6 REFINING OF COAL AND SHALE LIQUIDS

The refining of coal and shale liquids will require many of the processing steps now used in refining petroleum. The types, sizes, and numbers of processing units needed, however, will depend on the properties of the feedstocks and the desired product slates. The feedstocks, in turn, will vary with the coal liquefaction or shale retorting process used.

Shale oils extracted by different processes, in fact, do not differ radically from one another, but coal liquids vary widely from process to process. Pyrolysis, for example, yields highly unsaturated liquids containing high-boiling-point tarry fractions contaminated with coal solids. Direct liquefaction without the addition of catalysts produces high-boiling-point solvent-refined coal that may also be contaminated with solids. Catalytic hydroliquefaction can produce either an all-distillate synthetic crude oil or a liquid containing high-boiling-point fractions and nondistillable material that may contain solids. Indirect liquefaction via synthesis gas yields all-distillate liquids or methanol, both quite different in character from direct liquefaction products. Table 25 lists, for several coal, shale, and petroleum liquids, the characteristics that determine the requirements of refining.

Large-scale pilot plant tests of shale retorting have been carried out for many years, yielding relatively large amounts of liquids for evaluation, and studies of the refining characteristics of shale oil have been carried out in considerable detail. Experimentation with coal liquids, on the other hand, has been much more recent and only relatively small quantities of the product have been available. Thus, while it is possible to present some quantitative data on shale oil refining, the refining of coal liquids must be handled in a more qualitative manner.

For reference purposes, Figure 28 is a simplified schematic diagram of a typical sour crude refinery, with the gas processing steps omitted. The relative size and severity of treatment in the various process units vary, of course, with the sulfur content and boiling range of the crude as well as the desired product slate.

Table 25 Characteristics of several coal, shale, and petroleum liquids

	SRC product	H-Coal	Synthoil	COED product
Composition				
Carbon, wt %	87.93	89.00	87.62	83.05
Hydrogen, wt %	5.72	7.94	7.97	8.35
Oxygen, wt %	3.50	2.12	2.08	7.15
Nitrogen, wt %	1.71	0.77	0.97	1.10
Sulfur, wt %	0.57	0.42	0.43	0.35
Nickel, ppmw	2	1	1	1
Vanadium, ppmw	7	3	2	7
Titanium, ppmw	130	80	150	1
Iron, ppmw	140	20	375	350
Kinematic viscosity, cSt at 100°C	Solid	318	28.6	1090
Pour point, °C	Solid	50	4	50
Type of coal used	High volatile (Illinois No. 6)	High volatile bituminous (Illinois No. 6)	High volatile bituminous (Pittsburgh seam)	High volatile bituminous
Reference	Callen *et al.* (1976)	Callen *et al.* (1976)	Callen *et al.* (1976)	Johns *et al.* (1972)

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[a] In another West Texas vacuum residue (not the one described by Callen *et al.*),

[b] Measured at 250°F at a shear rate of 1.98 (sec.^{-1}).

CFFC Product	Paraho Shale Oil Colo. 28	El Palito No. 6 Fuel Oil	540 C West Texas Sour Residuum
88.4	84.5	86.4	83.88
7.0	11.2	11.2	9.97
1.5	1.6	0.3	0.48
0.69	1.96	0.41	0.4[a]
0.25	0.64	1.96	4.19
1	3.5	59	34[a]
1	0.2	275	52[a]
9.5	--	78	--
57	100	6	--
71[b]	177	--	--
--	72	--	--
Bituminous (Illinois No. 6)			
Sze (1980)	Table 19	Callen *et al.* (1976)	Callen *et al.* (1976)

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the fraction boiling above 975°F had these metal contents (Sze, 1980).

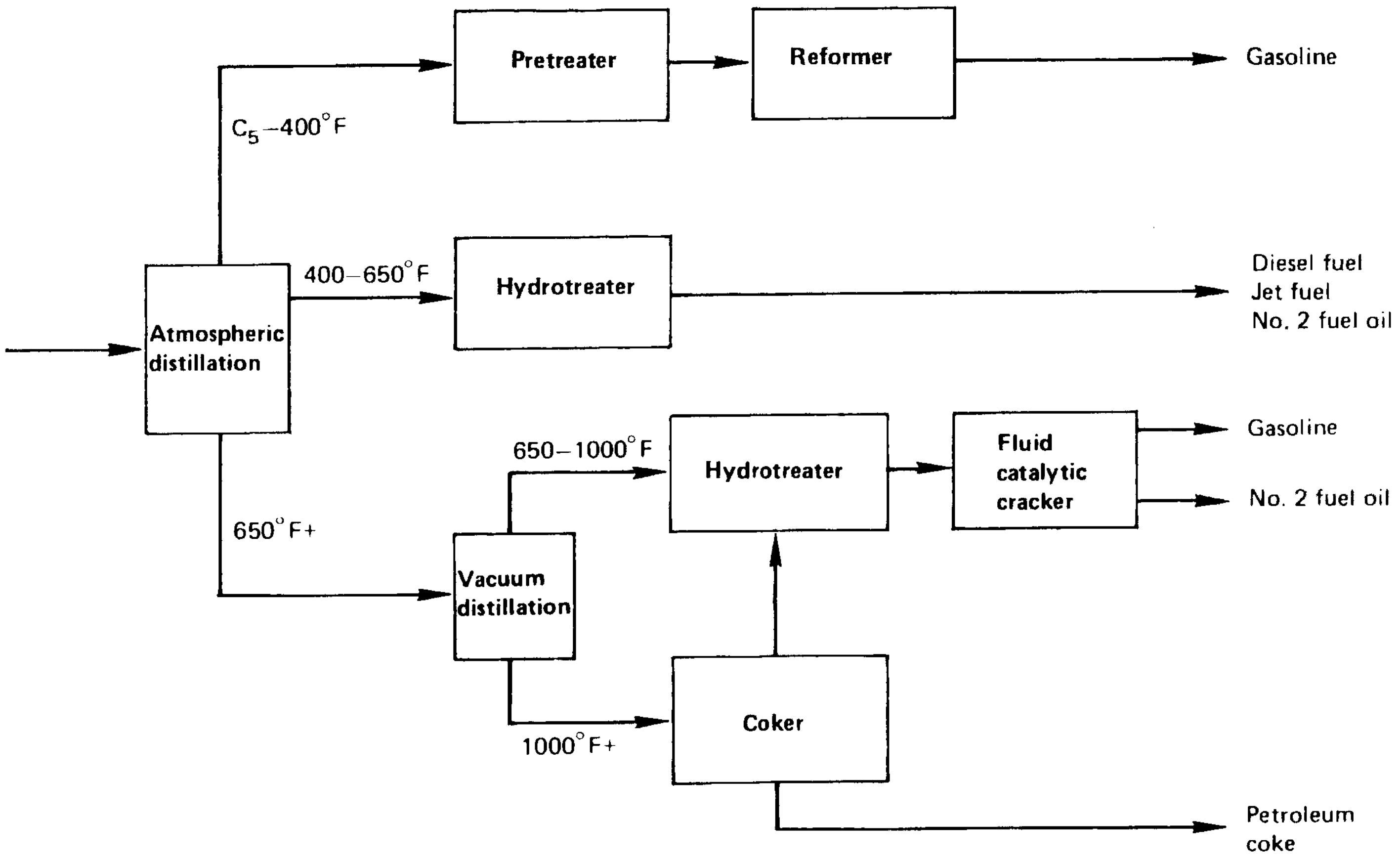

Figure 28 Flow diagram of typical sour crude refinery, omitting gas processing steps

REFINING COAL LIQUIDS

Heavy Liquid Feedstocks Containing Nondistillable Materials

Typical of the heavy liquid feedstocks obtained from coal are (a) solvent-refined coal (SRC), (b) catalytically hydroliquefied coal liquids containing nondistillable fractions, and (c) pyrolysis liquids.

As has already been noted in this report, the most effective way of using these heavy liquids at first may be to replace the petroleum fractions now being used for boiler fuels with coal-derived liquids that have undergone a minimum of refining. The petroleum fractions now used in boilers could then be refined to lighter products. This scheme would probably be cheaper than refining the coal liquids to lighter products. If coal liquids are put through a mild to moderate hydrotreating step to stabilize them and remove sulfur and nitrogen, the product will be usable not only as an environmentally acceptable boiler fuel but also as a refinery feed, as discussed below.

If, on the other hand, it is transportation fuels that are required, the refining could be carried out as shown in the schematic block flow diagram of Figure 29. The object of this processing sequence is to maximize the production of transportation fuels at the lowest practical level of hydrogen consumption. For heavy SRC-like feedstocks and the COED raw pyrolysis liquids, a liquid fluidized-bed front-end hydrocracking process such as LC-Fining or H-Oil could be used. If a fixed-bed mode of contacting is used, the particulate content of these liquids (0.1-0.2 percent by weight) will cause premature fouling or clogging of the catalyst bed. The relatively high residue contents of these two feedstocks require the use of front-end hydrocracking, which is more readily carried out with all-distillate syncrude-type feedstocks, as described further on.

In the first processing step of the refinery in Figure 29, the raw pyrolysis liquid or molten (or fluxed) heavy coal-derived liquid such as SRC would be mixed with recycle oil and fed to a liquid fluidized-bed hydrocracker containing a sulfur- and nitrogen-resistant catalyst. The objective of this step would be to reduce the fraction boiling over 850°F in the feed, to increase the H/C atomic ratio, and to remove a substantial amount of the heteroatoms (S, N, O). Hydrocrackate or effluent product from this step would then be atmospherically distilled into a full-range naphtha, an atmospheric gas oil, and atmospheric bottoms products. Following this, the atmospheric bottoms would be vacuum distilled into a vacuum gas-oil product and a vacuum bottoms product (boiling at more than about 900°F). The latter could be fed either to a hydrogen plant converting steam and carbonaceous feedstocks into hydrogen via a partial oxidation process, or to a coker. The product slate from the coker would consist of a coker gas oil, coke, and minor amounts of coker naphtha and gas. Whether coking were desirable would depend on the amount of additional liquid it would produce. The coke obtained could also be used in the production of hydrogen or fuel gas by partial oxidation.

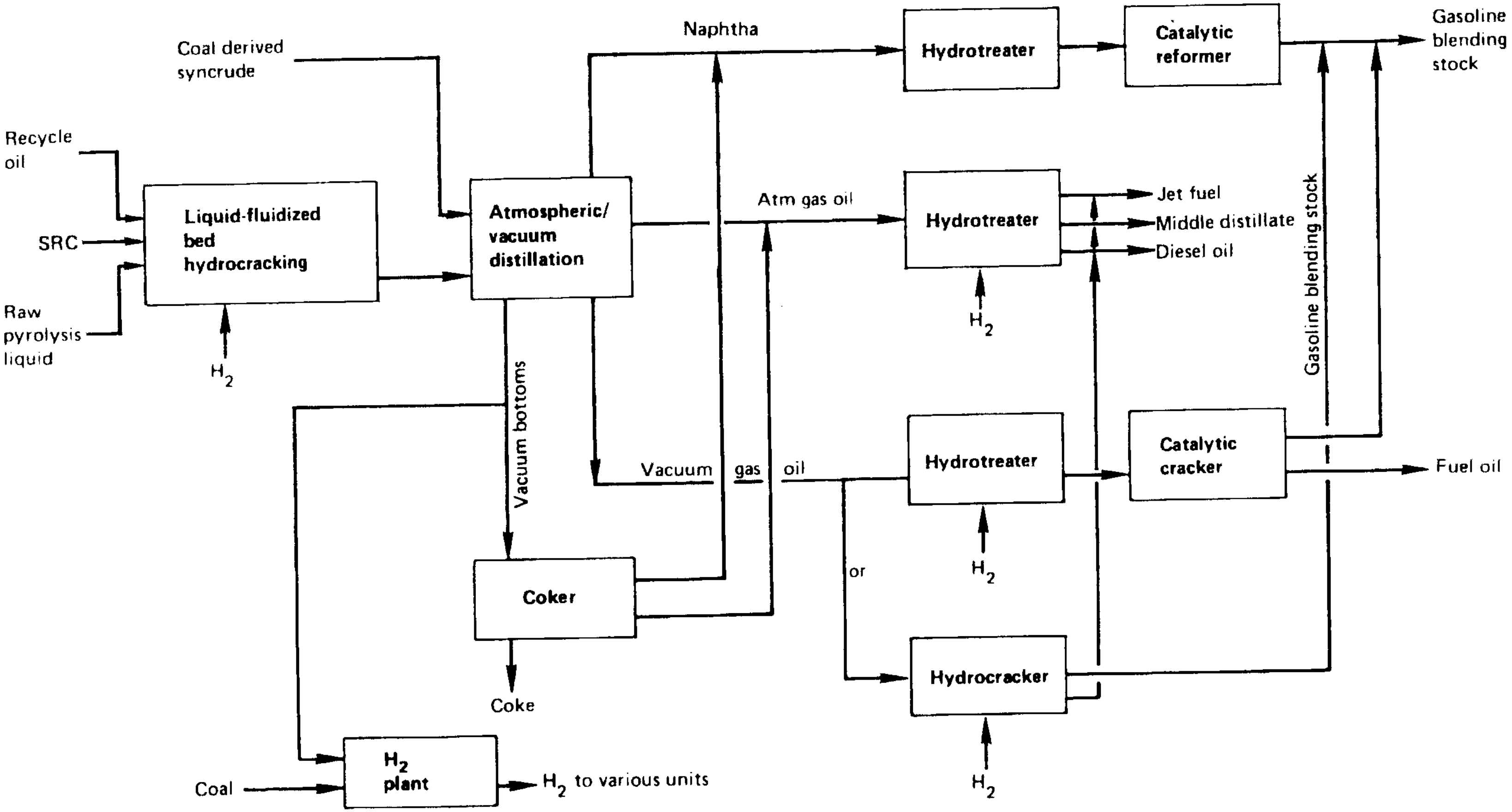

Figure 29 Coal liquid refining steps for producing transportation fuels

Naphtha from the atmospheric distillation step and from the coker, if available, would be hydroprocessed before being catalytically reformed to reduce the sulfur and nitrogen contents, a step normally carried out prior to conventional catalytic reforming with noble metal catalysts. Catalytic reforming would increase the aromatic content and octane number of the hydrotreated naphtha feedstock and yield a net hydrogen make. The product of the reforming would be a uniquely suited gasoline blending stock.

The atmospheric gas oil generated by the atmospheric distillation would be combined with coker gas oil, if available, and fed to a hydrotreater where the H/C ratio would be increased, the feedstock aromatic content decreased, and the heteroatoms content also decreased. If sufficient hydrogen were added and the aromatic content sufficiently reduced (both goals expensive to realize), the products would be usable as jet fuels and diesel oils. Less hydrogen would be required to produce mid-distillate heating oils.

The vacuum gas oil prepared during the vacuum operation could also be hydrotreated and then catalytically cracked. This combination of steps would produce both gasoline and fuel oil. The vacuum gas oil material could, on the other hand, be hydrocracked to produce a product slate of gasoline, jet fuels, mid-distillates, and diesel fuels. The gasoline so produced might or might not require reforming, depending on the pool octane requirement.

This refining scheme will require a hydrogen plant. The heavy vacuum still bottoms would probably be a convenient feed for hydrogen production; if additional hydrogen were required, it could be obtained by the partial oxidation of additional coal.

All-Distillate Synthetic Crudes from Direct Liquefaction

All-distillate synthetic crudes obtained by direct coal liquefaction are lighter (i.e., have a lower boiling range) than the heavy coal liquids and are free of particulate contaminants. As a result, the refining of such feedstocks for the production of gasoline and heating oil is relatively straightforward. As indicated in the block flow diagram of Figure 29, these syncrudes can be processed without the front-end hydrocracking step. If, however, they have a significant concentration of diolefins and require substantially lower temperatures in the primary distillation steps to avoid coking, it may prove advantageous to subject them first to a mild hydrotreating to improve their stability. The addition of this step would reduce the severity of the hydrotreating required downstream.

The following fractions may be obtained from the atmospheric and vacuum distillation units: a light naphtha cut, a heavy naphtha fraction, a light mid-distillate cut, and a heavy mid-distillate stream. The light and heavy naphthas would be hydrotreated and catalytically reformed as required, the light mid-distillate might be hydrotreated to produce No. 2 heating oil, and the heavy mid-distillate would be either hydrotreated and catalytically cracked or hydrocracked. There would be no need for a coker to process any heavy residue.

Refining all-distillate crudes is simpler because of the more severe hydroliquefaction used to produce them. It is too soon, however, to generalize on whether it would be more economical to produce and ship an SRC or an all-distillate syncrude from a primary liquefaction plant. The economics certainly favor the production of the maximum liquid product with minimum overall hydrogen consumption.

Indirectly Produced Coal-Derived Liquids

Indirectly produced coal-derived liquids (e.g., Fischer-Tropsch liquids, methanol, gasoline derived from methanol) are characterized by their lower boiling ranges and the essentially complete absence of combined sulfur and nitrogen, a result of the elaborately purified syngas (H_2 and CO) used in the production of these liquids. Although the refining of these indirectly produced liquids was not considered within the scope of this study, a few fundamental facts should be noted:

- Fischer-Tropsch liquids contain straight-chain olefins and paraffins, with almost no aromatics. Diesel fuels are easier to produce from them than from the highly aromatic products of direct liquefaction. The gasoline boiling range fraction has a low octane rating, requiring octane improvement processing steps (e.g., catalytic reforming of the naphtha and isomerization of the C_5/C_6 fractions).

- Gasoline from methanol contains aromatics and has a higher octane rating than Fischer-Tropsch liquids. The process produces in addition LPG and small amounts of fuel gas, and almost no materials with boiling points above that of gasoline.

REFINING SHALE LIQUIDS

Raw shale oil may have to be subjected to either visbreaking or mild hydroprocessing at the retorting site (depending on the retorting process) to improve its handling characteristics and reduce its pour point before it is sent to a refinery. It is not expected, in general, that the refining would be carried out at the retorting site. Figure 30 shows the various processing alternatives, with the product slate and product quality dictating the viable options. For a particular situation studied, the yields and product qualities of the shale oil after processing by the various options indicated in Figure 30 are as given in Table 26. In this study, the light ends were used internally for plant fuel or hydrogen plant feed. Although the results in other situations would be somewhat different, Table 26 serves as a good illustration.

