



CO₂ Abatement Through a Methanol Production Process

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A CO₂ to methanol process was simulated and optimized with Aspen Plus. The CO₂ comes from the capture by chemical absorption from the flue gas of a coal thermoelectric plant. The thermoelectric plant provides electrical energy for CO₂ capture and the methanol plant. Hydrogen is produced from the electrolysis of water using a carbon-free source of electricity. The methanol plant provides 46 % of the steam necessary for CO₂ capture, which remarkably reduces the impact of CO₂ recovery on the performance of the thermoelectric plant. The CO₂ balance showed that it is possible to abate a large amount of CO₂ from the production of methanol if carbon-free hydrogen is available.

1. Introduction

Carbon dioxide is the main anthropogenic greenhouse gas, and its emissions increased significantly during the last decades. At present, the carbon cycle, where CO₂ is the major factor, does not work in a balanced way. Anthropogenic emissions of CO₂ were 26·10⁹ t in 2004, and keeping the current trends, they are likely to double by 2050 (IFP, 2007). About 40 % of global anthropogenic CO₂ comes from thermoelectric plants fueled by natural gas and coal (Amann, 2007).

The use of CO₂ as a raw material transforms what today is considered as a constraint on economic opportunity. In this context, the recycling of CO₂ as a feedstock for the production of hydrocarbon substituents appears of great economical and environmental interest. Methanol can be produced from the hydrogenation of CO₂ and could replace gasoline, which therefore can potentially reduce the consumption of fossil fuels and enhance CO₂ recycling.

Methanol is a powerful candidate for replacing the gasoline due to its excellent combustion and lower pollution. In addition, DME (dimethyl ether) is a possible substitute for conventional diesel and is synthesized from the dehydration of methanol. Besides, methanol is a commodity of the chemical industry where it appears as an intermediate in many reactions.

Nowadays, methanol is mostly produced from the catalytic conversion of synthesis gas which is a mixture of CO, CO₂ and H₂. The synthesis gas can be produced from various carbon components; however, today the majority of large-scale methanol is derived from natural gas.

Mignard et al. (2003) proposed a methanol synthesis process from CO₂ captured from flue gas and electrolytic hydrogen. In order to have a significant abatement of CO₂, the process depends on availability of waste heat in the power plant to provide thermal energy to the process. In the absence of these thermal sources CO₂ abatement is almost null. Mignard and Pritchard (2006) compared the production of liquid fuels from the hydrogenation of CO₂, including methanol.

2. CO₂ to methanol production process design

The process proposed in this paper uses CO₂ captured from flue gas of a coal thermoelectric plant and hydrogen produced from electrolysis of water. The electrical energy used in the recovery of CO₂ and methanol synthesis comes from the coal plant, and that used in the electrolysis of water comes from a renewable source or at least a carbon-free one (e.g. nuclear).

The feed is stoichiometric with 88.0 t/h of CO₂ and 12.1 t/h of hydrogen. Aspen Plus™ V7.2 software was used for process simulation and design.

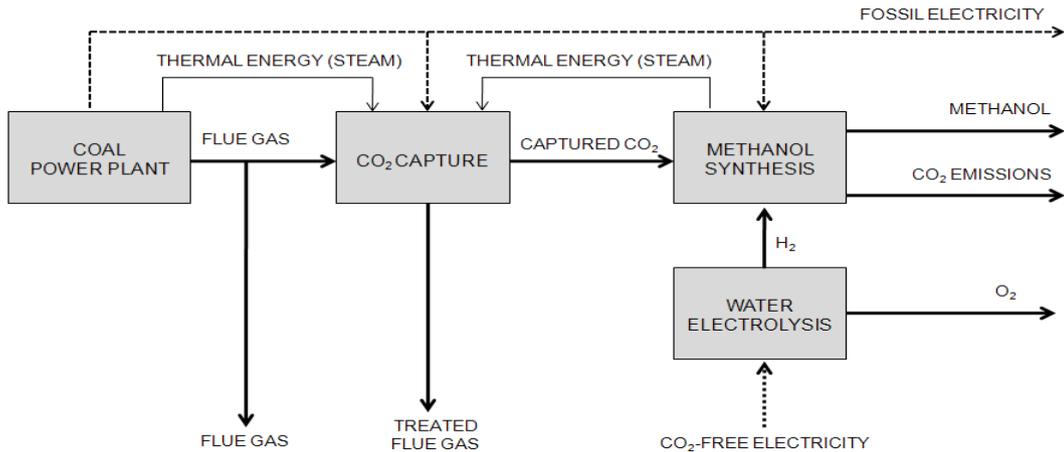


Figure 1: Bloc diagram of the process

The thermodynamic model used in equipments at more than 10 bar was the Redlich-Kwong-Soave equation of state with modified Huron-Vidal mixing rules. In equipments of less than 10 bar, the model used was NRTL-RK.

