COAL GASIFICATION -ROUTES TO AMMONIA AND METHANOL

by

F. C. BROWN, B.Sc.(Eng), A.C.G.L, M.I.Chem.E.
and
H. G. HARGREAVES, B.Sc, F.I.Chem.E., F.I.GasE.

HUMPHRIES AND GLASGOW LTD.

Paper read before The Fertiliser Society of London
on 18th October, 1979

TABLE OF CONTENTS

Page

COAL GASIFICATION -
ROUTES TO AMMONIA AND METHANOL

1. SUMMARY

The production of ammonia or methanol from coal starts with the gasification of coal Most older gasification processes operated at around atmospheric pressure, while modern developments use higher pressures. The two main advantages of the latter route are a reduction in compressor power consumptions, and much more compact gas cleaning equipment.

Comparison of two high pressure with two low pressure processes shows that for both ammonia and methanol production, the high pressure routes have advantages in bdth capital investment and coal consumption. Of the two high pressure gasification processes, the Texaco entrained flow system gives the simpler flowsheet, but the British Gas Corporation/Lurgi Slagging gasifier has the higher efficiency.

2. INTRODUCTION

In this paper it is our intention to demonstrate the effects of pressure gasification on the flowsheet of ammonia and methanol plants when compared with low pressure processes. It is not suggested that the flowsheets shown are necessarily the only ones suitable for these products or that they are necessarily the best. They represent the utilization of proven technology and, in the case of the older processes, they are the routes which are commonly offered commercially. Each scheme has been considered only in terms of a single product although it is quite likely that many future plants will be constructed to make several products from the same gasifier exit gas. In fact, we are currently working on a flowsheet where, after removal of sulphur compounds and CO_2, the gas is cryogenically separated to yield fractions used to manufacture ammonia, methanol and fuel gas for combined cycle power generation.

Several features of coal gasification processes distinguish them from processes based on natural gas, naphtha and even heavy fuel oil. Coal is much more variable than any of the other feedstocks and not all gasifiers can handle the whole range of coals. Coal based plants are much more complex and expensive than reforming processes. For this reason, a theoretically more efficient process may be rejected in favour of a simpler and cheaper process. The older processes have a lot of operating experience which often reduces rather than enhances confidence. Newer processes have little or no commercial operating experience and are often judged on highly expectant promotional data. Over the next few years, largely due to government financed projects in Western Europe and the USA, a great deal more will be understood about these processes.
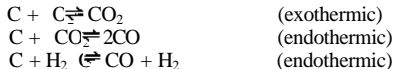
3. CHEMISTRY OF THE GASIFICATION PROCESSES

Coal, like other fossil fuels, is basically a mixture of compounds of carbon and hydrogen, but also containing appreciable amounts of oxygen, nitrogen, sulphur and mineral matter. For the manufacture of ammonia or methanol, we need to convert as much of the coal into hydrogen or carbon monoxide as possible, and in the case of light sulphur-free hydrocarbons, this is normally done by the endothermic reaction between steam and hydrocarbon, known as steam reforming. For example:

$$CH_4 + H_2 \rightleftharpoons CO. + 3H_2 \qquad \text{(endothermic)}$$
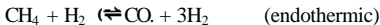
This can be carried out at moderate temperatures (around 800°C) in the presence of a solid catalyst which is packed in tubes, and the heat for the reaction is supplied by the external combustion of some fuel.

In the case of heavier hydrocarbons and coal, this catalytic route is not possible, and higher temperatures are required. The coal gasification processes to be described all involve partial oxidation of the coal, which is an exothermic reaction, to provide heat for the other reactions. Considering only the carbon in the coal, the following are three of the main reactions taking place:

$$
\begin{aligned}
C + C &\rightleftharpoons CO_2 & \text{(exothermic)} \\
C + CO_2 &\rightleftharpoons 2CO & \text{(endothermic)} \\
C + H_2 &\rightleftharpoons CO + H_2 & \text{(endothermic)}
\end{aligned}
$$

This is obviously an oversimplification, but it gives some idea of the desired reactions. Additionally, some byproducts are formed: about 90% of the sulphur forms hydrogen sulphide, and methane is formed both by the reverse of the steam reforming reaction shown above, and by the reaction between hydrogen and carbon:

$$C + 2H_2 \rightleftharpoons CH_4 \qquad \text{(exothermic)}$$

The yield of methane, an undesirable byproduct for syngas applications, is very dependent on reaction conditions, and is minimised by high temperature and low pressure.

In order to avoid the introduction of large quantities of nitrogen into the gas, which is then difficult to remove, the oxygen should be supplied as pure oxygen, rather than as air.

For ammonia production, the carbon monoxide is readily converted to hydrogen by the shift reaction ;

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

6
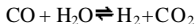
Then, after purification, the hydrogen is mixed with nitrogen and ammonia is produced by the high pressure synthesis reaction over an iron catalyst:

$$3H_2 + N_2 \rightleftharpoons XNH_3 \qquad \text{(exothermic)}$$

In the case of methanol synthesis, some carbon monoxide is allowed to remain in the gas, and methanol is synthesised catalytically:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \text{(exothermic)}$$

4. THE EFFECTS OF PRESSURE GASIFICATION

4.1 Effect on the Gasification Process

The available gasification processes are, as we have seen, all partial combustion processes. This means that at some point in the gasifiers the temperature is very high, generally very much higher than commercially available metals are able to withstand. Consequently, an effective, reliable refractory has to be found that will keep the metal of the shell in a suitable temperature range to enable low alloy material to be used.

For operation at pressure a means has to be found to introduce safely granular or powdered coal into a hot pressure vessel. Up till now the economic solution of this problem has probably been the biggest obstacle to efficient pressure gasification. A corollary of gasifying coal is that the ash has to be removed safely and efficiently from the same vessel. The only significant process effect is that as the pressure is raised the residual methane increases for a constant gasifier operating temperature.

We see at once that the major effect of pressure is to increase the material and mechanical problems associated with the gasifier. The increase in methane in the product gas is generally very small so that it can normally be ignored, or the gasifier temperature can be increased by a few degrees to obtain much the same value as at a lower pressure. In this paper we shall see how four gasification processes cope with these problems.

4.2 Effect on the Upgrading Process

With all the added problems which have to be faced when a gasifier is pressurised, why should we want to operate at pressure? There are two main reasons. The first and most important is to effect a very big reduction in compression power and cost; the second is to reduce the size of plant.

Whether a gas is produced under pressure or not the amount of gas made from a ton of coal is very much the same. The volume of gas product compared with the oxygen feed is very large. When the gasification is carried out at about 55 bar the power saving compared with a similar atmospheric pressure process is 15-25 MW for a 1000 MTD ammonia plant.

The space saving at pressure is partly due to a reduction in the number of gasifiers; for example, the Texaco gasifier output is nearly linear with pressure. However, the major reduction in plot area of the process units is in the dust removal equipment. Low pressure processes require large numbers of cyclones followed by wash towers, with electrostatic precipitators for final cleanup. The gas then needs a gas holder to smooth out production variations before a very large compressor can compress it to 30-50 bar. These items take up a very large portion of the process area. The pressure processes are able to remove dust to the same level as obtained by an electrostatic precipitator, using reasonable pressure drop through a venturi or similar scrubber. Not only does his part of the plant require much less space, it is also very much cheaper than the same part of the atmospheric pressure plant. However, some of the pressure processes have high cost units concerned with preparing the coal and introducing it at pressure into the gasifier.

