

ONCE-THROUGH FISCHER-TROPSCH WITH POWER PRODUCTION

Introduction

The Once-Through Fischer-Tropsch With Power Production (OTFT) concept is an example of a coal refinery in the Gasification category. Fischer-Tropsch products are the largest consumer of synthesis gas production by coal gasification, with 86,000 barrels of liquid products generated per day from 66,000 tons of feed coal by SASOL in South Africa [1]. The general idea of integrating Fischer-Tropsch (F-T) synthesis with electric power production is to take advantage of the synergy that exists to manufacture a broad range of saleable chemicals at a reduced cost due to coproduction of electricity.

In 1925, the German team of Franz Fischer and Hans Tropsch described a catalytic indirect liquefaction process that generated a broad and complex mixture of hydrocarbons, alcohols, aldehydes (e.g. formaldehyde), ketones (e.g. acetone), and carboxylic acids (e.g. acetic acid). Later versions of classical Fischer-Tropsch synthesis aimed for maximum gasoline production, having a low probability of forming long chain molecules and leading to coproduction of relatively large amounts of unwanted methane and ethane. The production of gasoline, diesel, and paraffins by Fischer-Tropsch synthesis provided a significant contribution to the energy requirements of wartime Germany, supplying nearly 15,000 barrels of military fuels per day. The current F-T concept is to maximize the yield of middle distillates and high molecular weight wax, while minimizing the production of light gases. The wax is then cracked to low molecular weight fuel products. The primary products of F-T synthesis are predominantly straight-chain in structure with the carbon double bond at the end of the chain, making them ideal starting materials for further chemical processing [2].

The coal refinery based on the OTFT concept is shown in Figure 1. The system would integrate the continuous generation of synthesis gas by Shell gasification technology, chemical production by a slurry phase Fischer-Tropsch unit used in an once-through configuration, and combined-cycle electric generation using the unconverted syngas. The necessary inputs to this coal refinery would include run-of-mine coal, water and air, while major products include high quality transportation fuels (gasoline, diesel), LPG and excess electricity. Sulfur and ammonia would be byproducts of this coal refinery.

Detailed Process Description

The technical aspects of coupling F-T synthesis with electric production has been assessed by the MITRE Corporation [3], based on a plant converting 30,000 tons per day of moisture-free Illinois No. 6 coal to various ratios of chemicals and electricity. A detailed flow diagram based on this reference is given in Figure 1. The feed coal is taken to be high-sulfur bituminous (Illinois No. 6), with a higher heating value of about

11,500 Btu per pound (dry basis) and a sulfur content of 3.9 percent by weight (see Table 1 for more details). Generation of synthesis gas is by Shell gasification technology, due to the high degree of energy integration and the low quantities of light gases other than carbon monoxide, CO, and hydrogen, H₂, formed during gasification.

In the Coal Preparation section, the feed coal is first pulverized and then dried to about 7 to 9 percent moisture. The pulverized coal is blanketed under carbon dioxide and introduced into the gasifier by a dry-feed lock-hopper type system. Oxygen is added with the coal, and also steam (if required).

The Shell gasifier is an oxygen-blown, entrained-flow gasifier that operates at slagging conditions. Typical operating conditions are 2,500 to 3,000° F and 350 to 400 psig. The entrained-bed unit produces a raw synthesis gas high in H₂ and CO content without liquid hydrocarbons, and low in CH₄ and CO₂ (see Table 2 [3]). The sulfur and nitrogen in the coal were assumed to be converted to hydrogen sulfide (H₂S) and ammonia (NH₃), respectively. The high temperature gasification process converts the mineral matter (ash) into a molten slag which runs down the gasifier inner wall into a water bath where it is removed as a slurry. Most of the ash within the coal is removed as a molten slag, with the remainder leaving with the raw synthesis gas. The raw syngas exiting the gasifier at about 2,700° F is quenched by cooled, recycle gas to below the ash deformation temperature. Steam is generated in the Syngas Cooler section during further cooling of the syngas, and in the waterwalls of the Gasifier.

The required oxygen stream for the gasifier is produced from air in the Air Separation plant. Nitrogen in excess of process requirements can be used for increased power production in the Gas Turbine/Generator section, stored on-site as a liquid for sale as a marketable byproduct, or vented to the atmosphere, as warranted by the process economics.

The raw gas is scrubbed to remove flyslag (fly ash) in the Solids Removal area after which it is sent to the COS/HCN Hydrolysis area, where the carbonyl sulfide (COS) and hydrogen cyanide (HCN) are hydrolyzed (chemical decomposition involving the addition of the elements of water) to form H₂S and ammonia (NH₃), respectively (along with CO, etc.). Ammonia is removed by contact with an aqueous stream in the Ammonia Scrubber section, with the chemical-grade ammonia (containing less than 5 percent water) recovered using steam stripping and scrubbing in the Ammonia Recovery section for possible byproduct sale. The clean sour gas is then sent to the Acid Gas Removal system.

The sour gas from the Solids Removal area can contain H₂S and CO₂ which are removed in the Acid Gas Removal area. The H₂S and (some) CO₂ will be separated from the remainder of the sour gas by a Selexol® acid gas removal unit. In the Selexol® process, the sour gas enters an absorber after having been cooled. Almost all of the H₂S is removed by physical absorption as the sour gas flows up through the absorber tower.