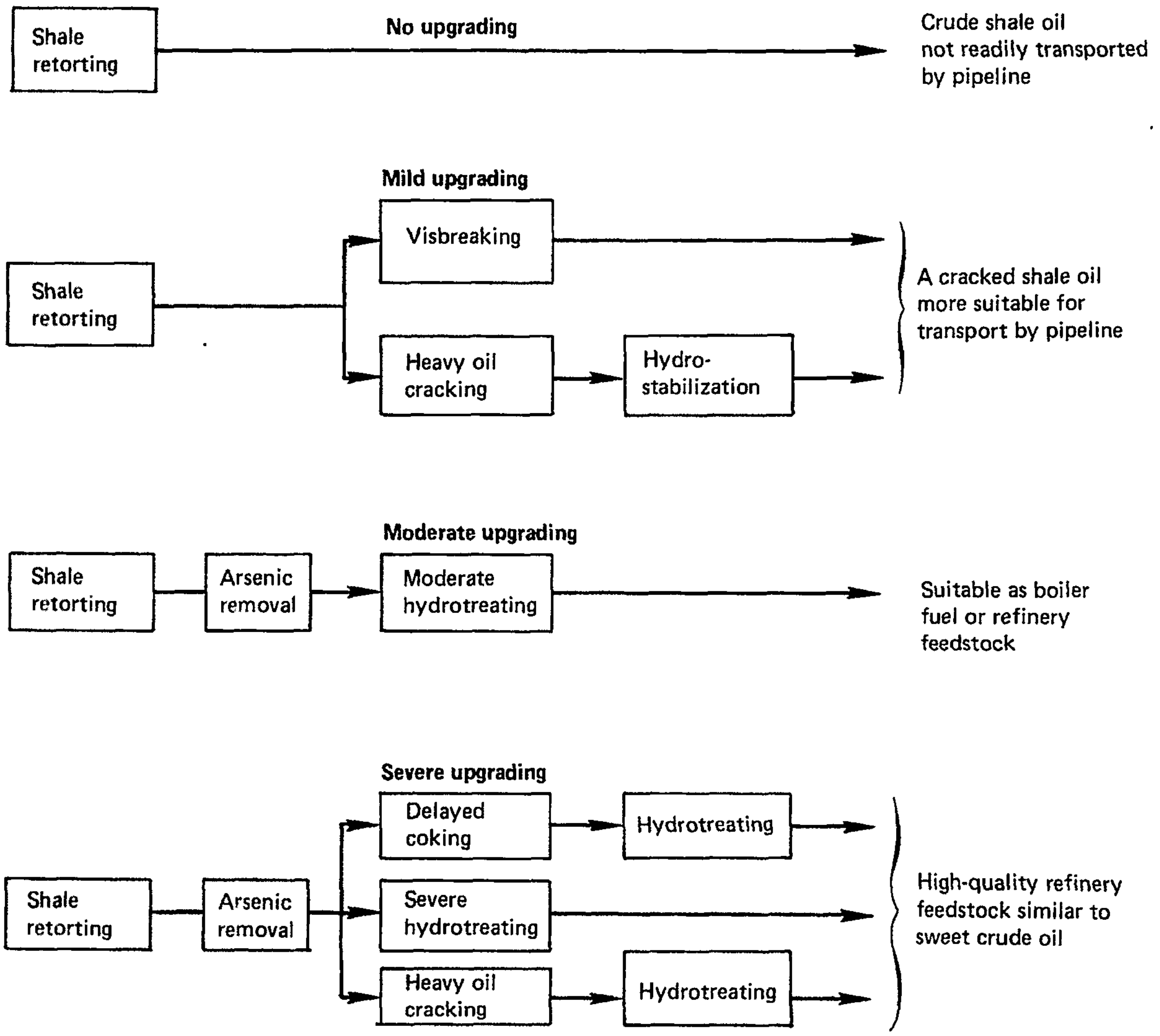

Figure 30 Processing alternatives for shale liquids according to quality of end product

TABLE 26 Oil shale facility process summary (based on 100,000 barrels per calendar day crude shale oil)

	Crude shale oil	Visbreaking	Heavy oil cracking/ hydrostabilization
C_4+ liquid oil product recovered, barrels per calendar day	100,000	100,300	88,920[a]
Heating value of oil recovered, 10^9 Btu per calendar day	605	605	490
Shale oil product quality			
Gravity, °API	19.8	20.4	34.0
Pour point, °F	85.0	20.0	35.0
Viscosity, cSt at			
40°F	460[e]	370	8
100°F	45	35	3
Reid vapor pressure, psi	3.5[f]	1.0	7.0
C_5-430°F			
Volume, percent	7.0	11.2[f]	37.7
Sulfur, ppmw	8,000	9,200	5,400
Nitrogen, ppmw	5,000	10,000	7,000
430-600°F			
Volume, percent	16.0	21.8[f]	22.5
Sulfur, ppmw	7,000	6,400	7,700
Nitrogen, ppmw	14,000	16,500	21,000
600-1050°F			
Volume, percent	70.0	61.0	34.3
Sulfur, ppmw	6,300	5,800	5,700
Nitrogen, ppmw	24,100	23,500	26,000
1050°F+			
Volume, percent	7.0	6.0	5.5
Sulfur, ppmw	--	--	--
Nitrogen, ppmw	--	--	--
Total			
Volume, percent	100.0	100.0	100.0
Sulfur, ppmw	7,000	6,700	5,600
Nitrogen, ppmw	21,000	20,300	17,200

[a] Shale oil product has 5.5 percent C_4 by volume.

[b] Shale oil product has 1.7 percent C_4 by volume.

[c] Shale oil product has 0.2 percent C_4 by volume.

Crude shale oil hydrotreated for		Delayed coking	Coking/ hydrotreating	Heavy oil cracking/ hydrotreating
Boiler fuel	Refined shale oil			
96,000	96,000	88,000[b]	87,020[c]	87,930[d]
581	568	508	506	500
36.3	40.0	29.7	43.0	43.0
60.0	50.0	35.0	35.0	35.0
20[e]	13[e]	20	8.5	8
5.5	4	5	3.3	3
1.0	1.0	3.0	1.5	5.0
16.5[f]	23.6[f]	21.1[f]	29.1	40.1
50	-	10,000	1	1
400	1	10,000	1	1
29.7[f]	32.0[f]	32.2[f]	39.1	31.5
--	50	8,500	20	20
--	200	16,000	200	200
49.4	40.0	45.0	31.6	25.3
600	500	6,000	20	20
2,500	600	21,000	1000	200
4.4	4.4	--	--	--
--	--	--	--	--
--	--	--	--	--
100.0	100.0	100.0	100.0	100.0
500	250	7,000	15	13
2,200	340	18,000	410	385

[d] Shale oil product has 3.1 percent C4 by volume.

[e] With addition of pour depressant.

[f] 400°F TBP cut point.

The first step in almost any scheme for refining shale oil will be the removal of arsenic, because the high arsenic concentrations in shale oils will severely poison most of the catalysts used in refining. Arsenic removal is generally carried out in an atmosphere of hydrogen under pressure at intermediate temperatures (450-600°F) in a fixed bed; a disposable adsorbent catalytically promotes the deposition of the arsenic in much the same way that other metals are deposited on hydroprocessing catalysts. The cost of satisfactory removal is currently estimated to range from 25 to 50 cents per barrel. The panel believes that much more research is needed into the nature of the arsenic compounds in shale oils, possible mechanisms and better materials for removing these compounds, and better methods for disposing of the spent adsorbent.

As shown in Figure 30, a moderate hydrotreating of shale oil will yield environmentally acceptable boiler fuels and suitable refinery feedstocks. Direct hydrogenation at moderate pressures (1000-1500 psig) will reduce the nitrogen and sulfur contents of shale oils to the point at which they can probably be burned in boilers and process heaters without exceeding the emissions standards for SO_x and NO_x. Moderately hydrotreated shale oil could also be admixed with crude fractions being used in various refinery processes.

It may be desirable to upgrade the shale oil even more, producing a synthetic crude that is compatible with conventional crudes, allowing it to be mixed with petroleum-based streams in existing refineries. This upgrading can be accomplished in several ways, the principal methods being (a) coking plus hydrotreating of the coker distillates, (b) severe hydrotreating of full-boiling-range raw shale oil, and (c) heavy oil cracking followed by hydrotreating. Let us examine these three alternatives briefly:

(a) Where coking plus hydrotreating of the coker distillates is employed, the primary problems are handling the high-nitrogen coke produced (about 4 percent N) as well as low liquid yields. The coke could be gasified to produce hydrogen but the economics of all the options would need to be carefully examined because of the low liquid yields (see Table 26).

(b) Severe hydrotreating of full-boiling-range raw shale oil may be the most attractive processing route for shale oil, since it provides the greatest flexibility in the choice of the final product slate and the least severe environmental problems. As indicated in a Chevron study (Sullivan and Stangeland, 1978), acceptable catalyst life can be achieved and fully acceptable feedstock quality produced for downstream refining (e.g., catalytic cracking and reforming). The Chevron study shows the optimal product nitrogen level to be about 500 ppm; the conditions required to achieve this level are the following: a pressure of about 2200 psig (1850 psia H_2 partial pressure) and approximately 2100 cubic feet of hydrogen per barrel. In this process, significant ring fracturing and saturation occur, resulting in a sharply reduced aromatic content and corresponding increases in paraffin and naphthene contents. The resulting naphtha cut is a better feedstock for reforming than is found in most petroleum crudes.

(c) The third processing alternative for producing high-quality refinery feedstock is the use of heavy oil cracking (HOC-fluid catalytic cracking technology licensed by Phillips/Kellogg), followed by hydrotreating of the cracked naphtha, light gas oil, and heavy gas oil in separate units. Since the coke produced is far in excess of that required to maintain a heat balance, a very considerable amount of high pressure steam is generated, requiring efficient utilization. This process is similar to that of (a) above, but coke is not obtained as a product; instead, the coke is burned in the regenerator, the heat recovery being in the form of high pressure steam. As with the process described in (a), the product requires reasonably severe hydrotreating for nitrogen removal.

The processing route that is optimal will depend on whether the refining takes place at the mine site as an integral part of the total mining-retorting-upgrading process, in a separate new refinery specifically designed for this purpose, or at an existing refinery to which facilities for handling shale oil are added. Many factors must be taken into account in choosing the location, including the total energy balance, the availability of feed streams for hydrogen generation, and the desired product mix. There are additional factors, such as the availability of water, the labor pool, the availability of space for expansion, and the means for transporting raw materials and products.

Figure 31 is a process chart for a fully integrated raw shale refinery designed to maximize the production of transportation fuels with the minimum use of hydrogen. After arsenic removal and hydrotreating, the shale oil feedstock is atmospherically distilled into a full-range naphtha, an atmospheric gas oil cut, and an atmospheric bottoms product that is subsequently vacuum distilled into a vacuum gas oil fraction and a vacuum bottoms product (900°F+). If the vacuum bottoms product is large, it could be fed to a coking process step or, alternatively, to a solvent de-asphalting process step that produces a decarbonized oil and/or asphaltic residuum that could be used for the generation of hydrogen in a partial oxidation process. If the feedstock has not been sufficiently hydrotreated, the de-asphalted oil would be fed to a hydrotreater and then catalytically cracked.

If the atmospheric residuum does not contain too large a quantity of heavy material or asphaltenes, the entire atmospheric residuum can be charged to a hydrotreater and catalytic cracker.

In the coker, the vacuum bottoms would be converted primarily into coker gas oil and coke with minor amounts of coker naphtha and gas. If

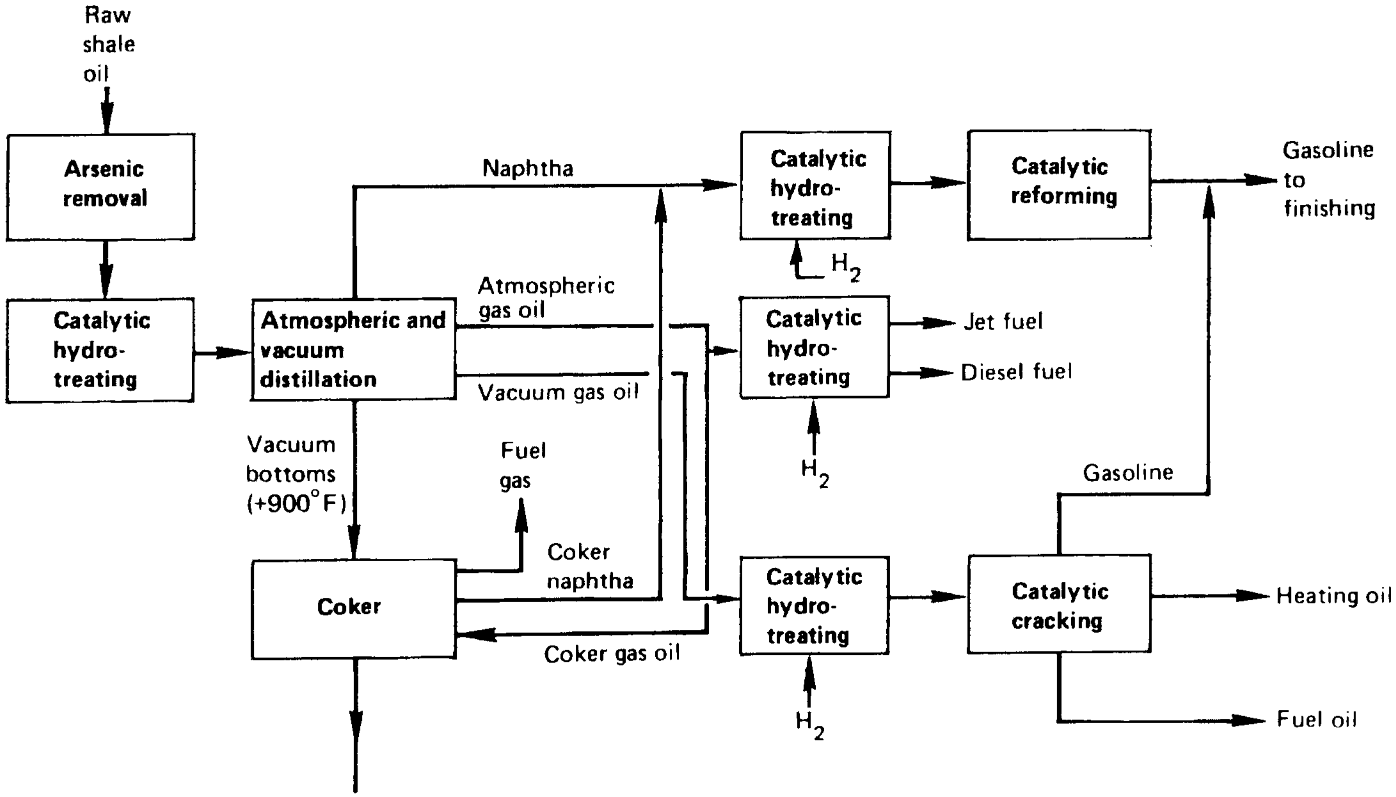

Figure 31 Shale oil refining steps to produce transportation fuels with minimum use of hydrogen

aluminum anode coke is desired, a delayed coker should be employed. If, on the other hand, low-quality coke is satisfactory and higher gas oil yields are desired, fluid coking could be considered. In either case, coke might be used to produce fuel gas or hydrogen by partial oxidation, although flexicoking (a combination of fluid coking and partial oxidation) may provide another option.

Coker naphtha and straight-run naphtha from the atmospheric distillation could be combined and hydrotreated to produce a low-sulfur (less than 5 ppm), low-nitrogen (less than 1 ppm) naphtha suitable for catalytic reforming. For octane improvement, conventional catalytic reforming would be entirely satisfactory.

Atmospheric gas oil obtained from the initial atmospheric distillation operation could be combined with coker gas oil and put through a hydrotreating step to remove heteroatoms and saturate aromatic rings, yielding jet and diesel fuels.

Straight-run vacuum gas oil could be hydrotreated to reduce the concentrations of nitrogen, sulfur, and polynuclear aromatics prior to catalytic cracking. (If a de-asphalting process option is used, the decarbonized oil would be combined with the straight-run vacuum gas oil before it is hydrotreated.) The product slate from this part of the refinery would consist of gasoline, heating oil, fuel oil, and gas.

Another alternative processing strategy would be to eliminate the coker and substitute a hydrocracking process step for (or combine it with) the catalytic hydrotreating and catcracking combination, as shown in Figure 32. Hydrocracking should increase the quantities of naphtha and/or diesel and jet fuel produced, but the naphtha from the process would require catalytic reforming. If a sufficiently nitrogen-resistant hydrocracking catalyst is not available, nitrogen would have to be removed prior to hydrocracking in a hydrotreatment step.

REFINING TECHNOLOGY FOR CATALYTIC HYDROPROCESSING

Overview

Catalytic hydroprocessing should be given the greatest attention in future research efforts because of its importance in the refining of shale oil and direct-route coal liquids. It is essential for the removal of heteroatoms (particularly nitrogen and sulfur, which are present in large concentrations), and for the cracking of the high-molecular-weight coal liquids to more usable fractions.