The commercial Cu/ZnO/Al₂O₃ catalyst was retained in this study. The kinetic model used is that of Vanden Bussche and Froment (1996) with readjusted parameters of Mignard and Pritchard (2008). The thermodynamic equilibrium constants are given by Graaf et al. (1986).

2.1 Water electrolysis

Hydrogen is produced from the electrolysis of water, with energy consumption of 4.8 kWh_{el}/Nm³. Hydrogen is supplied to the process at 30 bar and 25 °C, the conditions under which it leaves the electrolyser. Oxygen is generated as a by-product of electrolysis.

2.2 Oxygen by-product

Carbon credits are generated by the sale of by-product oxygen via pipeline to a chemical plant which uses it as feedstock. The ordinary production of oxygen by cryogenic air distillation consumes 0.42 kWh per tonne of O₂ (Bolland et Sæther, 1992). If a cryogenic process is used for the production of oxygen, CO₂ is emitted due to the consumption of electrical energy from fossil fuels. Thus, the carbon credits generated are equivalent to the amount of CO₂ that would be emitted if the oxygen is produced by the cryogenic process.

2.3 CO₂ capture

Amann (2007) studied the process of CO₂ capture by chemical absorption of the flue gas of a subcritical coal thermoelectric plant with desulfurization.

The net electrical power delivered by the plant is 556 MW_{el} with a CO₂ emission ratio of 857 g/kWh_{el}. For a capture rate of 85%, consumption is 44 kWh_{el} per tonne of CO₂ for the compression of feed and

3.2 GJ_{th} per tonne of CO₂ for the regeneration of the solvent. This thermoelectric plant is considered for this study.

In thermoelectric power plants where CO₂ capture is present, LP steam used in the capture is bled from the steam cycle of the plant. Given that there is an oversupply of steam in the methanol synthesis unit, this steam is sent to the capture unit. Therefore, the amount of steam bled from the plant is lower so is its impact on electricity production. The amount of steam sent corresponds to 46 % of the thermal energy necessary to CO₂ capture. Carbon dioxide is supplied to the process at 1 bar and 25 °C, conditions under which it leaves the capture unit.

2.4 Methanol synthesis and purification

Reactor

The reactor operates under adiabatic conditions, and is packed with 44500 kg of Cu/ZnO/Al₂O₃ commercial catalyst. The conversion of CO₂ is 33 % per pass in the reactor and the recycle ratio is 5.0. The present models do not consider the generation of by-products in the reactor. However, 0.4 % of by-product can be expected, most in form of methyl formate (NEDO and RITE, 1998; Mignard and Pritchard, 2006).

Distillation

Methanol is purified in a distillation column. The column was simulated with the rigorous model RadFrac Rate-Based of Aspen Plus. The BX structured packing was adopted, with 32.2 m of height and 3.6 m of diameter. Aspen Plus calculates the pressure drop in the column by a vendor correlation.

