Methanol Production by Gasification of Heavy Residues

by C. A. A. Higman
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Christopher Higman

1 Introduction

Approximately 2.5 million metric tons per year or about 10% of the estimated 1994 world methanol production capacity is based on the gasification of coal or heavy residues. 87% of this gasification- based capacity is located in only two countries, namely the United States of America and Germany. Over 90% of gasification-based methanol production operates with LURGI isothermal reactors. This includes all the large capacity ones. Against this background of current experience it is clear that there is a case to be made for the statement that, given the right circumstances, gasification can be an alternative to natural gas. The kind of synthesis gas produced by a gasification plant has, however, certain implications for the synthesis technology. The purpose of this paper is to review the technological aspects of methanol production from residual oil gasification using the SHELL Gasification Process ("SGP") as a typical proven oil gasification process for this application and to review the economic circumstances in which such a technology is a real alternative to natural gas.

2 Technology

2.1 Block Flow Diagram

The block diagram in Figure 1 provides an overview of the overall methanol process.

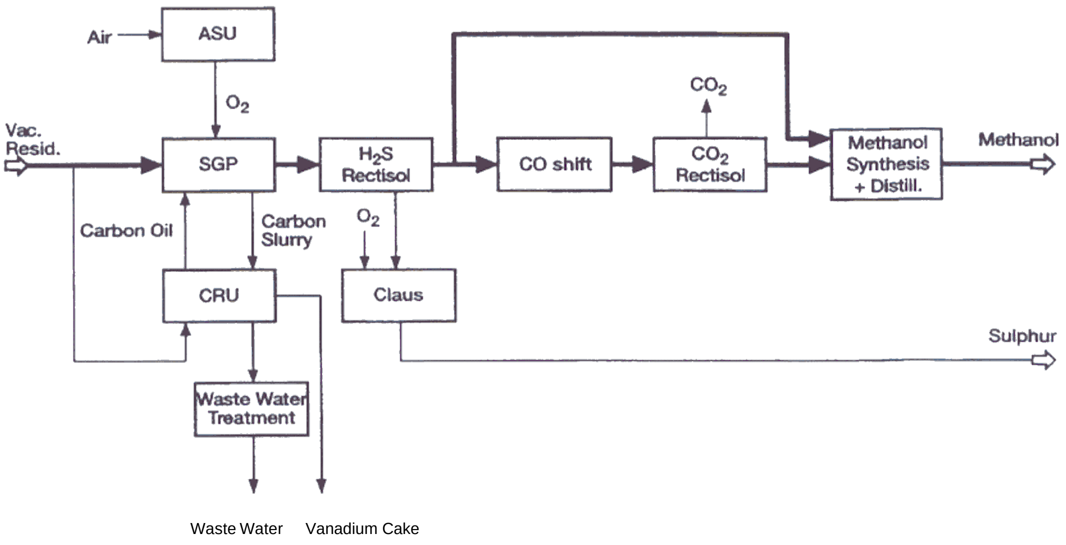

Figure 1: Block Diagram, SGP-based Methanol Plant

The feedstock is gasified in the SGP reactor with oxygen to produce raw synthesis gas at a temperature of about 1300° C and a pressure of typically about 60 bar. This gas is a mixture of hydrogen and carbon monoxide which, however, also contains CO_2, H_2S and COS together with some free carbon and the ash from the feedstock.

The hot gas is cooled in the synthesis gas cooler by generating high-pressure steam. Particulates are removed from the gas using a water wash prior to desulphurization.

Desulphurization is effected using the Rectisol process in which cold methanol is used as the solvent. A side-stream of gas is shifted to achieve the correct H_2: CO ratio for the methanol synthesis process before CO_2 removal, also using Rectisol. The methanol synthesis itself would operate at low pressure (about 50-80 bar) using typically the LURGI Low Pressure Methanol Process followed by a distillation step to achieve a product quality specification.

The wash water from the particulate removal is treated in the Soot Ash Removal Unit. Carbon and ash are removed from the water by filtration. The carbon is burnt off in a special furnace leaving a vanadium pentoxide ash as by-product. The bulk of the water is recycled to the water wash. The desulphurization solvent regeneration system operates selectively and without an additional concentration step produces a gas of sufficiently high H_2S content to allow it to be processed in a Claus unit, which converts the hydrogen sulphide into elemental sulphur using typically the Lurgi OxyClaus Process.

