

3.0 PROCESS DESCRIPTIONS

The descriptions which follow are somewhat brief and intended to describe the reaction system for the actual conversion of the coal. Subsequent purification operations are generally similar among coal conversion processes and, in practically every case, the same kinds of processing are used in industrial chemistry operations. Excellent descriptions, flow diagrams and progress reports are given in the Department of Energy, Division of Coal Conversion Quarterly Reports (July - September 1977 is publication No. DOE/ET 0026). The various coal conversion processes are in different states of development. These differences are reflected by the Process Confidence Index shown in Table 4.3 and this system is explained in Section 4.2.2.

3.1 SOLID PROCESSES

Two solid fuel products from coal are considered. These come from completely different processes. The first is solvent refined coal (SRC-I) from a federally sponsored development project. The intention for this product is to have a material which is very similar to coal but with much less pollutant content, particularly sulfur and ash. The SRC-I process achieves this and is on the verge of commercial demonstration. This material may eliminate the alternative for existing coal-fired equipment which is to process all of the flue gas to remove the sulfur and solid materials to make the plants environmentally acceptable. SRC-I boiler fuel is a solid material, with low ash and sulfur, capable of burning cleanly. Appendix 1 shows product specifications.

The other solid fuel material derived from some coal gasification processes is char. Char is principally carbon and the ash residue of the coal. Because much of the volatile matter has been removed and the coal molecule has been broken down into much smaller units, char can be a more reactive form of carbon than raw coal. Char can be used as a fuel or as a feed for gasifier systems. Gasifier systems use the char feed with air or oxygen to provide a mixture of carbon monoxide and hydrogen. Carbon monoxide and hydrogen mixtures have wide application and have been used for many years in various ratios to synthesize more valuable chemical compounds. This same gas mixture can also be used to

synthesize methane, the chief ingredient of natural gas and the most desirable pipeline gas. For all practical purposes methane may be considered exactly equivalent to natural gas. Most of the gasification processes produce some char. These processes are described in Section 3.3. The sulfur content of the char is an important factor dependent upon feed coal and the process. A high sulfur content reduces char value considerably.

3.1.1 SRC-I

Development of the Solvent Refined Coal process began in 1962. A pilot plant has been in operation since 1974. A second pilot plant operates completely independently on process development. The process was designed to dissolve the coal, remove the impurities and produce a non-polluting solid fuel. Hydrogen is added and liquid and gas produced as by-product fuels.

The coal is mixed with a process derived solvent, pumped to reaction pressure and combined with hydrogen, preheated and fed to a dissolver vessel. Well over 90% of the carbon materials in the coal dissolve in the reactor. Most of the sulfur in the coal combines with hydrogen to form hydrogen sulfide which leaves the reactor as a gas. The effluent slurry from the reactor is depressurized and then goes to a solid separation step. In this step ash plus unreacted coal are separated from the solvent and liquids. The clean liquid is distilled. A portion of the distillate liquid, process derived solvent, is recycled back to the dissolver. The SRC-I fuel is allowed to solidify. The melting point of the solid is about 180°C. The major use for this material is projected to be boiler fuel.

Development is still underway to determine the best system for removing solids from the slurry. The best possibilities include filtration, anti-solvent processing and critical solvent deashing. Filtration has been used in the pilot plant. Development is in progress by U.S. Filter for commercial scale equipment to eliminate the high cost and poor reliability of older style filters.

There has been one successful test of SRC-I product in a commercial power plant. There were no problems handling or using SRC-I fuel and performance was better than coal. Both the sulfur reduction and oxides of nitrogen limitation were achieved in the commercial test. It is likely that SRC solid could find wide application in utilities and possibly very large commercial boilers if cost incentive exists. This is a very large potential market. SRC-I properties depend on process conditions.

3.2 LIQUID PROCESSES

Fluids are more desirable from a handling standpoint than solids. Liquid fuels are desired to replace liquid petroleum products. Liquids have the general advantage over gases of lower storage cost. Gas fuels with characteristics as close to natural gas as possible are desirable for the purpose of replacing existing natural gas. There are a vast variety of liquids produced by several approaches to the conversion of coal. Pyrolysis is an historic method for producing liquids and gas from coal. It is difficult to control the kinds of products which result. The COED process is a successful improvement which pyrolyzes in stages.