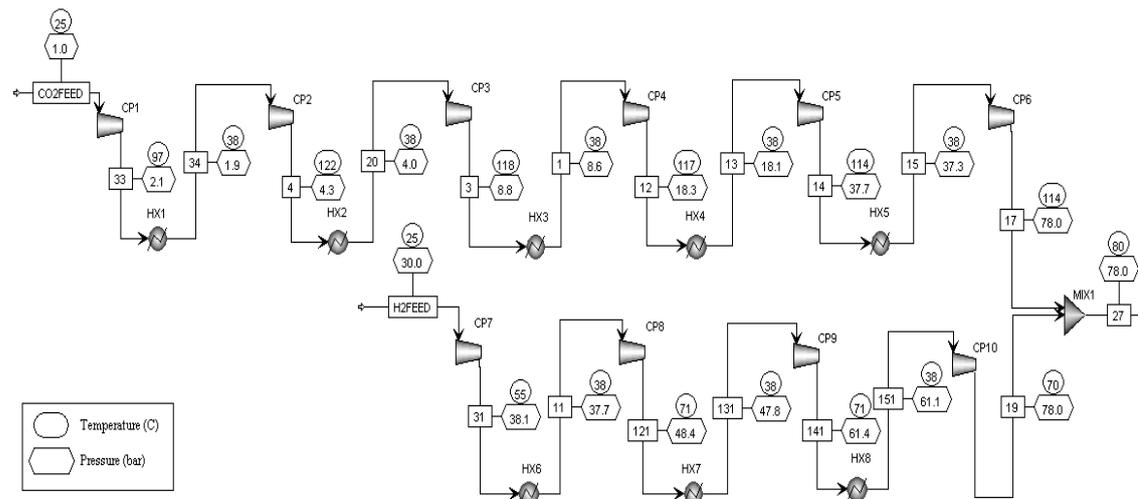


Figure 2: Flowsheet of compression unit

Heat and electricity

Heat exchanger network design was based on Pinch analysis performed with Aspen Energy Analyzer™ V7.1. All heat exchangers were designed with Aspen Exchanger Design and Rating™ V7.1. Steam is generated from the combustion with air of the purge and the gas stream leaving the top of the second flash tank (stream 16).

The streams of hot water leaving the heat exchangers HX1, HX2, HX3, HX4, HX7, HX8, E103 and bottom of the distillation column are used to generate electricity through an organic Rankine cycle. The work fluid is the R245fa.

