composition of gasoline and resulting vehicle exhausts have been reported by Gross.[46,47,48] Hangebrauck[52] includes motor vehicle emissions and fuel oil combustion in his study of sources of polycyclic aromatics in the atmosphere, basic investigations of conditions leading to the formation of polycyclic aromatics have been reported[10,60,61,8] and reports continue to appear on the composition of airborne particulates,[7,95,57,17,35] diesel[76,107] and automobile exhausts[11,16,30,72] and all facets of combustion-generated polycyclic aromatic hydrocarbons. The reviews prepared by the National Academy of Sciences on Particulate Polycyclic Organic

Matter[109] and Vapor Phase Organic Matter[143] point to energy sources as a primary contributor of polycyclic aromatics to the environment.

The PAH content of vehicle exhausts and of stack effluents is related to the PAH content of the fuel. Begeman[8] found higher emissions of BaP when a test engine was operated using fuels higher in PAH content than commercial gasolines. The NAS review[69] reports Gross[46,47,48] as finding that increasing the aromaticity of the fuel from 12% to 46% resulted in an increase of from 8-74% in the PAH emissions depending on the vehicle and emission control conditions. The data reported by Hangebrauck et al[52] indicates that 2-5 times more BaP, perylene, and fluoranthene is produced on combustion of a No. 6 Fuel Oil than No. 2 Fuel Oil to produce process heat under similar operating conditions. No. 6 Fuel Oil would be expected to contain higher concentrations of PAHs and higher molecular weight organics which could serve as precursors for PAH production. The importance of PAH precursors in the fuel is underscored by emission factors for BaP of 11,000 μg/gal for two-cycle engines (e.g., outboard motors, motorcycles, lawnmowers) which operate on oil:fuel mixes (typically 1:30) as compared by 170 μg/gal for automobiles.[109]

While aromaticity of the fuel clearly influences PAH emissions, combustion characteristics are far more important. A major factor is the air:fuel ratio used for combustion. The NAS review[109] reports Begeman as finding a 30 times greater production of BaP at an air:fuel ratio of 10:1 than at 14:1 for automobiles. It is also pointed out that BaP emissions increase with increasing engine use such that emissions are five times higher after 50,000 miles of use than at 5,000 miles and ten times higher when oil consumption reaches 200 mi/qt rather than 1600 mi/qt. The deteriorating engine alters its fuel composition and resulting combustion characteristics by drawing lubricating oil into the cylinders. The importance of combustion and combustor characteristics is readily apparent in the data provided by Hangebrauck et al[52] who reports emission factors of from 40-470 μg BaP/gal for eight automobiles tested, from 40-1450 μg BaP/gal for four trucks, and from approximately 1-18 μg BaP/lb of fuel oil for six conditions of process or space heating. Emission factors are more consistent than is indicated by these extremes but, with the exception of inadvertent combustion of lubricating oil, the influence of fuel aromaticity is relatively minor in comparison. The efficient, controlled combustion of coal as is sought in electric power generation can produce less BaP per pound of fuel than does the less efficient combustion of oil or even natural gas[52,128] as might occur in space heating. Oil and natural gas produce significantly lower quantities of PAHs than does coal when conditions of comparable combustion efficiency are considered.

BaP emission factors (Table 5) are useful for identifying major sources of environmental contamination by PAHs. Expressed per quantity of material combusted, the factors may also suggest sources of high localized concentrations of BaP and, thus, regions and periods of significant carcinogenic potential. Measurement of BaP alone obviously provides an underestimate of total PAH emissions and is likely to be inadequate for estimating the relative carcinogenicity of the emissions. As is illustrated by the data in Table 6, pyrene, a documented[142] co-carcinogen is present in both motor vehicle emissions and fuel oil-generated process heat emissions at concentrations much exceeding that of BaP. BaP constitutes between 0.5 and 4.2% of the ten PAHs reported and presumably a much smaller percentage of the total PAHs present. While the quantities (Table 6) of BaP emitted by two home heating units are similar, quantities of pyrene, phenanthrene, and fluoranthene differ by two orders of magnitude.

A more recent study[16] of automobile exhausts reports the presence of chrysene and 2,3 benzofluorene at levels of approximately 120-240 μg/gal and 160-

1000 μg/gal for the same fuels. Other recent examples of the chemical complexity of emissions are found in high resolution chromatographic profiles of automobile exhausts[11,30] and in a high resolution mass spectrometric analytical study[107] of diesel exhaust particulates. The latter study identified constituents with the molecular formulas corresponding to 48 known hazardous compounds including napthalene, anthracene/phenanthrene, pyrene, and chrysene/benzo[c]pyrene/benzo(b)fluoranthene/benzo[j]fluoranthene in diesel exhausts. One sample produced a molecular formula corresponding to 7,12-dimethylbenz[a]anthracene.

An additional factor important to judging the carcinogenic potential of emissions is the morphology of the carcinogenic constituents-particle size distribution and the nature of the particles. Several studies[2,82,110] have shown that PAHs tend to be concentrated on the smaller, more respirable, airborne particles indicating that the hazard may be greater than predicted by total BaP mass particulate loading. The work of Stanton[138] has clearly demonstrated the importance of a continuous localized dose of PAHs to lung epithelium as a factor in the etiology of experimental lung cancer. The vehicle (dissolved in a liquid particle as with tobacco smoke, adsorbed on a solid particle as with flyash, etc.) with which the carcinogenic polycyclic aromatic is dosed may be as important as is the total dose of PAH. Boyer and Laitenen[11] have demonstrated that respirable and nonrespirable particulates generated in automobile exhausts differ widely in elemental composition. Particle characteristics, including surface properties, must be known before the specific carcinogenictiy of an emission can be estimated.

With the exception of the low efficiency combustion of coal for space heating, the combustion of petroleum products contributes as much BaP to the respiratory environment as does any other energy source.

Table 5. BaP Emission Factors for the Combustion of Petroleum Products in Motor Vehicles

	μg BaP/gal fuel		tons BaP/year		
	Hangebrauck	NAS	Hangebrauck	NAS 1968	EPA 1972
Gasoline-Automobiles	170	170	8.6	10	10
Gasoline-Trucks	>460	∿500	>10	∿12	
Diesel	690	62	2.0	0.4	<1
			>20.6	∿22.4	∿11

From references 52, 109, 128.

Table 6. Distribution of Polycyclic Aromatic Hydrocarbons in Petroleum Combustion Effluents[a]

Source	Benzo(a)pyrene	Benzo(a)pyrene	Pyrene	Benzo(e)pyrene	Perylene	Benzo(ghi)perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene
	µg/gal	micrograms per vehicle mile									
Automobiles (1956-1964)	170	12	111	~16	1	49	1	20	5	32	74
Trucks (1956-1964)	>455	40	745	>48	6	199	-	105	78	485	475
Diesel Powered	690										
	µg/lb	micrograms per million BTU heat input									
Process Heat											
No. 2 Fuel Oil	<0.3	<20	49								56
No. 6 Fuel Oil	0.9	47	300							1800	270
Home Heating											
Sectional Boiler	<0.9	<40	1800							8900	5000
Hot Air Furnace	<1	<60	15								76
Institutional Heating											
Low Pressure air-atomized firing	18	900	6100			300		2100	3900	3500	1900

[a] From reference 52.

Coal

Approximately 18% of the energy consumed[135] in the United States in 1974 was supplied by coal while coal constitutes 63% of the national energy reserve. The increasing cost of oil and increasing dependence on foreign sources of oil are providing strong incentives to increase coal utilization. Plans are being made to double the current level of coal production to one billion tons per year as soon as practical. Coal will continue to supply heat and electric power and is likely to become a major source of liquid fuels for transportation and of crude oils for the chemical industry. The conversion of coal to gaseous or liquid fuels is further attractive in that it provides an alternative to expensive environmental control devices now required at power plants. A recent study[6] concludes that the production of electricity from pipeline quality natural gas produced from coal is less expensive than electricity produced directly from coal in certain areas. The predominant end-use of coal will continue to be through combustion. As is evident from the Wiser[148] conceptualization of coal, figure 1, combustion and conversion are accompanied by the possible production of polycyclic aromatic hydrocarbons.

Coal Extraction and Conventional Processing

Freudenthal, et al[36] have reviewed the carcinogenic potential of types of coal processing and conclude that there is little to no carcinogenic risk associated with the mining operation. This is in spite of the fact that coal dusts are inhaled (as is evidenced by the incidence of pneumoconiosis) and known to contain PAHs. Ianov is reported[36] to have determined the presence of PAHs including BaP in mine dusts collected after blasting operations. Mentser and Sharkey[107] have recently surveyed mine dusts by high resolution mass-spectrometry and report the presence of constituents with the formula $C_{18}H_{12}$ and $C_{20}H_{12}$ (possibly chrysene and BaP, respectively). Evidence of the presence of other

PAHs and of aliphatic hydrocarbons was also found; particularly from the section of the mine which employed diesel rather than electrical haulage.

Lebowitz et al[93] has surveyed other stages (e.g., crushing and grinding) of conventional coal processing. Coal dusts are itemized among the potentially hazardous emissions but PAHs were not.

Clearly the most important source of PAHs (a major contributer[109,128] to the national airborne BaP burden, and a documented[106,115] occupational hazard) from conventional coal processing is the coking operation. Coke is produced by heating coals to temperatures as high as 1400°C in the absence of air. Ammonia, coke-oven gas, a light oil, tar, and coke result from the process. As a measure of the magnitude of the industry, approximately 87 x 10^6 tons of bitumonus coal were processed to produce 60 x 10^6 tons of coke in 1972.

Coke oven batterys are difficult to sample because emissions are diffuse rather than from a point source. Most studies examine samples from personal monitors or from the general vicinity of the coke ovens. Results are generally expressed as "Coal Tar Pitch Volatiles" (CTPV), the cyclohexane or benzene soluble constituents of the particulates, or BaP is determined. Concentrations of BaP above the gas works retorts of a coke oven have been reported[92] as high as 216,000 ng/m^3. Jackson et al[68] report concentrations up to 16,000 ng/m^3 on the coke oven battery.

Of the references surveyed for this review, only Hangebrauck[52] reports quantitative data on other PAHs. Air samples taken from the general vicinity of a combined steel and coking industry ranged from 440 to 8600 ng/m^3 in concentrations of BaP, benzo(e)pyrene, pyrene, perylene, benzo(ghi)perylene, anthanthrene, coronene, anthracene, and fluoranthene. BaP was present at the greatest concentration of the constituents determined.

