olefins are produced from petroleum. In 1974, natural gas liquids supplied approximately 64% of the olefin production (DZ-003), although recent estimates give a 50-50 split of olefin feedstocks between natural gas liquids and petroleum. The chemicals presently being produced from natural gas and natural gas liquids are illustrated in Figure 3-1. Ethylene is the major olefin and provides the basis for a large and important part of the organic chemicals industry. It is the fifth largest volume chemical produced in the United States. Propylene, which is produced with ethylene, is the fourteenth largest volume chemical. Butadiene ranks thirty among the top volume chemicals.

Aromatics

The top volume aromatics, benzene, toluene and xylene, are produced primarily from petroleum liquids. A small percentage of these chemicals is currently being produced from coal in by-product coke ovens. The projected increases in coal usage can greatly increase aromatic production from coal, both from by-product coke ovens and liquefaction technologies.

3.2 Projected Feedstock Requirements

Projections of demands for chemical feedstocks have been compiled by several groups including Shell Oil (RE-149) and

TABLE 3-1

Projections of Demand for Major Categories of Petrochemicals (10^9 lb/yr)

Category	1975	2000	Annual Growth
Synthesis Gas	36.74	112.68	4.6%
Olefins	30.03	155.7	6.8%
Aromatics	16.54	75.75	6.3%
Total	83.31	344.13	5.8%

Chem Systems (SH-236). These forecasts were integrated into the data given in Table 3-1. Projections are given for the year 2000 using the base year 1975. These projections show a four-fold increase in overall petrochemical production and a five-fold increase for olefin feedstocks from 1975 to 2000.

It is anticipated that advances in technology and changing economic factors, as discussed in Section 5, will cause significant changes in the feedstocks that will be required by the chemical process industry. It is not felt, however, that drastic changes will occur for the general feedstock categories shown on Table 3-1. This is because shifts in feedstocks are most likely to occur within one of the defined categories. As an example, ethylene is an olefin, and the ethylene plants that are now in the planning stage will crack heavier hydrocarbon fractions than are used at present. These heavier feeds will yield a product slate with a larger percentage of longer chain olefins, such as butylene. Butylene may then replace ethylene in certain applications thereby resulting in a feedstock change while not affecting the olefin category projection.

Additional perspective may be gained from examination of Table 3-2 where a listing of primary chemicals and their projected growth are given. It is noteworthy that several chemicals on this list, ammonia, benzene, methanol, toluene, acetic acid, and xylene, can and have been derived from coal based technology. The acetic acid projections could change drastically if a low cost source of naphtha from coal is developed such that established U.S. and British technology for liquid phase oxidation becomes economically feasible.

3.3 Present and Projected Feedstock Sources

Chemical feedstocks accounted for some 6% of the domestic production of natural gas, natural gas liquids and crude oil

TABLE 3-2

U.S. PRODUCTION OF PRIMARY ORGANIC CHEMICALS FROM NATURAL GAS, PETROLEUM AND COAL

	1975 Production billions of lbs	Estimated 2000 Production billions of lbs	Average Annual Growth (%)
Ammonia	31.56	82.13	3.9
Ethylene	19.78	97.50	6.6
Benzene*	5.59	32.70	7.3
Propylene	7.60	49.75	7.8
Toluene	5.87	15.05	3.8
Methanol	5.18	30.55	7.4
Xylene	5.08	28.00	7.1
Carbon Black	2.76	7.21	3.9
Butadiene	2.65	8.45	4.0
Acetic Acid**	0.97	0.00	-
Total	87.04	351.34	5.7

