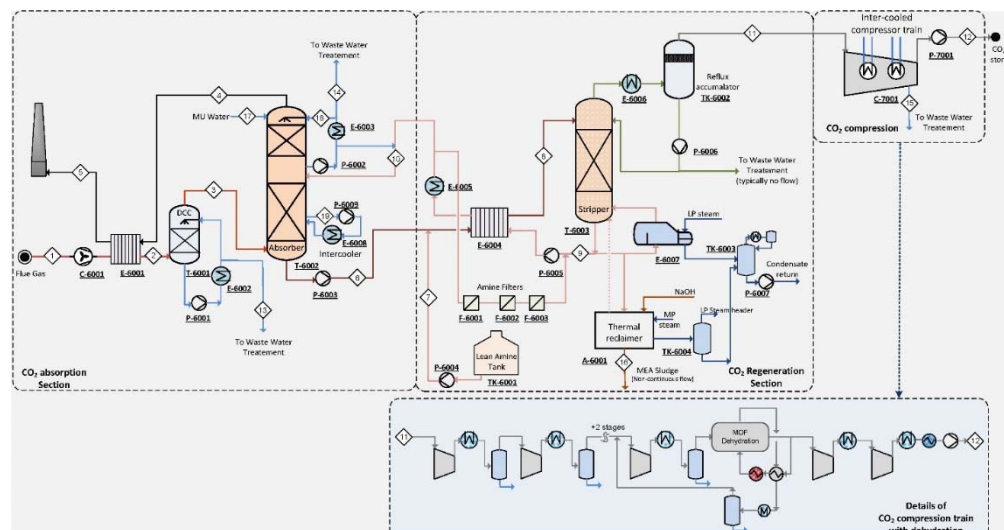# Report

Understanding the Cost of Retrofitting CO2 capture in an Integrated Oil Refinery

Performance analysis of CO2 capture options

Authors
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Report

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ABSTRACT
Post combustion capture with MEA from four generic refineries was modelled and simulated. Refinery nominal capacity is 100 000-350 000 bbl/day, with CO_2 emissions of 729-3350 ktonnes/year. Altogether 16 different capture cases were investigated (3-6 per generic refinery). Each capture case included CO_2 capture from between 1 and 5 stacks, and CO_2 capture rate from each stack was 90%. Cases with capture from several stacks have multiple absorbers and one common stripper. Flue gas desulfurization is included for CO_2 capture from Fluid Catalytic Crackers and CDU/VDU units.

Specific reboiler duty varies slightly between different CO_2 capture cases, due to varying CO_2 concentration in flue gases but is 3.64-3.69 GJ/t CO_2 in most cases.

An additional CHP plant without CO_2 capture was included in each refinery capture case to provide the additional steam required for MEA regeneration, and electric power required for CO_2 compression, flue gas fans, pumps and chillers. The CO_2 emissions from the CHP plant reduce the net CO_2 avoided from the streams with CO2 capture to about 60%.

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VERSION	DATE	VERSION DESCRIPTION
1	2017-04-28	First version with results for all post-combustion capture cases. CO_2 avoided missing.
2	2017-04-28	Second version: Modified according to input from Concawe to V1. Added CO_2 avoided for Base Case 4 and report summary.
3 (final)	2017-06-20	Final version incorporating comments from CONCAWE, IEAGHG. Updated the report to include Base Cases 1-3.

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Summary

This report describes the technical performance of CO_2 capture technologies integrated into four different generic refineries:

- Base Case 1) Simple refinery with a nominal capacity of 100 000 bbl/d
- Base Case 2 and 3) Medium and highly complex refineries with nominal capacity of 220 000 bbl/d
- Base case 4) Highly complex refinery with a nominal capacity of 350 000 bbl/d

The focus of the project is on post-combustion capture. The primary emission sources in each refinery were identified and CO_2 capture cases for the different refineries were established to explore CO_2 capture from a range of refinery CO_2 sources that vary in both capacity and CO_2 concentration. The capture cases were set up to include an absorber for each emission source and a common regenerator due to space constraints and to minimize expensive ducting in the refinery. Altogether 16 post-combustion capture cases using MEA have been investigated. Main focus is on capture from CO_2 emission sources from the highly complex generic refinery (i.e. Base Case 4) where a total of 6 capture cases were investigated.

Results

Overall, CO_2 capture with solvents (reactive absorption) is considered the most mature and relevant capture technology for post combustion or end-of-pipe capture. The solvent considered in this project is Mono Ethanol Amine (MEA). The MEA process for post-combustion capture has been simulated in HYSYS where a simple configuration with intercooler in the absorber is modelled. The tables below present an overview of the main results. It should be noted that the CO_2 capture process has not been optimized for the different cases. The table includes flue gas flow rate at operating point (OP) and design point (DP), with the latter being used to size the capture plant.

Table 1: Summary of main CO_2 emission sources and the absorber section in Base Case 1

		CO_2 [t/h] @ OP	% of total CO_2 emissions	CO_2 %vol	CO_2 %wt	Flue gas [t/h] @ OP	Utilization factor	Flue gas [t/h] @ DP	Absorber D (m)	Absorber H (m)	CO_2 captured t/h	CO_2 loading (mol/mol) lean	CO_2 loading (mol/mol) rich
A1	POW	42.3	48.80%	8.2	13.4	316.4	-	348.8	6.3	36	38.1	0.181	0.513
A2	CDU	23.6	27.20%	11.3	17.2	137.3	100%	151.2	4.2	36	21.3	0.181	0.516
A3	CRF	8.9	10.30%	8.4	13.4	66.5	92%	79.6	3	36	8	0.181	0.512

Table 2: Summary of selected CO_2 capture cases and the regenerator section in Base Case 1

		CO_2 emissions [t/h] @ OP	CO_2 emissions [t/h] @ DP	Avg CO_2 vol%	% of total CO_2 emissions	Regenerator D (m)	Regenerator H (m)	CO2 captured t/h	Flow rate (t/t CO2 cap) lean	Flow rate (t/t CO2 cap) rich	SRD GJ/t CO2	Lean/Rich HX duty kW
01-01	A1	42.3	46.6	8.2	48.80%	3.5	21	37.6	12.71	13.74	3.66	32795
01-02	A1+A2	65.9	72.6	9.2	76.00%	4.3	21	59.3	13.05	14.09	3.67	53468
01-03	A1+A2+A3	74.8	83.2	9.1	86.30%	4.7	21	67.3	13.06	14.09	3.67	60695