2.2 Residue Gasification and Soot Ash Removal

Gasification

The non-catalytic partial oxidation of hydrocarbons by the SHELL Gasification Process (Figure 2) takes place in a refractory-lined reactor, which is fitted with a specially designed burner.

The oxidant is preheated and mixed with steam prior to being fed to the burner. The burner and reactor geometry are so designed that this mixture of oxidant and steam is intimately mixed with the preheated feedstock.

Waste Heat Recovery

The product of the partial oxidation reaction is a raw synthesis gas at a temperature of about 1300 °C, which contains particles of residual carbon and ash. The recovery of the sensible heat in this gas is an integral feature of the SGP process.

Primary heat recovery takes place in a waste heat exchanger generating high-pressure (100 bar) saturated steam in which the reactor effluent is cooled to about 340°C. The waste heat exchanger is of a special design developed specifically for these operating conditions and used in about 135 installations worldwide. A small part of the steam thus generated is used for feedstock and oxidant preheating; the remainder is superheated for use in CO Shift and in steam turbine drives.

Secondary heat recovery takes place in a boiler feed water economizer immediately downstream of the waste heat exchanger.

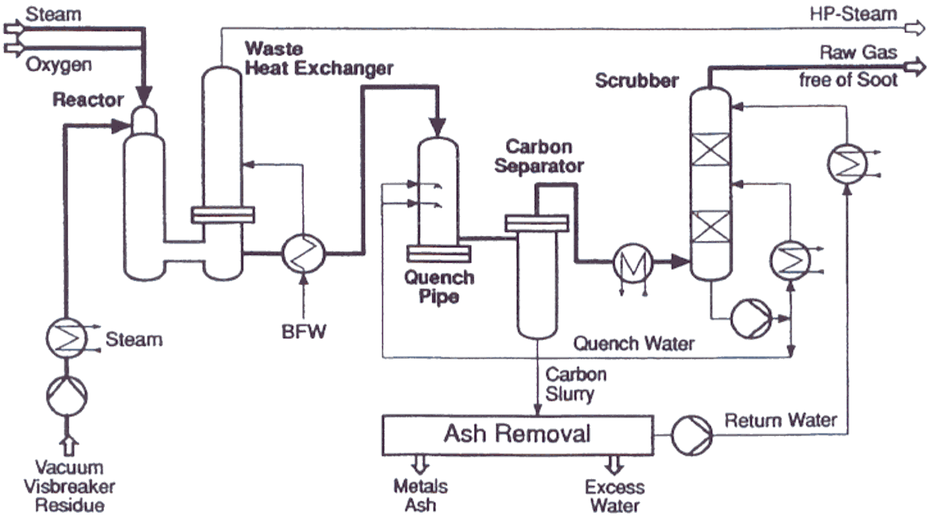

Figure 2: **Residual Oil-based SGP Unit**

Carbon Removal

The partial oxidation reactor outlet gas contains a small amount of free carbon. The carbon particles are removed from the gas together with the ash in a two-stage water wash. The carbon formed in the partial oxidation reactor is removed from the system as a carbon slurry together with the ash and the process condensate. This slurry is subsequently processed in the ash removal unit described below. The product syngas leaves the scrubber with a temperature of about 40° C and is essentially free of carbon. It is then suitable for treatment with any commercial desulphurization solvent.

Some 140-150 units have been installed worldwide with a processing capacity of some 7 million t/y of residue. One typical reference plant processes about 240,000 t/y of residues of varying quality, which are bought on the open market, for the production of ammonia. Another which was started up in 1972 produces a mixed product slate of ammonia, methanol and hydrogen and is fed with about 350,000 t/y residue directly out of a visbreaker.

Ash Removal Unit

Handling the carbon slurry is an important aspect of partial oxidation processes. The trend to using heavier feedstocks with a higher ash content has led to a re-evaluation of traditional extraction methods, in particular the possibilities of recovering the vanadium for metallurgical use.

Figure 3 illustrates the principles of the Soot Ash Removal Unit. The carbon slurry from the SGP unit is flashed to atmospheric pressure in the slurry tank. The slurry is then filtered on an automatic filter to recover a filter cake with about 80% residual moisture and a clear water filtrate. The filter cake is subjected to a controlled oxidation process in a multiple hearth furnace. This type of furnace, which is well established in many industries and specifically in the vanadium industry, allows the combustion of the carbon to take place under conditions where the vanadium oxides neither melt nor corrode. The product is a vanadium concentrate, which contains about 75% V_20_5. The process is autothermal, the heat of combustion of the carbon being sufficient to evaporate the moisture content of the filter cake.

