

**An Opportunity for Methanol;  
the Production Starting from Coal**

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presented at the  
**2008 WORLD METHANOL CONFERENCE**  
**Libson, Portugal**  
**8-10 December 2008**

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# **An opportunity for Methanol; The production starting from Coal**

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## **Abstract**

The Chemical Industry is facing a difficult challenge: how to deal with natural gas supply security and price volatility.

Solid Gasification is a promising answer to these needs: it is a commercially proven technology, available for the production of chemicals from coal and petcoke

A case study is developed in the paper in order to depict a possible technical alternative for Methanol production based on a feedstock that is available and abundant in the world; production of Methanol from coal gasification.

Methanol is considered either a final product or an intermediate for production, through Methanol to Olefins step (MTO), of the required petrochemical products.

The technical alternative, based on oxygen blown entrained bed gasification, is sized to produce 5000 t/day of Methanol. Overall performance and investment costs are evaluated and discussed through a sensitivity analysis on cost of coal.

The plant design offered includes two exclusive advanced technologies, the first being the CASALE axial-radial sour shift design and the latter being the CASALE methanol synthesis section and 'IMC' methanol converter designs.

Through these technologies it is possible to render plants more efficient and reliable.

## **Basis of design**

The study is based on commercially available technologies and evaluates costs and plant performance of a plant that can be presently engineered and built.

Two alternative plant configurations for the combined production of chemicals and power are investigated:

- Bituminous coal-based gasification, designed to produce 5,000 t/d of methanol
- Petcoke-based gasification designed to produce 5000 t/d of methanol

The gasification plant is designed to process bituminous coal and petcoke.

Main fuel characteristics are:

- Bituminous Coal (BC): LHV equal to 25,870 kJ/kg and a sulphur content of 1.1% wt (dry, ash free).
- Petcoke (PC): LHV equal to 32,450 kJ/kg and a sulphur content of 6.7% wt (dry, ash free).

Location for cost estimate is a generic European coastal site. The reference ambient conditions for performance evaluation are 15°C, ambient relative humidity of 60% and an average seawater temperature of 15°C.

- Methanol: Liquid Methanol at 99.85% wt purity is produced
- Sulphur: Sulphur is a by-product of the gasification plant with the following characteristics: Liquid, Purity: 99.9 wt.%, H<sub>2</sub>S content: 10 ppm wt (max). Solid by-products: Slag and filter cake are produced by the gasification plant.

### **Description of the IGCC complex**

The following description makes reference to Figure 1 showing the IGCC block flow diagram and the main process streams. The main process blocks of the complex are the following:

- Feedstock storage and preparation;
- Air separation (cryogenic technology);
- Gasification, including black water/grey water treatment;
- Syngas treatment and conditioning;

- Acid Gas Removal (AGR);

These basic blocks are supported by other ancillary units, such as sulphur recovery, tail gas treatment, and a number of utility and offsite units, such as cooling water, flare, plant/instrument air, machinery cooling water, demineralized water, auxiliary fuels.

Each process unit of the complex may be a single train for the total capacity or split into two or more parallel trains, depending on the maximum capacity of the equipment involved or on the necessity to assure, through the use of multiple parallel trains, a superior degree of reliability.

The key and first process step is the entrained flow gasification, which is suitable both for solid and liquid feed. In this type of gasifier the feed (petcoke slurry or coal slurry) flows co-currently with the gasification agents ( $O_2$  and steam). Residence time is very short, between 0.5 and 5 seconds; the temperature inside the gasifier is uniform and very high, from  $1,300^\circ\text{C}$  to over  $1,500^\circ\text{C}$ , well above the ash fusion temperature.

Recovery of gasifier sensible heat is made through a water quench inside the gasifier. The quench system allows efficient removal of solids from the raw gas, before entering the downstream facilities. In addition, water quench is beneficial for the downstream carbon monoxide (CO) shift reaction, which increases the  $H_2/CO$  ratio. In fact CO shift requires large amounts of water which are directly present in syngas at the quench outlet.