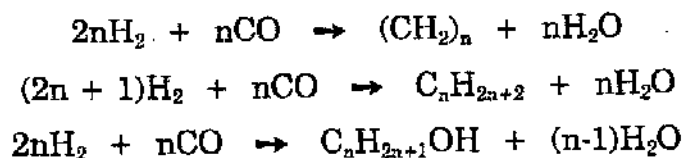
A syngas stream with low levels of contaminants is produced. About 15 percent of the CO₂ is removed, along with minor amounts of other gases. The absorbed gases are recovered by a series of pressure let-downs and stripping. A concentrated acid gas stream is produced that contains between 24 and 39 percent H₂S, which is routed to the Claus® unit. In the Claus® unit, H₂S is oxidized to form SO₂ and water, and then reacts the SO₂ with H₂S to produce elemental sulfur and water. The tail gas stream from the Claus® unit contains significant concentrations of H₂S and SO₂, and is routed to the SCOT (Shell Claus offgas treating) unit. In the SCOT unit, the sulfur species are catalytically reduced to H₂S and scrubbed (absorbed) by a regenerable amine solution. The H₂S is then steam stripped from the amine solution and returned to the Claus® unit. The elemental sulfur produced in the Claus® unit can be sold as a byproduct.

The syngas from the Acid Gas Removal area is a medium-Btu gas which contains 10 to 20 ppmv sulfur compounds, essentially in a reduced form (i.e., H₂S) [4]. To protect the F-T catalyst from deactivation by sulfur poisoning, the portion of the syngas stream for F-T synthesis is "polished" with zinc oxide (ZnO) by the following reaction:



to obtain an ultraclean product syngas with a total sulfur content of less than 0.06 ppm.

The heavy paraffin stage where the F-T chemistry proceeds is now detailed. Carbon monoxide, CO, and hydrogen, H₂, are converted by F-T synthesis via the following reactions [5]:



where "n" is the number of carbon atoms in the F-T synthesis product. These reactions represent the formation of olefins, paraffins and alcohols, respectively [6]. Another important reaction is the water-gas shift reaction:



which determines the equilibria between the amounts of hydrogen and carbon monoxide. The H₂-to-CO ratio in the raw gas is initially 0.4 (see Table 2) and is shifted to a value of approximately 0.67, while an approximate molar ratio of 2:1 is most appropriate in conventional F-T synthesis to minimize carbon formation from carbon monoxide (2 CO → CO₂ + C) and other problems [7].

F-T synthesis requires use of thermally efficient reactors, as the heat generated is considerable, being about 20 to 25 percent of the heat of combustion of the synthesis

gas [3, 8]. Higher temperatures lead to increased rate of reaction but also favor formation of lower hydrocarbons (methane, etc.). In addition, local overheating leading to higher temperatures detrimentally affect catalyst life. The controlling mechanism for optimum product liquid production is to maintain an uniform reaction temperature to achieve greater yields, but with a rapid removal of the heat of reaction so as not to allow an undesirable rise in the reaction temperature.

This coal refinery concept uses a slurry reactor for the F-T synthesis step. The use of an oil slurry reactor for F-T synthesis has the following advantages [2, 9]:

- (1) uniform reactor temperature and a high rate of heat dissipation
- (2) high single pass conversion [1]
- (3) ability to process CO-rich syngas [1]
- (4) high selectivity towards higher molecular weight products
- (5) flexibility in operation
- (6) continuous catalyst regeneration, and
- (7) simple construction and low investment cost.

The slurry F-T reactor operates by passing synthesis gas through a suspension of finely divided catalyst in an oil reactor medium (such as molten wax). The syngas flows as small bubbles through the catalyst suspension. The F-T synthesis products that are volatile under the operating conditions employed are removed with the unconverted portion of the syngas. These vapors are cooled and separated into a gaseous phase (containing C_1 to C_4 hydrocarbon gases, CO_2 , etc.), an aqueous phase (containing alcohols, ketones, aldehydes), and liquid hydrocarbon oils (C_5 and greater). Approximately 50 weight percent of the total product is a high molecular weight wax.

The high molecular weight (C_{15}^+) product wax formed in the F-T synthesis that will not vaporize is continuously removed from the reactor slurry as a liquid. The majority of the catalyst particles within this stream are separated from the product wax by a hydroclone (a liquid-solid cyclone) and returned to the reactor, while the high molecular weight wax is sent to a final filtration stage for removal of catalyst particles before further upgrading (by hydrocracking). The heat of reaction is removed by passing water through heat exchanger tubes in the slurry reactor, generating steam.

High single-pass (once-through) synthesis gas conversions (greater than 80 percent H_2 plus CO conversion) have been achieved with low (~ 0.6) H_2 -to-CO ratios [7]. Low temperature operation is possible with a slurry reactor, which is desirable for high wax production. The products of low temperature F-T synthesis consist almost entirely of straight-chain hydrocarbons and are free of aromatics.

The assessment of the OTFT concept by the MITRE Corporation analyzed the technical and economic consequences of different plant configurations and ratios of F-T liquid to electricity (based on the degree by which the raw F-T liquids are upgraded and

refined) [3]. The following four scenarios were examined in reference [3], as shown in Tables 3 and 4:

- Case 1: Maximum Liquid Production. This case is essentially a F-T synthesis plant dedicated to production of transportation fuels (gasoline, diesel), with only secondary electric power generation. Any wax produced is hydrocracked (large molecules converted into two or more smaller molecules by catalytic action with hydrogen) to produce a C_7 to C_{11} stream for gasoline production, and a C_{12} to C_{18} stream for diesel production.
- Case 2: Refining of C_5^+ Product. The C_1 to C_4 hydrocarbon gases produced by F-T synthesis and any unconverted syngas are combusted for electric power generation. The C_5^+ raw F-T product is refined to produce gasoline and diesel. As in Case 1, the wax is hydrocracked to maximize gasoline and diesel production.
- Case 3: Unrefined C_8^+ Product. The C_1 to C_7 hydrocarbons and alcohols produced by F-T synthesis, together with any unconverted syngas, are combusted for electric power generation. The C_8^+ hydrocarbons are not refined or further upgraded, but are sold as raw diesel blend stock. In this case, the operating conditions are modified such that essentially no wax is produced.
- Case 4: Unrefined C_7^+ /Alcohol Product. The C_1 to C_6 hydrocarbons produced by F-T synthesis, together with any unconverted syngas, are combusted for electric power generation. The C_7^+ hydrocarbon liquids and alcohols are sold as unrefined products. As in Case 3, no wax is essentially produced.

