CARBON MONOXIDE AS A FUEL

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The purpose of this talk is twofold. First, to familiarize you with a process for the separation of CO from gaseous mixtures which is called COSORB. COSORB cheaply and efficiently produces pure carbon monoxide from an ambient temperature and pressure gaseous mixture. Second, to discuss a coal gasification process which would produce pure CO for transmission and use as a fuel. This coal gasification process consists of (1) a slagging-ash gas producer using compressed air as oxidant, (2) gas processing units to extract the sensible heat of the producer gas as steam, isolate the tar and benzols produced and separate the sulfur, dust, and nitrogen containing compound from the gas, (3) COSORB which separates the CO from the rest of the purified producer gas (mostly nitrogen).

R. M. Jimeson, at the recent Dallas meeting of this division, outlined at length why a coal refining industry needs to evolve in the immediate future. 85% of the total chemical fuel reserves of this country are coal. Yet coal is dirty. In addition to smoke problems, the sulfur and nitrogen content of coal go out the stack during its combustion in a boiler plant. Environmental problems will not allow future expansion of raw coal burning. Yet scrubbing stack gases for environmental clean-up is very expensive and only partially effective. The proposed process to be discussed here hopefully is an economically sensible way to use coal as an energy source. It refines the coal by gasification near the mine, purifies the gas, removes sulfur and nitrogen containing impurities, and then transports the pure CO by pipeline to the energy consumer. Pollution problems faced by the consumer would be practically nil.

It is to be emphasized that this process is completely unthinkable without an efficient, cheap separation of CO from nitrogen by a process such as Tenneco's COSORB. No such process has even been proposed before because COSORB did not exist before.

On the first slide, a diagram of COSORB is shown. The process has two packed towers, an absorber and a stripper. A copper containing solvent is circulated through the absorber where the solvent is contacted with a gaseous mixture, for illustrative purposes, a mixture of N_2 and CO. The copper cation in the solvent "coordinately" complexes the CO and absorbs it into the solvent. N_2 is untouched and dissolves in the solvent only by physical forces. It is quite easy to get the CO content of the nitrogen down to less than 1000 ppm. The CO rich solvent flows from the bottom of the absorber to a heat exchanger where it gives up a large fraction of the dissolved CO to the gas phase. In the stripper, a boiling aromatic compound drives the CO quantitatively out of the solvent. The hot lean solvent flows through the heat exchanger where it is cooled and then fed into the absorber to complete the circuit. A turbine compressor is shown in the diagram that may be used to compress the CO by letting down the nitrogen from its pressure in the absorber to one atmosphere. The stripper is run at some 5 psig or so pressure.

The entire apparatus for COSORB is built of simple mild steel. No corrosion problems exist.

Packed towers no taller than thirty feet are more than adequate to allow the quantitative separation at million lb/day carbon monoxide rates. The only utilities necessary are cooling water, low pressure steam, and electricity sufficient to pump the solvent from the stripper column to the absorber.

Having acquainted you with the COSORB process, I now turn to discuss a coal to CO energy complex.

Figure 5 is a diagram of a slagging-ash producer. The coal entering the top is mixed with a flux (limestone) and the residual ash from burning the coal exits the producer as a liquid. These producers can be built in very large units (the blast furnace, a prototype of this producer, is built in standard sizes of 1000 tons coke per day). Under pressure, they also can be run at very high specific rates of production. These producers have a specific production rate fourfold that of the Lurgi process oxygen gasifiers. With pure carbon, the gas exit temperature is from 1000 to 1200C. The gases exiting a coal fed producer will be at a lower temperature because part of the sensible heat arising from the reaction of C to CO will be used to distill the tar, benzol, and moisture in the coal out of the coal on top of the very hot reaction zone. 72% of the energy of the carbon reacted will exit the producer as latent heat of combustion of CO while the remaining 28% will be sensible heat in the gas.

On slide 2, a line diagram of the coal to CO complex is shown. The heated producer gas goes to a steam generation unit where all possible sensible heat is transformed to steam. This steam is used as the driver in the succeeding units and also in the COSORB process to separate CO from the producer gas.

Tar and benzol are made in quantities similar to those obtained by low temperature coking of the coal in question.

One of the several developed efficient processes is then used to desulfurize the gas.

An activated carbon unit is then used for final clean-up to remove all heavier organics and nitrogen and sulfur from the gas.

A drying step (very probably a glycol-solvent absorber and stripper) is then used to finally prepare the gas for feed to COSORB. At this stage, the dry producer gas will be 33% CO with small amounts of H_2, CH_4, and CO_2 and the balance nitrogen.

This dry gas is then fed to COSORB (Fig. 1). In the absorber at 100 psig and ambient temperature, the CO is quantitatively absorbed in the solvent while the nitrogen goes overhead. A turbine lets down the pressurized nitrogen and compresses the pure CO. Considerable excess energy is available here and would be used to compress part of the air needed in Fig. 2 for the gas producer.

This energy complex would be at the mine. The product CO could be transported up to 400 miles to power generation stations or industrial complexes for use as fuel.

On slide 3, I have put down some salient points of interest about CO as a fuel. Its fuel value per unit volume is only 1/3 that of methane. This is a disadvantage for transport by pipeline, but not a severe one as long as the distances are reasonable. CO may be transported 400 miles by pipeline at an energy cost of only 13% of its fuel value.

As fuel, CO is superior to methane. It contains no water in its combustion gas. Its gross and net heat of combustion are the same. Methane uses only 90% of its gross heat of combustion in almost all of its fuel uses. CO has a higher octane number than methane. In a gas engine, fully 25% more horsepower can be delivered with CO than with methane as fuel.

CO can produce a completely dry hot gas if the combustion air is dried. This might be of great practical use in places where a very hot, but completely dry gas product is needed.

Engineering estimates for a COSORB based process and summarized on Fig. 4 for a very large CO producing complex, the complex size is 668 x 10^6 SCF/day CO. This is equivalent in delivered BTU's to a 250 million SCF/day rate of methane.

The unit gasifies 10,800 tons of carbon per day. The tons coal would be larger than this by the amount of tar and benzol distilled in the gas producer. Twenty-eight percent of the heat value of carbon would appear as sensible heat in the producer gas upon oxidation to CO. This heat is equivalent to 3.5 million pounds of steam per hour. About 2.2 million pounds of steam is enough to drive all the purification units for the gas feed and also to operate a COSORB unit for the separation of CO from nitrogen.

One primary process driver (100,000 H.P.) operates from exhausting nitrogen. A second process driver is used (112,000 H.P.) for air compressing. Only the latter would need fuel. This fuel in a turbine would be about 14% of the heating value of the CO produced.

It is my opinion that the process discussed is a much more promising economical method of coal gasification than any method which uses oxygen as oxidant and which synthesizes methane as product.

CO does not have the BTU per SCF to substitute for methane in the present gas network. However, it needs emphasis that two-thirds of the present use of methane is in industrial or electricity use. Only 1/3 of the methane presently used goes to homes or other non-industrial usage.

Industrial and electrical generating uses of methane could be switched from methane to CO without great problems. This would conserve methane, so that an ample supply could be assured to continue home heating.

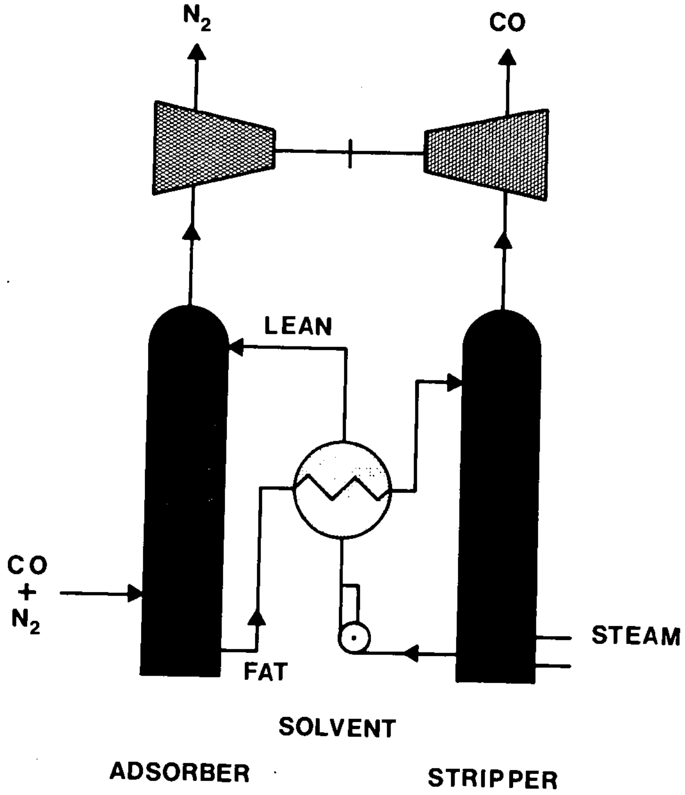

FIG. 1 - COSORB UNIT

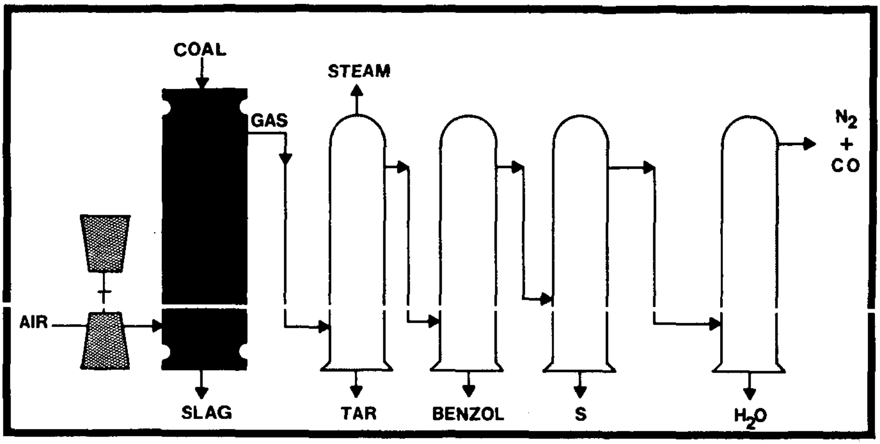

FIG. 2 - ENERGY COMPLEX: COAL-CO

CARBON MONOXIDE AS FUEL

HEATING VALUE: 340 BTU/SCF

COMBUSTION EQN: $CO + \frac{1}{2}O_2 + 2N_2 \rightarrow CO_2 + 2N_2$

CO/CH_4 RELATIVE ENERGY DENSITY: 1.25/1

USEABLE COMPRESSION RATIO
IN OTTO CYCLE ENGINE: >9

COAL-CO ENERGY COMPLEX

- SIZE: 668 x 10^6 SCF CO/DAY
- GASIFIER P: 115 PSIG
- CO P: 100 PSIG
- CARBON GASIFIED: 10,800 TONS/DAY
- DRIVE: TRANSFER TURBINE 100,000 H.P.
  AIR COMPRESSION 112,000 H.P.
- COSORB SOLVENT: 67,000 GPM
- STEAM USED: 2.23 x 10^6 #/HR.
- STEAM EQUIVALENT
  OF GAS SENSIBLE HEAT: 3.56 x 10^6 #/H.R.