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Table 3: Summary of main CO₂ emission sources and the absorber section in Base Case 2

		CO₂ [t/h] @ OP	% of total CO₂ emissions	CO₂ %vol	CO₂ %wt	Flue gas [t/h] @ OP	Utilization factor	Flue gas [t/h] @ DP	Absorber D (m)	Absorber H (m)	CO₂ captured t/h	CO₂ loading lean	CO₂ loading rich
B1	POW	92.2	35.90%	8.3	13.2	697.5	-	769.3	9.3	47	82.8	0.181	0.512
B2	FCC	44.3	17.20%	16.6	24.6	180.1	100%	198.1	5.5	36	39.8	0.181	0.522
B3	CDU-B /VDU-B	33.2	12.90%	11.3	17.2	193.7	100%	212.7	6.7	38	51.2	0.181	0.515
B4	CDU-A	23.6	9.20%	11.3	17.2	137.4	100%	151.2					
B5	SMR	3.7 / 15.7	7.50%	17.8	26.8	72.4	88%	90.7	3.6	36	17.5	0.181	0.526

Table 4: Summary of selected CO₂ capture cases and the regenerator section in Base Case 2

		CO₂ emissions [t/h] @ OP	CO₂ emissions [t/h] @ DP	Avg CO2 vol %	% of total CO₂ emissions	Regenerator D (m)	Regenerator H (m)	CO2 captured t/h	Flow rate (t/t CO2 cap) lean	Flow rate (t/t CO2 cap) rich	SRD GJ/t CO2	Lean/Rich HX duty kW
02-01	B1	92.2	101.8	8.3	35.90%	5.2	22	82.8	13.13	14.17	3.68	75165
02-02	B1+B2	136.5	150.5	9.9	53.10%	6.2	24	122.5	13.02	14.05	3.66	109782
02-03	B1+B2+ B3+B4+ B5	212.7	237.2	10.7	82.70%	7.8	28	191.1	13.00	14.02	3.65	171110
02-04	B2+B3+ B4	101.1	111.2	13.1	39.30%	5.3	23	91.0	12.92	13.97	3.64	81140

Table 5: Summary of main CO₂ emission sources and the absorber section in Base Case 3

		CO₂ [t/h] @ OP	% of total CO₂ emissions	CO₂ %vol	CO₂ %wt	Flue gas [t/h] @ OP	Utilization factor	Flue gas [t/h] @ DP	Absorber D (m)	Absorber H (m)	CO₂ captured t/h	CO₂ loading lean	CO₂ loading rich
C1[1]	POW (NGCC)	28.0	28.60%	4.9	7.6	364.9	-	408.7	6.2	36	25.2	0.181	0.494
	POW (B)	51.3		8.1	12.9	397	-	436.7	7	38	46.3	0.181	0.511
C2	FCC	53.1	19.10%	16.6	24.6	225.4	100%	237.4	5.7	36	47.7	0.181	0.522
C3	CDU-B /VDU-B	34.2	12.30%	11.3	17.2	199.2	100%	219.1	9.7[2]	48[2]	98.5[2]	0.181	0.513
C4	CDU-A	23.8	8.50%	11.3	17.2	138.6	100%	152.5					
C5	SMR	5.8 / 25.5	11.30%	17.7	26.7	108.8	91%	141.8	4.5	36	28.1	0.181	0.526

[1] The combined heat and power plant consists of an natural gas combined cycle, POW(NGCC), and a natural gas boiler with a steam cycle, POW(B). They have independent absorbers.

[2] This is a combined absorber for CDU-B/VDU-B, CDU-A and POW(B).

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Table 6: Summary of selected CO₂ capture cases and the regenerator section in Base Case 3

		CO₂ emissions [t/h] @ OP	CO₂ emissions [t/h] @ DP	Avg CO2 vol %	% of total CO₂ emissions	Regenerator D (m)	Regenerator H (m)	CO2 captured t/h	Flow rate (t/t CO2 cap) lean	Flow rate (t/t CO2 cap) rich	SRD GJ/t CO₂	Lean/Rich HX duty kW
03-01	C1	79.3	87.3	6.6	28.60%	4.9	22	71.5	13.46	14.49	3.74	66576
03-02	C1+C2	132.4	145.8	8.7	47.70%	6	23	119.3	13.16	14.21	3.69	108418
03-03	C1+C2+C3+C4+C5	221.7	247.4	10.0	79.80%	8.1	30	199.6	13.05	14.08	3.67	179337

Table 7: Summary of main CO₂ emission sources and the absorber section in Base Case 4

		CO₂ [t/h] @ OP	% of total CO₂ emissions	CO₂ %vol	CO₂ %wt	Flue gas [t/h] @ OP	Utilization factor	Flue gas [t/h] @ DP	Absorber D (m)	Absorber H (m)	CO₂ captured t/h	CO₂ loading (mol/mol) lean	CO₂ loading (mol/mol) rich
D1[1]	POW (NGCC)	76.0	20.87%	4.2	6.6	1160.5	-	1276.6	10.6	48	68.4	0.181	0.489
	POW (B)	21.4		8.1	12.9	165.5	-	182.0	4.5	32	19.3	0.181	0.512
D2	FCC	53.1	11.38%	16.6	24.6	215.9	100%	237.4	5.9	36	47.8	0.181	0.522
D3	CDU-A/VDU-A	49.2	10.54%	11.3	17.2	286.5	100%	315.2	9.7	48	107.7	0.181	0.514
D4	CDU-B/VDU-B	49.2	10.54%	11.3	17.2	286.5	100%	315.2					
D5	SMR	19.8 / 97.5	25.13%	17.7	26.7	438.6	88%	548.3	8.9	44	105.8	0.181	0.526

[1] The combined heat and power plant consists of an natural gas combined cycle, POW(NGCC), and a natural gas boiler with a steam cycle, POW(B). They have independent absorbers.

