Cost Effective CO₂ Capture from Flue Gas for Increasing Methanol Plant Production

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Abstract

Many methanol plants utilize steam-methane reforming (SMR) to produce syngas that is fed into a synthesis loop for producing methanol. As is typical for SMR-based methanol plants, the stoichiometry of the reactants is not at a value that is optimum for the most efficient reactor loop. In order to increase the methanol production capacity, the stoichiometry of the make-up gas can be corrected by injecting CO₂ into the process. A case study is presented in which Fluor’s Econamine FG Plus™ technology is used for recovering sufficient carbon dioxide from the SMR flue gas to expand the plant capacity by approximately 20%.

Keywords: Fluor; Econamine FG Plus™; EFG+; CO₂; CO₂ Capture; Methanol; Syngas; Methanol Production

1. Introduction

For natural gas based methanol plants, typical options available for synthesis gas production are: 1) Steam Methane Reforming (SMR) and 2) SMR followed by oxygen blown auto thermal reforming (ATR). SMR-based synthesis gas production is normally used for methanol plant capacities up to 2500 metric tons per day (t/d). The SMR followed by oxygen-blown ATR option is normally used for plant capacities greater than 2500 t/d.

In SMR-based methanol plants, the stoichiometry of the reactants in the synthesis gas is not at a value that is optimum for methanol production; there is about 30% more hydrogen relative to the carbon oxides. In order to increase the methanol production capacity by correcting the stoichiometry of the make-up gas, CO₂ can be injected into the process. The optimal methanol reaction stoichiometry can be described by the following ratio (also known as the stoichiometric number, SN):

\[
SN = \frac{H_2 - CO_2}{CO + CO_2} = 2.0 \text{to} 2.05
\]
In SMR-based methanol plants, the SN is normally about 2.95. When this ratio is decreased to 2.05 through the injection of CO₂; the hydrogen usage efficiency increases in the methanol synthesis loop resulting in an increase in the methanol production. This means both lower natural gas consumption and lower emissions from the SMR furnace per ton of methanol produced.

The source of CO₂ can be the SMR flue gas rather than purchase from an outside supplier. Advantages of recovering CO₂ from the SMR flue gas are:

- Cost certainty (i.e. control of source, quality and quantity of CO₂)
- No pipeline or rail/road transportation
- Carbon footprint reduction

Fluor’s Econamine FG PlusSM (EFG+) technology is a proven, cost-effective process for the removal of CO₂ from low pressure gases containing oxygen, such as an SMR flue gas. Fluor has extensive experience recovering CO₂ from steam reformer stacks. Furthermore, Fluor continually focuses on improving the EFG+ process configuration to lower the energy consumption by developing solvent and flow sheet enhancements.

This paper presents the main features of the Fluor’s EFG+ process and its implementation in a natural gas based 1200 t/d methanol plant.

**Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>DCC</td>
<td>Direct Contact Cooler</td>
</tr>
<tr>
<td>EFG+</td>
<td>Econamine FG PlusSM</td>
</tr>
<tr>
<td>kg/t</td>
<td>Kilogram per Metric Tonne</td>
</tr>
<tr>
<td>SMR</td>
<td>Steam Methane Reforming</td>
</tr>
<tr>
<td>SN</td>
<td>Stoichiometric Number</td>
</tr>
<tr>
<td>ST/d</td>
<td>Short Tons per Day</td>
</tr>
<tr>
<td>t/d</td>
<td>Metric Tonne per Day</td>
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**2. Implementation Strategy**

Fig. 1 shows a simplified block flow diagram of the natural gas-based methanol plant (Base Case).

![Fig. 1. Methanol Plant Simplified Block Flow Diagram (Base Case).](image)

The recovered carbon dioxide can be returned to the process in different ways. It can be injected either into the feed to the steam reformer, or directly into the make-up gas to the methanol plant prior to compression, or some
combination of the two. In any case, sufficient carbon dioxide needs to be returned to the process such that the stoichiometric number of the make-up gas is 2.05.