Additional study, particularly of the composition of CTPVs and of the morphology of the particulates, would be very important to provide reference data for advanced coal conversion technology development.

Coal Conversion

Coal "conversion"[19,51,85] is a generic term encompassing more than 100[65] specific processes designed to produce liquid, gaseous, or refined solid fuels as energy sources or substitute petrochemical feedstocks from coal. Undesireable ash and sulfur is removed and the coal is converted into a form suitable for direct use as low BTU or high BTU gas or for further refining to produce gasoline, fuel oil, and other products typical of petroleum processing. Processes designed to produce liquid fuels are optimized to maximize production of saturated hydrocarbons. Processes designed to produce petrochemical feedstocks are optimized to generate low molecular weight aromatics. Most processes generate a mixture of gaseous, liquid, and solid products some of which become an integral part of the process being consumed at the plant to enhance the yield of the specific product of interest.

Cochran[19] points out that the common chemical objective of the processes is to increase the atomic hydrogen to carbon ratio of the coal from its typical value of 0.8 to 1 to a ratio of 1.75 to 1 as is typical of oil. Higher ratios, ideally 4 to 1 as for methane, are sought in the production of gaseous fuels. It is necessary to depolymerize the coal and hydrogenate the resulting fragments to adjust the H/C ratio.

Cochran[19] divides the many conversion technologies into four basic categories, (a) carbonization, (b) direct hydrogenation, (c) extraction, and (d) synthesis. A coal is "carbonized" by heating (typically at 1000°F) in the absence of air causing the release of gases and tars. Hydrogen may be added at relatively low pressure, e.g. 600 psi, to result in "hydrocarbonization" to increase the yield of volatiles and tars. The remaining solid char is used to generate synthesis gas for the production of process hydrogen. "Direct hydrogenation" involves heating a coal slurry to approximately 850°F in the presence of hydrogen at pressures of 3500 psi and, usually, a catalyst. The "extraction" process requires that the coal be dissolved in a petroleum solvent. Dissolution occurs at approximately 500°F and 300 psi pressure and the resulting liquid is hydrogenated to produce a crude oil and additional solvent for extraction. The Fischer-Tropsch "synthesis" involves burning the coal in a gasifier in the presence of oxygen and steam to produce primarily carbon monoxide and hydrogen. The gas is purified and passed over a catalyst yielding liquid products ranging from methanol through waxes and oils. Substitute natural gas, liquid petroleum gas and liquid fuels are produced.

State of the art engineering technology is required to make these conceptually straight-forward operations commerically practical. Process flow diagrams are reminiscent of those for large scale petroleum refineries. Adequate technology is at hand for commercially viable small scale conversion as is evidenced[19,65] by the successful operation of the Sasol synthetic fuel plant for 20 years in South Africa. It is the size of the projected conversion plants and conversion industry in the United States that challenges engineers and concerns environmentalists. The Sasol plant processes approximately 3500 tons of coal per day while U.S. planners visualize at least 20 plants, each processing approximately 25,000 tons of coal per day, preferably 40 plants processing a total of 10^6 tons/day and possibly as many as 100 such plants. One plant processing 25,000 tons of coal each day would produce[19] 205 x 10^6 scf of gas, 5000 barrels of liquid petroleum gas, 40,000 barrels of motor fuels, and 5,000 barrels of fuel oil daily for a capital investment of $1.5 billion. Twenty such plants would produce one million barrels of liquid products and 4.1 x 10^9 cubic feet of gas daily to provide 6 percent of the nations present energy demand.

An industry of this size might be expected to have some impact on the environment and, considering the similarity to coking and coal tar works, on the health of the worker. An increasing number of documents are appearing which outline and evaluate specific processes for environmental impact. General studies have been reported by Glazer et al[38] and Katz.[78] The Energy Research and Development Administration (ERDA) coal gasification program is undergoing an environmental assessment at Carnegie - Mellon University.[105] Gasification processes which have been reviewed include the CO_2 acceptor,[69,104] Synthane,[75] Bi-Gas,[70] Lurgi,[133] Koppers-Totzek,[102] and Hygas[69] processes. The solvent refined coal (SRC) process[70] and COED pyrolyses process[75] are among the specific liquifaction technologies which have been evaluated. A comprehensive review of the environmental and health aspects of coal conversion has been prepared[12] by the Information Center Complex of Oak Ridge National Laboratory. The results of these and other studies are forming the basis of Envionmental Development Plans,[33] documents being prepared by the USERDA to guide energy-related enviornmental and health research.

The threat of an increase in occupational and/or environmental carcinogenesis is the major health impact receiving attention.[15,36] A firm epidemiological basis for this concern exists for occupational cancer. As is summarized in Table 7, technologies closely related to those comprising the projected coal conversion industry are known to be accompanied by an elevated risk of occupational carcinogenesis. Laboratory, clinical and epidemiology studies[31,83,129,130,146] in support of the Union Carbide Corporation coal conversion plant at Institute, W. Virginia confirm (Coomes[22] has questioned this conclusion) the carcinogenic nature of the process materials and document a substantial increase in skin cancer rate for employees in spite of protective measures taken. Concern about an increase in environmental carcinogenesis is less well-founded but cannot be ignored until it is demonstrated that carcinogenic materials can be contained within plant boundaries and the transportation and end-use of the products are not accompanied by an increased cancer risk. Sauter[120] has strongly urged that both the occupational and environmental cancer risk be given maximum attention in national policy decisions affecting the development of a fossil fuels conversion industry.

Polycyclic aromatic hydrocarbons are implicated as primary carcinogens in coal derived materials by virtue of their carcinogenicity and common occurance in coal tars. The experimental carcinogenicity of coal derived materials increases with increasing boiling point and is correlated with process conditions which favor the formation of PAHs.

The Bartlesville Energy Research Center is engaged in a systematic study of coal-derived liquids using modifications of the API-60 method for characterizing petroleum crudes. Reports are available on Syncrude from the COED Process using two coals,[29,139] on two oils from the H-Coal Process,[63] and the product of the Synthoil Process.[149] Distillates[29,63,139,149] prepared from the crudes are predominantly hydrocarbon in nature but also contain acidic, basic, and heteroaromatic constituents. Rubin et al[119] has reported as much as 15% removal of constituents from COED Syncrude by acid-base extraction. Jones et al,[74] using a newly developed Sephadex LH-20 procedure, reports 3% of the Syncrude is hydrophilic with an additional 8% being capable of strong hydrogen bonding.

Table 8 summarizes the distribution[149] of compound types in distillates from two coal conversion processes. Polyaromatics 3 rings and larger are seen to constitute from 5-40 wt. % of the products depending on process type, coal feed, and distillate boiling range. Diaromatics are present at twice the concentration of polyaromatics in the lower boiling distillates and at equal concentrations for two of three higher boiling distillates considered. The coal used influences the distribution of the products but has a smaller affect on polyaromatic content than does the process. The crudes examined contain from approximately 7.5-14 wt. % polyaromatics if it is assumed that all of the polyaromatic constituents are recovered in the two distillates. Separation at this laboratory[74] of a COED Syncrude from a Western Kentucky coal by Sephadex LH-20 chromatography produced a polycyclic aromatic fraction constituting 5 wt. % of the Syncrude. Preparative scale polycyclic aromatic isolates recently generated[18] by solvent extraction and adsorption chromatography for mouse dermal testing[62] corresponded to 6.0 and 5.1 wt. % of the experimental COED Syncrude and Synthoil products, respectively, under study at this laboratory. Synthetic crude oils thus appear to contain from two to five times the quantity of PAHs normally found in petroleum crudes. Tars and other high boiling residues produced as by products of the conversion process may contain ten times more PAHs than do the synthetic crude oils.

The Pittsburgh and Bartlesville Energy Research Centers are examining[29,63,139,149,147,77,132,131] the polyaromatic component of syncrudes and related products by mass spectrometric and nuclear magnetic resonance techniques designed to identify and quantitate classes of constituents. Results indicate the presence of a wide variety of hydrocarbon and heteroatomic constituents and the presence of many alkyl substituted derivatives. Data, some of which appears in Tables 9 and 10, has been reported[37,39,49,87,134] on the quantities of individual polycyclic aromatic hydrocarbons in coal conversion related materials. Results confirm the presence of a variety of known tumorigenic constituents, possible tumor promoters, and co-carcinogens.

Essentially no data is available on the unambiguous identification and subsequent quantitation of PAHs in synthetic fuels materials at the isomeric level. The potent carcinogens 3-methyl cholanthrene and 7,12-dimethylbenzanthracene have been reported[9] in shale oils and we have noted cochromatographic and mass spectrometric evidence for the presence of 3-methylcholanthrene in a variety of synthetic crude oils but their presence has not been positively identified. We have analyzed synfuels and related materials for benzo(a)pyrene (BaP) content by isotope dilution/fluorescence spectrometry/gas chromatography/ following extensive purification by solvent extraction and adsorption or cellulose acetate column, paper, or thin layer chromatography and found from approximately 40 ppm BaP to less than 2 ppm BaP for the same sample type. Our application[39] of Hecht's procedure[54] to the analyses of one syncrude for methyl chrysene content indicates that chrysene and its 2-methyl and 3-methyl derivatives are present at concentrations of approximating 100 ppm but that the highly carcinogenic[54,55] 5-methyl derivative constituted less than 20 ppm, if any, of the syncrude. Limitations of existing analytical methodologies and/or resources for detailed chemical studies has impeded the identification and quantitation of known tumorigenic agents at the isomeric level.

Phenols[58,125,134] are the major organic contaminants of by-product and process waters from coal conversion. As is illustrated in Table 11, polycyclic aromatic hydrocarbons are also found in the waters. The condensate from Synthane gasification is seen to contain predominantly napthalenes with the 2-methyl derivative being present at a greater concentration than all the other isomers combined. The raw process water from the Solvent Refined Coal process is seen to contain a larger variety of PAHs at much higher concentrations than is found for the gasification water or for by-product water from oil shale retorting. Concentrations are in the sub-ppm range for most constituents. As is the case for synthetic oils, these identifications are based primarily on co-chromatography or, at best, mass spectrometry and require confirmation.

