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Study of the CO_2 conversion into methanol: catalytic process and heat integration optimizations with a CO_2 capture unit.

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Abstract

The EU's target of climate neutrality by 2050 needs to systematically increase energy efficiency and decarbonize the industrial sector. Carbon capture and utilization (CCU) to produce chemicals and fuel are one of the most effective measures to address global warming and energy security. The energy demand of chemical processes can be reduced by heat integration. The purpose of this study is to evaluate the interest of a heat integration for two different configurations of CO_2 to methanol process to reduce external heat consumption. Using H_2 produced by electrolysis and CO_2 captured from a cement plant, a CO_2 catalytic conversion into methanol process is investigated and simulated in Aspen Plus™. More precisely, the conversion unit implemented is designed to convert 1310 kg of CO_2 per hour coming from a conventional cement plant equipped with the Best Available Techniques (with a flue gas CO_2 content of 20 mol.%). An advanced amines-based CO_2 capture process is considered. The captured CO_2 is then sent to the conversion unit together with green hydrogen to produce methanol. The heat released by the exothermal reaction of methanol production is recovered. To optimize the heat recovery in the process, two different reactor configurations have been studied: the first one completely isothermal and the second one using a reactor with two sections, respectively adiabatic and isothermal. It has been proved that the second configuration leads to the same CO_2 conversion performances as the first one with a reduction of 9.5% of heat requirement at the reactor inlet. In addition, an external heat source is necessary in the first case while the second one is fully autonomous on an energetical point of view.

Keywords: CO_2 conversion to methanol; Catalytic process; Heat integration; Aspen simulation.

1. Introduction

Clinker is the main ingredient in cement, and the amount used is directly proportional to the CO_2 emissions generated in cement manufacturing, due to both the combustion of fuels and the decomposition of limestone in the clinker production process, receptively 30% and 70% of CO_2 emissions. Producing enough cement to meet demand while reducing CO_2 emissions is challenging [1]. Carbon Capture Utilization and Storage (CCUS) is crucial to reduce cement sector CO_2 emissions as the main part of CO_2 emissions comes from the process and is unavoidable. The CO_2 captured from the cement flue gas can be used as a feedstock and converted to various chemicals, fuels, and other CO_2-based products. Methanol is an example of alternative fuels that can be produced from CO_2 [2]. Renewable

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methanol can be produced using CO_2 captured from cement plant flue gases and green hydrogen from water electrolysis (using excess of renewable energy as source of electricity). Globally, the reactions involved in the methanol formation are exothermal with a reduction of reaction mole number. It is thus favoured by temperature decrease and pressure increase. Methanol can be produced from CO_2 following three reactions: methanol synthesis from CO_2 (A), reverse water gas shift (B) and methanol synthesis from CO (C).

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad (A)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (B)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad (C)$$

The process modeling at an industrial scale is necessary in order to make the energy balance calculations and to determine parameters such as the heat released and the energy consumptions in the process, which are not easily calculated otherwise. Different papers studied the techno-economic feasibility of methanol production from CO_2 [3], [4], [5]. Despite the similarity of the main steps of methanol production, from one work to another, there are several key differences such as the source of CO_2, the hydrogen production route, the operating conditions (reactor temperature and pressure, final methanol purity, the type of reactor (adiabatic or isothermal), the unit capacity etc.). There is an agreement on the molar ratio of $H_2/CO_2 = 3$ in the feed-streams of the unit. The reaction occurs under high pressure (50-75.5 bar) and relatively low temperature for such kind of catalytic process (220-280°C) [6].

The heat released from the exothermal reactions can be recovered to reduce the energy demand of the process. The heat losses can be minimized by optimizing the parameters (e.g., optimisation of the energy used by the rectification column reboiler) or by modifying the configurations of the process (e.g., the reactor configuration). In this context, the current work focuses on providing an original process configuration to optimize its heat consumption for an optimal heat integration. More precisely, two process configurations are investigated and their energy performances are assessed in order to identify the case minimizing the external heat demand. In addition, the design of the rectification column has been optimized on order to minimize its energy consumption.

2. CCU process description

The Carbon Capture and Utilization (CCU) process chain considered includes (i) a polymer electrolyte membrane electrolysis (PEM), (ii) an amine(s)-based CO_2 capture unit applied to a flue gas coming from a BAT (Best Available Technology) cement plant and (iii) a catalytic CO_2-to-methanol conversion unit. As performed by [8], the scale of the entire process was defined considering the amount of renewable energy available for the hydrogen production. An overall capacity of 10 MW for the PEM is assumed which is equivalent to a hydrogen mass flow of 180 kg/h. The electricity used for electrolysis is produced using excess energy from renewable sources. It should be noted that the H_2 production has not been considered in the present paper. The Fig. 1 shows the conceptual CO_2 to methanol unit combined with a CCU process.

