

Design and simulation of a methanol production plant from CO₂ hydrogenation



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ABSTRACT

There has been a large increase in anthropogenic emissions of CO₂ over the past century. The use of captured CO₂ can become a profitable business, in addition to controlling CO₂ concentration in the atmosphere. A process for producing fuel grade methanol from captured CO₂ is proposed in this paper. The process is designed and simulated with Aspen Plus. The CO₂ is captured by chemical absorption from the flue gases of a thermal power plant. The hydrogen is produced by water electrolysis using carbon-free electricity. The methanol plant provides 36% of the thermal energy required for CO₂ capture, reducing considerably the costs of the capture. The CO₂ balance of the process showed that it is possible to abate 1.6 t of CO₂ per tonne of methanol produced if oxygen by-product is sold, or 1.2 t if it is not.

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1. Introduction

Anthropogenic emissions of carbon dioxide have increased vertiginously in the last century. Despite the uncertainty about the consequences of this phenomenon in the long term, great part of the scientific community believes that increasing the CO₂ concentration in the atmosphere is closely linked to the recent global temperature increase. Thus, great efforts have been made to capture CO₂ (Rivera-Tinoco and Bouallou, 2010) and re-inject it in the underground (Câmara et al., 2013), so as to minimise the increase of its concentration in the atmosphere.

Approximately 40% of anthropogenic CO₂ emissions originate from coal or natural gas power plants (Amann, 2007). Therefore, the capture of CO₂ emitted by thermal power plants is of major importance. However, the costs of capture are still high since the reduction on the power plant efficiency caused by the CO₂ capture unit is still considerable (Harkin et al., 2012).

If the captured CO₂ were used as raw material in the production of a marketable product, its capture and sale could become not only economically viable but also a profitable business. Another major challenge of this century is to substitute fossil fuels by renewable ones. Thus, the recycling of CO₂ as a feedstock for the production of hydrocarbons substituents presents great economic and environmental interests.

Methanol is widely used in the chemical industry, mainly in the production of formaldehyde, MTBE (methyl tert-butyl ether) and acetic acid. Moreover, methanol has excellent combustion properties, which allows its use as a fuel in vehicles, although it has only about half the energy density of gasoline. Furthermore, methanol is less polluting than conventional fossil fuels (Olah et al., 2008).

Methanol can be used in a wide range of concentrations mixed with gasoline, from small concentrations where it is an additive up to high concentrations such as the M85 (15% gasoline and 85% methanol). Vehicles fuelled by pure methanol (M100) are also viable and even more efficient (Olah et al., 2008). However, the toxicity of methanol is often cited as restriction for its use as fuel. Methanol is extremely toxic when ingested in large quantities, causing blindness and possibly death.

DME (dimethyl ether), which is a possible substitute for conventional diesel, can be synthesized from the dehydration of methanol. Therefore, the production of methanol from captured CO₂ may cause a reduction in the consumption of fossil fuels and enable CO₂ recycling.

The main objective of this study is to evaluate and quantify the abatement of CO₂ through the production of fuel grade methanol by the process proposed in this paper.

1.1. Conventional methanol production process

Most of the methanol produced industrially today is derived from the catalytic conversion of synthesis gas (gaseous mixture of

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CO, CO₂ and H₂). Although it may be produced from various carbonaceous components, most of the synthesis gas currently produced is derived from natural gas.

The commercial catalyst Cu/ZnO/Al₂O₃ is commonly employed in the production of methanol from synthesis gas. It allows the production of methanol under relatively “soft” conditions (210–270 °C and 50–100 bar), with a selectivity of 99% in relation to CO_x (Ullmann, 2002). By-products produced are mainly higher alcohols, methane, methyl formate and DME.

Considering the natural gas used as reagent and fuel, a typical plant consumes between 29 and 33 GJ of natural gas per metric ton of methanol produced (Uhde).

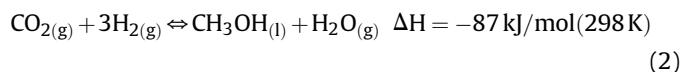
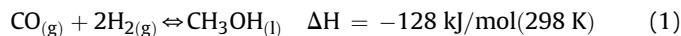
1.2. CO₂ to methanol process

1.2.1. Overview

Methanol can be produced from CO₂ in two different ways: in one step or in two steps. The one step conversion is the direct hydrogenation of CO₂ to methanol. In two steps conversion, CO₂ is first converted into CO through the Reverse Water Gas Shift (RWGS) reaction and then hydrogenated to methanol. In this paper, the conversion of CO₂ in one step was employed. Some routes of conversion of CO₂ to produce fuels are shown in Fig. 1.

The source of CO₂ may be the flue gases from thermal power plants (e.g. coal, natural gas) or factories producing steel, cement and other major emitters of CO₂. Hydrogen must be produced in a carbon-free way, such as biological production from algae or the electrolysis of water using carbon-free electricity (Demirci and Miele, 2013).

Exothermic reactions (Eqs. (1) and (2)) produce methanol. The RWGS reaction (Eq. (3)) occurs in parallel.