While one of the major concerns with petroleum has been the sulfur in the crude, there are problems with nitrogen as well in coal and shale liquids because of increasing restrictions on NO_x emissions from fuels and the severe poisoning effect that nitrogen-containing compounds have on refinery catalysts. The concentration of organically bound nitrogen

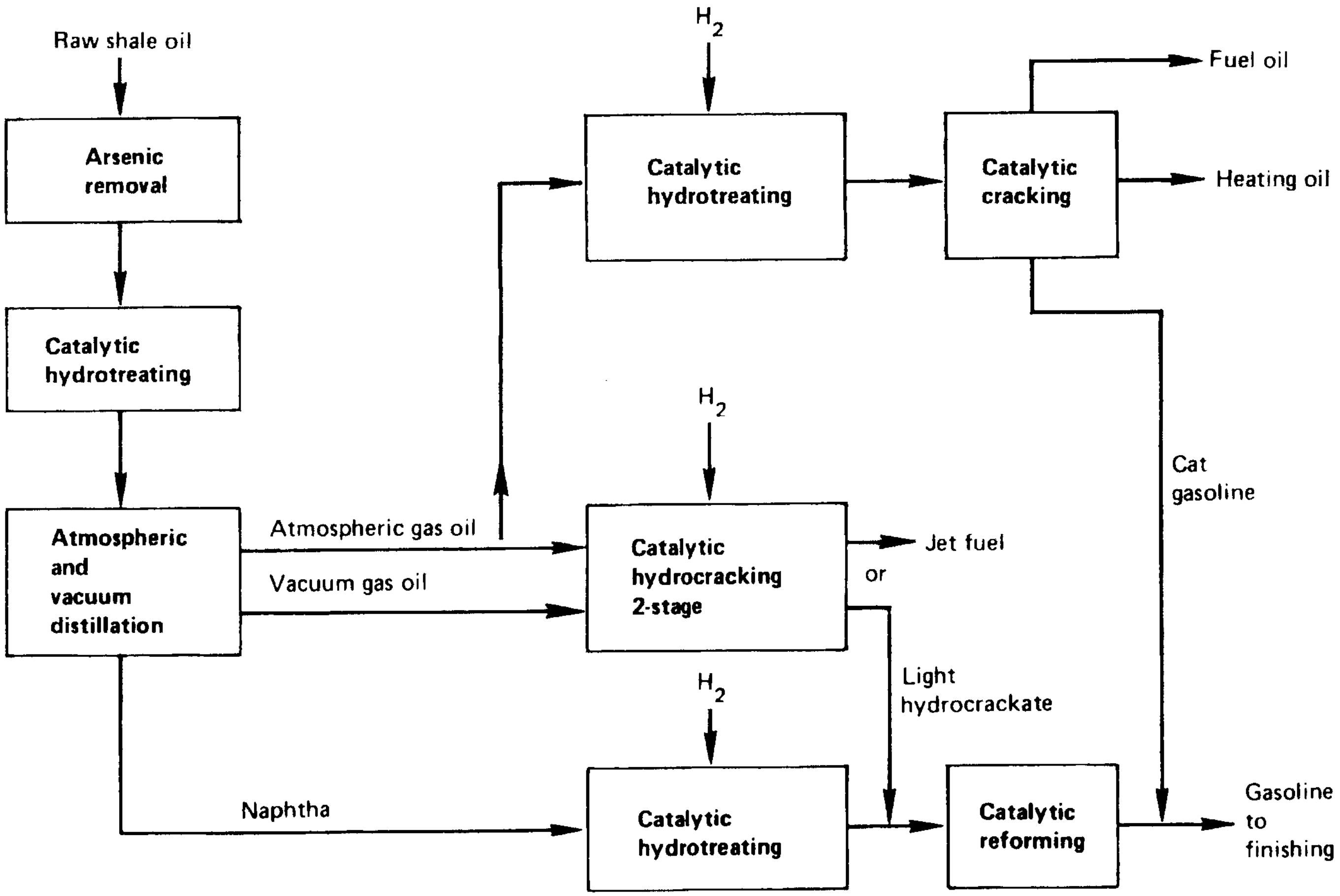

Figure 32 Shale oil refinery using substitute hydrocracking process step

in coal and shale liquids is several times higher than that found in petroleum. Figure 33 shows the effect that nitrogen has on a noble metal molecular sieve catalyst during hydrocracking. The 100°F temperature increase required to maintain constant product quality results in a severe increase in the rate of catalyst deactivation and a corresponding reduction in catalyst life.

In practice, the removal of nitrogen is generally more difficult than the removal of sulfur. Table 27 shows the extent to which nitrogen and sulfur can be removed by hydroprocessing from a shale oil, solvent refined coal, Synthoil (a coal-derived liquid from an earlier process), and three different petroleum distillates. The figures show that a lower percentage of the nitrogen is removed, generally, even when the hydroprocessing removes a high percentage of sulfur.

As the boiling point of the feedstock increases, a given degree of sulfur and nitrogen removal requires a progressively higher severity (i.e., higher temperature, pressure, or hydrogen recycle rate, or lower space velocity), and may result in a shortened catalyst life.

The need for increasing the severity of the operating conditions with the boiling point of the feedstock results from several factors. In the higher-molecular-weight feedstock:

- The compounds from which the heteroatoms are to be removed are less reactive.
- The more highly aromatic molecules of the feedstock compete with the heteroatom-containing molecules for catalyst sites, reducing their rate of reaction.
- The more highly aromatic molecules deactivate catalysts more severely, requiring higher hydrogen pressures to reduce coke formation to an acceptable level.

The higher aromaticities of coal and shale liquids make them more difficult to hydrocrack and require a higher hydrogen consumption.

Catalysts

Typical catalysts for the processes described here consist of combinations of cobalt, nickel, molybdenum, and tungsten supported on alumina. Such catalysts are normally 3-6 percent cobalt or nickel and 12-18 percent molybdenum or tungsten. Under operating conditions, these metals are in the form of sulfides on the alumina. The preferred catalyst for hydrodesulfurization is $Co\text{-}Mo/Al_2O_3$ (cobalt molybdate on Al_2O_3). The frequent choice for hydrodenitrogenation is Ni-Mo or NiW on Al_2O_3. The preferred catalyst for hydrocracking is Ni and W on an acidic support such as $SiO_2\text{-}Al_2O_3$.

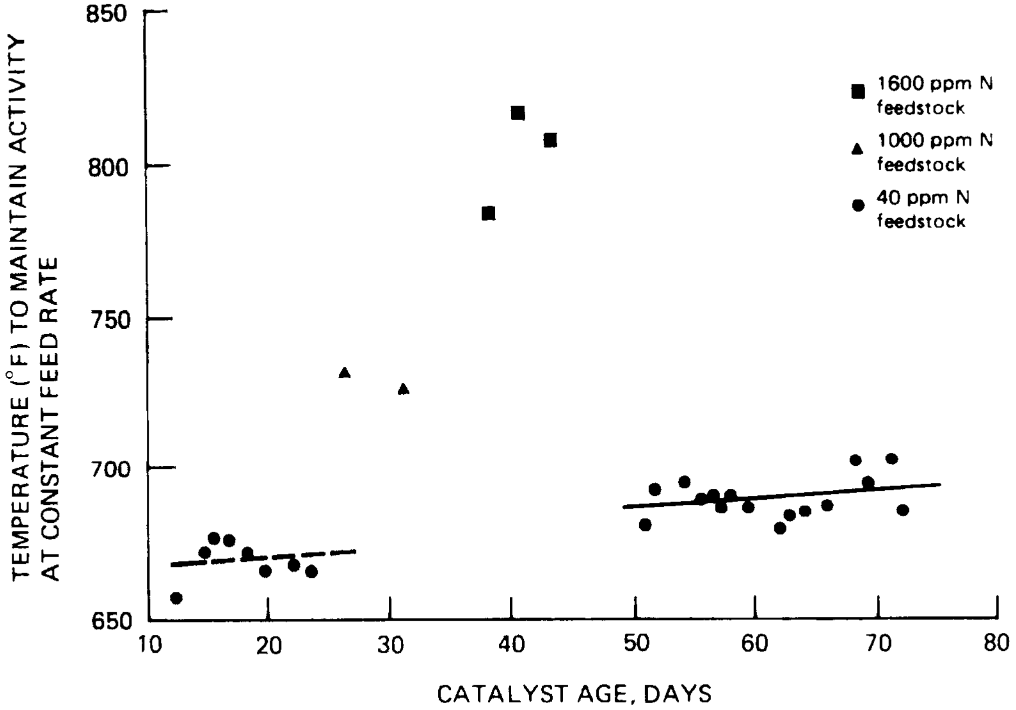

Figure 33 Effects of nitrogen content of feed on noble metal acid molecular-sieve catalyst in Unicracking-JHC process (Retallick, 1964)

Table 27 Sulfur and nitrogen removal from shale and coal liquids and three petroleum distillates, by hydroprocessing, in percent by weight

	Sulfur			Nitrogen		
	In original	In product	Percent removed	In original	In product	Percent removed
Shale oil[a]	0.6	0.0025	99.6	2.2	0.07	97
Solvent-Refined Coal II[b]	0.29	0.001	99.6	0.85	0.05	94
H-Coal[c]	0.32	0.001	99.6	0.46	0.014	70
Three petroleum distillates[d]	0.8	0.05	94	0.015	0.007	53
	1.19	0.07	94	0.056	0.041	27
	1.58	0.14	91	0.012	0.007	42

[a] Sullivan *et al.* (1977).

[b] Sullivan *et al.* (1980).

[c] Using Illinois No. 6 coal.

[d] Thomas (1970).

Any of these will catalyze all three reactions but with different selectivities. The best hydrogenation catalyst is probably Ni-W/Al_2O_3 but hydrocracking may also be catalyzed by nonacidic catalysts with an active hydrogenation-dehydrogenation component. Such catalysts, using a thermal cracking mechanism, are frequently preferred for very heavy feedstocks that would severely coke a strongly acidic support. For clean feeds, hydrocracking catalysts made up of a zeolite base with palladium or platinum are also employed (Ward, 1973).

Catalysts are generally extrudates. The particle size (1.5-3mm) is usually made as small as possible to minimize intraparticle mass transfer limitations, particularly for heavy feedstocks. The lower limit of particle size is set by the pressure drop allowable in the catalyst bed. Liquid fluidized-bed reactors have the advantage of allowing the use of very fine catalyst particles.

Reactors and Processes

For petroleum feedstocks that are free of solids, the reactors used are generally the trickle-bed type, with the oil "trickling" down over the catalyst in the presence of high-pressure hydrogen.

With heavy coal or shale liquids that are contaminated with solids, liquid fluidized-bed reactors (e.g., LC-Fining or H-Oil reactors) must be used to avoid plugging. This type of reactor (essentially a stirred tank reactor) has the added advantage of permitting the intermittent addition of fresh catalyst and withdrawal of spent catalyst while the unit is on stream. It also allows the use of smaller catalyst particles (less than 0.8 mm), reducing the mass transfer problem encountered with heavier feeds. The greater volume requirement of this type of reactor can be largely offset by operating at higher average temperatures but the increased hydrocracking that results may be undesirable. The design of both reactor types is straightfoward because of the considerable experience gained from the petroleum industry. What are needed are the catalyst deactivation rates with the feedstocks to be used. In operation, the reactor temperature can be increased with time to compensate for the deactivation of the catalyst and maintain constant conversion. If the deactivation is due to coking, the catalyst can be regenerated by controlled combustion of the coke. If, however, the deactivation of the catalyst is due to the deposition of metals, regeneration will not be possible.

Catalyst costs for processes that involve direct contact between coal and a particulate catalyst may be as high as $1.00 per barrel, but the cost may be much lower when solids separation is carried out prior to hydroprocessing.

Reactor systems include a preheat furnace, reactor, hydrogen recycle and purification system, and product separation train (Figures 34 and 35). For dirty feeds, the life of the catalyst can be extended by first passing the feed through a guard chamber with a cheap disposable catalyst to remove metals and rapid-coking components.

For the more severe operations with coal and shale liquids that would lead to undesirably high temperatures in the catalyst bed (hydrogenation and hydrocracking being quite exothermic), trickle-bed reactors are staged and cold gaseous hydrogen injected between the stages to reduce the temperature of the reactant stream. When two stages are necessary (because the feed is high in nitrogen and sulfur and particularly heavy, and considerable hydrocracking is required), more efficient process operation can be achieved by placing each stage in its own recycle loop. By this means, NH_3 and H_2S can be separated from the hydrogen before it is fed to the second catalyst bed (Figure 35). With the removal of sulfur and nitrogen in the first stage, hydrocracking can be carried out more effectively in the second stage.

The costs of processing coal and shale liquids can be reduced by using better grades of syncrudes, developing better catalysts, and

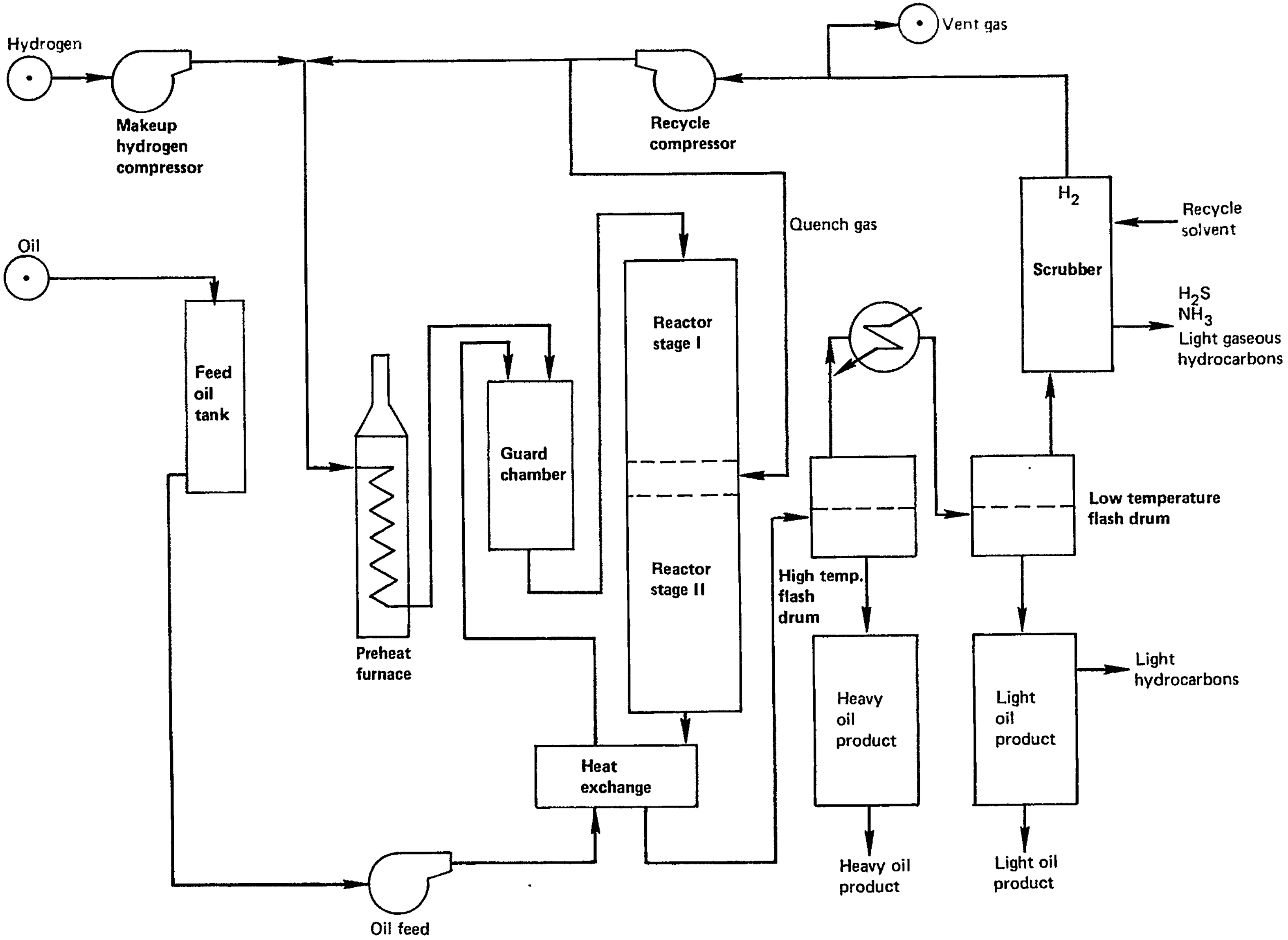

Figure 34 Hydroprocessing reactor system design for processing coal-derived liquids

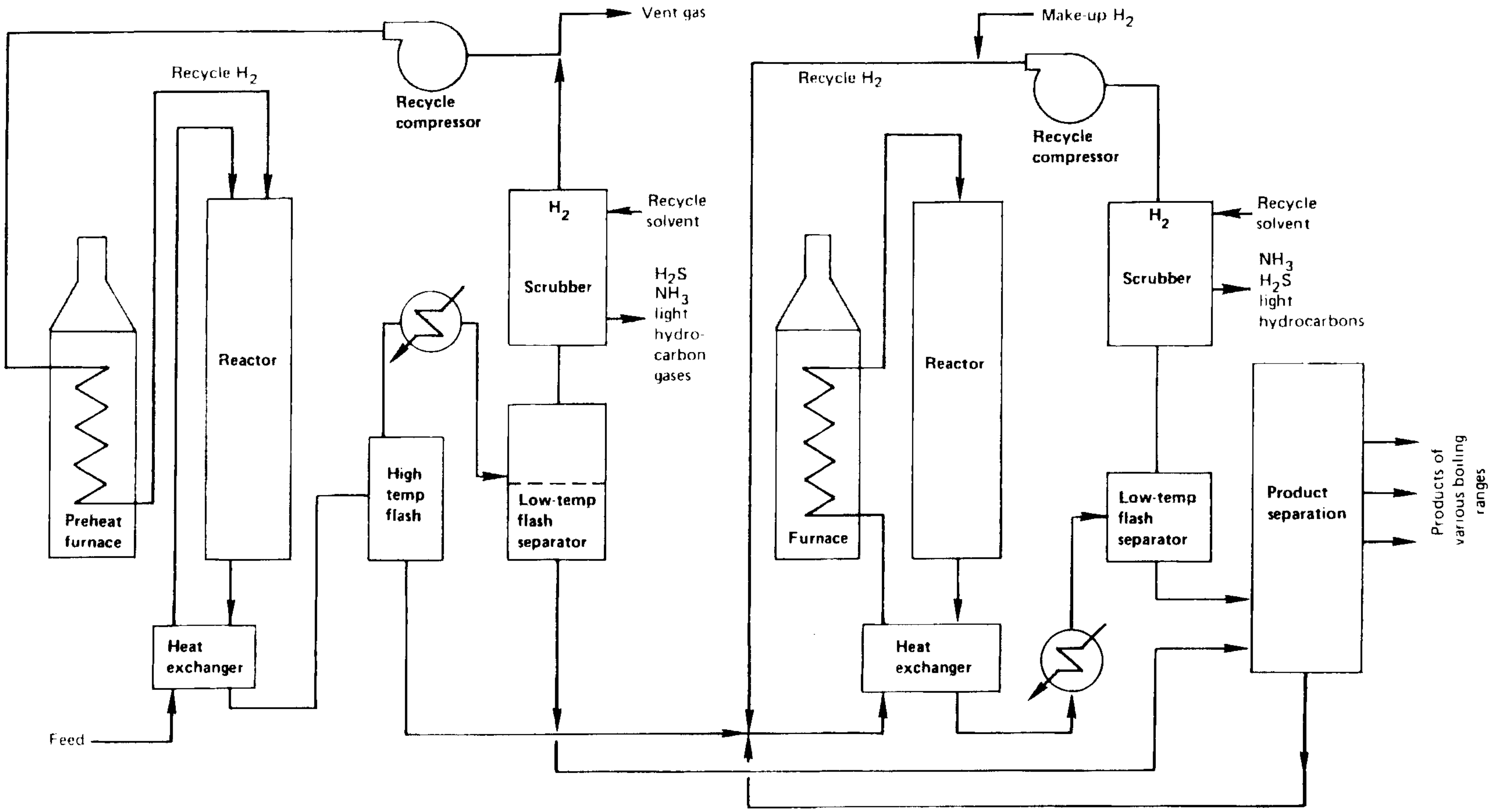

Figure 35 Two-stage hydroprocess-hydrotreating system, with parallel recycle loops for hydrogen

reducing the cost of hydrogen. The potential for the development of new and improved catalysts is enormous, but it will require a large research and development effort with particular attention to improvements in activity and selectivity.