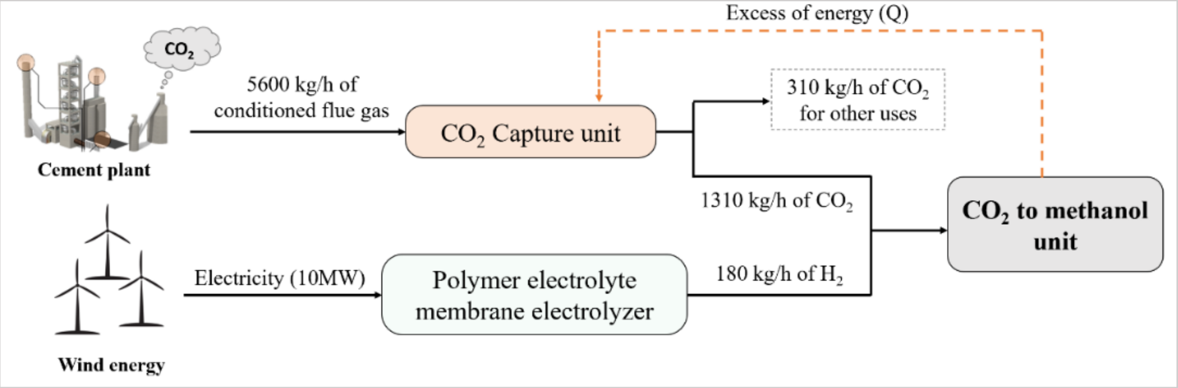

Fig. 1. Conceptual CO_2 conversion to methanol unit system combined with CCU process.

The conditioned flue gas to be treated enters the CO_2 capture unit with a flow rate of 5600 kg/h, at 1.20 bar and 146.4 ◦C. It is composed of N_2 (64.7 mol.%), CO_2 (20.4 mol.%), O_2 (8.6 mol.%) and H_2O (6.3 mol.%), based on average values coming from the Brevik Cement plant (Norcem company) in Norway. The implemented CO_2 capture process is based on the works of Dubois and Thomas [7] considering, a Rich Vapor Compression (RVC) process combined with an Inter-Cooled Absorber (ICA) and two Water-Wash (WW) sections, coupled to a conventional absorption-regeneration process. A methyl diethanolamine (MDEA) 10 wt.% + Piperazine (PZ) 30 wt.% aqueous blend has been considered as the solvent. About 10% of a cement plant flue gas are treated with a CO_2 absorption ratio of 90 mol.% corresponding to a production of 1620 kg/h of CO_2 (98 mol.% purity) but only 1310 kg/h of CO_2 are sent the conversion unit to respect the molar ration $H_2/CO_2 = 3$ at the inlet of the installation. The capture unit flowsheet is presented in Fig. 2. More details on the capture unit dimensions can be found in [8].

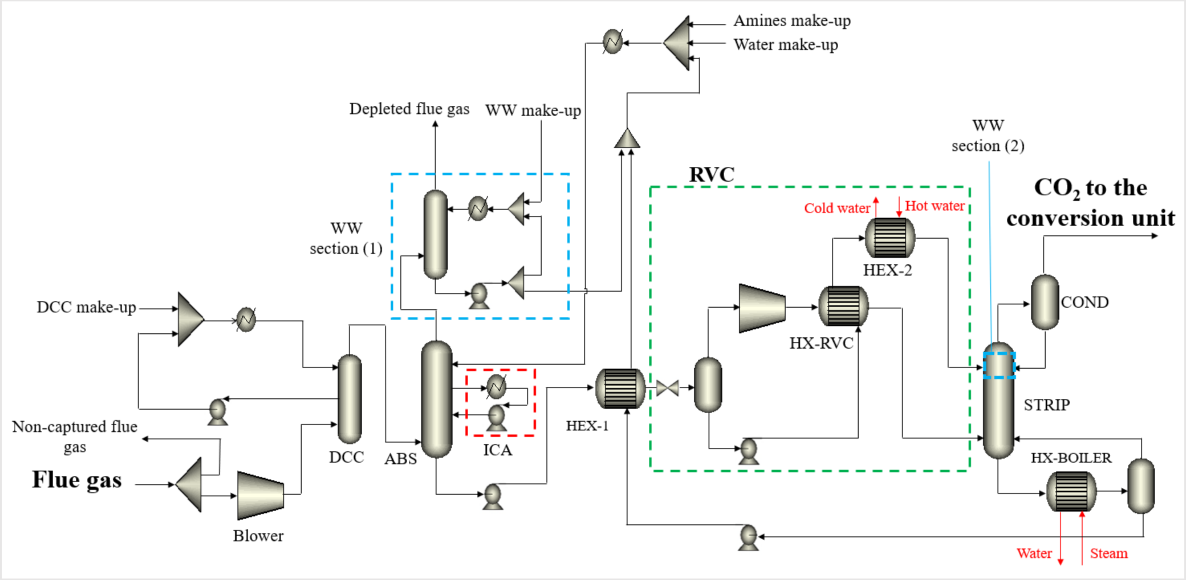

Fig. 2. Flowsheet of the CO_2 capture unit

3. Materials and methods

3.1. Simulated CO_2 conversion unit

The simulation of the CO_2 conversion unit has been carried out using Aspen Plus software V12. The implemented flow sheet and the corresponding simulation parameters of the CO_2 conversion unit are presented in Fig. 3. The Redlich Kwong equation of state [9] was used for the calculation of gaseous properties. The UNIFAC model has been considered for the equilibrium liquid-gas calculation [10].