The production of methanol from CO₂ hydrogenation has been the subject of many recent studies. Joo et al. (1999) studied the production of methanol in two steps and concluded that it has a higher yield than the process in one step. Mignard et al. (2003)

proposed a methanol synthesis process from CO₂ captured from flue gas of a coal power plant and electrolytic hydrogen. The process depends on availability of waste heat in the power plant to provide thermal energy to the process in order to have a significant abate of CO₂. In the absence of these thermal sources, CO₂ abatement is almost null. Mignard and Pritchard (2006) compared the energy efficiencies of production processes of methanol, ethanol and gasoline from the CO₂ hydrogenation. The methanol process showed the highest efficiency. Pontzen et al. (2011) carried out experiments to compare methanol from CO₂ production over Cu/ZnO/Al₂O₃ catalyst with the conventional syngas production process. The CO₂-based process showed lower productivities when compared to the conventional one. Soltanieh et al. (2012) studied and analysed economically the co-production of methanol and electricity from captured CO₂ and carbon-free hydrogen. Van Der Ham et al. (2012) designed a CO₂ to methanol process using a fluidised-bed membrane reactor. The process provided significant CO₂ abatement, but did not present economic viability.

1.2.2. Catalysts

The commercial catalyst Cu/ZnO/Al₂O₃ has been studied by several authors (Mignard and Pritchard, 2006; Mignard et al., 2003; Pontzen et al., 2011; Sahibzada et al., 1998) for the production of methanol from CO₂, although it is less efficient with supply of CO₂ than CO/CO₂ (ADEME, 2010).

Catalysts better adapted to CO₂ feed have been extensively studied. In many cases, the proposed catalysts are based on Cu-Zn oxides containing additives such as ZrO₂, Ga₂O₃ and SiO₂ over alumina. Guo et al. (2011) investigated the effects of the procedure of preparation on the performance of a Cu/ZnO/ZrO₂ catalyst. Zhang et al. (2006) studied the effect of zirconia addition on γ-Al₂O₃ support of a Cu based catalyst. Raudaskoski et al. (2009) reviewed papers about copper-based zirconia-containing catalysts. Chiavassa et al. (2009) studied the synthesis from Ga₂O₃-Pd/silica catalyst. Sahibzada (2000) reviewed kinetic results of Pd-promoted Cu/ZnO catalyst.

1.2.3. Installations

Carbon Recycling International installed at the end of 2010 a unit capable of producing 3000 t/y of methanol in Iceland (ADEME, 2010). This unit have a capacity of about 10 t of methanol from 18 t of CO₂ (Carbon Recycling International, 2009). The CO₂ used comes from the Svartsengi geothermal plant and an aluminium production plant. Hydrogen is generated from the electrolysis of water using a renewable source of electricity.

Mitsui Chemicals Inc. has a pilot unit in Japan capable of producing 100 t of methanol per year. CO₂ used comes from an ethylene production plant of Osaka Works Petrochemical Complex (ADEME, 2010).

The economic viability of plants depends on several factors, such as the price of a barrel of oil, electricity price, CO₂ price and use of by-products.

2. Methods

This paper proposes an enhancement of the process proposed by Van-Dal and Bouallou (2012), and also provides greater detail on the calculations as well as a deeper analysis. CO₂ captured from flue gases of a coal power plant and hydrogen generated from water electrolysis are fed into a methanol plant. An overview of the process is presented on Fig. 2.

Electrolysis of water is carried out using carbon-free electricity source, such as renewable (e.g. hydraulic, eolic, solar or biomass) or nuclear. However, the CO₂ capture unit and methanol unit are supplied with electricity from the coal power plant. Thus, hydrogen can be imported from somewhere where carbon-free energy is available and used in methanol plants installed in places where only fossil

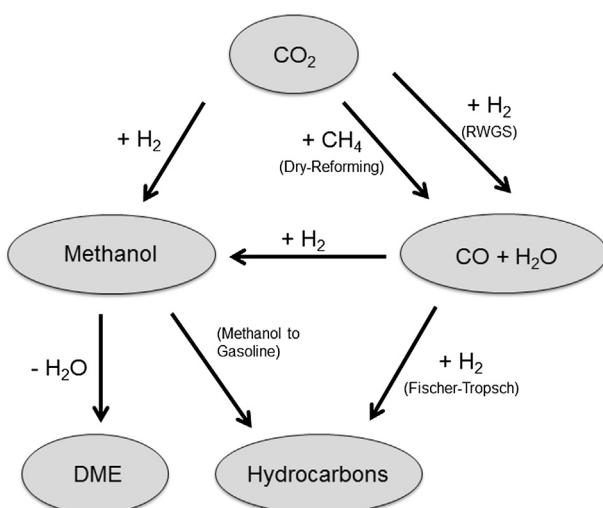


Fig. 1. CO₂ utilisation diagram.