Aside from pyrolysis, the two different basic routes to coal liquefaction are:

Direct Liquefaction

Crushed coal is slurried in a process-derived oil and reacted directly with hydrogen at high temperature and pressure conditions. Some solid always remains in the reactor effluent. This solid consists of unreacted coal and ash. The separation and subsequent treatment of this material is an important area of process development for each of the liquefaction processes. The liquid produced has properties similar to certain petroleum hydrocarbons. The actual yields and physical properties depend directly on reactor conditions and degree of hydrogenation. The direct liquefaction processes include SRC-II, EDS and H-Coal, all described in further detail below.

Indirect Liquefaction

Coal is first gasified to produce a hydrogen and carbon monoxide mixture. These materials are then recombined with the aid of catalysts to produce liquid compounds.

A particular advantage of indirect liquefaction is that essentially all of the sulfur and nitrogen present in the coal can be separated in the gaseous phase and thus eliminated from the liquid products.

These materials are difficult and expensive to remove to a very low concentration with direct hydrogenation processes. The practical processes for indirect liquefaction include methanol and Fischer-Tropsch. Process descriptions follow.

Each of the liquefaction processes produces several types of product and some gas. In some cases the gas is used within the plant. A summary of products from each process is shown in Table 5. Product properties are given in Appendix 1.

The liquefaction processes share many of the same production problems. Some are specific to the particular coal feed. An example of this is calcium carbonate deposition in the reactor. Alkali content tends to be higher in Western coals. This can be an advantage for indirect liquefaction as calcium catalyzes the gasification reaction. Otherwise the deposition can be avoided by feed coal pretreatment with sulfuric or sulfurous acid. Other problems such as the handling of residue slurries are common to many processes. The particular techniques found satisfactory by any one process developer can often be applied to another process.

3.2.1 SRC-II

The Solvent Refined Coal-II process was developed in the mid-1970's to eliminate two problems considered inherent with SRC-I. The first was the solids separation problem and the second was market acceptability for the product.

The SRC-II process is the same as SRC-I except proportionally more hydrogen is used and a portion of the slurry is recycled to increase the degree of conversion. Fuel oil is separated by vacuum distillation and residual materials are gasified. Only liquid and gas products result from the process.

A feed coal type limitation has been suggested for this process because certain trace minerals are required and these elements are found in the ash of particular coals. These trace elements are required in the liquefaction reactor to act as catalysts for the breakdown of solid to liquid. Where the problem is concentration rather than kind of trace elements,

the process developer has suggested that a recycle of residue would seem capable of broadening allowable coal feeds.

3.2.2 EDS

The Exxon Donor Solvent process development by Exxon began in 1966. The process is similar to SRC-II described above with the exception that a major portion of the hydrogen is supplied as a part of the solvent, chemically combined rather than as a free or dissolved gas. The process-derived solvent literally contributes hydrogen atoms to the coal molecule in the dissolver vessel. The solvent is rehydrogenated using a proprietary catalytic process. As a part of their process development, Exxon has been designing their proprietary Flexicoking process for the treatment of residual slurry produced in the liquefaction reactor.

3.2.3 H-Coal

Work on the H-Coal process began in 1964 as a natural extension of the commercially successful H-Oil process. In the H-Coal process, crushed and dried coal is slurried with recycle oils, mixed with hydrogen and liquefied in direct contact with catalyst in an ebullated bed reactor. This reactor utilizes an upward flow of liquid to expand the catalyst bed and maintain the suspended catalyst particles in random motion. The finely divided coal and ash particles flow through the ebullating bed and are removed with the liquid and vapor products.

The reactor effluent is separated into recycle and net product streams in conventional processing equipment under conditions more severe than existing applications. Conversion and yield structure are determined by reactor conditions, catalyst replacement rate and recycle slurry oil composition.

Two different modes of operation for H-Coal are used in this study. The one emphasizes distillate production and the other maximizes total fuel oil. Product from the distillate mode is termed syncrude as the liquid material produced is similar to low grade petroleum crude oil. Considerable upgrading is required to prepare this material for use as a refinery feedstock.

3.2.4 Fischer-Tropsch

The Fischer-Tropsch reactions were discovered in 1923. They include a range of combinations using iron/cobalt catalyst to react hydrogen and carbon monoxide to form paraffins, olefins and alcohols. These reactions are exothermic and not specific to the formation of any single compound.