We have been collaborating with J. L. Epler[34] and his staff on a study of the Ames Test[3] as a short-term screening bioassay of coal-derived materials. Oils and organic constituents of process derived waters are subjected to the acid-base solvent partition and adsorption chromatographic fraction procedure[119] found useful in biological studies of tobacco smoke condensates and the resulting fractions are biotested. Early quantitative results have been reported.[49] These and more recent studies show that two coal-derived oils are more active in the Ames system than are a shale derived oil or a petroleum crude oil. Biological activity is concentrated in the basic fractions and neutral fractions thought to contain polyaromatic constituents. A recent study here[59] has indicated the presence of azapyrene and possibly other azaarenes in a biologically active subfraction of one basic fraction. The utility of the Ames test for predicting carcinogenic activity is presently under study here[62] through a mouse dermal carcinogenicity bioassay of materials previously studied by Epler.

It is not possible to directly extrapolate the results of analysis summarized here to the production or environmental release of PAHs by an eventual coal conversion industry. Samples which have been analyzed come from very small scale operations without emission control modules and often from engineering experiments where process conditions are being manipulated to extremes. Materials from more realistic operations, those processing up to 100 tons of coal per day (still far from the 25,000 ton/day commercial plant projected), are only now becoming available. Product, process streams, waste streams, and the working environment of the 30 ton/day Solvent Refined Coal Plant in Fort Lewis, Washington are presently undergoing[15] a systematic chemical and biological study.

The quantities and variety of polycyclic aromatic hydrocarbons found in synfuels related materials clearly indicates the existence of a cancer threat. There is some evidence[103] that the conversion process can be modified to reduce

Table 7. Epidemiological Basis for Synfuels/Carcinogenesis Concern

Reference	Exposure/Experiment	Cancer
Pott, 1775[112]	English chimney sweeps	Scrotum
Volkmann, 1875[144]	Handling tar and paraffin from carbonization of lignite	Scrotum
Rehn, 1895[116]	Production of synthetid dyes from coal tar	Bladder
Lueke, 1907[97]	Carbon workers	Skin
Henry, 1931[56]	Coal tar workers	Bladder
Kuroda, 1936[90]	Coal gas workers	Lung
Kennaway, 1936[80]	Coal carbonization workers	Lung, larynx
Kennaway, 1947[81]	Street pavers, asphalters, coal gas workers, chimney sweeps	Lung
Doll, 1952[24]	Gas retort workers	Lung
Anon, 1958	Coal gas and coke workers	Stomach, Kidney, and pancreas
Bruugaard, 1959[14]	Gas retort workers	Bladder
Sexton, et al, 1960[31,83, 129, 130,146]	Coal liquefaction	Skin
Doll, 1965[26]	Gas works	Lung, bladder
Kawai, 1967[79]	Gas works	Lung
Lloyd, Redmond, et al, 1969-1974[96,99,100,101,113,114]	Steelworkers, coke producers	Lung
Doll, 1972[25]	Gas works	Lung, bladder, scrotal
Mazumdar, 1975[106]	Coke Oven workers	Lung

Abstracted in part from reference 36.

Table 8. Distribution of Constituents in Synthetic Crude Oil Distillates

Process Coal Distillate	Synthoil W. Virginia 207°-363°C	COED W. Kentucky 205°-380°C	COED Utah 204°-381°C	Synthoil W. Virginia 363°-531°C	COED W. Kentucky >380°C	COED Utah >381°C
Saturate	16	25	27.8	9.7	23.8	25.8
Monoaromatic	27.3	42	25.1	4.7	25.1	14.4
Diaromatic	21.6	13	17.5	22.6	24.3	18.4
Polyaromatic	7.9	5.4	7.1	41.1	20	25.1
Heteroaromatic	22.2	4.4	15.2	15.6	4.5	7.4
Distillate % of crude	42.6	54.2	45.4	27.3	24.2	40.3

From reference 149.

Table 9. Polycyclic Aromatic Hydrocarbons in Coal Derived Oils and Related Materials

milligrams per gram of Sample

	SRC Process Materials		Coal Derived Crude Oils			
	Wash Solvent	Process Solvent	Catalytic Hydrogenation	Pyrolysis	La-Miss Petroleum Crude	Shale Derived Crude Oil
Napthalene	32	0.1	1.6	1.7	0.9	1.4
Methylnapthalenes	44	5	3.8	4.6	1.6	1.6
Dimethylnapthalenes	18	18	3.7	6.3	2.1	2.2
Isopropylnapthalenes	0.2	1.5				
Biphenyl	10	6	0.2	0.4		<0.1
Dimethylbiphenyls	<0.1	2.6				
Fluorene	0.2	6.6	0.3	0.5	0.2	0.9
9,10-Dihydroanthracene			1.7			<0.1
9-Methylfluorene	0.1	3.1	0.1	0.1		0.4
1-Methylfluorene	<0.1	3	1.9		0.1	1.0
Anthracene	0.1	23	1.4		0.3	0.6
Phenanthrene						
Fluoranthene	<0.1	10.5	0.4		0.1	0.4
Pyrene	<0.1	11.2	4.3			0.2
1,2-Benzofluorene					<0.1	0.1
2,3-Benzofluorene					<0.1	0.1
1-Methylpyrene			0.6	0.1	<0.1	0.1

Table 9 (Cont'd)

Polycyclic Aromatic Hydrocarbons in Coal Derived Oils and Related Materials

milligrams per gram of Sample

	SRC Process Materials		Coal Derived Crude Oils			
	Wash Solvent	Process Solvent	Catalytic Hydrogenation	Pyrolysis	La-Miss Petroleum Crude	Shale Derived Crude Oil
Chrysene Triphenylene			0.1	<0.1		
Picene			0.4			
1,12-Benzoperylene			1.5			
Anthanthrene			0.1			

From References 37, 49, 87.

Table 10. Napthalenes in Synthetic and Natural Crude Oils

	Milligrams per gram				
	Coal Derived				
	Cat. Hydrogen.	Pyrolysis	Shale Oil	LMS Crude	Alaskan Crude
Napthalene	1.6	1.7	1.4	0.9	1.4
2-Methylnapthalene	2.9	3.5	0.9	0.9	1.8
1-Methylnapthalene	0.9	1.1	0.7	0.7	1.4
Biphenyl	0.2	0.4	0.1		0.4
2,6 Dimethylnapthalene	0.4	0.8	0.1	0.1	0.5
1,3 + 1,6 Dimethylnapthalene	1.8	3.0	1.6	1.3	2.3
2,3-Diemthylnapthalene	1.0	1.5	0.3	0.2	0.4
1,5-Dimethylnapthalene	0.2	0.7		0.1	0.2
1,2-Diemthylnapthalene	0.3	0.2	0.2	0.4	0.5
Acenapthylene	1.3	2.2	0.2	0.2	0.6
Acenapthene	0.5	0.3			
TOTAL	11.5	15.4	5.5	4.8	9.5

From Reference 44.

Table 11. Polycyclic Aromatic Hydrocarbons in Coal and Shale Conversion Waters

Constituent	Milligrams per Liter (ppm)		
	Synthane Gasification Condensate	Solvent Refined Coal Raw Process Water	Simulated In-situ Shale Retort By Product Water
Napthalene	0.2	5	0.1
2-methylnapthalene	1.3	2	0.3
1-methylnapthalene	<0.1	-[a]	0.1
2,6-dimethylnapthalene	<0.1	-	<0.1
1,3 + 1,6-dimethylnapthalene	0.1	-	0.2
1,5 + 2,3-dimethylnapthalene	<0.1	-	0.1
1,2-dimethylnapthalene	<0.1	-	<0.1
Dimethylnapthalenes	-	2.3	-
2-isopropylnapthalene	-	0.7	-
1-isopropylnapthalene	-	2	-
Biphenyl	<0.1	0.2	<0.1
Acenapthalene	-	<0.1	-
Acenapthene	1R[b]	-	<0.1
Dimethylbiphenyls	-	0.7	-
Fluorene	<0.1	0.3	0.2
9,10-dihydroanthracene	<0.1	-	<0.1
9-methylfluorene	-	0.3	-
1-methyl fluorene	ND[c]	0.2	0.2
Anthracene/phenanthrene	ND	1.1	0.3
2-methylanthracene	ND	-	0.2
1-methyl phenanthrene	ND	0.2	0.1

Table 11 (Cont'd)

Polycyclic Aromatic Hydrocarbons in Coal and Shale Conversion Waters

Constituent	Milligrams per Liter (ppm) Synthane Gasification Condensate	Solvent Refined Coal Raw Process Water	Simulated In-Situ Shale Retort By Product Water
9-methylanthracene	ND	-	0.4
Methylphenanthrene	-	0.3	-
Fluoranthene	ND	0.4	<0.1
Dihydropyrene	-	<0.1	-
Pyrene	ND	0.6	0.1
1,2-benzofluorene	ND	-	<0.1
2,3-benzofluorene	ND	-	<0.1
1-methylpyrene	ND	-	0.1
1,2-benzanthracene	ND	-	<0.1
Chrysene/triphenylene	ND	-	<0.1

[a] not reported
[b] incomplete resolution
[c] not detected

From References 37, 49.

the production of undesirable constituents without lessening the quality of the final product. Industrial hygiene practices will have to be carefully followed to limit occupational carcinogensis. Recycling hazardous waste streams as is presently planned in several processes and the development of control technologies optimized to remove PAHs may be required to avoid the environmental release of potential carcinogens.

Coal Combustion

Most of the coal mined in the United States is eventually consumed by combustion to produce process, residential, or institutional heating or electric power. An additional quantity is consumed by destructive distillation to produce coke. As is illustrated in Table 12, these sources combined with the open burning of coal refuse, account for approximately 90% of the national inventory of airborne benzo(a)pyrene. Of the 600-800 metric tons of BaP estimated to be emitted in 1972, controlled combustion and open burning contributed approximately 280 metric tons each.

Analytical results[128] on samples acquired from the National Air Sampling Network (NASN) for BaP content over the period 1966 to 1970 from urban and non-urban areas further emphasize the importance of coal combustion as a source of atmospheric polycyclic aromatic hydrocarbons. Average seasonal concentrations of airborne BaP ranged from 0.1 ng/m^3 to 50 ng/m^3 for rural and urban areas respectively. Concentrations are consistently higher in the winter months regardless of the region sampled in most cases and are always highest for heavily coal-based industrialized regions. The Pittsburgh and Birmingham areas, both heavy coal consumers, were found to contain maximum annual average concentrations of 14 and 18 ng/m^3 of BaP, respectively, over the five sampling years reported. Perhaps most importantly, the carcinogenicity of organic extract of particulates collected in Birmingham are reported[66] to be greater than that of comparable extracts from Los Angeles area particulates. While well-noted for its "smog", very little of the airborne particulates in the Los Angeles area are coal-derived.