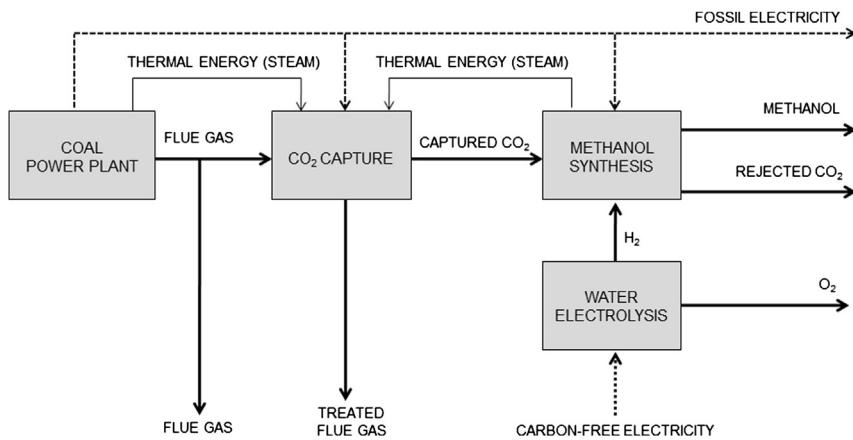


Fig. 2. Bloc diagram of the process (Van-Dal and Bouallou, 2012).

energy is available. Since renewable energies depend on climatic factors such as the wind and the average hours of sunshine to be viable, there is a limited number of places where they can be installed.

The commercial software Aspen Plus™ V7.3 was used for process design and simulation. The process is fed with 88.0 t/h of CO₂ and 12.1 t/h of hydrogen, i.e. stoichiometric feed. Redlich–Kwong–Soave equation of state with modified Huron–Vidal mixing rules (RKSMHV2) was used to calculate the thermodynamic properties of streams at high pressure (>10 bar). For streams at low pressure (<10 bar), NRTL-RK model was employed.

2.1. Water electrolysis unit

The energy consumption for the production of hydrogen by electrolysis of water (Eq. (4)) is equal to 4.8 kWh_{el}/m³ (m³ at 0 °C and 1 bar) (AFHPAC, 2011). The hydrogen leaves the electrolyser at 30 bar and 25 °C to be fed to the methanol plant.



A large amount of oxygen is also generated as a by-product of electrolysis. It could be sent to the power plant to carry out oxy-combustion, which would increase the concentration of CO₂ in flue gases and reduce the energy consumption of its capture. Another possible destination for the oxygen is its sale to a nearby chemical plant via pipelines. The second option was considered in this paper.

2.2. CO₂ capture unit

The CO₂ capture unit considered in this paper was based on the work of Amann (2007). CO₂ is captured by chemical absorption of

the flue gases of a subcritical coal power plant with desulfurization. MEA (monoethanolamine) in a mass concentration of 30% is used as solvent. Fig. 3 shows the process of CO₂ absorption with MEA and solvent regeneration by heating.

The flue gases to be treated are compressed before the capture process to compensate the pressure drop in the absorption column. They are then introduced at the bottom of the absorption column whereas the solvent poor in CO₂ is introduced at the top of the column. Throughout the column, MEA reacts with CO₂. The gas recovered at the top of the absorption column contains low levels of CO₂. The CO₂-rich solvent leaving at the bottom of the absorption column is sent to the regeneration column after being preheated by the regenerated solvent that leaves the regeneration column. The regeneration column includes a reboiler and a condenser. The reboiler recovers the energy from the condensation of low pressure (LP) steam for reversing the reaction between the amine and CO₂. The water vapour contained in the gas flow of the regeneration column is condensed and re-injected into the column. The regenerated solvent is fed back to the absorption column after having preheated the CO₂-rich solvent. The gas recovered at the top of regeneration column is mainly composed of CO₂ and water vapour. This gaseous flow is then completely dehydrated and compressed.

Without CO₂ capture, the net electrical power delivered by the power plant is 556 MW_{el} with a CO₂ emission ratio of 857 g/kWh_{el}. The efficiency of the plant is 38.5% (Lower Heating Value). The flue gases come out at 95.2 °C and 0.913 bar, with the composition shown in Table 1.

Considering a CO₂ capture rate of 85%, 44 kWh_{el} per tonne of CO₂ are consumed for feed compression and 3.2 GJ_{th} per tonne of CO₂ are employed for solvent regeneration. LP steam used in the capture is bled from the steam cycle of the coal power plant. The

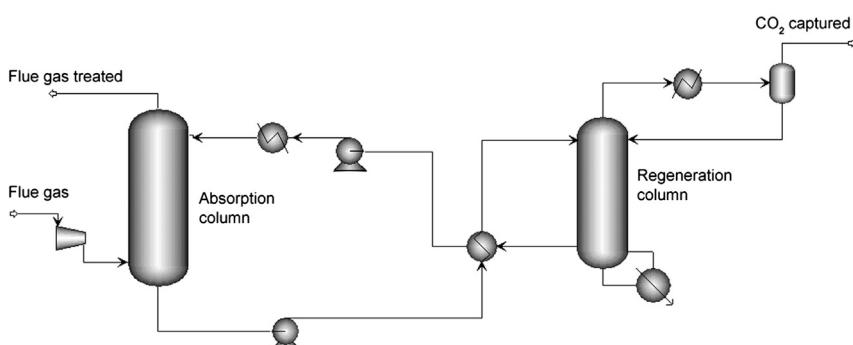


Fig. 3. Flowsheet of the CO₂ capture unit.