For a complete process to convert coal to hydrocarbons, a gasification section is required to precede the Fischer-Tropsch reactor section. There are a number of possibilities for the gasifier system. The choice is important because of the effect on final cost. The data used in this study are based on use of a British Gas Corporation (BGC) Slagging Lurgi gasifier. This choice is based on high conversion efficiency and ability to handle a broad range of coal types. This unit is still in the final development stage and so not yet in commercial use. Other gasifiers are under development which should be competitive with the BGC Slagging Lurgi.

The Fischer-Tropsch process has the advantage of being in commercial use with a conventional Lurgi gasifier. It has the disadvantage of producing a wide variety of compounds which do not fit well into existing markets. Mobil Oil Corporation has developed catalysts which improve the quality and quantity of gasoline from the F-T process.

3.2.5 Methanol and M-Gasoline

The production of methanol from a gas mixture of carbon monoxide and hydrogen is a specialized application of a Fischer-Tropsch reaction. The yield of methanol is maximized by a combination of optimum reactor conditions, catalyst and recycle of the unreacted gases.

The conversion of methanol to M-Gasoline is a separate catalytic conversion which can be done in fixed or fluid beds. This reaction is also exothermic. The thermal efficiency for the final M-Gasoline conversion step can be as high as 93%. Methanol has high potential as a fuel for peak-shaving turbine-driven generators and possibly boilers and vehicle fuel.

3.3 GAS PROCESSES

While a variety of solids handling, gas contacting and gas quality upgrading techniques may be employed in the various gasification processes, the primary goal is the same; to convert a sulfur-containing solid to an essentially sulfur-free gaseous product. The gaseous product may be a mixture of hydrogen and carbon monoxide with nitrogen. The definitions are not rigorous, but high Btu gas is generally over 900 Btu/scf and low-Btu gas is generally below 350 Btu/scf. Medium or intermediate gas falls between these values. High Btu gas production is the more difficult task as it requires additional upgrading of a low to intermediate-Btu gas stream to produce a commercially acceptable product. The carbon/hydrogen ratio is adjusted either by rejecting a portion of the carbon, increase of hydrogen, or a combination of both. The chemical processing steps include: production of a gas containing carbon oxides and hydrogen by the reaction of carbon and steam, gasification; reaction of hydrogen and coal to form methane, a hydrogasification process; reaction of hydrogen and carbon monoxide to produce methane, methanation; and the removal of impurities.

The gasification processes share a number of common techniques. The coal received at the plant site must be further cleaned and crushed or ground before it can enter the gasifier. Conventional cleaning methods are used to remove extraneous materials such as metal, rocks, etc. For some processes the coal must be finely ground so it may be fluidized or entrained in a flowing gas stream. For other processes crushing and sizing is all that is required. Agglomerating coals may be pretreated by heating, mild oxidation with air, or other procedures to assure smooth gasifier operation and avoid reactor plugging. Non-agglomerating coals such as lignite and sub-bituminous coal normally do not require pretreatment. Feeding a solid material such as coal to a higher pressure reactor is a difficult task. Dry feeders using a series of pressurized lock hoppers or wet systems in which a slurry is pumped into the reactor are used.

The gasification step is the heart of the process. Here the solid feed material is contacted with synthesis gas (carbon monoxide and hydrogen). The coal is devolatilized and a portion of the fixed carbon converted

to methane. The gas-solids contacting methods used include fixed beds, fluidized beds, moving beds, entrained beds and free-fall systems. The gasification process, overall, is endothermic and the heat required to maintain reaction rates is usually supplied by burning a portion of the coal feed. External heat sources such as electric resistance heating, molten salt or solid heat carriers, and the introduction of a hot hydrogen stream have also been tested. Following the gasification step the particulate materials and heavy hydrocarbons contained in the reactor effluent are removed by a water quench and solids separation system. If low-Btu gas or synthesis gas are the desired products, the raw gas is scrubbed to remove carbon dioxide and sulfur compounds and then used directly. However, if high-Btu gas is desired, methanation is necessary.