Early F-T synthesis and also that practiced at SASOL in South Africa [10] generates relatively large amounts of light gases which would be unwanted when maximizing liquid fuels production. Light hydrocarbon gases are generated in greater quantity in Cases 3 and 4, due to a shift in the molecular weight of the products away from the heavier waxes towards the lighter middle distillates. However, the light gases that are generated can be easily utilized in this coal refinery concept through combustion to generate electricity.

The fuel for the Advanced Power Generation system can potentially include the unconverted syngas from the F-T Synthesis section, light (C_1 to C_4) hydrocarbons produced in the F-T synthesis, and a fuel gas stream (C_4^+ and/or alcohols) produced by F-T synthesis. The overall concept is similar to an Integrated Gasification Combined-Cycle (IGCC) plant [11]. Compressed air is mixed and burned with the synthesis gas and the resulting hot gases (at about 2,200° F) are expanded through the Gas Turbine/Gener-

ator to produce the majority of the electric power. Steam is injected in the combustion zone to lower the flame temperature, suppressing NO_x formation. Another option, based on economic considerations, is to use a high-pressure N_2 stream from the Air Separation plant in place of steam as a flame diluent to suppress NO_x formation and to boost the mass flow in the Gas Turbine/Generator for higher electrical production [12].

The exhaust gases from the Gas Turbine Generator leave at around $1,000^\circ\text{F}$, and therefore contain significant energy that can be utilized. These exhaust gases pass through the Heat Recovery Steam Generator, generating superheated steam.

The superheated steam generated in the F-T Synthesis section and the Heat Recovery Steam Generator is sent to the Steam Turbine/Generator system to produce electricity. Additional electricity (approximately 20 percent of the coal's energy) is generated by the high-pressure (900 psig) steam generated by the Shell gasifier. The exhaust steam is condensed and recycled to the Heat Recovery Steam Generator. The fraction of power produced in the Steam Turbine is approximately 40 percent of the total coal refinery output [13].

Types of Feed Coal

Entrained-flow gasifiers in general have the ability to gasify all ranks of coal. The dry pulverized feed system developed by Shell theoretically enables utilization of all types of coal, including lignite [14]. The Shell gasification process is reported to be relatively insensitive to coal properties such as size, caking, moisture, ash, etc. [15], except as they affect operating conditions such as the required gasifier operating temperature level. The Shell Coal Gasification Process (SCGP) demonstration plant at Deer Park, Texas can process approximately 250 tons per day of bituminous coals and 400 tons per day of lignite. The coals that have been successfully gasified in the SCGP-1 plant include eleven U.S. bituminous, a foreign (Australian) bituminous coal, a western subbituminous (Buckskin from Powder Basin) coal, and a Texas (Alcoa) lignite [16].

Products

This coal refinery concept can produce varying ratios of electric power and chemicals. The main products from this coal refinery include electricity and F-T synthesis liquid hydrocarbons that can be sold as petrochemical feedstock (raw diesel blend stock) or further refined to transportation fuels (gasoline, diesel). The different ratios of the amount of electricity to F-T liquids are given in Tables 3 and 4, with a maximum liquid production of about 2.8 barrels of F-T liquids per ton of moisture, ash-free coal (Case 1).

Approximately 0.96 barrels of gasoline and 1.25 barrels of diesel fuel can be coproduced with 0.43 kWh of electricity from one ton of moisture, ash-free coal (Case 2). The sulfur content of both gasoline and diesel fuels is very low (0.06 ppm), with a cetane number of 70 for the diesel product (the cetane number is a measure of the ignition quality of a diesel fuel, with a lower value of 45 standard), making them both premium transportation fuels. This scenario is analogous to a conventional petroleum refinery where the higher hydrocarbons (C_5^+) are converted into transportation fuels and other petroleum products, while the C_1 to C_4 gases are used as fuels and as chemical feedstocks.

Marketable byproducts include (elemental) sulfur and anhydrous ammonia (NH_3). Assuming a sulfur recovery factor greater than 99.9 percent, the sulfur production rate would essentially equal the percentage of sulfur in the feed coal, i.e., approximately 3.5 pounds per 100 pounds of moisture, ash-free (maf) feed coal. Approximately 2.2 pounds of ammonia are produced per 100 pounds of maf feed coal.

Likely Applications

This coal refinery concept can produce transportation fuels as well as electricity. It could be expected that the commercial entities interested in this concept would include the petroleum as well as the electric utility industry (including independent power producers, IPP). Given the character of the product output, that certain processes are required in both operations (e.g., distillation of the raw liquids to give the desired type of products, hydrocracking, final upgrading of liquids to value-added products), and similarity of certain processes (e.g., the slurry reactor for F-T synthesis is similar in nature to an ebullating three-phase bed used for hydroprocessing of the petroleum liquids), it would be expected that the principal commercial entity interested in pursuing this concept would be the petroleum refining industry.

Status of Development

This coal refinery concept in essence consists of three totally integrated sections: generation of clean synthesis gas by Shell gasification, F-T synthesis in a slurry reactor followed by upgrading of the raw F-T products, and combined-cycle power generation. In general, any type of second-generation gasifier (including Texaco and Dow) can be used for synthesis gas generation.

Commercial scale demonstration of the Shell technology for coal gasification is targeted to start up in late 1993, with construction of a single train Shell gasifier with a 2,000 ton per day capacity underway in Buggenum, Netherlands [17]. The Shell gasifier will produce clean turbine fuel gas for a 250 MW_e IGCC power plant, with an expected efficiency of 46 percent (based on LHV).

