CASALE COAL-BASED METHANOL SYNLOOPS

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Abstract

METHANOL CASALE has recently started-up the first two methanol synthesis loops based on coal gasification in China. The first one was put on-stream in 2008 and the second one in 2009 with the respective capacities of 1350 MTD and 2000 MTD. This paper describes the experience that embraces the particularity of the gas composition, the behavior of these two plants and their locations, acquired with the two synthesis loops and converters. The paper also considers the collaboration with the design institutes at the project execution level, the installation pre-commissioning and commissioning in collaboration with the Chinese companies, the start-up and operating experience gained so far in these large size plants.

1) INTRODUCTION

Today most of the world methanol production is achieved with natural gas as feedstock. In the last few years a new scenario started to appear, in which the attention switched to the exploitation of new types of feedstock, such as coal and petroleum coke, that are abundant and, so far, less expensive.

China leaded this revolution, with the construction and commissioning of several methanol plant based on coal gasification and reaching almost 25% of world methanol production with an annual growth of 33%.

Nevertheless, the utilization of these solid feed-stocks implies different technological approaches, both in the preparation of the synthesis gas, and in its utilization to produce methanol, mainly because of the composition of the synthesis gas obtained from gasification, that is rich in carbon oxides and low in hydrogen, and may contain several catalyst poisons.

Thanks to its advanced technologies in methanol synthesis converters, Casale could enter this market and provided license, BEP/PDP of the synthesis section and in some cases distillation, proprietary internals of reactor and site services for eleven Chinese methanol projects. The first two plants have been recently put on stream: SHANGHAI COKING AND CHEMICAL CORP., Shanghai, in June 2008 and XINNENG ENERGY LIMITED - XIN'AO GROUP, Erdos City, Inner Mongolia in July 2009.

2) TECHNICAL ASPECTS

Make-up gas composition

The gas composition obtainable from coal gasification can be adjusted to the necessity of the methanol synthesis, but, in general, its stoichiometric ratio is lower than two, and the inert content is low.

Table 1. Typical Make-up gas composition

Item		Unit	Material balance
Composition	CO	% mol	30.48
	H_2		66.14
	CO_2		2.72
	CH_4		0.12
	Ar		0.15
	N_2		0.39

Moreover, it has to be considered the possibility that the make-up gas could contain catalyst poisons, such as sulfur and arsenic. These compounds should be washed away in the gas treatment upstream the synthesis loop (Rectisol), but, there may also be problems due to upset, mal-operation or under performance of some treatment units that may leave more impurities than desired in the gas.

As these poisons are irreversible, it is advisable to protect the catalyst by providing a guard on the make-up gas, which is able to absorb these dangerous substances. The type of guard bed that is most frequently installed protects the synthesis loop from sulfurous components. This guard bed can be installed either at the suction or at the discharge of the syngas compressor (before circulator) and can work in a temperature range from ambient up to 100°C. In the same vessel it is loaded a layer of hydrolization catalyst and a layer of zinc oxide catalyst.

Synthesis loop design (make reference to figure 3, 5 and 6)

The synthesis loop then has to be designed to take into account and to take advantage of the available gas composition.

This is normally done by providing some features that are not common in natural gas fed plants. One of these features is a hydrogen recovery unit on the loop purge gas. The recovered hydrogen needs to be added to the make-up gas to increase its stoichiometric number to a value around two, which is optimal for stoichiometric and kinetic reasons.

The high carbon monoxide concentration raises also the problem of the formation of carbonyls, such as iron and nickel. Once formed they will decompose on the catalyst reducing its activity and promoting undesired side reactions. The formation of carbonyls can be avoided by utilizing appropriate types of steel, that are higher grades than in gas based plants, in the areas where carbon monoxide concentration is high and the temperature is roughly in the range of 100 to 200°C.

The fact that the make-up gas normally has a low inerts content, and is rich in carbon, on the other hand, 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. For this reason it is very important to provide the right reactor, as discussed in the following chapters.

Overall the synthesis loop can be very simple. It consists in the 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 six main items overall, to which a guard bed may be added on the make-up gas, for protection from possible spikes in poisons content.

