# THE SYNTHANE PROCESS - RESEARCH RESULTS AND PROTOTYPE PLANT DESIGN

by

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## INTRODUCTION

The Synthane Process is a gasification system developed by the Bureau of Mines for converting bituminous coal, subbituminous coal, and lignite to a satisfactory substitute for natural gas (1), (2), (3).3/ The basic process steps are (1) coal pretreatment to destroy caking properties, (2) carbonization plus steam-oxygen gasification of the pretreated coal in a fluidized bed, (3) shift conversion of the gasifier synthesis gas to a $H_2$:CO ratio of 3:1, (4) purification of the shifted product gas, and (5) catalytic methanation of the hydrogen plus carbon monoxide.

About 15 years ago, the Bureau developed the hot carbonate system (4) for removing acid gases such as $CO_2$ and $H_2S$ from gas streams, which is used for step (4). This process is now commercial, as is the water gas shift step.

The Bureau recently has been concentrating its research on the gasification and methanation steps, but solutions to possible environmental problems are also being investigated. A contract has also been given to HRI (Hydrocarbon Research, Inc.) to operate its gasifier

3/ Numbers in parentheses (underlined) refer to list of references at the end of this paper.

modified to the Synthane operation to test the Synthane gasification step on a larger scale than done so far at Bruceton. Lummus Company has designed a 75-tpd plant to be installed on the Bruceton, Pa., grounds in 1973-1974; the plant is scheduled to operate in 1974.

Research at Bureau of Mines Laboratories, Bruceton, Pa.

A schematic of the Bruceton gasifier is shown in Figure 1. It originally combined the operations of free-fall pretreatment, carbonization, and gasification in one reactor when using a 70% through 200 mesh coal as the feed stock. Because of the limitations of the free-fall pretreater, the present equipment has a separate fluid-bed pretreater, although the product gas still consists of gas from all three operations. The fluid-bed pretreater can handle a coal which is 30% through 200 mesh (20 x 0) and therefore has raised the permissible linear velocity in the gasifier from below 0.2 ft/sec to 0.4, which raises the gasifier throughput of coal.

The Bruceton gasifier operates at 40 atmospheres' pressure and a maximum temperature of 1800° F. Some recent test results given in Table 1 show a satisfactory methane yield and an economic product gas yield of $H_2 + CO + CH_4 + C_2H_6$. The desirable carbon conversion is about 65%, permitting the gasifier char to be burned to raise steam. The steam decomposition has been low--less than 40%.

The pretreating step has operated satisfactorily to render caking coals non-caking; Pittsburgh seam coal with an FSI (free swelling index) of 8 to 9, and Illinois No. 6 coal with an FSI of 3 to 5. We have no trouble with agglomeration of the coal in the high temperatures of the gasifier when the FSI is reduced below 2. Usual conditions of operating the fluid-bed pretreater at 40 atmospheres are 0.8 to 1 ft/sec gas linear velocity, 0.6 to 0.8 scf $O_2$/lb coal, and a temperature of 750-800° F.

The Bureau has developed two methods of converting the purified product synthesis gas to methane: the hot gas recycle (HGR) (5), and the tube-wall reactor (TWR) (6). Both presently use Raney nickel catalyst flame-sprayed into tubes or onto plates. The HGR utilizes the heat capacity of the recycle gas to remove the exothermic heat of reaction (65 Btu/cu ft of feed gas) from the catalyst. In the TWR system the heat of reaction is transferred through the sprayed tube wall to boiling Dowtherm. Both operate at about 750° F and the highest pressure used at Bruceton has been 400 psig. Results of a recent TWR test, operated for about 4 months, are shown in Figure 2. In this test the reactor contained 7 tubes sprayed externally with Raney nickel. The latest arrangement, Figure 3, shows a single tube with the catalyst coated on the inside of the tube. This permits easier replacement of the catalyst because the tubes do not have to be removed from the tube bundle in a multi-tube reactor.

Research at Hydrocarbon Research, Inc.

Because of the small size of the Bruceton gasifier (4-inch-diameter by 6-foot-high fluid bed) and because the length of the tests has been limited by the storage capacity of the feed hopper (150 lb), a contract was let to HRI to revise their continuous gasifier (26-inch diameter by 80 feet high) to simulate a Synthane gasifier. Revisions are complete. A sketch of the HRI gasifier is shown in Figure 4. The unit consists of coal handling equipment, a pretreater, gasifier, an incinerator plus a bag filter. Results of their work should be known in the fall of 1972. Thermal patterns and gas, liquid, and tar compositions should predict more accurately the behavior of larger gasifiers.

## The Lummus Company Design

The Lummus Company designed a 75-tpd plant to demonstrate the Synthane process. The design was discussed in detail in an earlier paper (7). A sketch of the overall plant, which will operate at a maximum of 1000 psig, is shown in Figure 5. Operations which are not being demonstrated in this plant but will be needed in a commercial plant are (1) a heat exchanger to cool the gas (and raise steam) from 1400° F to 800 ° F after the gasifier (the 1400° F gas in the Lummus design passes directly to the Venturi scrubber); (2) a plant to clean up the water effluent from the gasifier (this water is passed to a thermal oxidizer); and (3) a combustor to burn the char to raise steam for the overall plant needs (the char is being carted to a land fill). While there is space at the plant site for these operations, it was believed these would direct too much attention to peripheral development and were not needed to prove the main steps in the process.