5. THE PRODUCTION OF AMMONIA

5.1 **Introduction**

This paper is based on the results of a study carried out by Humphreys & Glasgow. For this, we considered two pressure processes and two atmospheric or close to atmospheric pressure processes. The pressure processes are Texaco, using a coal water slurry feed system, and the British Gas Corporation/Lurgi Slagging Gasifier, operating with a lock hopper feed system. The low pressure processes are Koppers Totzek, at just above atmospheric pressure, and Winkler, which can be operated at 1-4 bar pressure. Both of the low pressure processes use screw feed systems.

Both Texaco and the Slagging Gasifier can be considered as second generation processes. The conventional Lurgi process is not considered separately since it is felt that the Slagging Gasifier will be sufficiently developed to be offered by the time any new coal gasification project is required. Its consumption and performance figures compare favourably with those of the conventional Lurgi but its big advantage is the very large increase in output of dry gas per gasifier.

Each gasifier system will now be considered in turn. The descriptions correspond to the figures at the end of this paper. It is not the intention of this paper to concern itself too much with gasifier details. However, those features which affect the overall scheme will be highlighted.

5.2 Koppers Totzek Process (Fig. 1)

This is the most widely used gasification system for ammonia production. The KT gasifier is fed with pulverised coal 70% of which can pass through a 200 mesh screen. In the screw feeders it is mixed with steam and oxygen and then partially combusted atl600-1800°C in the gasifier, which has either two or four feeders. The ash melts and some forms a thick layer on the thin refractory lining of

the shell of the gasifier. This molten ash runs out into a slag quench tank attached to the base of the gasifier. The steam raised by the quenching action flows up through the gasifier to leave with the hot gases through an exit in the top of the gasifier. In this exit there is a small water spray to cool the gas down below the ash fusion temperature so that the ash dust does not stick to the surface of the radiant boiler located vertically immediately above the spray.

After passing through the radiant boiler the gas turns and enters another boiler before it enters a wash column. The gas from the wash column then enters a wet mechanical contactor where more dust is removed as a slurry. The gas is then finally cleaned of dust in an electrostatic precipitator. The dry clean gas is then held in a holder before being compressed to about 30 bar for sulphurous gas removal.

The gas from a KT gasifier contains about 11% of CO_2 and generally less than 1% of sulphur compounds, about a tenth of which are COS. The sulphurous gas removal process should be very efficient and selective to produce a gas off the stripper containing about 30% H_2S, so that the Claus unit will operate efficiently. The gas remaining after sulphur removal should contain less than 1 ppm of sulphur. So far these conditions have been most easily achieved using the cold methanol (Rectisol) process. Other processes like Sulfinol, Selexol, Alkazid have been used with some measure of success.

After sulphurous gas removal the gas is normally compressed to about 50 bar before being saturated with water for carbon monoxide shift conversion. For ammonia plants it is essential to convert as much CO as possible. The economic limit with 3 beds is to achieve a residual CO level of about 3%. A conventional iron oxide shift catalyst is used.

After carbon monoxide conversion the gas is dehumidified and cooled down to — 50° C for CO_2 removal in the second part of the Rectisol plant. This process is very efficient at removing the CO_2 down to a few ppm. The two parts of the Rectisol unit are integrated. The sulphurous gases are removed by a stream of liquid taken from part of the way down the CO_2 absorber which has a CO_2 loading equivalent to that of the CO_2 partial pressure in the H_2S absorber. The liquid fed to the top of the CO_2 absorber is the regenerated fluid from the H_2S stripper.

There are four streams of regenerated gas leaving the Rectisol plant, a sulphur-rich stream to the Claus unit, a sulphur-lean stream to the Claus incinerator, a pure (98% plus) CO_2 stream and an impure CO_2 stream from the nitrogen stripping stage.

After CO_2 removal the cold gas enters the Nitrogen Wash section. Remaining traces of CO_2 are removed by a molecular sieve while the CO, CH_4 and most of the argon are removed cryogenically by condensation and washing with liquid nitrogen. The purge gas from this unit is used for firing the steam superheater since all of the waste heat derived steam produced in the plant is saturated.

The gas leaving the top of the column is warmed up, and more nitrogen is

9

added to correct the hydrogen:nitrogen ratio before the gas is compressed for ammonia synthesis. The pressure of the ammonia loop is likely to be between 150 and 250 bar. Since the make-up gas is pure, the loop is about 15% smaller than an equivalent output loop on a conventional natural gas-based plant.

The ash from the gasifier is separated in the form of a slurry and generally sent to settling ponds where the supernatent liquid runs off. The small amount of ammonia and cyanide in the gas are dissolved in water in the wash system. The cyanide reacts with iron compounds in the ash to be completely eliminated. However, in some plants it has been found advantageous to let some HCN remain in the gas stream. This inhibits the formation of elemental sulphur in the Rectisol unit which can be a nuisance as it blocks heat exchangers. There is also a small tendency for elemental sulphur to be formed in the raw gas compressors. There is a build up of solid sulphur and sulphur compounds which it has not so far proved possible to eliminate completely. Part of the problem is due to the very high oxygen use which results in a few ppm of SO_2 being present in the gas.

Another gas problem with this flowsheet is due to the nitric oxide which is present in the raw gas up to about 70 ppm. If this is not removed it is condensed out as a solid in the nitrogen wash unit. This not only blocks the exchangers but could cause more serious problems. It has been found that high levels of iron in the humidifier section of the CO shift unit catalytically reduce the NO to nitrogen in the presence of ammonia which is there primarily to prevent corrosion.

The KT process is particularly high on power requirements; for a 1000 MTD plant the major compressors have a total power of about 75 MW. The steam production in the gasifier boilers is just about sufficient for the CO shift system. Some boiler feedwater heating or steam raising is available in the CO shift system and in the ammonia synthesis loop, but the bulk of the energy requirements must be met by steam raised in the auxiliary boiler. The plant can be made much cheaper if imported electric power is used to power all the machinery.

5.3 **Winkler Process** (Fig. 2)

The Winkler Gasifier can be operated, according to the Licensor, up to a pressure of 4 bar. This gasifier is a very large throughput gasifier for such low pressure operation. One of the largest gasifiers is just sufficient to make enough gas for 1000 MTD of ammonia.

The coal is crushed to under 8 mm and provided it contains under 18% of water need not be dried. It is advisable not to feed too many fines to the gasifier as they are easily transported out before gasification is complete. The bed is fluidized by steam and oxygen, the rates and ratio of which are adjusted to give the necessary bed temperature of between 850 and 1000°C. The older the coal the higher the temperature. The process works best on reactive young coal when the operating temperature is about 900°C. The operating temperature with young coal is mainly determined by the need to eliminate benzene in the outlet

gas.

Some of the oxygen is admitted toward the top of the fluid bed. This has been found to improve the proportion of the feed which is gasified and helps to reduce the hydrocarbon emission. However, since a fluid bed is very close to a perfectly mixed system the ash which is drawn off will contain the same proportion of combustible char as in the bed. In fact the char content is arranged so that the ash has good combustion characteristics.

The gas leaving the top of the fluid bed is cooled in a waste heat boiler before dust removal. The main advantage of pressure operation is that venturi scrubbers can then be used to reduce the final dust loading to the same sort of figure as would be obtained from an electrostatic precipitator. The bulk of the dust that is carried over is removed by dry cyclones and is combined with the char and burnt in the auxiliary boiler. About 15% of the char is lost in the wet scrubbing stage and is generally rejected along with the ash from the boiler.

Since the gasifier operates at below the ash fusion temperature it uses less oxygen than Koppers Totzek unit in spite of not having such a high carbon efficiency. The residual methane is also a little higher at about 2% but this is unimportant when a nitrogen wash unit is being employed.

Since the amount of ash being carried over is very large, erosion of the boiler surface is a problem with this gasifier as it is with the KT gasifier. However, the operation of the gasifier itself is always very safe. Even if the oxygen flow is doubled for a short while there is no immediate danger, due to the high inventory of the bed with its coal residence time of over 1/2 hour. A similar mismatch on the Koppers Totzek gasifier would be much more serious and would require an immediate shutdown for safety.