Adding the CO\(_2\) into the steam reformer feed gas (Option 1, Fig. 2) results in a higher ratio of CO to CO\(_2\) in the make-up gas, which leads to less water in the crude methanol stream. However, because the CO\(_2\) is sent through the steam reformer, the increased reformer throughput increases the reformer heat duty. For an economical revamp or in cases where the original plant has sufficient margin, lowering the steam to carbon ratio could be considered to maintain the original reformer heat duty.

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**Fig. 2.** Econamine FG Plus\(^{SM}\) Unit with CO\(_2\) Addition to the SMR Natural Gas Feed (Option 1; Preferred).

**Fig. 3.** Econamine FG Plus\(^{SM}\) Unit with CO\(_2\) Addition to the Make-Up Gas (Option 2).
Option 2 (Fig. 3), in which CO₂ is directly injected into the make-up gas to the methanol plant, has minimal impact on the steam reformer heat load and the process steam demand for a given methanol production as compared to Option 1. However, the implementation of Option 2 results in higher water content in the crude methanol product and this might adversely impact the methanol distillation system.

After careful consideration of the plant design and hydraulics, Option 1 (Fig. 2) was selected for this study.

2.1. Impact on SMR Flue Gas Composition

The injection of CO₂ into the methanol plant as per Options 1 or 2 will affect the steam reformer flue gas composition as compared to the Base Case. Hence, the flue gas composition needs to be recalculated before it can be used as the basis for the design of the Econamine FG Plus℠ plant.

Methanol plant simulations were developed to determine the effects of adding the recovered carbon dioxide and hydrogen back to the process. From these calculations, it can be seen that when the SN of the make-up gas is corrected, the methanol loop becomes more efficient, resulting in the following effects:

- The hydrogen consumption efficiency increases
- The purge gas rate decreases
- The hydrogen concentration of the purge gas decreases (and the CO₂ concentration increases)

The changes to the purge gas rate and composition results in an increase in the rate of natural gas firing (as fuel) in the SMR. The net result is an increase in the CO₂ concentration of the flue gas. The calculated change in flue gas from the Base Case is shown in Table 1. (Note that the compositions shown in this table assume that the reformer convective section is air tight, i.e. there is no air infiltration into the convective section.)

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Base Case</th>
<th>Option 1</th>
<th>Option 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>4.2</td>
<td>8.7</td>
<td>8.6</td>
</tr>
<tr>
<td>N₂</td>
<td>67.8</td>
<td>70.7</td>
<td>70.1</td>
</tr>
<tr>
<td>O₂</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>27.0</td>
<td>19.6</td>
<td>20.3</td>
</tr>
</tbody>
</table>

The flue gas composition listed in Table 1 for Option 1 (or alternatively Option 2) can be used for the basis of the Econamine FG Plus℠ plant.

In addition to an increase in CO₂ concentration, the quantity of CO₂ available for recovery also increases for Option 1 and 2 over the Base Case. This is important, since the amount of CO₂ recovery required to achieve a stoichiometric ratio of 2.05 was greater than the amount of CO₂ even available in the Base Case flue gas. At the modified flue gas composition and flow rate for Option 1, approximately 59% of the carbon dioxide from the flue gas would have to be recovered for injection to the process.

Because of the change in carbon dioxide concentration and flow rate in the reformer flue gas that accompanies CO₂ injection into the methanol plant, the Base Case flue gas should not be considered for CO₂ recovery.

If the same radiant heat duty were used for the Option 1 configuration as what was required for the Base Case, the syngas production would be sufficient for a 22.5% increase in the methanol production rate (increase in nominal capacity from 1200 t/d to almost 1500 t/d).

When considering CO₂ injection for adjustment of the stoichiometric ratio, consideration must also be given to the operating/expansion limits of the methanol plant. Specific items to consider include:

- Operating/expansion limits of the SMR, including the convective section
- Operating/expansion limits of the syngas compressor
- Operating/expansion limits of the methanol reactor loop
- Best location(s) for adding CO₂ to the process to improve the make-up gas stoichiometry
3. Carbon Capture Unit (Econamine FG Plus™)

Calculations indicate that if the same SMR radiant heat duty were used for the Option 1 configuration as what was required for the Base Case, the syngas production would be sufficient for an approximate 20% methanol production rate increase. A carbon dioxide recovery unit with 500 t/d (550 ST/d) nominal capacity is predicted.