CONCLUSIONS

The conclusions reached on the processing of coal and shale liquids are as follows:

- Since shale liquids are more nearly like petroleum than are coal-derived liquids, shale liquids are more easily processed to diesel and jet fuels. Minimally upgraded shale oil could initially enter the market as a boiler fuel or refinery feedstock.
- If coal and shale liquids can be transported economically, they could be refined in existing refineries, suitably modified, without requiring the construction of new ones.
- The refining of coal and shale liquids will involve many of the processing steps used in petroleum refining, although they may vary in some detail. Refineries for processing coal and shale liquids will, consequently, resemble modern petroleum refineries.
- The most important step in refining coal and shale liquids is hydroprocessing to remove the heteroatoms (S, N, O), reduce the average molecular weight to that required for the products being produced, and reduce the aromaticity. In shale liquids, high hydrogen consumption during hydrodenitrogenation makes nitrogen removal the single most important problem in refining. In coal liquids, high hydrogen consumption is required to reach acceptable nitrogen contents and to reduce the aromatic content.
- Hydrogen consumption represents a major fraction of the cost of processing coal and shale liquids, and needs to be minimized.
- Coal and shale liquids can be hydroprocessed with the use of catalysts, as is done at present with petroleum. The lighter fractions of coal and shale liquids, behaving much like light petroleum feeds, can be hydroprocessed and refined with existing technology, requiring little further research. But fractions of coal and shale liquids require more severe hydroprocessing than the corresponding petroleum fractions and cause more severe catalyst deactivation. They also require more hydrogen. Particular attention must be given to the development of catalysts that can remove nitrogen with less hydrogen consumption. Catalysts with greater activity maintenance are also needed.
- Hydroprocessing costs are increased by the severity of the processing conditions. The costs can be reduced by using coal and shale liquids of better quality.

- Arsenic, a severe catalyst poison, is present in shale liquids in concentrations that pose a more serious problem than the arsenic concentrations occasionally found in petroleum. The arsenic contents of coal-derived liquids are much lower and pose no problem.

- After coal and shale liquids have been adequately hydroprocessed, they generally can be processed in much the same way as petroleum feed stocks. Since the refining technology for petroleum has been so well developed, a major R&D effort is not needed on downstream processes for coal and shale liquids (i.e., catalytic cracking, catalytic reforming, isomerization, etc.).

RECOMMENDATIONS

- Although some processes for refining coal and shale liquids are already available, the costs are still high, due primarily to the high rate of hydrogen consumption required at present for boiling point reduction and the removal of sulfur and nitrogen heteroatoms. A reduction in the cost of hydrogen should therefore be an important objective of research and development efforts.

- The lighter components of coal and shale liquids after refining could be used initially as gasoline blending agents.

- Research and development should be carried out on the refining (particularly the hydroprocessing) of liquids with a wide range of properties. None of the three routes for direct coal liquefaction (i.e., pyrolysis, solvent extraction, and catalytic liquefaction) can, as yet, be considered out of the running. Each has its advantages and each produces liquid products with different properties.

- A fundamental research program is required for a better understanding of hydrodenitrogenation catalysis and the development of improved and new catalysts. The Department of Energy should actively sponsor such a program. Also needed are a better understanding of the forms of arsenic and mineral matter in coal and shale liquids and better ways of removing these catalyst poisons.

- The Department of Energy should continue its program of sponsoring tests of industrial proprietary processes to keep abreast of the current state of the art.

- The Department of Energy should sponsor considerably more fundamental research on the reactions involved in the refining of coal and shale liquids. A better understanding of the reaction mechanisms is essential to the development of new and improved processes.

- Government agencies should give high priority to activities directed toward finding optimum combinations of new fuels and end-use equipment. Facilities should be established for the supply of adequate quantities of fuels with a wide range of compositions for testing and research in fuel-consuming devices. Full cooperation with the fuel and equipment manufacturing industries is essential.

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7 HYDROGEN PRODUCTION

The preceding chapters have emphasized the importance of reducing hydrogen consumption in the conversion of coal to liquids meeting normal product specifications. Liquefaction plus subsequent refining might typically require about 6,000-9,000 cubic feet of hydrogen per barrel of refined products. Since the production of hydrogen from coal costs approximately \$3 per thousand cubic feet (Cart _et al_., 1978), the cost of hydrogen will obviously be a major component of the total product cost. The incentive for producing hydrogen more cheaply is clearly great. A projection of the hydrogen demand for conventional uses is shown in Table 28.

If, by the year 2000, 1 million barrels per day of coal and shale liquids were refined using an average of 4,000 cubic feet of hydrogen per barrel, hydrogen use would come to 0.5 x 10^{15} Btu per year, a major but not radical increase when compared to the projected range of 2.3-3.4 x 10^{15} Btu per year for conventional uses. (A comparable amount might be used for coal liquefaction to produce the liquids for refining.) Further growth in the refining of coal and shale liquids could increase the hydrogen demand by an order of magnitude.

PRODUCTION PROCESSES

Steam Reforming

At present, hydrogen is generally manufactured by "steam reforming," a process in which natural gas and steam are reacted at high temperature to produce a mixture of carbon dioxide, carbon monoxide, and hydrogen. (In petroleum refining, most of the hydrogen is produced as a by-product from the catalytic dehydrogenation of naphtha in producing high-octane gasoline, but any major increase in hydrogen demand for refining will require an increase in the use of manufactured hydrogen.) Steam reforming has been gradually improved during its many years of commercial use. The process is carried out by reacting a light hydrocarbon feedstock (e.g., methane) with steam in the presence of a nickel catalyst at about 1500°F and 250 psig. The synthesis gas that results is a mixture of carbon monoxide and hydrogen, according to the reaction,

Table 28 Demand projections for industrial hydrogen (10^{15} Btu/yr)[a]

	Year		
	1973	1985	2000
Petroleum refining	0.34	0.51	0.5-1.6[b]
Ammonia production	0.34	0.54	0.92
Methanol and other chemicals	0.12	0.22	0.61
Other uses	0.04	0.10	0.25

[a] Based on 322 Btu gross heating value per standard cubic foot.

[b] Quantity will depend on whether residuum cracking is done by coking or hydrocracking.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (1)$$

Energy for the reaction is produced by burning some of the hydrocarbon feedstock separately in a furnace. The reaction products of the feedstock-steam mixture are then cooled and reacted with additional steam in the presence of a metallic iron catalyst at about 660 F, resulting in the following reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (2)$$

The net reaction becomes

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \qquad (3)$$

with half the hydrogen product coming from the methane feedstock and half from the steam.

Hydrogen can be produced from any light hydrocarbon feedstock that either exists in a gaseous state at the reaction temperature or can be vaporized. Methane is the most desirable feedstock because it has the highest H/C ratio of all the hydrocarbons.

Partial Oxidation

The catalytic reforming process cannot be used with high-boiling-point, high-sulfur feeds. With feeds of this kind, the oil is burned to carbon monoxide and hydrogen in a reaction with oxygen and steam. When a residual feedstock with an H/C ratio of 1.8 is brought in contact with steam and oxygen in a gasification (partial oxidation) reactor at about 2400°F, the following reactions take place:

$$CH_{1.8} + H_2O \longrightarrow CO + 1.9\ H_2 \qquad (4)$$

$$CH_{1.8} + 1.45\ O_2 \longrightarrow CO_2 + 0.9\ H_2O \qquad (5)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (6)$$

The heat for the endothermic reaction of equation (4) is supplied by the oxidation reaction of equation (5). Pure oxygen is used instead of air for reaction (5) to avoid diluting the synthesis gas with nitrogen. When the products from the gasification reactor are cooled to about 700°F, any remaining CO is shifted to H_2 by reaction (6). The net reaction for partial oxidation of residual oil thus becomes

$$CH_{1.8} + 0.98\ H_2O + 0.51\ O_2 \longrightarrow CO_2 + 1.88\ H_2 \qquad (7)$$

Hydrogen from Coal

Although hydrogen can be produced from coal by a partial oxidation process similar to the partial oxidation of residuum , the process is more difficult to carry out, coal being harder to handle and relatively unreactive. The use of coal adds an additional problem in the need to remove the ash from the gasification reactor. The net result is substantially higher operating costs.

Another problem with coal is its low H/C ratio of about 0.8. With coal as a feedstock, as with residua, hydrogen is produced by reforming, oxidation, and shift reactions:

$$CH_{0.8} + H_2O \longrightarrow CO + 1.4\ H_2 \qquad (8)$$

$$CH_{0.8} + 1.2\ O_2 \longrightarrow CO_2 + 0.4\ H_2O \qquad (9)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (10)$$

The net reaction is

$$CH_{0.8} + 0.70\ O_2 + 0.60\ H_2O \longrightarrow CO_2 + H_2 \qquad (11)$$

With coal as a feedstock, the gasification reactor is usually run at about 2700°F, the heat required for gasification reaction (8) being supplied by burning part of the coal with oxygen, as in reaction (9). When coal is gasified at a lower temperature, the product is substitute natural gas.

Other Processes

Hydrogen can also be produced by the electrolysis of water. Current state-of-the-art electrolysis plants require a very high capital investment, but significant progress is being made in reducing capital costs by raising pressures and improving electrodes and electrolytes. (In the discussion of costs below, the cost of hydrogen production by electrolysis is based on a performance similar to that projected for the General Electric Solid Electrolyte Process.)

Presently under investigation in various parts of the world are a number of processes that produce hydrogen from water by a series of heat-driven multiple-step reactions. While these exploratory studies are in too early a stage to make accurate estimates of system efficiency and costs, it appears unlikely at this time that they will be competitive with the current method of releasing hydrogen from water by combining the oxygen in the water with the carbon in coal. Processes using nuclear-generated heat to break water down into hydrogen and oxygen in a closed cycle must compete with processes in which nuclear-generated heat is used to produce electricity that is then used to remove the hydrogen from water by electrolysis.

The best of the thermochemical processes, offering efficiencies in the 40-50 percent range, appear to be at least as efficient as electrolysis with a Rankine-cycle generator working over the same temperature range, and may be somewhat more efficient.

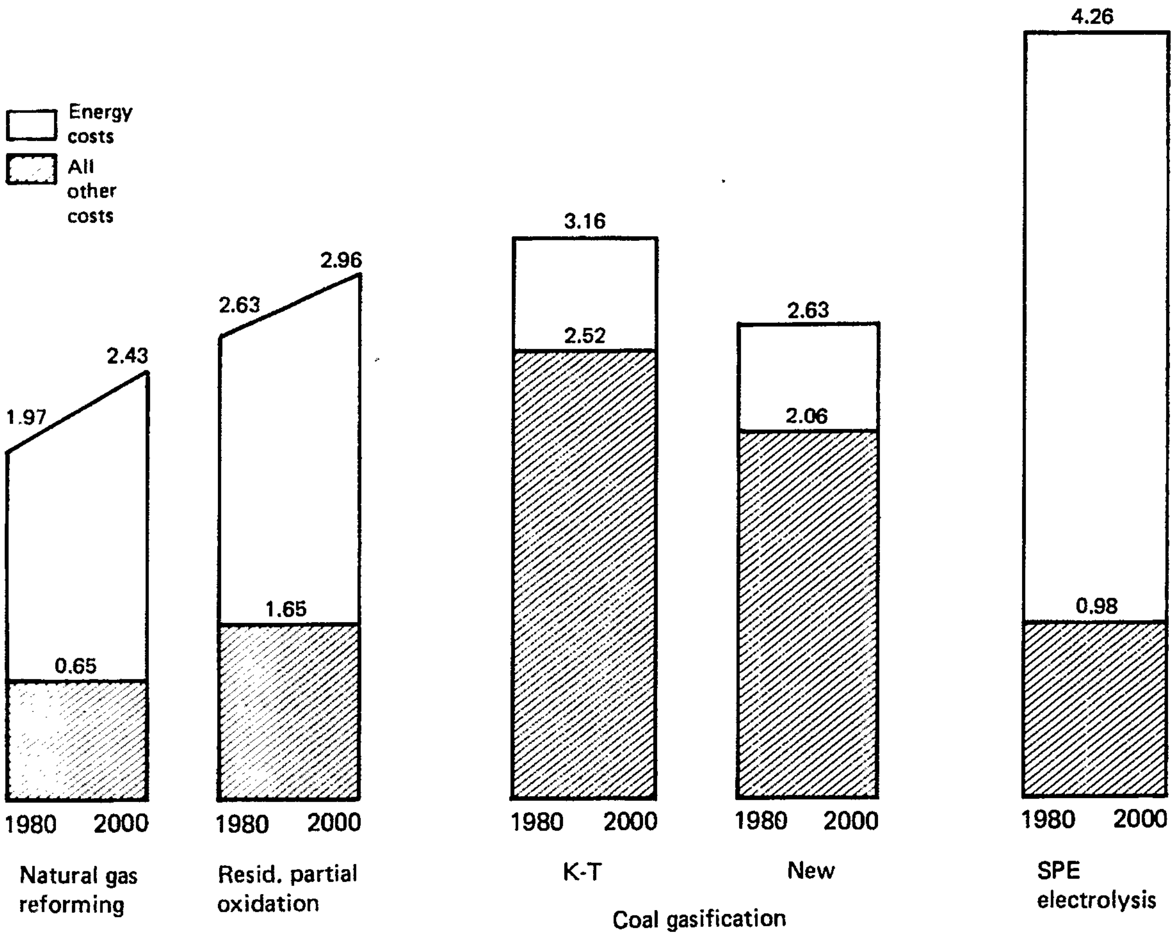
A number of other ways of producing hydrogen are of interest. One involves the use of iron to decompose water. The hydrogen in the water is released by the formation of iron oxide, which is then converted back into iron in a reduction process using gas produced from coal. A version of this process, under development at the Institute of Gas Technology with support from a number of utility and industrial groups and the U.S. Department of Energy, was carried to the pilot plant stage on a scale that used two tons of coal per day.

The use of CO_2 and H_2S acceptors such as limestone during the gasification of coal can yield refining grade hydrogen in one step, but the problems, involving limestone life and regeneration, are still serious.

The use of air instead of oxygen in multiple-bed fluid solids systems has considerable potential if the problems can be overcome. Advances in technology and design could make this approach attractive.

Comparative Costs

In comparing the costs of the various processes, we assume that the new generation of closed-cycle thermochemical processes will have costs and efficiencies comparable to those of new electrolysis processes. Figure 36 shows the projected costs (in 1980 dollars) of plants producing



Figures on bars are 1980$/1000SCF
1000 SCF = 0.322 x 10^6 Btu (gross heat of combustion)

Figure 36 Projected costs of hydrogen production by various processes, in plants producing 100 million standard cubic feet per day, at a midcontinent location (Corneil, *et al.*, 1977). Numbers represent 1980 dollars per thousand standard cubic feet (0.322 million Btu gross heat of combustion).

100 million standard cubic feet of hydrogen per day (the quantity required to refine approximately 25,000 barrels of coal and shale liquids). The estimates are based on the work of Corneil et al. (1977). Feedstock and energy costs as given in Table 29 were assumed, along with a before-tax return of 20 percent per year.

As seen in Figure 36:

- Natural gas reforming, with gas at $3.15 per million Btu, provides the lowest cost hydrogen due to the low capital and operating costs.
- Petroleum residuum conversion requires a larger capital investment. Although the feedstock is cheaper than natural gas, the low thermal efficiency combined with the low-hydrogen, high-sulfur content of the residuum results in total feedstock costs that are about the same as the cost of natural gas.
- Partial oxidation of coal (using available Koppers-Totzek technology, for example) requires a very high investment that more than makes up for the lower feedstock costs. The figures shown for the "new" technology are for the same type of process run at a higher pressure (400-500 psi), resulting in high coal conversion and the formation of little methane. (Such a process is currently under development in a program in which Koppers and Shell are taking part.) The "new" technology lowers the costs of the Koppers-Totzek process by about 15 percent, making it competitive with residuum oxidation.
- The projected solid polymer electrolyte (SPE) process will involve a relatively low capital investment for the electrolysis equipment, but electric power costs will be high, depending largely on the capital costs of the generating equipment. The hydrogen produced by this process will very likely cost substantially more than hydrogen produced by the alternative processes. The use of lower cost off-peak electricity will not help to any extent, the saving in power costs being balanced out by the cost of storing the hydrogen.

Although the lowest cost process for hydrogen production at present is steam reforming of methane, a 50 percent increase in the cost of methane would raise the cost of hydrogen to that estimated using the "new" coal gasification technology. The trends now being seen in the discovery and production of methane from the conventional drilling of permeable formations point to short supplies and increasing costs over the years ahead.

It will be possible, however, to produce hydrogen from the large reserves of "unconventional" gas that are known to exist in geopressured brine, coal, and low-permeability formations. The cost of recovery is not yet known, but it will probably be higher than current conventional discovery and production costs. While there is a chance that such

Table 29 Projected feedstock and energy costs

Feedstock	1980 dollars per million Btu
Natural gas	\$3.15
Petroleum residuum	\$2.60 (at \$15 per barrel)
Coal	\$0.96 (at \$21.80 per ton)
Electricity	\$8.80 (at 3¢ per kWh)

reserves will prolong the economic life of hydrogen production from methane, it seems prudent at this time to assume that the production of hydrogen from coal will eventually displace production from methane.

The cost of producing hydrogen from coal is now nearly competitive with the cost of producing it by residuum conversion, and the projected worldwide shortage of petroleum after 1990 provides a powerful incentive for using coal. During the next century, shortages of coal and concern about the buildup of carbon dioxide in the atmosphere may bring about a transition to hydrogen production by the electrochemical or thermochemical splitting of water, however.

The capital costs for plants that produce hydrogen from coal are shown in Table 30.

The bulk of the cost is in the synthesis gas production,but the cost of shift conversion and methanation and the cost of carbon dioxide removal are sufficiently high to warrant efforts toward cutting these costs also.

The capital costs for synthesis gas production shown in Table 30 can be broken down as shown in Table 31. There are no easy targets here for a major reduction in costs, although the optimization of the pressure levels can result in a substantial gain.

CONCLUSIONS AND RECOMMENDATIONS

- The hydrogen required for the liquefaction of coal and the refining of raw coal and shale liquids represents a large part of the

Table 30 Capital investment costs for plants producing hydrogen from coal, with a capacity of 100 million standard cubic feet per day

Process	Millions of 1980 dollars	
	Koppers-Totzek plant	"New" technology plant
Synthesis gas production (including O_2 plant)	106.4 (72.5%)	82.1 (67.1%)
Shift conversion and methanation	16.7 (11.4%)	16.7 (13.6%)
CO_2 removal	23.6 (16.1%)	23.6 (19.3%)
Total	146.7 (100.0%)	122.4 (100.0%)

Table 31 Breakdown of capital investment costs for synthesis gas production

Process	Percent
Coal preparation and storage	10
O_2 plant and H_2 compression	70
Gasification	20

total cost. The search for ways of reducing this cost should be given a high priority in the synthetic fuels programs of the Department of Energy and of private industry.