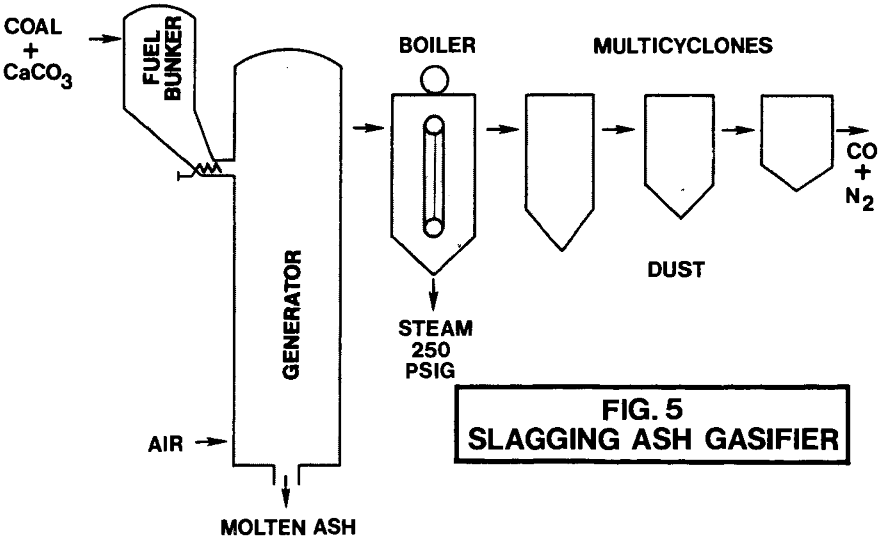

FIG. 5
SLAGGING ASH GASIFIER

Very Large Steam Reformers

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INTRODUCTION

Recent forecasts of future natural gas requirements in the United States indicate that demand will exceed locally utilised production by 6,800,000,000,000 cubic feet during the year 1980 - (a 18,600,000,000 CFD deficit) (Reference - The Economist Intelligence Unit Ltd).

Japan similarly will have a deficit by 1980 for which estimates vary widely. The Economist Intelligence Unit forecast the figure for the year 1980 as 600,000,000,000 cubic feet (1,640,000,000 CFD).

Trans-oceanic transportation of natural gas in the liquid form (LNG) from countries with surplus supplies has been seen as one means of making up these deficits.

A major problem associated with the LNG scheme is the provision of transportation vessels. Cryogenic tankers are required which at present are on a 5 to 7 year delivery schedule and their costs are extremely high and still escalating rapidly.

An alternative means of transporting "natural gas" is now being studied in great detail. The idea is to convert the natural gas at its source to fuel quality methanol (or Liquid Chemical L.C.F) and to ship the methanol in conventional tankers for burning direct as fuel at the user location, or convert the methanol to SNG (Substitute Natural Gas) to supplement the locally produced natural gas.

Economic comparisons between the two schemes have been discussed elsewhere and the general opinion is that both types of plant will be built.

The plants to produce "methanol fuel" in economic quantities will be far larger than the methanol plants now being built for "chemical quality methanol".

LARGE PLANT

Contractors in the process industry and equipment vendors are being continually asked to supply larger plants in order that the chemical producer, refinery operator and fuel supplier, can keep pace with the ever increasing demand for more and cheaper product. For example, single stream ammonia plants have increased in size from 150 TPD of ammonia to 1,500 TPD in about one decade. The industry now faces a much larger increase in the size of methanol plants when the "fuel quality methanol" schemes proceed.

In a period from 1968 until 1975 we are expecting to see an increase in capacity of a methanol plant from 150 TPD to 25,000 TPD. In order to achieve the minimum production costs, this 25,000 TPD plant should be made up from the minimum number of single streams.

PROCESS ROUTE TO METHANOL FUEL

The natural gas which is currently being or that will be flared in areas such as the Middle East can be converted to methanol by the following process route. (See Fig. I).

The process consists of three basic steps:-

Steam reforming of desulphurised natural gas.
Compression to, and synthesis at, 100 atmospheres.
Dehydration to the required calorific value quality by distillation.

1 Reforming

Desulphurised natural gas is mixed with steam, reformed under optimised conditions in a tubular reformer, and then cooled.

2 Compression and Synthesis

Cold synthesis gas is fed by centrifugal compression to the synthesis loop where the methanol is formed.

Excess hydrogen is purged directly from the loop and burned in the reforming furnace, thus maintaining the overall plant efficiency at a high level.

3 Dehydration

Separation of water and dissolved gases from the L.C.F is achieved in a simple single-column distillation system.

THE STEAM REFORMER IS THE MAJOR PIECE OF EQUIPMENT IN THE METHANOL PLANT

The steam reformer is the most important and expensive single item of equipment in the methanol plant. It is therefore important to optimise the size and number of steam reformers required to produce 25,000 TPD of methanol within technical limitations. To date, the largest steam reformer is operating in a methanol plant at Clear Lake Texas (Celenese Chemicals Co) and contains 600 reforming tubes. This plant can produce 1,500 TPD of methanol by a similar route to that described above, or 1,800 TPD by slightly modified process route.

The following table shows the number of reforming tubes required for the range of methanol plants discussed.

Methanol Output TPD	Reformer Tubes (approx) 4'' I.D; 40' heated length
150	60
1,500	600
5,000	2,000
25,000	10,000

OPTIMUM PLANT SIZE

The basis of this paper is that a single stream methanol plant can be built to produce 5,000 TPD of methanol. Five such identical plants will be required to produce 25,000 TPD. We are thus talking of a reforming furnace containing approximately 2,000 tubes, which is in excess of three times the world's largest operating single stream furnace.

Improvement to catalysts and reformer equipment are continually being implimented. Increases in output from these improvements are disregarded in this paper because they are insignificant with respect to the magnitude of the increase in output required for the economic production of L.C.F.

The reasons for selecting 5,000 TPD methanol plant are two fold:

1 Equipment other than the reformer is proven commercially at this sizing.

2 The increasing size of reformers over the years projected to 1976 show a progression to approximately 2,000 reforming tubes. (Figure II).

This paper continues with the description of a single stream 2,000 tube reformer.

STEAM REFORMER

A steam reformer contains a number of reforming tubes which are basically heat transfer tubes filled with catalyst. The process reactants, (steam and hydrocarbon) are passed through the tube where they react endothermically. These tubes are held vertically in a direct fired furnace box. The output of the plant is dependent on the following:

1 The number of tubes.

2 The physical dimension of the tubes.

3 The operating conditions.

4 The analysis of the total feed to the reformer.

5 The activity of the catalyst.

TUBE DESIGN PARAMETERS

Some of the important design parameters of the reforming tubes and the limitations imposed upon them are as follows:

Tube Length

It is possible to increase the output of a furnace by lengthening a given number of reformer tubes and thereby increasing the volume available for catalyst.

Actual costs prove it is more economical to increase the length of a given number of tubes than to maintain tube dimensions and increase the number of tubes. Benefits from increasing the length are available until limited by one of the following factors.

a Pressure Drop through the catalyst packed tube.

In order to limit the pressure drops through the plant to an acceptable level, the maximum heated length of a tube, currently being considered, is 50 feet giving a pressure drop through the tube in the order of 70 psi.

b Thermal Expansion.

As the reformer tubes operate at elevated temperatures, the tubes expand when heated from the ambient to operating temperatures. This expansion has to be taken up by the adjoining pipework, making its design rather cumbersome.

c Compression Load at elevated temperatures.

It is necessary, due to the length and relative small diameters of the tubes, to minimize the self weight compressive load on the tube. This is done by partially supporting the tube at the top by either counter-weights or by tensioning springs. Whichever method is used, a tube length from 40-50 feet seems to be the optimum.

Tube Diameter

Increasing the diameter of the tube achieves a larger volume available for catalyst for a given number of furnace fittings, as does lengthening the tube. Although in increasing this dimension consideration must be given to the following:

a Increasing the hoop stress in the tube.

This will increase the thickness of the tube wall, offering a higher resistivity to heat transfer, resulting in higher tube wall temperatures. The higher tube wall temperature again increases the wall thickness and therefore an economic optimum diameter must be chosen.

b Decreasing the tubes' heat transfer surface area for a given volume of catalyst.

This increases the tube wall metal temperatures and hence the tube wall thickness resulting from the higher heat fluxes required to pass the heat of reaction.

c Reduction in the gas side heat transfer coefficient.

Resulting again in higher tube wall temperatures and hence thicker tube walls.

The cost of tube material in its fabricated form is approximately \$1.25 per pound weight (compared with \$0.25 per pound for carbon steel), the need for optimisation then is critical on reformers containing 2,000 tubes.

Taking into account the above, also the heat flux and catalyst loading limitations imposed by the catalyst suppliers, the economical diameters for reformer tubes vary between 3½" and 4½" ID dependent upon operating conditions.

Tube Pitch

Take one row of tubes firstly it is necessary to select the tube pitch. This choice is governed by mechanical limitations of how close together tubes can be placed and an economic evaluation of tube wall thickness against the pitch selected. In general terms, the closer the tubes are together, the hotter the tubes will be for a given set of operating conditions. As the metal thickness of the tube is highly dependent upon the metal temperature of the tube an economic tube pitch is essential on large furnaces. Tube pitches of 9 to 11 inches are normally chosen after economic optimisation.

Other Variables

Consideration must also be given to catalysts and their activity, the temperature and pressure of the reaction, the steam to hydrocarbon ratio, of the catalysts' loading: all of which can be optimised to give the best possible output from a given number of tubes.

The above considerations leads the designer to the dimensions of the tube and the proximity of the tubes to each other within a single row.

TYPE OF FURNACE

Secondly we must consider the basic type of furnace which is best suited to large steam reformers.

Furnaces are generally classified into two types:

i Vertically fired multirow furnaces.

ii Side fired furnaces.

Side Fired

The side-fired furnace relies upon the tube being bounded on two sides by a refractory wall. The heat is received by the tubes from the radiating refractory wall. This, in fact, limits a dimensional freedom when trying to increase the size of the furnace. As we have already discussed, the heated length of a tube is fixed at say 40'-50' and each tube must be bounded on two sides by a refractory wall : this leaves just one dimension for expansion.

Vertically Fired Furnaces

Conversely on an up-fired or down-fired furnace the heat to the tubes is supplied by the radiating products of combustion and not radiating refractory. This means that we can have more than one row of tubes within the furnace box. This then allows for two dimensions of freedom. (See Figure III).

Single cell multi-row steam reformer furnaces have been operating for many years. In fact the majority of reformers outside the United States are of this type. The choice between up and down firing of the multi-row furnace generally breaks in favour of down firing when the size of the furnace and its convection section is large enough to require an induced draught fan to ensure good operation. This breakpoint is generally a furnace containing about 10 tubes.

The fundamental difference between a side-fired and vertically fired furnace is that the former requires refractory wall to effect heat supply to the tubes whilst the latter relies upon radiant heat transfer from the combustion gases. Thus multirow vertically fired furnaces are constructed without inter-row refractory walls.

Side Fired or Top Fired Furnaces for very large Steam Reformers

The maximum number of tubes than can be satisfactorily contained within a single cell side-fired furnace is approximately 150. This means about 13 radiant boxes would be required to produce 5,000 TPD of methanol and 65 boxes to produce 25,000 TPD.

The largest multi-row furnace now operating contains 600 tubes* which reduces the radiant box requirements to 4 and 16 for the 5,000 TPD and 25,000 TPD plants respectively.

Furnaces of the multi-row type containing 2,000 tubes will reduce the radiant box requirement to only 1 and 5 respectively.