Diehl et al[23] have demonstrated a dependence of emission factors for benzo(a)pyrene, benzo(e)pyrene, and benz(a)anthracene on the type of coal but conclude, as was previously noted for the combustion of petroleum products, that combustion efficiency is the primary factor influencing PAH emissions. The annual "BaP Inventories" (Table 12) identify small residential furnaces as the overwhelming source of heat-generation related BaP. Process-or institutional-heat generation combustors are identified as more important to the inventory are than large scale power plants. The studies summarized by Hangebrauck et al[52] provides the basis for these conclusions and illustrates that PAHs other than BaP follow the same trend. The data summarized in Table 13 further illustrate that the type, and presumably the efficiency, of combustion is a more important factor than is the size or purpose of the combustor.

Coal fired power plants contribute relatively little to the natural particulate BaP burden. A high combustion efficiency combined with effective emission control methods reduce the annual emission to one ton or less of BaP. A low annual emission does not eliminate this source as a contributer to the PAH related cancers. Local concentrations may be high. Diehl et al,[23] for example, report the release of up to 50 mg/hr of BaP from power plants rated from 1 x 10^6 to 2 x 10^6 lbs steam/hr. A release of 46.6 mg BaP/hr may be calculated from the more recently summarized[1] results of Hangebrauck[52] for a power plant consuming 59 metric tons of coal per hour. While only 840 μg of BaP are released per metric ton of coal consumed, the process releases large quantities of BaP and presumably larger quantities of PAHs into a localized environment.

Emissions estimates are dependent on accurate sampling and analysis methods. PAHs are thought[128] to be released from the combustor flame in the vapor state later to condense on inorganic particles or to coalese to form particles of pure condensate. The recent study of sampling techniques by Jones et al[73] addressed the problem of vapor state PAHs by designing a sampling system which incorporated an organic adsorbent in the sampling train. The authors determined the concentrations of anthracene, pyrene, fluoranthene, chrysene, benz(a)anthracene, and benzopyrenes in effluents from the small scale combustion of natural gas and residual oils and from effluents of a carbon black manufacturing facility using the adsorbent sampling system and standard sampling systems. Expressed as total polycyclic organic matter (POM), Jones et al report from two to ten times as much POM in the effluents using the adsorbent sampler. Enhancements by a factor of ten seem to be associated with the combustion of sulfur-containing fuels. It should be noted that the most volatile PAHs, the napthalenes, were not studied. The logical conclusion is that emissions from coal-fired power plants may be as much as an order of magnitude greater than has been predicted using traditional sampling methods. Methodological limitations, combined with changes[128] in combustion techniques designed to meet NO_x emission standards, may result in a significant underestimate of the importance of coal-fired power plants to the national particulate BaP inventory. Regional affects, particularly during periods of atmospheric conditions which localize the dispersion of emitted particulates, may be much greater than would be predicted by annual national inventories of BaP.

Differences[66] in carcinogenicity for airborne particulates from different geographic locations suggest that the composition of adsorbed organic matter may be important. The data summarized in Table 13 illustrates that pyrene and fluoranthene are consistently present at concentrations equal to or greater than

BaP in coal combustion emissions as is also noted (Table 6) for residual oil combustion. Benzo(e)pyrene (BeP) is reported present at concentrations approximating that of BaP for coal combustion while BeP was generally present at levels below the detection limit for oil combustors studied.[52] Diehl reports[23] that concentrations of benz(a)anthracene are within a factor of two of those for BaP for the coal-fired power plants he has sampled.

Griest et al[45] of this laboratory have recently surveyed the hydrocarbon content of an ash taken from the stack of a Tennessee Valley Authority coal-fired power plant. The ash was extracted with benzene after adding carbon-14-BaP to the ash to determine recoveries, and the extract was analyzed by fluorescence spectrometry and gas chromatography. The extract was further purified by florisil and alumina column chromatography to remove paraffins after these components were found to predominate on the ash. Results of these analyses for PAHs are summarized in Table 14. Normal paraffins 16-through 34-carbons in chain-length inclusively constituted 8.6 ppm of the ash while the PAHs visualized constituted less than 0.2 ppm. Benzofluorenes and alkyl-substituted napthalenes, pyrenes, phenanthrenes, and anthracenes were found in addition to the commonly reported pyrene and fluoranthene. The separate analysis for BaP by fluoresence spectrometry and carbon-14 isotope dilution indicated that BaP constituted 35 ppb of the ash. The results cannot be converted to quantitative emission factors because the plant operating characteristics and the sampling protocol were not specified. The data clearly demonstrate, however, that the composition of adsorbed organic matter is considerably more complex than would be indicated by results of analyses for a small number of pre-selected constituents.

The contribution, if any, of coal fired power plants directly to the aquatic or terrestrial environment is less well known. Mass flow levels reported[86] for a trace element balance study within a power plant consuming approximately 88 metric tons of coal per hour show that 8.43 x 10^{14} gm of fly ash are collected by the precipitator per minute while only 0.037 x 10^{4} gm/min of fly ash are released into the environment through the stack. Slag and precipitator ash, 394.5 tons per ton of released ash, are often disposed of in ash ponds. It is not known how efficiently the spectrum of PAHs contained on the ash are leached or acted upon by micororganisms and subsequently leached into the aquatic environment.

Present technologies are effectively controlling the annual emissions of particulate BaP (and presumably other PAHs) from coal-fired power plants. The projected increasing national reliance on coal-based electric power and the possible regional contribution to environmental carcinogenesis from a high point-source emission of PAHs, require a continued surveillance of this source of energy-related polycyclic aromatic hydrocarbons.

Oil Shale

Certain shales, particularly those in the Green River Basin of Colorado are sufficiently rich in organic matter ("kerogen") to allow the production of petroleum substitutes by retorting. Shale is being slighted in this review only because polycyclic aromatic hydrocarbon carcinogeneses problems are conceptually similar (but less severe) than those which have already been discussed as accompanying the liquefaction of coal. High grade shales yield only 25 gallons of oil per ton as compared to 1-3 barrels per ton of coal. The high grade oil shale deposits in the Green River formation of Colorado, Utah, and Wyoming are so massive, however, as to allow estimates[89] of some 600 billion barrels of recoverable oil from the 600 square miles containing the shale. This quantity of oil is reported[89] to be equivalent to the known reserves of petroleum oil including the 10 billion barrels in the Prudhoe Bay area of Alaska. Oil is presently produced[71] by heating ("destructive distillation," "retorting") shale

Table 12. Estimated Annual Airborne Emission of Benzo(a)pyrene in the United States

	Metric Tons per Year	
	1968	1972
Coal		
Hand-stoked and underfeed-stoked residential furnaces	380	270
Intermediate size furnaces	9	6
Steam power plants	1	<1
Open burning, coal refuse	308	281
Coke production	0.05-153	0.05-153
Total, Coal	∿700-850	∿550-700
Petroleum and Natural Gas		
Oil, residential through steam power plants	2	2
Gas, residential through steam power plants	2	2
Petroleum catalytic cracking	5	6
Asphalt air-blowing	<1	<1
Asphalt hot-road-mix plant	<1	
Gasoline-powered, automobiles and trucks	20	10
Diesel-powered, trucks and buses	<1	<1
Rubber tire degradation	9	10
Aircraft		
Lawn mowers and motor cycles		
Total, Petroleum	∿41	∿32

Table 12 (Cont'd)

Estimated Annual Airborne Emission of Benzo(a)pyrene in the United States

	Metric Tons per Year	
	1968	1972
Other Materials		
Wood, home fireplaces	36	23
Enclosed incinerator, apartment through municipal	31	3
Open burning, domestic and municipal waste	22	
Open burning, vehicle disposal	45	5
Open burning, forest and agriculture	127	10
Open burning, other		9
	∿261	∿50
U.S. Annual Total	100-1150	640-780

From results summarized in reference 128.

Table 13. Distribution of Polycyclic Aromatic Hydrocarbons in Coal Combustion Effluents

Heating Plant	Fuel Rate	Benzo(a)pyrene µg/lb	Benzo(a)pyrene	Pyrene	Benzo(e)pyrene	Perylene	Benzo(ghi)perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene
			milligrams per million BTU heat input									
Power Plant A	~60 tons/hr	0.25	.020	.160								.20
Power Plant B	~60 tons/hr	3.1	.220	1.025	.395	.017	.200		.005			.075
Process Heat A	~5 tons/hr	0.43	.032	.24	.092					.370		.55
Process Heat B	~300 lbs/hr	140	10	16	7.9	1.6	4.5	.29	.33	.85	10	38
School Heat B	~200 lbs/hr	1.6	.12	1.7	.23						1.0	3.2
Residential Heat A	~5 lbs/hr	52	3.8	7.7	5.4		.58		1.2		29	47
Residential Heat B	~6 lbs/hr	25	1700	2700	870	220	1400	270	49	1100	2300	4300

From results summarized in Reference 52.

Table 14. Polycyclic Aromatic Hydrocarbons on Fly Ash from a Coal Fired Power Plant

PAH	Concentration, ng/gm
Naphthalene	8.3
2-Methylnaphthalene	5.0
1-Methylnaphthalene	5.2
Biphenyl	10.3
1,6- and/or 1,3-Dimethylnaphthalene	T
2,6-Dimethylnaphthalene	T
1,5- and/or 2,3-Dimethylnapthalene	T
9,10-Dihydroanthracene	12.6
Phenanthrene	17.6
2-Methylanthracene	9.1
1-Methylphenanthrene	<24.8
Fluoranthene	<13.4
Pyrene	<19.0
1,2-Benzofluorene	36.8
2,3-Benzofluorene	11.8
1-Methylpyrene	T
Picene	T
TOTAL	0.2 ppm

T, trace

From reference 45.

extracted by surface or underground mining to approximately 1000°F in above ground retorts. Research is underway at the Laramie Energy Research Center, Laramie Wyoming, on methods to allow the in-situ conversion of shale to oil.