The captured CO_2 is fed in the conversion unit with a mass flow of 1310 kg/h at 4.96 bar and 45°C. It is compressed to the operating pressure (65 bar) using three compressors with intermediate intercooling. The H_2 (180 kg/h) is fed at 30 bar and 80°C and it is compressed using one compressor. CO_2 and hydrogen are then mixed with the recycle stream and preheated (using Heater 1) before being injected in a plug-flow reactor. Two reactor configurations have been studied:

- Case 1: an isothermal reactor operating at 250 °C.
- Case 2: a reactor comprising a first adiabatic section, with an inlet temperature of 230°C followed by a second isothermal section. In this second case, the flow exiting the adiabatic section is setting at 250°C.

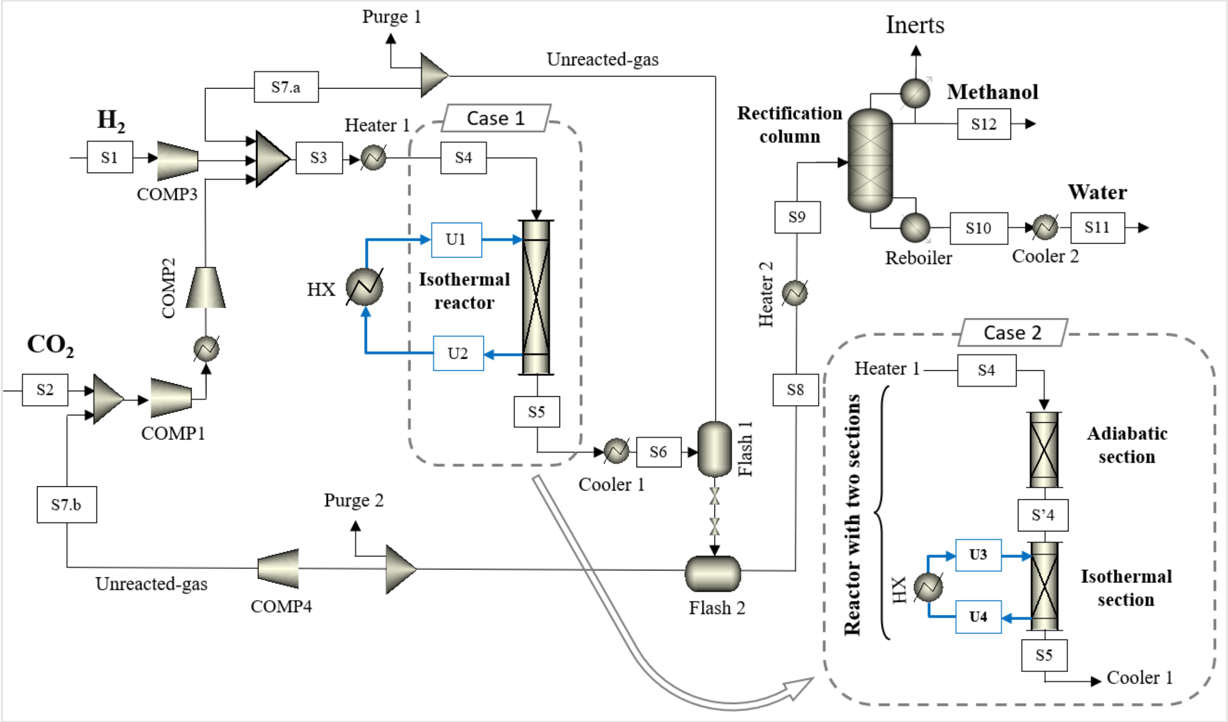

Fig. 3. Flowsheet of the CO_2 conversion unit: Case 1 using one isothermal reactor and Case 2 using a reactor with two sections (adiabatic and isothermal).

The $Cu/ZnO/Al_2O_3$ catalyst in the reactor enhanced the production of methanol. To describe the catalytic reactions kinetics through the catalyst, the model of Graaf has been considered [11]. In this model, all reactions are assumed to be based on a dual-site Langmuir-Hinshelwood-Hougen-Watson mechanism: CO and CO_2 adsorb competitively on site 1, while H_2 and H_2O adsorb competitively on site 2. The adsorption of methanol is assumed to be negligible and H_2 is believed to adsorb dissociatively on its site. The kinetic rate expressions of Graaf's model are expressed as following:

$$r_{(A)} = \frac{k_{CH_3OH,CO_2}\, K_{CO_2} \left(f_{CO_2} f_{H_2}^{1.5} - \dfrac{f_{H_2O}\; f_{CH_3OH}}{K_{p,C}\; f_{H_2}^{1.5}} \right)}{(1 + K_{CO}\, f_{CO} + K_{CO_2}\, f_{CO_2})(\, f_{H_2}^{0.5} + \,(K_{H_2O}/K_{H_2}^{0.5})\, f_{H_2O}\,)} \tag{1}$$

$$r_{(B)} = \frac{k_{RWGS}\;\; K_{CO_2} \left(f_{H_2} f_{CO_2} - \dfrac{f_{H_2O}\, f_{CO}}{K_{p,B}} \right)}{(1 + K_{CO}\, f_{CO} + K_{CO_2}\, f_{CO_2})(\, f_{H_2}^{0.5} + \,(K_{H_2O}/K_{H_2}^{0.5})\, f_{H_2O}\,)} \tag{2}$$

$$r_{(C)} = \frac{k_{CH_3OH,CO}\, K_{CO} \left(f_{CO} f_{H_2}^{1.5} - \dfrac{f_{CH_3OH}}{K_{p,A}\;\, f_{H_2}^{1.5}} \right)}{(1 + K_{CO}\, f_{CO} + K_{CO_2}\, f_{CO_2})(\, f_{H_2}^{0.5} + \,(K_{H_2O}/K_{H_2}^{0.5})\, f_{H_2O}\,)} \tag{3}$$

where: r_i represents the rate of reaction i ($mol.s^{-1}.kg^{-1}{}_{catalyst}$), k_i is the kinetic constant of the reaction i, K_J is the adsorption constant of the component j, $K_{p,i}$ is the equilibrium constant of the reaction i (based on partial pressure) and f_J the fugacity of the component j.