Table 1
Composition of flue gases.

Composition	% Molar
H ₂ O	6.6
CO ₂	14.0
O ₂	3.8
N ₂	75.6

fact of extracting a flow rate of 100 t/h of LP steam at 4.14 bar involves a decrease of 18.3 MW_{el} in electricity production for the power plant (Amann, 2007).

Since there is steam available in the methanol synthesis unit, this steam is used in the CO₂ capture unit. Consequently, the amount of steam bled from the power plant is lower and so is its impact on electricity production. The steam provided by methanol synthesis unit corresponds to 36% of the thermal energy needed to CO₂ capture.

After capturing 88.0 t/h of CO₂, the net electrical power delivered by the power plant is equal to 537 MW_{el} with a CO₂ emission ratio of 723 g/kWh_{el}. An amount of about 1 kg of MEA per tonne of CO₂ absorbed is necessary to compensate losses due to degradation and evaporation of the amine. The CO₂ captured is fed to the methanol plant at 1 bar and 25 °C.

2.3. Methanol synthesis and purification unit

The process flowsheet is presented in Fig. 4. The main improvements over the process published by Van-Dal and Bouallou (2012) are the optimisation of the number of compressors and also not considering perfect separation in the flash tank located before the distillation column.

The reduction in the number of compressors, and hence in the number of heat exchangers, caused a decrease in capital cost without a large increase in energy cost. Furthermore, without considering perfect separation between liquid and gas in the flash tank has made the simulation of the distillation column more realistic since a fraction of gases was also considered in the feed of the column.

2.3.1. Flowsheet description

CO₂ is fed at 1 bar and hydrogen at 30 bar, both at 25 °C. CO₂ is compressed to 78 bar in a series of compressors with intercooling. Hydrogen is compressed to 78 bar in a single stage. The two gases are mixed (MIX1) and then re-mixed with the recycle stream (MIX2). The stream is then heated (HX4) to 210 °C and injected into the fixed bed adiabatic reactor. The gases leaving the reactor are divided (DIV1) into two streams: the first (60% of initial stream) is used to heat the fresh feed (HX4), while the second is used in the reboiler (DT1REB) and also to heat the feed of the distillation column (HX5). The two streams are re-mixed (MIX3) and cooled to 35 °C by water (HX6). Water and methanol, which were condensed in exchanger HX6, are separated from the non-reacted gases in a knock-out drum (KO1). Some of the non-reacted gases (1%) are purged to minimise the accumulation of inerts and by-products in the reaction loop.

The liquid stream leaving the knock-out drum (KO1), called crude methanol, is composed of methanol, water and residual dissolved gases. The crude methanol is expanded to 1.2 bar in two valves (VLV1 and VLV2). Then, the residual gases are almost completely removed in a flash tank (TKFL1). The remaining stream is heated to 80 °C in exchanger HX5, and then sent to a distillation column (DT1). The water comes out of the bottom of the column at 102 °C containing 23 wt-ppb of methanol. Methanol comes out of the top at 1 bar and 64 °C, in gaseous form, containing 69 wt-ppm of water and some non-reacted gases. Methanol is then compressed (CP7) and cooled (HX8) to 40 °C. In a knock-out drum (KO2), non-reacted gases come out of the top, and methanol product comes out of the bottom in liquid form.

2.3.2. Reactor

The adiabatic reactor is packed with a fixed bed of 44,500 kg of Cu/ZnO/Al₂O₃ commercial catalyst. For this catalyst, the model proposed by Vanden Bussche and Froment (1996) is able to describe with good precision the reactions of methanol production and the RWGS reaction. The model assumes that the CO₂ is the main source of carbon for the synthesis of methanol and that it does not cause direct inhibition of the reaction represented by Eq. (2), which was demonstrated by Sahibzada et al. (1998). In