In most gasification processes the hydrogen content of the gasifier effluent is too low for effective conversion to methane. Therefore, the shift reaction is employed to react a portion of the carbon monoxide with steam to form more hydrogen. Fixed bed reactors charged with catalyst are used in this process. The CO_2 formed is then removed. A number of commercially available processes are effective in removing both CO_2 and sulfur compounds. The off-gas from the purification processes is treated to recover the sulfur and minimize objectionable effluents.

Synthesis gas which is mostly hydrogen and carbon monoxide has a heating value much too low for direct injection into the natural gas network. The heating value of the gas is increased by catalytically reacting the hydrogen and carbon monoxide to form methane. This methanation process is highly exothermic and a number of techniques have been developed to control reactor bed temperatures. Fixed beds and fluidized beds with reactor system variations have been tested. The final step to prepare high-Btu gas for transmission is to remove water to specification levels and compress if necessary.

3.3.1 CO_2 Acceptor

The CO_2 Acceptor process was designed to accomplish two important functions within the same reactor; coal gasification and carbon dioxide (CO_2)

removal. The commercial process uses three fluidized bed reactors. The gasifier achieves coal gasification and the combination of CO₂ formed with acceptor solid. The acceptor solid is regenerated in a second vessel. The acceptor is a lime material which reacts with CO₂ in the reactor and incidentally provides reaction heat which contributes to the heat input required for the coal gasification reaction. Heat for the acceptor regeneration is generated by burning residual char withdrawn from the top of the gasifier bed. The combustion takes place within the acceptor regenerator.

Lignite and sub-bituminous coals are preferred feeds because of their high reactivity. With these the gasification temperature is sufficiently low to avoid ash fusion and consequent solid deposition and particle agglomeration.

The hydrogen-rich gas mixture from the gasifier is purified, methanated, compressed and dehydrated to produce pipeline quality gas. The CO₂ Acceptor process is unique among the high-Btu gas processes as it does not require a separate acid gas removal system. It also has the lowest water requirement. It has the particular disadvantage of poor operability on feeds other than lignites or sub-bituminous coals.

A second mode of operation for the CO₂ Acceptor process produces syngas by not going through the methanation step. Syngas is a useful medium-Btu intermediate which may be used to synthesize methanol, other hydrocarbons or alcohols.

3.3.2 Hygas

Development of the Hygas process began in 1954. Pilot plant operation began in 1972.

The Hygas reactor is a single vessel containing four separate, vertically stacked contacting zones. Coal is pumped into the reactor as a slurry containing up to 50 weight percent solids in recycle oil. The slurry is dried in the top zone with hot gases rising from the lower reactor zones. The dried coal is then gravity fed down through the remaining reactor zones, countercurrent to the ascending reacting gas

stream. There are two hydrogasification zones; the first, a short residence time (1-10 seconds) low temperature (650 - 760°C) dilute-phase transport reactor, followed by a longer residence time (20-40 minutes) higher temperature (870 - 925°C) dense-phase fluid-bed reactor. Sixty to seventy percent of the total product methane is produced in these two hydrogasification reactors. In the bottom zone the remaining residual char is converted to high hydrogen-content synthesis gas by dense-phase, fluid-bed steam-oxygen gasification at temperatures of 950 - 1010°C and 10-20 minutes residence time. This hot synthesis gas is the hydrogen source for the two upper hydrogasification zones. Ash is withdrawn from the bottom zone, water-quenched and removed from the process as a water slurry.

The raw gas mixture from the reactor is scrubbed, then passed through an acid-gas removal system. A final methanation process converts most of the unreacted hydrogen and carbon monoxide present to methane.

A pretreatment step is required for caking coals which would otherwise agglomerate in the reactor. The pretreatment consists of mild air oxidation which destroys the coals' agglomerating properties and reduces product yield.

3.3.3 Bigas

Process development began in late 1963. The process hypothesis was that a high methane yield would result from reactions of coal with steam at high temperature and pressure.

Coal is fed into the first gasifier stage as a water slurry. Steam is injected separately, combines with the coal, and the mixture is contacted by hot gas from the oxygen-fed lower stage causing conversion to methane, carbon monoxide, carbon dioxide, hydrogen and char. This mixture rises through the gasifier and is discharged from the gasifier to a water quench. The gas is scrubbed further, then treated in a shift reactor which combines carbon monoxide and steam to form more hydrogen. The gas is then passed through acid gas scrubbers to remove hydrogen sulfide and carbon dioxide. This is followed by a methanation reactor which combines most of the carbon monoxide and remaining hydrogen

and forms more methane raising the heating value of the product gas significantly.