*This 600 tube furnace was designed on the Modular concept (detailed description to follow) such that by repeating proven modules any number of tubes can be accommodated.

Summary of Number of Radiant boxes required by the different furnaces.

	Number of Radiant Boxes.		
Output (Methanol)	Side Fired. 150 tubes per radiant box	Top Fired. 600 tubes per radiant box	Top Fired. 2,000 tubes per radiant box
5,000 TPD	13	4	1
25,000 TPD	65	16	5

This table shows the magnitude of the variance in designs when applied to very large reformed gas requirements.

The economic and operational advantages of selecting a low number of radiant boxes are considerable. Each radiant box will have its own piping, valving, instrumentation, burners and flue gas exhaust fan and all will require attention from plant operators.

MODULAR FURNACE

A radiant box containing approximately 2,000 tubes is the economic design for the proposed 5,000 TPD methanol plant, we now describe the Davy Powergas Modular Steam Reformer. The "MODULAR" concept that allows for an almost limitless expansion of the reformers.

This design has been developed over many years and is based upon the experience gained by our company in supplying over 170 steam reformers.

PRIMARY REFORMER (RADIANT SECTION)

General (See Figure IV)

The modular reformer is basically a box shaped refractory lined chamber, encasing the tubes.

The reformer tubes are supported vertically in straight rows and are connected to the feed stock header and reformed gas header systems by means of small bore tubes called pig tails. These pig tails protrude from the top and bottom of the furnace respectively.

The feedstock and steam flow downwards inside the catalyst filled reformer tubes. The heat for reaction is supplied by the products of combustion passing co-currently down the furnace outside the tubes.

The flue gases from the furnace flow into flue gas coffins or chambers of firebrick construction which run the entire width of the furnace. These are situated between the rows of tubes. The openings or ports in these coffins offer a resistance to flow which ensures even distribution of the flue gases within the furnace box.

The flue gas coffins empty into a refractory lined collecting duct which is located along the entire length of the furnace. This duct transfers the flue gases to the Convection section. See Figure IV.

MODULAR CONCEPT

The MODULAR concept entails the detailed design of a standard module or section of the steam reformer which is repeated until the reformer is of the required size. The module consists of 2 rows of reforming tubes and their associated burners. It can contain up to 74 tubes and is designed such that it may be repeated with respect to process, mechanical, and structural considerations. It is the prime requirement of the concept that extrapolation of the basic design is eliminated.

Reformer Tube

The reformer tubes packed with catalyst are simply guided and part supported on steel work below the furnace hearth plate.

The tubes are generally centrifugally cast 25% Cr - 20% Ni - 0.4% Carbon alloy steel. 24% Cr - 24% Ni - 1.5% Niobuim steel which has a higher stress valve may be used in place of the above material but the economics must be calculated on a case by case basis.

Burners

The burners are arranged in rows on each side of the tube lines and are fired vertically downwards. The burners can be designed to fire either liquid, or gaseous fuels or combinations of both. Normally forced draught combustion air (either ambient or heated) is used. With gaseous fuels the burners can be designed to be self inspirating.

Inlet and Outlet Header System

The inlet and outlet header systems consist of a number of subheaders arranged symmetrically about the furnace and these headers are connected to the tubes by inlet and outlet pigtails.

Each inlet header is connected to one row of tubes by small bore pipes called pig tails. These pigtails are designed to absorb, the horizontal expansion of the headers, the vertical expansion of reformer tubes and self expansion. These small bore pipes also assist even feedstock distribution to all reformer tubes by having a significant pressure drop through them.

Each outlet header is connected to two rows of tubes by small bore tubes called outlet pigtails made from 32% Ni - 20% Cr (Alloy 800). These pigtails are designed to accommodate both vertical and horizontal expansions of outlet headers and self expansion of the pigtail.

The reactants outlet sub-headers are fabricated from 32% Ni - 20% Cr material. Each subheader has a central tee connection and transition piece to the refractory lined main which transfers the product to the next process unit downstream of the reformer.

CONVECTION SECTIONS FOR LARGE REFORMERS

With increasing capacities of reforming furnaces the convection section duties have increased proportionately. The steam generation on a 5,000 Te/day Methanol plant can be as much as 1,500,000 lb/hour.

During the last decade, maximum steam pressures on reforming plants have increased from 400 to 1500 psig. Due to the above factors, convection sections have changed and are now in design similar to conventional type of power station boiler plant.

Convection sections must be "purpose" designed to meet the individual mechanical requirements and operational flexibility of the individual plant.

In determining the performances of convection sections the following factors must be considered.

i Thermal Design

Correct thermal design is most important, operational problems are encountered with oversurfacing while undersurfacing means a lack of performance.

ii Cavity Radiation

Cavity Radiation emitted by the furnace refractory and the flue gases coming from the radiant box are directed at the first heat transfer unit in the convection section. This radiation is dependant upon the flue gas temperature and the volume of the cavity upstream of the first unit, but is independent of the output of the plant. It is then necessary to safeguard convection units with varying operating duties from this constant source of cavity radiation.

If the first unit in the convection section was a process steam superheater, this unit would have a varying heat load dependant upon the process requirement. When the plant is operating at reduced loads or a plant start-up it would be subjected to the full radiation causing high metal temperatures. This results in the choice of higher alloy for the fabrication of the unit which increases the cost and may introduce metallurgical problems not experienced with the lower temperatures and alloys.

Radiant Shield Water Tube Boilers are therefore installed to absorb cavity radiation, and their purpose is:

a To absorb high radiant loads providing the flexibility to include auxiliary firing within the furnace collecting duct. This is sometimes necessary for steam raising and/or process control.

b Protection of downstream units.

iii Flue Gas Distribution

Natural draught furnaces have known problems of gas distribution in furnace "bridging" sections due to relative low gas velocities. With the MODULAR furnaces induced draught is provided, giving higher gas velocities which offer ideal gas distribution and the elimination of unbalanced gas temperature streams.

iv Induced Draught

Higher rates of heat transfer are achieved with an induced draught system offering more compact designs. Convection sections need not conform to the radiant box dimensions, and can be designed to suit the individual plant requirements.

In the Modular furnace waste gases are collected in a separate duct, elsewhere and the convection section is independent of main point.

v Compact Tube Banks

Economic use of tube configurations and pressure drop evens out irregular flow patterns or irregular firing of auxiliary burners in modular furnace collecting duct.

This is a particular problem area in side-fired furnaces. Normally their design constraints result in the supply of units that are both long and narrow, and have large bore heat transfer tubing which can give maldistribution of flue gases and uneven metal temperatures.

vi Circulation

Boiler Water circulation is a most important factor. Usually failures of boiler systems can be attributed in one form or other to circulation problems eg:

a Pump failure in forced circulation systems.

b Dry-out caused by water loss.

c Interference with circulation by extraneous matter.

d Water chemistry causing build up of deposits, or corrosion in high flux zones with subsequent failures.

Circulation can be either Natural or Forced.

Natural Circulation Systems are preferred as they do not require any "prime movers", circulation is maintained by the "thermodynamics" of the system. Higher circulation rates exist with Natural Circulation Systems than with Forced circulation Systems.

With modular designed furnaces, the natural circulation systems is always offered.

vii Materials

Careful selection of materials to cater for all conditions of operation and start up duties. As stated in this text the design of the Modular furnaces convection section assist in reducing the serverity of the various operating conditions and makes for safer designed units.

viii Steam Drums

Steam drums must be adequately sized, not only to provide steam of high quality demanded by modern chemical plant, but, also to provide a sufficient reserve of water "hold up" to maintain circulation to "radiant" steam generators during emergency conditions.

ix Air Preheat

Combustion air preheaters improve the overall efficiency of the units, and these are becoming increasingly important as fuel prices continue to rise. For large reforming furnaces, rotary regenerative airheaters are economically more attractive than the conventional shell and tube types.

x Flexibility of Operation & Control

Controlled supplementary firing in furnace collecting ducts can be incorporated to produce additional steam which may be required to obtain the optimum steam/power balance.

The control of steam superheat is by adjustments of firing rates and/or the use of spray water attemperators at an intermediate stage in the steam superheater.

The facility for bypassing flue gases around heat transfer units is incorporated in the design.

Further supplementary firing at intermediate points in recovery duct is a further method of control which is sometimes incorporated.

Manufacture

Where possible, units should be designed to minimise field erection. During shop manufacture more stringent control can be applied to material identification, workmanship, inspection and non-destructive testing. Field erection costs are usually more expensive than "shop" charges.

STRUCTURAL DESIGN OF LARGE STEAM REFORMING FURNACES

Radiant Section

The structure forming the radiant section of the Modular Reforming Furnace can be considered in three separate parts :-

1 Top Housing - supporting and providing weather protection to the process pipework the burners and to the suspended refractory brickwork.

2 Casing - supporting the refractory brickwork, burners and reforming tubes, and providing weather protection to the brickwork forming the walls.

3 Sub-frame - supporting the casing and providing a rigid "table" over which the casing is free to thermally expand. This thermal expansion takes place radially from an anchor point and movement is guided on the rectangular axes of the furnace.

All the design methods and fabrication techniques used for the structural steelwork of the radiant section are as specified in standard structural codes.

In accordance with the modular concept the major part of the structural steelwork of the radiant section is formed by assembling a series of standard designed and shop fabricated units. Included in this category are all hearth frames, side and end casing panels, intermediate columns, beams supporting the suspended refractory roof and the top housing members. By using standardised units, fabrication time and erection periods are minimised and the possibility of fabrication errors reduced.

The maximum size of the radiant section is not governed by steelwork design, considerations. The modular concept has eliminated almost all the structural design problems which are encountered in designing large conventional furnaces.

Convection Section

The structural steelwork of the convection section duct is of similar construction to that of the radiant section although it is purpose designed. Prefabrication is maximised to reduce the erection period.

When designing the structural steelwork arrangement for the duct, consideration is given to the initial installation of boiler and superheater units; also to their removal and replacement should there be a failure during operation.

Sections of steelwork are provided which can be easily removed, normally complete with the refractory insulation.

As with the radiant section, thermal expansion of the steelwork of the duct is catered for by the provision of expansion joints at strategic places and PTFE sliding bearings in the case of a horizontal duct. Spring suspension systems are installed where the convection section is a vertical duct.