Fluor can offer its proprietary Econamine FG Plus™ (EFG+) technology for the carbon dioxide recovery unit. The EFG+ technology is a proven, cost-effective process for the removal of CO₂ from low-pressure gases containing oxygen. Fluor has built or licensed 28 amine plants worldwide based on its EFG+ technology.

The EFG+ technology utilizes a solvent formulation that is specially designed to recover carbon dioxide from low pressure, oxygen-containing streams, such as a boiler and reformer stack gas and gas turbine flue gas streams. One of the challenges to installing a carbon dioxide recovery unit on any of these types of gas streams is the pressure sensitivity of the upstream unit. Fluor has successfully installed EFG+ units on the exhaust duct of a gas turbine in a power plant, where neither backpressure nor pressure fluctuations can be tolerated. The technology is also located on steam-methane reformer flue gas lines in Brazil and Singapore. These plants have consistently removed the carbon dioxide from the flue gas without disturbing the upstream pressure.

The two EFG+ plants that were installed on steam-methane reformers in Brazil were each designed with a capacity of 90 t/d (99 ST/d) CO₂ with the first being commissioned in 1997. The CO₂ recovered was used both for the food industry and to increase methanol production. The EFG+ plant installed in Singapore was commissioned in 2002. This plant was designed to recover 36 t/d (40 ST/d) of CO₂ from a steam reformer flue gas with the recovered CO₂ being used in the food industry.

The CO₂ produced from the EFG+ process is of high purity (>99.9% dry basis). A simplified depiction of an EFG+ based Carbon Capture unit is shown in Fig. 4.

![Fig. 4. Simplified Depiction of an Econamine FG Plus™ for recovery of 500 t/d (550 ST).](image-url)
lean solvent flash configuration, and large column design. Many patents have been issued and more are pending on various other design aspects to improve performance and remain a world leader in the industry of carbon capture.

The above list serves as a menu of options from which a customized plant design can be developed. Each CO₂ removal application has unique site requirements, flue gas conditions and operating parameters. Based on the given CO₂ removal application, it may be beneficial to implement only some of the enhancement features listed above. In this way, every plant will be optimized for its specific CO₂ removal application. The overall energy demand associated with a customized EFG+ plant can be up to 25% lower compared to that of a non-customized plant.

3.1. Improved Solvent Formulation

Generic solvent based plants operate at low concentrations of approximately 18-20 wt%. Fluor’s previous EFG plants were based on a solvent concentration of 30 wt%. Current EFG+ plants are designed with solvent concentrations greater than 30 wt%.

The improved solvent formulation results in increased reaction rates, which decreases the required packing volume in the absorber, thereby lowering capital cost. Utilizing both the low-pressure drop structured packing along with the improved solvent formulation, the packing volume required for CO₂ absorption is reduced by up to 40%. Furthermore, the improved solvent also has higher solvent carrying capacity for carbon dioxide, thus decreasing the solvent circulation rate; this reduces the plant steam requirement by up to 10% along with lowering the capital cost for solvent circulation equipment.

3.2. Absorber Intercooling

As the EFG+ solvent absorbs CO₂, heat is released and the solvent warms. The warming has two effects:

- Increased reaction kinetics between the CO₂ and the solvent leading to improved absorption.
- Decreased CO₂ carrying capacity of the solvent leading to decreased absorption.

Fluor has developed Absorber intercooling to optimize the absorption temperature profile by removing excess reaction heat from the column, thereby improving absorption while also increasing the solvent’s CO₂ carrying capacity. With intercooling, less solvent needs to be circulated for every ton of CO₂ that is absorbed. Solvent regeneration energy is also reduced since a smaller quantity of solvent needs to be regenerated. When applied, absorber intercooling reduces the EFG+ plant energy consumption by 5-10%.