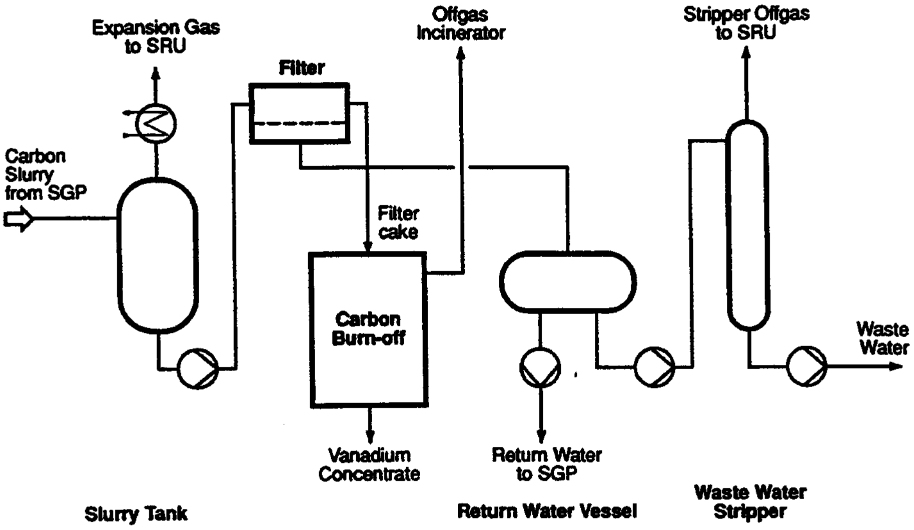

Figure 3: **Soot Ash Removal Unit**

The bulk of the filtrate is recycled as wash water to the SGP unit. However, the overall system generates a net water surplus, which must be further treated before final discharge. The first step is a sour water stripper in which dissolved gases, such as H_2S, CO_2 and ammonia are removed. The stripped gases are incinerated in a special burner in the Claus unit and therefore kept entirely within the system. Final water clean up takes place in a flocculation-sedimentation system for trace metal (ash) removal and a biological wastewater treatment unit.

2.3 RECTISOL Desulphurization and CO2 Removal

Looking further at the Block Flow Diagram, we see the desulphurization and CO2 removal stages using the selective RECTISOL process.

RECTISOL (Figure 4) is a physical washing system, which uses cold methanol as its solvent. The incoming raw gas is cooled down to about -30°C, the operating temperature of the H_2S Absorber. Both H_2S and COS are washed out with the cold methanol to a residual total sulphur content of less than 100 ppb. Part of the desulphurized gas is then shifted outside the Rectisol unit, the degree of shift being dependent on the requirements of the synthesis unit. Carbon dioxide is then removed from the shifted gas in the CO_2 Absorber. This column is divided into two sections, a bulk CO_2 removal section using flash regenerated methanol and a fine CO_2 removal section in which hot regenerated methanol is used. The CO_2 removal section operates at lower temperatures, typically about -60° C. The permissible CO_2 slip is dependent on the application. For methanol synthesis gas 1% residual CO_2 is quite adequate.