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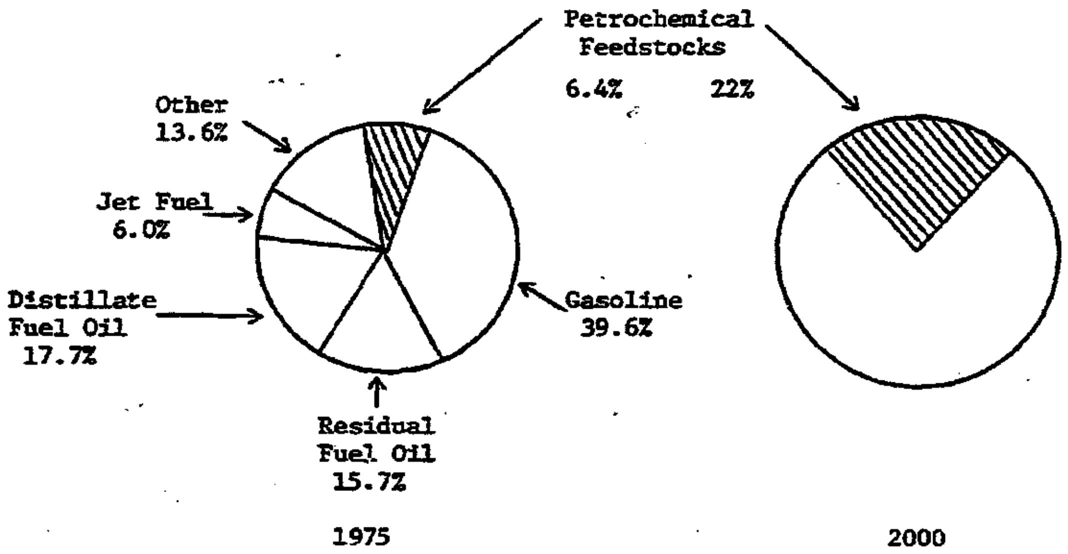
*In 1975 27% and in 2000 15% of benzene was manufactured from toluene (SH-236). The toluene production values shown do not include toluene used for benzene production.

**Estimated production of acetic acid by liquid phase oxidation of butane.

in 1975. (It should be emphasized that this feedstock demand does not include any process energy requirements.) Currently petroleum and natural gas are the hydrocarbon sources for 100% of the olefin production in the U.S. (DZ-003). They are also the source for 95% of the ammonia production and 97% of the basic aromatics. The remaining aromatic and ammonia production is by-product recovery in coking operations. Total domestic production of these oil and gas resources is expected to increase by approximately 30% by the year 2000 (RE-149). Chemical feedstock demand as shown in the previous section will require some 22% of the domestic production in the year 2000 if no new sources for these feedstocks become available. Figure 3-3 illustrates petroleum usage patterns in 1975 and projected chemical feedstock usage in 2000, and shows that the growth in chemicals will outstrip the growth in production of natural gas and petroleum resources.

FIGURE 3-3
Comparison of Petrochemical Demands To Other Petroleum Uses



However, superimposed on the growth in chemicals is a projected doubling of the U.S. energy requirements by the year 2000 (US-730). Figure 3-4 shows graphically the feedstock requirements in relation to overall energy supply and fossil fuel availability. The total U.S. energy usage in 1975 was the equivalent of approximately 37 million barrels of oil per day (LI-192). Domestic crude, natural gas and natural gas liquids accounted for 54% of this total, with coal adding another 20% (FE-153). Six percent of this 54% was required for petrochemical feedstocks, which amounted to three percent of the overall U.S. energy demand.

The total energy demand of this country has been rising since 1950 at a rate of 3.6% per year (FE-153). This rate will not continue as prices continue to rise, but a growth rate of 2.5-3% is certainly a reasonable projection. For a growth rate of 2.5%, energy consumption in 2000 will increase 85% over what is today, and with a rate of 3% it will double. At the same time, crude oil production is expected to peak around 1985 at a level 40% greater than 1975 and then gradually decline to a production level 30% higher than in 1975 by the year 2000 (RE-149). Natural gas production should decrease substantially by 2000, and natural gas liquid production levels should hold about the same as present (RE-149). Thus, in 2000, crude oil production is expected to be 30% over what it is today, and with this limited production increase, combined natural gas and natural gas liquids production will decline. At the same time energy requirements will about double and petrochemical feedstock demands will be approximately four times what they are presently.