After raw gas compression the gas is processed in exactly the same way as for the Koppers Totzek process route. Once again the bulk of the process steam is produced from the gasifier waste heat and although the overall energy requirements is still large the main gas compressors take between 5.0 and 8.0 MW less than the Koppers Totzek process. The higher figure corresponds to operation at the higher gasification pressure.

There is no serious effluent problem as cyanide in the char slurry is again rendered harmless by the iron present in the ash. The process gas stream contains less nitric oxide than the Kopper Totzek gas due to the lower gasification temperature.

5.4 **British Gas Corporation (BGc)/Lurgi Slagging Gasifier** (Fig. 3)

This gasifier is a development by BGC of the conventional Lurgi gasifier. The gasifier works at 25-30 bar pressure and has countercurrent flow of reactants and products. In this way a large amount of the fresh coal is carbonised before it is gasified. Consequently the product contains tar, light oils and a high level of methane apart from the normal gasification products CO, CO_2 and H_2. This feature is particularly useful when making Substitute Natural Gas (SNG), but

means that further reforming is necessary before the gas can be used for ammonia or methanol synthesis.

Coal is crushed and the 15-25% of undersize is separated for use in the auxiliary boiler plant. The remainder is then fed to the overhead lock hopper of the slagging gasifier from where it is discharged into the gasifier the top of which is at about 550°C. The coal first dries and then pyrolises as it increases in temperature while moving down the bed. At the base of the bed the coal char is gasified with oxygen and steam at a sufficiently high temperature to fuse the ash which leaves through a slag tap at the base of the gasifier.

The gas from the top of the gasifier is cooled to 160°C to condense most of the tar and some of the other hydrocarbons present. The tar is separated from the water and hydrocarbons and some is pumped back to the gasifier where it is sprayed on to the top of the coal bed. This decreases the carry-over of coal dust. Most of this tar re-evaporates and leaves with the gas; surplus tar can be recycled and gasified.

The hot moist gas is warmed up and more steam is added before it is passed over the CoMo type shift catalyst. Apart from converting carbon monoxide most of the COS is also hydrogenated. The CO can be reduced to about 3.0 mol percent. This gas is then cooled down before entering the Rectisol unit.

The Rectisol unit is designed to remove selectively virtually all of the sulphur compounds plus a little CO_2 in the first part of the absorber and the remainder of the CO_2 in the second part of the absorber. The remaining carbon monoxide and methane are then removed in the nitrogen wash unit.

Since the purge gas from the nitrogen wash unit contains so much methane it is compressed to 30 bar and reformed with steam in a conventional tubular reformer. The gas leaving the reformer is cooled and then the carbon monoxide is shifted in a high temperature stage. The gas is cooled and then returned to the main stream at the Rectisol stage.

The pure synthesis gas from the nitrogen wash has its nitrogen level adjusted before it is compressed into the ammonia synthesis loop.

The molten slag from the gasifier is quenched with water in the slag lock hopper. The solid is then discharged and the slag is separated for disposal. Part of the water is discarded and part is recycled to the slag hopper.

The tar, oil and water mixture goes to a tar separator where the tar settles at the bottom in a dusty layer which gets clearer towards the top. Above the tar is a layer of dirty phenolic water and above this is a layer of light oil. The bottom portion of the tar is recyled to the gasifier, the top portion is disposed of or gasified, and the light oil is taken off and distilled. The distillate is used as reformer fuel in this application. The phenolic water is treated with a solvent to remove the phenol and related compounds. They are recovered from the solvent by distillation. The remaining liquor is steam stripped to remove H_2S, ammonia, etc. before it is sent for biological treatment. This extensive plant requires considerable space and utilities.

12

5.5. **Texaco Coal Gasification Process** (Fig. 4)

This process is a development of the Texaco Synthesis Gas Generation Process for the partial oxidation of heavy fuel oil. Coal is ground, slurried with water to a thin paste, and pumped into the gasifier where it is gasified with oxygen at a high temperature. The gas and molten gas are then quenched with water in the base of the gasifier and the ash is discharged through a lock hopper. The gasifier can be operated at pressures up to 175 bar and produces a gas containing very little methane which after processing is ideal for ammonia production.

The coal is crushed and then ground in special mills to give a size distribution which will not only give a strong slurry of low viscosity but will have good gasification characteristics. The finely ground coal is slurried with fresh water and with the soot water returned from the carbon scrubber and slag disposal system. A system of slurry tanks ensures that a constant slurry concentration is maintained for gasification. The slurry is pumped to the gasifier by high pressure slurry feed pumps. These pumps are similar to those used in Urea plant for carbamate duty.

A 1000 MTD ammonia plant would use a gasifier operating at between 55 and 85 bar pressure which represents the limit of available technology for centrifugal oxygen compression and economic nitrogen wash equipment.As the size of plant is increased the pressure would be 75 to 80 bar since this reduces the number of gasifiers required. One of the largest gasifiers will make enough gas at 55 bar pressure for 1000 MTD of ammonia.

In the gasifier the coal slurry is partially combusted with pure oxygen in a special burner. The temperature of operation is just above the slag fusion temperature. Too high a temperature would result in high rates of refractory erosion while too low a temperature would cause large lumps of slag to form which would block the exit to the lock hopper.

The hot gas and slag are quenched in a water bath at the base of the gasifier. The slag solidifies to form a coarse frit. The gas leaves saturated with water and still loaded with unburnt carbon. The slag discharges into a slag lock hopper which is periodically discharged on to a slag screen. The liquid falls into the slag water sump from which it is pumped to the thickener.

The hot gas leaving the gasifier is scrubbed in a venturi scrubber and the carbon water slurry is separated in a knockout drum. The clean saturated gas then goes to the CO shift system. The liquor is partly recirculated to the venturi scrubber and to the quench area in the base of the gasifier. Fresh condensate is fed into the system to supply the venturi scrubber preferentially. Dirty water is discharged from the base of the gasifier and used to heat fresh water before it is cooled and sent to the thickener. The clear water from the thickener overflows into a surge drum where it is mixed with some sour process condensate before being pumped back through the carbon water exchanger into the carbon scrubbing system. The bottoms from the thickener, which contain carbon and fine ash suspended in water, are pumped to the coal slurry preparation tank. The

13

amount of carbon lost with the slag from the slag screen is very small. The carbon efficiency of the gasification stage is about 99% due to the efficient carbon recycle system.

The CO shift system again uses a sulphur resistant catalyst as with the Slagging Gasifier. Due to the quench system there is sufficient steam in the gas to complete the conversion of the CO to a residual value of 3.0% without any further steam addition. As the gas from the second shift reactor is cooled down it is used to heat boiler feed water, raise steam at various pressure levels, and to reboil an absorption refrigeration system.

The process condensate is separated and pumped to the gasification stage as makeup. The gas then enters the Rectisol unit where sulphur compounds and CO_2 are selectively removed. The gas is then further purified in the nitrogen wash unit before it is synthesised into ammonia.

6. THE PRODUCTION OF METHANOL

6.1 **General**

In all cases the gasification stage is carried out in exactly the same manner for methanol production as for ammonia production. The differences are in how the gas is processed. Gas derived from coal gasification contains too much carbon for methanol production. This excess carbon must be removed in the form of carbon dioxide.

Methanol synthesis catalyst is even more sulphur sensitive than ammonia synthesis catalyst; consequently all of the sulphur must be removed before the gas meets the methanol synthesis catalyst. Any purge from the methanol loop is normally used to assist in the superheating of the waste heat derived steam.

