Enhancing Methanol Production by CO_2 Injection

BY:

ABDULATIF M. AL-MUSABBEH
Saudi Methanol Co., Jubail, K.S.A.

SAYER M. AL-SHAMMARI
Saudi Methanol Co., Jubail, K.S.A.

Date

15th APRIL 2006

ABSTRACT

Ar-Razi had conducted a feasibility study about enhancing the methanol production by 20% via CO_2 injection. This injected CO_2 will be recovered from existing Reformer Flue Gas. The advantage of CO_2 injection had resulted in attractive economical cost for methanol production as well as high contribution to reduce the emission of CO_2 to atmosphere.

However, the remarkable achievement in this study is not only the production increase that will reach 20%, but also the CO_2 source, which will be recovered from existing steam reformer Flue Gas. Recovery of CO_2 from flue gas and use it in boosting methanol production can make Ar-Razi Pioneer in the industries.

ARRAZI own the largest methanol complex in the world within one fence through 4 independent plants, with nameplate capacity equivalent to 3.1 million Metric Tons per Year. Methanol is produced through well-known conventional technology, which consists of steam reformer, methanol Converter, and distillation. ARRAZI steam reformers can approximately emit 1880 KNM3/h of flue gas from which CO_2 can be recovered.

In conventional Methanol process CO_2, CO and H_2 (SynGas) are produced by reforming natural gas and then react together on synthesis catalyst to produce crude methanol. Since the H_2 exists in excess quantity, injecting CO_2 to SynGas can increase methanol production.

Brief description about the project is as follow: flue gas will be pulled from two reformer stacks via blower, and then cooled down by direct contact with cold water. Next, flue gas will be treated in two-column absorption technology using amine-based solvent to capture CO_2. Purified CO_2 will be pressurized and then injected in the methanol process.

The technical evaluation showed that de-bottlenecking the methanol plants is feasible from operation and maintenance point view. In addition, Economical evaluation had showed attractive return and payback period.

Introduction:

Feasibility study had been conducted to de-bottleneck Ar-Razi methanol plants. The purpose of de-bottleneck study was to inject the methanol plants by CO_2 in order to increase the production considering methanol demand growth, improve the production cost and sustain against the impact of Natural Gas change.

Three methanol plants were considered in CO_2 injection which will result in 20% overall production increase; approximately 1515 Ton/day.

CO_2 source will be the flue gas emitted by two existing steam reformers, which will be recovered through Amine-Based Chemical Absorption process.

As result of recovering CO_2, AR-RAZI will contribute in reduction of CO_2 emission, which is one of the worldwide environment concerns.

This paper will focus on the CO_2 source since it was found the major subject in the de-bottlenecking the plants.

De-bottleneck Configuration:

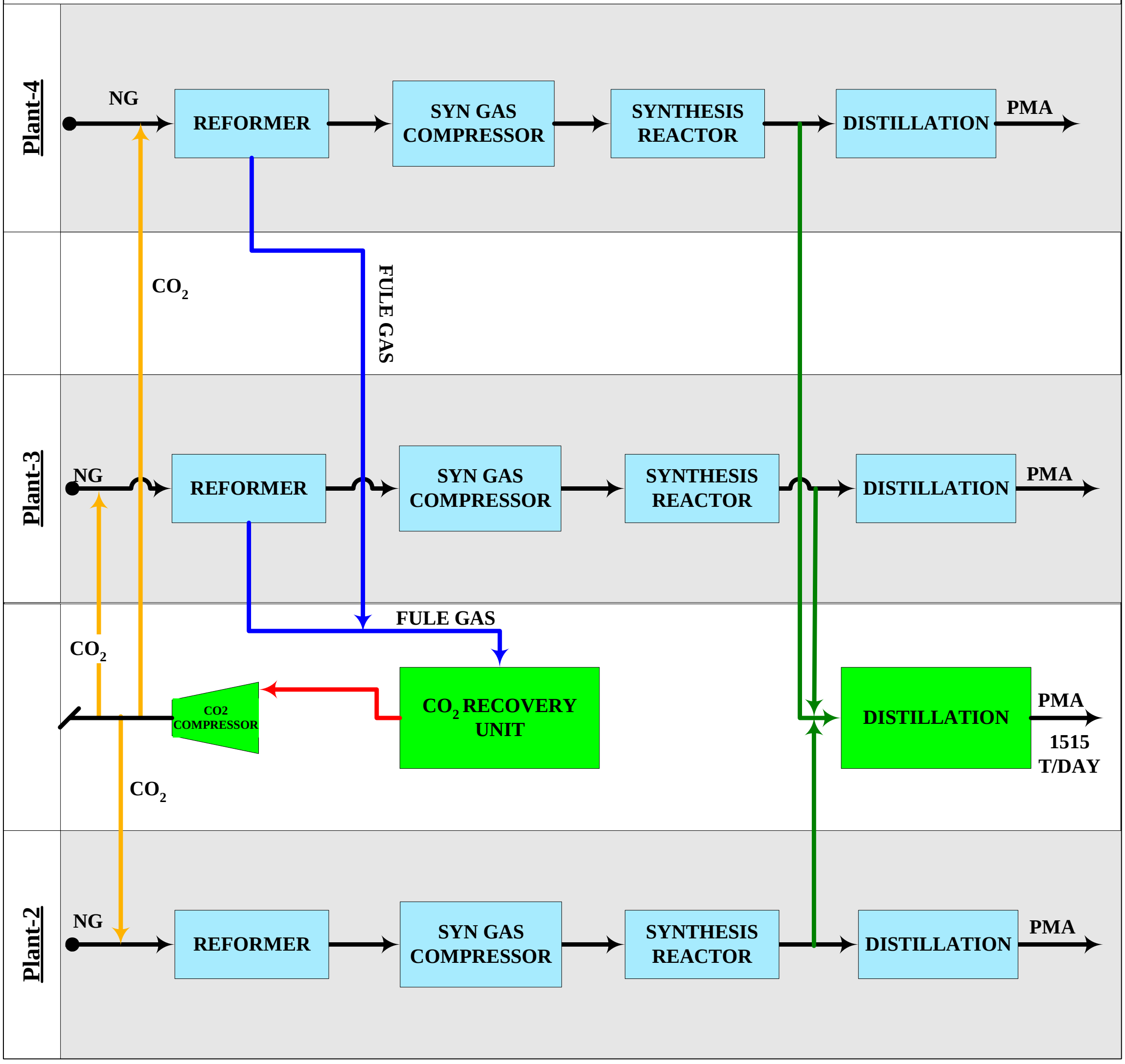
Production of three plants will be increased by injecting CO_2 to upstream of the reformer section, which will increase the Methanol production by 20% as overall. The incremental crude methanol will be treated in additional distillation unit with design capacity of 1515 ton/day.

The CO_2 source will be the flue gas emitted by two steam reformers that will be treated in chemical absorption recovery process to capture the CO_2 from flue gas; the capture solvent will be amine based solution. The design capacity of the CO_2 recovery process will be 3000 ton/day of CO_2.

Beside the process changes, it had been found that an additional cooling duty is necessary mainly to quench the flue gas and cool the additional crude methanol. In addition, electrical substation is required to supply additional power requirement.

Configuration of Debottleneck Methanol Plants

Note: Green Filled Blocks Will Be The New Units.



Legend: PMA is Pure Methanol Product

So, the de-bottlenecking of three plants will require the following additional facilities:

1. Distillation unit
2. CO_2 recovery unit.
3. Cooling system
4. Additional Electrical station

Background of CO_2 Source:

Carbon dioxide is used in the food industry in carbonated beverages, brewing, and flash drying. Its industrial uses include enhanced oil recovery (EOR), welding, chemical feedstock, inert gas, firefighting, and solvent extraction as a supercritical fluid. It is an essential ingredient in medical oxygen, where in low concentrations it acts as a breathing stimulant.