Syngas main components are  $H_2$ , CO,  $CO_2$ ,  $H_2O$ , as well as  $H_2S$  and COS that need to be removed, and inerts. Downstream gasification, the shift reaction occurs on a catalyst suitable to process  $H_2S$  containing syngas (sour shift) to convert CO and water to  $H_2$  and  $CO_2$ . The shift catalyst promotes also the COS hydrolysis with its conversion to  $H_2S$  and  $CO_2$ . Raw syngas after cooling with heat recovery through steam generator and water heating, is then treated in the AGR unit with a physical solvent that removes the acid gases ( $H_2S$ , less than 1 ppm and  $CO_2$ ). The resulting syngas is free of any contaminant and prepared to produce both methanol.

In the sulfur recovery unit, the H<sub>2</sub>S rich stream coming from the AGR regenerator is burned with oxygen in a muffle furnace, followed by two reactors in series where the Claus reaction takes place to produce liquid sulfur.

The oxygen required for both the gasification reaction and the Claus reaction is produced in the air separation unit (ASU), where air is fractionated by cryogenic distillation. The target of this alternative is to produce 5000 t/d of methanol.

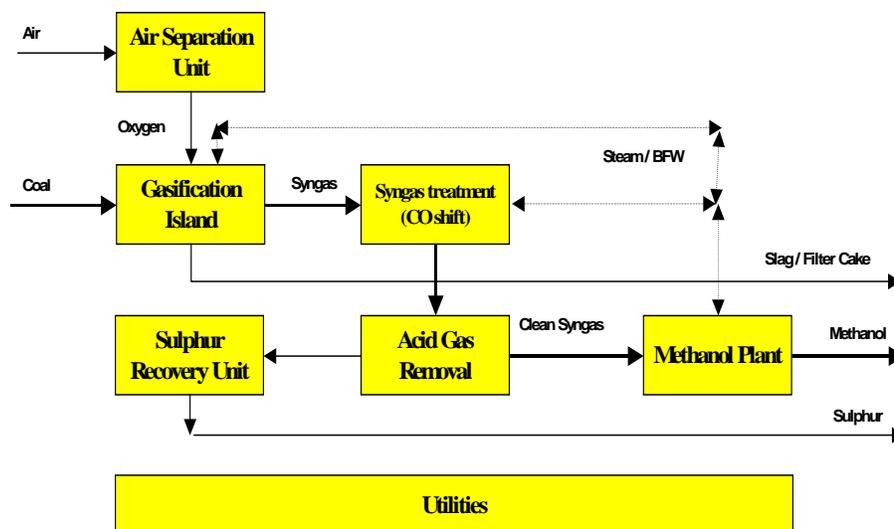


Fig. 1 – IGCC Block flow diagram for Methanol Production.

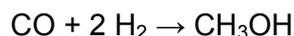
Downstream the shift reactor and the heat recovery, shifted syngas is cleaned in the AGR. The composition of the clean syngas at the AGR outlet shall meet the following specification, in order to be suitable for the methanol production:

$$(H_2 - CO_2) / (CO + CO_2) = 2.0$$

This specification is met with an average CO shift conversion of approx. 53% and a CO<sub>2</sub> capture rate equal to approx. 80%.

At AGR outlet the syngas goes to the methanol plant.

In the methanol plant syngas is compressed in order to enter the methanol synthesis reaction. The main reaction involved in this catalytic process is:



Due to the limitation imposed by chemical equilibrium, the conversion achieved in the reactor is only partial. For this reason it is necessary to recycle the non-converted

reactants. The liquid mixture of methanol and water is finally distilled in different columns to achieve the desired methanol purity

### **Performance and investment cost data**

The performance data of the two cases considered are summarised here below:

#### Case 1

Production of 5000 t/day of methanol starting from coal

Coal consumption. 300 t/h (7200 t/day)

Syngas from gasification section. 70000 Nm<sup>3</sup>/h

Clean syngas to methanol synthesis loop. 23500 Nm<sup>3</sup>/h

Auxiliaries consumption: 180 Mwe

Investment cost (Methanol synthesis and purification, syngas production and conditioning, balance of the plant): 1790 Million Euros