6.2 **Koppers Totzek and Winkler Processes** (Figs. 5 and 6)

After sulphurous gas removal at 30 bar the gas is compressed to about 50 bar and is then humidified and partially shifted. The gas is then dehumidified and further cooled before entering the CO_2 removal stage. If this stage can be designed so that any remaining trace of sulphur is removed but about 3% of the CO_2 remains then this is preferred. If this cannot be achieved then part of the gas must be shifted after CO_2 removal to give a minimum level of about 3%, which is essential for good performance and long catalyst life in the methanol loop.

The methanol loop would operate at about 50 bar thus requiring only a gas circulator. After each pass the gas leaving the methanol converter contains about 5% of methanol which is removed by cooling. Now the gas contains small quantities of nitrogen and methane which build up in the loop and are continually purged as they would otherwise slow down the reactions. The Winkler process has a higher methane level and consequently a higher purge rate from the loop.

6.3 Slagging Gasifier (Fig. 7)

The clean gas from the first tar and condensate separation stage contains too much methane for methanol synthesis. To reduce this methane to an acceptable level we have chosen a catalytic partial oxidation process similar to the one that our company used in the design of a methanol plant, taking acetylene plant tail gas as feedstock, in China. However, this catalytic process requires the gas to be sulphur-free; consequently some or all of the CO_2 adjustment and all the sulphur removal is done before the reforming stage. Passing all the gas from the gasifier over the shift catalyst is a good idea as, apart from converting most of the COS to H_2S, it improves the quality of the light oil whicch is condensed out once the gas is cooled after the shift. The Rectisol unit which follows removes the sulphur compounds and the CO_2 selectively. The purified gas is then warmed up to a high temperature before it enters the catalytic reformer. Steam and oxygen are added and the gas leaves the catalyst bed at about 900°C with only a small amount of methane still present. The gas is cooled and if necessary excess CO_2 is removed in a second acid gas removal stage. The gas is then compressed to 50 bar and synthesised into methanol. The purge gas from the methanol loop is used to help superheat the waste heat-derived steam.

6.4 Texaco Gasification (Fig. 8)

Since only part of the carbon monoxide has to be shifted a waste heat boiler could be used after the Texaco gasifier instead of a quench arrangement. At this stage we feel that the simplicity of the quench arrangement plus the unproven nature of the directly connected waste heat boiler leads to the choice of the quench arrangement for methanol plants as well as ammonia plants.

After carbon scrubbing, the gas all passes through the CO shift system to adjust the carbon dioxide to give a suitable methanol synthesis gas. It also reduces the COS level by converting most of it to H_2S. All sulphur compounds and the excess CO_2 are then removed in the Rectisol process.

The Rectisol process must be used in order to give both a concentrated stream of H_2S for the Claus plant and a sufficiently pure gas for methanol synthesis. Other processes are unlikely to meet these two objectives.

If about 3% CO_2 cannot be safely slipped through the Rectisol absorber then part of the product gas will have to be humidified and the CO converted so as to give this level, which is necessary for the methanol synthesis process.

The methanol synthesis will be undertaken at about 50 bar. The type of distillation system will depend on the product specification required. A single column will be sufficient for dewatering; two columns will produce Federal Grade A which is adequate for most uses, while the low ethanol Federal Grade AA specification requires either two tall columns or a three-column system. All the compressors would be driven by steam turbines using mainly waste heat-derived steam.

7. PERFORMANCE AND CAPITAL COST DATA

7.1 General

The four processes have been calculated operating with a sub-bituminous coal analysis. This coal represents a typical moderately high ash coal containing a high level of water most of which is only physically adsorbed.

The figures for process coal have all been calculated from either published data on gas composition at the exit of the gasifiers or from other non-confidential sources. The gas composition out of each gasifier has been calculated to correspond to the following as delivered coal analysis:

H_2	26.14	Mol%
N_2	0.58	Mol %
C	69.59	Mol %
O_2	2.17	Mol%
S	1.52	Mol%
Total ash + H_2O free	100.00	
ash	14.5% ww	
Water	10.0% ww	

Nett Calorific Value (as delivered) 5777 kcal/kg

All the coal figures refer to the "as delivered" coal. The auxiliary boiler has been assumed to have a thermal efficiency of 85%. There is an electrical consumption for each plant to cover all the drives other than those listed below. An absorption refrigeration system is used with all schemes. The following machines are driven by steam turbines:

Air Compressor for Air Separation Unit
Oxygen Compressor
Raw Gas Compressor(s)
Synthesis Gas Compressor and Circulator
Nitrogen Compressor (including any Nitrogen Wash refrigeration)
Rectisol Flash Gas Compressor
Not all these compressors are required for every scheme.

7.2 Ammonia Production

(a) *Daily Consumptions*. Table 1 below gives the consumption of coal for process and power for each gasification process as well as the daily consumption.

Table 1
Daily Consumption for 1000 MTPD Ammonia Production

Process	O_2 Plant Capacity MTPD	Process Coal MTPD	Power Coal MTPD	Total Coal MTPD
Koppers Totzek	1310	1630	800	2430
Winkler	720	1410	410	1820
Slagging Gasifier	570	1250	330	1580
Texaco	1400	1550	300	1850

E ach plant has an additional electrical consumption of between 200 and 300 KW/tonne of ammonia excluding the cooling water pumps but including coal preparation.

(b) *Capital Cost.* Capital costs for the four schemes are summarised in Table 2.

Table 2
Erected Cost (Mid-1978 Basis)

Process	Million US Dollars
Koppers Totzek	200
Winkler	180
Slagging Gasifier	165
Texaco	145

These costs include coal reception, preparation, process units, auxiliary steam plant, cooling water system, treated water unit and ammonia storage. Excluded are buildings and land, escalation, financing charges, working capital, spares, shipping and any construction premiums due to a remote location.

It is estimated that from date of order to completion will take 4 to 5 years.

7.3 Methanol Production

(a) *Daily Consumption.* Table 3 below gives the daily consumption of coal for process and power for each gasification process as well as the daily oxygen consumption.

Table 3
Daily Consumption for 1000 MTPD of Methanol

Process	O_2 Plant Capacity MTPD	Process Coal MTPD	Power Coal MTPD	Total Coal MTPD
Koppers Totzek	1440	1800	540	2340
Winkler	800	1560	390	1950
Slagging Gasifier	1020	1570	290	1860
Texaco	1550	1720	170	1890

Each plant has an additional 200-300 KW hr per tonne of methanol excluding cooling water pumps but including coal preparation.

(b) Capital Cost. Capital costs for the four schemes are summarised in Table 4.

Table 4
Erected Cost (Mid-1978 Basis)

Process	Million US Dollars
Koppers Totzek	180
Winkler	165
Slagging Gasifier	155
Texaco	130

The same qualifications apply as for the ammonia plant costs.

8. COMMENTS ON THE CONSUMPTION AND CAPITAL DATA

8.1 Gasifier Operation

The Slagging Gasifier produces by far the best performance for ammonia and just the best for methanol production. It is unfortunate that this is the process with the least amount of published up-to-date data. Our calculations are based on one gas analysis published following work in 1976 on the large Slagging Gasifier at Westfield in Scotland plus a lot of data published many years earlier on a much smaller research gasifier at the Midland Research Station of British Gas Corporation at Solihull. We have made the simplifying assumption that 10% of the coal is converted into tar, phenol and light oil. This quantity will no doubt vary depending upon the quality of the coal. Another problem with the

18

Slagging Gasifier is that with certain coals there may be 25% of undersize in which case there would be more than is needed for power generation for either ammonia or methanol. This fine coal can, however, probably be gasified by adjustment to the gasification conditions.

The stirrer arrangement in the top of the standard Lurgi Gasifier can also be used in the Slagging Gasifier, thus making the process suitable for a wide range of coals. For methanol production the Slagging Gasifier requires the second gasification stage which makes it much more comparable with the other processes.