The low recycle ratio that can be used implies that these items are also quite small, enabling very large capacities in a single train, much larger then ever achieved so far in any plant of any type, provided, again, that the converter is of the right design.

Converter design

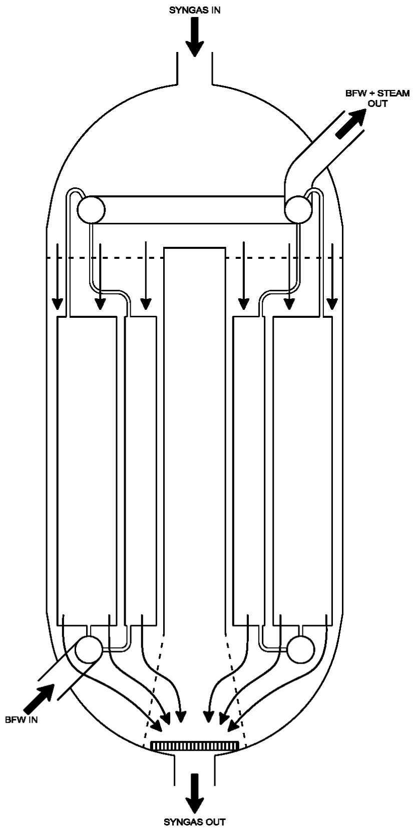

Figure 1. Simplified layout of IMC converter

The type of converter that is proposed by METHANOL CASALE for this type of service is the "**IMC**" that stands for **I**sothermal **M**ethanol **C**onverter. This reactor design is characterized by the fact that the catalyst bed is cooled by plates immersed in the catalyst, containing boiling water as cooling fluid.

In the case of gasification plants, the amount of carbon monoxide and dioxide present in the synthesis gas is very significant. Normally the concentration of these gases is of about 15%v for CO and of 5%v for CO_2 at reactor inlet. These high concentrations of carbon oxides imply that the converter must be provided with an heat sink, to control the reaction temperature. This heat sink is normally boiling water generating medium pressure steam that is around 25-30 bar. This pressure is selected because its corresponding temperature level matches the operating temperature in the catalyst bed well, and the steam produced can be usefully utilized in the plant in turbines

As mentioned above, the plate-cooled converters make use of cooling plates immersed in the catalyst mass for heat removal. The boiling water enters the converter shell and is distributed at the bottom of the plates. It then flows inside the plates from the bottom to the top. The mixture water/steam is collected in a manifold and exits the converter.

The construction of the converter internals is conceived so that there is no tube sheet, therefore there is no constraint in the converter size, and the construction is light, consisting of a normal pressure vessel containing the catalyst bed and the plates.

The plates are dimpled, obtained in an automatic production process consisting in their welding with a laser controlled by a computer. This results in a very high quality consistency, where the manual input is minimal.

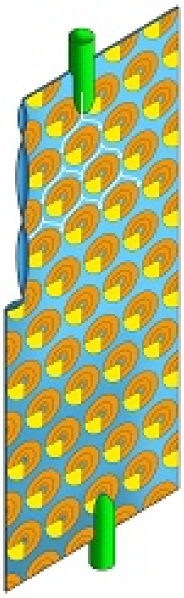

Figure 2. Steam rising plate

The plates are surrounded by the catalyst mass where the process gas is flowing. The process gas flow can be axial or axial-radial. In the latter case very large capacities in a single vessel with a low pressure drop, can be obtained.

The main advantages of Casale IMC design are in terms of:

- better performances, resulting from the advanced design, ensuring the best catalyst temperature profile with the highest uniformity;
- highest reliability thanks to the industrialized and automated production process of the reactor's internal components;
- easier catalyst replacement and maintenance of the internals.
- easier mechanical construction
- Casale experience in designing synthesis converters

3) PROJECT AND INDUSTRIAL EXPERIENCE

All the above advantages are proven in the industry: there are already seven **IMC** converters in operation and all of them running fine.

Two of these seven units are of special importance as a reference for coal based plants: SHANGHAI COKING AND CHEMICAL CORP. and XINNENG ENERGY LIMITED - XIN'AO GROUP. These are the first two methanol synthesis loop from coal gasification with Casale design put on stream.