The primary environmental problems facing the shale oil industry appear to be locating adequate supplies of water for processing, avoiding contaminating the limited western water supply, and disposing of solid wastes. Approximately two tons of spent shale accompanies the production of each barrel of oil. Because of its decreased density following processing, it is not possible to return all of the spent shale to the mine. Almost 600 million tons of spent shale would have to be disposed of annually from an oil shale industry producing one million barrels of oil per day.[89]

A report by Schmidt-Collerus[126] suggested that a carcinogenic hazard could be associated with spent shale. Coomes[22] has recently responded to this and the Sauter[120] paper. He reports that hairless mice living in a bedding of spent shale exhibit no greater incidence of skin cancer than those living in normal bedding and suggest that this is evidence of the non-carcinogenic nature of spent shale. Coomes also reports results from three laboratories which show that the benzo(a)pyrene content of processed shale is no greater than 40 ppb, well within the range of concentration, reported for coconut oil, oysters, and oak leaves. Bonomo has reported[9] concentrations of BaP of from 15-115 ppb in weathered spent shales.

Crude shale oil contains[22] approximately 3 ppm of BaP, one hundred times that found in spent shale and approximately that found in petroleum crude oils. A shale oil produced by an above ground simulated in-situ retort has recently been subjected to solvent extraction and adsorption chromatographic separations here to prepare a polycyclic aromatic hydrocarbon enriched isolate for biological study. The isolate composed approximately 2.0 wt. % of the shale oil. This is less than the quantity of isolate prepared (3.2 wt. %) from a mixture of petroleum crude oils using the same procedure. The product of simulated in-situ retorting contains the same variety (Table 9) of polycyclic aromatic hydrocarbons as is observed in petroleum and coal-derived oils. The highly carcinogenic isomers 3-methylcholanthrene (MCA) and 7,12-dimethyl benzanthracene have been reported[9,120] in both raw and processed shale but identifications are based principally on chromatographic retention. We have observed gas chromatographic and mass spectrometric evidence for the presence of trace quantities of MCA in a crude shale oil produced by simulated in-situ retorting but do not consider the data adequate for positive identification.

Mouse dermal bioassay remains the most widely accepted measure of carcinogenicity. Coomes[32] has published the results summarized in Table 15 from a report by the Colony Development Operation.[21] The data suggest that crude shale oil is no more carcinogenic than is commonly used fuel oil. It also suggests that subsequent upgrading (by hydrogenation) further reduces the carcinogenicity of the oil.

Reports of polycyclic aromatic hydrocarbons in shale retort derived waters cannot be extrapolated directly to environmental releases. Data in Table 11 were generated using the water recovered by centrifuging the oil-water product of a simulated in-situ retort. The distribution of paraffins in the water was identical to that found in the oil. The polycyclic aromatics may be dissolved in the oil remaining in the water due to incomplete separation. Control technologies optimized to remove "hydrocarbons" may reduce the polyaromatic content of the water to acceptable levels.

The commercial scale conversion of shales to oil will involve processing large quantities of polycyclic aromatic hydrocarbons. The possibility of PAH related occupational and environmental carcinogenesis cannot be ruled out based the limited experimental data and process experience available.

Table 15. Mouse Dermal Carcinogenicity of Shale Oils and Related Materials

Material	P_{mc}[a]	Material	P_{mc}[a]
Whole Shale Oil	0.1	Coke Oven Coal Tar	0.54
Upgraded Shale	0.03	Cracked Sidestream	0.26
Industrial Fuel Oil	0.17	Napthenic Distillate	0.06

[a] "carcinogenicity" relative to 3-methylcholanthrene[64]

From reference 22.

Conclusions, Comparisons, Comments

Fossil fuels provide more than 90% of the nations energy and are the primary technological source of polycyclic aromatic hydrocarbons. Combustion, coal coking, and petroleum catalytic cracking are the primary fossil energy sources of airborne PAHs. Transportation and processing of petroleum are the primary technological sources of PAHs contaminating the water environment. Energy related operations accompanied by the greatest hazard of occupational carcinogenesis are those involving contact with petroleum- and coal-"residuals" (e.g., coal tars) and respiration of heavily PAH-contaminated environments (e.g., coking).

Coal and shale conversion will constitute a new source of PAHs. A single commercial coal liquefaction plant will produce (assuming 25,000 tons of coal/day, 2 bbl oil/ton of coal, 140 kg oil/bbl, 3 wt. % PAH) 210,000 kgs of PAHs and (assuming 1 ppm BaP) 7 kgs of BaP daily as a component of the product. An industry processing 10^6 tons of coal per day would produce approximately 100 metric tons of BaP annually. The quantities, if any, of PAHs generated as wastes or emitted during processing is unknown.

Technology appears to exist to handle the increased PAH burden. The petroleum industry, for example, processed 780 metric tons of BaP (assuming 0.78 x 10^9 MT petroleum crude oil consumed, 1 ppm BaP) in 1972. Secondly, much of the coal-derived oil is expected to be consumed by combustion and it is well documented that combustion efficiency is more important than is the aromaticity of the fuel in determining final PAH emissions. Conversion technologies remain a potential occupational health and local environmental health threat because it is not known how efficiently the hazardous constituents can be contained in a commercial scale plant.

Based on the very limited data (Table 16) available, coal and shale derived crude oils contain only 2-3 times more BaP than do petroleum crudes. Some processes, particularly those optimized to produce chemical feedstocks, produce products containing 10-100 times the BaP and/or PAH content of petroleum crudes. Tars and high boiling products produced in the conversion processes can consist of 40 wt. % PAH but thses must be compared to their peotroleum counterpart, e.g., pitches, rather than crude oils in judging the added impact of the conversion industry on the environmental PAH burden. In general, coal- and shale-derived oils may be expected to contain larger quantities of alkylated PAHs, heteroatomic constituents, and hydroaromatics than does petroleum.

The experimental carcinogenicity of shale oil is reported to be about equal to that of petroleum crude oil. Coal tars are well known to be highly carcinogenic. Mutagenicity screening shows two coal derived oils to be more active than a shale oil which, in turn, is approximately equal in activity to a petroleum crude oil. In all cases, the mutagenic activity is concentrated in the polycyclic aromatic enriched fractions and the basic fractions.

With the possible exception of airborne particulates, knowledge of the PAH content of energy-related materials falls far short of existing analytical capabilities and of needs of biologists to estimate carcinogenic potential. A systematic study of the types reported by Sawicki and by Hangebrauck are required to generate the data base necessary. PAHs other than BaP must also be determined, the matrix in which the PAHs reside must be determined, and the presence or absence of unusually bioactive isomers, e.g. 3-methylcholanthrene, must be established. The extent of bioaccumulation and of chemical transformation due to environmental processes must be determined to fully evaluate the relevance of source terms to the impact on receptor organisms including man.

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Table 16. Benzo(a)pyrene Content of Energy Related Materials

Materials	∿ppm BaP
Crude Oils	
Petroleum	1
Libya[42] 1.3 Venezuala[42] 1.6	
Persian Gulf[42] 0.04 Arabian[88] 1.5	
Shale Derived	3
Crude Oil[22] 3.1	
Hydrotreated[22] 0.7	
Coal Derived	3
Catalytic Hydrogenation[88,134] 1.6, 41	
Pyrolysis[88] 4.1	
Petroleum Products	
Gasoline	0.4
Commercial[108] 0.46, 0.03, 0.55	
Catalytically Reformed[108] 6.2	
Nationwide Composite Premium[140] 0.48	
Nationwide Composite Regular[140] 0.21	
Motor Oil, new[42]	0.03
Motor Oil, used[42,108] 2.4, 6.0	4
Diesel Fuel[42,108] 0.03, 0.07	.05
No. 2 Heating Oil[108] 0.01-0.05	.03
Asphalt[145] 0.1-27	2
Petroleum Pitch[43]	2000

Table 16 (Cont'd)

Benzo(a)pyrene Content of Energy Related Materials

Materials	~ppm BaP
Miscellaneous	
Creosote[98]	200
Coal Tar[98,124] 1800, 5000	3,000
Coal Tar Pitch[145]	10,000
Raw Shale[22]	.015
Processed Shale[22]	.03
Bitumonus Coal[124]	<.001
Reference Envionmental Materials	
Waters	
Uncontaminated ground water[4]	<0.00001
Drinking water[4]	<0.00003
Contaminated by industrial effluent[4]	0.01
Heavily contaminated by coking, oil shale, oil-gas processing[4]	0.5-1.0
Miscellaneous	
Foods[124]	<0.001
Earths upper crust[4]	0.1-1.0
Biosynthesized per weight dried material, wheat and rye[4]	0.01-0.02

REFERENCES

1. "A National Energy Plan for Energy Research, Development, and Demonstration: Creating Energy Choices for the Future," (1975). Volume 1, The Plan, U. S. Energy Research and Development Administration, ERDA-48, June 28, Washington, D.C.

2. Albagli, A., Oja, H, and Dubois, L. (1974). Size-distribution pattern of polycyclic aromatic hydrocarbons in airborne particulates. Enviornmental Letters, 6(4), 241-251.

3. Ames, B. N., McCann, J., Yamasaki, E. (1975). Methods for detecting carcinogens and mutagens with the Salmonella/microsome test. Mutat. Res. 31:347-364.

4. Andelman, J. B., and Suess, J. J., (1970). Polynuclear aromatic hydrocarbons in the water environment. Bull. Wld. Hlth. Org., 43, 479-508.

5. Andelman, J. B., and Snodgrass, J. E. (1974). Incidence and significance of polynuclear aromatic hydrocarbons in the water environment. CRC Critical Reviews in Environmental Control, 4(1), 69-83.

6. Anon, (1977). How to use coal: gas judged superior all round to electricity. The Energy Daily, Vol. 5, No. 87, pp. 2-3, May 4, LLewellyn King, ed., Washington, D.C.

7. Bartle, K. D., Lee, M. L, and Novotny, M. (1974). High-resolution GLC profiles of urban air pollutant polynuclear aromatic hydrocarbons. Intern. J.

Anal. Chem., 3, 349-356.

8. Begeman, C. R. (1964). Carcinogenic aromatic hydrocarbons in automobile effluents, pp. 163-174. In Vehicle Emissions (Selected SAE Papers). (Paper 440C presented January 1962 at the SAE Atuomotive Engineering Congress) New York:Society of Automotive Engineers, Inc.

