yields of olefins and aromatics from these technologies. Product slates can be varied according to the downstream processes employed, the manner of their operations, and the basic process flows established within the plant. If enough processing is employed, all three feedstock categories can be produced from any one of the basic conversion starting points (coal pyrolysis, coal gasification, coal liquefaction, and oil shale retorting).

In the following sub-sections, methods of applying conversion technology and downstream processing to produce each of the feedstock categories (synthesis gas, olefins, aromatics) will be described.

4.2.1 Synthesis Gas Production

Synthesis gas production may be readily accomplished by the gasification of coal. Commercial and developing gasification processes which could be used for synthesis gas production are shown in Table 4-2. Of these processes, the Winkler, Lurgi, and Koppers-Totzek (K-T) have been in commercial use since the early 1950's. Gasification processes that are presently used in coal-based synthetic ammonia plants are shown in Table 4-3. The gasifier most commonly associated with an ammonia plant for synthesis gas production is the Koppers-Totzek.

The K-T process combines oxygen and finely divided coal material through jet nozzles into a partially empty reactor. The coal is ignited by heat radiation from the reactor walls and is completely gasified. The temperature of the gas mixture is normally 1500-1600°C and due to these high temperatures all of the reactred coal is cracked into CO, H_2, CO_2, and H_2O. Ash flows down the reactor as liquid slag and also leaves with the gases as fine-grained dust. After heat recovery the gas is scrubbed with water to remove particulates and is ready for the use as a chemical feedstock (WI-106).

TABLE 4-3
COAL BASED SYNTHETIC AMMONIA PLANTS

Customer and Location	Gasification Process and Ammonia Production (tons per day)			Construction Start
	Winkler	Lurgi	Koppers-Totzek	
Azot Gorazde, Yugoslavia	50			1950
Empreso Nacional Calvo Sotelo, Puertolano, Spain	140			1950
Azot Sanayii, Kutahya, Turkey	120			1950
Typpi Oy, Oulu, Finland			60	1950
Nippon Suiso, Onahama, Japan			100	1954
Empreso Nacional Calvo Sotelo, Puentes, Spain			100	1954
Typpi Oy, Oulu, Finland Extension			60	1955
Daudhkel, Pakistan		60*		1956
Nitrogenous Fertilizer, Ptolemais, Greece			300	1959
Neyveli, South Ascot, India	300			1960
Naju Fertilizer, Korea		150*		1962
Chemical Fertilizer, Mae Moh, Lampang, Thailand			100	1963
Azot Sanayii, Kutahya, Turkey			250	1966
Industrial Development Corp., Kafue/Lusaka, Zambia			100	1966
Nitrogenous Fertilizer, Ptolemais, Greece			75†	1969
Fertilizer Corp. of India, Ramagundam, India			900	1969
Fertilizer Corp. of India, Talcher Plant, India			900	1970
Nitrogenous Fertilizer, Ptolemais, Greece			150	1970
Fertilizer Corp. of India, Korba Plant, India			900	1972
AE & Cl Ltd., Modderfontein, Republic of South Africa			1000	1972
Industrial Development Corp., Kafue/Lusaka, Zambia			100†	1974
Total	610	210	5195 = 6015	
Percent of Production	10%	4%	86% = 100%	

* exact production rate unknown

† ammonia production calculated from the increased synthesis gas production

Source: WI-106

The K-T crude gas composition is shown in Table 4-4. This gas is excellently suited as a feedstock for the synthesis of ammonia, methanol or hydrocarbons.

The K-T raw gas from coal has a CO to H_2 ratio of 2:1. By adjusting this ratio the K-T synthesis gas could be used as the starting material for a variety of petrochemical feedstocks.

- For ammonia synthesis all of the CO in the stream would be shift converted with H_2O to maxmize H_2.
- In modern commercial methanol synthesis technology a CO to H_2 ratio of 1:2.2 is used (DA-145).
- For the synthesis of hydrocarbons using the Fischer-Tropsch process a CO to H_2 ratio of 1:2-3.5 is required depending upon the specific process being used (RO-199).

Radian has calculated that the price of gas from a Gulf Coast operated K-T gasifier would be about \$3.50 per 10^6 Btu gas in 1976 dollars. This cost was determined based on using Illinois No. 6 coal at a cost of \$15.50/ton mine month cost (\$23.10/ton delivered or \$1.05/10^6 Btu coal delivered).