In all Chinese projects Casale works in collaboration with local design institutes, typically playing the role of EPC contractors of the project. For the two projects mentioned above the design institute were respectively SCCDI (Shanghai Pacific Chemical Group Co Coking & Chemical Design Inst) and TCC (China Tiancheng Chemical Engineering Corp). Design institutes are involved in the project since the very preliminary phases, so that the design basis is agreed upon during contract negotiation.

Casale typical scope of supply consists of basic or process design of the synthesis loop and in some cases of distillation section, while detail design and material supply is limited to the proprietary internals of synthesis converter (plates). BEP e PDP are provided by Casale in double language English/Chinese and according to relevant Sinopec standard.

After BEP or PDP delivery, a design review meeting is held with the participation of Client and Design Institute experts, in which Casale gives detailed explanations and Client reviews and comments all the basic design documents, as necessary for the assessment of the documentation, allowing Design Institute to proceed with the detailed engineering work. Typically Client and Design Institute participate to this meeting with a delegation of about 10 people including project managers and experts from all the major engineering disciplines, like process, mechanical, piping, instrumentation, electrical etc.

Detail engineering design is then developed by Design Institute and Casale reviews this work to check compliance with the process design requirements. Also this phase is very important for a smooth development of the project and it ends with a Detail Design Review Meeting in the offices of the Design Institute.

Typical project duration from contract signature to detail design review meeting is 12 months, with basic design review after 5 months from kick-off meeting.

The collaboration between Casale and Client does not end with the design phase but it continues on field. In fact, one of the features of Casale converter internals is their modularity and their assembly on field with the same technique developed by Casale for in-situ retrofit. The installation is performed by the Client, under the supervision of Casale field engineers. Also the first catalyst loading is performed under Casale supervision.

Casale assistance goes on with commissioning and start-up activities, including catalyst reduction. During this period Casale personnel also provides training to Client staff operators. Finally, last commitments for site activities concern parameters optimization and test-run.

From the experience with these two Chinese projects, Shanghai Coking and Xin'ao, Casale has learnt once more how the assistance at site is important for a successful project. Therefore, Casale keep on maintaining close cooperation with the Client and full assistance in troubleshooting even after test-run period expiration.

SHANGHAI COKING & CHEMICAL CORPORATION

Design capacity of this methanol loop is 1350MTPD. Syngas is coming from a combination of two thirds of the slurry coal gasification duty and one third of the COG gasification.

Synthesis loop is characterized by relatively low operating pressure (75 bar design) and a design composition of the syngas slightly less reactive than other coal-based process (CO partial pressure is ~7 bar at converter inlet, while in other projects can be higher than 13 bar).

Methanol converter is equipped with IMC internals steam raising type and the generated steam can be fed to steam turbine after superheating.

The plant was started up on June 15th of 2008 and fed with feedstock on June 24^{th}. The plant could easily achieve 100% load. Successful test run certificate was signed in January 2010 after analyzing December 2009 data.