The situation that presents itself is that the demand for hydrocarbons will be much higher than the natural liquid and gaseous supply. The role that coal will play in supplying petrochemical feedstocks could be one of two ways, or a combination of the two. These two scenarios are:

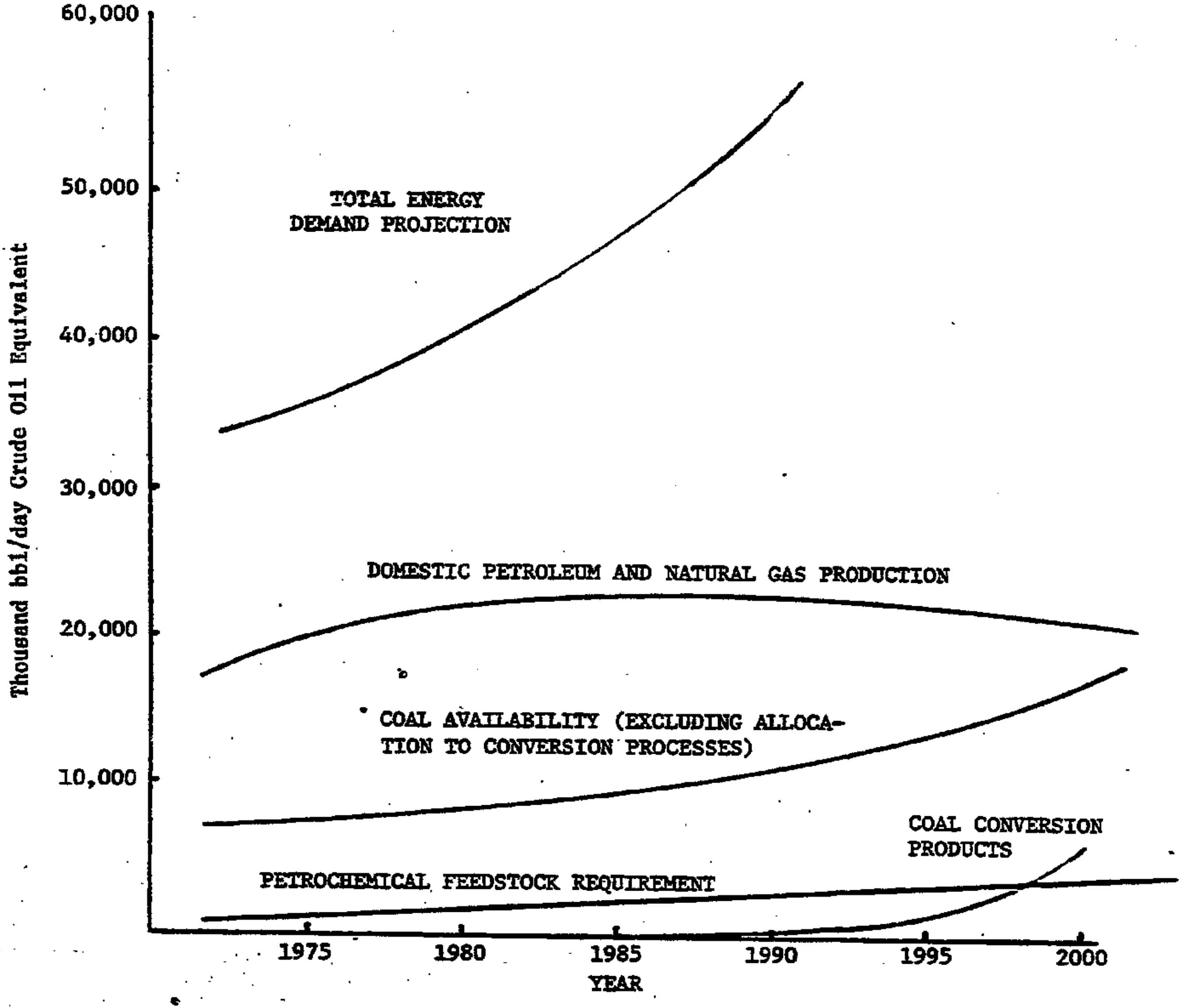


FIGURE 3-4. RELATIONSHIP OF PETROCHEMICAL FEEDSTOCK DEMAND TO FOSSIL FUEL AVAILABILITY AND TOTAL ENERGY DEMAND

1) Petrochemical feedstocks will be derived primarily from crude oil, natural gas and natural gas liquids. With this alternative, feedstocks will require over twenty percent of the domestic hydrocarbon production in 2000, a percentage much higher than today's six percent.
2) The same percentage of oil and gas is processed to feedstocks as is today, with coal and oil shale conversion technologies supplying the added demand.

Complete adherence to either scenario is unlikely. More probably petrochemical feedstocks will be supplied by a combination of the two scenarios. In this event, conversion technologies will supply some fraction of the petrochemical feedstocks in the future. As petroleum and natural gas supplies decrease, the role that coal and oil shale will play in supplying feedstocks cannot help but increase. To meet such large scale production, major processing changes will be required of the refining industry. Process advances will also be needed. These needs must be addressed soon as technological changes and widespread industry acceptance are traditionally slow.

4.0 CHEMICAL PRODUCTION FROM COAL AND OIL SHALE

This section examines the technical feasibility of producing chemicals from coal and oil shale resources. First the chemical nature of coal and oil shale is reviewed to illustrate that these resources are suitable for chemical production and then the technical feasibility of chemical production is examined by relating coal and oil shale conversion technology to chemical processing routes.

This review illustrates that technology does exist to produce the basic petrochemical feedstock categories of synthesis gas, olefins, and aromatics from coal and oil shale and, therefore, that chemicals can be produced from these resources if desired. The fact that chemicals are not being derived from these resources to any extent indicates that at present the economic driving forces are not sufficient to justify usage at the current level of technical capability. An identification and assessment of factors which are constraining chemical production from coal and oil shale is conducted in Section 5.