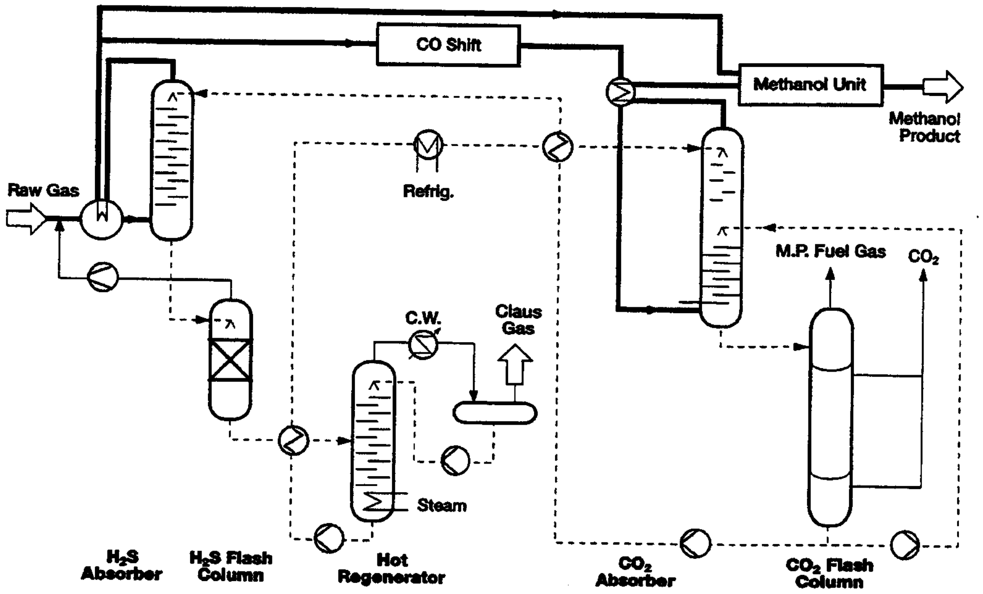

Figure 4: RECTISOL Acid Gas Removal Unit

Following the solvent circuit, we see first an intermediate H_2S flash from which co-absorbed hydrogen and carbon monoxide are recovered and recompressed back into the raw gas. The flashed methanol is then reheated before entering the Hot Regenerator. Here the acid gas is driven out of the methanol by reboiling and a Claus gas with an H_2S content of 25-30% (depending on the sulphur content of the feedstock) is recovered. Minor adaptations are possible to increase the H_2S content if desired.

The hot regenerated methanol, which is the purest methanol in the circuit, is used for the fine CO_2 removal. The methanol from the CO_2 removal is subjected to flash regeneration in a multi-stage flash tower. The configuration shown is typical for the methanol application with only atmospheric flash regeneration. Finally the loop is closed with the flash regenerated methanol returning to the H_2S Absorber.

2.4 CO Shift Conversion

In the CO Shift Conversion Unit (Figure 5) the carbon monoxide produced in the gasification unit is converted with steam to hydrogen and carbon dioxide according to the equation

$$CO + H_2O \Rightarrow H_2 + CO_2$$

The flow sheet shows a saturator-cooler system, which uses the heat of reaction of the CO shift reaction to generate two-thirds of the thermodynamic steam requirement of the reaction. Only the stoichiometric steam requirement is drawn from the header. In the methanol case this represents approximately 18% of the nett steam produced in the SGP unit, the balance being available for steam turbine drives. For methanol a two-stage reactor system using conventional HT -Shift catalyst is used to achieve a CO slip of about 3.2%.

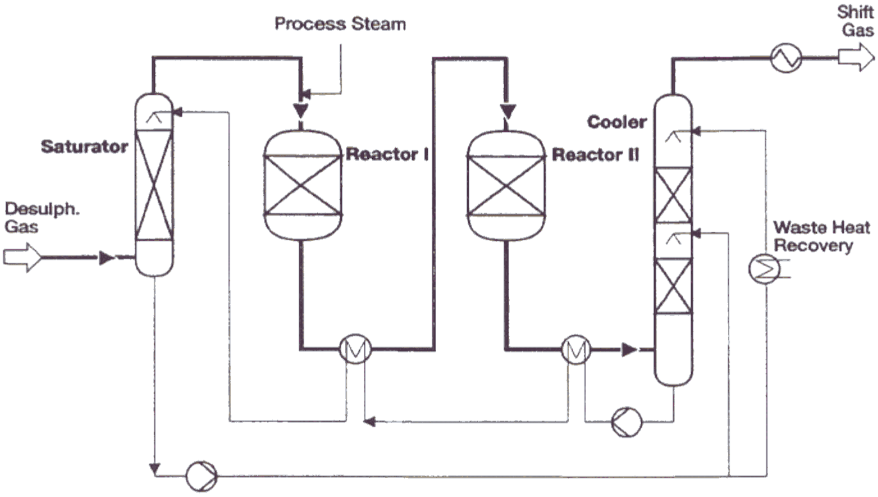

Figure 5: **Lurgi CO Shift Process**

2.5 LURGI Low Pressure Methanol Process

Methanol Synthesis

Correct adjustment of the bypass around the CO Shift unit will allow the production of a synthesis gas with an optimum value of just over 2 for the stoichiometric ratio $(H_2\text{-}CO_2)/(CO+CO_2)$. The selection of the exact pressure to run the methanol synthesis loop will depend on an OPEX/CAPEX optimisation. For medium size units of for instance 600 t/d the loop would operate at about 50 bar, i.e. without any intermediate syngas compression. For a large unit of say 2,000 t/d, the pressure would be somewhat higher. The principles are shown on Figure 6.