- The most appropriate and economical sources of hydrogen for this purpose appear to be coal and coal char, in view of the inadequacy of the natural gas and petroleum resource base. While electrolysis and thermochemical water splitting are substantially more expensive techniques, research and development work should continue in these areas since, at some future date, coal resource limitations and/or environmental considerations may lead to the need for alternatives.

- The cost of hydrogen might be reduced by 10 to 15 percent by optimizing and further developing existing partial oxidation processes for converting coal to hydrogen. An additional 15 percent cost reduction may be obtainable by fully optimizing and developing processes that are now less well developed (e.g., air oxidation in a multiple fluid bed system, the use of CO_2 acceptors such as CaO, or the use of oxygen acceptors like iron).

- The U.S. Department of Energy should give a high priority to the identification and support of R&D and systems approaches to lower cost processes for converting coal and char to hydrogen.

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8 ENVIRONMENTAL EFFECTS

Substituting coal and shale liquids for the prevailing feedstocks of petroleum refineries will require a careful examination of all of the environmental effects to be encountered. While modern petroleum refineries are generally in compliance with the regulations covering air and water pollution and solid waste disposal,[a] substituting synthetic crudes for petroleum feedstocks can have adverse effects.[b]

The potential adverse effects of substituting synthetic crudes for petroleum depend on the location of the refining operation, the refining scheme required, the methods for handling the products, and the effects encountered in combustion or other end use. A key factor, of course, is the chemical composition of the synthetic crude as compared with that of petroleum. Although pilot-scale tests on shale liquids indicate it is possible and practical (using petroleum refining techniques) to keep the gaseous, liquid, and solid wastes within the limits established by current environmental regulations, the refining of coal liquids is not so far advanced. Problems that have resulted in the past from new economic and technological developments underline the need for better assessments of the environmental, economic, social, and institutional impacts of such developments.

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[a] Pollution control and the impacts of the standard crude petroleum producing and consuming industries have been reported extensively in the literature. Various studies have dealt with the occupational exposure of refinery workers, the health effects of refinery products on handlers and users, and the effects of emissions and effluents from refineries, blending stations, and service stations on the general population (Baird, 1967). Work on fugitive emissions is now in progress.

[b] The site-specific environmental effects associated with the production of synthetic crudes are not considered in this chapter, because these been examined elsewhere (National Research Council, 1977). This report restricts itself to the environmental effects of the subsequent refining.

This chapter deals with the important differences between the impacts of refining synthetic crudes and those of refining petroleum. Although considerable research has been carried out in an attempt to establish acceptable environmental standards, there is still a great need for additional data that can be used to establish conservative, yet practical, parameters for environmental quality. Research is needed to identify and evaluate the risks of exposure to hazardous substances, estimate the costs of reducing the risks, and place the costs and risks in proper perspective. It is well established that the presence of a hazardous substance does not necessarily mean that it will be harmful. There are elements that are essential to life at one concentration and hazardous to life at other concentrations. A substance may be harmless as it exists in nature (or under similar circumstances) but harmful under other circumstances.

The impact of a substance on human health and the environment is a function of the mode of occurrence, concentration, and time. For this nation to become self-sufficient in energy, it is imperative that we know as much as possible about the distribution of the toxic materials that result from our technology and the impacts of these materials on health and the environment. The state of the art is such that identifying and measuring some elements and compounds are often possible at levels well below those that may be harmful.

LOCATION OF THE REFINING OPERATION

The most likely source of shale oil in the relatively near term is the Green River formation at the junction of Colorado, Wyoming, and Utah. The most likely sources of coal oil are the western, midwestern, and Appalachian reserves, with the western reserves now being given the greatest attention.

The production of shale liquids will require extensive mining and extraction operations in areas that have thus far been unaffected by industrial activities. Some of the same problems will be encountered with coal liquids produced from western coals. Even if their viscosities are low enough to permit pumping at ambient temperatures, their chemical instability and immiscibility with heavy petroleum fractions or crude may make it desirable to refine coal liquids at their sources. Thus, in both cases refining will have an additional environmental impact at the source of the raw materials.

CHEMICAL COMPOSITION OF SYNTHETIC CRUDES

The chemical constituents of coal and shale liquids of most importance in determining the refining schemes to be used are the concentrations of heteroatoms (oxygen, sulfur, and nitrogen), polycyclic organic matter (POM), and trace elements in the feedstocks. Table 32 summarizes the carbon, hydrogen, and heteroatom concentrations of several shale

Table 32 Chemical composition of typical shale-derived, coal-derived, and petroleum crudes

	Shale Liquids[a]		Coal Liquids[b]		Petroleum[c]	
	Range	Average	Range	Average	Range	Average
Main constituents, wt %						
Carbon	83.1-85.9	84.5	83.0-89.0	86.0	--	86.5
Hydrogen	11.1-12.0	11.5	5.7-11.6	8.6	--	12.3
Heteroatoms, wt %						
Oxygen	0.9-1.89	1.4	0.38-7.15	3.8	--	0.5[d]
Sulfur	0.5-0.9	0.7	0.35-0.57	0.5	0.1-5.3	1.0
Nitrogen	1.3-2.18	1.7	0.77-1.71	1.2	0.02-0.9	0.2
Trace metals, ppmw						
Nickel	1.6-20	--	1-59	--	0.2-124	14.0[d]
Vanadium	0.4-20	--	0.2-275	--	0.1-220	25.4[d]
Iron	40-142	--	6-375	--	--	--
Copper	0.15-11	--	--	--	--	--
Arsenic	10-52	--	--	--	--	--
Titanium	--	--	1-150	--	--	--

[a] See Table 20, Chapter 5.

[b] See Table 25, Chapter 6.

[c] Derived from Fryback (1980), except where noted.

[d] Petroleum Publishing (1973).

liquids, coal liquids, and (for comparison) petroleum crudes, along with their concentrations of some trace metals.

Heteroatoms

Because of their higher heteroatom contents and lower hydrogen contents shale and coal liquids will in general require more hydrogenation than petroleum crudes, but subsequent processing will very likely be similar to the conventional processing of petroleum crudes.

Since the oxygen contents of coal and shale liquids are about 3 to 8 times those of petroleum crudes on the average (Table 32), correspondingly more condensate water with high concentrations of polycyclic organic matter will be produced during the hydrogenation of coal- and shale-derived crudes. However, petroleum refining generates considerably larger amounts of wastewater (from desalting and conversion processes) that contains similar compounds.

The nitrogen contents of coal and shale liquids, 4 to 9 times those of petroleum crudes on the average (Table 32), will result in the generation of significantly more ammonia during hydrogenation. This nitrogen must be removed from the product stream because it would otherwise poison downstream catalysts and degrade the products.

The sulfur in coal and shale liquids must also be removed during hydrogenation to protect downstream catalysts and meet product quality specifications. The sulfur contents of coal and shale liquids are lower than those of petroleum crudes on the average[a] (Table 32), and lower quantities of hydrogen sulfide will be produced. Where the balance between nitrogen and sulfur is conducive to the production of the fertilizer ammonium sulfate, as is frequently the case in the refining of petroleum crudes, it may be possible to use this production to minimize the discharge of sulfur and nitrogen to the environment.

Polycyclic Organic Materials (POMs)

The higher oxygen and polycyclic organic matter contents of synthetic crudes, as compared with petroleum, create the potential for greater concentrations of organic matter in the process wastewater. However, little quantitative information is available. The wastewater results from the separation by condensation of the water generated from the product stream during processing. Since the condensates are saturated solutions under the prevailing process conditions, and since polycyclic materials are more water soluble than paraffinic materials, the condensate waters from the processing of synthetic crudes will have higher concentrations of organic matter than the condensate water from petroleum crudes.

The presence of polycyclic organic materials and hazardous volatile elements in fuel oils will necessitate careful combustion control because of the combustion sensitivity of POMs; incomplete combustion will release particulates, hazardous POMs, and adsorbed toxic elements. POMs can also be created during some complete combustion processes. The use of such fuel oils will need to be carefully monitored if environmental problems are to be avoided. The formation of particulates and the fates of stack gas emissions are not well understood, but the potential for adverse

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[a] Part of the sulfur originally in the shale and coal is removed during the production of the liquids.

impacts is significant. Known carcinogens have been identified in the stack gas emissions from a utility boiler burning a fuel that was 49 percent shale oil (Southern California Edison, 1976).

The relatively high POM contents of synthetic crudes increase the potential for pollution not only from the hydrogenation step but also from subsequent refining steps. Since the impact will be refinery-specific, it is difficult to predict magnitudes at this stage, but it is certain that the higher POM contents of synthetic crudes will increase the likelihood of carcinogenic, mutagenic, and teratogenic substances in the waste products.

The most noxious POMs of synthetic crudes (i.e., phenols, cresols, and carbolic acids) can readily be degraded biologically. From the limited data available, it appears that biological treatment plus effluent polishing will effectively remove the most important pollutants. Although effluents that are treated biologically show no acute toxic effects on fish, they frequently contain significant concentrations of organic matter that cannot be biologically degraded any further. Little is known of the impact of these substances on the environment.

Trace Elements

Serious environmental problems may also be created by the trace elements in coal and shale liquids; the effects depend largely on the distribution of these elements during processing. The concentrations in the product, by-product, and water phases; on the catalysts; and in the emissions to the environment could range from levels that are not harmful to levels that can affect refinery personnel, users, and the general public. The concentrations in the water phase could create the need for additional wastewater treatment and increase wastewater treatment sludge disposal problems. The concentrations on catalysts could limit the use of thermal regeneration, increasing catalyst requirements by 5 to 20 times and creating serious disposal problems. New methods need to be developed for economically recovering the critical metals in spent catalysts without producing environmental problems.

A serious problem may result from the combustion of end-products that contain high concentrations of trace metals. A test with conventional fuel oil in a utility boiler has shown that the quantities of barium, nickel, arsenic, lead, and mercury in the stack gas can range from a moderate to large fraction of the concentration of these elements in the fuel--13, 16, 32, 78, and 100 percent, respectively (Southern California Edison, 1976). The substitution of synthetic fuels for conventional petroleum-based fuels can therefore seriously aggravate the air pollution problem.

The limited data presented in Table 32 would indicate that the problems with shale and coal liquids are likely to be about equivalent; shale liquids contain significant quantities of copper and arsenic, and coal liquids contain titanium. However, it should be kept in mind that coal contains many other trace elements that could find their ways into coal liquids.

Additional information on the fates of trace elements during the refining of coal and shale liquids is needed to more clearly delineate the nature of the problems that are likely to be met with gaseous, liquid, and solid effluents. More studies like those made by Battelle-Northwest (Fruchter et al., 1977), TRW, and Denver Research (U.S. Environmental Protection Agency, 1977c) would be useful and could be carried out in conjunction with process R&D. The toxic, mutagenic, teratogenic, and carcinogenic nature of the final products and the possible effects of these products on the general public will also need to be examined in more detail.

REGULATIONS AND CONSTRAINTS

Federal, state, and local governments are now concerned with more than the protection of the health of the general public. In addition to the regulation of the workplace and the quality of the air and water affecting human beings, existing laws and policies protect fish and wildlife life, endangered biological species, scenic rivers, and historical and cultural sites. Public participation is now encouraged in matters affecting the environment.

The most important federal laws on the control of the environment are the following:

- National Environmental Policy Act of 1969 (PL 91-190)
- Clean Air Act Amendments of 1977 (PL 95-95)
- Clean Water Act of 1977 (PL 95-217)
- Safe Drinking Water Act of 1974 (PL 93-523)
- Resource Conservation and Recovery Act of 1976 (PL 94-580)
- Toxic Substances Control Act of 1976 (PL 94-469).

Under the National Environmental Policy Act, the responsible official must file with the Environmental Protection Agency a detailed environmental impact statement for any proposed major federal action significantly affecting the environment. The statement must include descriptions of alternatives to the proposed action, the effects on the "maintenance and enhancement of long-term productivity," and "irreversible and irretrievable commitment of resources" that would be involved.

The Clean Air Act regulates the emission of particulates, sulfur oxides, nitrogen oxides, carbon monoxide, oxidants, lead, and hazardous compounds by major industries by means of the New Source Performance Standards (NSPS), and the Act controls air quality by means of the National Ambient Air Quality Standards (NAAQS). Regional areas that have an air quality better than the NAAQS are designated Prevention of Significant Deterioration (PSD) areas and are allowed incremental increases in emissions for new developments depending on the type of area (e.g., national parks and the like). Areas that do not meet NAAQS are required to obtain offsets in emissions from some other source to accommodate development.

Under the Clean Water Act, various requirements must be met for a permit to discharge wastes into bodies of water. While no specific effluent standards have been set for such discharges from coal liquefaction and oil shale retorting facilities, the refining of synthetic crudes would be subject to the same standards as petroleum refining. For dredge-and-fill operations in a navigable stream, a Section 404 permit must be obtained from the Army Corps of Engineers, with the concurrence of the Environmental Protection Agency. Exceptions to the act may be required for wastewater discharges in western energy-development areas where natural waters, without the discharge of wastes, do not meet water quality criteria. Effluent limitations imposed on the petroleum industry on July 1, 1977, were based on the use of the best practicable control technology currently available. Limitations on water pollution by the industry were also affected by the Settlement Agreement between the National Resources Defense Council and EPA (June 7, 1976) and a U.S. Court of Appeals ruling (August 11, 1976). The settlement agreement now covers a list of 129 priority pollutants that must be taken into account in defining the permissible control technology. Effluent limits have been set on cadmium, copper, cyanides, lead, mercury, zinc, arsenic, nickel, silver, selenium, phenol, and chromium.

The Safe Drinking Water Act regulates the injection and reinjection of fluids into the ground, specifying monitoring and mitigation measures to protect groundwater systems. Permits must be obtained for the reinjection of fluids into the ground in Colorado.

The Resource Conservation and Recovery Act regulates the transportation, storage, and disposal of solids, semisolids, liquids, and contained gaseous wastes from the point of generation to the point of disposal. Under this Act, wastes with certain levels of reactivity, corrosivity, ignitability, toxicity, radioactivity, teratogenicity, mutagenicity, infectiousness, and phytotoxicity are to be classified and listed as hazardous, requiring special transportation to and disposal at waste sites that have EPA or state permits. Waste lubricating oil is already on a special chemicals list and is classified as hazardous. A list of processes generating hazardous wastes includes kerosene filter cakes, lube oil filtration clays, slop oil emulsion solids, and API separator sludge.

The Toxic Substances Control Act deals with recordkeeping, reporting, production conditions, the handling of toxic substances, and the testing of the effects of toxic substances. An inventory of all commercially produced chemical compounds is now being compiled in accordance with the provisions of the Act, which also requires that the producers of any new chemical substance notify the Environmental Protection Agency 90 days prior to its manufacture, providing the agency with information on its use, the quantities to be produced, by-products, disposal practices, and any available data related to health and environmental effects. In addition, the Act stipulates that the manufacturer of any new chemical substance may also be required to carry out epidemiological, carcinogenic, mutagenic, and environmental tests. Environmental Protection Agency regulation of the use of a chemical may take one of three forms: (a) manufacture with no restrictions, (b) manufacture with conditions placed on the handling and use of the chemical, or (c) an outright ban.

CONTROL TECHNOLOGIES

Current policy places emphasis on "best practicable," "best available," and "best conventional" control technology, with one exception: suitable control technology must be developed where environmental protection criteria are more stringent than current technology can accommodate.

There are two basic levels of technology for environmental protection:

- The simplest and narrowest approach is effluent or emission treatment, as required by current policy.
- A more comprehensive approach is pollution abatement, an approach to optimum pollution control by means of a technological and economic evaluation of the entire pollution generation system as well as the effluent/emission treatment system.

Government and industry both regard pollution control as the control of three separate and independent types of wastes: those discharged to the air, those discharged as liquids, and those discharged as solids. Although they may appear as separate and independent types of wastes to some, they are interrelated. There is consequently a need to integrate the treatment of these three types of wastes at their source. An evaluation of the entire system in terms of pollution generation, control, treatment, and disposal will provide the most feasible and cost-effective means of protecting the quality of the environment. The need for technological effectiveness and economy in the national energy program should provide the motivation for the development of a multipollutant (air, water, solid waste) release management system.

Although a comprehensive mass balance study of the distribution of pollutants among stack gas, wastewater, and solid wastes will be obtainable only during full-scale runs with synthetic crudes, as much data as possible should be obtained from pilot-plant operations to broaden the base of knowledge needed to deal with full scale problems.

PUBLIC CONCERNS

The general public has voiced its concern in recent years about industrial pollutants and the effects they may have on the environment and the various forms of life on this planet. Considerable controversy and confusion has resulted from the inability, so far, to accurately assess the risks posed by the emissions and effluents from industrial activity.

One must assume that each of the regulations now in effect is well intended, but each has a cost that should be justified by hard evidence, not supposition. Without generally accepted assessments of the risks and benefits that are likely to result from technological developments, the regulations that ensue will tend to engender public cynicism and slow technological and economic progress.

What is a "safe" level of pollution? Most of the regulations that call for the absence of "traces" of one or another material from air or drinking water were written in an earlier day when the limits of analysis were in the order of parts per million. Current techniques frequently permit the identification of concentrations of parts per trillion, a level at which adverse physiological effects for most, but not all, pollutants are extremely unlikely. Some chemicals have been called into question only because modern ultrasensitive analytical techniques have shown them to be ubiquitous.

In siting new facilities of any kind anywhere, three basic questions need to be answered if potential conflicts among local, regional, and national interests are to be avoided or, at least, resolved. The first question is whether the need for such a facility outweighs its undesirable impacts. If the answer is yes, the next question is whether or not the proposed site is the logical site, or the best site, for such a facility. If the need and the site are accepted, the final question is what must be done to protect the interests of the people that will be affected.

There is, consequently, a need for research on impacts, risks, and other costs, aimed at helping decision makers and the public establish acceptable safeguards and evaluate trade-offs and alternatives. Obviously, means of quantifying such costs at specific sites (especially those that have in the past been little touched by industrial development) are important and should be developed. No matter how precisely we can quantify a risk, an impact, or a benefit, however, it will never be possible to reduce cost/benefit analysis to a matter of mathematical certainty; social values and political interaction will always play the decisive role in determining what is acceptable. Research in the social sciences will help establish decision-making procedures by which the many disparate costs and benefits of development may be weighed in a more orderly fashion.

RECOMMENDATIONS

The committee recommends that efforts be made to do the following:

- Develop principles, criteria, and methodologies for identifying environmental impacts; coordinating the control of gaseous, liquid, and solid wastes; evaluating alternatives and trade-offs, and resolving conflicts among regional and national interests.

- Determine the mass balance and distribution of hazardous substances among the products and wastes of synfuel refineries in order to evaluate potential environmental and health effects.