4.1 Chemical Nature of Coal and Oil Shale

Any source of hydrocarbons can be used as a starting material for the synthesis of other organic compounds. However, the practical limits of this processing are more narrowly defined. This section is intended to give the reader an idea of why coal and oil shale are theoretically suitable as substitutes for petroleum and natural gas as primary feedstocks for the petrochemical industry.

Chemical Nature of Coal

Coal is a natural solid combustible material consisting of amorphous elemental carbon with various amounts of hydrocarbons, complex organic compounds and inorganic materials (HA-264). Although the exact structure of coal is not precisely known, evidence suggests that the molecular structure of vitrinite (principle fragment of plant debris in bright coal) is of the following form in bituminous coals and anthracites (TA-058).

- The coal molecule contains a number of small aromatic nuclei or clusters of aromatic nuclei, each incorporating for the most part between one and four fused benzene rings. The number of clusters varies a little between molecules of the same coal, but the average for a large number of these molecules is characteristic of the rank of the coal.
- These aromatic clusters are interlinked in the molecule mainly by ring structures containing six carbon atoms.* The six membered rings can be both aromatic as well as alicyclic. By loss of hydrogen these six membered ring structures can merge with the aromatic clusters and increase the average size of the latter.
- A large portion of the hydrogen, both in the aromatic and nonaromatic rings, is substituted by aliphatic groups such as methyl and possibly larger groups.
- A small portion of the rings, both of the aromatic and hydroaromatic type, may contain oxygen or sulfur in place of one of the carbon atoms, and in addition, some of the rings containing oxygen may be five membered.
- Some of the aromatic units may be interlinked through oxygen in the ether form.