For the smaller unit the clean gas from the CO2 removal unit is fed to the suction side of the loop gas circulator while the CO shift by-pass gas has sufficient pressure to enter the loop on the discharge side. For the larger plant the gases are mixed together at the suction of the booster compressor. The gas is preheated in the Feed-Effluent-Exchanger and fed to a tubular reactor in which the carbon oxides and hydrogen are converted to methanol. The tubes are filled with catalyst, which is cooled by the boiling water on the outside of the tubes.

The steam pressure of about 40 bar maintains the desired gas outlet temperature of 250 °C. The unconverted gas together with the methanol leaves the reactor and is cooled successively in the Feed-Effluent-Exchanger, an air-cooler and a final water cooler, thus condensing the methanol. The crude methanol is separated out in a separator and led to the distillation section. Inerts (mainly methane and nitrogen) are purged from the loop before the remaining gas is fed back to the circulator. The purge gas, which in the case of a partial oxidation based methanol plant is relatively small, contains also some H_2 and CO and can be used as a sulphur-free fuel gas.

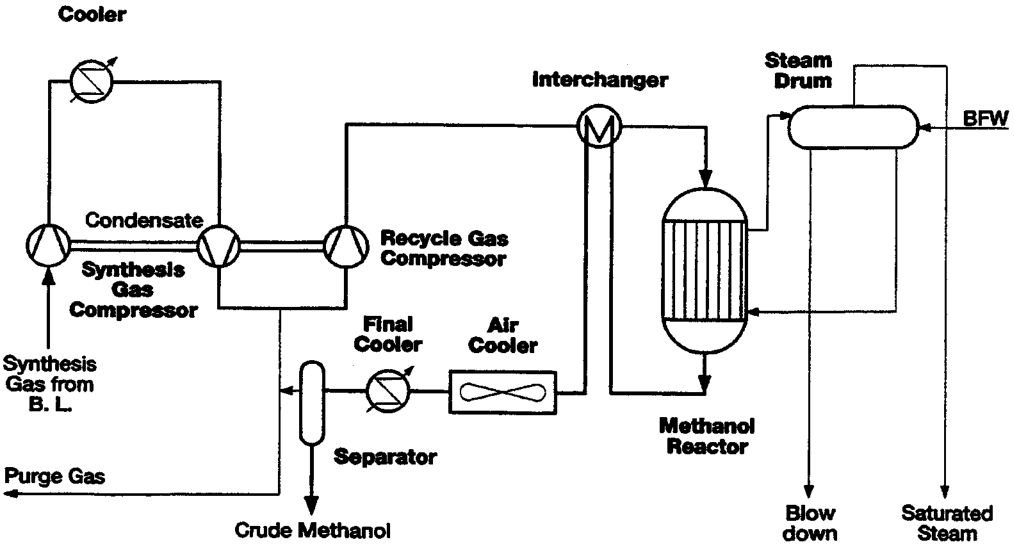

Figure 6: Lurgi LP Methanol Synthesis

For the methanol synthesis it is important to recognize the difference between an optimised synthesis gas produced from a partial oxidation unit or a gas produced from steam reforming of natural gas. Table 1 shows typical analyses for three different gas production schemes - residue gasification, conventional steam reforming and LURGI's combined reforming.

Process	**Gasification**	**Conventional Reforming**	**Combined Reforming**
Feedstock	**Heavy Residue**	**Natural gas**	**Natural gas**
CO2 mol %	3.52	7.30	7.68
CO mol %	27.86	16.80	21.62
H2 mol %	67.97	72.10	67.78
CH4 mol %	0.21	3.70	2.84
Inerts mol %	0.44	0.10	0.08
$\frac{H_2 - CO_2}{CO+CO_2}$	2.05	2.7	2.05