The Texaco performance figures are very much influenced by the ash level in the coal. Not only does the ash add to the water required for slurrying, and hence increase the oxygen requirement, but a proportion of the ash joins the carbon in the soot, and is thus recycled to the gasifier. An important subject for process development is a better separation of ash and carbon so that the ash recycle can be reduced. The major power consumers of the Texaco process are the Air Separation Unit and the Oxygen compressor at about 25 MW; consequently, any power saving could be very significant. In spite of the quench system reducing the temperature at which heat is available for recovery, it is still possible to be very efficient with this process. Steam is raised at several pressure levels, the boiler feed water for process and auxiliary steam production is heated and there is still sufficient to power the absorption refrigeration unit. Unfortunately, all this heat recovery equipment is very expensive due to the very corrosive nature of the gas. However, the overall simplicity of the process train from the exit of the gasifier to the ammonia loop helps to keep the overall erected cost to less than that of the other processes.

The Winkler process shows good performance figures and has about the same erected cost as the Slagging Gasifier process. However, satisfactory performance is confined to young coals and dust removal is still a troublesome and expensive area.

The Koppers Totzek process has very poor figures for both ammonia and methanol production. To compensate it has much more operational experience than all the other processes and it can handle successfully almost any coal. The very high operating temperature produces both very low residual methane and refractory corrosion problems. The latter is more significant than the low methane since the Winkler gas with up to 2% of methane is still very suitable even for methanol synthesis.

8.2 Process Routes

It is in the integration of the gasifier with the treatment and synthesis stages that the benefits of certain gasifiers become more apparent.

Both the low pressure processes have great difficulty in removing sufficient particulates from the gas stream. It is important that compressors should handle a very clean gas if seal and impeller life is to be satisfactory. Koppers uses an

expensive electrostatic precipitator to achieve a low dust level while Winkler use most of the pressure increase of their modern gasifier in impact scrubbers to achieve the same quality.

Once the gas is free from particulates it must be compressed for sulphur removal. This gives several problems. The compressor must withstand both sulphur and CO_2 corrosion. Any leak of this gas is very dangerous due to both the H_2S and CO present. Great care has to be taken to minimise the possibility of leaks, especially those caused when dust increases the clearances in seals.

Although the Slagging Gasifier produces its gas at a suitable pressure for sulphur removal and further processing, some of the gas enters the lock hopper and must be recompressed into the process train in order to maintain a high plant efficiency. Before compression the gas must be carefully handled due to its high H_2 S and CO loading.

The Texaco process is the only one where dangerous process gases do not require compression. The only gas which might be put in this category is oxygen, the technology for which is very well understood. Texaco also has the advantage that particulate removal can be very efficiently done in a venturi scrubber. Once the carbon has been removed the gas is then processed in exactly the same way as for the partial oxidation of oil except that the amount of carbon dioxide is much larger.

The Slagging Gasifier only partially reforms the coal; this is a very good feature of making SNG but means that expensive, complex facilities have to be added to reduce the methane to acceptable levels. It is mainly this extra equipment which results in the capital cost of the Slagging Gasifier based plant being greater than that of the Texaco based plant.

When making either ammonia or methanol, processes which use a CoMo shift catalyst stage have several advantages. Over this catalyst COS is hydrogenated to H_2S to give close to equilibrium conditions. Consequently in the Rectisol plant it is very much easier both to remove the bulk of the sulphur compounds selectively and to remove more sulphur compounds in the first stage. In the case of ammonia plants this also has the effect of reducing the sulphur in the CO_2 product which is usually required for Urea production. In methanol plants it should mean that the gas leaving the CO_2 removal stage should be low enough in sulphur not to require ZnO guard in front of the methanol synthesis catalyst.

8.3 Production Economics

(a) *Ammonia.* An expensive sub-bituminous coal costs $25/MT. Taking this price, the difference in coal consumption between the Slagging Gasifier and Koppers Totzek represents a saving of over $20/MT ammonia. Texaco and Winkler occupy an intermediate position, both having a coal cost about $6/MT ammonia less than that for Koppers Totzek. Since other operating cost differences are small compared with the cost of coal, the annual advantage of the Slagging Gasifier over Winkler or Texaco is about $2 million. Now the capital

20

cost difference between Texaco and the Slagging Gasifier is $20 million which would take 10 years to pay off. For this type of plant in Western Europe the maximum payoff period is 3 to 4 years and consequently the capital cost difference would have to be reduced to $8 to $20 million to make the two processes comparable. This could make the Slagging Gasifier more attractive as plant sizes increase since then the capital cost difference per tonne output would decrease.

The Slagging Gasifier could be operated to its advantage in another mode which has so far not been discussed. The purge gas from the nitrogen wash unit which is rich in methane could be used to feed an existing natural gas based ammonia plant, particularly where supplies of natural gas were about to run out, or a more suitable use could be found for them. This could have the effect of considerably improving the economics of the Slagging Gasifier. Another way of using the Slagging Gasifier would be to integrate it with the Texaco process for those locations where sulphur emission regulations are severe. In this case the Slagging Gasifier would be used to make a cheap sulphur-free fuel gas with the undersize coal joining the feed to the Texaco unit. Sulphur removal would be done by a side stream from the main Rectisol unit.

Koppers Totzek has the most expensive plant with the highest consumption. However, their extra experience and more certain construction costs may still lead to this process being chosen particularly for smaller plants and where a wide range of coals is to be handled. The cost data for all the other processes are based on paper studies and it is possible that the price of these may increase more than that of Koppers once an actual plant is ordered. However, the figures for the Texaco process have the backing of a major study which our company is currently carrying out for a US government department.

(b) *Methanol*. The performance figures for three of the processes are very close, with the Koppers consumption again being very much higher. It is in the erected cost advantage that Texaco gain over the others. By operating the gasifier at about 60 bar a very simple flowsheet is obtained with the Texaco process which is clearly reflected in the price. No synthesis gas compressor is required while the duty, and hence cost, of the CO shift and Rectisol units are much lower than with the ammonia route. The extra size of the gasifier and the air separation plant tend to offset this, so that the final price is only $15 million less than for the ammonia plant. The other processes are so much more expensive that the Texaco process would normally be the automatic choice. However, at the moment, a little more operational data is required before too many projects can be committed to this process. Of the more well-tried gasifiers the Winkler process, particularly at 4 bar, would be an interim choice. However, coal-based plants are unlikely to be ordered in any numbers for a few years during which time more experience would be available on the Texaco process from plants in Germany and the USA.

21

9. OPERATIONAL AND ENVIRONMENTAL CONSIDERATIONS

All the extra environmental problems not found on natural gas plants are located around the gasifier and in the separation and disposal of the sulphur from the feedstock.

Due to the low temperature at the top of the bed the Slagging Gasifier produces the biggest liquid effluent problem. It is estimated that the facilities for removing phenol cost over $4 million while tar handling and light oil distillation cost several millions of dollars more. Once these problems are dealt with the Slagging Gasifier has no more problems than the other three processes in the sulphur recovery area.

The two very high temperature processes produce only very small quantities of toxic gases. The small quantity of cyanide reacts with iron in the ash to form harmless ferrocyanides. Ammonia is present in very small quantities and can normally be disposed of without treatment from the gasifier wash liquor blowdown. However, the Koppers Totzek and Winkler processes use ammonia in the humidifier-dehumidifier system to control corrosion. The blowdown from this system must be treated to remove ammonia before it is disposed of. The Texaco system does not have this problem.

With certain coals the lower temperature Winkler process produces aromatic compounds which separate out in the wash system. Apart from needing treatment for environmental reasons, naphthalene is particularly troublesome as it is a solid at room temperature and sticks to heat exchanger and other surfaces causing blockages and poor performance.