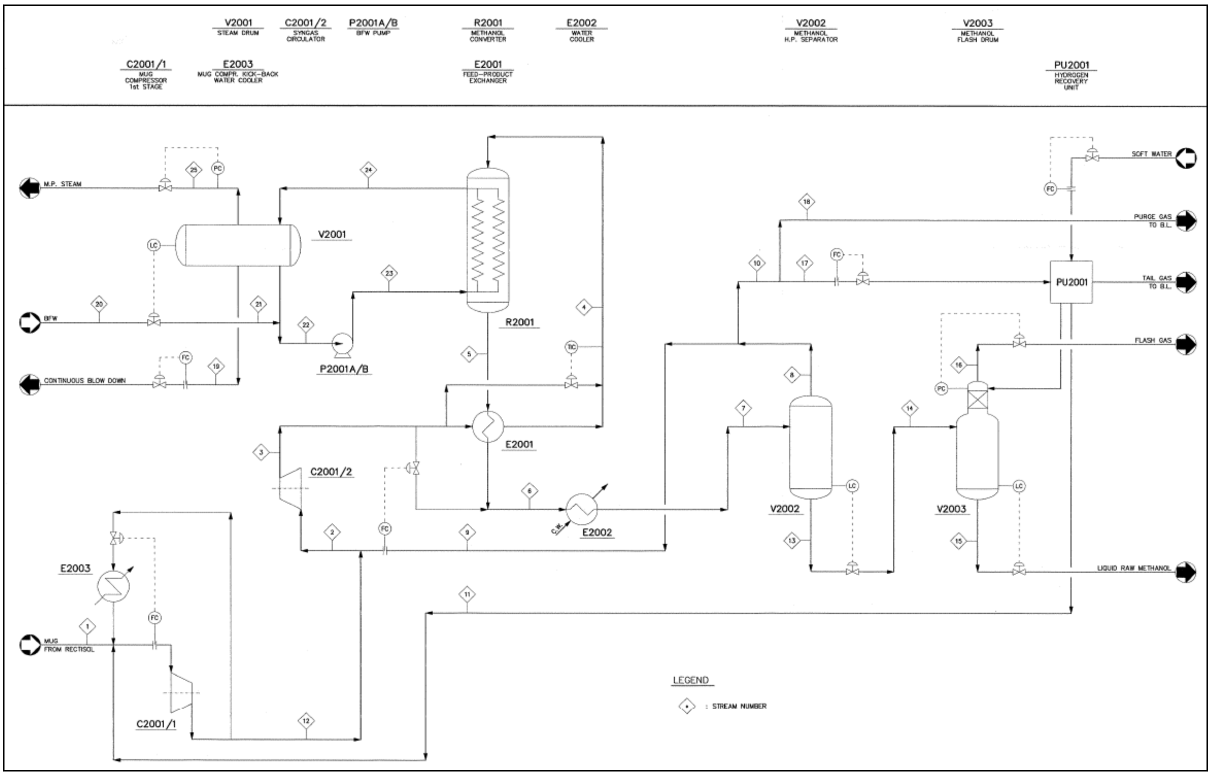

Figure 3 Shanghai Coking synthesis loop process flow diagram

Table 2. Operating data in comparison with design data

	Design operating conditions (SOR)	December 2009 operating conditions
Time on stream [months]	0	~16
Plant Load	100%	93.3%÷97.2%
Steam generated [t/h]	64.6	60÷75
Operating pressure at converter inlet [barg]	~ 74	~ 65
MeOH in/out converter [%mol] (simulated value)	0.36 / 10.67	0.27 / 10.1

From table 1, it is evident that synthesis loop is running at almost 9 bar less than design, denoting good converter performances. Also steam production is higher than expectations.
Differently from tube cooled converter, where only the inlet and outlet temperature are reliably measured, IMC allows to check the internal temperature profile. In the case of Shanghai Coking, temperature profile is stable since start-up not showing any catalyst deterioration in one year and half of operation.

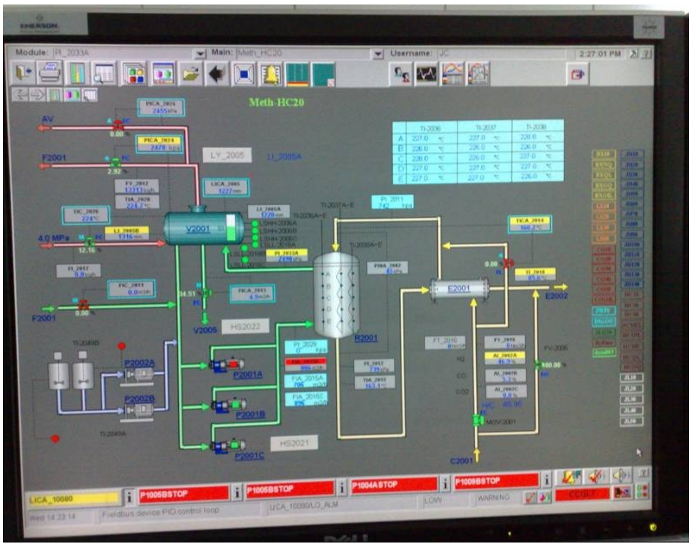

Figure 4. Picture of Shanghai Coking DCS system

XINNENG ENERGY LIMITED - XIN'AO GROUP

Design capacity of this methanol loop is 2035 MTPD, with syngas coming from coal gasification. Because of uncertainties in gas impurities, two guard beds have been installed for COS hydrolyzing and H_2S adsorption, loading Chinese catalyst.