4.2.2 Olefin Production

Olefins can potentially be produced from both coal and oil shale. Olefin production from coal could be accomplished by Fischer-Tropsch synthesis of a synthesis gas stream followed by a cracking operation, or by cracking of a coal liquefaction effluent stream. Olefins may potentially be obtained from oil shale either as a fraction of the gas product (if indirect combustion is used) or, as in coal liquefaction, by cracking of a shale oil distillate product. At present, the only commercially operated method for producing olefins from these resources is cracking a coal synthesis gas derived Fischer-Tropsch product.

TABLE 4-4
K-T GASIFIER CRUDE GAS COMPOSITION

Feedstock	Hard Coal[1]	Lignite[1]
Moisture wt. %	2.40	52.50
Ash wt. %	15.23	15.45
C wt. %	67.72	20.83
H wt. %	3.87	1.62
S wt. %	0.57	0.86
N wt. %	1.65	0.64
O wt. %	8.56	8.10
Crude Gas		
$CO_2 + H_2S$ vol. %	12.0	13.0
CO vol. %	58.1	55.9
H_2 vol. %	28.3	29.0
CH_4 vol. %	0.1	0.1
N_2 + Ar vol. %	1.5	2.0

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[1] Before gasification hard coal is dried to a rest moisture of 1 wt. % and lignite to a rest moisture of about 6.8 wt. %.

Source: FR-218

Cracking of Fischer-Tropsch Synthesis Product

The Fischer-Tropsch reaction is actually the formation of hydrocarbons from a carbon monoxide-hydrogen synthesis gas. Thus, the Fischer-Tropsch process involves gasifying the coal to synthesis gas and then reforming hydrocarbon liquids. The Fischer-Tropsch process was used during World War II by the Germans to produce commercial industrial quantities of synthetic hydrocarbon liquids for use as fuels. After World War II, the European energy market changed with the decrease of fuel prices and the simultaneous increase of coal cost. This caused the closing of most plants using the Fischer-Tropsch process by the 1960's. However, in South Africa plentiful coal deposits could be mined economically versus importing petroleum. South Africa has been producing oil from coal since 1955 using the Fischer-Tropsch synthesis process.

The South African Coal, Oil and Gas Company (SASOL) operates a fixed-bed ARGE Fischer-Tropsch process and a fluid bed Synthol Fischer-Tropsch process for the synthesis of petroleum fractions from a Lurgi coal gasification process. Table 4-5 shows the product distribution from these two Fischer-Tropsch processes. For the fixed bed ARGE process, the liquid reaction fractions above C_5 consist of 32% gasoline, 21% diesel and 47% higher paraffins. From the fluid bed Synthol process, nearly 70% of the liquid mixtures above C_5 are in the gasoline boiling range (FR-139). The combustion of both Fischer-Tropsch processes gives a spectrum of products very similar to highly paraffinic petroleum. This highly paraffinic naphtha is an excellent cracking stock for the manufacture of ethylene. Table 4-6 shows the product distribution from the cracking of this naphtha.

Because of the success of the existing SASOL I plant to produce oil from coal using the Fischer-Tropsch process, SASOL is building a new plant with three times the oil production capacity of the SASOL I plant.

TABLE 4-5

PRODUCT DISTRIBUTION FROM FIXED BED AND SYNTHOL FISCHER-TROPSCH SYNTHESIS ON IRON CATALYSTS

Process	Fixed bed		Synthol	
Temperature °C	220-240		320-240	
Pressure, bars	26		22	
H_2/CO ratio in feed gas	1.7:1		3:1	
Primary products	Wt.% Total	Wt.% Olefins	Wt.% Total	Wt.% Olefins
C_1	7.8	-	13.1	-
C_2	3.2	23	10.2	43
C_3	6.1	64	16.2	79
C_4	4.9	51	13.2	76
C_3-C_{11}	24.8	50	33.4	70
C_{12}-C_{20}	14.7	40	5.1	60
$>C_{20}$	36.2	~15	-	-
alcohols, ketones	2.3	-	7.8	-
acids	-	-	1.0	-
	100.0	100.0		

Source: FR-139

TABLE 4-6
PRODUCT DISTRIBUTION FROM NAPHTHA (C_5-C_{11}) CRACKING

	Wt.%
Ethylene	26.5
Acetylene	0.4
Propylene	15.6
Crude butadiene	9.5
Crude BTX	26.1
Fuel	21.9
	100.0

Source: FR-139

Cracking of Coal Liquefaction Reactor Effluent

Another potential method of producing olefins from coal is to crack a naphtha or middle distillate effluent stream from a coal liquefaction process. Table 4-7 shows the results of steam coil cracking of straight run naphtha and middle distillate fraction from the H-Coal liquefaction process. The cracking of these fractions yields sizeable amounts of olefins and aromatics suitable for chemical feedstocks.