Table 1: Methanol Synthesis Gas Analysis

The interest in this table focuses on the stoichiometric ratio and the CO_2-content of the gas. Both gasification and combined reforming produce a stoichiometric ratio of 2.05, which results in optimum hydrogen utilization. The conventional reforming of natural gas produces a surplus of hydrogen, which leaves the loop as purge gas. When one reviews the details of the two reactions

$$CO + 2\,H_2 \Rightarrow CH_3OH$$

and

$$CO_2 + 3\,H_2 \Rightarrow CH_3OH + H_2O$$

It is necessary to take account of the fact that methanol formation from CO has a significantly higher heat of reaction than that from CO_2. Furthermore, the production of impurities from side reactions increases with increasing temperature in the catalyst pores. The higher proportion of methanol produced from CO when using syngas from coal or oil gasification means that in such a plant additional attention must be paid to the issue of heat removal. It is necessary not only to remove the larger quantity of heat compared with a natural gas-based unit. It is also necessary to perform this in a manner, which prevents the slightest local overheating in order to avoid by-product formation. The intense and intimate cooling provided by the boiling water in the LURGI isothermal reactor has therefore made it the preferred reactor system for gasifier-based methanol plants.

Methanol Distillation

The Crude methanol contains a small amount of co-formed products as well as some physically dissolved gases. The dissolved gases are flashed off in a Flash Vessel and low boiling impurities removed in a Prerun Column. The stabilized methanol is then distilled in a two-stage system (Figure 7), first under pressure and then at atmospheric pressure to obtain a specification product.

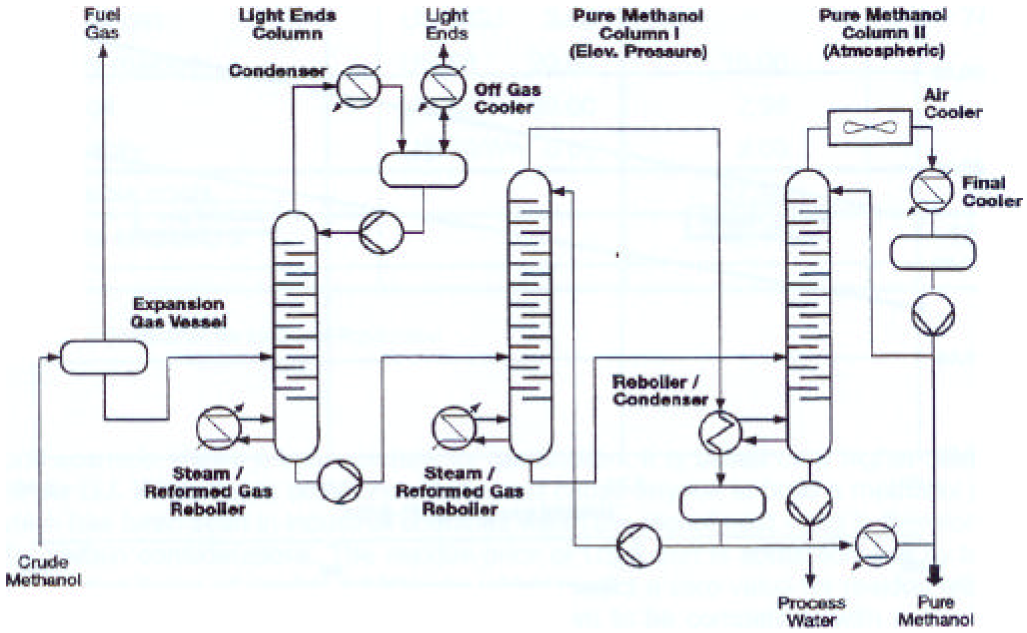

Figure **7:** **Three Column Distillation**

3 Comparative Economics

We are all aware of the fact that in terms of investment gasification will never be a cheap option. On the other hand its inherent flexibility provides the opportunity to operate with cheap feedstocks and this is what can prove to be an attraction in the right circumstances. Table 2 provides a number of key figures for establishing the economic comparisons. The data is based on a 2000 t/d world scale unit using either residue gasification or Combined Reforming of natural gas. Both technologies use oxygen (either in the gasifier or in the secondary reformer of the natural gas unit) and it has been assumed for both cases that the oxygen plant will be purchased and operated as an integral part of the methanol plant.

Process		**Gasification**	**Combined Reforming**
Feedstock		**Heavy residue**	**Natural Gas**
Product rate	t/a	660 000	660 000
Investment cost	Million US$	380	250
Main consumption figures			
Natural gas	GJ/t MeOH		29.9
Heavy residue	kg/t MeOH	800	
Fuel oil	kg/t MeOH	37	
Electricity	kWh/t MeOH	180	

Table 2: Key Data for a 2000 t/d Methanol Plant

In table 3 two different feedstock price scenarios have been compared. The first scenario is typical for today's conditions with relatively cheap natural gas and residue prices holding up remarkably well compared with predictions from the last few years. Under these circumstances it is clear that residue gasification is not competitive with combined reforming of natural gas - even if one adds a transport burden onto the costs of producing from natural gas in a remote area.