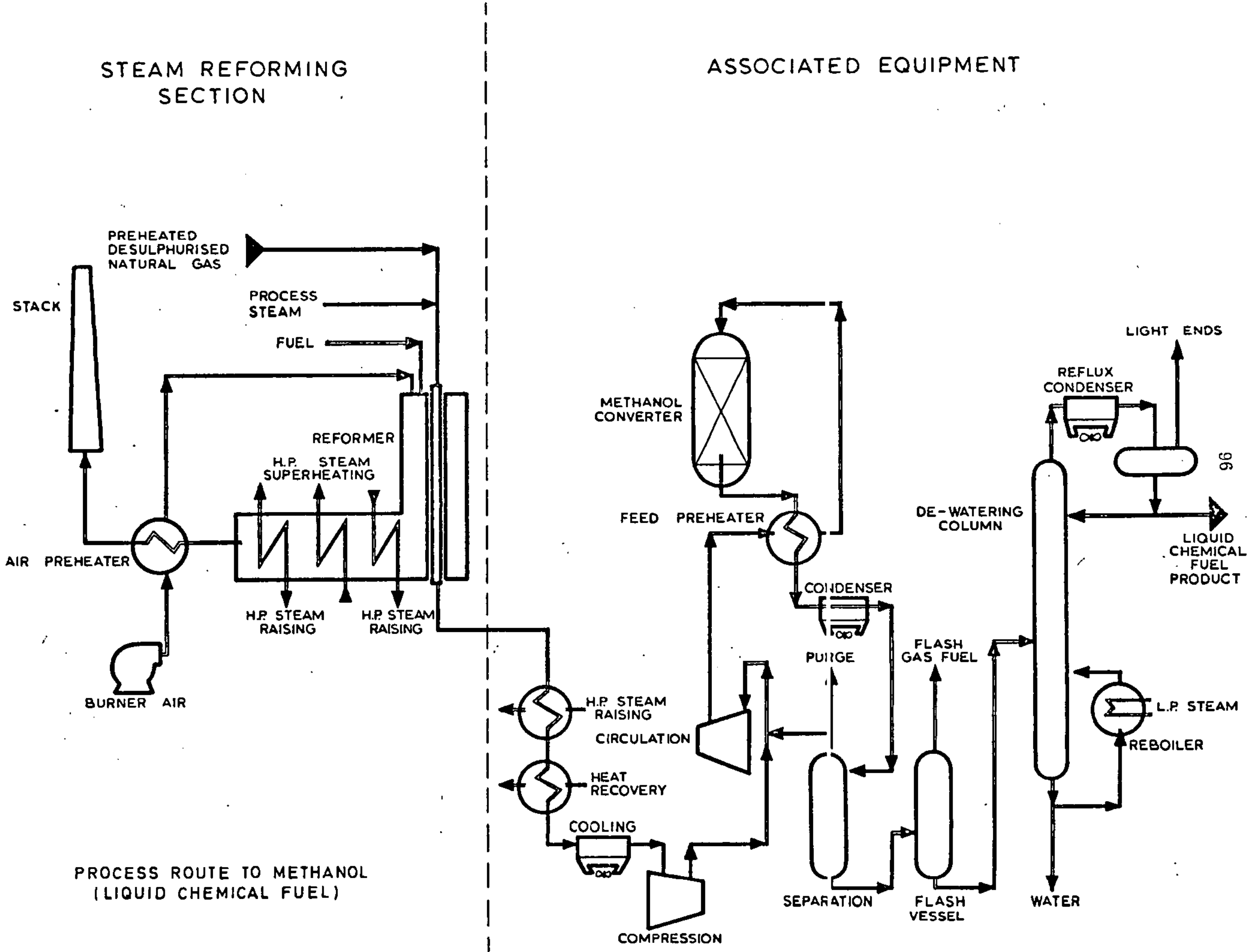
Conclusion

The energy shortage in certain areas of the world is leading the suppliers to investigate various methods of transporting the readily available natural gas from areas such as the Middle East to these areas in need of energy.

One method that is gaining interest and support is to produce and transport "fuel quality methanol".

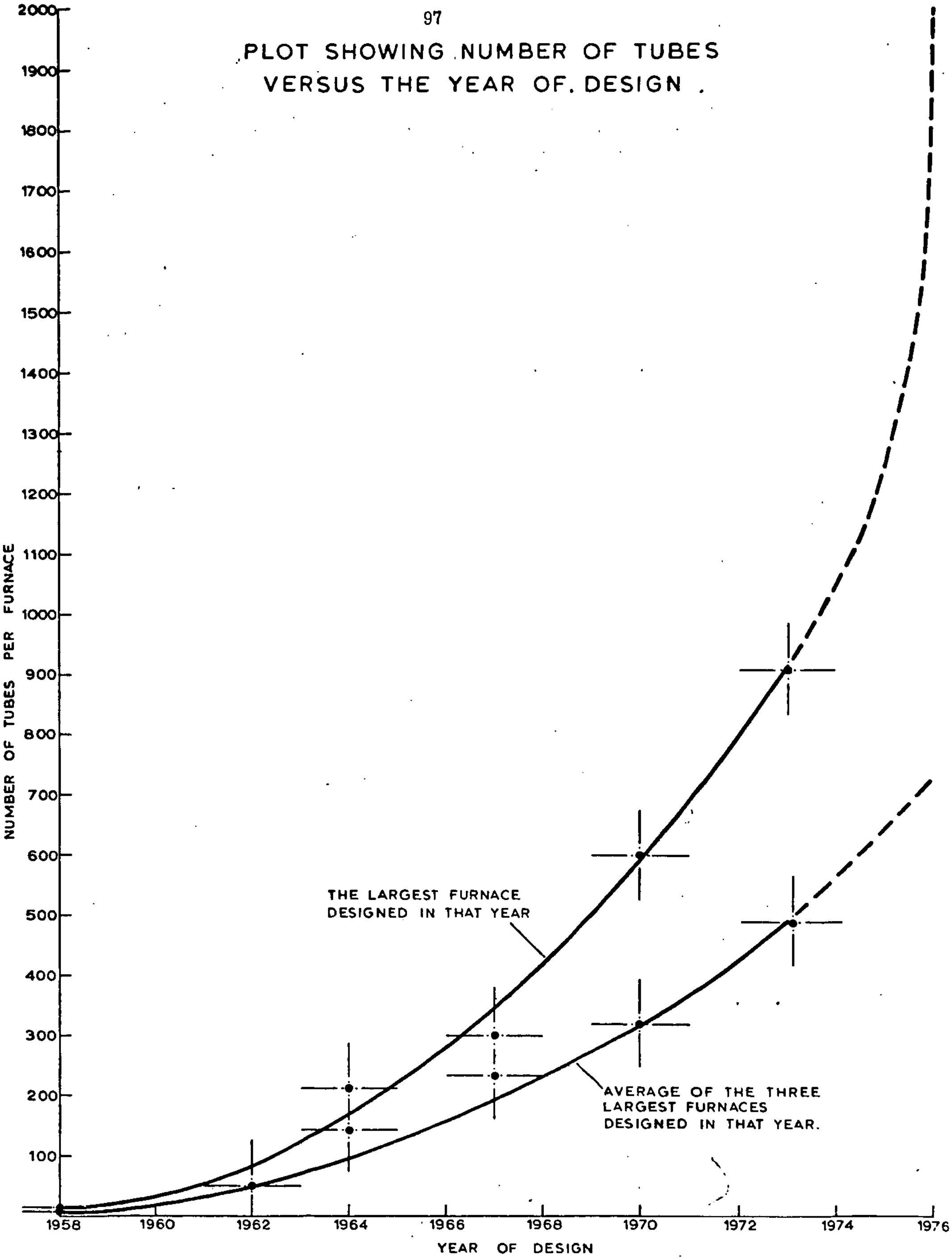
Economic studies indicate that 5,000 TPD methanol plants are the optimum size. The critical item in these plants is the steam reformer and this paper discusses the various types of reformer available. Side fired furnaces are considered unsatisfactory for this duty due to their basic design precluding this type of furnace from increasing in physical size.

The vertically fired modular type furnace as developed by Davy Powergas, has the design capability to increase in size. The worlds largest furnace is designed to this concept, and from the design, erection and operating experience gained from this furnace we describe a steam reformer satisfactory in all aspects to meet the new requirements in the production of fuel quality methanol.



PROCESS ROUTE TO METHANOL
(LIQUID CHEMICAL FUEL)

Figure I

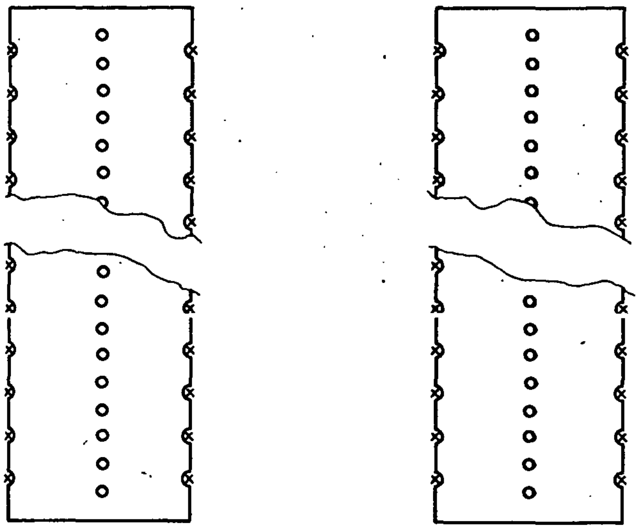


PLOT SHOWING NUMBER OF TUBES VERSUS THE YEAR OF DESIGN.