A review of the relevant literature on the F-T slurry process up to 1980 is given in reference [8] from which it was concluded that in comparison with the fixed-bed and entrained fluidized bed reactors used at SASOL, the slurry F-T reactor gives better catalyst performance (higher yield per unit weight of catalyst) and higher single pass conversions. Mobil Research and Development Corporation has developed a two-stage F-T/ZSM-5 Process for the conversion of coal to high-quality motor fuels [7, 18]. The Mobil design combined a slurry-phase F-T synthesis technology with a fixed-bed ZSM-5 reactor to convert the vaporized F-T products from the first-stage slurry reactor into high quality gasoline. Bench-scale pilot plant experiments were performed in a slurry F-T reactor (2 inch ID by 25 feet high) which yielded high H₂+CO conversions (80 to 85 mole percent), high reactor-wax yields (50 to 65 weight percent), and low methane and ethane yields (2 to 4 weight percent). To minimize the yield of methane and ethane while maximizing liquid fuel (gasoline and middle distillate) yields, it was necessary to increase the reactor-wax yield from the F-T slurry reactor. To achieve a methane and ethane yield of 2 weight percent required the wax yield to be approximately 80 weight percent, so that it was necessary to convert and upgrade the F-T slurry wax into high quality fuels. The design basis for the F-T slurry reactor in this coal refinery concept is that recommended by Mobil [7].

Comparison of the overall economics of the different cases in Tables 3 and 4 is given in references [3] and [19].

Environmental Aspects

The main environmental intrusions from this coal refinery include atmospheric emissions of SO₂ and NO_x, and solid wastes. Integration of the IGCC portion within this coal refinery results in very low emissions of SO₂, NO_x and particulates. The majority of the sulfur and nitrogen in the feed coal is recovered from the process in the form of elemental sulfur and ammonia. Approximately 98 to 99 percent of the sulfur compounds are removed in the Shell gasification process, with a NO_x emission rate of about 50 to 75 ppmv (based on 15 percent excess oxygen) [15, 17, 20]. The flue gases emitted to the atmosphere are virtually free of sulfur oxides and low in nitrogen oxides. Both are reported to be well within the limits of NSPS [4]. Emissions of trace toxics, such as halogens, heavy metals, ammonia and organic compounds are assumed to be extremely low as the metals are fixed in the slag, which is non-leachable [17].

Conventional petroleum refineries may require large amounts of process water, which may be unavailable in areas with restricted water supplies. The Shell gasification process is normally designed to be self-sustaining in water requirements, with only loss makeup necessary.

The amount of slag produced from coal gasification is equal to the quantity of ash that results from burning coal. The solids (slag, flyslag) produced in the SCGP-1 demonstration plant have been shown to be environmentally clean [21]. The sulfur

within the coal is recovered and sold; it therefore generates a revenue stream instead of a disposal concern. The average solid waste production rate would be on the order of the slag production rate, which for this example is 0.11 lb per lb feed coal (dry basis).

Research Needs

This conceptual design of a F-T synthesis facility does not consider the coproduction of non-fuel liquids. SASOL markets as many as 80 non-fuel coproducts from its F-T units that contribute approximately 25 percent of SASOL's income [22]. Sensitivity studies that include the formation of non-fuel products would determine their resulting economic impact.

F-T synthesis is the catalytic conversion of synthesis gas to liquid hydrocarbons and/or oxygenated fuels. Further development of poison-tolerant catalysts, higher catalytic activity, scaling up of catalyst production, and separation of catalysts and product waxes would increase the selective conversion of the Fischer-Tropsch liquids [23].

Slurry-phase F-T synthesis has been performed at the bench-scale level. Successful scaleup of the process would allow commercial-scale demonstration of F-T synthesis in this country.

The mechanism of F-T synthesis chemistry limits the selectivity of the reaction, which in turn determines the distribution of the hydrocarbon products that could be expected from the F-T synthesis [24]. This difficulty may be circumvented by use of shape-selective supports and/or unsteady-state operation of the F-T reactor [23].

Table 1: Feed Coal Analysis

ULTIMATE ANALYSIS (weight percentage, dry basis)						
Carbon	Hydrogen	Oxygen	Sulfur	Nitrogen	Chlorine	Ash
70.5	5.4	10.1	3.9	1.3	~ 0.01	8.8
PROXIMATE ANALYSIS						
Total Moisture (weight percent)			12.0			
Higher Heating Value (dry basis)			~ 11,500 Btu per lb			

Table 2: Shell Gasifier Product Gas Composition

COMPOUND	YIELD, mole percent, ash-free basis
Carbon Monoxide, CO	64.4
Hydrogen, H ₂	26.2
Carbon Dioxide, CO ₂	3.4
Methane, CH ₄	< 0.01
Nitrogen, N ₂	0.4
Hydrogen Sulfide, H ₂ S	1.3
Ammonia, NH ₃	1.0
Water, H ₂ O	3.3
TOTAL	100.0

Table 3: Product Distribution for the Different Scenarios: Cases 1 and 2

PRODUCT OUTPUT (barrel per ton coal; moisture, ash-free basis)		
SCENARIO	Case 1: Maximum Liquid Production	Case 2: Refining of C ₅ ⁺ Product
Propane, C ₃	0.16	0.0
Butane, C ₄	0.23	0.0
Gasoline (C ₅ to C ₁₁)	1.26	0.96
Diesel (C ₁₂ to C ₁₉)	1.42	1.25
Alcohols	0.07	0.07
Excess Electricity (kWh per lb coal maf)	0.02	0.43