The pretreatment-gasifier arrangement is shown in Figure 6. One fluid-bed pretreater is modeled after the Bruceton work and is 10-3/4 inch in O.D. by 48.5 feet long. The other is 20 inches in O.D. by 15 feet long. The second design will result in a linear velocity only one-fourth that of the first but should not have the slugging flow conditions which may cause problems in the first. The gasifier itself is 4.75 feet in O.D. by 94 feet high. It will have an 8-foot fluid bed topped by internals to create a disengaging zone; this will be topped by another fluid bed for carbonization. Above that will be a 15-foot free-fall section to the coal inlet. This design is based on the need for a separate carbonizing zone to maximize methane formation.

Figure 7 shows the raw gas scrubbing system. The hot 1400° F gas passes directly to a Venturi scrubber where the gas is cooled to 450° F to condense the steam and remove fines. The cooled stream then passes to a gas scrubber to remove tars and dusts. An oil scrubber may be used if necessary.

Figure 8 shows the apparatus which cools the char from 1800° F to 600° F. The char flows from the gasifier to a bed fluidized with steam by water sprays being used to cool the char. Flow of the char is controlled by the differential pressure between the gasifier and the cooler.

The Lummus design incorporates both methanation systems developed by the Bureau. The TWR methanator reactor, Figure 9, consists of 22 2-inch-diameter tubes 20 feet long inside a 16-inch diameter shell.

The HGR reactor, Figure 10, consists of 28 plates 10 feet long, of varied widths to fit into a 14-inch-O.D. pipe. (A section used in the Bruceton HGR is shown in Figure 11 which also shows the flame-spraying technique. Fig 12 shows the gun used to spray tubes internally.)

The tubes are thermal sprayed internally, and the plates are sprayed on both sides with Raney nickel to a thickness of 0.020 inch.

The gas purification stream consists of the Benfield activated hot potassium carbonate process plus activated carbon and sponge iron boxes for removal of traces of sulfur. A Stretford plant will be provided to recover sulfur from the $H_2S$ from the Benfield regenerator.

## Pollution Aspects

### Water

The gasifier condensate water analysis is shown in Table 2. The water is very similar to the weak ammonia liquid from a byproduct coke plant. Bethlehem Steel Company, at its Bethlehem, Pa., plant (8) has reduced the phenol level to loo ppb by bacteriological treatment and has reduced the thiocyanates by an average of 70%. In our present plans this water is disposed of in a thermal oxidizer. There is space on the grounds to put in a treatment system later if desired.

Gas

Analysis of gas from the gasifier is shown in Table 3. The Benfield system will remove the $H_2S$, the COS, the mercaptans, and $SO_2$ and $CS_2$ components to a total level of 5 to 10 ppm but only partially remove the thiophenes. Those components that are left must be reduced to a total level of 0.1 ppm before methanation. This is accomplished by the activated carbon and sponge iron boxes. After regeneration, the sulfur-containing gas passes to a Stretford unit (rather than a Claus) to lower the sulfur level so that there is no air pollution problem due to off gases from the Stretford.

Char

Sulfur analyses of some typical chars are shown in Table 4. Most of our work at Bruceton recently has been directed at the gasification of Illinois No. 6 coal. As can be seen, this char could not serve as powerplant feed because the $SO_2$ content of the flue gas would exceed present EPA requirements (1.2 lb $SO_2$/MM Btu). It is believed if the tar were desulfurized and burned with the char to provide the heating value (9) needed because of the low volatile content of the char, the effluent would meet the EPA requirement in most cases.

Trace Compounds

Certain compounds could not be detected by the mass spectrometer, and other methods were used. Table 5 shows the analyses of those we have found so far. HCN is of importance because of its effect on the Stretford process (10). The limit on HCN must be below 20 ppm and apparently, based on our results, the gas contains less than this maximum. The Hg level of 0.1 ppb is also within limits.

It should be stressed that there will be a difference in the temperatures of the gas leaving the Bruceton gasifier, the gas leaving the Lummus design gasifier, and the gas leaving a gasifier of the projected commercial size. The Bruceton gasifier exit gas is at 800-900° F, while the gas from the larger ones will be at about 1400° F. This higher temperature will result in a decreased phenol yield and perhaps in a decreased tar yield, but we do not believe it will significantly affect the components in the gasifier gas. An area of development being investigated at Bruceton is hot clean-up of the gasifier gas to remove tars, sulfur, and dusts. This alternative would remove the need for a water wash and permit the gas to be sent directly to the shift converter, at a savings in heat-exchange equipment and a diminishing of the quantity of polluted water.

## CONCLUSION

The Synthane process has been developed to the extent that a 75-tpd plant has been designed and the contract let for the construction to start in 1972. The plant will demonstrate the main steps of the process but is not designed to solve the problems of water treatment and char combustion. The prototype plant should be in operation by 1974.