All the processes have a heavy metals problem with certain coals. The amount of metals in the ash which dissolve in water is very low but in some areas it is still considered too high and these need to be precipitated and separated before the liquor is disposed of.

All processes are noisy, the coal handling and crushing being particularly difficult to quieten completely. Other noise areas are the reversing vents on the air separation plant and all the process compressors. These are definitely not the sort of plants to build close to residential areas.

It is generally the case that the simpler a plant is, the easier it is to operate. This holds good for these units studied here. The low pressure processes have considerable operational problems in the area of dust removal and raw gas compression. Once past the gasifier the Texaco process has the simplest flowsheet with the smallest number of machines. When this gasification system has more operational experience then its simpler flowsheets for both ammonia and methanol production should make this the easiest of all the processes to operate and maintain. If the gasifier turns out to be less successful, the Slagging Gasifier based routes are more likely to have the advantage.

10. CONCLUSIONS

The low pressure processes are at a considerable disadvantage to the high pressure processes for ammonia and methanol production. In the case of Winkler this is mainly due to the extra costs associated with the raw gas cleaning and compression. It is probable that higher pressure Winkler operation may considerably reduce this disadvantage.

Of the high pressure processes the Texaco process has the simpler flowsheet and a much smaller environmental problem. Once the gasifier is more proven, this is likely to be the best process for ammonia and methanol. The Slagging Gasifier is likely to be developed into an attractive competitor particularly where fuel gas or feed for an adjoining existing plant is required.

MATERIAL BALANCES FOR 1000 MTD AMMONIA PLANT
BASED ON VARIOUS COAL GASIFICATION PROCESSES

Part 1

Components	Feeds to Gasifier	Streams ex Gasifier		Purge Gas ex Nitrogen Wash	Make up Syngas
KOPPERS TOTZEK GASIFIER (Figure 1)					
Gas (kg mol/hr)					
CO₂	–	565		–	–
O₂	1688	–		–	–
H₂	–	1364		60	3675
CO	–	2587		205	–
CH₄	–	5		5	–
CₙHₘ	–	–		–	–
N₂	17	46		208	1225
S Compounds	–	26		...	–
Dry Gas Total	1705	4643		478	4900
H₂O	472	354		–	–
Others (kg/hr)					
Coal (as received)	67960	–			
Char (30% wt C)	–	14000			

Components	Feeds to Gasifier	Streams ex Gasifier		Gas ex Acid Gas Removal	Purge Gas ex Nitrogen Wash	Make up Syngas
WINKLER GASIFIER (Figure 2)						
Gas (kg mol/hr)						
CO₂	–	924		–	–	–
O₂	933	–		–	–	–
H₂	–	2217		3713	37	3675
CO	–	1651		186	186	–
CH₄	–	147		134	134	–
CₙHₘ	–	–		–	–	–
N₂	9	35		35	292	1225
H₂S	–	65		–	–	–
Dry Gas Total	942	5039		4068	649	4900
H₂O	2750	1628		–	–	–
Others (kg/hr)						
Coal (as received)	58500	–				
Char (30% wt C)	–	11900				

MATERIAL BALANCE FOR 1000 MTD AMMONIA PLANT
BASED ON VARIOUS COAL GASIFICATION PROCESSES

Components	Feeds to Gasifier	Streams ex Gasifier	Gas ex Main Shift	Reformed Purge Gas	Gas ex Acid Gas Removal	Purge Gas ex Nitrogen Wash (30% is fuel to fire reformer)	Make up Syngas
SLAGGING GASIFIER (Figure 3)							
Gas (kg Mol/hr)							
CO_2	—	86	1982	308	—	—	—
O_2	720	3	—	—	—	—	—
H_2	—	940	2836	919	3755	79	3675
CO	730	2051	158	47	205	205	—
CH_4	—	256	253	70	323	323	—
C_nH_m	—	15	15	—	15	15	—
N_2	7	29	29	356	1734	508	1225
H_2S	—	58	58	—	—	—	—
Dry Gas Total	737	3438	6331	1700	6032	1130	4900
H_2O	963	1117	2475	551	—	—	—
Others (kg/hr)							
Coal	51250						
(as received)							
Coal Tar	—	16250					
Slag	—	7500					

Components	Feeds to Gasifier	Streams ex Gasifier		Gas ex Acid Gas Removal	Purge Gas ex Nitrogen Wash	Make up Syngas
TEXACO GASIFIER (Figure 4)						
Gas (kg mol/hr)						
CO_2	—	1185		—	—	—
O_2	1765	—		—	—	—
H_2	—	1841		3744	69	3675
CO	—	2107		203	203	—
CH_4	—	43		43	43	—
C_nH_m	—	—		—	—	—
N_2	18	46		46	258	1225
S Compounds	—	73		—	—	—
Dry Gas Total	1784	5295		4035	573	4900
H_2O	741	2186		—	—	—
Others (kg/hr)						
Coal (as received)	64600	—				
Total Water in Coal Slurry	52700	—				
Char (50% wt C)	7850	7850				
Slag	—	9500				

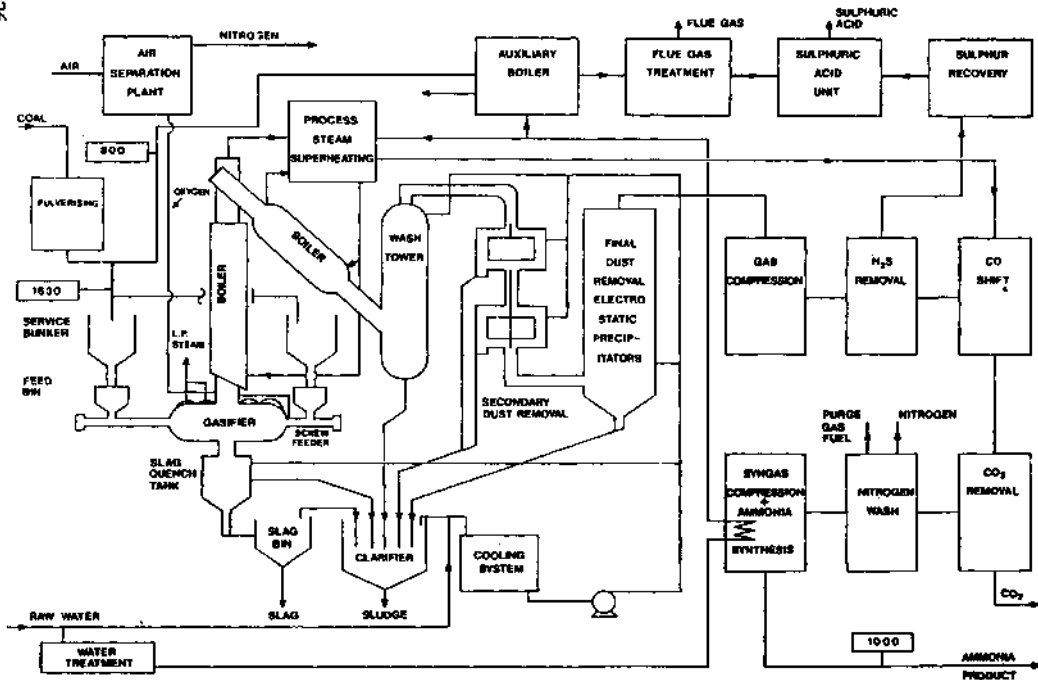Figure 1   1000 MTD Ammonia using Koppers Totzek Process
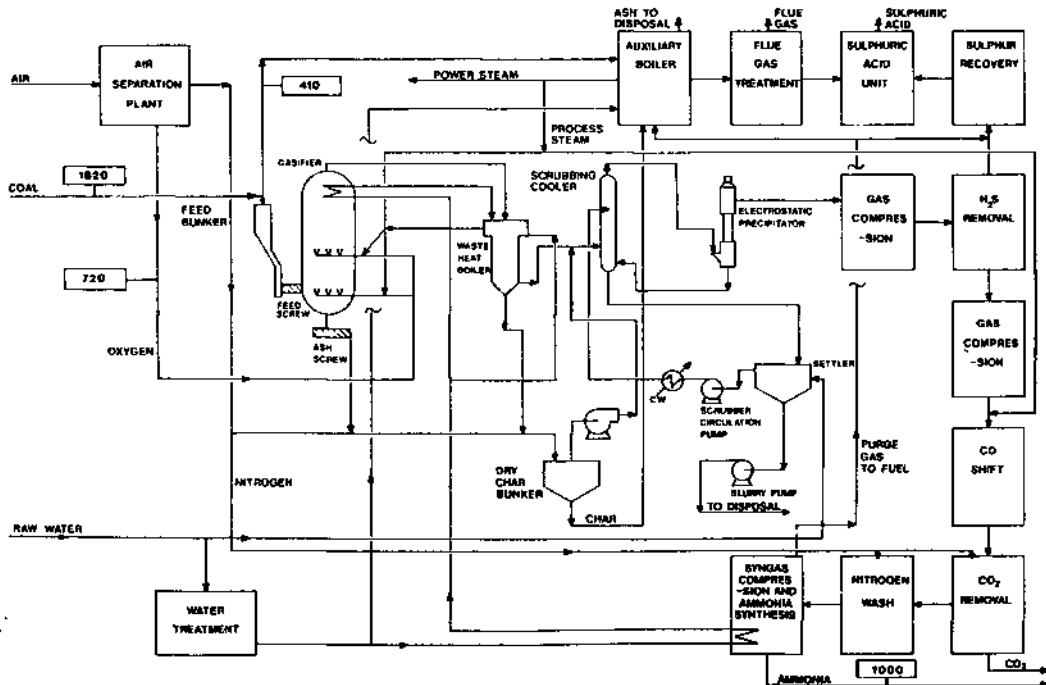
Figure 2. 1000 MTD Ammonia using Winkler Gasifier