- Better establish the toxicity, mutagenicity, teratogenicity, and carcinogenicity of liquid, gaseous, particulate, and solid effluents from the refining of coal and shale liquids and the use of the end products, and determine the fates of the hazardous constituents of these wastes in the food chain.

- Develop more cost-effective technology for the treatment of refinery wastewater.

- Develop environmentally acceptable methods for the removal and disposal of the arsenic in shale liquids.

- Develop acceptable processes for regenerating spent catalysts and the recovering of metals from them for reuse.

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9 HEALTH EFFECTS

For over a hundred years coal tars, heavy petroleum fractions, and shale oil have been known to cause abnormal skin growths and sometimes fatal skin cancer in workers exposed to them. The occupational health risks of refining and handling coal- and shale-derived liquids must therefore be given careful study, along with the risks to consumers who use the refined products. Of greatest importance is the ability of coal tars to cause skin cancers and possibly other cancers, due to relatively high contents of high-boiling-point polynuclear aromatic and heterocyclic compounds. Shale oil and petroleum crudes contain less of these substances, although severe thermal treatment greatly increases their concentrations, so that certain heavy petroleum fuel oils produced by severe cracking are today given special handling in refining and use.

During the development of the petroleum industry over the past century, increasing attention has been paid to the environmental and health effects of their refining and use. Of particular importance have been occupational health problems and pollution of the environment by refinery effluents and combustion of refined products.

The introduction of coal- and shale-derived liquids will tend to increase the potential for health impacts. This chapter discusses the specific hazards, concentrating on the problems posed by carcinogens, cocarcinogens, and mutagens in the liquids and in their refined products. The experience of the petroleum industry, where similar problems have been successfully dealt with, will be reviewed as a model from which we may draw inferences about the safe handling of synthetic liquids.

HEALTH EFFECTS OF PETROLEUM REFINING AND HANDLING

The carcinogenic potential of petroleum crudes is low, varying from crude to crude (Leitch, 1922; Twort and Twort, 1931; Schwartz, 1934; Antonov and Lints, 1960; Emmet, 1975). Differences in the carcinogenicity of 16 different crudes have been reported by Leitch (1922), and Heiger and Woodhouse (1952) have shown the carcinogenicity of petroleum crudes to be lower than the carcinogenicity of certain distilled fractions. Twort and Twort have made extensive studies of various crude petroleum stocks, examining boiling point fractions and other factors. In experiments reported by King (1969) and the United Kingdom Medical Research Council (1968), crudes that boiled at temperatures above 650°F (350°C) were found to be the most carcinogenic, but specific carcinogens were not isolated. As a result of these experiments, the carcinogenic potency of a petroleum crude was thought to be due to the interaction of weak carcinogens.

Studies to date show that the carcinogenic potentials of various coal, oil shale, and petroleum products generally correlate with their boiling points. Animal tests also indicate a general correlation between carcinogenicity and the presence of certain aromatic compounds, such as benzo(a)pyrene. The question is whether the increase in carcinogenicity with temperature is due to the selection and concentration of carcinogens that are already present in the crude or to de novo synthesis by pyrolysis during refining. When Smith et al. (1951) compared the carcinogenicity of certain virgin gas oils, crudes, and high-boiling-point catalytically cracked oils, they found that the virgin feed to the cracking process showed moderate carcinogenic activity while the residuals and the crudes from which they were distilled showed none.

Experiments carried out with animals showed that the high-boiling-point fractions of catalytically cracked oil had carcinogenic activities comparable to those of active coal tars. In skin painting tests on mice, rabbits, guinea pigs, and rats, the mice were found to be susceptible to the development of cutaneous malignancies and the rabbits were found to be prone only to early papilloma (benign epithelial tumors). The guinea pigs and rats were unresponsive. When different boiling fractions were distilled from catalytically cracked oil, a sharp cut-off in carcinogenicity was noted. The 700-800°F (371-427°C) fractions produced only papillomas. Higher boiling-point fractions produced carcinomas, the effect peaking with the fractions in the 950-975°F (510-524°C) range.

Dietz et al. (1952) investigated the conditions under which carcinogenic compounds formed in refining processes and found that the major carcinogenic component of the refinery product was in the 700-985°F (370-550°C) fractions. They also found, by chemical analyses and carcinogenic potency tests with mice, that the materials in the boiling point range associated with carcinogenicity could be reduced to zero by recycle catalytic cracking, and studied the effect of varying the recycle percentages.

Dietz et al. (1952) also investigated the possibility of disposing of high-boiling-point catalytic stocks by blending them with noncarcinogenic refinery streams. As a result of these studies, they suggested that the carcinogenic potential of a 10 percent blend be considered a low hazard. Their data indicated a straight-line relationship between the percentage of high-boiling product (up to 10 percent by volume) and carcinogenic potency. They state that the thermal cracking of clarified catalytically cracked oil boiling above 700°F (371°C) will produce lower boiling-point fractions, but the process appears to increase the quantity of aromatics of four or more condensed rings in the remaining fraction boiling above 800°F (427°C) and decrease the quantity of nonaromatics. Despite the increase in the quantity of aromatics, tumor potency does not seem to be appreciably higher than that of the clarified oil feedstock. Thus, further thermal cracking of catalytically cracked oil will reduce its carcinogenic potency.

OCCUPATIONAL STUDIES

Some years back, a number of investigators reported on the incidence of skin cancer in certain petroleum refinery workers and the occurrence of skin lesions on machinists using petroleum-derived cutting oils (Davis, 1914; Kennaway, 1925; Schwartz, 1934).

Since then, additional studies have shown that the tumor-induction potency of the low-boiling-point fractions of petroleum may be enhanced by the presence of some substances that are not, by themselves, carcinogenic. Holt et al. (1951) found that a 1:1 mixture of distillate oils with boiling points above and below 700°F (370°C) usually produced more tumors than fractions from the same crude with boiling points in the 700-810°F (370-500°C) range. They attributed this paradox to the presence of noncarcinogenic long-chain paraffins (C_{10}-C_{16}) and alkyl derivatives of cyclohexane, benzene, and naphthalene in the lower boiling point fraction.

Subsequently, Horton et al. (1965) attributed the tumorigenic activity of cutting oils to the elemental sulfur and organic sulfur compounds added, finding that the addition of elemental sulfur, benzyl disulfide, and tetrabutyl polysulfide shortened the latency period in tumor experiments.

The toxicity of highly volatile petroleum products affects the workers in a variety of industries that use these products (e.g., industries that produce paints, solvents, and cleaning compounds). Even the slight exposure of gasoline handlers has a significant effect. A correlation between urinary phenol and exposure to gasoline has been reported in the literature (Sherwood, 1972), and there is anecdotal evidence that an unusual exposure to gasoline from industrial accidents can lead to toxic disturbances. The toxic effects of gasoline are believed to be due to the benzene and benzenelike single-ring aromatics and phenols that are present in gasoline in low concentrations. Benzene concentrations of 0.3-3.2 ppm have been measured in the air near bulk-loading installations for gasoline with 3.1-5.8 percent by volume benzene. Gasolines with higher benzene concentrations have given atmospheric concentrations of up to 9.4 ppm (Parkinson, 1971).

Until recently, benzene was not generally considered a significant health hazard in normal refinery or gasoline-handling operations; in the latter, atmospheric concentrations of benzene did not often exceed the threshold limit of 10 ppm set by the American National Standards Institute for the handling of gasoline with a benzene content of 5 percent or less (American National Standards Institute, 1969, 1975).

Now that benzene is known to be a leukemogenic agent (Eckhardt, 1973), the potential hazards inherent in gasoline-handling and petroleum refinery operations cannot be dismissed. Although a 1974 epidemiological survey of 38,000 refinery workers exposed to low-level benzene concentrations for 10 years did not show the health conditions of these workers to be statistically different from those of the general populations in the countries studied (Thorpe, 1974), this survey suffered from the lack of proper controls, as have many other occupational risk assessments in the past.

The potential risk of leukemia from petroleum products should continue to be examined. A 1975 survey of rubber industry workers indicates that the incidence of lymphatic leukemia in workers exposed to solvents is twice that of unexposed workers (McMichael et al., 1975).

In 1974, the American Petroleum Institute published the results of a survey of causes of death among petroleum refinery workers (Tabershaw/Cooper Associates, 1974, 1975). The study selected workers in 17 of the nation's 251 refineries, to provide a representative sample according to location, ownership, and size. The mortality study involved 20,163 workers with a total of 142,298 years of observation. Every worker included in the study had worked in one of the refineries for at least one year between January 1, 1962 and December 31, 1971. Ninety-nine percent had been successfully traced as of the final report on September 23, 1975.

Sixty-four percent of the group, representing 76 percent of the years of observation, were men hired before 1952; the average length of service was 20 years. There were 1,194 deaths in the group, and death certificates were obtained for 1,185.

The major findings of the study were as follows:

1. The Standardized Mortality Ratio (SMR) for all causes was 69.1, compared to 100 for a comparable U.S. male population.

2. Mortality from CV-renal disease (SMR 74), digestive cancer (SMR 86), and ulcers of the duodenum (SMR 88) was inversely related to estimated exposure to atmospheric hydrocarbons.

3. Mortality from respiratory cancer increased with increased estimated exposure, but remained below the expected value even in the high exposure group (SMR 82).

4. Mortality from lymphomas was greater than expected (SMR 123), but the excess was not statistically significant. There was a suggestion of increased mortality with higher exposures.

5. Mortality from genital cancer (SMR 111) was also greater with increased exposure, though the excess was again not significant.

A similar study in the United Kingdom (Rushton and Alderson, 1980) has recently published findings that tend to corroborate these results.

SHALE OIL REFINING AND HANDLING

Plants for the commercial production of fuels, waxes, and chemicals from oil shale have been operated during the last 140 years in France, Australia, Estonia, Sweden, Spain, Manchuria, the Republic of South Africa, Germany, and the People's Republic of China. Information on the associated health effects has come mainly from Scotland, Estonia, and the United States.

Scottish Studies

In Scotland, oil shale has been used since the late 19th century for the production of ammonia, naphtha, lubricating and illuminating oils, and solid paraffin (Leitch, 1922). During the early 20th century, reports began to appear of an increased incidence of cancer among paraffin and oil workers in the shale oil industry and among workers in textile factories (Scott, 1922; White, 1926; Henry, 1937). The lubricating oils used extensively in the spinning-mules of textile factories began to be linked to cases of cutaneous, penile, and scrotal "mule-spinner's cancer." Extensive experiments with animals (Twort and Twort, 1931) showed not only that shale oil products were more carcinogenic than comparable petroleum products but also that the high-boiling-point fractions of shale oil were more potent than the low-temperature fractions; the carcinogenicity increased in fractions boiling at temperatures over 750°F (400°C).

Twort and Twort concluded that "shale oil contains compounds easily rendered carcinogenic at relatively low temperatures (as compared to coal tars), while at higher temperatures additional and more active compounds are formed." When medicinal liquid paraffin was autoclaved at 715°F (380°C) they found that it too gave definite evidence of tumorigenicity.

Twort and Twort were unable to identify the carcinogenic compounds in shale oil, but Berenblum and Schoental (1943), using spectrofluorometry, reported approximately 1 percent benzo(a)pyrene (BaP) in blue shale oil, but no significant evidence of BaP in unretorted shale. Berenblum and Schoental also showed the presence of other carcinogenic compounds in the shale oil, reporting the tumor potencies of different fraction groups.

Estonian Studies

In Estonia, shale is retorted using two procedures: (a) a low-temperature (930°F, 500°C) process that yields oil containing paraffins, naphthalenes, olefins, aromatic compounds, oxygen, phenols, sulfur-containing compounds, and nitrogen-containing compounds, and (b) a high-temperature (1830-2200°F, 1000-1200°C) chamber-oven process yielding more aromatics. Estonian shale and its derivatives contain a relatively large amount of phenol-related compounds (Veldre and Janes, 1979).

After an examination of 215 shale oil workers, Kung (1972) reported symptoms of intoxication (including headaches), sleep disorders, irritability, fatigue, and disturbances of the central nervous system (Veldre and Janes, 1979). Urinary excretion of phenols was noted in exposed workers but it did not appear to be correlated with the length of exposure.

In a subsequent study of 2,069 workers who had been employed in the Estonian shale oil industry for 10-20 years, Purde and Rahu (1979) found that the incidence of skin cancer in the women in the group was significantly higher than it was in the general population, and that the cancers tended to appear at an earlier age.

Since 1951, animal tests of the carcinogenic potency of Estonian oil shale tars, retort oils, and commercial products have been carried out by painting them, in either concentrated or diluted form, on the backs of mice (Bogovski and Vinkmann, 1979). In addition to irritation of the skin and mucous membranes, investigators noted signs of neuromuscular excitability and systematic alterations that indicated the possible absorption of toxic components through the skin, symptoms similar to those reported by Kung (1972). The most carcinogenic fractions were those retorted at high temperatures; blends containing as little as 10 percent of the most carcinogenic material (chamber-oven oil) were found to have the same effect as the undiluted oil. Experiments with chromatographic fractions of aromatic compounds of chamber tar showed no strong correlation between tumor potency and BaP content. Studies of the effect of coking on BaP concentrations and tumorigenicity showed that the distillate from coking had less than 25 percent of the BaP content and essentially none of the BaP tumor potency of its chamber-oven tar precursor (Bogovski and Vinkmann, 1979).

In animal studies of the carcinogenic and cocarcinogenic action of water-soluble phenols from Estonian oil shale, Bogovski and Mirme (1977) detected only weak carcinogenic activity in crude water-soluble phenols recovered from process wastewater. Two-stage experiments they designed to promote the formation of tumors showed that crude phenols had positive effects and more refined products had weak or undetectable effects.

Studies have indicated that the general toxicity of Estonian shale oil is greater in the higher boiling-point materials (Veldre and Janes, 1979; Blinova _et al._, 1974). The studies made suggest that the major toxic effects are caused by phenols, which are present in crude Estonian shale oil in concentrations of 25-30 percent. Experiments with various phenolic fractions all showed considerable toxicity.

In animal studies using acute exposures, death was associated with various neurological signs. With the longer exposures, there were signs of dysfunction of the central nervous system, anemia, and leukopenia (a severe reduction in the blood's white cell count), and decreases in the catalase and perioxidase enzymes, SH groups, and glucose levels in the blood. There was also evidence of decreased kidney and liver function.

U.S. Studies

Very few studies of oil shale-related health effects were made in this country until recently. A 1955 report on skin lesions was inconclusive (Birmingham, 1955), but a report the following year showed that crude shale oil and several fractions boiling above 1300°F (700°C) were carcinogenic to the skin of mice, although their potencies were less than that of heavy oils from coal hydrogenation (Hueper, 1956a, 1956b). Later reports on tests with mice showed that crude shale oil and petroleum products had approximately one-fifth the carcinogenic potency of coal tar, and that hydrotreated shale oil was approximately one-fifteenth as potent (Atwood and Coomes, 1974; Coomes, 1976). Another recent study shows the following incidence of skin cancer in mice from acute doses of petroleum, shale, and coal crudes: 53 percent from a centrifuged Synthoil coal crude, 40 percent from a shale crude from a modified _in situ_ pilot plant, 37 percent from a COED coal crude, and 0 percent from a blend of petroleum crudes from California, Alberta, Alaska, Iran, Louisiana, and Arabia (Holland _et al._, 1979).

Considerable experimental data have been obtained in the past decade from short-term tests of mutagenic action (e.g., the Ames test, forward and reverse mutations with _E. coli_ and _Saccharomyces cerevisae_, and the sex-linked recessive test in _Drosophila_). A useful first-order predictor of mutagenesis, the Ames test is also being considered as a predictor of carcinogenesis, because of the strong correlation between the mutagenicity and carcinogenicity of pure compounds (Ames, _et al._, 1973; Ames _et al._, 1975). This test has been carried out with various petroleum, shale, and coal crudes, process water effluents, and so on. A central repository now exists for the collection and distribution of materials for biological and chemical testing to cooperating investigators (Coffin, 1980; Coffin _et al._, 1979). Preliminary findings now available from short-term testing may be relevant to problems associated with refining. Additional data are to be presented at an intergovernmental agency workshop sponsored by the Environmental Protection Agency and Oak Ridge National Laboratory in mid-1980.

A great deal of useful information has also been obtained by combining short-term animal tests with an innovative chemical fractionation and compound identification technique (Rubin _et al._, 1976; Jones _et al._, 1977;

Guerin et al., 1979; Epler et al., 1977). Extractive fractionation (Table 33) has shown that the basic fraction has the strongest mutagenic activity, on a weight/weight basis, although a comparison on the basis of relative concentrations shows that it is the neutral fraction that contributes most to the total activity. Chemical fractionation has shown that the hydrophobic H-bonding fractions (amines, phenols, etc.) and the tetra-aromatic fractions have the greatest mutagenic activity. Guerin et al. (1979) and Epler et al. (1979) found, on further examination of the basic fractions, that the mutagenic activity is contained largely in an acetone subfraction from the ether-soluble base fraction containing such compounds as dibenzacridenes and azobenzopyrenes. However, continued studies by Guerin et al. (1979) indicate that the unusual mutagenicity of the basic fraction in raw coal and shale liquids may be due to the presence of polycyclic aromatic primary amines; Pelroy et al. (1979) also demonstrated the presence of amines in this fraction. No significant basic fraction is contained in crude petroleum. These data suggest that the presence of the highly mutagenic compounds such as the primary amines most probably explain the differences in the mutagenicity and carcinogenicity of coal and shale liquids and petroleum. Hydrotreating would remove the mutagenic activity of the basic fraction as well as that of the neutral fraction.

The Tosco Corporation has been looking into the toxicity (particularly the carcinogenicity) of shale oils for a number of years. Animal studies from 1975 to 1978 at the Eppley Institute for Research in Cancer and Allied Diseases (Omaha, Nebraska) and at Bioresearch Consultants (Cambridge, Massachusetts) have shown that petroleum crude oil and shale oil coke have carcinogenic potentials equivalent to, or lower than, those of common petroleum refinery products and intermediates. The studies have effectively demonstrated that the refining of shale oil by hydrotreating significantly reduces its carcinogenicity:

- Animals constantly exposed over their lifetimes to massive concentrations of oil shale and Tosco II spent shale by skin contact, ingestion, and inhalation did not develop cancer or any acute toxicities.

- Intratracheal instillation of oil shale, Tosco II spent shale, Tosco II atmospheric effluent, or shale oil coke in hamsters did not cause lung cancer.

The American Petroleum Institute has conducted a major testing program to determine the biological impact of raw shale, spent shale, and shale liquids from various sources and processes (Table 34). Related studies are being carried out by Colony Development, the U.S. Environmental Protection Agency, and the National Institute of Occupational Safety and Health (NIOSH). The results, combined with those of other studies made in the past, will provide the basis for an industrial hygiene program for oil shale workers (Cameron Engineers, 1978b).