#### Case 2

Production of 5000 t/day of methanol starting from petcoke

Petcoke consumption 250 t/h

Syngas from gasification section 62000 Nm<sup>3</sup>/h

Clean syngas to methanol synthesis loop 23100 Nm<sup>3</sup>/h

Auxiliaries consumption: 150 Mwe

Investment cost (Methanol synthesis and purification, syngas production and conditioning, balance of the plant): 1750 Million Euros

### **Methanol production costs**

The production cost of methanol has been evaluated on the basis of the following main assumptions:

- Price of sulphur: 240 €/t.
- No solid by-products cost/revenue is considered.
- 7,621 equivalent operating hours (reference: 100% capacity) corresponding to 87% equivalent availability.
- 8% discount rate on the investment cost over 25 operating years
- 10% IRR
- Maintenance cost equivalent to approx 3.0% of the total capital costs.
- Cost of imported electric power: 40 €/MWh

In case of methanol production from coal the calculated methanol production cost is 350 €/t when coal is valued 60 €/t and 320 €/t when coal is valued 40 €/t.

In case of methanol production from petcoke the calculated methanol production cost is 280 €/t when petcoke is valued 20 €/t and 255 €/t when petcoke is valued 5 €/t.

### **CASALE Axial-Radial Sour Shift Converter**

In most of the gasification plants the shift converters designed so far are axial catalyst bed reactors. This arrangement has several drawbacks.

The pressure drop is inherently high, and, to be maintained within reasonable values, it needs wide and short pressure vessels. These vessels operate at relatively high temperature, and often also quite high pressure, and therefore, require thick walls, with consequent high weight and cost.

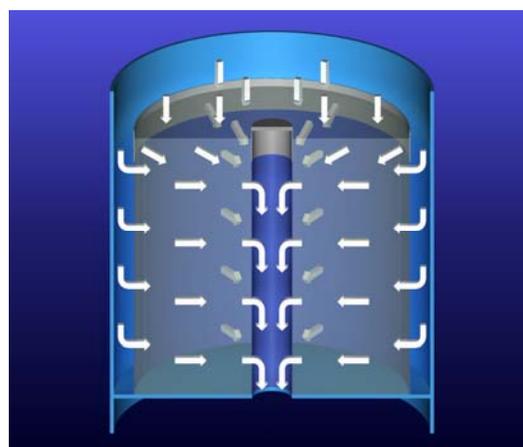
The axial catalytic bed reactors have pressure drops all concentrated in the catalyst, as no gas distribution is provided. The consequence of this situation is that the reactor pressure drop increases during the operation due to the catalyst deterioration. This pressure drop increase can be substantial, due to the presence of water droplets and particulate in the incoming gas. The increase in pressure drop augments the energy consumption in the compressor sending the synthesis gas into the synthesis loop, and may reduce the plant capacity, if the suction pressure of this compressor drops considerably.

To overcome these problems, CASALE has introduced a new shift converter design providing an axial-radial catalyst bed.

#### **The Axial-Radial Flow Concept**

The axial-radial flow is a concept utilized to design fixed catalyst beds, invented and patented by CASALE in 1980. The concept is very simple, and consists mainly in a radial bed the top of which is left open, to let

a minor part of the gas flow downward axial-radially, while most of the gas flows radially. This arrangement has many advantages, such as:



**CASALE Axial-Radial**

- The bed pressure drop is low;
- The bed is mechanically simpler as there is no top cover;
- The replacement of catalyst is simpler, as there is full access to the bed, without having to go through manholes;
- The catalyst utilization efficiency is high as there is no unused catalyst portion under the top cover;

The advantages described above have made this design a wide success, and it is now used in more than 500 different catalysts beds in ammonia converters, shift converters, pre-reformers, and methanol converters.

### **Axial-Radial Shift Converters' Advantages in Gasification Plants**

The advantages of the axial-radial flow in sour shift converters are summarized here below.