[2] This is a combined absorber for CDU-B/VDU-B, CDU-A and POW(B).

Table 8: Summary of selected CO₂ capture cases and the regenerator section in Base Case 4

|		CO₂ emissions [t/h] @ OP	CO₂ emissions [t/h] @ DP	Avg CO2 vol %	% of total CO₂ emissions	Regenerator D (m)	Regenerator H (m)	CO2 captured t/h	Flow rate (t/t CO2 cap) lean	Flow rate (t/t CO2 cap) rich	SRD GJ/t CO2	Lean/Rich HX duty kW
04-01	D1	97.4	107.2	4.7	20.87%	5.1	22	87.6	13.95	15.06	3.85	85481
04-02	D1+D3+D4	195.8	215.4	6.7	41.95%	7.3	28	176.0	13.5	14.54	3.76	164682
04-03	D1+D2+D3+D4+D5	366.2	420.4	9.4	78.45%	10.2	38	329.7	13.10	14.13	3.68	298219
04-04	D5	117.3	146.6	17.7	25.13%	6.2	24	105.3	12.68	13.7	3.57	115594
04-05	D1+D3+D4+D5	313.1	362.0	8.7	67.08%	9.5	33	282.0	13.16	14.19	3.69	256441
04-06	D1+D2+D3+D4	248.9	273.8	7.7	53.32%	8.1	30	223.8	13.33	14.38	3.72	206691

The steam consumption as a function of CO₂ captured is fairly linear (Figure 1), since the variation in specific reboiler duty is rather small between the different capture cases. There are 5 main flue gas CO₂ compositions that arise from natural gas combined cycle (NGCC), natural gas + refinery fuel gas

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combustion, fuel oil combustion, fluid catalytic cracker (FCC) catalyst regeneration and steam methane reformer (SMR) furnace exhaust. Of these, the NGCC flue gas and SMR exhaust are the outliers with the NGCC having a CO_2 concentration of around 4vol% while the SMR furnace exhaust has a CO_2 concentration of around 18%. The specific reboiler duty (SRD) of the NGCC unit is higher than that of the SMR exhaust. However, as most of the cases have absorbers with a combination of flue gas compositions, the effect of this variation is diluted. The highest SRD is 3.85 GJ/t CO_2 captured for Case 04-01 (NGCC) and the lowest is 3.57 for Case 04-04 (SMR). Most of the other cases have SRDs in between 3.64-3.69 GJ/t CO_2 captured.
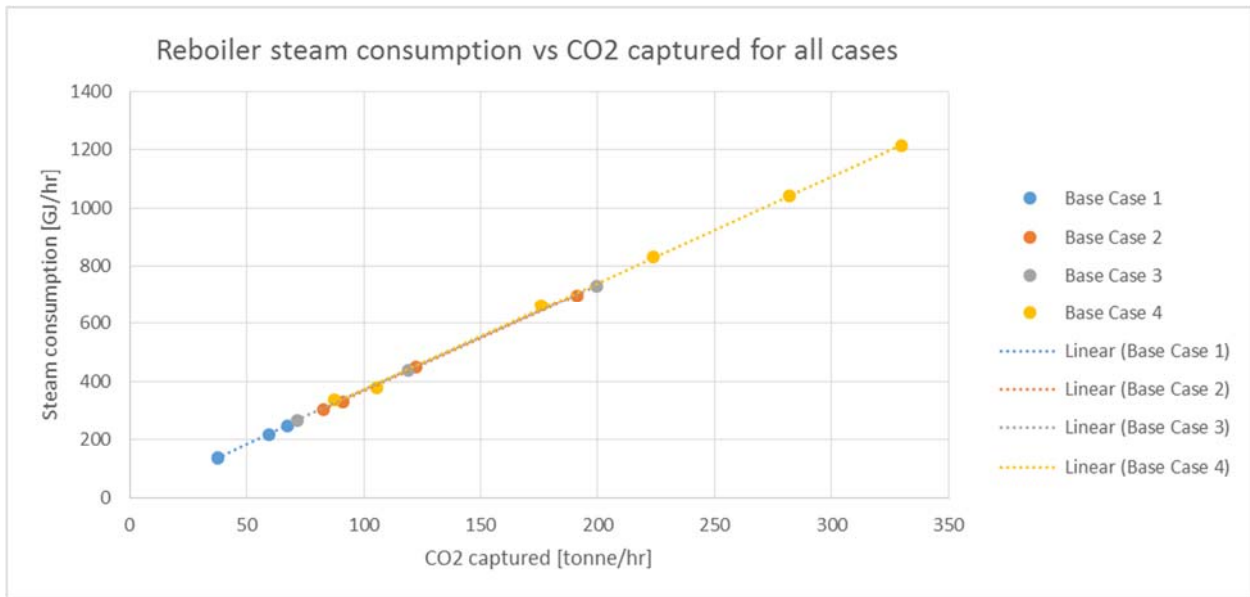

Figure 1. Reboiler steam consumption dependency on captured CO_2 for all investigated capture cases.