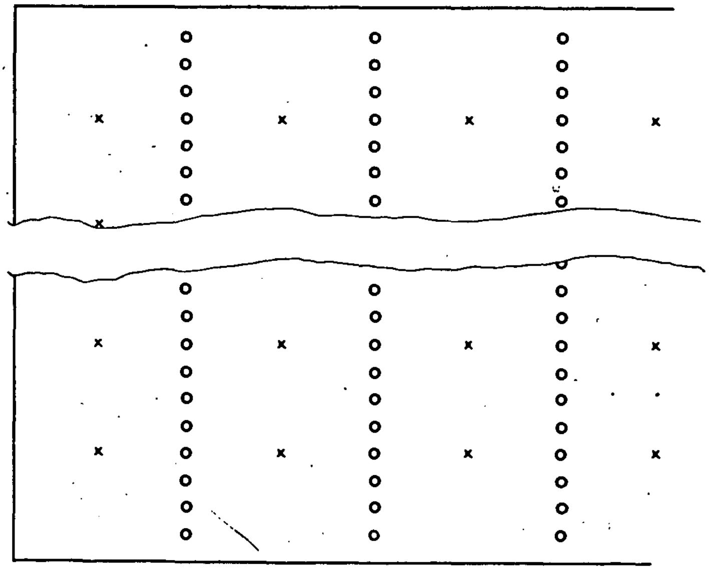
Figure II

PLAN VIEW OF SIDE FIRED FURNACES

SHOWING NEED FOR 2 REFRACTORY SIDE WALLS
FOR EACH ROW OF TUBES



x BURNERS
o REFORMER TUBES

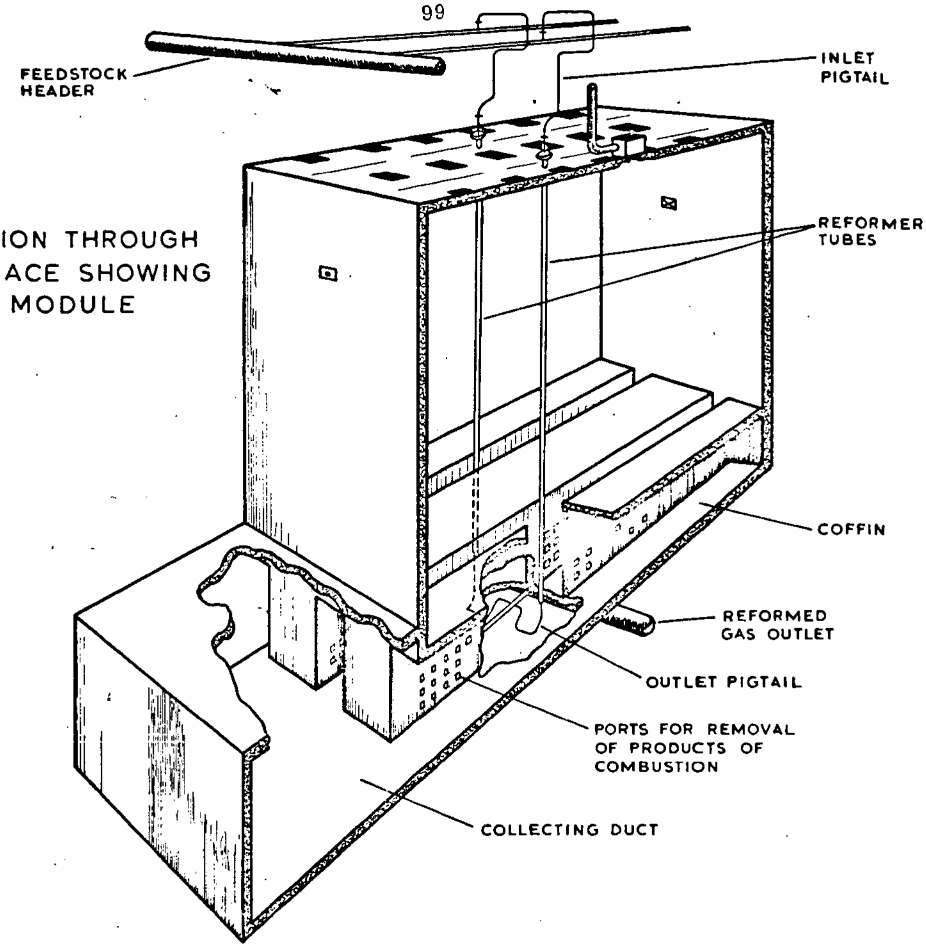


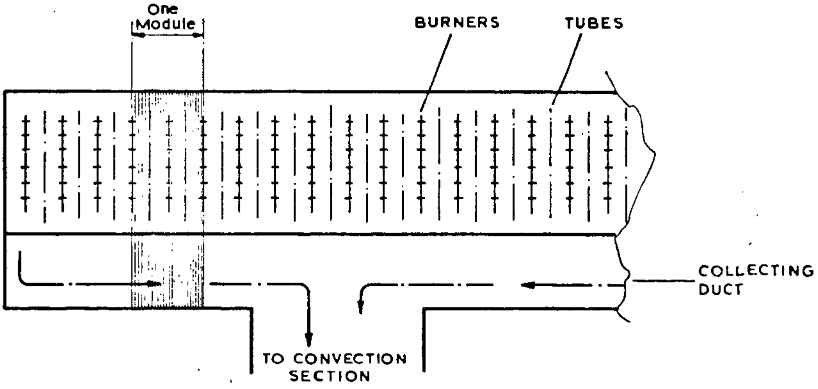
PLAN VIEW OF A VERTICALLY FIRED FURNACE

INTERMEDIATE REFRACTORY WALLS BETWEEN TUBE ROWS
ARE ABSENT FROM THE DESIGN

Figure III

SECTION THROUGH FURNACE SHOWING ONE MODULE





PLAN VIEW

Figure IV

CLEAN FUELS FROM COAL - AN ALTERNATIVE TO SNG

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INTRODUCTION

A major portion of current coal gasification research is directed toward processes for production of substitute natural gas (SNG). These processes rely typically on relatively low temperature, high pressure gasification to enhance methane yield in the gasifier, followed by extensive water gas shifting and acid gas removal, and finally a catalytic methanation step. Those portions of the SNG processes most critical to their success—high pressure gasification and methanation—are farthest from being proven technology.

The Methyl Fuel process, however, produces a clean liquid fuel, primarily methanol, from synthesis gas produced at medium pressures bypassing the problems of high pressure gasification. The process, shown schematically in Figure 1, is composed of operations each of which has been proven in commercial applications.

PROCESS DESCRIPTION

Synthesis begins with steam/oxygen gasification at 22 atm. or below and at temperatures well above 1500K (2240F). These conditions insure rapid reaction rates and high carbon utilization, with minimal problems in coal handling and feed. Steam gasification is accomplished in the upper chamber of a two-stage suspension gasifier, with heat being provided by combustion with oxygen of ungasified char recycled to the lower chamber. The resulting synthesis gas is virtually methane-free, consisting principally of hydrogen, steam and carbon oxides. Gasifiers of this type have been available commercially for many years. One example is the Belle, W. Va., gasifier built by B&W for duPont in the early 1950's.

Particulate removal is achieved by a cyclone system, which recycles the bulk of the unburned char back to the combustion zone of the gasifier, followed by a venturi-water scrub system which also cools the "make" gas.

Gaseous sulfur compounds are removed by a conventional hot carbonate scrubbing system, which also removes a portion of the CO_2 produced in the gasifier. Elemental sulfur is recovered as a salable byproduct in a conventional Claus plant. The sweetened synthesis gas is then reacted catalytically with steam in a water gas shift reactor to adjust the relative concentrations of hydrogen and carbon monoxide for Methyl Fuel synthesis. Shift requirements are about two-thirds of those needed for methanation.

A second hot carbonate scrubber removes most of the remaining CO_2, which is vented to the atmosphere. Hot carbonate systems were chosen here because of their well-known commercial acceptance and economy for removal of large quantities of acid gas, although other systems, such as the Rectisol system could also be used. In the latter case, methane absorption would be no problem in the Methyl Fuel process.

The sweet synthesis gas is then dewatered and compressed for alcohol synthesis, the degree of compression depending on the synthesis process used. In this study, we have chosen the Vulcan-Cincinnati, Inc. high pressure process partly because of the rugged nature and regenerability of its zinc-based catalyst.

Composition of the gas at this point is hydrogen and carbon monoxide in about a two-to-one ratio, with small amounts of CO_2, water, nitrogen, and methane. The carbon oxides react with hydrogen over a catalyst to form methanol and small amounts of higher alcohols and water. A condenser removes liquid products, which pass to a small refinery operation for purification. The finished product, trademarked Methyl Fuel, is a clean, sulfur and nitrogen-free liquid fuel suitable as a blending agent for gasoline and a substitute for light fuel oils. The fuel has a gross heating value just over 5500 kcal/kg (10,000 Btu/lb), and burns cleaner than natural gas.

A preliminary process study has shown that for suspension gasification without char recycle, where carbon losses are about 12 percent, we can expect an overall thermal efficiency of about 63.5 percent for the process. These figures are based on actual performance of the B&W Morgantown gasifier built for the Bureau of Mines in the early 1950's(1).

The above thermal efficiency seems low compared to efficiencies of 65-70 percent now being reported for competitive SNG processes, suggesting that some means may be available for improving process efficiency. Because of the nature of the high temperature gasification process, only a small number of products (CO, CO_2, H_2 and H_2O) are formed in significant quantities in the gasifier; and these are related through a mass balance and shift equilibrium. Thus a very simple expression can be derived to show the effects of certain gasification variables on Methyl Fuel production and thermal efficiency. Methyl alcohol is formed through the reactions:

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (1)$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \qquad (2)$$

which are related through the water gas shift reaction,

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad (3)$$

A simple molar balance based on these reactions shows that the maximum production of methyl alcohol is directly proportional to the moles of carbon monoxide and hydrogen formed in the gasifier, assuming that a shift converter is available to optimize the relative concentrations of CO and hydrogen, and that reactions (1) and (2) go to completion:

$$[CH_3OH] = 1/3\ ([CO] + [H_2]) \qquad (4)$$

If gasification is complete and methane and tar formation are negligible,

$$[CO] = [C]_f - [CO_2] \qquad (5)$$

$$[H_2] = [H_2]_f - [H_2O] \qquad (6)$$

$$[O_2]_f = [CO_2] + 1/2\ [CO] + 1/2\ [H_2O] \qquad (7)$$

where $[C]_f$, $[H_2]_f$ and $[O_2]_f$ are the moles of carbon, hydrogen and oxygen fed to the gasifier, excluding char recycle since it is already included in the coal feed, but including hydrogen and oxygen in the coal and steam feeds; and $[CO]$, $[CO_2]$, $[H_2]$ and $[H_2O]$ are the moles of carbon oxides, hydrogen, and steam in the synthesis gas leaving the cyclone separators. Substituting and rearranging,

$$[CO] + [H_2] = 2([CO]_f - [O_2]_f) + [H_2]_f \qquad (8)$$

From equation (4), then, recognizing that neither carbon gasification nor methyl alcohol formation may go to completion, and that side reactions occur

$$[CH_3OH] = n_M \frac{2(n_G [C]_f - [O_2]_f) + [H_2]_f}{3} \qquad (9)$$

where $[CH_3OH]$ is the maximum number of moles of methyl alcohol produced, n_M and n_G represent the conversion efficiencies of methyl alcohol synthesis and gasification, respectively. Then $n_G [C]_f$ represents the number of moles of carbon leaving the gasifier as gaseous carbon oxides. For the purpose of this paper, we will assume complete conversion in the Methyl Fuel synthesis loop.

EFFECT OF CHAR RECYCLE

Using Equation (9), one can determine the effects of char recycle, CO_2 recycle, and steam addition on overall product yield and thermal efficiency. The B&W Morgantown gasifier may be used as a reference, producing 2.641 kmoles of Methyl Fuel for each 100 kg of West Virginia coal. Addition of char recycle raised the carbon utilization efficiency to 95 percent, the production of Methyl Fuel to 2.894 kmoles, and the overall thermal efficiency to 69.3 percent.

EFFECT OF CO_2 SUBSTITUTION

Substitution of CO_2 for oxygen represents one method for reducing oxygen costs. Off-gas from the hot carbonate scrubbers could be compressed and recycled back to the gasifier to take advantage of the Boudouard reaction:

$$C + CO_2 \longrightarrow 2CO \qquad (10)$$

Treating CO_2 as totally gasified carbon and oxygen, equation (9) shows that, with char recycle, a 10 percent molar substitution of CO_2 for oxygen increases the methanol yield to 3.048 moles/100 kg of coal, and the thermal efficiency of the synthesis process to 73.4 percent.

In actual practice, this efficiency would not be achieved since the Boudouard reaction places a heat penalty on the gasifier reducing the amount of process steam available for the remainder of the process. If this heat penalty is made up by combustion of coal in an auxiliary boiler, the overall process thermal efficiency is reduced to 70.6 percent as shown in Figure 2. Further substitution of CO_2 continues to improve the thermal efficiency of the process at the expense of gasification temperature until carbon utilization efficiency decreases, and methane and tars begin to form. At this point, equation (9) no longer holds, and gasification is not suitable for Methyl Fuel production.

EFFECT OF STEAM/OXYGEN RATIO

The effect of altering the steam/oxygen ratio may also be shown by equation (9). Steam substitution has the beneficial effect of increasing the hydrogen yield of the gasifier while decreasing the production of CO_2. Again using char recycle, a 10 percent molar substitution of steam for oxygen also increases the methanol yield to 3.048 moles/100 kg coal, and the apparent thermal efficiency to 73.4 percent. The steam gasification reaction

$$C + H_2O \longrightarrow CO + H_2 \qquad (11)$$

is also endothermic and places a heat penalty on the system. This reaction is less endothermic than the Boudouard reaction, however, resulting in a practical thermal efficiency of 70.8 percent.

The thermal penalties produced by CO_2 recycle and steam substitution are shown in Figure 3, expressed as percent of process heat available compared to that of the Morgantown gasifier. The thermal advantage of steam substitution is quite evident, especially at higher steam/oxygen ratios.