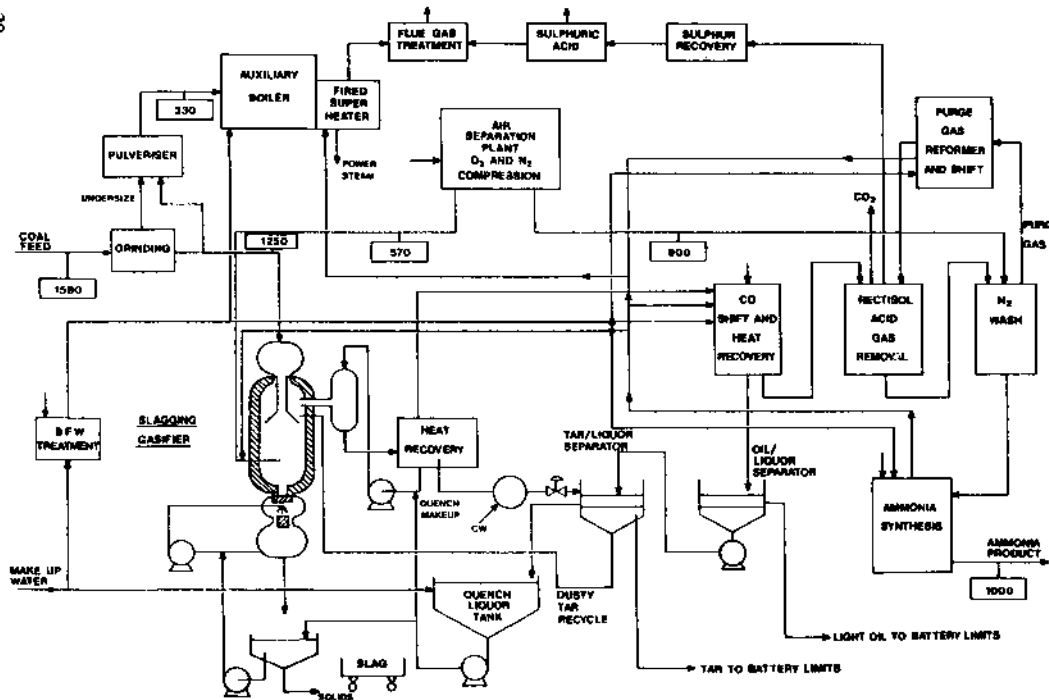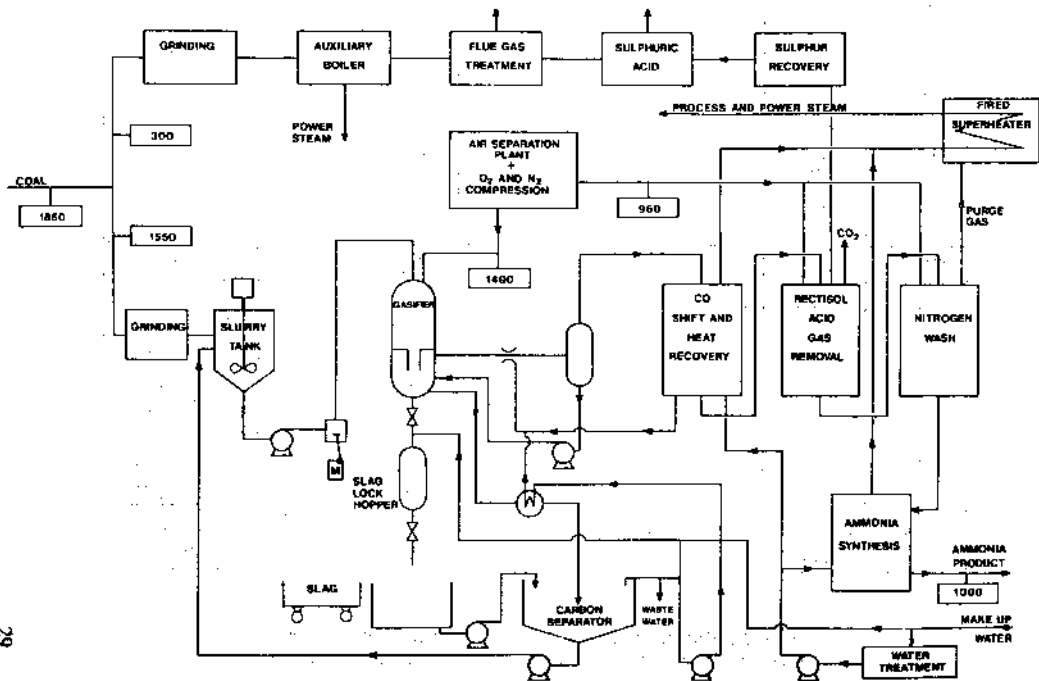**Figure 3. 1000 TE/DAY Ammonia Plant - Slagging Gasifier**

Figure 4. 1000 MPTD Ammonia Plant Texaco Coal Gasification

MATERIAL BLANACE FOR 1000 MTD METHANOL PLANT
BASED ON VARIOUS COAL GASIFICATION PROCESSES

Part 1

Components	Feeds to Gasifier	Streams ex Gasifier			Make Up Syngas	Methanol Loop Purges
Koppers Totzak Gasifier (Figure 5)						
Gas (kg mol/hr)						
CO_2	—	619			135	16
O_2	1857	—			—	—
H_2	—	1496			3019	301
CO	—	2836			1309	126
CH_4	—	5			5	5
C_nH_m	—	—			—	—
N_2	19	51			51	51
S Compounds	—	84			—	—
Dry Gas Total	1876	5091			4519	501
H_2O	520	388			—	—
Others (kg/hr)						
Coal (as received)	75000	—				
Char (30% wt C)	—	15500				