Process **Fixed costs for scenarios 1 and 2**		**Gasification**	**Combined Reforming**
Capital charge	US$/t MeOH	74.10	48.75
Maintenance	US$/t MeOH	14.26	9.38
Personnel	US$/t MeOH	6.60	4.50
Overheads, etc.	US$/t MeOH	19.27	12.78
Total fixed costs		**114.23**	**75.41**
Variable costs for scenario 1			
Natural gas	US$/GJ 1.25		37.38
Heavy Residue	US$/t 50	40.00	
Fuel oil	US$/t 80	2.96	
Electricity	US$/kWh 0.05	9.00	
Total variable costs		**51.96**	**37.38**
Total costs scenario 1		**166.19**	**112.79**
Variable costs for scenario 2			
Natural gas	US$/GJ 2.50		74.75
Heavy Residue	US$/t 20	16.00	
Fuel oil	US$/t 80	2.96	
Electricity	US$/kWh 0.05	9.00	
Total variable costs		**27.96**	**74.75**
Total costs scenario 2		**142.19**	**150.16**

Table 3: Cost Breakdown for Methanol Production

The second scenario shows a better picture for gasification. It is based on a higher natural gas price of US-$ 2.50 per GJ. While this is not a price that would cause anyone to build a methanol plant today, it is a price which has been seen in industrial countries within the recent past - and is therefore not totally un-realistic for certain considerations. The residue price of US$ 20/t is admittedly low by today's standard but it is well above those oil market projections, which predict a zero value for residue within the next ten years. Under these conditions gasification can be shown to be competitive with natural gas reforming. Figure 8 shows the cost relationship over a full range of feedstock prices.

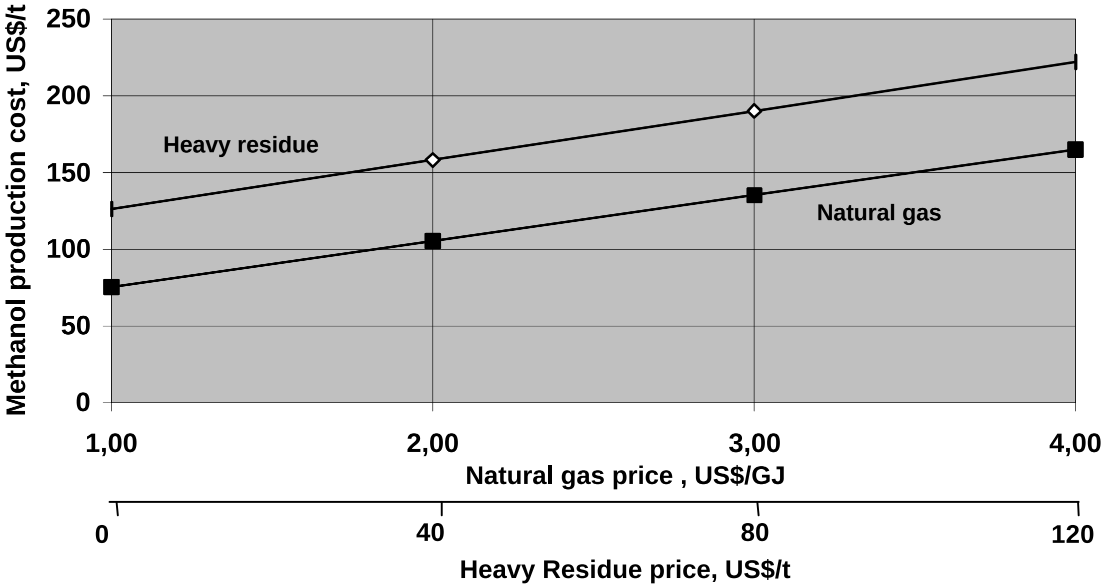

Figure 8: Methanol Production Cost from Natural Gas and Heavy Residues

4 Conclusion

Methanol production by gasification of heavy residues is a current and proven technology, accounting for about 10% of world methanol production. It would under today's economic conditions not be competitive to build such a plant compared with importing methanol produced from cheap natural gas in a remote location. If, however, strategic or other considerations demand that production be located in one of the major industrial countries, then a fall in the residue price could make additional capacity of this sort more attractive.

References

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