EFFECTS ON GAS TREATMENT

If it is assumed that the feed to the Methyl Fuel synthesis loop is balanced— i.e., in a two-to-one ratio of hydrogen to equivalent CO— then all excess carbon will leave the system as CO_2 via the carbonate scrubbers. Equation (9) and a simple carbon balance

$$[CO_2]_{\text{scrubbed}} = n_G\,[C]_f - [CH_3OH] \qquad (12)$$

will then show the effects of char recycle, CO_2 recycle and steam substitution on acid gas scrubbing load. Figure 4 illustrates these effects clearly, showing CO_2 absorber load as a percent of that required for the Morgantown gasifier case.

Raising carbon utilization efficiency to 95 percent by char recycle increases the ratio of CO to CO_2 in the gasifier and enhances the production of hydrogen. More usable carbon is produced, and the CO_2 absorber load drops to 91.7 percent of its original value. Since acid gas removal represents about 15 percent of the capital cost in a Methyl Fuel plant, and is one of the major users of process steam and electric power, the cost savings are significant.

CO_2 recycle has the effect of increasing the amount of CO_2 that must be absorbed. For every three moles of CO_2 recycled, one additional mole of CO_2 is absorbed. In a practical system, then, the cost of CO_2 compressors, added CO_2 absorber capacity, and additional process steam capacity would tend to offset any advantages due to an increase in overall process thermal efficiency.

Steam substitution has the reverse effect, reducing the amount of CO_2 discarded. For every three moles of steam substituted, two moles of CO_2 do not have to be absorbed. In addition to the capital cost savings, this route represents a more economical use of the process steam, since a typical hot carbonate stripper requires about three moles of steam for each mole of CO_2 absorbed. Operating with char recycle, a 10 percent steam substitution would reduce CO_2 absorber load by about 6 percent.

CONCLUSIONS

With few exceptions, today's SNG processes are years from commercialization or even demonstration. The Methyl-Fuel process, on the other hand, consists of components each of which has been demonstrated commercially, and thus could be readily commercialized. Overall process thermal efficiency is comparable to present SNG processes.

Because of the simplicity of the process and the gasification products produced, a simple expression relates gasifier feeds to Methyl Fuel output. This expression shows that char recycle, CO_2 recycle and steam substitution can all improve thermal efficiency, but all impose a heat penalty on the system. The combination of char recycle and steam substitution has been found most advantageous, since it maximizes thermal efficiency while minimizing the gasifier heat penalty and reducing capital costs and process steam requirements.

REFERENCES

1. P.R. Grossman and R.W. Curtis, "Pulverized-Coal-Fired Gasifier for Production of Carbon Monoxide and Hydrogen," Trans. ASME 76, pp. 689-95 (1954).

FIGURE 1

METHYL FUEL PROCESS FLOWSHEET

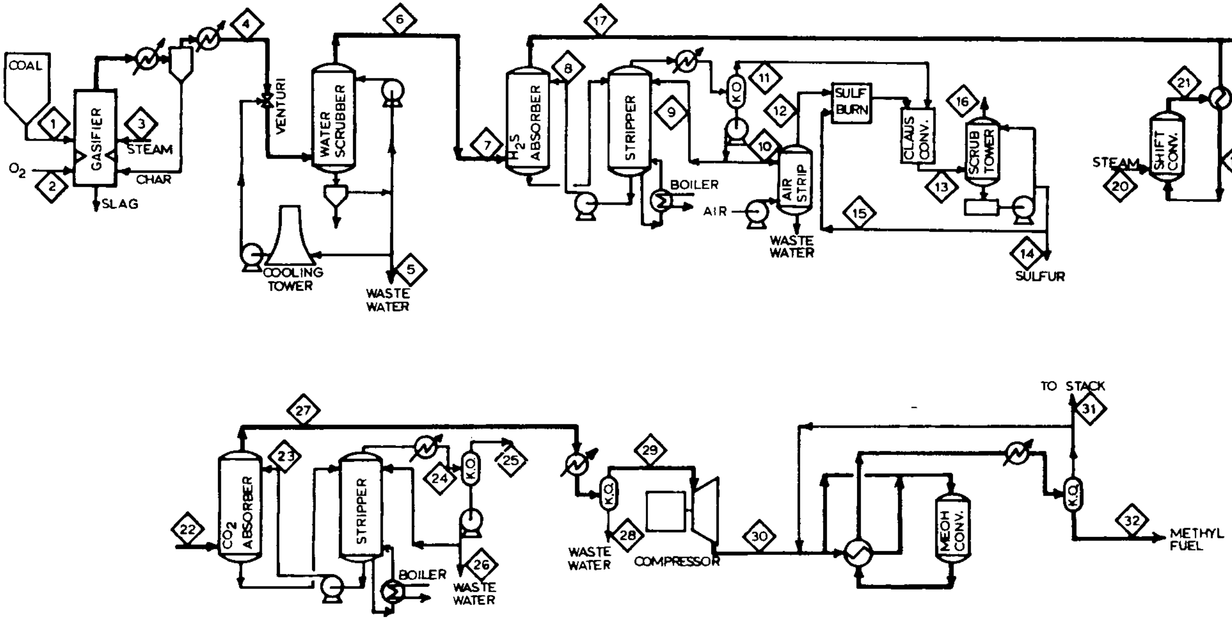


FIGURE 2

EFFECTS OF MODIFICATIONS IN GASIFIER OPERATION-THERMAL EFFICIENCY

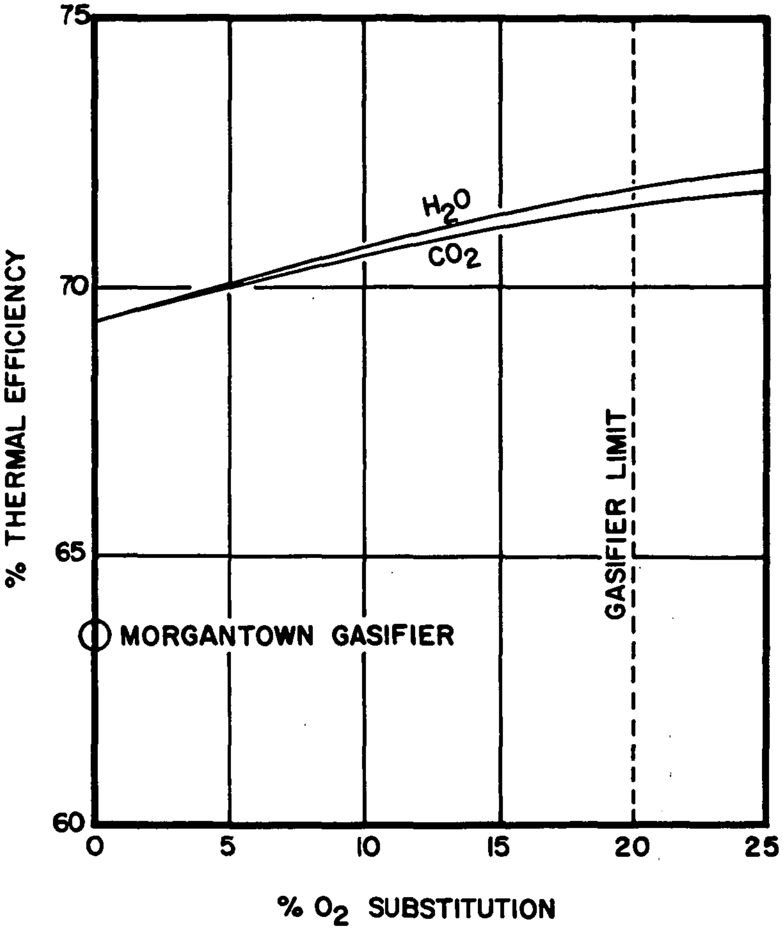


FIGURE 3

EFFECTS OF MODIFICATIONS IN
GASIFIER OPERATION-
ACID GAS REMOVAL

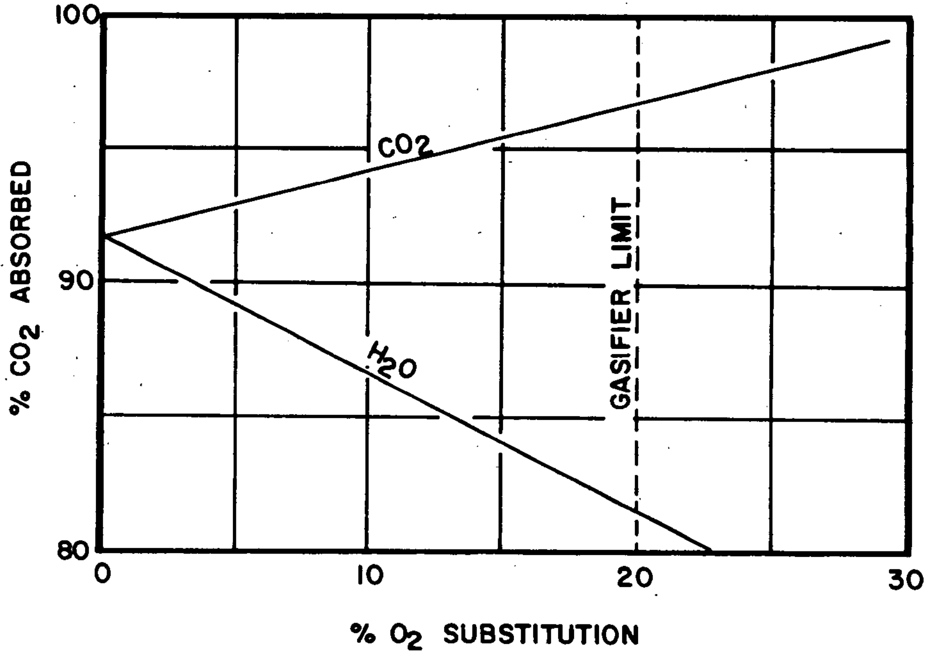
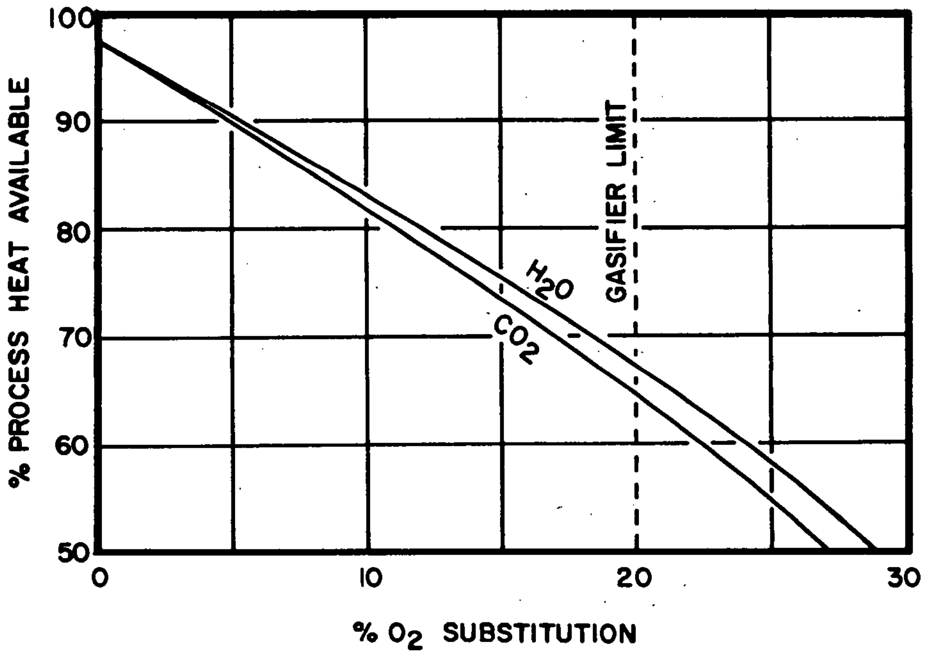


FIGURE 4

EFFECTS OF MODIFICATIONS IN GASIFIER OPERATION-STEAM GENERATION



Methyl-Fuel — A New Clean Source of Energy, David Garrett, T. O. Wentworth, Vulcan-Cincinnatti, Inc., 1329 Arlington, Cincinnatti, Ohio 45225

A new liquid fuel has been developed with all the advantages of natural gas or fuel oil, but which is actually less polluting than natural gas. This liquid fuel, designed for use in power plants, large industrial furnaces and boilers and for gas turbines, is a mixture of predominately methanol with controlled percentages of higher alcohols. The fuel has been named METHYL-FUEL, a trademark registered for Vulcan-Cincinnatti, Inc. The METHYL-FUEL process produces liquid fuel with essentially zero sulfur, nitrogen and metals content, at costs competitive with very low sulfur fuel oils and with imported LNG on a "Btu delivered to burner" basis. Actual combustion tests showed NO_x emissions in flue gas are lower than that for natural gas. METHYL-FUEL may be regasified to methane if desired, at costs competitive with naphtha gasification. METHYL-FUEL may also be added to gasoline as an effective octane improver and gasoline extender replacing lead additives for this purpose. The technology for METHYL-FUEL production and regasification is reviewed and results from combustion tests are discussed.