As expected, the power consumption for CO_2 compression as function of captured CO_2 is linear (Figure 2)
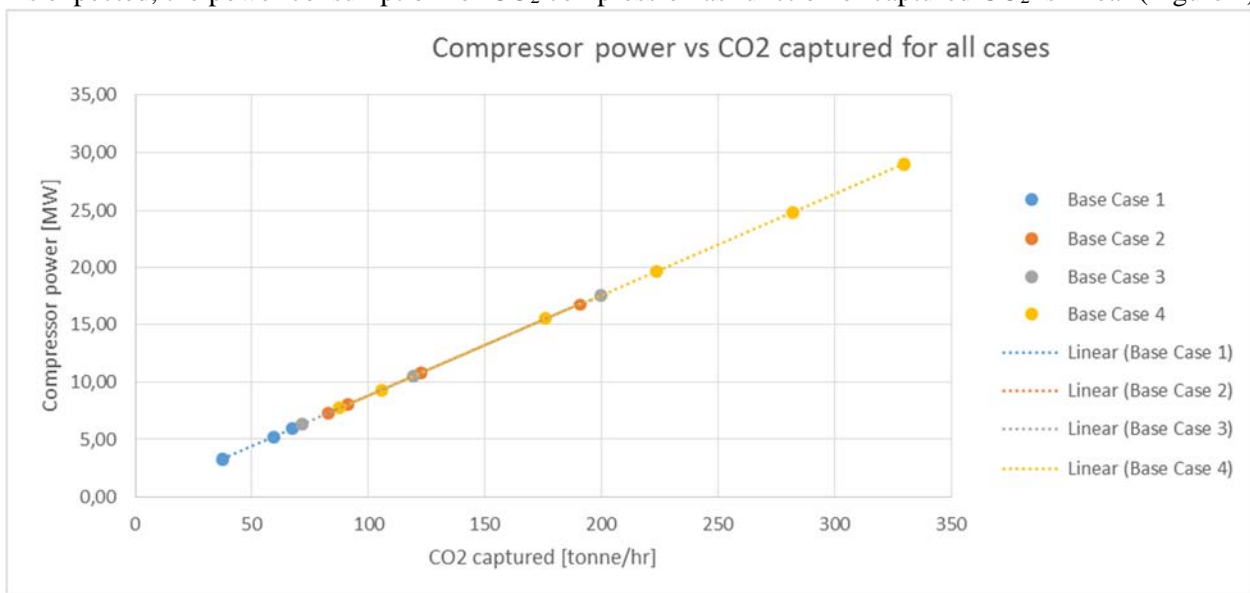

Figure 2. Compressor power dependency on captured CO_2 captured for all investigated capture cases.

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The fan power required for flue gas compression is not linear. The required fan power depends on the CO_2 concentration in the flue gas. In other words, two flue gas streams with exactly the same amount of CO_2 but different compositions will require different compression work as the total volume of gases to be compressed will be different in the two case. For examples Cases 04-01 and 04-04 capture similar amount of CO_2, however Case 04-01 required significantly higher fan power due to low CO_2 concentration compared to Case 04-04. Furthermore, flue gas desulphurization (FGD) units are required only for certain flue gases. When an FGD is required, addition power is required to overcome the FGD pressure drop. No trendlines were therefore added in Figure 3. Still, the figure provides a rough picture of the order of magnitude of fan power requirement.
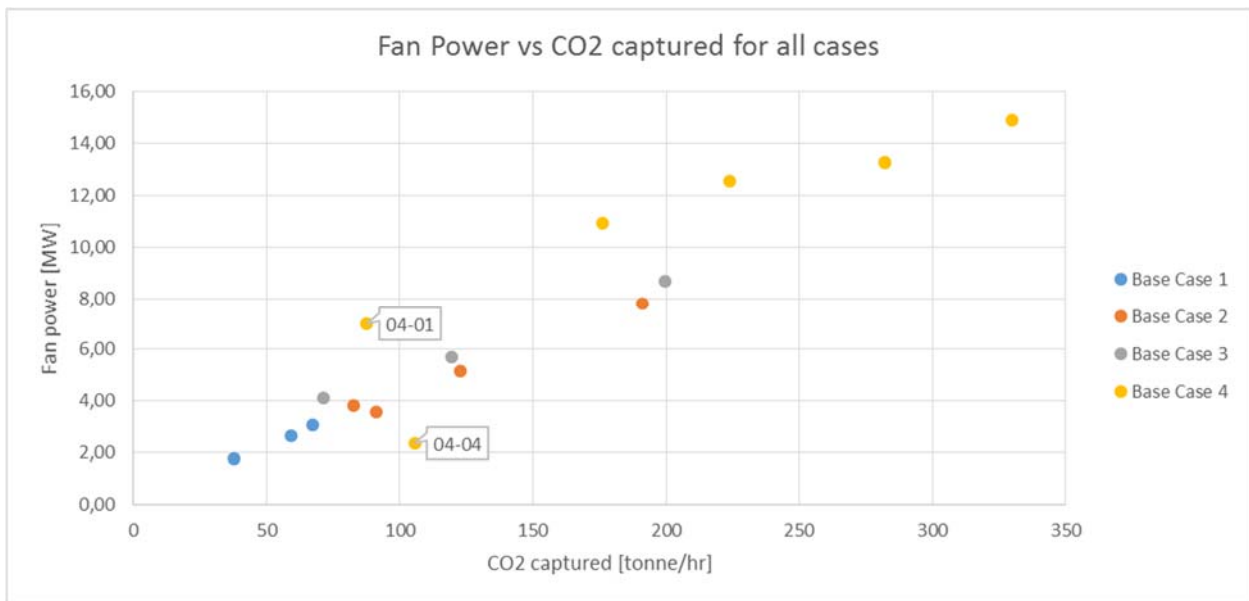
Figure 3. Fan power requirement vs CO_2 captured for all investigated capture cases