The largest potential market for CO_2 is EOR and chemical Industries. The major CO_2 sources that can be considered for industrial market are (1):

1. Natural sources
    a. CO_2 wells
2. Industrial byproducts
    a. Natural gas sweetening
    b. Synthesis gas production
3. Flue gases
    a. Fossil fuel-fired power plants
    b. Industrial furnaces
    c. Cement plants
    d. Engine exhausts
    e. Lime kiln exhausts

The most economical sources of carbon dioxide are CO_2 wells and natural gas sweetening or synthesis gas purification byproducts. However, the price of methanol justifies the recovery of CO_2 from flue gas sources (1).

Flue gases have long been important sources of CO_2 for the merchant CO_2 market, especially in remote locations or when by-product CO_2 sources are unavailable or insufficient. In the simplest case, fuel is combusted to produce flue gas then CO_2 is extracted from the flue gas.

CO2 Recovery from Flue Gas

There are several methods to capture CO_2 beside the amine based chemical absorption technology, which is well known since long time. Some of these are not practically economic for capturing CO_2 from flue gas, while some are not yet proven or technically not applicable for capturing CO_2 from flue gas. Below is brief description about theses methods (1 & 2).

1. **Higher Pressure Absorption Process:** Absorption at atmospheric pressure severely handicaps processes that rely on higher pressures. For these process, the driving force for CO_2 absorption and the cyclic loading between absorption and de-sorption will be insufficient for economical CO_2 recovery. Alternately, compression costs to put the flue gas into the operational range of these processes are prohibitive.

2. **Hot Potassium Carbonate:** Hot potassium carbonate (HPC) or "Hot Pot" is effectively used in many ammonia, hydrogen, ethylene oxide and natural gas plants. The most widely licensed of these are the Benfield process. This process was proposed for treating flue gases but optimum operating pressure for the process found to be 7.0 Bar (g), which will be uneconomical for large scale flue gas recovery.

3. **Membranes:** Membranes suffer from both the cost of compression, heat exchange and flue gas components to obtain high pressure feed and in that they produce an impure CO_2 product. There are currently no commercial applications of membranes for recovery of CO_2 from flue gases, though they have been used in large EOR projects to recycle CO_2 from the associated gas.

4. **Cryogenic Liquid Purification:** Cryogenic methods for CO_2 capture options are considered for only Integrated Gasification Combined Cycle (**IGCC)** and the combustion in pure O_2 / CO_2, since the low concentration of CO_2 in the flue gas makes this uneconomical for other cases like steam reformer.

5. **Adsorption:** Consideration of the gas-solid adsorption options concentrated on the use of molecular sieves in fixed beds. Adsorption may not be an attractive option for CO_2 capture mainly because the

capacity of solids to absorb gas and the selectivity are relatively low. The removal of CO_2 from gas streams by an adsorbent is most effective when the CO_2 content is between 400ppm and 1.5 % by volume.

As result of above survey, chemical absorption using amine-based solvent was concluded to be the most reliable option for CO_2 recovery from flue gas; especially that flue gas is low-pressure environment. It is commercially available, proven, being significantly improved and routinely used for small plant and skid mounted units for chemical and food industries.

Provider of Amine-Based CO_2 Recovery Process

Among the chemical absorption of CO_2 recovery process the following chemical companies were found involved in this field:

1. **ABB** (Jointly by Kerr-McGee & ABB Lummus)
2. **Flour Daniel** (Econamine FG^{TM})
3. **MHI** (jointly by MHI&KEPCO)
4. **Wittcold**

In next page, table can show the contribution of those engineering companies about the CO_2 recovery process:

ABB, Flour Daniel and MHI have own propriety CO_2 recovery process. All of them had built CO_2 Recovery plant at small scale.