This reactor system is able to handle all types of coals without pretreatment. There are materials problems due to the high operating temperature. The slagging section is particularly prone to flow interruptions due to solidification of the molten ash. Solids circulations throughout the system are a difficult problem. The process has never operated satisfactorily.

3.3.4 Synthane

Development of the Synthane process began in the early 1960's.

The sized coal is fed by a weigh-bin lock hopper system into the fluidized bed pretreater where the coal is dried before flowing to the single stage fluid bed reactor. Steam and oxygen are injected below the fluidized bed. Gasification occurs within the fluidized bed. Unreacted char flows downward into another bed fluidized and cooled by steam. Char is removed from the pressurized system as a water slurry.

Product gases are scrubbed prior to shift conversion which gives the proper carbon monoxide-to-hydrogen ratio for methanation.

Large quantities of char are produced and exported from the plant as boiler fuel. This solid fuel is undesirable compared to fluid fuels and has been assigned an appropriate value factor in this study. In late 1978, DOE made a decision to cease operations of the Synthane pilot plant.

3.3.5 Lurgi Process, Dry Bottom

The Lurgi process employs a moving bed technique wherein the coal charge moves downward as a continuous bed and is contacted by an upward flowing steam-oxygen mixture. The feed coal is crushed and screened to size range of about one-eighth to one and one-fourth inch size. Fines are separated and used as fuel. The sized coal is continuously fed to the top of the reactor through a pressurized lock hopper system. As the coal

moves downward through the reaction zone the steam-oxygen mixture reacts with the coal to form synthesis gas. The hot synthesis gas hydrogasifies and devolatilizes the raw coal in the upper zones and is withdrawn from the reactor for further cleaning and upgrading. The coal bed is supported on a revolving grate. Ash is discharged as a dry granular solid to the ash disposal system.

While the Lurgi reactor system has principally been used to gasify non-agglomerating or slightly agglomerating coals, the range of usable coals has been extended by the addition of stirrers to break up the agglomerates. In order to avoid sintering of the ash and plugging of the bed, the reactor normally operates with a steam/oxygen volume ratio of 6 to 10. This leads to high residual unreacted steam in the off-gas stream and increases the oxygen requirement. As detailed in section 3.3.6, the Slagging Lurgi Process has reduced these requirements and improved overall process efficiency.

The off-gas is cleaned for use as low-Btu fuel gas (heating value in the range of 300 Btu per cubic foot) or cleaned and methanated to produce a high-Btu gas. The Lurgi process gas clean-up system includes quench vessels, steam generators and coolers. A heavy tar oil is recovered from the quench water while other gaseous contaminants are removed in subsequent gas clean-up processes. If necessary, the hydrogen/carbon monoxide ratio is adjusted in a shift reactor for methanation. The shifted gas is scrubbed to remove the carbon dioxide. The hydrogen and carbon monoxide in the purified gas stream are then catalytically converted to methane to produce a final product gas with a heating value near 950 Btu per cubic foot.

3.3.6 Slagging Lurgi Process

The Slagging Lurgi Process utilizes a moving bed system in which down-flowing coal is contacted with a rising gas stream in a manner quite similar to the conventional dry bottom Lurgi reactor. The principal difference between the two is the method of discharging ash. The Slagging Lurgi operates at a higher bed temperature and the ash is melted. The molten ash then flows from the bottom of the reactor through a slag discharge system. The primary advantage of the slagging Lurgi

is the reduction of steam input per unit of gas produced and the much higher rate of conversion obtainable at the higher bed temperature. Process efficiency is higher and the cost of the reactor section of the gasification plant may be significantly reduced. While the need to maintain gasifier operability requires care in selecting coals with the proper ash fusion temperature, this process is expected to extend the range of coals which can be successfully gasified in the Lurgi reactor. Coals with lower ash fusion temperatures and lower reactivity can be gasified under slagging conditions while the higher ash content coals with high ash fusion temperatures are gasified in a standard dry bottom Lurgi.