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*Some controversy exists over the type of internal linkages which are present in coal. Historically these linkage have been thought to be ring structures; however, work performed by Mobil Research and Development Corp. for ERDA under Contracts EP-77-C-01-2447, EC49-187-2276, and EC49-182-1773, suggests that the linkage may well be predominantly straight chains.

- The majority of oxygen in the vitrinites occurs as hydroxyl functional groups substituting for hydrogen on the aromatic rings.
- A small amount of oxygen occurs in the carbonyl groups, e.g., in quinone forms of the aromatic rings or possibly as ketone attached to the nonaromatic rings.
- Nitrogen is the atom next in abundance to oxygen in vitrinites. It probably occurs in heterocyclic ring structures and to some extent as amine groups.
- The sulfur in coal exists in two forms, organic and inorganic. The total amount of sulfur varies from almost negligible to 7-8%. The organic and inorganic sulfur distribution depends on the coal genesis.
- Much of the inorganic sulfur can be removed by physical means, but the organic variety probably exists in a manner analogous to that described for nitrogen.
- The coal substance can be represented as being composed of parallel stacked planar aromatic units linked to nonplanar nonaromatic structures. This explains why the shape of coal can be complex in three dimensions and the spatial structure of the molecule may be fairly open.
- Overall the evidence suggests that the molecular weights of extracts, representing 5 to 10% of the coal substance, contain molecules with a wide range of sizes with molecular weights averaging 1,000 to 3,000. It is possible that those parts of coal that cannot be extracted by solvents without thermal decomposition contain even larger molecules than those found in solution.

These factors illustrate the complex nature of coal and give some reasons to the highly variable reaction of coal to processing. The general products, however, are fairly well known. Destructive distillation in pyrolysis (such as with coking operations) results in the release of the coal volatile matter, which includes products all the way from hydrogen and methane to heavy aromatics and other high molecular weight organic compounds. The aromatic nature of the products of pyrolysis of coal have made coal an important source of the primary aromatic chemicals, benzene, toluene, and xylene (BTX) for some time. The processing problems with coal derived liquids are mainly with regard to the sulfur, oxygen and nitrogen heteroatoms, and the complex molecular structure and large molecular weights of the products.

Partial oxidation of coal in a gasifier yields a stream of H_2 and CO which is often used as synthesis gas. Process conditions can be controlled to form liquid condensate by-products or methane.

Chemical Nature of Oil Shale

Oil shale is a sedimentary rock with a relatively high organic content (30 to 60%) that yields a crude oil (shale oil) when heated in absence of air (HA-264). Typical shales may yield from 20 to 50 gallons of crude oil per ton. Shale oil has long been considered as a possible supplement to petroleum reserves since a crude oil may be obtained from oil shale by destructive distillation followed by hydrotreating.

As an example of oil shale the structure of shale from the Green River Formation is described below. The shale contains approximately 16 weight percent kerogen which represents about 80% of the total organic matter. Thus the structure of kerogen is a good approximation of the nature of shale oil. The remaining 20% of the organic matter is bitumen.

Present X-ray diffraction methods strongly support the following features for Green River oil shale kerogen (YE-026):

- There are few aromatic carbon skeltons in kerogen. Aromaticity for this kerogen is extremely low (approaches zero). There is a possibility of the presence of isolated double-bonded carbon structures.
- The bulk of the carbon structure is naphthenic containing 3-4 rings. It is possible that these are clusters and that they are linked by heterocyclic atoms and short-chain bridges.
- No free-end and flexible long-chain linear polymethylene structures are present in this kerogen.
- The C/O atomic ratio of kerogen is 18. The distribution of oxygen functional groups in this kerogen is predominantly of ether type (53%) and ester type (25%). The crosslink sites of the naphthenic structures are anticipated to be largely oxygen.
- The structure of kerogen is a multipolymer consisting of monomers which are the molecules so far identified from bitumen origin. There is as anticipated not only the primary bonding but secondary and tertiary bonding as well.