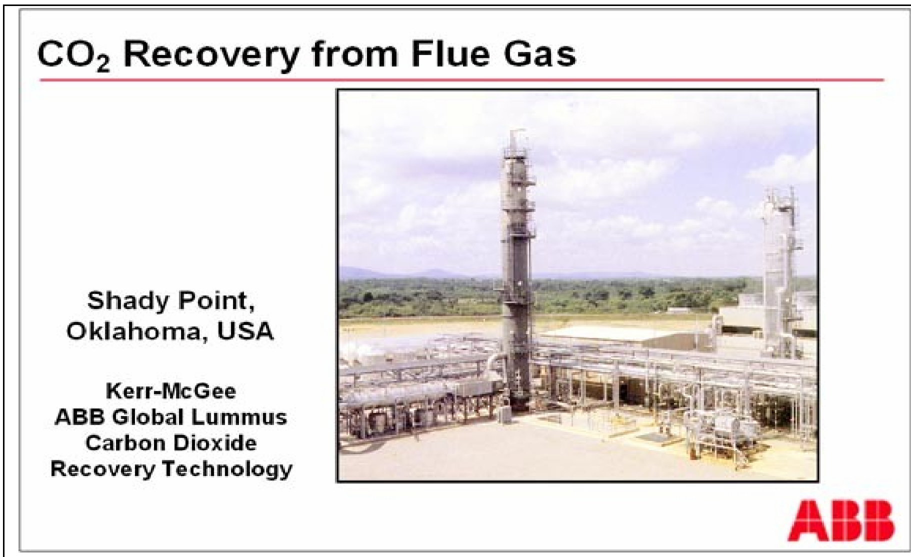
In addition, ABB, Fluor Daniel and MHI had conducted feasibility study for large CO_2 recovery from flue gas; these studies had concluded that the CO_2 recovery from flue gas is technically feasible.

CO2 Recovery Process Provider				
	ABB	**Flour Daniel**	**MHI**	**Wittcold**
References (Built & Commissioned Plant)	4 Plant + 1 Pilot plant	Over 21 plants	2 Plants + 1 Pilot Plant	8 Plants
Maximum Capacity built	400 t/d **(Fired with Coal)**	350 t/d **(Gas turbine exhaust)**	160 t/d **(Fired with natural gas)**	50 t/d
Conducted Feasibility Study for Large Unit?[1]	Yes	Yes	Yes	-
Solvent	15~20 % MEA + Inhibitor	30% MEA + Inhibitor	Strictly Hindered Amine (KS-1)	MEA
Absorption Contactor	Random or Structural Packing	Random Packing	Low pressure packing (KP-1)	Structural Packing

[1] Defined Criteria for large scale is a minimum 2400 t/d of CO_2 if flue gas result of NG firing and 4600 t/d if flue gas result of firing of Coal.

Proven CO_2 Recovery on Gas Turbine Exhaust; Bellingham Plant, USA - Aerial View (350 t/d) **(Fluor Daniel)**

CO_2 Recovery plant in Kedah, Malaysia (160 t/d) **(MHI/KEPCO)**



Process Description of CO_2 Recovery Unit:

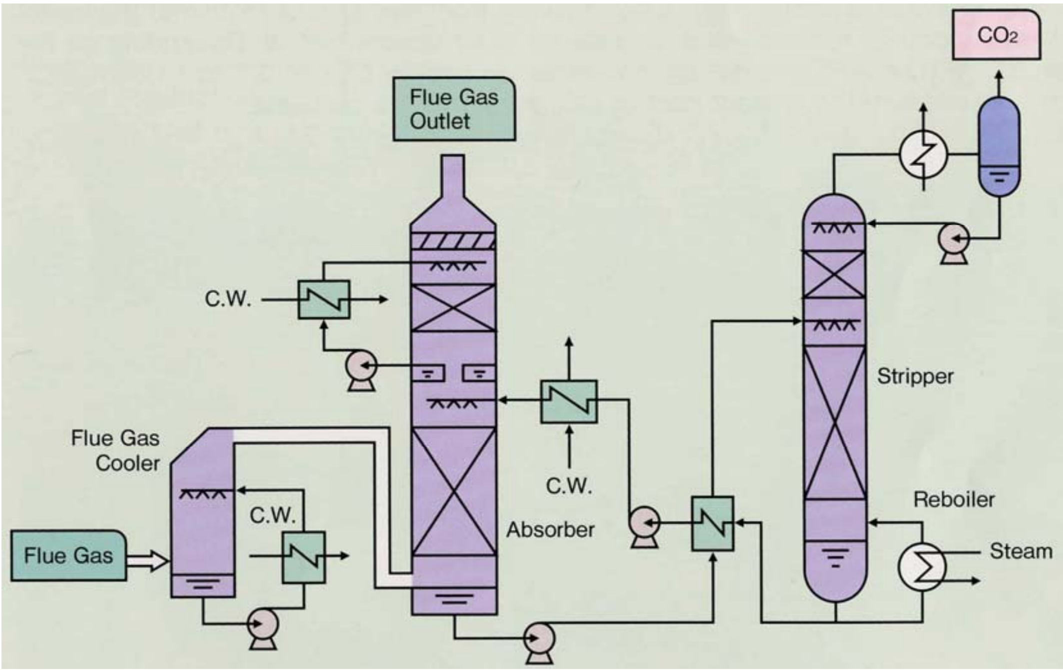
The flue gas contains approximately 9.8% (vol. %, dry basis) of CO_2 and at 200^oC will be pulled from two reformer stacks by blower through rectangular duct. The flue gas from the stack is slightly pressurized by the Flue Gas Blower and sent to the Flue Gas Water Cooler. In the Flue Gas Water Cooler, the flue gas is quenched by direct countercurrent contact with circulating cooling water