The gas produced from the Slagging Lurgi is roughly similar in composition to the dry bottom Lurgi product gas. Downstream treating and upgrading process steps are essentially the same. As stated above, process efficiency is better than dry Lurgi. This process is still in the early development stage and is proprietary. Sufficient data were not available to give an economic appraisal. This descriptive information was given because of the high current development activity.

3.4 OTHER PROCESSES

The final group of processes studied use both chemistry and thermal energy conversion to produce electricity as the final product. These processes convert the coal to the most convenient gaseous products and then burn the gas in simple efficient turbine driven generator equipment to utilize pressure, thermal and chemical energy to achieve conversion efficiencies potentially better than modern coal burning electric power plants.

The following two power processes were included in this report for a broader comparison and because they are receiving active federal R&D support. There are many other systems for electric power generation with all of the same potential advantages which are being developed in the U.S. and abroad. These systems could have also been evaluated as low-Btu gas producers. They have potential as medium gas producers if oxygen instead of air is used in the reactors.

3.4.1 Combustion Engineering

Development of the Combustion Engineering system began in 1974. This process is a method for production of low-Btu gas for electricity production. It is based on an air-blown, atmospheric pressure, entrained gasifier.

A portion of the coal is burned in a combustion section of the gasifier to supply heat for the gasification reaction. The ash from the combustion section is removed as molten slag from the bottom. The remainder of the coal is fed to the reduction section where it contacts hot gas. The conversion process takes place in an entrained area where fresh coal contacts hot gas and devolatilization and gasification occur. The hot gas is cooled and solids are separated. After Stretford process sulfur removal the gas is ready for use as turbine or boiler fuel.

The ability to treat all coals without pretreatment and the complete carbon conversion are advantages. The low pressure operation necessitates relatively large vessels and piping for a given fuel rate. Low-Btu gas must be recompressed and utilized close to the source for the same reasons. All design and material-of-construction problems have not been resolved for this process. It has not yet operated on a significant scale.

3.4.2 Westinghouse

This process is called the "Advanced Coal Gasification System for Electric Power Generation". Development began in 1972 and the 15 ton/day system has been operating since 1975.

The initial concept for the Westinghouse coal gasification system was a two-reactor system. Both reactors, the devolatilizer and the gasifier, contain fluidized beds. The first reactor, the devolatilizer, is used to devolatilize and decake coal as required. Devolatilized char circulates around a draft tube and prevents coal particles from agglomerating as they pass through their sticky stage during heating. The second reactor, the gasifier, is used to gasify char from the

devolatizer and agglomerate the residual ash at high temperature. The gasifier also provides heat for the process.

The initial concept also included adsorption of hydrogen sulfide with dolomite in the devolatizer. Hydrogen sulfide removal with dolomite in the devolatizer is currently not under consideration for initial commercialization; however, work in this area is still being explored at the Westinghouse Research Laboratories.

Initial testing of the Westinghouse process at the 15 ton/day PDU located near Madison, Pa. began in 1975. Testing philosophy was aimed at demonstrating the technical feasibility of each reactor, the devolatizer and then the gasifier, before running them together as an integrated system.

Tests on the devolatizer ran from mid-1975 to mid-1976. Gasifier tests began late in 1976 and have continued through 1978. The tests on each reactor demonstrated the feasibility of each reactor's conceptual design. Tests on the integrated system, devolatizer and gasifier combined, will begin in 1979.

Extensive development work on the gasifier has been done at the PDU. Tests on the gasifier have been successful with run times in excess of 200 hours. In addition to char, caking and non-caking coals without pretreatment have been successfully processed in the gasifier. Also, the gasifier has been run on air and on pure oxygen. From the development work on the gasifier, the concept of a single-stage system has evolved in addition to the original two-reactor system.

This coal gasification process is being developed for a variety of low-Btu and medium-Btu applications. These include:

- a. Combined cycle power generation
- b. Fuel cell power generation
- c. Industrial fuel gas
- d. Chemical feed stock

The size used in this study would require multiple gasifiers.

The pressurized gasifier operation should give an efficiency advantage over gasifiers which operate at atmospheric pressure. This theoretical advantage is slight as evidenced by the higher products efficiency shown for the Combustion Engineering combined cycle process. The advantage of the latter process is due to a selection of a better steam cycle for the waste heat recovery part of the system.