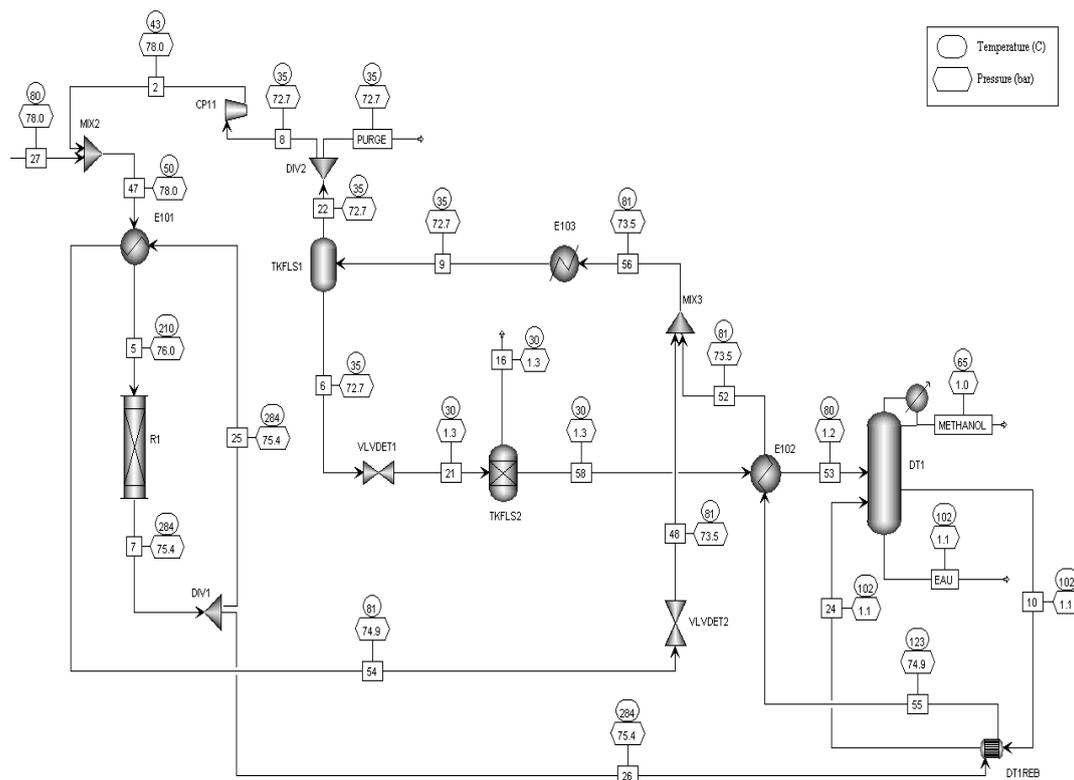


Figure 3: Flowsheet of reaction and purification units

Flowsheet description

CO₂ is fed at 1 bar and hydrogen at 30 bar, both at 25 °C. They are compressed to 78 bar in a series of compressors with intercooling. The two gases are mixed (MIX1) and then re-mixed with the recycle stream (MIX2). The current is then heated (E101) to 210 °C and injected into the adiabatic reactor. The gases leaving the reactor are divided (DIV1) into two streams: the first (60 % of initial current) is used to heat the fresh feed (E101), while the second is used in the reboiler (DT1REB) and also in the heating the feed of the distillation column (E102). The two streams are re-mixed (MIX3) and cooled to 35 °C by water (E103). Water and methanol, which were condensed in exchanger E103, are separated from the non reacted gases in a flash tank (TKFLS1).

The liquid stream leaving the flash tank, called crude methanol is composed of methanol, water and residual dissolved gases. Some of the non reacted gases (1 %) are purged to minimize the accumulation of inerts and by-products.

The crude methanol is expanded to 1.3 bar in a valve (VLVDET1). Then, the residual gases are removed in a second flash tank (TKFLS2). The remaining stream, which is composed of methanol and water, is heated to 80 °C in exchanger E102, and then sent to a distillation column (DT1). The water comes out from the bottom of the column at 102 °C, and contains 53 wt-ppm of methanol. Methanol comes out from the top at 1 bar and 65 °C, in liquid form, containing 10 ppm of water.

3. Results and discussion

The result of material, energy and CO₂ balances are presented in Tables 1, 2 and 3, respectively. Not including CO₂ emissions caused by energy consumption, the yield is 0.67 tonnes of methanol per tonne of CO₂ supplied. As it is shown in Table 2, the energy used for electrolysis of water corresponds

to 97 % of the net electrical power consumed. The methanol synthesis unit does not need external heat input, so 100 % of the thermal energy consumed is used in CO₂ capture.

As shown in table 3, if the oxygen by-product is sold, the process developed in this study may abate 1.7 tonne of CO₂ per tonne of methanol produced. If it is not sold, the figure is 1.2 t of CO₂ per t of methanol. However, if only 22 % of the power used in electrolysis comes from the coal plant, the CO₂ balance becomes null.

Table 1: Global mass balance

Compound	In (tonne/h)	Out (tonne/h)
CO ₂	88.0	6.6 ^c
H ₂ O	108.1	41.4
Methanol	0	59.3
O ₂	7.1 ^a	96.0 ^b
MEA	0.09	0.09

^a Oxygen from air used to burn the purge and the stream 16.

^b Oxygen generated by water electrolysis.

^c Sum of CO₂ content in the purge and in the stream 16 with the CO₂ produced by the combustion of these streams.

Table 2: Energy balance

Unit	Operation	Amount	
Water electrolysis	Power to electrolysis	645.1	MW _{el}
	CO ₂ capture		
CO ₂ capture	Compressing flue gas	3.9	MW _{el}
	Steam to regeneration column	77.7	MW _{th}
Methanol synthesis	Compressing fresh feed	15.9	MW _{el}
	Compressing gas recycle	2.9	MW _{el}
	Steam to methanol distillation	0	MW _{th}
	Steam generated	35.7	MW _{th}
	Electricity generated	1.9	MW _{el}

Table 3: CO₂ balance

In/Out	With sale of O ₂ (tonne/h)	Without sale of O ₂ (tonne/h)
CO ₂ fed to the process	- 88.0	- 88.0
CO ₂ rejected by methanol synthesis	+ 6.6	+ 6.6
Electricity consumption	+ 12.2	+ 12.2
Carbon credits generated	0	- 34.6
CO ₂ balance	- 69.2	- 103.7

4. Conclusions

A CO₂ to methanol process was simulated and optimized with Aspen Plus. The methanol plant provides 46 % of the steam necessary to CO₂ capture, which remarkably reduces the impact of CO₂ recovery on the performance of the thermoelectric plant. The CO₂ balance showed that it is possible to abate a large amount of CO₂ from the production of methanol if carbon-free hydrogen is available. Thus, methanol production is a viable way of CO₂ abatement; the main challenge remains to produce large flows of carbon-free hydrogen.

References

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