Table 4: Product Distribution for the Different Scenarios; Cases 3 and 4

PRODUCT OUTPUT (barrel per ton coal; moisture, ash-free basis)		
SCENARIO	Case 3: Unrefined C ₈ ⁺ Product	Case 4: Unrefined C ₇ ⁺ /Alcohol Product
* C ₇ to C ₁₁	Not Applicable	0.87
* C ₈ to C ₁₁	0.65	Not Applicable
C ₁₂ to C ₁₈	0.46	0.46
C ₁₉ to C ₂₄	0.14	0.14
C ₂₅ ⁺	0.01	0.01
Alcohols	0.0	0.13
Excess Electricity (kWh per lb coal maf)	0.88	0.75

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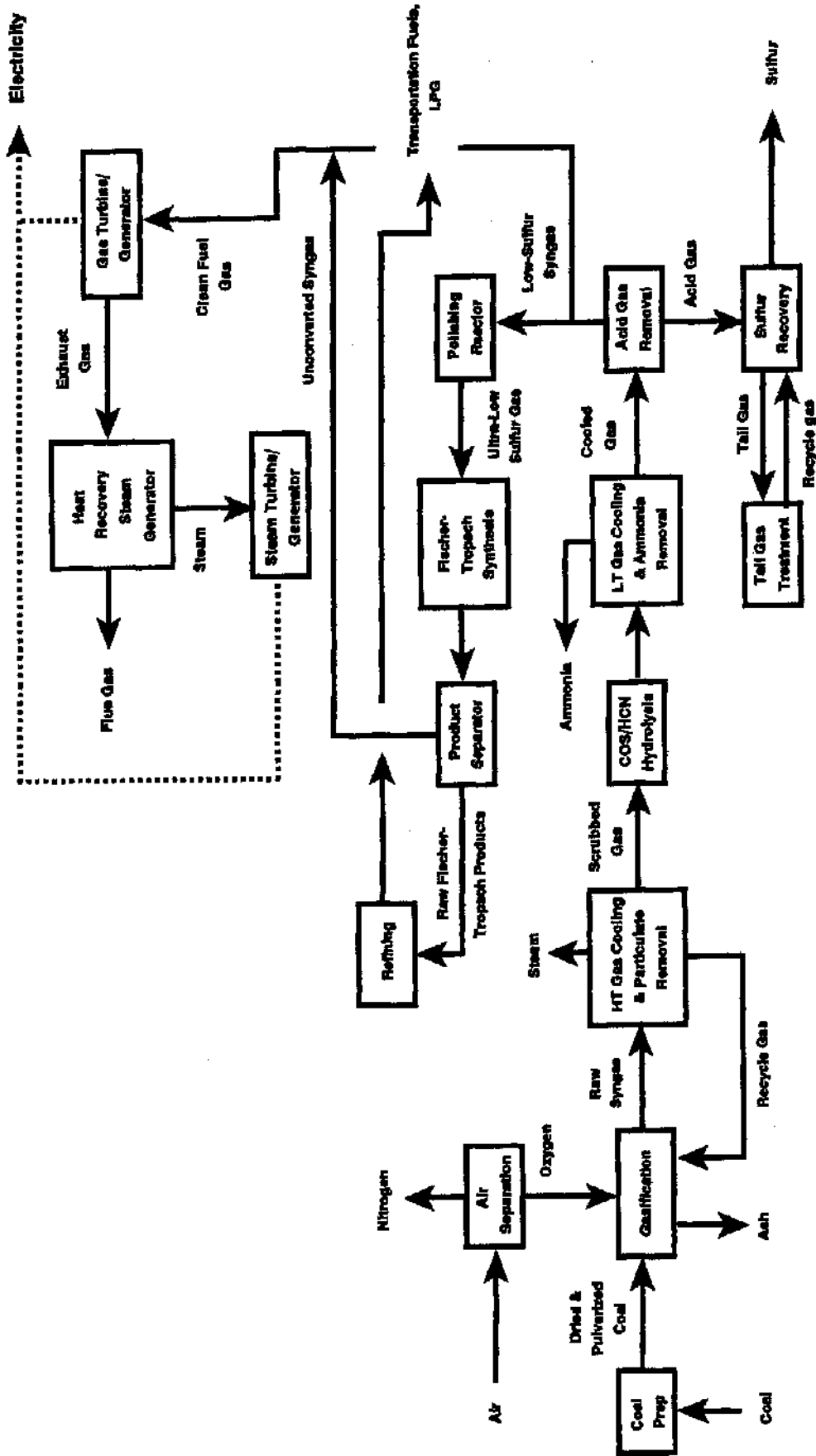


FIGURE 1: Overall Block Diagram of the Once-Through Fischer-Tropsch Process with Power Generation Concept

SHELL MIDDLE DISTILLATE SYNTHESIS

Introduction

The Shell Middle Distillate Synthesis (SMDS) process employs a modern variation of the classical Fischer-Tropsch (F-T) technology which uses a two-stage process that permits variation of the liquid product yields [1, 2]. Synthesis gas is converted into long-chain hydrocarbons which are then upgraded into naphtha for gasoline, kerosene for jet fuel, and gas oil for diesel. The original intent of the SMDS process is the conversion to liquid hydrocarbons of natural gas reserves at remote locations that are not served by pipelines [1]. Currently, this natural gas is often flared and wasted because it cannot be brought to market economically and so it would be converted by this process into liquid hydrocarbons that can be easily stored and transported. The intermediate synthesis gas required for F-T conversion can also be produced from a number of feedstocks other than natural gas, including heavy residues and most importantly coal. This coal refinery concept would employ partial oxidation of coal to generate the required synthesis gas.

The coal refinery based on the SMDS process is shown in Figure 1. The system would integrate the generation of synthesis gas from coal by Shell gasification technology coupled with the conversion of the syngas by the Fischer-Tropsch reaction to chemical feedstocks. The necessary inputs to this coal refinery would include run-of-mine coal, air, and electricity, while the major products would include liquid hydrocarbons (naphtha, kerosene, and gas oil). Sulfur and ammonia would be byproducts of this coal refinery.