As highlighted by [6], the optimal Gas Hourly Space Velocity (GHSV) for the conversion of CO_2 into methanol was of the order of 10000 h^{-1}. The GHSV can be expressed as following:

$$GHSV = \frac{Q_{v_0}}{\rho_{catalyst}\ m_{catalyst}} \tag{4}$$

where: $\rho_{catalyst}$ is the bed apparent density ($\rho_{catalyst}$ =1300kg/m^3), $m_{catalyst}$ is the mass of catalyst and Q_{v_0} is the volumetric flow rate of the gas mixture entering the reactor under standard conditions.

The design (volume) of the reactor for the first configuration is based on the use of the optimal GHSV. Unlike the first case, this second case is more complicated to size because it consists of dividing the reactor into two sections and this implies to adapt the reactor dimensions to fix the GHSV at the selected value (10000h^{-1}). The outlet flue temperature (T_{OUT}) of the adiabatic section depends on its length ($L_{\ adiabatic}$) and the mass of catalyst loaded ($m_{adiabatic}$). In a first time, a study of the temperature profile was carried out as a function of the reactor length considering that the entire reactor is adiabatic with the temperature inlet T_{in}= 230°C (< 250°C). In a second time, the length of the isothermal section is defined according to an iterative method (using Aspen Plus^{TM} and Excel tools).

The product stream exiting the reactor is then cooled down to 40°C to be fed to a first flash tank (Flash 1) for the separation of the gaseous and liquid phases. The pressure of the liquid stream is reduced to 1.3 bar using two valves and then fed in a second flash (Flash 2) operating at 40°C. The unreacted gases (vapor phase of the two flashes) are then recycled to the inlet of the reactor. It should be noted that the gas flue exiting the second flash is compressed up to 4.69 bar before being injected with the CO_2 to be compressed up to 65 bar. A fraction of the recycled gases is purged (Purge 1 and 2) to prevent the accumulation of inert gases and by-products in the reaction loop (1.5% for each). The crude methanol (≈ 60 wt.% of methanol) leaving the second flash is sent to the rectification column after being heated to 90°C (Heater 2). To reach high methanol purity in the distillate (S12) (99.85 wt.% according to the methanol market [12]) and high water purity in the waste (S10) to avoid its treatment (99.9 wt.%), a Design of Experiments conducted by JMP® software has been considered to define the most favourable parameters combination allowing to achieve these specifications. Six parameters have been considered to optimize the rectification column: the reflux ratio, the reboiler duty, temperature of crude methanol, temperature of condenser, the number of stages and the feed stage number. The optimization of the rectification column allows the minimization of the reboiler heat consumption.

3.2. Heat integration evaluation

To evaluate the heat integration potential of each configuration, the heat released from cooling hot streams and that required for heating the cold streams are calculated. It should be noted that flows with low temperature levels and or low mass flows have not been considered in this work. Indeed, these hot streams do not have a sufficient level of energy to supply it to another cold stream in the process. The heat released from the isothermal reactor (isothermal section in case 2) is recovered using a medium pressure steam at 174°C and 8 bar as utility flow (U) (U1 and U2 for case 1, U3 and U4 for case 2, see Fig.3). The Table 1 presents the different hot and cold streams with their temperature levels

Table 1. Hot and cold streams in the conversion unit.

	Exchanger	Streams	
		case 1	case 2
Hot streams	Cooler 1	S5 to S6	
	Cooler 2	S10 to S11	
	HX	U2 to U1	U4 to U3
Cold streams	Heater 1	S3 to S4	S3 to S4.a
	Heater 2	S8 to S9	
	Reboiler	-	

4. Results and discussions

4.1. Engineering assessment

The reactors dimensions in each case are presented on the Table 2. In case 2, the adiabatic section represents 19.6% of the total reactor volume. This part of reactor is sufficient to heat up the gas mixture to T = 250°C. The Table 4 presents the streams data of the CO_2 conversion plant (two cases) derived from the process simulation. A difference is observed in the mass flow of the reactor inlet stream (S4), this is the reason of a slight difference in the conversion of the CO_2 over the reactor in case 1 (23%) comparing with the case 2 (22.4%). The overall CO_2 conversion in turn remains the same in both cases and achieves 99.6%. The methanol produced is quite the same for each configuration (818 and 813 kg/h for Case 1 and Case 2 respectively) using 3% more catalyst in the second one.

Table 2. Reactor(s) dimensions.

	Case 1 (isothermal)	Case 2	
		adiabatic section	isothermal section
Catalyst mass (kg)	1687	339	1393
Length (m)	4.6	0.9	3.8
Diameter (m)		0.6	

4.2. Design of the rectification column

According to the Design of Experiments conducted by JMP software, 32 simulations were performed by Aspen Plus^{TM} to identify the best parameters combination (presented in Table 3). The effect of the reboiler duty ($Q_{Rboiler}$) on the methanol and water purities is showed in Fig. 4. From the graphics, a compromise between maximum purity of methanol and water and minimum energy consumed by the reboiler is satisfied when $Q_{Reboiler}$ =199kW.