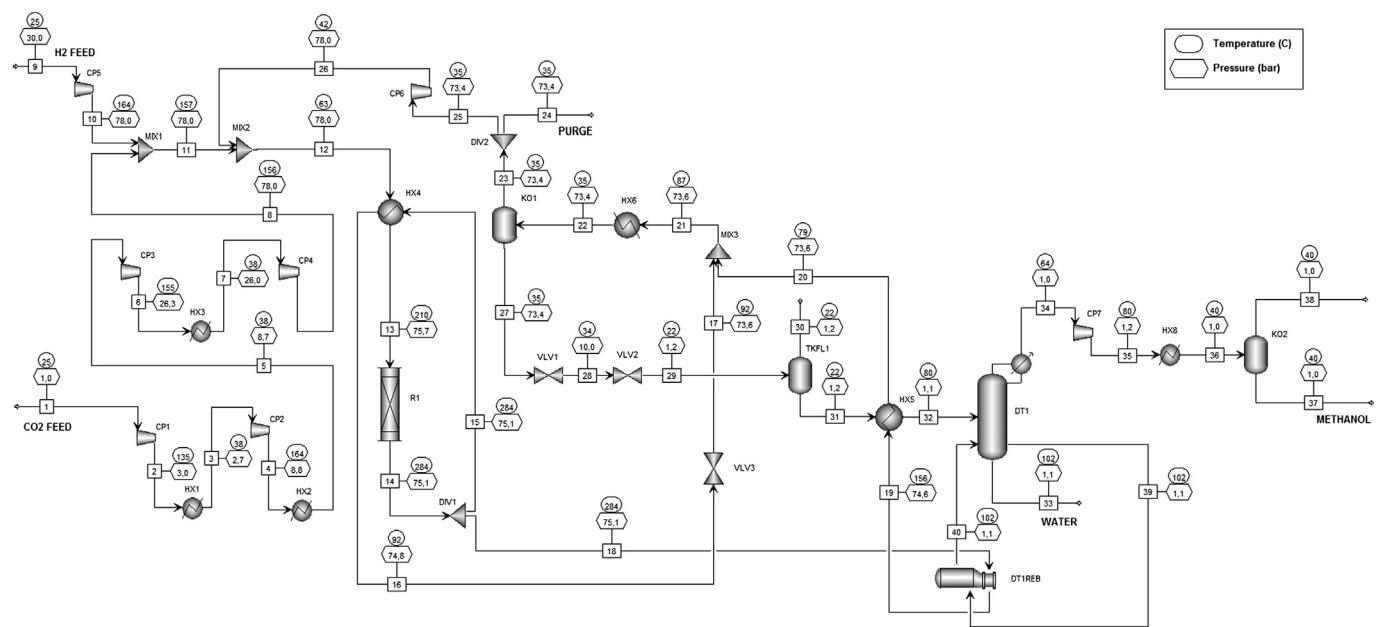


Fig. 4. Process flowsheet.

addition, the model considers the inhibitory effect of water formed by the RWGS reaction. The activation energies of reactions were readjusted by Mignard and Pritchard (2008) to better represent the experimental data, which also expanded the application range of the model up to 75 bar.

The kinetic model used in this paper is that of Vanden Bussche and Froment (1996) with readjusted parameters of Mignard and Pritchard (2008) (Eqs. (5) and (6), in which pressures are expressed in bar and temperatures in K). The kinetic constants follow the Arrhenius law (Eq. (7)), its parameters are shown in Table 3. The thermodynamic equilibrium constants are given by Graaf et al. (1986) (Eqs. (8) and (9)). However, the model as shown by Eqs. (5)–(9) could not be directly implemented in Aspen Plus because the software only accepts certain types of kinetic equations. Appendix A shows how the kinetic model was rearranged to allow the simulation of the reactor in Aspen Plus, and also its new parameters.

The pressure drop in the fixed bed is calculated by the Ergun equation, already implemented in Aspen Plus. The characteristics of the catalyst are described in Table 2.

Methanol synthesis

$$r_{\text{CH}_3\text{OH}} = \frac{k_1 P_{\text{CO}_2} P_{\text{H}_2} \left(1 - \frac{P_{\text{H}_2\text{O}} P_{\text{CH}_3\text{OH}}}{K_{eq1} P_{\text{H}_2} P_{\text{CO}_2}} \right)}{\left(1 + k_2 \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} + k_3 P_{\text{H}_2}^{0.5} + k_4 P_{\text{H}_2\text{O}} \right)^3} \quad [\frac{\text{mol}}{\text{kg}_{\text{cat}} \text{s}}] \quad (5)$$

Reverse water gas shift reaction

$$r_{\text{RWGS}} = \frac{k_5 P_{\text{CO}_2} \left(1 - K_{eq2} \frac{P_{\text{H}_2\text{O}} P_{\text{CO}}}{P_{\text{CO}_2} P_{\text{H}_2}} \right)}{\left(1 + k_2 \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} + k_3 P_{\text{H}_2}^{0.5} + k_4 P_{\text{H}_2\text{O}} \right)} \quad [\frac{\text{mol}}{\text{kg}_{\text{cat}} \text{s}}] \quad (6)$$

$$k_i = A_i \exp\left(\frac{B_i}{RT}\right) \quad (7)$$

$$\log_{10} K_{eq1} = \frac{3066}{T} - 10.592 \quad (8)$$

$$\log_{10} \frac{1}{K_{eq2}} = -\frac{2073}{T} + 2.029 \quad (9)$$

33% of CO₂ fed to the reactor is converted into methanol and the recycle ratio is equal to 5.0. Although the production of by-products was not considered in this model, 0.4% of by-products can be expected mainly in the form of methyl-formate.

2.3.3. Distillation

A distillation column is used to purify methanol. The column was simulated with the rigorous model RadFrac in Equilibrium mode of Aspen Plus. The column has 44 rectification and 13 stripping stages. The reflux ratio is equal to 1.2. The fluid used to recover energy from the condenser is air.

If the production of by-products was considered in the reactor, substances such as methyl formate, DME, and other hydrocarbons and alcohols would be present in the feed of the distillation column. Therefore, a small amount of these substances would leave

Table 2

Characteristics of Cu/ZnO/Al₂O₃ catalyst.