Table 33 Distribution of mutagenic activity in shale crude oil by fractionation procedures

Fraction[a]	Activity[b]	Weighted activity[c]
Extractive fractionation		
Sodium hydroxide insolubles	256	3
Weak acid 1 (WA_I)	185	1
Weak acid 2 (WA_E)	52	1
Strong acid 1 (SA_I)	0	0
Strong acid 2 (SA_E)	159	1
Strong acid 3 (SA_W)	160	1
Basic 1 (B_{Ia})	1,377	3
Basic 2 (B_{Ib})	800	2
Basic 3 (B_E)	952	68
Basic 4 (B_W)	223	1
Neutral	112	97
Total		178
Sephadex gel chromatographic fractionation		
Hydrophilic	1,300	78
Polymeric 1	54	3
H-bonding	1,040	52
Polymeric 2	0	0
Aliphatic	180	108
Mon/diaromatic	24	3
Tri/tetraaromatic	132	7
Tetraaromatic	1,220	49
Total		300

[a] Shale derived crude oil "B", separate aliquots about six months apart.

[b] Revertants per milligram of fraction using TA98, S-9, and Aroclor 1254 (Twort and Twort, 1931).

[c] Revertants per milligram of starting material computed by multiplying activity of fraction by weight percentage of total recovered weight constituted by the fraction.

Source: Guerin *et al.* (1979).

Table 34 API shale toxicity testing program

Material	Process	Subject area					
		Acute toxicity	Carcinogenesis	Chronic inhalation	Mutagenesis	Teratogenesis	Analytical
Raw shale							
Anvil Points		X	X	X	X	X	X
Colorado "C-a" tract		X	X				X
White River		X	X				X
Shale oil							
Parachute Creek	Tosco	X	X		X	X	X
Anvil Points	Paraho D[a]	X	X		X	X	X
Anvil Points	Paraho D[b]	X	X				X
Parachute Creek	Union B	X	X		X	X	X
Spent shale							
Parachute Creek	Tosco	X	X				X
Anvil Points	Paraho D[a]	X	X	X	X	X	X
Anvil Points	Union B	X	X				X
Parachute Creek	Union SGR	X	X				X

[a] Direct fired.

[b] Indirect fired.

COAL OIL REFINING AND HANDLING

Indirect Liquefaction

Although this report focuses primarily on direct liquefaction, at least passing reference should be made to the liquids produced by indirect liquefaction processes (Fischer-Tropsch, methanol, methanol to gasoline, and methanol to methyl tertiary butyl ether). Free of nitrogen and sulfur contaminants, all these liquids will have acceptable combustion emission levels. Toxic to varying degrees when ingested, inhaled, or absorbed through the skin, none of them is likely to contain "chronic toxins" (i.e., carcinogens).

The more complex mixtures (Fischer-Tropsch oils) have been tested on mice (Hueper, 1956a, 1956b). Cutaneous applications and injections did not result in any observable cancers, but liver degeneration was noted in heavily dosed animals. The absence of carcinogenic activity was undoubtedly related to the aliphatic (as opposed to polynuclear) structure of Fischer-Tropsch liquids.

Direct Liquefaction

The incidence of skin cancers among individuals working with the products of coal pyrolysis and coal combustion has been noted for more than 200 years (Pott, 1775; von Volkmann, 1875; Yamagawa and Ichikawa, 1915; Hueper, 1942). During the early 20th century, attempts were made to understand the problem by inducing malignant growths and tumors in animals with cutaneous applications of coal tar and extracts from coal and soot (Yamagawa and Ichikawa, 1915; Tsuitsui, 1918).

A decade or so later, Kennaway and Hieger (1930) showed that it was possible to produce cancer with a synthesized compound (1,2,5,6 dibenzanthracene) that is a component of coal tar, and Cook et al. (1933) established the carcinogenicity of benzo(a)pyrene. Other investigators subsequently reported on the carcinogenic activities of polynuclear aromatics, dibenzacridines, dibenzcarbazoles, aniline dyes, and many other compounds synthesized from coal, petroleum, and other feedstocks (Shubik and Hartwell, 1957; Gerarde, 1960). Gerarde discusses the toxicity of aromatic hydrocarbons at some length.

Pyrolysis

Various forms of coal pyrolysis were used prior to 1920 to produce illuminating gas, tar, refined tar products, and coke. The health problems of the workers have been reported in a number of U.S., British, and German publications (von Volkmann, 1875; Tillmanns, 1880; Schuchardt, 1885; Legge, 1911, 1922a, 1922b; Kennaway, 1924a, 1924b; Heller, 1930). Despite the attention given to the problems between 1875 and 1930, no conclusions were reached on the causes. The only conclusion was that epithelioma was extremely prevalent among the workers of the time.

Although pyrolysis is one of the processes for direct liquefaction now under study and pyrolysis products are produced in at least some of the gasification processes under consideration, the risk of cancer from these processes cannot be equated to the risks associated with the production of coke for blast furnaces (and, at one time, for water gas production) (Bruusgaard, 1959; Doll et al., 1965; Batteye, 1966; Doll et al., 1972; Redmond et al., 1972; National Research Council, 1977). Coke ovens are batch devices in which the emissions during charging and discharging are unavoidable (Lawther et al., 1965; Batteye, 1966; Treibl, 1967; Bee et al., 1974). The synthetic fuel processes now under study, on the other hand, are continuous processes in which products are withdrawn under controlled conditions, as in petroleum refineries. There will still be risks, however, since the primary liquid products are carcinogenic (Forney et al., 1974). Such risks must be minimized by appropriate plant design and hygienic operating practices.

Little has been published on the health effects of the trace elements in coal that are carried into the coal liquids during each of the liquefaction processes. A start has been made on the concentrations of these elements in crude coal liquids (see Table 25, Chapter 6), but more definitive data on the fates of these trace elements during the liquefaction and refining processes are needed. A total of 38 elements (in addition to the basic carbon, hydrogen, and oxygen) have been identified in coal (National Research Council, 1977).

Coal Hydrogenation (Solvent Extraction and Catalytic Liquefaction)

As solvent extraction and catalytic liquefaction are alternative forms of coal hydrogenation, it is reasonable to expect their health effects to be similar.

In 1956, Hueper reported that eight of the nine fractions from the hydrogenated coal liquid products of the U.S. Bureau of Mines' Bergius pilot plant produced cancers in rats, mice, and rabbits; the carcinogenic potency increased as the boiling point of the fraction increased. Some activity was still present in unfinished gasoline, but none was found in finished gasoline.

Since solvent-refined coal (SRC) liquids are highly aromatic and contain large quantities of material boiling above 600°F (315°C), one would expect them to be carcinogenic. Cutaneous applications on mice at the Kettering Laboratories showed that, while the solution of SRC used was weakly carcinogenic, the hydrogenated bottoms and solvent were moderately potent (National Research Council, 1977).

At the close of World War II, eight volumes were written on all aspects of coal and tar hydrogenation by specialists from I. G. Farben Industrie, Ludwigshafen (Prev, 1945). No detailed health data were included in this extensive summary, but a discussion on condensed aromatics showed that the authors were aware of the health hazards:

> Production of condensed aromatics was not specially intended in any of the processes heretofore discussed; any aromatics found were more in the nature of byproducts, in most cases undesired, in many cases even to be considered harmful, and efforts were therefore made to keep their amounts as low as possible.

Despite their awareness of the carcinogenicity of high-boiling-point condensed aromatics, it seems reasonable to assume there were no major health problems in German industries because of the low boiling points of the products handled.

In 1952, a 300-ton-per-day hydrogenation pilot plant, set up by Carbide and Carbon Chemicals to produce various chemicals from coal, began to affect the skin of a large number of workers (Ketcham and Norton, 1960; Lowry, 1963). When 2537 Å ultraviolet light was used to study the exposure of the workers, the examiners noted various patterns of fluorescence, ranging from a general fluorescence of the face to streaks and/or smudges of fluorescence on various parts of the body. Air samplings showed concentrations of BaP that varied from 0 to 1870 mg/m^3. In clinical studies of 359 of the male workers with a mean age range of 36-40 years, 51 were found to have a total of 63 skin abnormalities. After an examination of most of these abnormalities, 18 were classified as cancerous and 36 were classified as precancerous; 2 others were suspected of being cancerous but the evidence was not clear cut. An analysis of the exposure times led to the conclusion that exposures of nine months or more were increasing the skin cancer rate significantly, possibly to as much as 16-37 times the rate for the same age group in the general population.

By means of skin painting tests on mice, various process streams at Carbide and Carbon Chemicals were compared with a positive control (methyl cholanthrene). The results showed that the tumorigenicity of the streams was proportional to the boiling point, the light oil portion indicating no activity (Table 35). Although the tumorigenicity was still substantial when the amount of pasting oil remaining in the mix was as little as 2 percent, it could be reduced appreciably by washing the skin after exposure or applying protective cream before. In tests of the effect of dilution (with benzene), the latent period was found to increase in proportion to the percentage of benzene.

Carbide and Carbon Chemicals later required that its workers wear protective clothes and that they follow a regimen of showers and changes of clothing. However, the plant was closed shortly thereafter; follow-up studies are underway but incomplete. The company's safety and health procedures and their clinical, experimental, and control programs indicate the type and magnitude of effort necessary to cope with the problems encountered in coal hydrogenation (Sexton, 1960; Weil and Condra, 1960; Ketcham and Norton, 1960).

Table 35 Relationship of carcinogenicity to boiling points of all streams (except light oil)

Material	Boiling Point (^oC)	Tumor index	Cancer index	Tumor ratio[a]	Cancer ratio[a]
Middle oil stream	260 to 320	46	15	35	31
Light oil stream residue	260 to 380	66	38	46	45
Pasting oil	320 to 450	94	75	60	76

[a] Ratio of mean latent period of methyl colanthrene to the mean latent period of material, multiplied by 100.

Source: Weil and Condra (1960).

HANDLING AND USE OF OIL SHALE AND COAL PRODUCTS

Gasoline

Since it is reasonably certain that gasoline produced from oil shale and coal will be indistinguishable from gasoline produced from petroleum, no new problems are anticipated in handling and using synthetic gasolines.

Mid-Distillates

The problems of handling and using mid-distillates from petroleum (e.g., heating oils, diesel fuels, and kerosene) have been relatively minor, since they contain little or none of the more active polynuclear aromatics. But the situation will be quite different with mid-distillates produced from coal and oil shale. The problem may be more severe with the former, since coal liquids are more highly aromatic and have a carcinogenic activity that is comparable to or greater than that of the more active cracked petroleum fractions. Limited tests indicate hydrotreated shale oils are significantly less potent (Atwood and Coomes, 1974; Coomes, 1976).

Further study is needed of ways of reducing the hazards of handling and using mid-distillates from coal and oil shale if these products are to be made available to the general public. Trace metal concentrations will also need to be determined and evaluated before these products are brought into general use.

Residual Fuels

Since SRC and heavy hydrogenated coal oils are environmentally acceptable as boiler fuels, they will very likely be used for this purpose initially. These liquids are actively carcinogenic, however, and will require special handling by industrial users to avoid prolonged cutaneous contact. If the heavy refined shale oils are also actively carcinogenic, they will require similar precautions. Information on the trace metals in the heavy synthetic liquids has not yet been published.

Combustion Particles

Added to a long-standing concern about the carcinogenicity of soot from the incomplete combustion of coal is a newly discovered concern—the carcinogenicity of the polynuclear hydrocarbons (PNH) that result from the incomplete combustion of organic matter.[a] An active study of this matter is being carried out at the Massachusetts Institute of Technology using new quantitative assay techniques that are similar to the Ames test (Shopek et al., 1978a, 1978b). An extensive program to evaluate the mutagenicity of particles from diesel exhausts is being carried out by the U.S. Environmental Protection Agency; some preliminary information has already been published.

Since the formation of combustion particles is a primary function of combustion conditions, the potencies of the particles cannot be related simply to the fuel source.

CONCLUSIONS AND RECOMMENDATIONS

The mutagenicity and carcinogenicity of coal, shale, and petroleum crudes tested to date can be ranked in that order, with coal at the top of the scale. Although raw shale liquids fall between coal liquids and petroleum in this list, their activity is closer to that of petroleum.

The differences between the mutagenicities of synthetic and petroleum crudes may be explained by the presence in the former of highly mutagenic alkaline constituents (the polycyclic aromatic primary amines).

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[a] Common sources of PNH: gasoline and diesel engines, steam plants, power plants, coke ovens, the burning of refuse, and the decomposition of organic matter in soil and sediments (Kaden et al., 1979).

Refining with hydrogen (as described in Chapter 6) removes heteroatoms and saturates some organic constituents. Both tend to reduce the mutagenic and carcinogenic activities of the liquids. The mutagenic and carcinogenic activities of hydrotreated shale liquids, for example, differ little from those of petroleum crudes (Cowser, 1980).

Since the hydrocarbons of coal and shale liquids tend to have more complex structures and higher molecular weights than petroleum crudes, the correlation between boiling point and carcinogenicity in petroleum crudes may not be directly applicable to coal and shale liquids. This is an area that requires study (already underway on Paraho shale oil). Additional information is also needed on the toxicity of the highly volatile compounds produced from coal and shale liquids.

Biological testing should be carried out as part of the effort to develop a synthetic fuels industry, to determine the nature and extent of the potential risks to the health of workers in such an industry and of the general population.

Since toxicity may be a feature of a particular resource or a function of the mode of processing, or both, every aspect requires attention.

It would be prudent to have the biological data in hand before making a major investment in production facilities. This calls for an integrated effort by fuel technologists and toxicologists on every stage of the production process, from the extraction of the resource to the use of the final product.

While it is recommended that classical toxicological techniques be used to provide definitive information, attention should also be given to new techniques (e.g., bacterial mutagenic tests) that appear useful.

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10 RESEARCH AND DEVELOPMENT

Federal funding of research and development should focus on activities that augment but do not duplicate the R&D that private industry can carry on effectively.

Federal support is appropriate for (a) high-priority projects whose costs or risks limit support by private enterprise, (b) long-term development programs with distant payoffs, and (c) programs that, for strategic reasons, are needed to develop technologies earlier than they would be developed if left to market forces. Another responsibility of the government is research and development directed specifically at protecting the environment and the health and safety of the public and the work force.

Synthetic fuels can, at present, be refined with known or partly developed processes based on privately developed petroleum refining technology. The necessary research and development, in the judgment of industrial experts, is low in both cost and financial risk and is a direct extension of ongoing research programs devoted primarily to petroleum refining. Given reasonable expectations of a market in the relatively near future, the private sector can provide the necessary refining technology without federal R&D funds. Many private concerns, in fact, are reluctant to seek federal support, which, in their views tends to stifle incentives for industry to spend its own funds on R&D, threatening the traditional competitive conduct of proprietary research and development.

The Department of Energy has a responsibility for ensuring that the necessary technology will be available when needed, however, and some participation in refining R&D appears necessary so that advanced technology for refining synthetic fuels will be available at the same time as production techniques and facilities for crude synthetic fuels. The Department of Energy could, alternatively, accelerate the establishment of an economic and efficient synthetic fuel refining industry by guaranteeing a market for the products, leaving it to industry to develop the necessary technology.

To gain a better perspective on current efforts and the need for future research, the panel conducted a survey of private industry on the refining of hydrocarbon liquids for use as burner and transportation fuels. In addition, current projects sponsored by the Department of Energy were reviewed informally with members of the Department and their contractors.

FEDERALLY FUNDED R&D

The Department of Energy sponsors a limited amount of basic and exploratory research in fields pertinent to synthetic liquid refining and the indirect liquefaction of coal. At one point, the government planned a 100-barrel-per-day plant to test refining processes and produce products for evaluation but this was dropped because of budget limitations.

The basic and exploratory work sponsored by the Department of Energy is done by universities, federal laboratories, and industrial concerns, with pilot-scale projects handled by contract with industry. A number of universities are investigating the chemical, physical, and thermal properties of various coal-derived liquids, and the Bartlesville, Laramie, and Pittsburgh Energy Technology Centers are carrying on similar work with coal and shale liquids. Federally sponsored programs at universities, federal Energy Technology Centers, and at least one private R&D firm are studying the chemistry of catalytic refining.

Also being carried on at government laboratories are limited attempts to apply modern petroleum refining practices to synthetic crudes; the projects are mainly bench-scale experiments with variations in catalysts and process conditions. Some universities are also experimenting with process and catalyst variations.

Chevron Research Co. began conducting bench-scale refining tests of shale oil and coal liquids in 1977 with Department of Energy support, using conventional refining techniques. This effort is currently focusing on cutting costs. Universal Oil Products is conducting similar contract work.

The Navy contracted early in fiscal year 1977 for 60,000 to 100,000 barrels of shale oil from the Anvil Points Facility, operated jointly by industry and the Department of Energy. This oil is being refined to military product specifications so that full-scale tests of the resulting products can be conducted. The Air Force is also funding research and development work to determine the most cost-effective way of refining whole shale oil to low-nitrogen turbine fuel.

The canceled pilot-scale plant, planned by the Department of Energy, to produce transportation fuels from coal liquids will still be needed to produce fuels for full-scale testing in currently available engines. It is too large to be useful for testing and developing new refining processes, but it can be used to confirm design conditions.

Department of Energy In-House Refining R&D Capability

The Department of Energy's Energy Technology Centers at Bartlesville, Oklahoma, Laramie, Wyoming, and Pittsburgh, Pennsylvania, were visited as a part of this study. These centers are carrying out a wide variety of work in refining R&D.[a] Bartlesville has a unique thermodynamics laboratory and an engine-testing facility where, using a total systems approach, studies are being made of optimal combinations of refining facilities and engine types. Laramie is field testing in situ coal gasification processes and is also monitoring all of the DOE's shale contracts. Pittsburgh, the largest of the three centers, remains a leader in the conversion of coal to liquids and gases.

The analytical capabilities are excellent at all three centers, particularly at Bartlesville, where the equipment includes the latest in facilities of this type. The extensive analyses of liquids being obtained at all three locations will prove very helpful in guiding research and development in this area. Laramie concentrates on shale oils and Pittsburgh on coal liquids, with Bartlesville working on both. Laramie is the only center that has done a significant amount of work in refining, having made studies of coking, hydrotreating, and hydrocracking of shale oils for more than 20 years. However, the equipment at Laramie is old and limited in scope, and appears inadequate for the type of experimentation that will be needed in this area. Pittsburgh, on the other hand, has just installed modern continuous units for refining coal liquids; these units are being tested.

One of Bartlesville's major functions is monitoring contracts on enhanced oil and gas recovery. This center, with a staff of about 190, has a long background of cooperative work with the petroleum industry, including projects (sponsored by the American Petroleum Institute) in characterizing crude oils and individual compounds in petroleum. Efforts on refining have been limited to paper studies of the application of existing petroleum processes, but a small multipurpose hydrogenation unit installed recently will give the laboratory some "hands-on" experience in refining. Bartlesville's thermodynamics laboratory and engine test facilities have been used on a cooperative basis to carry out work for other government departments and for industry.