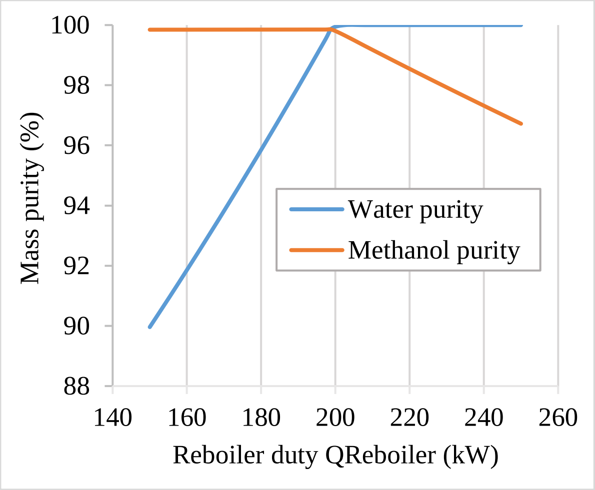

Fig. 4. Effect of $Q_{Reboiler}$ on the mass purity of methanol and water.

Table 3. Parameters of the rectification column.

Parameter	Value
Reflux ratio	1.66
Reboiler duty (kW)	199
Temperature of crude methanol (°C)	90
Temperature of the condenser (°C)	70
Number of stages	25
Feed stage (from bottom)	16

Table 4. Streams data of the CO_2 conversion plant (Case 1 and Case 2)

	Feed streams		**Reactor(s)**				**First recycled stream**		**Crude methanol**		**Rectification column**			
Stream	**S1**	**S2**	**S4**		**S5**		**S7.a**		**S9**		**S10 (Waste)**		**S12 (Distillate)**	
Case	**-**	**-**	**Case 1**	**Case 2**	**Case 1**	**Case 2**	**Case 1**	**Case 2**	**Case 1**	**Case 2**	**Case 1**	**Case 2**	**Case 1**	**Case 2**
Temperature (°C)	80	45	250	230	250		40		90		107	107	70	
Pressure (bar)	30	4.96	65		65		65		1.3		1.3	1.3	1.3	
Molar Vapor Fraction	1	1	1		1		1		1		0	0	0	
Mass flow (kg/h)	180	1310	6720	6898	6720	6898	5166	5343	1410	1407	508	507	818	813
Mass fractions														
CO_2	0	1	0.80		0.62		0.77		0		0		0	
H_2	1	0	0.13		0.10		0.12		0		0		0	
CH_3OH	0	0	0.01		0.14		0.01		0.64		0		0.9985	
H_2O	0	0	1.24E-03		0.08		0.001		0.36		0.999		0	
CO	0	0	0.06		0.06		0.08		0		0		0	

4.3. Energy analysis

The energy flows are presented in Fig. 5. The total energy available in case 1 is equal to 2151 kW with heat requirement of 1715 kW (excess energy = 436 kW). A quantity of 2073 kW is released in the case 2 against 1628 kW of required energy (excess of energy = 444 kW). The preheating of the flow injected into the reactor presents the most important quantity of energy in each configuration. This energy is reduced by 9.5% in the second one thanks to the two sections configuration of the reactor. In addition, a heat integration is less interesting when using only an isothermal reactor because of the need of external heat source. This need originates from the fact that there is no other stream in the process at a temperature higher than 250°C (temperature at the reactor inlet).