GASIFICATION OF CHAR WITH SULFUR DIOXIDE

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1.0 INTRODUCTION

The preliminary experiments summarized here were aimed initially at determining optimum conditions for reducing sulfur dioxide to elemental sulfur with char. However, an important secondary objective followed when we found that carbon monoxide (CO) was the main oxidized product generated in the reduction. In other words, this second objective was focused on the possibility of defining a novel gasification system based on the reaction:

$$2C + SO_2 \xrightarrow{\qquad\qquad} 2CO + 1/2\ S_2$$

Finally, supporting experiments were made using Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) to better understand the gasification of char with SO_2.

2.0 BACKGROUND

Because of current environmental considerations, many regenerative processes are being proposed to remove sulfur-containing products from the tail gases of coal burning systems. Some of these processes generate a concentrated SO_2 stream at some point. The SO_2 concentration may vary for the particular process; however, it is generally agreed that the most desirable end product is free sulfur. For example, one such process described in two previous papers,(1,2) is the hot iron/iron oxide desulfurization concept developed by the Babcock and Wilcox Company. Briefly, in this concept, hydrogen sulfide (H_2S) is removed from a fuel gas generated by air-blown suspension gasification of coal. Two overall steps are involved in the desulfurization concept:

$$\mathrm{Fe/FeO_x} + H_2S\ \text{(sour gas)} \longrightarrow \mathrm{Fe/FeS_x} + H_2O\ \text{(sweet gas)}$$

$$\mathrm{Fe/FeS_x} + \text{Air} \xrightarrow{\qquad\qquad} \mathrm{Fe/FeO_x} + SO_2 + N_2$$

After all of the available iron oxide surface scale has reacted to form iron sulfide, regeneration or recovery of the iron oxide is necessary. In practice, this regeneration is accomplished by purging the iron sulfide scale with air to recover iron oxide and a regenerant gas that contains from 10 to 13 vol. percent SO_2 in nitrogen. The overall process concentrates sulfur from less than 1.0 vol. percent in the fuel gas to 10-13 vol. percent SO_2 in the regenerant gas.

In a coal burning process, one readily obtainable reductant is a hot char produced by partial combustion of the coal feed.

The major difference between present-day and earlier coal gasification to medium Btu gas ($CO + H_2$) is the direct use of oxygen in the gasification process. Today, oxygen is used to burn part of the carbon to supply the endothermic heat necessary to drive the gasification reactions. For example, considering coal to be carbon at 1300F, the following reactions occur during oxygen or air gasification:

$$C + O_2 = CO_2 \xrightarrow{\hspace{6em}} \Delta H = -169{,}900 \text{ Btu (exothermic)}$$

$$C + CO_2 = 2CO \xrightarrow{\hspace{6em}} \Delta H = +\ 73{,}500 \text{ Btu (endothermic)}$$

The sum, $2C + O_2 = 2CO$, $\Delta H = -96{,}400$ Btu (exothermic), represents overall gasification with oxygen to yield carbon monoxide and recoverable heat.

Depending on the type of gasifier, the upper temperature level during gasification is of prime concern from the standpoint of reaction rates or kinetics. For example, in air-blown entrainment gasification, the short residence time in the high-temperature zone determines gas quality and the fraction of coal gasified.(3) In other words, any variable that reduces temperature, such as a heat loss or the presence of steam, detracts from gas quality. Using oxygen instead of air, however, generates such extreme temperatures that some steam addition is necessary to moderate gasification temperature. With steam addition, a second heat consuming reaction occurs, $C + H_2O + CO + H_2$, $\Delta H = +58{,}500$ Btu (endothermic).

The disadvantage of oxygen-blown gasification relates to the necessity and expense of providing an associated oxygen plant. However, using air as the oxygen source dilutes the gas produced with nitrogen to reduce its heating value to the range of 100 Btu/Scf as opposed to a theoretical 320 Btu/Scf for pure oxygen gasification. Moreover, nitrogen cannot be economically removed from the produced gas.

3.0 POSSIBLE CONCEPT

A second possible route for producing non-nitrogen diluted CO involves the use of SO_2 as the gasification agent. Sulfur dioxide can be separated from N_2. The following steps might constitute a possible concept for accomplishing this process:

(1) Sulfur is burned in air to produce a gas containing 19-21% SO_2.
(2) Using an acid gas scrubbing system, SO_2 is separated from the inert nitrogen diluent and fed, together with hot char, to a gasifier.
(3) Undiluted SO_2 reacts with hot char to yield CO and elemental sulfur, $2C + SO_2 \longrightarrow 2CO + 1/2\ S_2$.
(4) Product gases from the gasifier are quenched to separate sulfur from the product CO.

4.0 MAJOR CONCERN

From the standpoint of the basic chemistry involved, the area of greatest concern centers around the calculated endothermic gasification of carbon with SO_2. For example, the reaction $2C + SO_2 \quad 2CO + 1/2\ S_2$ at 2200F is endothermic to the extent of 880 Btu/lb of SO_2 reduced (50,400 Btu/mole). This calculation is based on the reaction of carbon in the standard state. The carbon in char may, of course, yield slightly different thermodynamics than carbon in the standard state; however, char may contain other consitutents like ash that react with SO_2. These reactions may provide additional heat.

In considering char gasification with SO_2, one logical question to be addressed is "What differences exist between SO_2 and CO_2?" On the surface, CO_2 gasification of carbon is more endothermic to the extent of 1600 Btu/lb of CO_2 reduced (70,400 Btu/mole). Other differences, as we shall see, center around the kinetics or reaction rates involved.

5.0 EQUIPMENT AND PROCEDURE

Basically, two test rigs were used. For the initial tests, a small (1-inch I.D.) externally heated mullite tube served as the reactor sketched in Figure 1. The feed gases (N_2 + SO_2) were metered and fed to a preheating section where the gas temperature was increased to about 900F. The hot char temperature was in the range of 1600 to 2000F where reaction occurred. As the products exited the reactor, quenching was accomplished by a device designed to condense sulfur by contact with water in a container filled with glass beads. Product gases were analyzed by gas chromatography.

Later tests were made in a 5-inch diameter tube using a fluidized bed of char. This reactor (sketched in Figure 2) consisted of a 36-inch long silicon carbide tube heated by an outer annular furnace firing natural gas. Bed temperatures of 2200F were easily attained in this furnace. Product gas samples were drawn through a water-cooled stainless-steel probe to quench temperature. As before, gases were analyzed by gas chromatography.

Thermal analysis (DTA and TGA) was performed on an instrument manufactured by Tracor. Kinetic measurements of the carbon, SO_2, and CO_2 reaction were made at constant temperature with a modified Tracor TGA balance. For the kinetic measurements, a 15 mg sample of graphite was placed in an inert gas while the system was heated to reactant temperature. At the desired temperature, SO_2 or CO_2 was substituted for the inert gas and the weight loss was monitored.

6.0 CARBON SOURCES

Carbon sources were as follows:

(1) Metallurgical coke (-16 + 30 mesh) with the following analysis:

Proximate Analysis, % of wt.		Ultimate Analysis (Dry), % of wt.	
Volatile Matter	0.5	C -	90.8
Fixed Carbon	92.0	H -	0.2
Ash	7.5	S -	0.7
		N -	0.8
		Ash -	7.5

(2) Coal char from FMC
(3) Pulverized graphite.

7.0 RESULTS

For discussion, the experimental results are broken down into three areas; each area represents a different approach at understanding the gasification step.

1. Bench scale test reactors
2. Differential Thermal Analysis (DTA)
3. Kinetic measurements

7.1 BENCH SCALE TEST REACTOR

Our bench scale test reactors ranged from a small fixed bed to a larger fluidized bed. In the fluidized bed reactor, provision was also made for air addition. The reason of course, for the scale up was to answer questions unanswered by the small reactor.

7.1.1 Fixed Bed Tests

Table 1 illustrates initial test results obtained with the 1-inch I.D. fixed bed reactor. The first two tests illustrated were made with 13 vol. percent SO_2 in nitrogen or a simulated regenerate gas from our hot Fe/FeO_x desulfurization process to determine whether SO_2 could be reduced with hot carbon. The results with both the simulated regenerant gas and pure SO_2 clearly illustrate that carbon was an excellent reductant at temperatures around 2200F and space velocities from 700 to 800. No SO_2 survived the reduction.

The second tests also showed that a significant amount of CO was formed. Unfortunately in the tests with pure SO_2, a significant amount of COS was produced. We felt that COS probably was formed from the gas phase reaction $CO + 1/2\ S_2 \longrightarrow COS$ as the gases slowly cooled while exiting the reactor. In other words, it was not possible to reduce temperature rapidly from 2200F in the small reactor.

7.1.2 Fluidized Bed Test

To quench the product gases rapidly, we switched to the water-cooled sample probe and the 5-inch diameter fluidized bed reactor. The objective, of course, was to reduce the time CO and S_2 were in contact with each other at temperatures from 1800F down to the condensation point of sulfur.

Results from the fluidized bed tests with coke were tabulated in Table 2. No SO_2 survived the reduction; all of the SO_2 fed to the char bed was reduced to elemental sulfur or COS. In comparison to the previous tests, quick quenching the product gases reduced the COS level. With simulated regenerant gas (13 vol. percent SO_2) only a trace of COS survived; however, with pure SO_2 the COS level was still quite high or at least 7 vol. percent.

7.1.3 Air Addition

Since the reduction was calculated to be endothermic, several experiments were made to see how much we could back off the external heat and still maintain the SO_2 - char gasification. This was done by decreasing the heat (natural gas) input to the outer annular furnace. Two other changes were made; i.e.,

(1) Some air was added to the SO_2 but not enough to compensate for the calculated heat uptake of the reaction.

(2) The bed consisted of coal char instead of metallurgical coke.