Then, the flue gas leaving the Flue Gas Water Cooler enters the bottom of CO_2 Absorber and flows upwards, countercurrent to the lean solution. CO_2 in the flue gas will be absorbed into the amine-based solution through direct contact. Packing is installed within the absorption section in order to increase surface area where the absorption reaction between the solvent and the CO_2 in flue gas takes place. The treated flue gas exits the top of the Absorber at low temperature.

The CO_2 absorbed in the rich solution is removed from solution by steam stripping in the CO_2 Stripper. The rich solution containing CO_2 contacts with steam from the reboiler through the packing to receive heat from the steam in order to dissociate the CO_2 from the solution. The CO_2 and steam rise to the top through the CO_2 Stripper and contact with the reflux water where the solution vapor is recovered. The overhead vapor is cooled to in the Stripper Condenser. The condensate accumulates in the Stripper Reflux, and is pumped by the Stripper Reflux Pump to be retuned to the top of the CO_2 Stripper.

The recovered CO_2 is sent to the suction drum of the CO_2 Compressor, and the mist is separated. The recovered CO_2 is then pressurized by centrifugal compressor and sent to the three methanol plants.

Next page, simple diagram for the CO_2 recovery can be shown.



Simple Diagram for

CO_2 Recovery System from Flue Gas

Technical Concerns

This section will discuss the concerns that had been identified to design large CO_2 recovery unit. No Carbon Dioxide recovery unit had been built more than 400 ton/day, while the target in this study is 3000 ton/day, however many studies have been conducted to prove that large scale is feasible. The limitation is the maximum diameter of absorption column and cooling vessel for the flue gas. The largest economic single train is 2400 t/d (based on the maximum column diameter is 12.8m). For very large vessel it will be more cost effective if constructed with rectangular cross section.

In addition, at certain level of study it had been found that large single blower should be adopted to pull the flue gas from two steam reformers, however, similar operating condition was identified in power plant, which was visited, and its operability and reliability had been confirmed.

Moreover, flue gas distribution and flow pattern through the cooling vessel and absorption column was also an important issue since the flue gas quantity is huge and shall flow through big duct and large cooling vessel and absorption column. It had been concluded that, careful fluid dynamic shall be performed at detail design stage and necessary countermeasure shall be taken.

Economical Evaluation Result:

The economical part of the project was executed in very molecules way covering all realistic data and information, several analysis process in terms of data authenticity and history. The results achieved were tested further and sensitivity analyses session identified final IRR, ROI, NPV and payback period.

Conclusion:

De-bottleneck of AR-RAZI methanol plant was found technically and economically feasible. The general concern about the CO_2 recovery from flue gas was identified with recommendations, the technology is commercially available, mature and being significantly improved. The de-bottleneck study can be brought to further level of project phases.

References

1. Chapel Dan G. and Mariz Carl L., “Recovery of CO_2 from Flue Gases: Commercial Trends”, 1999.

2. IEA Greenhouse Gas R&D program, “carbon dioxide capture from power station”.