Density	1775 kg _{cat} /m ³ _{cat}
Particle diameter	5.5 mm
Fixed bed porosity	0.4

Table 3
Parameters values for the kinetic model [B given in J/mol].

k_1	A_1	1.07
	B_1	40,000
k_2	A_2	3453.38
	B_2	—
k_3	A_3	0.499
	B_3	17,197
k_4	A_4	$6.62 \cdot 10^{-11}$
	B_4	124,119
k_5	A_5	$1.22 \cdot 10^{10}$
	B_5	-98,084

the column at the top with methanol. However, this would not preclude its use as fuel.

2.3.4. Heat exchanger network

Pinch analysis is a systematic methodology to reduce energy costs in processes. It was developed in the late 70's by Bodo Linnhoff from UMIST (University of Manchester Institute of Science and Technology) (Linnhoff and Flower, 1978). Kemp (2007) provides a comprehensive guide to pinch analysis, from the foundations to the advances made in recent years. Heat exchanger network design was based on pinch analysis performed with Aspen Energy Analyzer™ V7.1.

To design the heat exchangers and calculate their pressure drops, the software Aspen Exchanger Design and Rating™ V7.1 was used. The cooling fluid used in heat exchangers HX1, HX2, HX3, HX6 and HX8 is water supplied at 28 °C. The pinch in exchangers HX1, HX2, HX3 and HX6 is 10 °C. Table 4 shows details about the heat duty and utilities for all heat exchangers of the process.

2.3.5. Steam and electricity generation

Steam is generated from the combustion with air of the purge (stream 24) and the gaseous streams 30 and 38. These streams are composed essentially of hydrogen, CO, CO₂ and methanol. Combustion reactions that take place are represented by Eqs. (10), (11) and (12). It was considered 85% of efficiency in the boiler.



The Lower Heating Values are: H₂ = 121.0 MJ/kg, CO = 10.1 MJ/kg and CH₃OH = 19.9 MJ/kg.

The streams of hot water leaving the heat exchangers HX1, HX2, HX3, HX6 and bottom of the distillation column are mixed and used to generate electricity through an organic Rankine cycle. Fig. 5 shows the flowsheet of the organic Rankine cycle. The working fluid is the R245fa. The energetic efficiency of the cycle is 3% and the

Table 4
Heat exchangers details.

Equipment	Heat duty (MW _{th})	Utility
HX1	2.17	Water (In 28 °C, Out 125 °C)
HX2	2.94	Water (In 28 °C, Out 154 °C)
HX3	2.93	Water (In 28 °C, Out 145 °C)
HX4	62.4	Integrated
HX5	24.6	Integrated
HX6	33.8	Water (In 28 °C, Out 77 °C)
HX8	19.7	Water (In 28 °C, Out 40 °C)
DT1REB	21.2	Integrated
DT1COND	21.6	Air

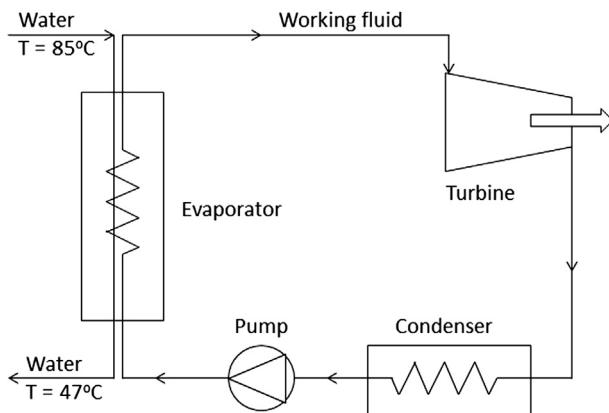


Fig. 5. Organic Rankine cycle.

exergetic efficiency is 36.3%. The water enters the cycle at 85 °C and leaves it at 47 °C. Afterwards, water is fed into a cooling tower.

3. Results and discussion

3.1. Mass and energy balances

Table 5 shows the mass balance and Table 6 the energy balance. Table 5 shows that the yield is 0.67 t of methanol per tonne of CO₂ supplied. The production of oxygen is 1.1 t per tonne of CO₂ supplied. Considering an operation of 8000 h/y, the annual methanol production of the plant is equal to 470,500 t.

Table 6 shows that water electrolysis corresponds to 97% of net electricity consumed by the entire process. Since the methanol synthesis unit does not need external heat input, all the steam produced by the combustion of streams 24, 30 and 38 is sent to the CO₂ capture unit. Therefore, the amount of steam bled from steam cycle of the coal plant is 49.4 MW_{th} instead of 77.7 MW_{th}, i.e. 36% lower.

3.2. CO₂ abatement

3.2.1. CO₂ emissions

CO₂ emissions occur in three different ways in the process: 1) CO₂ rejected from methanol synthesis unit, 2) thermal energy consumption, 3) electricity consumption. The details are as follows.