9. Bonomo, F. (1974). Environmental effects of carbonaceous solid wastes from commercial oil shale operations. Proceedings of the workshop on "Analytical Chemistry Pertaining to Oil Shale and Shale Oil," National Science Foundation, June 24-25, pp. 133-186, Washington, D.C.

10. Boubel, R. W., and Ripperton, L. A. (1963). Benzo(a)pyrene production during controlled combustion. J. Air Pollut. Control Assoc., 13:553-557.

11. Boyer, Kenneth W., and Laitinen, Herbert A.(1975). Automobile exhaust particulates-properties of environmental significance. Environmental Science & Technology, 9(5), 457-469.

12. Braunstein, H. M., Copenhaver, E. D, and Pfuderer, H. A. (Editors) (1976). Environmental, Health, and Control Aspects of Coal Conversion: An Information Overview, Volumes I and II. ORNL EIS-94 and EIS-95, Oak Ridge National Laboratory, August, Oak Ridge, TN.

13. Bridboard, Kenneth (1976). Carcinogenic and mutagenic risks associated with fossil fuels. National Institute for Occupational Safety and Health, November 15, Rockville, MD.

14. Bruusgaard, A. (1959). T. Norske, Laegeforen., 79, 755.

15. "Carcinogens Relating to Coal Conversion Processes (1976). USERDA-FE, FE-2213-1, TRW Systems and Energy, June 14, Washington, D.C.

16. Candeli, A., Mastrandrea, V., Morozzi, G., and Toccaceli, S. (1974). Carcinogenic air pollutants in the exhaust from a European car operating on various fuels. Atmospheric Environment, 6, 693-705.

17. Cautreels, W., and van Cauwenberghe, K. (1977). Fast quantitative analysis of organic compounds in airborne particulate matter by gas chromatography with selective mass spectrometric detection. J. of Chromatography, 131, 253-264.

18. Clark, B. R., Ho, C.-h., and Jones, A. Russell (1977). Approaches to the chemical class analyses of fossil derived materials. Preprints of the "Symposium on Analytical Chemistry of Tar Sands and Oil Shale," Division of Petroleum Chemistry, American Chemical Society New Orleans Meeting, March 20-25, pp. 811-822.

19. Cochran, Neal P. (1976). Oil and gas from coal. Scientific American, 234(5).

20. Coleman, H. J., Dooley, J. E., Hirsch, D. E., and Thompson, C. J. (1972). Compositional studies of a high boiling 370°-535°C distillate from Prudhoe Bay, Alaska, crude oil. Presented before the Divison of Petroleum Chemistry, Inc., American Chemical Society, Boston Meeting, April 9-14.

21. Colony Development Operation (1974). An environmental impact analysis for a shale oil complex at Parachute Creek, CO, Part I.

22. Coomes, R. Merril, (1976). Health effects of oil shale processing. Quarterly of the Colorado School of Mines, Proceedings of the Ninth Oil Shale Symposium, James H. Gary, Ed., Vol. 71, No. 4, October, pp. 101-123.

23. Diehl, E. K., du Breuil, F., and Glenn, R. A. (1967). Polynuclear hydrocarbons emission from coal-fired installations. Transactions of the ASME Journal of Engineering for Power, pp. 276-282, April.

24. Doll, R. (1952). Jour. Ind. Med., 9, p. 180.

25. Doll, R., et al. (1972). Mortality of gas-workers - Final report of a prospective study. Brit. J. Ind. Med., 29:394-406.

26. Doll, R., Fisher, R. E., Gammon, E. J., et al. (1965). Mortality of gasworkers with special reference to cancers of the lung and bladder, chronic bronchitis, and pneumoconiosis. Brit. J. Ind. Med., 22, 1-12.

27. Dong, Michael, and Locke, David C. (1976). High pressure liquid chromatographic method for routine analysis of major parent polycyclic aromatic hydrocarbons in suspended particulate matter. Anal. Chem., 48(2), 368-372.

28. Dooley, J. E., Hirsch, D. E., Thompson, C. J., Vogh, J. W., and Ward, C. C. (1974). Analyzing heavy ends of crude. U. S. Energy Research and Development Administration, Bartlesville Energy Research Center, Bartlesville, OK. Reprinted from Hydrocarbon Processing.

29. Dooley, J. E., Sturm, G. P., Jr., Woodward, P. W., Vogh, J. W., and Thompson, C. J. (1975). Analyzing syncrude from Utah coal. BERC/RI-75/7, August, Bartlesville Energy Research Center, Bartlesville, OK.

30. Doran, T., and McTaggart, N. G., (1974). The combined use of high efficiency liquid and capillary gas chromatogrphy for the determination of polycyclic aromatic hydrocarbons in automotive exhaust condensates and other hydrocarbon mixtures. J. Chromatographic Science, 12, 715-721.

31. Eckardt, Robert E. (1960). Hydrogenation of coal. Archives of Environmental Health, 1, 232-233.

32. Eckardt, Robert (1967). Cancer prevention in the petroleum industry. Int. J. Cancer, 2, 656-661.

33. Environmental Development Plan (Draft): Oil Shale Program. (1977). USERDA, (by Booz-Allen & Hamilton, Bethesda, MD), March 8, Washington, D.C.

34. Epler, J. L, Rao, T. K., and Guerin, M. R. (1977). Evaluation of feasibility of mutagenic testing of shale oil products and effluents. Presented at the US - Soviet Workshop on Health Effects of Shale Oil Development, May 18-20, Denver, CO.

35. Fox, Marye Anne, and Staley, Stuart W. (1976). Determination of polycyclic aromatic hydrocarbons in atmospheric particulate matter by high pressure liquid chromatography coupled with fluorescence techniques. Anal. Chem., 48(7), 992-998.

36. Freudenthal, R. I., Lutz, G. A, and Mitchell, R. I. (1975). Carcinogenic potential of coal and coal conversion products. A Battelle Energy Program Report, February 25.

37. Fruchter, J. S., Laul, J. C., Petersen, M. R., and Ryan, P. W. (1977). High precision trace element and organic constituent analysis of oil shale and solvent-refined coal materials. In Preprints of the "Symposium on Analytical Chemistry of Tar Sands and Oil Shale," Division of Petroleum Chemistry, American Chemical Society New Orleans Meeting, March 20-25, pp. 793-807.

38. Glazer, F., Hershaft, A., and Shaw, R. (1974). Emissions from processes producing clean fuels. Booz-Allen and Hamilton, Inc. Prepared for: Environmental Protection Agency, March.

39. Goeckner, N. A., and Griest, W. H. Determination of methyl chrysenes in a coal liquefaction product. Science of the Total Environment, in press.

40. Gordon, Robert J., and Bryan, Robert J. (1973). Patterns in airborne polynuclear hydrocarbon concentrations at four Los Angeles sites. Environmental Science & Technology, 7(11), 1050-1053.

41. Gordon, Robert J. (1976). Distribution of airborne polycyclic aromatic hydrocarbons throughout Los Angeles. Environmental Science & Technology, 10(4), 370-373.

42. Graf, W., and Winter, C. (1968). 3,4-Benzpyren in Erdöl. Archiv. fur Hygiene und Bakteriologie, Vol. 152, pp. 289-293.

43. Grienke, R. A., and Lewis, I. C. (1975). Development of a gas chromatographic - ultraviolet absorption spectrometric method for monitoring petroleum pitch volatiles in the environment. Anal. Chem., 47(13), 2151-2155.

44. Griest, W. H., and Olerich, G. (1977). Napthalene distribution in synthetic and natural crude oils. Coal Technology Program Quarterly Progress Report for the Period Ending June 30. Oak Ridge National Laboratory, Oak Ridge, TN.

45. Griest, W. H., Kubota, H., Holmberg, R. W. (1976). Analysis of flyash for POM content. October, Oak Ridge National Laboratory, Oak Ridge, TN.

46. Gross, G. P., First annual report on gasoline composition and vehicle exhaust gas polynuclear aromatic content. (CRC-APRAC Project CAPE-6-68) NTIS Publication PB-200-266.

47. Gross, G. P., Second annual report on gasoline composition and vehicle exhaust gas polynuclear aromatic content. (CRC-APRAC Project CAPE-6-68) NTIS Publication PB-209-955.

48. Gross, G. P., Third annual report on gasoline composition and vehicle exhaust gas polynuclear aromatic content. (CRC-APRAC Project CAPE-6-68) NTIS Publication PB-215-527.

49. Guerin, M. R., Epler, J. L., Ho, C.-h., and Clark, B. R.(1976). Determining fugitive emissions measurements needs for an emerging industry - advanced fossil fuels utilization. Proceedings of Symposium on Fugitive Emissions Measurement and Control, May, pp. 275-304, Hartford, CT.

50. Haines, W. E., and Thompson, C. J. (1975). Separating and characterizing high-boiling petroleum distillates: the USBM-API procedure. USERDA, July, LERC/RI-75/5, BERC/RI-75/2.

51. Hammond, Ogden, H., and Baron, Robert E. (1976). Synthetic fuels: prices, prospects, and prior art. American Scientist, 64, 407-417.

52. Hangebrauck, R. P., von Lehmden, D. J., and Meeker, J. E. (1967). Sources of polynuclear hydrocarbons in the atmosphere. U. S. Department of Health, Education, and Welfare, Public Health Service, Environmental Health Service, National Air Pollution Control Administration, Durham, NC.

53. Harrison, R. M., Perry, R., and Wellings, R. A. (1975). Polynuclear aromatic hydrocarbons in raw, potable, and waste waters. Water Research, 9, 331-346.

54. Hecht, S. S., Bondinell, W. E., Hoffmann, D. (1974). Chrysene and methylchrysenes: presence in tobacco smoke and carcinogenicity. J. Nat'l. Cancer Inst., 53(4), 1121-1133.

55. Hecht, S. S., Loy, M., Maronpot, R. R., and Hoffmann, D. (1976). A study of chemical carcinogenesis comparative carcinogenicity of 5-methylchrysene, benzo(a)pyrene, and modified chrysenes. Cancer Letters, 1, 147-154.

56. Henry, S. A., Kennaway, N. M., Kennaway, E. L. (1931). The incidence of cancer of the bladder and prostate in certain occupations. Jourittyg (Camb.), 31, pp. 199-202.