Synthesis loop is characterized by design operating pressure of 83 barg (SOR) and operation with very reactive synthesis gas (stoichiometric ratio of make-up gas is 1.91 with 30.48% CO), which influenced reactor sizing.

Methanol converter is equipped with IMC internals steam raising type. Generated steam is superheated in a fired heater using HRU tail gas as fuel (design scope inside Casale battery limit, see PFD in figure 5).

The plant of Xinneng Energy Company has been running for more than one year since startup of July, 2009. 100% load could be easily reached right after start-up. A successful performance test at 96% load has been signed at the end of October 2009. An additional internal performance test by the client at 98.5% load (2005MTPD) has been taken in March 2010.

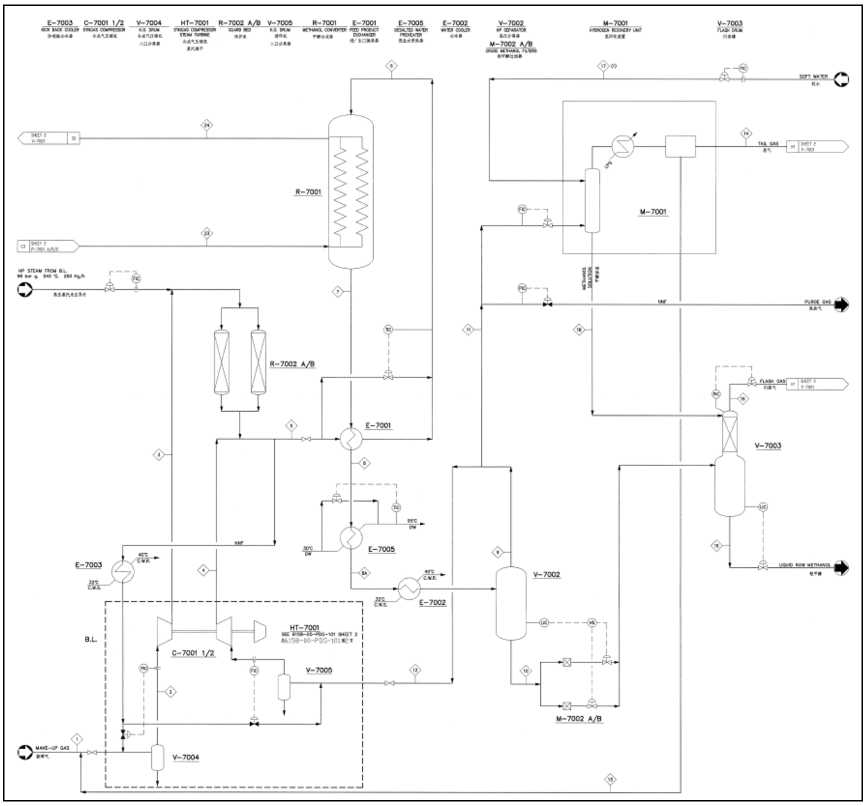

Figure 5. Xinneng Energy Limited - Xin'ao Group process flow diagram of synthesis section