Detailed Process Description

This process is a variation of the conventional Fischer-Tropsch technology designed to overcome the low sensitivity limitation of the F-T technology that results in products that range from light hydrocarbon gases to high molecular weight waxes. The SMDS process employs a catalyst with high activity and high selectivity towards higher molecular weight products. The process essentially consists of four steps: (1) generation of synthesis gas, (2) conversion of synthesis gas by F-T technology, (3) cracking and upgrading of the F-T product into smaller molecules, and (4) fractionation (separation) of the different boiling point fractions [1].

In the Coal Preparation section, the feed coal is first pulverized and then dried to about 7 to 9 percent moisture. The pulverized coal is blanketed under nitrogen and introduced into the gasifier by a dry-feed lock-hopper type system. Oxygen is added with the coal, and also steam (if required).

The Shell gasifier is an oxygen-blown, entrained-flow gasifier that operates at slugging conditions. Typical operating conditions are 2,500 to 3,000° F and 350 to 400

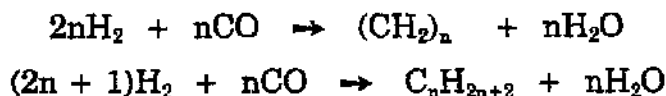
psig. The entrained-bed unit produces a raw synthesis gas high in H₂ and CO content, and low in CH₄ and CO₂ and without liquid hydrocarbons (see Table 1 [3, 4]); small amounts of H₂S and COS are also present (< 0.5 percent). The high temperature gasification process converts the mineral matter (ash) into a molten slag which runs down the gasifier inner wall into a water bath where it is removed as a slurry. Most of the ash within the coal is removed as a molten slag, with the remainder leaving with the raw synthesis gas. To make the ash non-sticky, the raw syngas is quenched at the gasifier exit by cooled, quenched recycle gas. Additional cooling occurs in the Syngas Cooler section, generating high-pressure superheated steam. Additional steam is generated in the waterwalls of the Gasifier. The power needs of the process can reportedly be met by the high-pressure steam [5].

The majority of the slag carried by the raw syngas (called flyslag) is removed in the Solids Removal area by cyclone(s) and may be recycled back to the Gasifier or removed from the process. The remaining flyslag is removed as a clarifier sludge and the gas cooled by wet scrubbing in the Solids Removal area. Ammonia and other trace water soluble contaminants are removed by contact with aqueous streams in the Acid Gas Removal section, with the ammonia recovered for possible byproduct sale. The clean sour gas is then sent to the Acid Gas Removal system.

The sour gas from the Solids Removal area contains H₂S and COS which are to be removed in the Acid Gas Removal area. Separation of H₂S and CO₂ from the remainder of the sour gas is by physical absorption using the Sulfinol acid gas removal unit commercially licensed by Shell. The tail gas stream from the Sulfinol unit contains H₂S which is routed to the Claus[®] unit for conversion into elemental sulfur. The elemental sulfur can be sold as a byproduct. The offgas stream may be used for additional power generation.

The required oxygen stream for the gasifier is produced from air in the Air Separation plant. A portion of the nitrogen produced is used for operating the gasification coal feed system, with the remainder typically vented to the atmosphere. Nitrogen in excess of process requirements can be stored on-site as a liquid for sale as a marketable byproduct, if warranted by the process economics.

The syngas from the Acid Gas Removal area is a medium-Btu gas which contains 10 to 20 ppmv sulfur compounds, essentially all as carbonyl sulfide [6]. To protect the F-T catalyst, the syngas is polished with ZnO to obtain an ultraclean product syngas with a total sulfur content of less than 0.1 ppm. The heavy paraffin stage where the F-T chemistry proceeds follows gasification. Carbon monoxide, CO, and hydrogen, H₂, are converted by F-T synthesis via the following reactions [7]:



where "n" is the number of carbon atoms in the F-T synthesis product. Carbon monoxide, CO, reacts with H₂O via the water-gas shift reaction to form H₂:



The equilibrium of the water-gas reaction favors hydrogen production at low temperature, with the converse (increased CO production) at higher temperatures [8]. Typical coal-derived synthesis gas has a low hydrogen-to-carbon monoxide molar ratio (about 1/2:1) that requires input of additional hydrogen to achieve the ratio of 2:1 to 2 1/2:1 necessary for F-T synthesis. The method typically pursued is to apply the water-gas shift reaction at low temperature to a portion of the synthesis gas, converting CO into H₂. This however would increase the amount of CO₂ in the synthesis gas which is initially very low (< 2 percent; see Table 1). The CO₂ generated will react with needed H₂ at higher temperatures, lowering the possible yield unless the CO₂ is removed. The SMDS process generates the required hydrogen for the overall process by the following methane reforming reaction:



in the Steam Reforming section, with the CO generated by the above reaction converted to H₂ by the water-gas shift reaction. The CO₂ in the H₂-rich gas is generally removed to generate a high-purity (95 to 98 percent) hydrogen stream.

The Shell design for the F-T reactor is a simple tubular fixed bed containing a proprietary catalyst which is reported to be very stable, can be regenerated in-situ, and has an expected life of about 5 years [2]. The Shell catalyst is partly or largely cobalt with iron or ruthenium present [9], with a high probability of forming long chain molecules, minimizing formation of unwanted light hydrocarbons [2]. The synthesis gas components (H₂, CO) react to form predominantly long chain paraffins that extend well into the wax range. This differs from classical F-T catalysts which were designed to maximize gasoline production with a low probability of forming long chain molecules, and lead to formation of methane and ethane. The F-T reactor operates at a temperature level where heat recovery by steam production leads to high energy efficiencies [1].