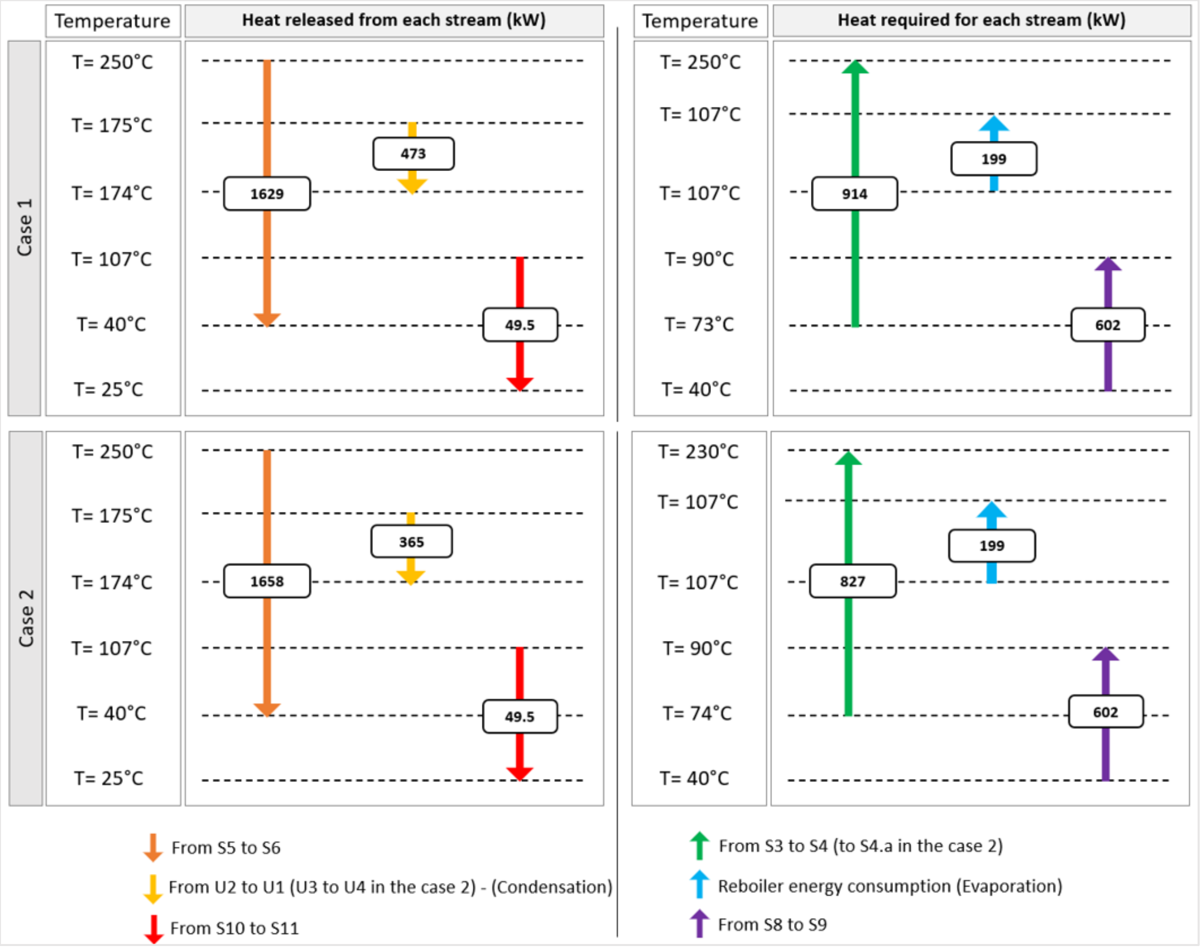

Fig. 5. The heat flows released/required for the heating up/cooling of the different streams of the conversion unit.

5. Conclusion

To reduce the CO_2 emissions and the use of fossil energy resources, the carbon capture and utilization technologies propose a wide range of solutions. The heat integration is one of the most important elements to reduce the energy demand of such processes. This work focused on the optimization of the process configuration and the rectification column optimization for an optimal heat recovery. Two cases have been studied, the first consisted in one isothermal reactor while in the second the reactor was divided into two sections (adiabatic and isothermal). It has been shown that an external energy source in necessary while using an isothermal reactor to complete the preheating of the gas mixture until 250°C before its injection in the reactor. In the new configuration of the reactor comprising two sections, the temperature of the inlet flue gas is reduced to 230°C and the adiabatic section allows the preheating of the gas mixture thanks to the exothermal reaction. In parallel, the process performances (CO_2 conversion and methanol production) remain the same while the catalyst mass is increased by only 3% in comparison with the first case. The optimization of the rectification column helped to minimize the reboiler duty, a compromise has been found between high methanol and water purity and the energy demand. As perspectives of this work, detailed heat integration with the CO_2 capture unit will be carried out considering the second configuration. Techno-economic studies and life cycle assessment will be also investigated.

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STUDY OF THE CO_2 CONVERSION INTO METHANOL: CATALYTIC PROCESS AND HEAT INTEGRATION OPTIMIZATIONS WITH A CO_2 CAPTURE UNIT.

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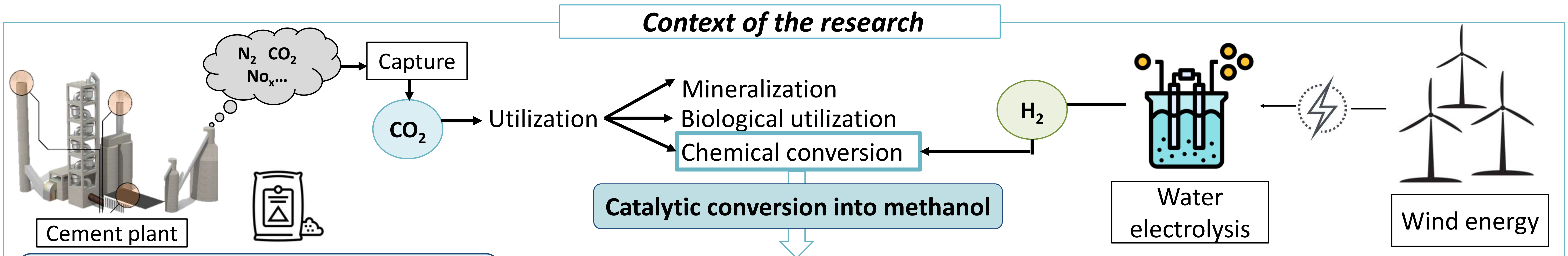
Context of the research



Capture

CO_2 → Utilization → Mineralization / Biological utilization / Chemical conversion