Components	Feeds to Gasifier	Streams ex Gasifier	Gas ex Acid Gas Removal		Make up Syngas	Methanol Loop Purges
WINKLER GASIFIER (Figure 6)						
Gas (kg mol/hr)						
CO_2	—	1028	—		140	23
O_2	1036	—	—		—	—
H_2	—	2461	2889		3029	311
CO	—	1833	1444		1305	122
CH_4	—	163	149		149	149
C_nH_m	—	—	—		—	—
N_2	10	38	38		38	38
H_2S	—	73	—		—	—
Dry Gas Total	1046	5594	4520		4661	643
H_2O	3053	1807			—	—
Others (kg/hr)						
Coal (as received)	64950					
Char (30% wt C)	—	13200				

MATERIAL BALANCE FOR 1000 MTD METHANOL PLANT
BASED ON VARIOUS COAL GASIFICATION PROCESSES

Part 2

Components	Feeds to Gasifier	Streams ex Gasifier	Gas ex Main Acid Gas Removal	Feeds to Reformers	Make up Syngas	Methanol Loop Purges
SLAGGING GASIFIER [Figure 7]						
Gas (kg mol/hr)						
CO_2	—	107	—	—	126	9
O_2	915	4	.	4	—	—
H_2	—	1177	1995	.	3018	301
CO	—	2567	1754	—	1317	134
CH_4	—	321	317	—	—	.
C_nH_m	.	19	19	—	—	—
N_2	9	37	—	4	4	4
$H_2S + COS$	—	73	—	—	—	—
Dry Gas Total	924	4305	4085	408	4465	448
H_2O	1206	1399	—	22778	—	—
Others (kg/hr)						
Coal (as received)	66450	—				
Coal Tar	—	20750				
Slag	—	9600				

Components	Feeds to Gasifier	Streams ex Gasifier		Make Up Syngas	Methanol Loop Purges
TEXACO GASIFIER [Figure 8]					
Gas (kg mol/hr)					
CO_2	—	1345		137	20
O_2	2005	—		—	—
H_2	—	2090		3035	318
CO	—	2392		1310	127
CH_4	—	49		49	49
C_nH_m	—	.		—	—
N_2	20	52		52	52
S Compounds	—	80		—	—
Dry Gas Total	2025	6008		4583	566
H_2O	842	2482		—	—
Others (kg/hr)					
Coal (as received)	71500	—			
Total Water in Coal Slurry	59850	—			
Char (50% wt C)	8850	8650			
Slag	—	10500			

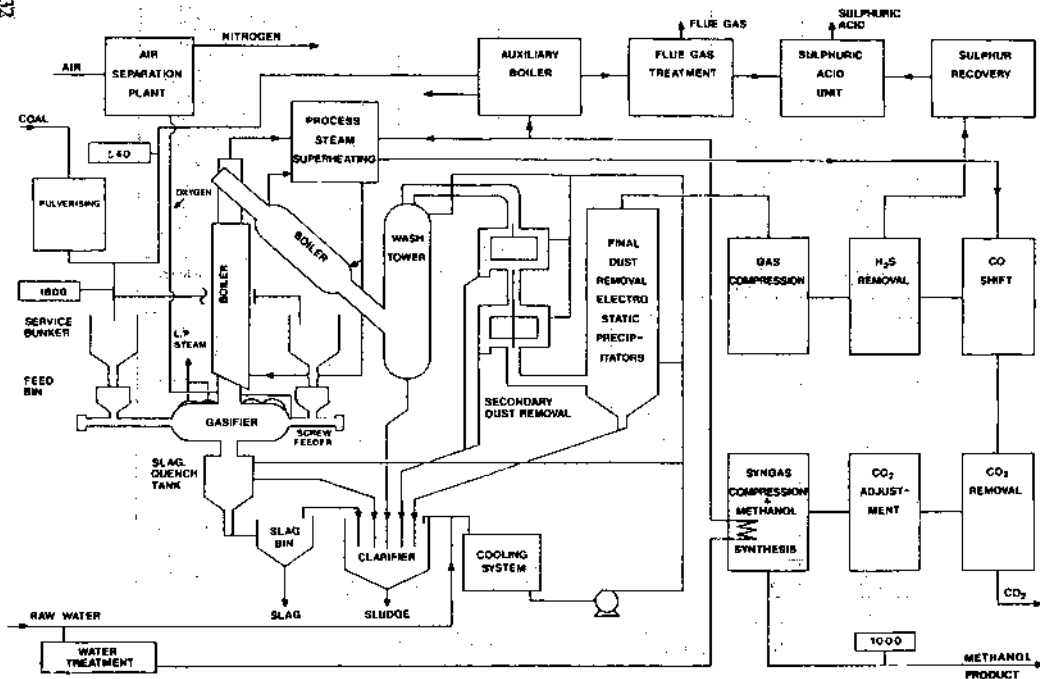Figure 5. 1000 MTD Methanol using Koppers Totzek Process
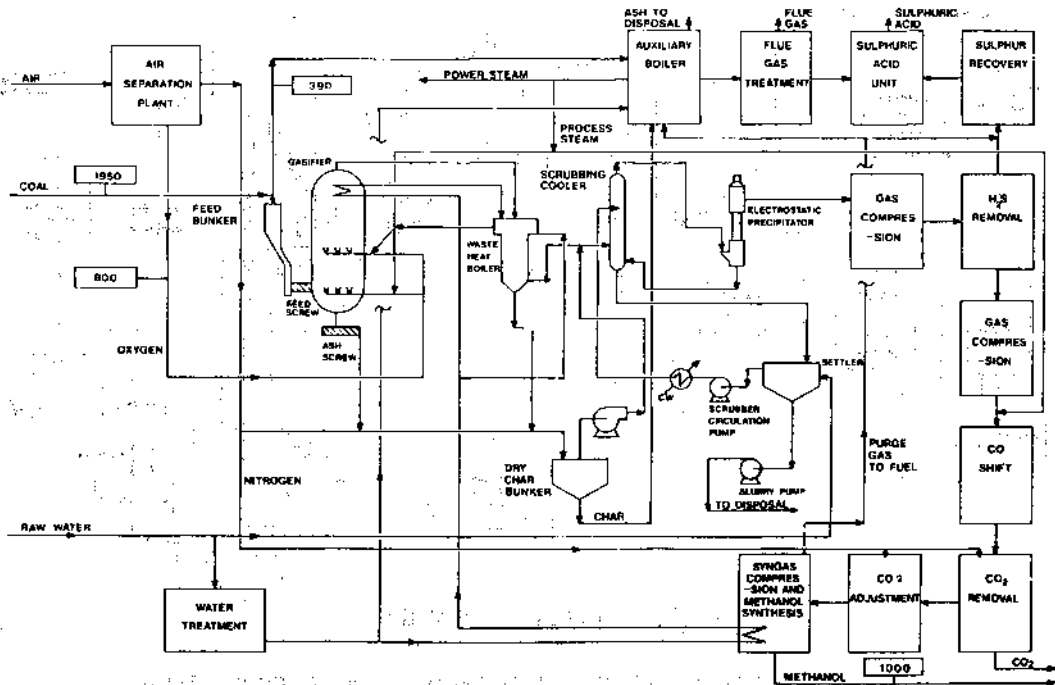
Figure 6. 1000 MTD Methanol using Winkler Gasifier

Figure 7. 1000 TE/DAY Methanol Plant - Slagging Gasifier

Figure 8. 1000 MPTD Methanol Plant Texaco Coal Gasification