57. Hill, H. H., Jr., Chan, K. W., and Karasek, F. W. (1977). Extraction of organic compounds from airborne particulate matter for gas chromatographic analysis. J. of Chromatography, 131, 245-252.

58. Ho, C. H., Clark, B. R., and Guerin, M. R. (1976). Direct analysis of organic compounds in aqueous by-products from fossil fuel conversion processes: oil shale retorting, synthane coal gasification and COED coal liquefaction. J. Environ. Sci. Health, A11(7), 481-489.

59. Ho, C.-h. (1977). Chemical composition of the mutagenic basic fraction of syncrudes, May, Oak Ridge National Laboratory, Oak Ridge, TN.

60. Hoffmann, D., and Wynder, E. L. (1963). Studies on gasoline engine exhaust. J. Air Pollut. Control Assoc. 13:322-327.

61. Hoffmann, C. S., Jr., Willis, R. L, Patterson, G. H., and Jacobs, E. S. (1971). Polynuclear aromatic hydrocarbon emission from vehicles. Presented to the 160th National Meeting of the American Chemical Society, March, Los Angeles, CA.

62. Holland, J. M. (1977). Dose response relationships in chemical carcinogenesis. In Coal Technology Program Quarterly Progress Report for the Period Ending December 31, 1976, ORNL-5252, Oak Ridge National Laboratory, Oak Ridge, TN.

63. Holmes, S. A., Woodward, P. W., Strum, G. P., Jr., Vogh, J. W., and Dooley, J. E. (1976). Characterization of coal liquids derived from the H-coal process, BERC/RI-76/10, November, Bartlesville Energy Research Center, Bartlesville, OK.

64. Horton, A. W., and Denman, D. T. (1955) Carcinogenesis of the skin: a re-evaluation of methods for the quantitative measurement of the potencies of complex materials. Cancer Rex, 15, p. 701.

65. Howard-Smith, I., and Werner, G. J. (1975). Coal conversion technology: a review. Millmerran Coal Pty. Ltd., May, Brisbane, Australia.

66. Hueper, W. C., Kotin, P., Tabor, P. C., Payen, W. W., Falk, H., and Sawicki, E. (1962). Carcinogenic bioassays on air pollutants. Arch. Pathol., 74:89-116.

67. Hudson, H. H. (1975). Water for Wyomings' coal. Water Spectrum, 7(2), Summer, 41-46.

68. Jackson, James O., Warner, Peter O., and Mooney, Thomas F. (1974). Profiles of benzo(a)pyrene and coal tar pitch volatiles at and in the immediate vicinity of a coke oven battery. American Ind. Hygiene Assoc. J., May, pp. 276-281.

69. Jahnig, C. E., and Magee, E. M. Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification: Section I: CO2 Acceptor Process, Exxon Research and Engineering Company, Linden, NJ, December 1974; EPA-650/2-74-009d, NTIS PB-241-141 and Section 6: Hygas Process, August 1975; EPA-650/2-74-009h, NTIS PB-247-225.

70. Jahnig, C. E., Evaluation of Pollution Control in Fossil Fuel Conversion Processes. Liquefaction: Secton 2. SRC Process, Exxon Research and Engineering Company. March 1975; EPA 650/2-74-009f, NTIS PB-241-792 and Section 5. Bi-Gas Process, May 1975; EPA 650/2-74-009g, NTIS PB-243-694.

71. Jensen, H. (1974). Historical survey of the study of the qualitative and quantitative nature of shale oil. Report of the Conference-Workshop entitled Analytical Chemistry Pertaining to Oil Shale and Shale Oil, June 23-25, pp. 20-28, National Science Foundation, Washington, D.C.

72. Jentoff, R. E., and Gouw, T. H. (1976). Analysis of polynuclear aromatic hydrocarbons in automobile exhaust by supercritical fluid chromatography. Anal. Chem., 48(14), 2195-2199, December.

73. Jones, Peter W., Giammar, Robert D., Strup, Paul E., Stanford, Thomas B. (1976). Efficient collection of polycyclic organic compounds from combustion effluents. Environmental Science & Technology, 10(8), 806-810.

74. Jones, A. Russel, Guerin, M. R., and Clark, B. R. (1977). Preparative scale liquid chromatographic fractionation of crude oils derived from coal and shale. Submitted to Anal. Chem., May.

75. Kalfadelis, C. D., and Magee, E. M., Evaluation of Pollution Control in Fossil Fuel Conversion Processes. Gasification. Section I. Synthane Process, June 1974, EPA-650/2-74-009b, NTIS PB 237-113; and Liquefaction. Section I. COED Process, January 1975, EPA-650/2-74-009e, NTIS PB 240-371, Exxon Research and Engineering Company.

76. Karasek, T. W., Smythe, R. J., and Laub, R. J. (1974). A gas chromatographic - mass spectrometric study of organic compounds adsorbed on particulate matter from diesel exhaust. J. Chromatography, 101(1), 125-136.

77. Karn, Fred S., and Brown, Fred R. (1976). Aging studies of the synthoil product Part II: effects of time, temperature, atmosphere. PERC/TRI-76/2, September, Pittsburgh Energy Research Center, Pittsburgh, PA.

78. Katz, D. L, Briggs, D. E., Lady, E. R., et al. (1974). Evaluation of coal conversion processes to provide clean fuels (fluidized bed combustion, coal beneficiation; pyrolysis; coal gasification; coal liquefaction) Parts I and II. Prepared under Research Project EPRI 206-0-0 by the University Of Michigan College of Engineering for Electric Power Research Institute, February, Palo Alto, CA.

79. Kawai, M., Amamoto, H., Harada, K. (1967). Epidemiologic study of occupational lung cancer. Arch. Environ. Health, 14:859-64.

80. Kennaway, N. M, and Kennaway, E. L (1936). A study of the incidence of cancer of the lung and larynx. Jour. Hyg. (Camb.), 36, pp. 236-267.

81. Kennaway, N. M, and Kennaway, E. L. (1947). A further study of the incidence of cancer of the lung and larynx. Brit. J. Cancer, 1, pp. 260-298.

82. Kertesz-Saringer, et al. (1971). On the size distribution of benzo(a)pyrene containing particles in urban air. Atmospheric Environment, 5, 429-431.

83. Ketcham, N. H., and Norton, R. W. (1960). The hazards to health in the hydrogenation of coal, iii. the industrial hygiene studies. Archives of Environmental Health, 1, 194-207.

84. Kireeva, I. S., Yanysheve, N. Ya. (1970). Loading of atmospheric air with carcinogenic polycyclic aromatic hydrocarbons from petroleum processing installations. Translated from Gig. Naseiennykh Mest, No. 9, 113-117.

85. Klass, Donald L. (1975). Synthetic crude oil from shale and coal. Chemtech, 499-510.

86. Klein, David H., Andren, Anders W., Carter, Joel A., Emery, Jeul F., Feldman, Cyrus, Fulkerson, William, Lyon, William S., Ogle, Jack C., Talmi, Yair, Van Hook, Robert I., and Bolton, Newell (1975). Pathways of

thirty-seven trace elements through coal-fired power plant. Environmental Science & Technology, 9, 973.

87. Kubota, H., Griest, W. H., and Guerin, M. R. (1975). Determination of carcinogens in tobacco smoke and coal-derived samples - trace polynuclear aromatic hydrocarbons. Reprint from Trace Substances in Environmental Health-IX, D. D. Hemphill, Ed., University of Missouri, Columbia.

88. Kubota, H. (1977). Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, personal communication.

89. Kuhn, E. A. (1974). National energy considerations involving shale oil. Report of the Conference-Workshop entitled Analytical Chemistry Pertaining to Oil Shale and Shale Oil, June 23-25, pp. 2-7, National Science Foundation, Washington, D.C.

90. Kuroda, S. and Kawahata, K. (1936). Uber die gewerbliche enstetehung des lungen krebses bei generatorgasarbeitern. Z. Krebsforsch, 45, pp. 36-39.

91. Lao, R. C., Thomas, R. S., Oja, H., and Dubois, L. (1973). Application of a gas chromatograph--mass spectrometric--data processor combination to the analysis of the polycyclic aromatic hydrocarbon content of airborne pollutants. Anal. Chem., 45, 908, May.

92. Lawther, P. J., Commins, B. T., and Waller, R. E. (1965). A study of the concentrations of polycyclic aromatic hydrocarbons in gas works retort houses. Brit. J. Ind. Med., 22, 13.

93. Lebowitz, H., Tam, S., Smithson, G., Jr., Nack, H., Oxley, J., Cavenaugh, G., Burklin, C., and Dickerman, J. (1975). Potentially hazardous emissions from the extraction and processing of coal and oil. April, EPA-650/2-75-078, NTIS PB241-803, Washington, D.C.

94. Lee, M. L., Bartle, K. D., and Novotny, M. V. (1975). Profiles of the polynuclear aromatic fraction from engine oils obtained by capillary-column gas-liquid chromatography and nitrogen-selective detection. Anal. Chem., 47(3), 540-542, March.

95. Lee, M. L., Novotny, M., and Bartle, K. D. (1976). Gas chromatography/mass spectrometric and nuclear magnetic resonance determination of polynuclear aromatic hydrocarbons in airborne particulates. Anal. Chem., 48(11), 1566-1572, September.

96. Lerer, T. J., et al (1974). Long term mortality study of steelworkers: vii mortality patterns among crane operators. Jour. Occup. Med., 16, p. 606.

97. Leuke, A. W. (1907). Ipithelioma in carbon workers. Cleveland Med. J., 6, pp. 199-202.

98. Lijinsky, W., Domsky, I., Mason, G., Ramahi, H. Y., Safavi, T. (1963). The chromatographic determination of trace amounts of polynuclear hydrocarbons in petrolatum, mineral oil, and coal tar. Anal. Chem., 35(8), 952-956.

99. LLoyd, J. W., and Clocco, A. (1969). Long-term mortality study of steelworkers: i. methodology. Jour. Occup. Med., 11, p. 299.

100. Lloyd, J. W. (1971). Long term mortality study of steelworkers: v. respiratory cancer in coke plant workers. Jour Occup. Med., 13, p. 53.

101. Lloyd, J. W., et al (1970). Long term mortality study of steelworkers: iv. mortality by work area. Jour. Occup. Med., 12, p. 151.

102. Magee, E. M., Jahnig, C. E., and Shaw, H. (1974). Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification; Section 1; Koppers-Totzek Process. Esso Research and Engineering Company, January, EPA-650/2-74-009a, NTIS PB-221-675.