3.3. Low Pressure Drop Packing in the Direct Contact Cooler (DCC)

Fluor employs structured packing in the DCC and Absorber columns specifically designed to provide a large area for mass transfer while maintaining very low pressure drops throughout the flue gas path. Low pressure drop through the flue gas path is imperative in order to minimize the Blower electrical power that is necessary to push the flue gas through the EFG+ plant. The low pressure drop packing in the DCC and Absorber columns reduce the pressure rise across the Blower by 40-50%. This smaller pressure rise in the Blower directly leads to reduced electrical power consumption resulting in a lower annual operating cost.

3.4. Lean Solvent Flash Configuration

In a standard EFG plant, the lean solvent from the Stripper, containing a low loading of carbon dioxide, is cooled and routed to the Absorber. Fluor now offers a lean vapor flash configuration (patent pending) in which the hot lean solvent from the Stripper is flashed at low-pressure in a flash drum. The resulting flashed vapor consists mostly of steam with small amounts of carbon dioxide and solvent. The flashed vapor is compressed in a thermo-compressor and returned to the bottom of the Stripper where it flows upward through the column while stripping CO₂ from the rich solvent.
With a portion of the stripping steam requirement being supplied by the flashed vapor, the reboiler steam requirement is reduced. Since the temperature of the lean solvent is reduced in the flash drum, the temperature of the rich solvent leaving the cross exchanger is also reduced, thereby lowering the temperature at the top of the Stripper. This results in a lower cooling load in the condenser and therefore, a lower overall plant cooling water requirement.

Both the capital cost and power requirements of the plant increase with the lean vapor compression configuration. However, the steam savings in the reboiler very often pay for the increased costs elsewhere. Ultimately, the benefits of this configuration are dependent on the relative costs of steam and power, but Fluor has encountered several cases for large-scale plants where this configuration pays out in a relatively short period of time due to an overall energy demand reduction of 5-15%.

3.5. Solvent Reclaiming and Waste Generation

Solvent reclaiming is required to remove contaminants from the circulating solvent loop that cannot be removed by the in-line cartridge filters or activated carbon filtration bed. These contaminants include heat stable salts and non-volatile degradation products. The solvent reclaimer concentrates and removes these contaminants as a waste that must be periodically hauled off-site for disposal. Without solvent reclaiming, these contaminants would build-up in the circulating solvent loop and continually degrade the plant performance until the entire solvent inventory would periodically need to be drained, disposed of, and replaced. Therefore, the reclaimer system serves to minimize the overall plant waste generation.

In addition to non-regenerated heat stable salts and non-volatile degradation products, the reclaimer waste consists of unrecovered solvent, water and soda ash or caustic solution. The quantity of reclaimer waste generated is highly dependent on flue gas characteristics including, but not limited to:

- SO\(_x\) and NO\(_x\) concentrations
- Oxygen partial pressure

For SMR-based flue gases, which typically have very low SO\(_x\), NO\(_x\) and O\(_2\), the reclaimer waste generation is on the order of 0.1-0.2 kg/t of CO\(_2\) recovered.

3.6. Coal Flue Gas Demonstration at Wilhelmshaven, Germany

In 2008, Fluor and E.ON Energie AG (E.ON) formed a partnership to construct a demonstration plant for the purposes of advancing CO\(_2\) capture technology. This plant is designed to capture CO\(_2\) from the flue gas of a coal fired plant using Fluor’s EFG\(^+\) technology. Many of the energy saving features described above have been demonstrated at the Wilhelmshaven plant. A picture of the Wilhelmshaven EFG\(^+\) Demonstration plant is provided as Fig. 5.
4. Conclusion

Correcting the SN of the make-up gas to 2.05 greatly improves the efficiency of the methanol reactor loop. As a result, the methanol plant capacity could likely be increased. Fluor’s analysis indicates that if the same SMR radiant heat duty were used, by just injection of CO₂ into the reformer feed, the syngas production would be sufficient for an approximate 20% increase in the methanol production rate. In order to achieve the 20% methanol production rate increase, a carbon capture unit with 500 t/d (550 ST) nominal capacity is required. This is approximately 59% of the carbon dioxide from the SMR flue gas.

Fluor’s EFG+ technology has been demonstrated to efficiently remove the CO₂ from the low pressure SMR flue gas without disturbing the upstream unit (Reformer) pressure.