Laramie, in addition to monitoring oil shale contracts, is carrying out in-house work on shale oil composition and in situ retorting. Its work on one of the fractions of shale oil, a very heavy tar, includes the characterization of this material and an evaluation of its use as asphalt for road construction. The annual reports that have been issued are

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[a] The National Laboratories (Oak Ridge, Argonne, Brookhaven, Sandia, and Lawrence Livermore) and the other Technology Centers (for example, Morgantown and Grand Forks) also have considerable capacity for research and development in the refining of synthetic fuels.

impressive and give an excellent picture of what has been accomplished by its staff of 205.

The Pittsburgh Energy Technology Center at Bruceton, Pennsylvania, with a staff of 470, is part of a complex which also includes facilities of the Department of Labor's Mining Safety and Health Administration and the Department of the Interior's Bureau of Mines. Other Department of Energy functions at that location include the 75-ton-per-day Synthane pilot plant, the 10-ton-per day Liquefaction Test Facility (formerly the Synthoil PDU), and the Pittsburgh Mining Operations Center, which is carrying out research in longwall and conventional mining. Until the summer of 1978, work on the refining of coal liquids at Pittsburgh had been limited to batch autoclave experiments, the results of which were difficult to translate into conclusions about large-scale continuous operation. Pittsburgh has since expanded its laboratory facilities and now has two flow-type hydrogenation units, instrumented to give a complete set of data. Its capability for catalyst and other process research has also been expanded.

In considering the general problem of research on the refining of coal and shale liquids, this panel concludes that major research and development on processes should be handled by industry, not only because they will be the ultimate users of the technology but also because they have built excellent facilities and have trained personnel to carry out the work. It is recommended that the Energy Technology Centers keep work of this type to the minimum level necessary to maintain familiarity with the field. This panel also concludes that long-range basic research on the refining of these liquids should be sponsored by the government; while a substantial amount of relevant basic and exploratory work being carried out by industry, government support can have the desirable effect of accelerating progress in the development of new processes.

In view of the relatively limited manpower and facilities available at Bartlesville and Laramie, it appears that neither is in a position to carry out in-house, longer range research. But Laramie can monitor development-type contracts on the refining of shale oils, drawing heavily on its staff's knowledge of the constitutions of these materials, and Bartlesville can do the same for coal liquids, based on its staff's analytical knowledge and their familiarity with petroleum processing techniques.

The center at Pittsburgh, where a Process Sciences Division has been set up with a Catalysis Branch, a Process Development Branch, and a Chemistry Branch, is in the best position to carry out some limited work in-house and to monitor contract work with universities, industry, and nonprofit institutions.

Thus, while the Energy Technology Centers do not have the resources to carry out a large fraction of the needed research in the refining of coal and shale liquids, they are equipped to monitor government-supported research based on their knowledge of the compositions of these liquids and their limited practical experience in carrying out refining studies.

PRIVATELY FUNDED R&D

The panel conducted an informal poll of 37 private concerns, including architect-engineers, petroleum refiners, and catalyst manufacturers, that are now conducting refining research and development and might be expected to continue developing technology for refining coal and shale liquids. It should be stressed that this was not a comprehensive survey. It was intended only to provide general information about efforts by private industry in this field. The questionnaire used is included as an appendix to this chapter.

Twenty-nine companies responded. The detailed responses must be kept confidential, but the aggregated statistics give a general picture of the efforts being made and of industry views on where (or if) federal funding can be effectively spent on these problems.

The results reveal that perhaps 2000 people, professional and nonprofessional, are working in private industry on all forms of refining research. Ten to twenty percent of the effort is devoted specifically to the refining of coal and shale liquids, including basic research and bench-scale and pilot-plant work. Approximately half the effort specifically devoted to synthetic fuel refining is funded by the federal government. The 29 responding companies have, in all, devoted more than 1000 person-years to coal and shale liquid refining problems.

Fifteen companies answered the question whether basic exploratory research in these subjects is needed, all of them in the affirmative. Four added that government and industry should sponsor such work jointly, and two stated that industry alone should be involved. Ten respondents answered the question whether development and demonstration work is needed, all in the affirmative; five recommended joint government-industry sponsorship, and two expressed the belief that industry itself should be the sole source of funds.

In their general comments, four companies favored government involvement in defining needed areas of research and coordinating the R&D effort. Five were opposed to government intervention, stating that refining research is low in both risk and cost, that the petroleum industry will develop the necessary technology, and that government funding in the synthetic liquid fuel field should be aimed at liquefaction processes rather than refining.

Most of the responding companies, in answer to a question about research needs, recommended that research be carried out on the following:

- Longer lived catalysts

- Catalysts for synthesizing fuels in the 400-600°F boiling range from coal
- Low-cost methods for producing hydrogen
- Inexpensive and effective means of removing nitrogen and sulfur from the products
- Improvements in product stability, to allow longer storage
- The chemistry of raw liquids and their chemical behavior during processing
- The economically optimum combination of various final products and end-use devices.

The panel is familiar with industrial research and development in this field, and has been able to identify strong and weak points. The major problem is not a technical one, but rather the uncertainty about economic factors. No one is certain when commercialization will occur, and there is consequently no incentive for a high-priority full-scale commitment by industry.

At present, most research and development in this area is carried out under government support, with cost-sharing by industry. Experimental work in the industrial laboratories is being done primarily on the following:

- The development of more selective catalysts for nitrogen and sulfur
- The development of catalysts with longer life
- The investigation of operating parameters affecting the upgrading of solvent refined coal via expanded bed catalytic hydrogenation
- Catalytic cracking and hydrocracking of hydrogenated coal-derived and shale-derived gas oils
- The removal of ash from coal-derived liquids without the use of filters or centrifuges.

In carrying out this work, industry is drawing on its accumulated experience and expertise in petroleum refining.

The scope and level of industrial activity appear sufficient to yield practical technologies for converting coal to liquid fuels, but a strong effort to optimize these technologies cannot be expected until the economics are favorable. The case of shale oil is somewhat different. Several private concerns are currently carrying out large-scale <u>in-situ</u> development projects and others have stated that their surface-retorting processes are ready for commercialization as soon as the economics are right. These firms believe that the time required for final pilot-plant studies, optimization and construction will be available during the time period between a decision to produce shale oil commercially and the need for production quantities.

R&D PRIORITIES

The informal and selective survey of R&D work in progress, and the experience of the members of this panel, permits identification of the most important fields for R&D in synthetic liquid fuels refining. They are summarized here; more detailed technical discussions appear elsewhere in this report.

Future Product Requirements

Liquids produced directly from coal and shale are considerably more costly to refine to meet current gasoline and distillate fuel specifications than is petroleum. The highest boiling fractions of coal liquids are expected to be used initially in applications where little refining is necessary, as in power plants and large industrial boilers. Fractions boiling in the same temperature range as gasoline will likely be used to produce gasoline because of their high octane numbers. But the use of coal liquids for the production of distillate fuels is expected to be delayed. Shale liquids, with their higher hydrogen contents, will be more attractive for the production of high-quality transportation fuels.

By the time synthetic fuels are produced in any quantity, the relative demand for various liquid fuels will probably have changed. Gasoline, for example, is expected to constitute a smaller proportion of total hydrocarbon demand in the future than it does today, while mid-distillate fuels of high hydrogen content (diesel and jet fuels, home heating oil, and the like) will grow in importance. This is something of a problem in view of the low hydrogen contents of coal liquids and the high cost of hydrogenation. Now under study are combustion equipment designs that can use fuels with lower hydrogen contents (e.g., gas turbines, stratified-charge engines, and Stirling-cycle engines), but they are not likely to be used on any significant scale before the turn of the century.

At present, engine manufacturers and fuel refiners are looking to each other for direction. The need for collaboration is recognized, but any shift in products and fuels will be slow in coming. Practical engine-fuel systems require considerable effort, not only on the technical and engineering problems but also on the financial and institutional arrangements that will be needed to optimize costs and efficiencies.

Catalyst Development

Petroleum refining catalysts are inadequate for the refining of synthetic liquids that have heavier burdens of nitrogen, sulfur, and various trace elements. As these impurities tend to deactivate conventional catalysts, it is vital to understand the deactivation mechanisms.

Especially important is the need for selective hydrodenitrogenation catalysts. Since nitrogen degrades product stability and pollutes the air when the products are burned, it must be removed from fuels that are to be used in many end-use devices. Unfortunately, available catalysts tend to saturate the raw liquids with hydrogen before removing nitrogen, resulting in high hydrogen consumption. Hydrodenitrogenation catalysts that are as selective as available hydrodesulfurization catalysts need to be developed. Federal support of basic research relevant to this problem is recommended.

Shale oils present a particular problem because their arsenic contents are generally high. Arsenic is highly toxic and, in addition, rapidly deactivates refining catalysts. Industry is already attacking this problem, but long-range studies of arsenic's chemical forms in shale oil, its specific catalyst deactivation mechanisms, and its removal would be helpful.

Disposal of Arsenic Wastes from Shale Oil Refining

Traces of arsenic remain in spent shale and enriched deposits of arsenic accumulate in spent guard chamber clays and hydrofining catalysts (probably as As_2S_3) during shale oil refining; these must be disposed of in an environmentally acceptable manner. As_2S_3 is reported to be pyrophoric; hence, a controlled incineration is probably required. Since impervious clay deposits are frequently found in underlying shale deposits, the disposition of oxidized spent clays and catalysts in compacted spent shale is a reasonable possibility. Evaluation and pilot testing of this procedure is needed.

An alternative, more expensive procedure is disposition through long term storage procedures at a national disposal site (U.S. Environmental Protection Agency, 1973).

Hydrogen Production

Because coal liquids are relatively low in hydrogen content, large amounts of hydrogen must be added during the refining process to produce high-quality hydrocarbon fuels. Hydrogen is also needed to remove the sulfur and nitrogen. All commercial methods of hydrogen production are costly and contribute heavily to the costs of the ultimate products. While some possibilities exist for reducing the cost of producing hydrogen from coal or char, the development of such processes is comparable in cost and complexity to the development of coal gasification processes. If a promising possibility developed, a sharing of R&D costs between DOE and industry would be desirable. Exploratory and basic work on new approaches to hydrogen production should be supported by the Department of Energy where good ideas and competent research teams can be identified.

Chemistry of Raw Liquids and Chemical Reactions in Refining

The chemical properties of shale liquids differ markedly from those of petroleum. They are, in general, more heavily laden with nitrogen, sulfur, and oxygen, and some contain wide varieties of trace elements. Coal liquids from direct conversion processes contain large concentrations of polycyclic aromatic compounds, a few of which are known carcinogens.

These characteristics have important implications for refining, the environment, and the health of synthetic fuel workers and the public. A comprehensive and accurate picture of the compositions of coal and shale liquids is obviously vital. While some federally funded work is being carried out at universities and federal laboratories, more effort is needed in these areas.

Indirect Liquefaction

Indirect coal liquefaction may prove competitive with direct liquefaction as a means of producing gasoline, diesel fuel, and jet fuels. The indirect process (involving gasification, gas purification, and subsequent liquefaction) has the advantage of removing all of the impurities of the feed coal but, in the Fischer-Tropsch process as operated commercially at SASOL, it results in an olefinic gasoline that requires further treatment. In addition, the SASOL gasoline contains a range of chemicals that must be separated out for other applications or further conversion.

If more selective catalysts for indirect liquefaction can be developed, this Fischer-Tropsch process, which now appears to be more expensive than direct liquefaction, will appear more competitive when the overall goal is considered. Research on new catalysts, with the objective of producing a greater proportion of transportation fuel of the desired quality should be encouraged. Some very promising developments have taken place recently; for example, industry has developed an indirect process for the selective conversion of synthetic gas to high-octane gasoline by converting the gas to methanol, which is then converted to high-octane gasoline over a zeolite catalyst.

Health and Environmental Impacts

The ecological and health impacts of introducing synthetic liquids into the refining system deserve and require careful study. Refinery effluents and emissions must be better characterized, and their potential impacts on ecological systems and the health of workers and the general public must be established with greater precision than is now possible. Finally, suitably effective control technologies must be made available.

In the human health field, the first task is to identify the populations most at risk, by means of multimedia exposure assessments that take into account all sources of exposure; presumably the most heavily exposed population will be that of workers in refineries, and those who must handle certain refined products. Complex mixtures of substances will be involved, and their possible interactions must be accounted for. Workers should be monitored for signs of exposure-related health problems, and a follow-up registry should be maintained so that their conditions may be checked periodically in the future. Clinical and laboratory studies of the metabolism of toxic, carcinogenic, co-carcinogenic, and mutagenic materials should be made to identify the main risks and useful indicators of exposure.

Studies of the ecological effects of refinery effluents and emissions should begin with accurate assessments of the compositions and release rates of all wastewaters, solid wastes, and emissions to the atmosphere. Site-specific studies of pollutant effects and pathways in the environment should begin early enough so that later recognition of the need for tighter control does not impose undue retrofit requirements on refining systems, and control technologies should be assessed in terms of their effectiveness in controlling all pollutants of concern.

RECOMMENDATIONS

Although refining processes capable of producing conventional fuels from oil and shale are available, high hydrogen consumption, poor selectivity, and, in some cases, low catalyst activity and life indicate the need for major improvements. The petroleum industry in the United States is capable of developing synthetic fuel refining processes and is carrying on a considerable amount of exploratory research, but the clearly distant need for major synthetic fuel refining facilities has delayed a major effort at commercialization. As complements to the research and development efforts of the petroleum industry, the panel recommends that the government support its own program, emphasizing basic and exploratory research.

Basic and Exploratory Research

As this chapter has emphasized, the fundamental government role in the conduct of research and development is to sponsor work on long term, basic research problems. The aim is to broaden the knowledge base as a foundation for applied research and process development, both of which are mainly the provinces of private industry.

The highest basic and exploratory research priorities in the refining of synthetic liquids should be accorded the following problems:

- Reaction mechanisms for the selective removal of nitrogen, as a means of reducing the consumption of hydrogen
- The deactivation mechanisms of selective catalysts for the removal of nitrogen, oxygen, and arsenic
- New catalytic materials.

The following problems should be given moderate priority:

- The forms in which arsenic is present in shale oil, and reaction mechanisms for its removal
- The mechanisms of the viscosity and solubility changes that occur during the storage of some coal liquids
- The factors that determine selectivity in indirect liquefaction.

The problems in the following list deserve relatively low priority in federal research and development:

- Reaction mechanisms for the removal of oxygen from synthetic liquids
- The deactivation mechanisms of desulfurization catalysts.

Applied Research and Process Development

While industry is able and willing to develop refining technology to accommodate synthetic liquids, the federal government should monitor progress and maintain enough expertise to allow efficient regulation and identification of emerging basic research problems. This will entail the funding of some small applied research projects in the Energy Technology Centers, universities, and industry.

In such a program, methods of selective nitrogen removal and techniques for lowering the cost of hydrogen, and synthetic gas, and the development of longer lived catalysts for removing nitrogen, oxygen, and arsenic deserve the highest priority; all could strongly reduce production costs. On the next order of priority are methods of selective arsenic removal, more selective catalysts for indirect liquefaction, and additives to improve the stability of coal and shale liquids. A lower priority should be given to methods of selective oxygen removal and development of longer lived catalysts for desulfurization.

Systems Development

Because the economics of synthetic fuels depend heavily on the extent to which they must be upgraded for use in engines and burners, it would be useful to optimize fuels and end-use equipment, considered as a system. The development of engines and burners that can use less refined fuels, for example, might pay large returns in overall efficiency and economy. Large scale engine and burner tests would be required in such a development effort, and suitably large supplies of refined fuels. The facilities, including a small refinery, would be too expensive for any private company to construct, and a government-industry cooperative program might be appropriate.

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APPENDIX:
LETTER AND QUESTIONNAIRE SENT TO 37 PRIVATE CONCERNS INVOLVED IN REFINING R&D

November 22, 1977

Dear Sirs:

At the request of the Department of Energy (formerly ERDA) the National Research Council has formed an ad hoc panel to investigate the research and development needs related to the refining of synthetic crude oils obtained from coal and oil shale. The specific objective of the ad hoc panel is to:

> Define the research and development needs in refining coal and shale liquids to a product slate emphasizing transportation fuels and other distillable fuels.

In order to accomplish this objective, the panel will:

> Survey the programs currently underway on processing techniques applicable to coal and shale upgrading. Programs are currently supported by Industry, Department of Energy, Department of Defense and the Electric Power Research Institute (EPRI).
>
> With the results of the above, define the areas in coal and shale refining and upgrading where research would be desirable from a benefit to cost standpoint and from the standpoint of national needs.

The current composition of the panel is attached to this letter.

As indicated in the statement of task, a measure of magnitude and nature of R & D programs aimed at advancing the technology of refining coal and shale liquids is needed in order to define research needs in this area.

It is recognized that a substantial fraction of petroleum refining technology is applicable to the refining of coal and shale liquids and that petroleum refining research and development capabilities could potentially be focused on research dealing with the special characteristics of coal and shale liquids such as high nitrogen content, high aromatic content, high oxygen content, etc. For hydrogen manufacture, programs aimed at cost reduction where coal or coal char is the starting material would be relevant. Similarly, studies of product composition requirements might focus on the effect of high nitrogen content on fuel stability or on the effect of low hydrogen content on burnability, for example.

We therefore request that your organization supply the panel with information on the magnitude of your current activity in the areas of petroleum refining research and development listed above.

For consistency, it is recommended that the information include

1. Total laboratory and staff professional personnel directly engaged in research and development on the refining of hydrocarbon liquids including those from tar sands, shale oil and coal, as well as from crude petroleum.

2. The fraction of this effort specifically devoted to refining of coal and shale liquids. This might include problems related to:

    a) sulfur removal
    b) nitrogen removal
    c) boiling range conversion
    d) hydrogenation
    e) hydrogen manufacture
    f) product composition
    g) fuel stability
    h) others

3. The split between Basic & Exploratory, Bench Scale and Pilot Plant.

4. Fraction of this work supported by government funds.

5. Your comments on research needs in this area.

The industrial information gained in this survey will be presented in aggregated form; thus we will not reveal, in any way, the specific activities of any one company. The information will be listed under the categories of:

- Petroleum companies

- Process research and construction companies

Please let me stress that the data provided will be used only to help the panel complete its objective; that is, providing meaningful recommendations to the Department of Energy on where research and development should be concentrated.

I would appreciate it if we could receive your response by Jan. 2, 1978. Your cooperation in gathering this information will be greatly appreciated.

Sincerely yours,

John O. Berga
Executive Director

JOB/vs
Attachments

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