The H-Coal process is a catalytic direct hydrogenation method for coal liquefaction. The coal is slurried with a process derived solvent and hydrogen, and pumped to a catalytic (Co/Mo) ebullated bed reactor. The catalyst is retained in the bed by size and density differences and the product stream is flashed to atomospheric pressure. The gas from this flash is sent to gas treatment, separation and hydrogen recycle. The liquid-solid slurry is sent to a hydroclone to separate a solvent stream for recycle to slurrying. The remaining liquid-solid slurry is filtered and the liquid is distilled as product. The solid from the filter is gasified for hydrogen production. The principle product of the process is a fuel oil (82%) with a fairly small naphtha stream (18%). Approximately four barrels of liquid product per ton of coal may be produced with this process (ST-209). H-Coal yields for bituminous and sub-bituminous coals are shown in Table 4-8.

Olefins from Oil Shale Retorting

Presently, all seriously considered processes for recovering oil from oil shale involve heating the shale to decompose the kerogen to volatile oil and gas (AT-051). One such process is the Tosco II Retorting Process.

TABLE 4-7
STEAM COIL CRACKING OF H-COAL FRACTIONS
Wt% OF PRODUCT[1]

Product	Straight Run Naphtha	Straight Run Middle-Distillate
Hydrogen	0.8	0.7
Methane	16.3	12.1
Ethylene	23.4	14.4
Propylene	8.5	5.9
Butadiene	3.0	1.5
Benzene[2]	23.6	18.5
Fuel	24.4	46.9

[1] Calculated yields assuming recycle gas extinction and hydrodealkylation of toluene and C_8 aromatics.

[2] Includes toluene and xylene equivalents.

Source: PE- 241

TABLE 4-8

H-COAL YIELDS FOR BITUMINOUS AND SUBBITUMINOUS COAL

ILLINOIS NO. 6 BITUMINOUS COAL

	Yields, % by Weight
Light gas, C_1-C_3	10.2
Liquid product	71.0
Unconverted char	10.7
Hydrogen sulfide, water, ammonia	14.0

$$\text{Conversion} = \frac{\text{maf coal-char}}{\text{maf coal}}\ (100) = 89.3\%\ \text{by weight}$$

LIQUID PRODUCT INSPECTIONS

ASTM Cut Points	% by Volume	Degrees, API	Liquid Yield % by Weight of Moisture and Ash Free Coal	Liquid Yield Barrels Per Ton of Moisture and Ash Free Coal	Nitrogen, p.p.m.	Sulfur, p.p.m.
C_4 to 400°F	31.6	49.2	18.5	1.35	1,000	990
400° to 680°F	39.7	21.1	27.5	1.70	1,700	1,600
680° to 975°F	15.8	0.3	12.7	0.67	4,100	1,000
975°F+	12.9	-20	12.3	0.55		
Total	100.0		71.0	4.27		

WYOMING SUBBITUMINOUS COAL

	Yields, % by Weight
Light gas, C_1-C_3	10.8
Liquid product	56.1
Unconverted char	18.6
Hydrogen sulfide, water, ammonia	12.9
Carbon monoxide and carbon dioxide	6.6

Conversion = 81.4% by weight

LIQUID PRODUCT INSPECTIONS

ASTM Cut Points	% by Volume	Degrees, API	Liquid Yield % by Weight of Moisture and Ash Free Coal	Liquid Yield Barrels Per Ton of Moisture and Ash Free Coal	Nitrogen, p.p.m.	Sulfur, p.p.m.
C_4 to 400°F	39.4	50	18.5	1.35	2,000	<700
400° to 650°F	27.6	21	15.5	0.95	3,000	<700
650° to 975°F	18.0	4	11.1	0.62	6,000	<700
975°F+	15.0	-16	11.0	0.52		
Total	100.0		56.1	3.44		