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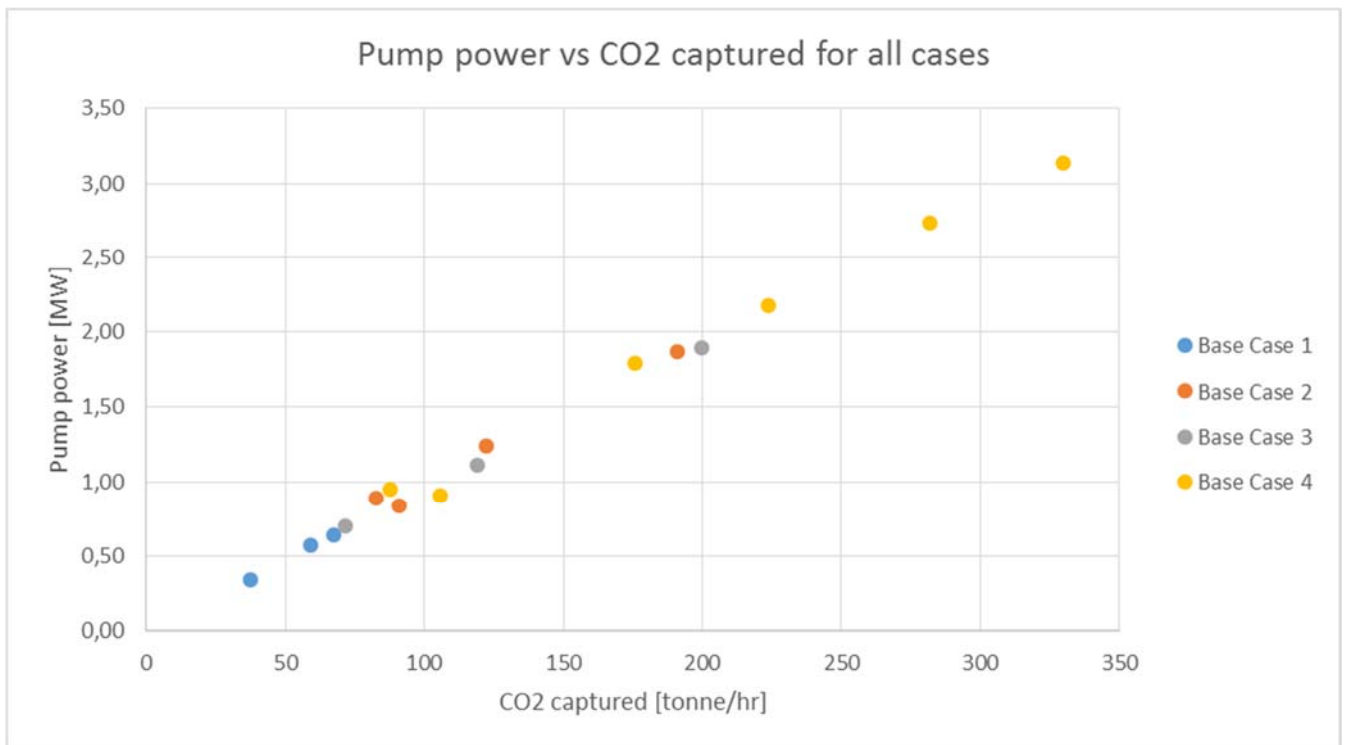
Figure 4. Pump power vs CO₂ captured for all investigated capture cases

The pump power requirement also depends on CO_2 concentration in the flue gas (Figure 4). Additionally, the CO_2 loading also has an effect on the pump power requirement. Compared to the fan power consumption, the pump power appears to show a small deviation from a linear relationship due to its smaller magnitude. For a quick, rough, back-of-the-envelope estimation, the pump power can be assumed to be linear.

All the absorbers in this work are designed to capture 90% of the CO_2 from the stacks. However, the net CO_2 avoided is significantly lower than the CO_2 capture rate of 90%. This is due to CO_2 emissions from the natural-gas fired CHP plant required for providing additional steam and power. The net CO_2 avoided is around 60% only.

Suggestions for future work on post-combustion capture from integrated oil refineries

The results in this report are used as the technology basis for estimating the cost of retrofitting post-combustion CO_2 capture to refineries, as presented in the subsequent report *Cost estimation and economic evaluation of CO₂ capture options for refineries*. The study does not pretend to cover all possible technical aspects of refinery post-combustion capture. Items that merit further attention are

- Investigating and quantifying the (expected reduced) energy consumption when applying a more modern solvent than MEA. Such solvents may require steam at different pressure/condensing temperature, and the reboiler/stripper may also operate at a different pressure than in the present case. The investigation is therewith more complex than just reducing the specific steam consumption.

- Advanced process configurations of post combustion capture process: Le Moullec et al.[1] provide an exhaustive review of 20 process modifications for improved process efficiency of solvent-based post-combtion CO_2 capture process. They are classified under process improvements for enhanced absorption, heat integration and heat pumping. Among then split flow arrangements are the most common where the general principle is to regenerate the solvent at two or more loading ratios.
- CO_2 capture from refineries integrated in industrial clusters. It is clear from the present report that generating the steam and power required for CO_2 capture and compression with a stand-alone natural-gas fired CHP plant significantly reduces the CO_2 avoided – although 90% of the CO_2 is captured from the investigated emission points, the net CO_2 avoided is only around 60%. Refineries located in industrial clusters with excess heat available should therefore be of interest to investigate from a CO_2 capture perspective – if the necessary steam can be provided with little or no additional fuel consumption this would be beneficial from a CO_2 emissions perspective. Power supply would then ideally come from a highly efficient thermal plant with CCS, or even from renewable energy.

CO_2 capture from H_2 production and Fluid Catalytic Cracker (FCC)

As mentioned earlier, the focus of this report is on post-combustion capture from refinery emission sources. However, CO_2 capture from syngas stream in an SMR and oxy-combustion capture from fluid catalytic cracking are receiving significant attention for CO2 capture from refineries. A brief study is provided of CO_2 capture from a refinery SMR based on the IEAGHG report *Techno-Economic Evaluation of Deploying CCS in Standalone (Merchant) SMR Based Hydrogen Plant using Natural Gas as Feedstock/Fuel*, report No 2017-02. This case is investigated in this report on CO_2 capture from the SMR in Base Case 4 ("Case 04-04" in Chapter 7).

Also, a literature review is provided in this report on oxy-combustion capture from Fluid Catalytic Crackers (FCC) in refineries, mainly relating to research undertaken by the CCP (CO_2 capture project)[2].

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[1] Le Moullec, Y., Neveux, T., Al Azki, A., Chikukwa, A., Hoff, K.A., 2014. Process modifications for solvent-based post-combustion CO2 capture. Int. J. Greenh. Gas Control 31, 96–112.

[2] http://www.co2captureproject.org/

1 Introduction

The aim of this study is to describe and analyse the technical performance of CO_2 capture from refineries. Four generic refinery Base Cases were developed and described by Amec FW in the document *Performance Analysis – Refinery Reference Plants*:

- Base Case 1) Simple refinery with a nominal capacity of 100 000 bbl/d
- Base Case 2 and 3) Medium to highly complex refineries with nominal capacity of 220 000 bbl/d
- Base case 4) Highly complex refinery with a nominal capacity of 350 000 bbl/d

All post combustion CO_2 capture studies in this document are related to one of these cases. Main focus is on CO_2 capture from refinery Base Case 4, which is seen as the most relevant reference for existing European refineries of interest for retrofit of CO_2 capture. The aim is that the work presented in this report together with *Performance Analysis – Refinery Reference Plants* should be a useful basis the European refinery industry to estimate the energy and utilities requirements for CO_2 capture from their own refineries.