The pressure drop is independent from the catalyst age. In fact, the bed pressure drop is concentrated in the perforated walls containing the catalyst and controlling the gas flow to the catalyst, and of course, the pressure drop of the perforated walls does not change with time, while the catalyst pressure drop in itself is negligible. For this reason even if the catalyst has mechanically deteriorated through ageing or by carry-over of water droplets, its pressure drop, with the axial-radial flow, remains still negligible compared with that of the perforated walls;

The catalyst life is longer, because the pressure drop is not affected by the catalyst ageing or mechanical wear and tear. Therefore, it is not necessary to replace the charge for its high pressure drop;

The plant production rate is higher. In fact, as the pressure drop of the shift converter is lower and remains stable, the pressure of the product gas delivery is higher during the catalyst life. It is further extended also because the catalyst life is longer, therefore, there is less needs of shut-downs for catalyst replacement;

The catalyst life can easily reach 4 years, as proven in the mentioned applications, even in the first shift converter;

The converters are less expensive, because the axial-radial bed is slimmer than the axial bed, therefore their pressure vessels are less expensive. As an example taken

from an actual design for a 5'000 MTD plant, a comparison of axial-radial vs. axial beds in both the first and second sour shift converters is the following:

Type	DP	ID	Construction Material	Vessel Weight
	bar	m		
1 <sup>st</sup> bed axial-radial	0.5	3.4	Low Alloy	Reference
1 <sup>st</sup> bed axial	1.0	4.7	SS Cartr. or Refractory Lin.	(*)
2 <sup>nd</sup> bed axial-radial	0.5	3.4	Low Alloy	Reference
2 <sup>nd</sup> bed axial	1.0	4.5	Low Alloy	+10%

(\*) Cannot be compared as explained below

An additional advantage of the axial-radial bed is to be noted for the first converter, due to the high operating temperature the axial bed has to be designed either with a SS cartridge, and an annulus for flushing the pressure vessel, or with a refractory lined vessel. For the axial-radial bed, with an inward flow, the hot gas is kept at the center of the bed, away from the vessel wall, so that only the outlet nozzle is exposed to high temperature. For this reason, it is not possible to make a comparison based only on weight.

### Application to Shift Converters

The axial-radial bed as been already applied to 22 shift converters, including HTS and LTS in steam reforming plants, HTS in POX plants and Sour Shift converters, while 11 more are under construction.

Out of these 22 units in operation, 2 are HTS in partial oxidation plants, while three are sour shifts, first and second converters.

The 2 HTS in Pox plants are revampings of existing axial units. The revamping, in both cases has been done to reduce the old units pressure drop, and to have a pressure drop that does not depend the age of the catalyst.



Revamping of a POX HTS in Brazil

The three sour shift converters are in operation in China since four years.

Among the 11 units under construction, three are sour shifts in coal gasification plants, two are the first and second converter in a new plant in the U.S.A., while the third is in China, and is a first converter.

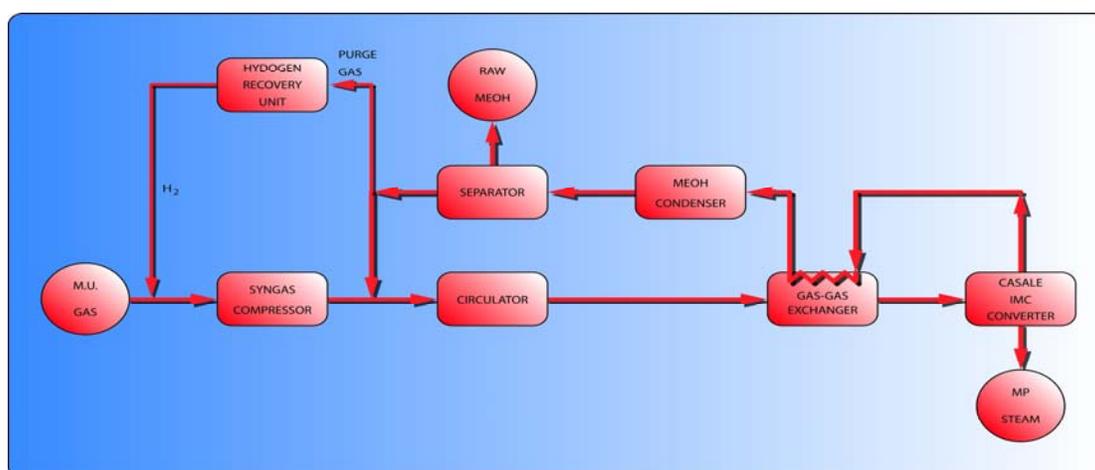
### **The synthesis loop downstream a gasification plant**

The technology for this section of the plant is based on the CASALE design for both the methanation section and the synthesis converter.