Results from part of the tests are found in Table 3. The SO_2-to-air ratio varied from 2 to 10 vol. SO_2 per vol. of air. Although the tests were not designated to give quantitative information, we were surprised to find that once the reduction started, it maintained itself without the addition of external heat. In other words, the char - SO_2 gasification approached a heat balanced reaction with some air addition.

7.2 DIFFERENTIAL THERMAL ANALYSIS (DTA)

To better define the relative heat uptake of the char/coke reaction with SO_2 and CO_2, differential thermograms were obtained using the two reactant gases with pulverized metallurgical coke. We found that, because of the highly endothermic fusion of the ash constiutents in the coke at 1800 to 2000F, it was necessary to preheat the coke sample blanketed with inert nitrogen to reactant temperature (2350F). Once the prefused ash had been heated and cooled back to ambient temperature, a second heating cycle in inert gas did not reveal the endothermic fusion of the ash. After one cycle in nitrogen, SO_2 or CO_2 was substituted for the DTA measurements. Two typical curves obtained with CO_2 and SO_2 are illustrated in Figure 3. Negative peaks represented endothermic or heat consuming reactions.

Although the differential thermograms were not quantitative, the results (Figure 3) presented a comparative picture of coke gasification with SO_2 and CO_2. The curves suggested that the CO_2 - coke reaction was far more endothermic at about 2000F where gasification occurs than was the corresponding reaction with SO_2. In fact, the coke - SO_2 reaction was nearly heat balanced.

7.3 KINETIC MEASUREMENTS

The last series of measurements made involved a comparison of the kinetics, or the rate of weight loss versus time of pulverized graphite in SO_2 and CO_2. For these measurements, graphite served as the source of carbon instead of metallurgical coke or coal char. The latter sources of carbon proved to be too reactive for accurate kinetic measurements.

For the weight loss-time measurements, a strip chart recorder was added to the basic X-Y recorder in the TGA apparatus to measure sample weight versus time. The weight loss was plotted as a function of time at constant temperature. Figure 4 illustrates a plot of the fractional weight loss versus time curve for graphite gasification with SO_2 at 2100F.

The simplified model used to interpret the weight loss-time curves assumes:

(a) that the heterogeneous graphite particle mix can be approximated by spheres with an average diameter, initially of r_o, and at some time later as r. The fractional weight loss, fw, is given by

$$fw = 1 - \frac{r^3}{r_o^3} ; \qquad (1)$$

(b) that the reaction of carbon is first order with respect to available carbon atoms; and

(c) that the concentration of SO_2 or CO_2 in a flowing system is constant,

$$\frac{dc}{dt} = -k\ Ca, \qquad (2)$$

where (dc/dt) represents the rate of carbon atom gasification and 'Ca' is the concentration of available carbon atoms on the surface of the graphite particle being gasified. The rate of decrease of the particle radius is constant, or

$$\frac{dr}{dt} = -k' \tag{3}$$

Differentiating equation (1), substituting for 'r' and integrating gives the following expression that relates the fraction reacted (fw) to time (t) by the temperature function of the reaction (k').

$$1 - (1-fw)^{1/3} = k't \tag{4}$$

The use of equation (4) to fit the experimental data is illustrated in Figure 4 by the dashed line. Similar fits are obtained for the other experimental weight loss-time curves.

The spherical model represents only a crude approach at defining the temperature function of the reaction. The Arhenius expression for the rate constant k' is:

$$k' = Ae^{-E/RT} \tag{5}$$

The utility, however, of the simplified approach is that it gives us a means of estimating the temperature-time performance of graphite gasification with SO_2 or CO_2.

From the rate constants, Figure 5 was constructed. These curves represented the time-temperature relationship to gasify 50, 75, and 90 wt. percent of graphite with SO_2 and CO_2. Several points were indicated:

1. The rate of gasification is faster at a given temperature with SO_2 than CO_2. For example, the time required to gasify 50 wt. percent of the graphite at 2300F ranges from 15 minutes for SO_2 to 60 minutes for CO_2 (no thermodynamic limitation at 2300F).
2. The predicted rates apply only for pulverized graphite. Char gasification would give a more rapid rate because of a higher specific surface area.
3. A few seconds at 3000F is worth tens of minutes at lower temperatures for equivalent gasification.

8.0 CONCLUSIONS

From this process oriented study, our conclusions are as follows:

(1) SO_2 in a nitrogen containing regenerant gas can be converted primarily to CO and sulfur by reaction with carbon (char) at temperatures in excess of 2000F.

(2) The gasification of char with SO_2 may proceed along several paths. Some of these may be exothermic such that the overall reaction is nearly heat balanced.

(3) The burning of sulfur in an air atmosphere and the subsequent separation to produce a highly concentrated SO_2 gas may prove to be an economical means of producing a high CO content gas without requiring an oxygen plant.

(4) SO_2 gasification of carbon proceeds at a faster rate at a given temperature than the CO_2-carbon reaction.

In terms of our initial objectives, SO_2 can be completely reduced to elemental sulfur by reaction with hot char. Further, aside from free sulfur, CO is the primary product formed from the reduction.

REFERENCES

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2. Kertamus, N.J., ibid, 18, No. 2 (131) 1973.

3. Sage, W.L., ibid, (211).

TABLE 1 FIXED BED (COKE)

Input Gas Flow Ft^3/hr	GHSV*	Input% SO_2	Avg. Temp. °F	Output %CO_2	%N_2	%CO	%COS	Test Length Min.
6.80	773	13	2230	5	77	18	-----	60
4.384	813	100	2100	32.5	---	43.0	24.5	30
4.384	776	100	2220	11.0	---	42.0	47.0	60

$$\text{*Gaseous hourly space velocity} = \frac{\text{Ft}^3 \text{ of gas/hr @60F}}{\text{Ft}^3 \text{ of bed (initial)}}$$

TABLE 2 FLUIDIZED BED (COKE)

Input Gas Flow Ft^3/min	GHSV	Input% SO_2	N_2	Avg. Temp. °F	Output %CO_2	%N_2	%CO	%COS	Test Length Min.
0.56	1.93	100	--	2240 -	< 1	4	80	7	15
0.9	391	100	--	2100 2250	< 1	5	76	7	35
0.9	315	100	--	2250	6	1	68	22	25
1.9	813	13	87	2000 - 2100	< 1	80	18	1	60

TABLE 3 AIR ADDITION TO SO_2 (CHAR)

Input Gas Flow Ft^3/min	GHSV	Input Gas% SO_2	N_2	O_2	Avg. Temp. °F	Output Gas% CO_2	N_2	CO	COS	Test Length Min.
1.13	276	13	87	----	1800	1	69	24	2.7	85
1.1	264	14.2	84.9	.903	1900	< 1	84	17	1	250
0.683	252	15.6	83.5	.945	2060	< 1	62	35	2.0	300
0.379	138	89.2	8.5	2.3	2210	< 1	3.7	87.0	9.2	153
0.45	164	100	----	----	2240	11.6	---	79.7	8.6	153

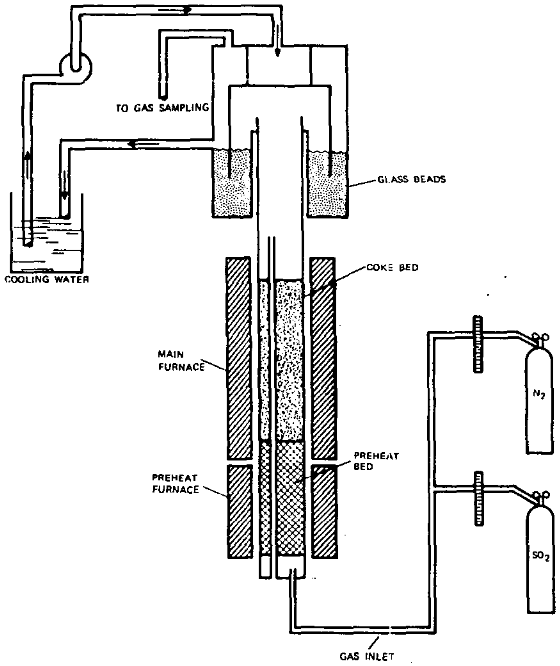


FIGURE 1. FIXED BED GASIFIER

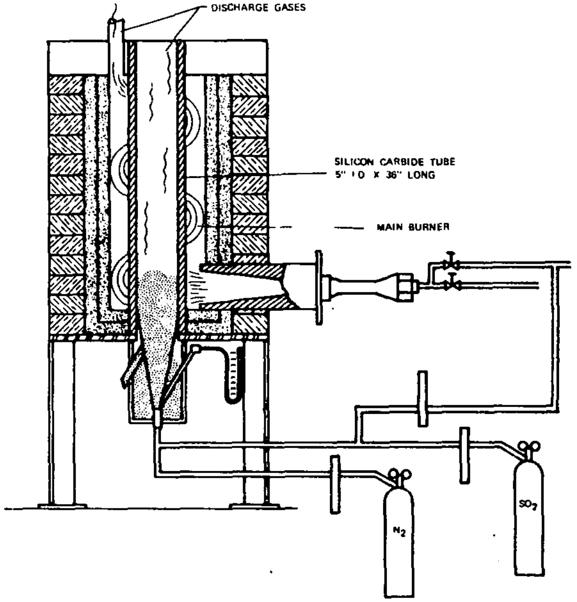
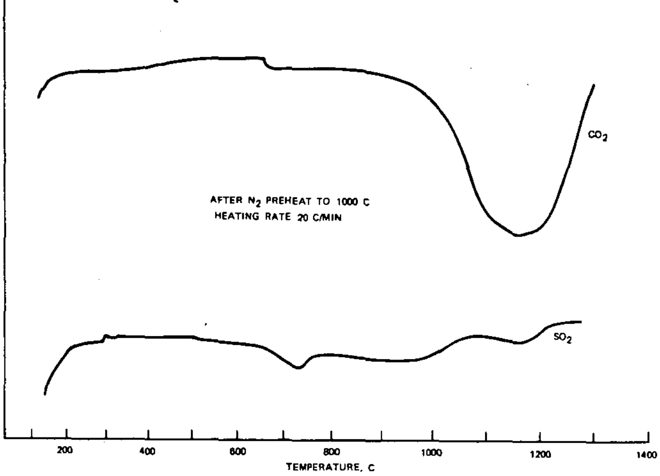


FIGURE 2. 5-INCH FLUIDIZED BED REACTOR

FIGURE 3. DIFFERENTIAL THERMAL ANALYSIS OF METALLURGICAL COKE IN CO_2 AND SO_2



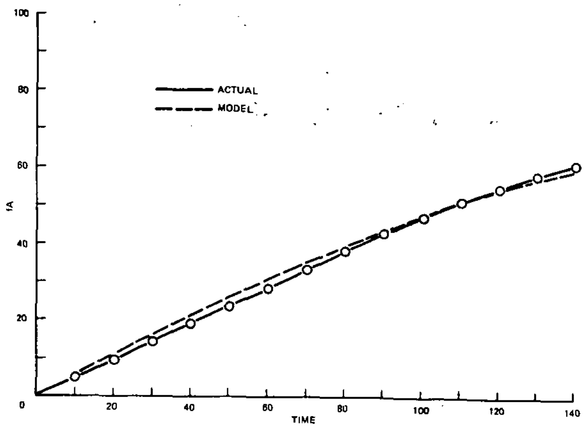


FIGURE 4. FRACTIONAL WEIGHT LOSS VS. TIME
GRAPHITE + SO_2 AT 2100 F

FIGURE 5. GASIFICATION OF GRAPHITE