Overall, CO_2 capture with solvents (reactive absorption) is considered the most mature and relevant capture technology for post combustion or end-of-pipe capture. The solvent considered in this project is Mono Ethanol Amine (MEA). MEA is used in this study primarily as it is considered as "standard" with well-known thermodynamics. It has also been used in many other IEAGHG CO_2 capture studies. Solvents are also considered mature technology for CO_2 capture from shifted syngas associated with Steam Methane Reformer (SMR) for hydrogen production. This option has not been investigated in detail in the present work. Instead, results are retrieved from the recently published IEAGHG report "Techno-Economic Evaluation of Standalone H_2 Plant (Merchant)", and related to the results for CO_2 capture from the SMR in Base Case 4 (Case 04-04). Finally, to cover oxy-combustion capture from refineries, a review on work done on oxyfuel capture for refineries in the CCP project is presented in chapter 9.

1.1 Assumptions

A basic assumption for this study of CO_2 capture from refineries is that the refinery production does not change, i.e. amount of crude fed to the refineries as well as the products and product quantities are unchanged. To provide the additional steam required for MEA regeneration and additional power required by the CO_2 capture unit and associated units, it is assumed that an additional natural gas-fired CHP plant is constructed on the refinery site. CO_2 capture from this CHP plant has not been included in the study. CO_2 capture can of course be added to such a CHP plant also, but this would require a scale-up of the plant to produce additional steam for this additional CO_2 capture.

1.2 Capture case selection rationale

For the emission sources from the four refinery Base Cases, a range of CO_2 capture cases were defined, focusing on the largest point sources among the refinery stacks. The rationale for selecting the cases was to have one case with a rather low capture rate (while ignoring really small, and hence impractical, emission sources), one with medium capture rate and one with high capture rate. After selecting the first 12 cases, one additional capture case was selected for Base Case 2 (case 02-04) and three additional capture cases were selected for Base Case 4 (cases 04-04, 04-05 and 04-06). The rationale for these selections is provided in sections 5.1 and 7.1.

## 1.3 Results generation and processing

The 16 CO_2 capture cases were simulated in Aspen HYSYS v9. The input data are defined in the report *Common Framework – technical*. Changes in this input (e.g. ambient conditions or cooling water temperature) would of course have an impact on the results.

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After simulating the CO_2 capture cases, Excel-based results files with the main results and stream data were generated. The main simulation results can be found in appendix A, where also process flow diagrams (PFDs) for each capture case are included. Key results (consumption of steam and power, cooling and makeup water requirement) are displayed graphically for all capture cases.

The process simulation results were used by Amec Foster Wheeler to establish the refinery balances, which can be found in appendix B. The CO_2 emissions from the CHP plants were used to calculate the net CO_2 emissions for each capture case. Process simulations of the capture cases were done at the *operating point*, i.e. matching the operating points of the refinery Base Cases, as listed in the report *Performance analysis – Refinery reference plants.* Also, the refinery balances were established for the operating point.

2 Post-combustion CO₂ capture process using MEA
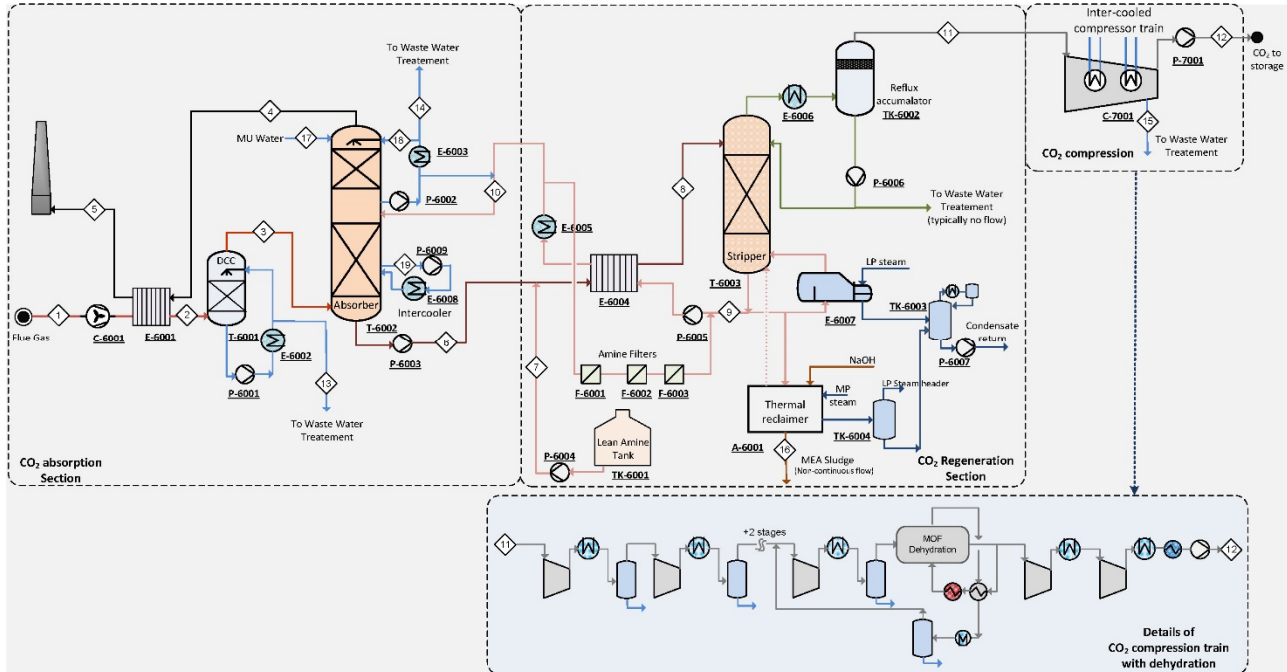
Figure 5: Process flow diagram of the MEA process for post-combustion CO₂ capture

This project makes use of reactive absorption of CO_2 using solvent as the end-of-pipe capture option for refinery flue gases. In reactive absorption CO_2 is chemically bound to the solvent through a slightly exothermic process. The reaction is reversed to release the CO_2 and regenerate the solvent by supplying heat to the process. The solvent considered in this project is Mono Ethanol Amine (MEA). MEA is used in this study primarily as it is considered as "standard" with well-known thermodynamics. It has also been used in many other IEAGHG CO_2 capture studies. It is recognized that modern proprietary solvents optimized for CO_2 capture from flue gases are likely to have reduced energy requirement. Investigating the impact of this is however beyond the scope of the present report.