A top medium grade oil shale will contain approximately 27 gallons oil per ton of shale (HE-191). A typical distillation range of this oil is as follows:

IBP to 400°F	18%
400 to 600°F	24%
600 to 900°F	34%
900°F+	24%
	100

The straight run oil distillates boiling to 600°F have the most potential for petrochemical feedstock utilization. In this stream saturates normally vary from 26-36 volume %, olefins from 36-50% and aromatics from 23-32% (AT-051).

Shale oil also tends to be high in nitrogen (2 wt.%) which means additional nitrogen must be removed in processing an oil shale derived synthetic crude. Typically this will involve hydrogenating the oil stream and recovering the resulting ammonia. If not upgraded, combustion of the untreated shale oil would produce higher NO_x emissions than petroleum derived stocks due to the higher nitrogen content. Characteristics of crude shale oil produced from different retorting processes are shown in Table 4-1.

TABLE 4-1

CHARACTERISTICS OF CRUDE SHALE OILS

	Retorting Process		
	Gas Combustion	Union	TOSCO
Gravity, ° API	19.7	20.7	28.0
Sulfur, wt. %	0.74	0.77	0.80
Nitrogen, wt. %	2.18	2.01	1.70
Pour Point, °F	80	90	75
Viscosity, SUS @ 100°F	256	223	120

4.2 Processing Routes and Conversion Technology

As illustrated in Figures 3-1 and 3-2, the primary "building block" chemicals of the petrochemical industry fall into the three basic feedstock categories of 1) synthesis gas derived, 2) olefins, and 3) aromatics. Therefore, to produce chemicals from coal and oil shale, conversion processing must be capable of changing these resources into a product resembling one of these basic feedstock categories.

Many commercial scale coal conversion plants and a number of coal and oil shale pilot and demonstration plants exist today. Table 4-2 shows a list of the commercial processes for

TABLE 4-2
COAL AND OIL SHALE CONVERSION PROCESSES

	Commercial Processes	Development Processes
Pyrolysis	Coal Carbonization (Coking)	COED Garrett Toscoal U.S. Steel
Gasification	Koppers-Totzek Lurgi Wellman-Galusha Winkler Woodall-Duckham Wilputte	ATGAS Bi-Gas COGAS CO_2 Acceptor Hydrane Hygas Kellogg Molten Salt
Liquefaction	Fischer-Tropsch	H-Coal SRC Synthoil Exxon Donor Solvent
Oil Shale	None	Hydrotorting In-Situ Paraho Petrosix Tosco II Union Oil

coal conversion and a list of coal and oil shale conversion processes in more advanced pilot or demonstration stages. These coal and oil shale conversion processes are of the following types:

- Coal pyrolysis,
- Coal gasification,
- Coal liquefaction, and
- Oil shale retorting.

Each of these basic conversion categories yields a different mix of compounds in the reactor effluent. The relation of these generic conversion processes to the production of petrochemical feedstock streams is shown in Figure 4-1.

It should be noted that if only straight run products from the reactor are considered, application of this conversion technology is rather limited. Coal gasification will produce a synthesis gas stream, coal pyrolysis an aromatic fraction, coal liquefaction an aromatic fraction, and oil shale retorting (in the case of indirect combustion) an olefinic gas stream. Only in the case of synthesis gas production would the stream be considered a primary product.

However, the use of downstream processing will greatly increase the flexibility and yield from these conversion processes. The use of Fischer-Tropsch synthesis followed by olefin cracking allows the production of olefins and aromatics from a synthesis gas stream. Therefore, synthesis gas, olefins and aromatics can ultimately be produced via gasification of coal as demonstrated by SASOL.