- 1) The CO₂ rejected by the streams 24, 30 and 38 of the methanol synthesis unit is shown in Table 5.
- 2) The methanol synthesis unit requires no external input of thermal energy. However, the combustion of the streams 24, 30 and 38 for the production of steam used in the capture unit emits CO₂ due to CO and methanol combustion (Eqs. (11) and (12)).

Table 5
Mass balance (not including CO₂ emissions from energy consumption).

Compound	In (t/h)	Out (t/h)
CO ₂	88.0	5.82 ^a
CO	0	0.51 ^a
H ₂	0	0.87 ^a
H ₂ O	108.1	33.7
Methanol	0	59.3
O ₂	0	96.0 ^b
MEA	0.09	0.09

^a Contained in stream 24, 30 and/or 38 before their combustion.

^b Oxygen generated by water electrolysis.

Table 6
Energy balance.

Unit	Operation	Amount	Amount/t _{MetOH}
Water electrolysis	Power to electrolysis	645.1 MW _{el}	39.3 GJ _{el} /t _{MetOH}
CO ₂ capture	Flue gases compression	3.9 MW _{el}	0.236 GJ _{el} /t _{MetOH}
	Steam to regeneration column	77.7 MW _{th}	4.74 GJ _{th} /t _{MetOH}
Methanol synthesis and purification	Fresh feed compression	16.9 MW _{el}	1.03 GJ _{el} /t _{MetOH}
	Compressors CP6 + CP7	2.9 MW _{el}	0.175 GJ _{el} /t _{MetOH}
	Steam to methanol distillation	0 MW _{th}	0 GJ _{th} /t _{MetOH}
	Steam generation	28.3 MW _{th}	1.72 GJ _{th} /t _{MetOH}
	Electricity generation	2.2 MW _{el}	0.131 GJ _{el} /t _{MetOH}
Total net electricity consumption		666.6 MW _{el}	40.6 GJ _{el} /t _{MetOH}
Total net thermal energy consumption		49.4 MW _{th}	3.0 GJ _{th} /t _{MetOH}

- 3) The net consumption of electricity of the methanol synthesis unit is 17.6 MW_{el}. After installing the capture unit, the rate of CO₂ emission of the power plant is equal to 723 g/kWh_{el}. Thus, the resulting emission from electricity consumption is 12.8 t of CO₂ per hour.

3.2.2. Carbon credits

Carbon credits are generated by the sale of by-product oxygen via pipeline to a nearby chemical plant, which uses O₂ as feedstock. Oxygen is commonly produced from cryogenic air distillation in industrial plants. O₂ production and compression to 35 bar consumes 0.42 kWh_{el} per kilogram of O₂ (Bolland and Sæther, 1992). Thus, if oxygen were produced using electricity from the coal power plant, CO₂ would be emitted. Therefore, the carbon credits generated are equal to the amount of CO₂ that would be released if the oxygen was produced through a cryogenic process using electricity from the coal plant. Since the production of oxygen is 96.0 t/h and the rate of CO₂ emissions of the coal power plant equal to 723 g/kWh_{el}, 29.2 t/h of carbon credits are generated.

3.2.3. CO₂ balance

CO₂ balance is shown in Table 7.

Table 7 shows that, if the oxygen by-product is sold, the process presented in this paper may abate 1.6 t of CO₂ per tonne of methanol produced. If it is not sold, the figure is 1.2 t of CO₂ per tonne of methanol. The consumption of fossil electricity is the main cause of CO₂ emissions in the process.

If only 20% of the electricity used in electrolysis comes from the coal plant, CO₂ balance becomes null (in the case where oxygen is sold). Therefore, for a significant CO₂ mitigation it is necessary that hydrogen is produced through a carbon-free way. However, it is important to notice that hydrogen production can be carried out through any carbon-free process, and not necessarily water electrolysis. Since the whole process presented in this paper uses fossil energy, except for the water electrolysis unit, the methanol plant can be installed in any region where a

Table 7
CO₂ balance.

In/out	Without sale of O ₂ (t/h)	With sale of O ₂ (t/h)
CO ₂ fed to methanol plant	-88.0	-88.0
CO ₂ rejected by methanol plant	+5.82	+5.82
Thermal energy consumption	+1.21	+1.21
Electricity consumption	+12.8	+12.8
Carbon credits generated	0	-29.2
CO ₂ abatement	-68.2	-97.4

thermal power plant exists, even if carbon-free energy is not available nearby. Thus, hydrogen can be produced in regions where renewable energy is available to be exported and employed in methanol plants.

4. Conclusions

The impact of the CO₂ capture unit on the power plant efficiency is remarkably reduced due to the steam supplied by the methanol synthesis unit, which corresponds to 36% of the steam used in CO₂ capture. The CO₂ balance shows that it is possible to abate 1.6 t of CO₂ per tonne of methanol produced if oxygen by-product is sold, or 1.2 t if it is not. In both cases, carbon-free hydrogen must be employed. Thus, if a large flow of carbon-free hydrogen is available, the production of methanol may mitigate large amounts of CO₂. The whole process uses fossil electricity, except for the hydrogen synthesis unit. So methanol plants are not limited to places where renewable energy is available for CO₂ mitigation. Hydrogen can be generated in places where renewable energy is available and then exported to methanol synthesis plants.