The simulated process as set up when capturing CO_2 from one low-sulfur CO_2 source is illustrated in Figure 5. Flue gas from refinery process units or utility is cooled down in a process heat exchanger where it heats up exhaust gas from the top of the water wash section to the stack. The flue gas is further cooled to 40 °C in a direct contact cooler (DCC). The cooled gas is sent to a packed bed absorber where it is contacted with 30 wt% MEA solvent that is added to the top of the absorber. The flow rate of the solvent is adjusted to ensure close to 90% CO_2 capture. The CO_2 lean exhaust leaving the top of the absorber contains MEA and other MEA degradation products. An amine water wash section at the top of the absorber removes MEA and other impurities by contacting it with cold water that is circulated as shown in Figure 5.

MEA with chemically bound CO_2 (also called rich solvent) from the absorber is preheated in a process heat exchanger called the lean/rich heat exchanger with hot solvent regenerated in the stripper (also called lean solvent) and sent to the stripper or regenerator where CO_2 is released and solvent is regenerated. Heat is supplied for the regeneration process in the form of LP steam at 4.41 bar (with a condensing temperature of 140°C). The lean solvent is further cooled to 40°C after the lean/rich heat exchanger and mixed with amine wash water prior to feeding it to the top of the absorber.

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The CO_2 released from the top of the regenerator contains mainly water and nitrogen as impurities. This is sent to a seven stage inter-cooled compression process to compress the CO_2 product stream to 85 bar. The water is flashed out after the first five intercooling stages and then sent to a molecular sieve dehydration process to achieve the 10 ppm water specification in the CO_2 product stream. 10% of the dry CO_2 stream from the dehydration process is used as a purge gas in the regeneration stage of the dehydration process, and then recycled back to the prior stage for recompression. After compression to 85 bar the CO_2 product is cooled with cooling water and a chiller (using propane as refrigerant) in series to reach 25°C and then pumped to 110 bars. The use of a chiller is not necessarily required, but this is a process design choice that was made for the present study.

MEA degrades in the presence of O_2, SOx and NOx in addition to thermal degradation. A portion of the lean amine is sent to the thermal reclaimer to remove the degraded MEA by forming heat stable salts with sodium hydroxide (NaOH). Heat is supplied to the thermal reclaimer as MP steam.

As mentioned earlier, the reaction is slightly exothermic that causes the temperature to increase along the height of the absorber column from the bottom to the top. While MEA absorption kinetics are favoured by high temperatures, the absorption capacity deteriorates. An intercooler is thus included in the process close to the bottom to cool the solvent to 40°C and boost absorption and reduce the specific energy for solvent regeneration, commonly referred to as Specific Reboiler Duty (SRD). The placement of this intercooler has not been optimised as part of this work. Another option to decrease the SRD is to increase the temperature at the top of the absorber to improve kinetics. Thus pre-cooled amine wash water is mixed with the cooled lean amine to achieve a temperature of around 50°C rather than 40°C for the lean amine feed to the absorber. It should be noted that the absorption profile is top heavy, i.e., most of the absorption of CO_2 in the MEA takes places at the top of the column.

In cases where CO_2 is captured from more than one stack, one absorber per stack is typically used in the simulations, while there is *one common stripper* for the refinery. It is common refinery practice to pipe rich solvents to one common stripper.

The simulations for the different cases were performed in Aspen HYSYS v9.

3 Flue gas desulfurization

The flue gases from the CDU/VDU and FCC have a sulfur content of 240.8 and 256.5 ppmv respectively. This would cause excessive amine degradation, and the sulfur content of the flue gas must be reduced prior to CO_2 capture. A SOx content of 10 ppmv is known as an economical limitation for MEA CO_2 capture processes. Flue Gas Desulfurization (FGD) units should thus be installed for sulfur removal prior to the CO_2 capture process.

In the wet scrubbing process applied here, the reagent is reacted with SOx in a wet scrubber where the flue gas passes through. The reagent in wet scrubbers can be limestone ($CaCO_3$), lime (CaO), magnesium enhanced lime (MgO and CaO) and sodium carbonate (Na_2CO_3). Limestone based wet FGD technology, which can achieve very high sulfur removal rates, has the largest number of industrial installations. The technology has been selected in this project. Limestone ($CaCO_3$) and SO_2 are converted into gypsum ($CaSO_4 \cdot 2H_2O$) with presence of water and oxygen. The overall reaction is shown in the following equation.

$$CaCO_3 + SO_2 + 2H_2O + 0.5O_2 \leftrightarrow CaSO_4 \cdot 2H_2O + CO_2$$
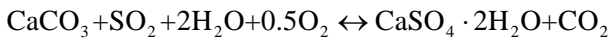
The mass balance of the FGD unit, such as the removal rate of SO_2, the consumption of limestone and O_2 as well as the production of gypsum, is mainly determined using the above reaction. The flue gas at the outlet of the wet scrubber is saturated with water. The flue gas is cooled mainly due to the evaporation of water vapor. The water content in the flue gas thus increases. Fresh water make-up is necessary to balance the water lost into the flue gas, the effluent as well as the water in gypsum. The impurities in the effluent is referred to the IEAGHG report (2010/05). The main energy consumption of the FGD unit is the additional electric power that is consumed to drive an additional induced draft fan to overcome the pressure drops in the unit, the oxidization air blower, the agitators and the pumps.

The wet FGD units are included for the CO_2 capture cases where the SOx content in the flue gas exceeds 10 ppmv, as can be seen from the process flow diagrams as well as the stream data for the cases.