The use of hydrotreating, hydrocracking, reforming, and olefin cracking on reactor effluent streams from coal liquefaction processes and oil shale retorts will greatly increase the

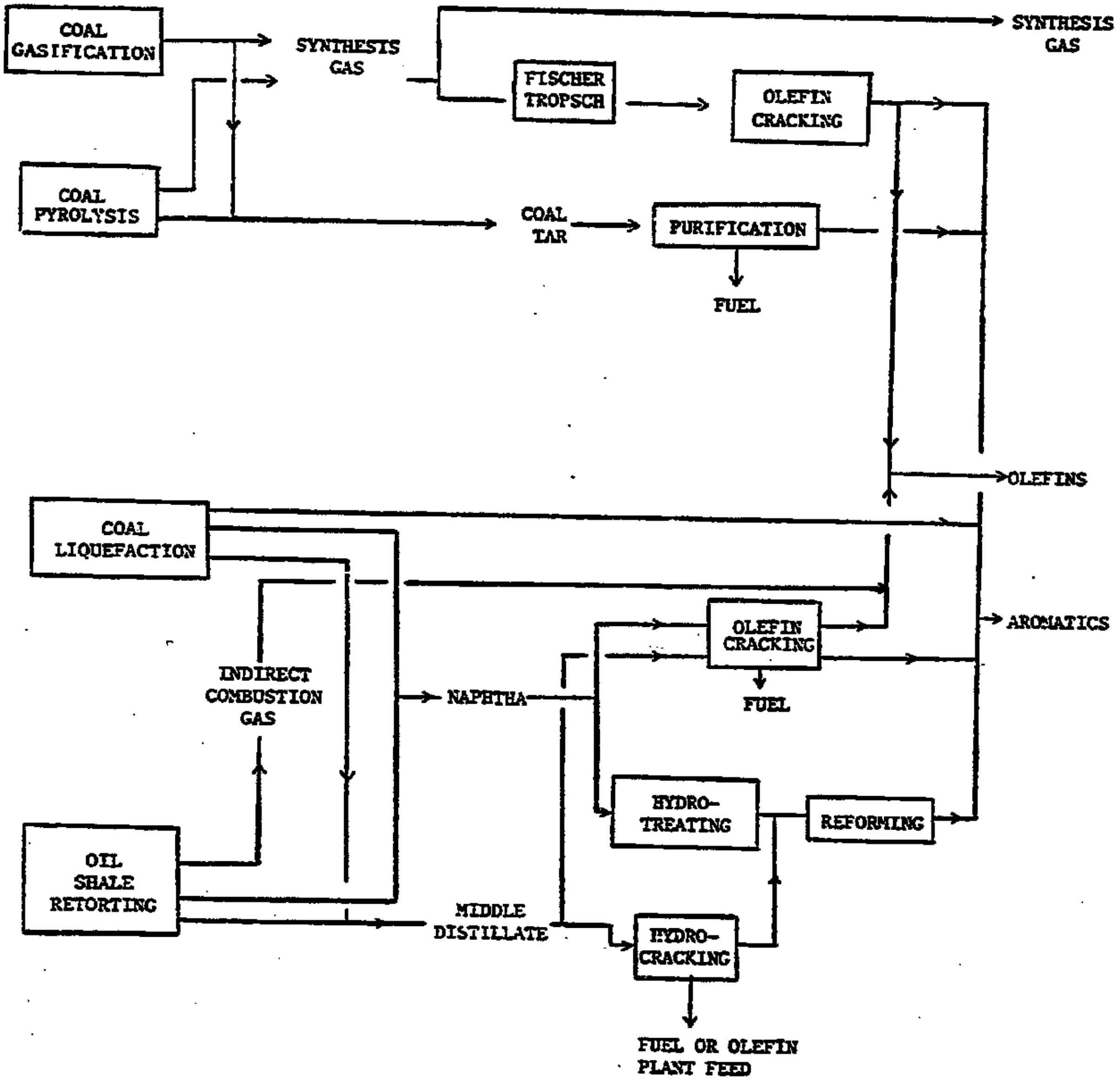

FIGURE 4-1. RELATIONSHIP OF CONVERSION TECHNOLOGIES TO PETROCHEMICAL FEEDSTOCKS