H_2 ← Water electrolysis ← Wind energy

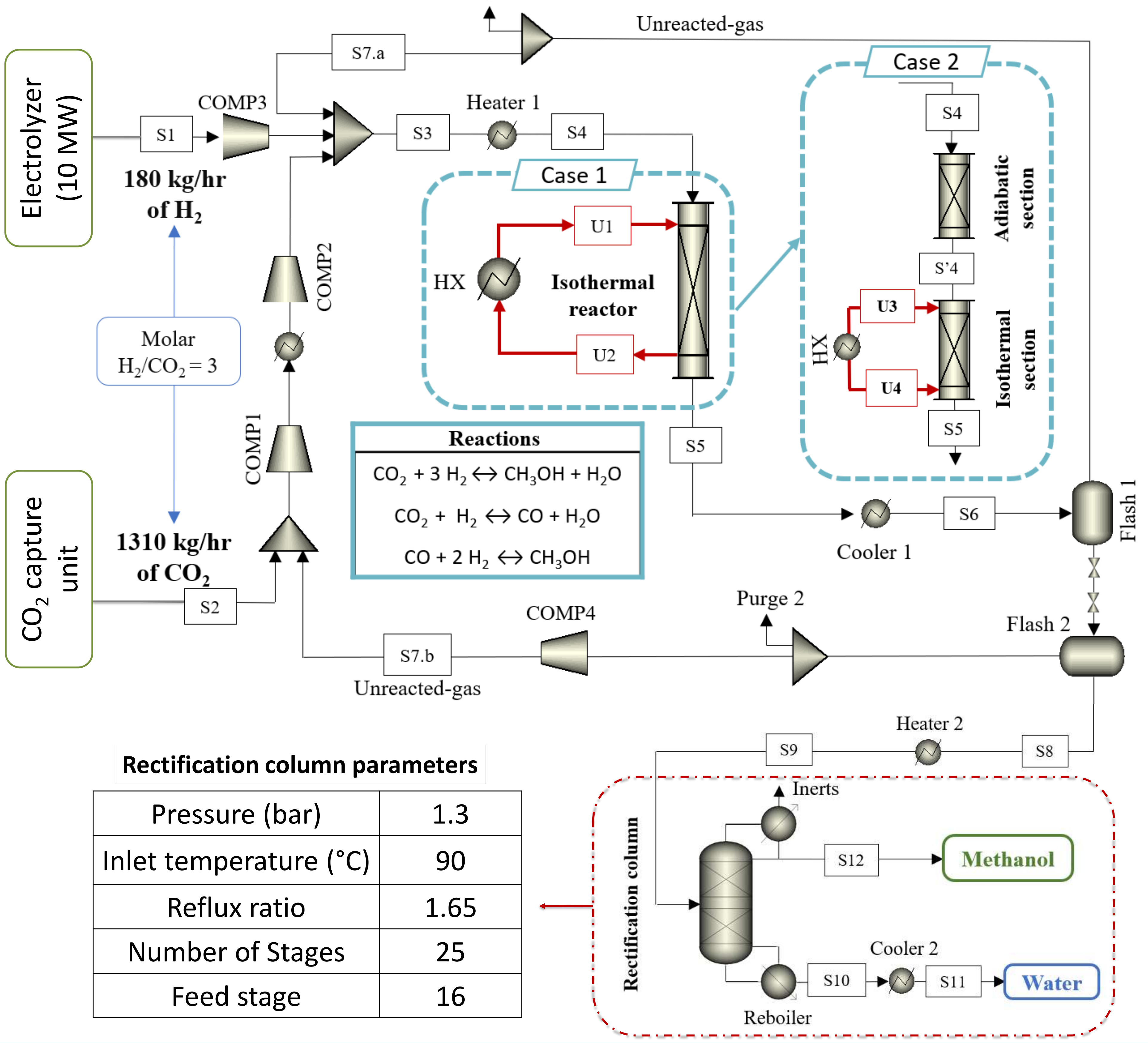
Catalytic conversion into methanol

Cement sector is responsible for 5% of global CO_2 emissions.

***Objective*: Simulation of the conversion unit and optimization of its energy demand**

Green Hydrogen production

Simulation works



Reactions

$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O$

$CO_2 + H_2 \leftrightarrow CO + H_2O$

$CO + 2\,H_2 \leftrightarrow CH_3OH$

Rectification column parameters

Pressure (bar)	1.3
Inlet temperature (°C)	90
Reflux ratio	1.65
Number of Stages	25
Feed stage	16

- **Reactions kinetics**

The model of Graaf (Graaf et al. 1988) has been used to describe the reaction kinetics. It has been developed using coper-based catalyst $Cu/ZnO/Al_2O_3$.

- **Operating and design parameters of the reactor(s)**

Inlet/Outlet temperature –Adiabatic = 230/250°C
Operating temperature –Isothermal = 250°C
Reactors pressure (bar) = 65 bar