The long chain waxy paraffins are subsequently cracked into smaller molecules of the desired size in a mild severity, trickle-flow hydrocracker (where the liquid is contacted with hydrogen and made to trickle over the catalyst) containing another Shell proprietary commercial catalyst. This step in effective thermally breaks down the coal-derived extract into products of lower boiling point range with the addition of hydrogen by catalytic reaction. It involves hydrogenation (addition of hydrogen) of olefins (unsaturated aliphatic hydrocarbons; i.e., ethylene), removal of oxygen-containing compounds (mainly alcohols), hydroisomerization (conversion of a compound to its isomer, such as butane to isobutane; for blending to high-octane gasoline), and hydrocracking of the normal paraffins to the desired chain length. The products from this step are

pure paraffins, with very low sulfur and nitrogen impurities as well as low aromatic content [2].

The product stream from the Product Upgrading step is separated by a series of continuous fractionation towers in the Distillation section. Naphtha (boiling point below 340°F), the main fraction taken from the top of the fractionation tower, is used mainly for motor gasoline and can be processed further for octane improvement by octane reforming (conversion of molecules in the gasoline molecular weight range to other with high octane, such as aromatics and cyclic carbon compounds). The next boiling fraction is kerosene (boiling point between 340 to 510°F), followed by gas oil (boiling point above 510°F).

Types of Feed Coal

Entrained-flow gasifiers in general have the ability to gasify all ranks of coal. The dry pulverized feed system developed by Shell theoretically enables utilization of all types of coal, including lignite [10]. The Shell gasification process is reported to be relatively insensitive to coal properties such as size, caking, moisture, ash, etc. [4], except as they affect operating conditions such as the required gasifier operating temperature level. The Shell Coal Gasification Process (SCGP) demonstration plant at Deer Park, Texas can process approximately 250 tons per day of bituminous coals and 400 tons per day of lignite. The coals that have been successfully gasified in the SCGP-1 plant include eleven U.S. bituminous, a foreign (Australian) bituminous coal, a western subbituminous (Buckskin from Powder Basin) coal, and a Texas (Alcoa) lignite [11].

Products

The SMDS process allows operating flexibility in the distribution of the product liquids, to match market demand. Either gas oil or kerosene may be emphasized in the product slate (shown in Table 3 [2]). In the gas oil mode, the products contain 60 percent gas oil, 25 percent kerosene, and 15 percent naphtha. In the kerosene mode, the kerosene percentage becomes about 50 percent, with 25 percent gas oil and 25 percent naphtha. This shift in the product distribution can (presumably) be accomplished through variation of the severity of the hydrocracking step; the gas oil mode can be achieved through less severe hydrocracking conditions which will lead to less breakdown of the high molecular weight waxy paraffins into smaller molecules (more high boiling components, thus more gas oil).

Likely Applications

Naphtha typically is a liquid intermediate in petroleum refining, usually further treated by catalytic reforming to produce high octane reformat suitable for blending to motor gasoline or petrochemical feedstock. Kerosene is a liquid fuel commonly used

in lamps, flares and stoves, while gas oil is similar in nature to No. 1 and No. 2 fuel oils and can (presumably) be used as such. The liquids can be used to displace petroleum-derived fuels in both commercial and electric utility applications.

The paraffinic nature of the product liquids, together with very low sulfur and nitrogen contents, make them excellent blending components for upgrading petroleum refinery fractions that would otherwise be used as fuel oil [2]. Given the characteristics of the product output and similarity of certain processes (the trickle-flow hydrocracker has a somewhat similar layout to a conventional gas oil hydrotreater [2]), it would be expected that the principal commercial entity interested in pursuing this concept would be the petroleum refining industry.

Status of Development

The SMDS process integrates mainly conventional, proven technology other than the modified Fischer-Tropsch step [1]. The process was first announced in 1985 by Shell for the production of kerosene and gas oil from natural gas [12]. The first commercial plant utilizing the SMDS process is under construction in Sarawak, Malaysia, with startup aiming for late 1992 [1, 2]. Capacity will be about 500,000 metric tons (551,200 short tons) per year from 100 million cubic feet of natural gas per day. Royal Dutch/Shell Group is also investigating other sites in the world where remote natural gas reserves would benefit from becoming the feedstock for a SMDS plant.

Commercial scale demonstration of the Shell technology for coal gasification is targeted to start up in late 1993, with construction of a single train Shell gasifier with a 2,000 ton per day capacity underway in Buggenum, Netherlands [3]. The Shell gasifier will produce clean turbine fuel gas for a 250 MW_e IGCC power plant, with an expected efficiency of 46 percent (based on LHV).

Estimates of the overall economics (i.e., capital investment, annual operating costs) of the SMDS process as applied to coal are reported in reference [2].

Environmental Aspects

Shell claims minimal environmental impact from the process [2]. The majority of the sulfur and nitrogen in the feed coal is recovered from the process in the form of elemental sulfur and ammonia. Approximately 98 to 99 percent of the sulfur compounds are removed in the Shell gasification process, with a NO_x emission rate of about 50 to 75 ppmv (based on 15 percent excess oxygen) [3, 4, 13]. The off-gases are consumed in the process for power generation. The flue gases emitted to the atmosphere are virtually free of sulfur oxides and low in nitrogen oxides. Both are reported to be well within the limits of NSPS [6].

Conventional petroleum refineries require large amounts of process water, which may be unavailable in areas with restricted water supplies. The Shell gasification process is normally designed to be self-sustaining in water requirements, with only loss makeup necessary. The SMDS process as a whole is a net producer of water (due to generation of water from the F-T synthesis reactions) which can be used for other purposes.

The catalysts used in the process are not an issue for waste disposal, as the spent metal catalysts are recycled for metals recovery [2]. The solids (slag, flyslag) produced in the SCGP-1 demonstration plant have been shown to be environmentally clean [14].