Appendix A

The model as shown by Eqs. (5)–(9) cannot be directly implemented in Aspen Plus, since the software only accepts certain types of kinetic models. Thus, in order to create a compatible kinetic model, the equations of the thermodynamic equilibrium were incorporated into the kinetic constants and the units of the equations were modified to suit Aspen Plus requirements. The rearranged kinetic model is shown in Eqs. (A.1), (A.2) and (A.3), where pressure is given in Pa and temperature in K. Table A.1 shows the model parameters.

Methanol synthesis

$$r_{\text{CH}_3\text{OH}} = \frac{k_1 P_{\text{CO}_2} P_{\text{H}_2} - k_6 P_{\text{H}_2\text{O}} P_{\text{CH}_3\text{OH}} P_{\text{H}_2}^{-2}}{(1 + k_2 P_{\text{H}_2\text{O}} P_{\text{H}_2}^{-1} + k_3 P_{\text{H}_2}^{0.5} + k_4 P_{\text{H}_2\text{O}})} \quad [\text{kmol}/\text{kg}_{\text{cat}}\text{s}] \quad (\text{A.1})$$

Reverse water gas shift reaction

$$r_{\text{RWGS}} = \frac{k_5 P_{\text{CO}_2} - k_7 P_{\text{H}_2\text{O}} P_{\text{CO}} P_{\text{H}_2}^{-1}}{1 + k_2 P_{\text{H}_2\text{O}} P_{\text{H}_2}^{-1} + k_3 P_{\text{H}_2}^{0.5} + k_4 P_{\text{H}_2\text{O}}} \quad [\text{kmol}/\text{kg}_{\text{cat}}\text{s}] \quad (\text{A.2})$$

$$\ln k_i = A_i + \frac{B_i}{T} \quad (\text{A.3})$$

Table A.1
Parameters of the rearranged kinetic model.

k_1	A_1	-29.87
	B_1	4811.2
k_2	A_2	8.147
	B_2	0
k_3	A_3	-6.452
	B_3	2068.4
k_4	A_4	-34.95
	B_4	14,928.9
k_5	A_5	4.804
	B_5	-11,797.5
k_6	A_6	17.55
	B_6	-2249.8
k_7	A_7	0.1310
	B_7	-7023.5

After rearranging the equations, the kinetic model LHHW (Langmuir–Hinshelwood–Hougen–Watson) from Aspen Plus could be used. The original kinetic model was implemented on Scilab 5.4 in order to validate the rearranged kinetic model from Aspen Plus.

The dimensions of the reactor and operating conditions selected for the simulation are the same as those of Vanden Bussche and Froment (1996). The reactor is a stainless steel tube of 0.016 m in diameter and 0.15 m long, in adiabatic regime. Details of the catalyst and the feed stream are shown in Tables A.2 and A.3.

Table A.2
Characteristics of the catalyst.

Density	1775 kg _{cat} /m ³ _{cat}
Fixed bed porosity	0.5
Mass	34.8 g
Pellet diameter	0.0005 m

Table A.3
Characteristics of the feed stream.

Mass flow	2.8 · 10 ⁻⁵ kg/s
Pressure	50 bar
Temperature	220 °C
Feed composition (molar%)	
CO	4.00
H ₂ O	0.00
Methanol	0.00
H ₂	82.00
CO ₂	3.00
Inert (Argon)	11.00

Fig. A.1 shows the molar fractions as function of reactor length for both Scilab and Aspen Plus kinetic models. Fig. A.1 reveals that Scilab and Aspen Plus kinetic models are equivalent. Therefore, the rearranged Aspen Plus kinetic model can be used to simulate the methanol reactor.

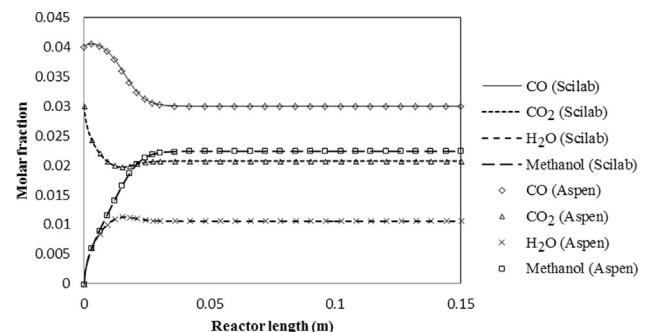


Fig. A.1. Comparison of Scilab and Aspen kinetic models.

The curves presented in Fig. A.1 strongly resemble those published by Vanden Bussche and Froment (1996). However, there is a significant difference in the first 0.03 m of the reactor, which is due to the adjustment made by Mignard and Pritchard (2008) on the reaction activation energies.

Nomenclature

r_i	Rate of reaction in relation to component i
k_i	Kinetic model constant
P_i	Partial pressure of component i
A_i	Kinetic model constant
B_i	Kinetic model constant

T	Temperature
K_{eqi}	Thermodynamic equilibrium constant

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