$$GHSV = \frac{Q_{v_0}}{\rho_{catalyst}\, m_{catalyst}} = 10000\,h^{-1}$$

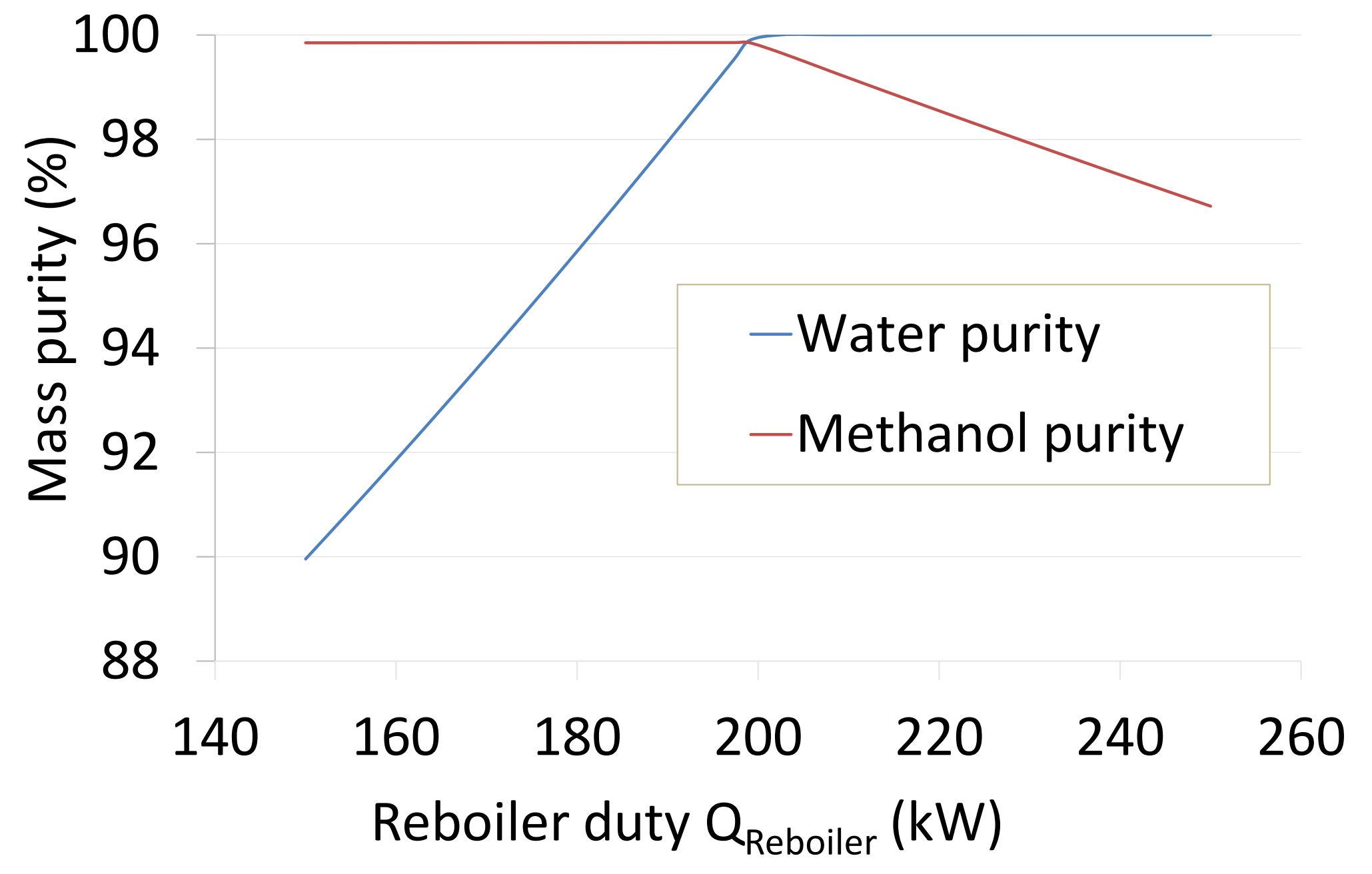
Case 1 → $m_{catalyst} = 1687\ kg$

Case 2 → $m_{(adiabatic)} = 339\ kg$; $m_{(Isothermal)} = 1393\ kg$

- **Engineering performance**

	Key indicator		value	
			Case 1	Case 2
Reactor	CO_2 conversion	Per-pass (%)	23	22.4
		Overall (%)	99.6	
Rectification column	Methanol flow (kg/h)		818	813
	Methanol purity (wt.%)		99.85	
	Water flow (kg/h)		508	507
	Water purity (wt.%)		99.9	

Heat integration evaluation



Effect of $Q_{Reboiler}$ on the mass purity of methanol and water.

Hot and cold streams in the conversion unit

	Exchanger	Temperature (°C)		Energy (kW)	
		Case 1	Case 2	Case 1	Case 2
Hot streams	Cooler 1	250 to 40		+1629	+1658
	Cooler 2	107 to 25		+49.5	
	HX	175 to 174		+473	+365
Cold streams	Heater 1	73 to 250		-914	-827
	Heater 2	40 to 90		-602	
	Reboiler	107		-199	

Discussion

- The total energy released Q → Case 1: Q = 2151 kW; Case 2: Q = 2073 kW
- The total heat requirement E → Case 1: E = 1715 kW; Case 2: E= 1628 kW
- The excess energy ΔE = 436 kW in case 1 and 445kW in case 2
- Case 2: The energy at the reactor inlet is reduced by 9.5%.
- Case1: Needs an external heat source. No other stream at temperature > 250 **°C**

Conclusions and perspectives

- To reduce the energy demand of the conversion unit, two reactor configurations cases have been studied, the first consisted in one isothermal reactor while in the second the reactor was divided into two sections (adiabatic and isothermal). Comparing to the Case 1, in Case 2 there is no need for an external heat. The optimization of the rectification column helped to minimize the reboiler duty.
- As perspectives of this work, detailed heat integration with the CO_2 capture unit will be carried out considering the second configuration. Techno-economic studies and life cycle assessment will be also investigated