SOURCE: HE-055

In the Tosco II process heated ceramic balls are used as the heat-carrying medium. The pyrolysis reaction is carried out in a rotating drum under 5 psig pressure in a reducing atmosphere. The circulating load of ceramic balls is separated from the spent shale and reheated in a separate furnace. Table 4-9 shows a typical gas yield from the Tosco II process after removal of CO_2 and H_2S, which were 32 wt% and 5 wt% respectively. The gas produced by the Tosco II process is rich in olefins (ethylene, acetylene, propylene and butenes) and could be a good feedstock source of the chemical industry.

Table 4-10 gives an analysis of the oil yield from the Tosco II process. The oil distillates boiling to 600°F have a distribution of 26 to 36 volume % saturates, 36 to 50 volume % olefins, and 23 to 32 volume % aromatics. As discussed for the coal liquefaction effluent, the shale oil can also be routed to a cracking process to increase the olefinic yield.

4.2.3 Aromatic Production

As shown in Figure 4-1, aromatic production from coal may be obtained via the coal tar from coal pyrolysis or coal gasifier by-product; as a by-product from olefin production; by separating aromatic fractions from the straight run coal liquefaction effluent; and by upgrading coal liquefaction and oil shale naphtha and middle distillate streams by hydrotreating, hydrocracking and reformining operations. Of these mechanisms for aromatic production from coal, the two which are at present in commercial operation are by-product recovery from pyrolysis of coal (in coke ovens) and by-product recovery from steam cracking of a Fischer-Tropsch product (SASOL).

TABLE 4-9
TOSCO II PROCESS TYPICAL GAS YIELD AFTER ACID GAS REMOVAL

	wt %	mol %	#/Ton Raw Shale
H_2	2.42	30.21	1.1
CO	5.33	4.79	2.4
CH_4	13.05	20.51	5.8
C_2H_6	16.66	13.88	7.5
C_2H_4	8.02	7.22	3.6
C_3H_8	9.49	5.43	4.3
C_3H_6	8.31	4.99	3.7
iC_4H_{10}	0.77	0.35	0.4
nC_4H_{10}	4.02	1.75	1.8
C_4H_8	8.09	3.63	3.6
C_5+	23.84	7.24	10.7
	100.00	100.00	44.9

Source: AT-051

TABLE 4-10
TYPICAL SHALE OIL FROM TOSCO II PROCESS
(33 GALLONS PER TON RAW SHALE)

Gravity, ° API	22.0
Pour Point, °F	30.0
Sulfur, wt%	0.8
Nitrogen, wt%	1.8
Carbon, wt%	84.7
Hydrogen, wt%	11.3
Distillation	Vol %
IBP to 400°F (gasoline & naphtha)	18.0
400 to 600°F (diesel)	24.0
600 to 900°F (fuel oil)	34.0
900°F + (residuum)	24.0
# of oil per ton of raw shale	252

Source: AT-051

Aromatic By-Product from Coke Ovens

During the early years of this century, the chemical industry obtained a large part of its chemical feedstock from the products of coal carbonization. The vast majority of these chemicals were the coproducts of coke manufacturing. Today most coke plants are built solely to provide fuel for blast furnaces and foundry cupolas. At some coke plants the productions of coproducts is considered a nuisance.

Practically all coke is made in chemical recovery, slot type ovens. High temperature carbonization is the predominant process used to make metallurgical coke and is carried out at temperatures ranging from 900° to 1150°C. Hot gases from carbonization leave the top of the coke oven and are cooled to 85°C by direct contact with a scrubbing liquor. Condensed tars are separated from the liquor which is then recirculated. The warm gases are further cooled to 35°C to condense water and more tar. Ammonia remaining in the gas is removed by direct contact with a sulfate or phosphate solution and used as fertilizer (PE-119).

By cooling the gas down to 25°C, the aromatics, naphathalene, benzene, toluene, and xylenes are recovered by contact with a petroleum oil wash. The remaining gas is then normally used as fuel.

An alternate method for recovering coal chemicals is the use of cryogenic system to condense everything but hydrogen. The hydrogen is then used for the synthesis of ammonia or methanol.

About 16% of the coal tar produced is burned, 38% is distilled for the use as a source of chemicals and 46% is sold to tar processors who make road tars, roofing pitches, pipeline enamels and carbon electrodes (PE-119).