In gasification plants the make-up gas normally has a low inerts content, and is rich in carbon, this makes it possible to achieve high production rates with low recycle ratios and low catalyst volumes, provided that the converter design is appropriate. In fact, as the gas is very reactive it can easily create problems of catalyst overheating and hot spots in the converter.

The synthesis loop is very simple, as illustrated in the flow sheet below. It consists in one synthesis converter, a gas-gas exchanger preheating the reacting gas entering the converter, a condenser to cool down the gas to the methanol condensation temperature, a separator to separate the liquid raw methanol from the unreacted gas, a purge recovery unit to recover hydrogen from the purge gas to correct the stoichiometric number, and the syngas and circulating compressor.

There are only seven items overall. This small number ensures a higher reliability of the system, a smaller pressure drop, with consequent lower energy consumption, and a lower overall investment cost.



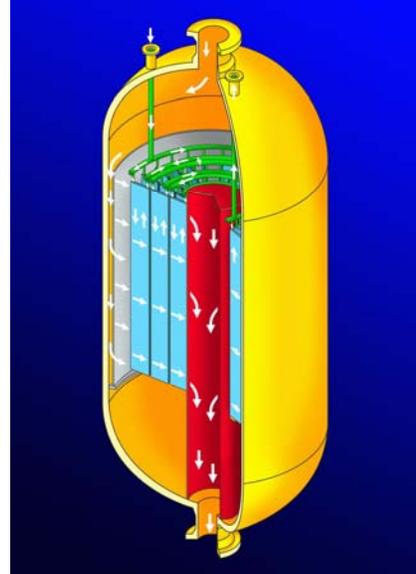
The low recycle ratio that can be used, implies that these items are also quite small, enabling very large capacities in a single train.

### **The Casale IMC converter**

The type of converter that is proposed by METHANOL CASALE for this type of service is the plate-cooled “IMC” converter, designed to utilize the reaction heat through direct steam generation.

As it is well known, the cooling elements inside the reactors are hollow plates.

These reactors are very well suited for this application as they ensure a very effective cooling of the catalyst, a very reliable and simple mechanical construction, an easy catalyst loading and unloading, and can be designed in a single vessel for very large capacities, as it can be furnished with the axial-radial catalyst bed design.



Furthermore, this design is now proven already for capacities exceeding 3'000 MTD in a single unit.

An important advantage of this design is that it allows, differently from other older ones, the temperature control of the temperature profile in the catalyst bed even in a steam raising design.

This aspect is very important because with this feature is possible to increase the conversion per pass in the reactor, to reduce the highest temperature reached by the catalyst and to optimize the design of the equipment external to the reactor.

### **Casale experience with IMC converters**

In addition to the IMC units in operation in several natural gas based plants, the first one in a coal based gasification plant is now on stream in China.

This converter has been started up in June of 2008, and has a design capacity of 1350 MTD. It generates medium pressure steam.

The methanation section has been designed by CASALE, while the procurement, except for the converter internals, has been done from China.

Nevertheless, the converter operations show a low peak temperature in the catalyst bed, confirming the ability of the converter internals to uniformly remove

the heat generated by the reaction even if the plant is running at partial load due to problems in the gasification section. The gas composition at present is also different from the design, and consists mainly of a mixture of CO and H<sub>2</sub> only.

In addition to this unit there are 6 more IMC converters being built using this design to be used in coal based plants, with capacities ranging from 1350 MTD to 3'000 MTD, and all of them are single vessel converters. The next start up is scheduled in early 2009.

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