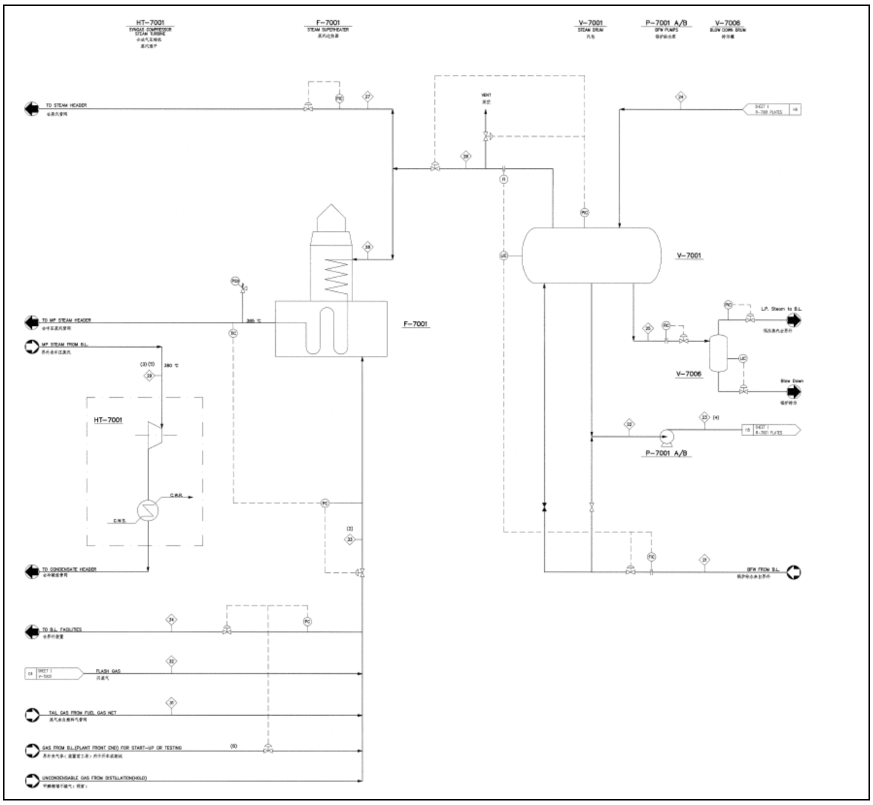

Figure 6. Xinneng Energy Limited - Xin'ao Group process flow diagram of steam section

At 100% of the load the saturated steam production was in line with the design value. Loop operating pressure is more than 10 bar below design value, showing that converter and catalyst are working very efficiently.

Table 3. Operating data in comparison with design data

	Design conditions (SOR)	29th October 2009	March 2010
Time on stream [months]	0	~4	~ 8
Plant Load	100%	96.2%	98.5%
Steam generated [ton/ton of methanol]	1.2	1.2	1.26
MUG consumption [kmol/ton of methanol]	101	97	98
MeOH converter out [%mol] (simulated value)	14	12.6	13.3
Converter pressure drop [bar]	2.0	1.06	N.A.
Operating pressure at converter inlet [barg]	82.3	71.0	79

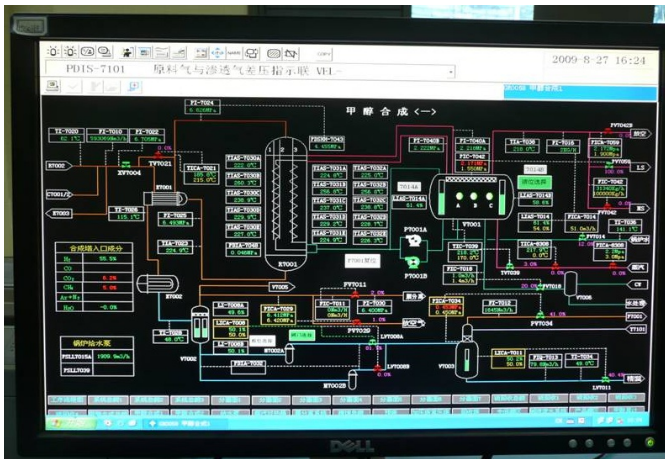

Figure 7. Picture of converter structure with steam drum on top level and DCS of Xinneng Energy Limited - Xin'ao Group plant

4) CONCLUSIONS

Producing methanol from gasification of coal or petroleum coke requires tailor made solutions that can differ significantly from those so far used in the more common gas based plants, to take full advantage of the peculiarities of the synthesis gas generated with this process.

Casale has acquired valuable experience in coal gasification projects thanks to the Chinese experience and the fruitful and close collaboration with Chinese Clients and Companies.

SHANGHAI COKING AND CHEMICAL CORP. and XINNENG ENERGY LIMITED - XIN'AO GROUP represent two milestones for Casale history and technology. Their smooth start-up and fast achievement of design load is a benchmark of Casale advanced technology and highlight the farsightedness of these two companies, making them a reference point in methanol industry.