Table 4-11 shows typical yields of coke and chemicals from high temperature coal carbonization tar. Table 4-12 shows the composition of high temperature coke-oven tar averaged from five typical tars. The by-products from the high temperature carbonization of coal are a valuable chemical feedstock source. Approximately 7% of the U.S. benzene supply comes from the carbonization of coal (FI-142).

By-Products from Olefin Cracking

The production of aromatics as a by-product of steam cracking for olefins is another commercially practiced method of obtaining aromatics. Aromatic yield for the cracking of a gasification Fischer-Tropsch derived stock is shown in Table 4-6. Aromatic yield for the cracking of a straight run liquefaction product is shown in Table 4-7. In both cases the aromatic fraction is significant.

Straight Run Aromatic Production

Coal liquefaction processes tend to produce liquids high in aromatics. These straight run aromatics can be separated from the reactor effluent and used as a chemical feedstock. In general, the composition of the raw liquid product varies in distillable fractions from around 17% up to 60% and are from 20% to 25% aromatics.

Processing of Liquefaction Effluent

The reactor effluent from a coal liquefaction or oil shale process can also be processed to enhance the aromatic yield. As shown in Figure 4-1, straight run naphthas may be hydrotreated and are reformed to produce aromatics while straight run middle distillates may be hydrocracked and the hydrocarackate naphthas routed to a reformer. The percentage increase in aromatics by reforming straight run and hydrocrackate naphtha fraction from H-Coal are shown in Table 4-13.

TABLE 4-11
TYPICAL YIELDS OF COKE AND CHEMICALS FROM HIGH-TEMPERATURE COAL CARBONIZATION

	Percent	Lbs. Per Ton
Coke (incl. coke breeze)	75	1500
Coal Tar	4	80 (8 gal)
Light oil		1
Naphthalene oil		8
Heavy creosote oil		9
Anthracene oil		14
Soft pitch		16
Medium pitch		14
Hard pitch		18
Light Oil	1	22 (3 gal)
Benzene		15
Toluene		3
Xylene		1.5
Other		2.5
Liquor	6	120
Ammonium sulfate		20
Gas	14	280 (10,500 cu ft)
Hydrogen sulfide		6
Carbon dioxide		18
Nitrogen		8
Hydrogen		32
Carbon monoxide		45
Methane		130
Ethane		11
Ethylene		20
Propylene		3
Light oil		3
Other (butylene, HCN, etc.)		4

Source: (PE-119)

TABLE 4-12

COMPOSITION OF HIGH-TEMPERATURE COKE-OVEN TAR[1]

	Percent by Weight
Liquor	1.6-5.8
Benzol	0.1-0.3
Toluol	0.1-0.4
Xylol	0.1-0.5
Total tar acids (phenols, cresols, xylenols)	2.0-3.9
Total tar bases (pyridine, picolines, quinolines)	1.4-2.0
Naphtha (coumarone, indene)	0.4-2.0
Crude naphthalene	7.7-11.7
Methylnaphthalene oil	2.1-2.9
Biphenyl oil	0.9-1.5
Acenaphthene oil	1.4-2.8
Fluorene oil (fluorene, diphenyl oxide)	1.9-3.6
Anthracene-heavy oil (anthracene, phenanthrene, carbazole)	9.6-12.3
Pitch	60.2-64.2
Distillation losses	0.9-2.8

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[1] Ranges of composition of five typical tars from "The Coal Tar Data Book". The Coal Tar Research Association, 2nd Ed., Section A1, 2-4, 1965.

Source: PE-119

TABLE 4-13
REFORMING OF H-COAL NAPHTHA FRACTIONS

Components [1]	Straight Run Naphtha		Hydrocrackate Naphthas	
	Feed	Products	Feed	Products
$C_1 - C_3$	-	5.0	-	6.6
$C_4 - C_5$	0.8	4.1	-	4.9
$C_6 - C_9$				
Paraffins	13.6	6.1	10.8	7.5
Naphthene	41.3	2.0	36.9	2.2
Aromatic	33.9	72.0	35.0	73.5
C_{10}+			17.2	5.3
	38.2	89.9	42.3	88.3

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[1] Product is in wt% of components $C_1 - C_{10}$+

Source: PE-246