103. Massey, Michael J., Nakles, David V., Forney, Albert J., and Haynes, William P. (1975). Role of gasifier process variables in effluent and product gas production in the synthane process. Presented at the Environmental Aspects of Fuel Conversion Technology II Symposium sponsored by the Environmental Protection Agency, December 15-18, Hollywood, FL.

104. Massey, Michael J., Dunlap, R. W., McMichael, F. C., and Nakles, D. V., (1976). Characterization of effluents from the hygas and CO_2 - acceptor pilot plants. Fossil Energy, USERDA, Work performed under Contract No. E(49-18)-2496, Carnegie-Mellon University, Interim Report, July-September, Pittsburgh, PA.

105. Massey, Michael, J. Dunlap, Robert W., and Luthy, Richard G.(1977) Environmental assessment in the ERDA coal gasification development program. Progress Report for the period July 1976 - December 1976, Carnegie-Mellon University, March 1977.

106. Mazumdar, Sati, Redmond, Carol, Sollecito, William, and Sussman, Nancy (1975). An epidemiological study of exposure to coal tar pitch volatiles among coke oven workers. J. of the Air Pollution Control Association, 25(4), 382-389.

107. Mentser, M., and Sharkey, A. G., Jr. (1977). Chemical characterization of diesel exhaust particulates. USERDA, March, PERC/RI-77/5, Pittsburgh Energy Research Center, Pittsburgh, PA.

108. Norris, M. S., and Hill, E. D. (1974). Polynuclear aromatic hydrocarbons in Petroleum products. Presented at Fossil Fuel Chemistry and Energy Workshop University of Wyoming Science Summer Camp, Laramie, Wyo., July 23-27.

109. Particulate Polycyclic Organic Matter: Biologic Effects of Atmospheric Pollutants (1972). National Academy of Sciences, Washington, D.C.

110. Pierce, Ronald C., and Katz, Morris (1975). Dependency of polynuclear aromatic hydrocarbon content on size distribution of atmospheric aerosols. Environmental Science & Technology, 9(4), 347-353.

111. Pierce, Ronald C., and Katz, Morris (1975). Determination of atmospheric isomeric polycyclic arenes by thin-layer chromatography and fluorescence spectrophotometry. Anal. Chem., 47(11), 1743-1748.

112. Pott, P., (1775). "Cancer Scroti" in Chirurgical Observations, Hawes Clark, and Collings, London, pp. 63-68.

113. Redmond, C. K. et al (1969). Long term mortality study of steelworkers: iii follow-up. Jour. Occup. Med., 11, p. 513.

114. Redmond, C. K. et al (1972). Long term mortality study of steelworkers: vi Mortality from malignant neoplasms among coke oven workers. Jour Occup. Med., 14, p. 621.

115. Redmond, Carol K., Strobino, Barbara Reiber, and Cypess, Raymond H. (1976). Cancer experience among coke by-product workers. Occupational Carcinogenesis, Annals of the New York Academy of Sciences, 271, 102-115.

116. Rehn, L. (1895). Arch. Klin. Chri., 50, p. 88.

117. Reid, George W., and Streebin, Leale, E. (1972). Evaluation of waste waters from petroleum and coal processing. Prepared for Office of Research and Monitoring, U. S. Environmental Protection Agency, EPA-R2-72-001, December, Washington, D.C.

118. The Registrar General's Decennial Supplement, England and Wales, 1951: "Occupational Mortality - Part II," Vol. 1 (Commentary), HMSO, London, pp. 104-5.

119. Rubin, I. B., Guerin, M. R., Hardigree, A. A., and Epler, J. L. (1976). Fractionation of synthetic crude oils from coal for biological testing. Environmental Research, 12, 358-365.

120. Sauter, D. Y. (1977). Synthetic fuel hazard. The Elements, 3-4, April.

121. Sawicki, E., Elbert, W. C., Hauser, T. R., Fox, F. T., and Stanley, T. W. (1960). Benzo(a)pyrene content of the air of American communities. Amer. Ind. Hyg. Assoc. J. 21:443-451.

122. Sawicki, E., Hauser, T. R., Elbert, W. C., Fox, F. T., and Meeker, J. E. (1962). Polynuclear aromatic hydrocarbon composition of the atmosphere in some large American cities. Amer. Ind. Hyg. Assoc. J. 23:137-144, March-April.

123. Sawicki, E. (1975). The chemical composition and potential genotoxic aspects of polluted atmospheres. Presented at the workshop for the "Investigations on the carconogenic burden by air pollution in man" in Hanover, Germany on October 22-24.

124. Sawicki, E. (1975). Analysis of atmospheric carcinogens and their cofactors. Presented at the Symposium on Environmental Pollution and Carcinogenic Risks at Lyon, France on November 3-5.

125. Schmidt, C. E., Sharkey, A. G., and Friedel, R. A. (1974). Mass spectrometric analysis of product water form coal gasification. December, NTIS PB 240-835, Pittsburgh Energy Research Center, Pittsburgh, PA.

126. Schmidt-Collerus, J. J. (1974). The disposal and environmental effects of carbonaceous solid wastes from commercial oil shale operations. NSF GI 3482X1, Denver Research Institute, Denver, CO.

127. Schneiderman, Marvin A. (1976). Carcinogenesis as an end point in health impact assessment. In Proceedings of the LASL Third Life Sciences Symposium, "Impact of Energy Production on Human Health - An evaluation of means for assessment," Anderson, E. C. and Sullivan, E. M., eds., Tech. Info. Center, USERDA, CONF-751022, pp. 65-74.

128. Scientific and Technical Assessment Report on Particulate Polycyclic Organic Matter (PPOM). March 1975, U. S. Environmental Protection Agency, EPA-600/6-74-001, Washington, D.C.

129. Sexton, Richard J. (1960). The hazards to health in the hydrogenation of coal, i. an introductory statement on general information, process description, and a definition of the problem. _Archives of Environmental Health_, _1_, 181-186.

130. Sexton, Richard J. (1960). The hazards to health in the hydrogena coal, iv. the control program and the clinical effects. _Archives of Environmental Health_, _1_, 208-231.

131. Sharkey, A. G., Shultz, J. L., Schmidt, C. E., and Friedel, R. A. (1975). Mass spectrometric analysis of coal derived fuel. _In_ Proceedings of the Third ERDA Environmental Protection Conference, September 23-26, CONF 750967, ERDA-92, pp. 687-701, CHicago, IL.

132. Sharkey, A. G. (1976). Mass spectrometric analysis of process streams for coal-derived fuels. _In_ Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism, and Carcinogenesis, Vol. 1, Ralph Freudenthal and Peter W. Jones eds., pp. 341-347, Raven Press, New York, NY.

133. Shaw, H., and Magee, E. M. (1974). Evaluation of pollution control in fossil fuel conversion processes; gasification; section i: lurgi process. Exxon Research and Egnineering Company. EPA-650/2-74-009c, NTIS PB-237-694.

134. Shults, W. D., ed., (1976). Preliminary results: chemical and biological examination of coal-derived materials. March, ORNL/NSF/EATC-18, Oak Ridge National Laboratory, Oak Ridge, TN.

135. Simon, J. A., and Malhorta, R. (1976). Place of coal in the total energy needs of the United States. California Geology, pp. 195-201, September.

136. Smith, N. A. C., Smith, H. M., Blade, O. C., and Garton, E. L. (1951). The bureau of mines routine method for the analyses of crude petroleum, 1. the analytical method. Bulletin 490, Bureau of Mines, U. S. Department of the Interior.

137. Smith, H. M., and Hale, J. H. (1966). Crude oil characterizations based on bureau of mines routine analyses. Bureau of Mines Report of Investigations 6846, U. S. Department of the Interior.

138. Stanton, M. F., Miller, E., Wrench, C., et al (1972). Experimental induction of epidermoid carcinoma in the lungs of rats by cigarette smoke condensate. J. National Cancer Institute, 49:867-873.

139. Strum, G. P., Jr., Woodward, P. W., Vogh, J. W., Holmes, S. A., and Dooley, J. E. (1975). Analyzing syncrude from Western Kentucky coal. BERC/RI 75/12, November, Bartlesville Energy Research Center, Bartlesville, OK.

140. Sullivan, James B.(1974). Marine pollution by carcinogenic hydrocarbons. Proceedings of a Symposium and Workshop held at NBS, May 13-17, Gaithersburg, MD.

141. Travers, W. B., and Luney, P. R. (1976). Drilling, tankers, and oil spills on the Atlantic outer continental shelf. Science, 194(4267), 791-796, November.

142. VanDuuren, B. L. (1976). Tumor promoting and co-carcinogenic agents in chemical carcinogenesis, pp. 34-52. In Chemical Carcinogens, ACS Monograph 173, C. E. Searle, ed., American Chemical Society, Washington, D.C.

143. Vapor-Phase Organic Pollutants (1976). Medical and Biologic Effects of Environmental Pollutants. National Academy of Sciences. Washington, D.C.

144. Volkman, R. (1875). "Beitrage Zur Chrirurgie," Druck and Verlag von Breikepf and Hartel.

145. Wallcave, L, Garcia, H., Feldman, R., Lijinsky, W., and Shubik, P. (1971). Skin tumorigenesis in mice by petroleum asphalts and coal tar pitches of known polynuclear aromatic hydrocarbon content. Toxicol. Appl. Pharm., 18, 41-52.

146. Weil, Carrol S., and Condra, Naomi I. (1960). The hazards to health in the hydrogenation of coal, ii. carcinogenic effect of materials on the skin of mice. Archives of Environmental Health, 1, 187-193.

147. White, Curt M., and Newman, John O. H. (1976). Chromatographic and spectrometric investigation of a light oil produced by the synthoil process. PERC/RI-76/3, September, Pittsburgh Energy Research Center, Pittsburgh, PA.

148. Wiser, Wendell H. (1973). Some chemical aspects of coal liquefaction. Presented at the Short Course on Coal Characterization and Coal Conversion Processes, Penn State University, October 29 - November 2, University Park, PA.

149. Woodward, P. W., Strum, G. P., Jr., Vogh, J. W., Holmes, S. A., and Dooley, J. E. (1976). Compositional analyses of synthoil from West Virginia coal. BERC/RI-76/2, January, Bartlesville Energy Research Center, Bartlesville, OK.