Research Needs

Commercial demonstration of the SMDS process based on coal-derived synthesis gas has not been demonstrated. A preliminary conceptual design (which includes the effect of differing coal rank) of a large-scale SMDS plant would be the first step towards commercial demonstration of this coal refinery concept using coal as the feedstock.

A detailed economic study has not been reported for application of the SMDS process for conversion of coal. The set of conditions that would merit full scale production of coal-based liquids by this process would be established by a series of sensitivity studies of the overall economics.

Table 1: Typical Shell Gasifier Performance Characteristics

COAL	Illinois No. 6 Bituminous	El Cerrejon Bituminous
GASIFIER PRODUCT GAS COMPOSITION (mole percent, dry basis)		
CO	62.62	62.59
H ₂	30.93	30.28
CH ₄	0.04	0.02
CO ₂	1.50	1.63
Inerts	4.91	5.48
OPERATING CONDITIONS		
lb O ₂ /lb coal	0.80	0.84
lb steam/lb coal	0.082	0.084
Carbon Conversion (%)	99%	99.7%
Sulfur Removal (%)	99%	99.4%

Table 2: Analysis of Feed Coals Used In Table 1

COAL	Illinois No. 6 Bituminous	El Cerrejon Bituminous
ULTIMATE ANALYSIS (weight percent, dry basis)		
Carbon	61.6	73.4
Hydrogen	4.2	4.8
Nitrogen	1.3	1.8
Sulfur	4.6	1.0
Chlorine	0.01	0.04
Ash	18.5	8.9
Oxygen	9.7	10.1
PHYSICAL CHARACTERISTICS		
Tot. Moisture (weight %)	9.5	16.7
Heating Value (Btu/lb, dry)	11,400	13,100

Table 3: Product Distribution from Example SMDS Coal Refinery

PERCENTAGE OF PRODUCT STREAM (weight percent)			
MODE	Naphtha	Kerosene	Gas Oil
Gas Oil Mode	15	25	60
Kerosene Mode	25	50	25

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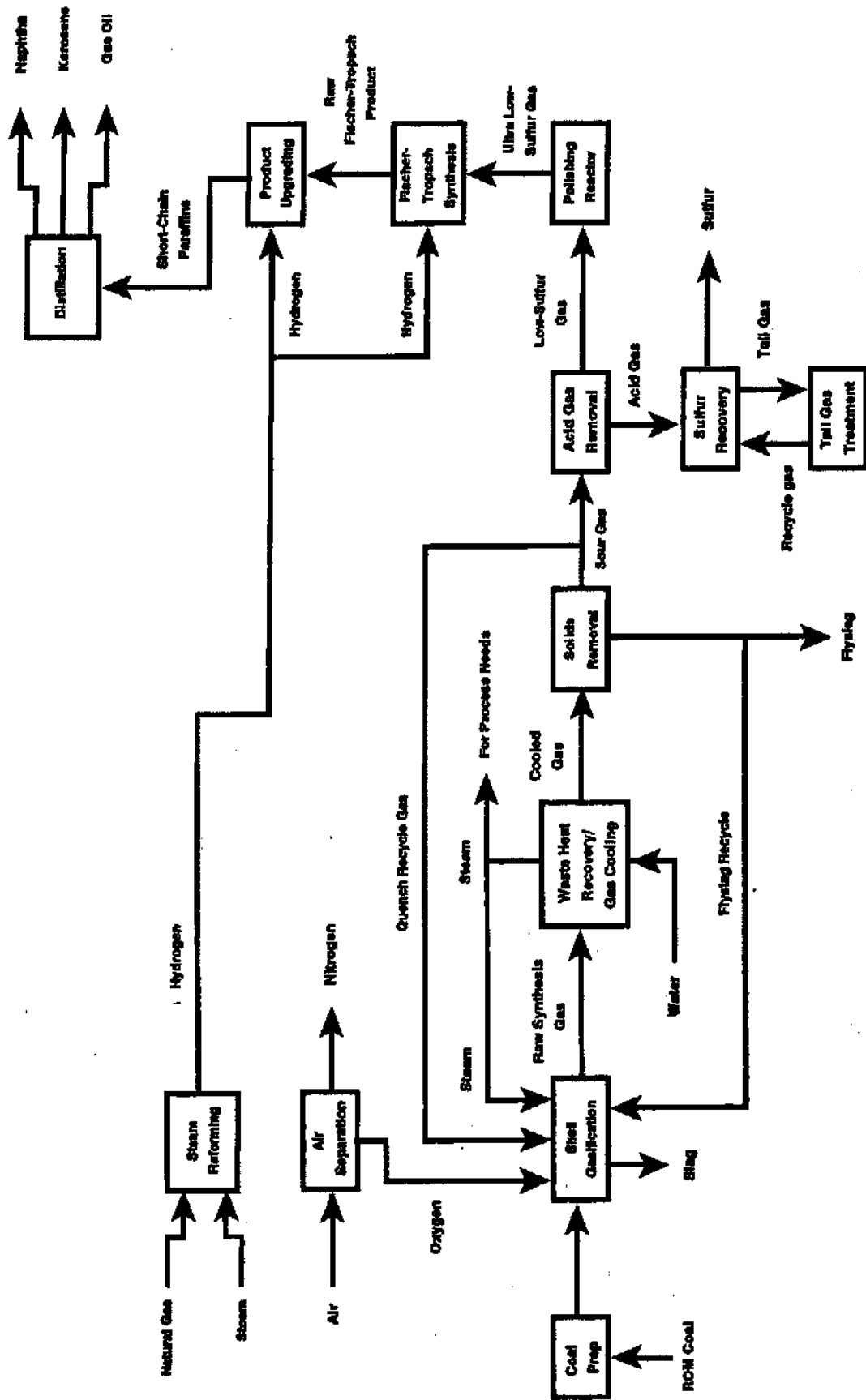


FIGURE 1: Overall Block Diagram of the Shell MDS Concept