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4 Base Case 1

It should be noted that all results provided for CO_2 capture from this and the other Base Cases in this report are for the refinery *operating point*, as determined in the report *Performance analysis – Refinery reference plants*. Sizing and costing in the subsequent report *Cost estimation and economic evaluation of CO_2 capture options* is done for the *design point*.

4.1 Capture case descriptions

The three largest emission sources in the refinery Base Case 1, the power plant (A1), the crude distillation unit (A2) and the catalytic reformer (A3), were selected as candidates for CO_2 capture (refer to Table 9). The emissions from the power plant (A1) are from natural gas and refinery fuel gas combustion in gas boilers. The emissions from the crude distillation unit (A2) come from fuel oil combustion in the fired heater related to the process while that of the catalytic reformer unit (A3) comes from natural gas and refinery fuel gas combustion in the fired heater related to the process.

Table 9. Emission sources selected for capture in refinery Base Case 1.

		CO_2 [t/h] @ operating point	% of total CO_2 emissions	CO_2 %vol	CO_2 %wt	Flue gas [t/h] @ operating point
A1	POW[1]	42.3	48.8%	8.2	13.4	317.1
A2	CDU	23.6	27.2%	11.3	17.2	137.4
A3	CRF	8.9	10.3%	8.4	13.4	66.6

[1]Reference should be made to section 1.1.1 in report *Performance analysis – Refinery reference plants* for explanation of abbreviations POW, CDU, CRF.

Based on the emission sources in Table 9, three post-combustion capture cases were defined for refinery Base Case 1 that capture an incrementally larger share of the refinery CO_2 emissions. The three capture cases selected are shown in Table 10.

Table 10. The three selected capture cases for refinery Base Case 1. Refer to Table 9 for definition of emission sources A1-A3.

		CO_2 emissions [t/h] @ operating point	% of total CO_2 emissions	Avg CO_2 vol%
01-01	A1	42.3	48.8%	8.2
01-02	A1+A2	65.9	76.0%	9.2
01-03	A1+A2+A3	74.8	86.3%	9.1

The refinery Base Case 1 without CO_2 capture is self-sustained with power. To cover the additional power consumption caused by the CO_2 capture and compression, an additional natural gas-fired CHP plant is included (see appendix B). CO_2 is not captured from this CHP plant in the present study.

4.2 Results

Key results from the CO_2 capture simulations, with capture of 90% of CO_2 from selected emission sources are presented below. All simulations and results presented are for the refinery operating point. Further results from the simulations, as well as process flow diagrams can be found in Appendix A. Results are presented without utilities unless specified otherwise.

4.2.1 Specific utilities consumption

A summary of the specific utilities consumption for the capture plant at the operating point is provided in Table 11. Further details can be found in appendix A. Note that the specific electricity and cooling water demands provided in appendix A are per process unit, i.e. per absorber, stripper and for the compression unit, whereas the total numbers are provided below. The CO_2 avoided for all capture cases is lower than the CO_2 captured, due to the additional CO_2 emissions from the utilities CHP plant (see appendix B).

Table 11. Specific utilities consumption for Base Case 1 capture cases.

|	01-01	01-02	01-03
CO_2 captured [t/hr][1]	37.5	59.3	67.3
Net CO_2 avoided [t/hr][2]	24.9	39.3	44.7
Specific reboiler duty [GJ / t CO_2 captured]	3.66	3.67	3.67
Electricity demand [kWh / t CO_2 captured]	148.0	146.1	146.8
Cooling water demand [t / t CO_2 captured]	104.4	94.7	96.4
Makeup of water [t / t CO_2 captured]	0.79	0.93	0.91

[1]Excluding dissolved water in CO_2 stream. [2]Including CO_2 emissions from utilities CHP plant.

4.2.2 Steam consumption

The very small variation in specific reboiler steam consumption gives a linear correlation between the amount of steam consumed (in MW) and the amount of CO_2 captured, as can be seen in

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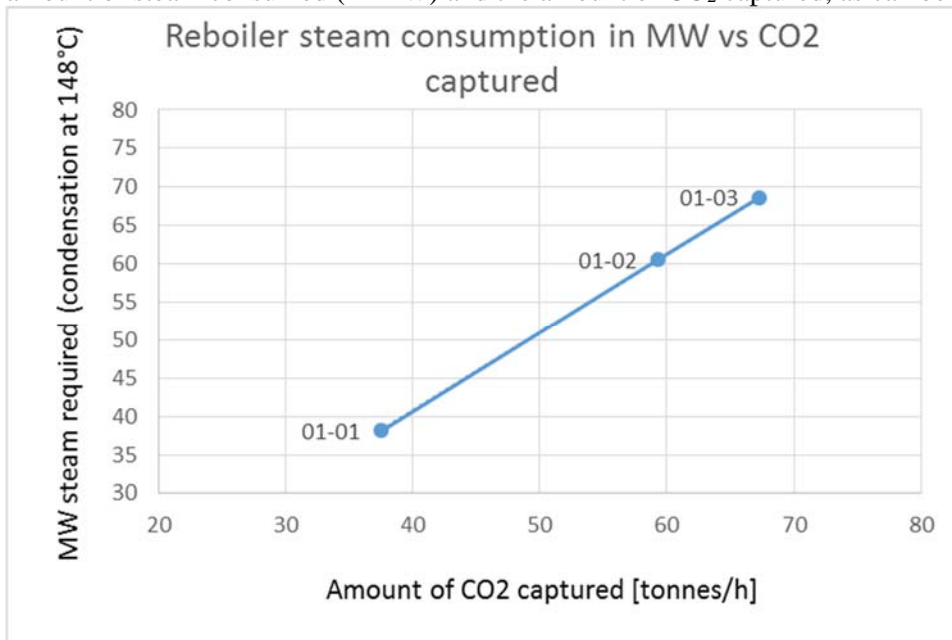
Figure 6. It should be recalled that the heat released from condensing steam varies4 with varying condensation temperature and pressure, results are valid for steam condensing at 147.7°C with the corresponding heat of condensation being 2121.37 kJ/kg steam (a temperature approach of 20°C was selected in the CO_2 capture process simulations).
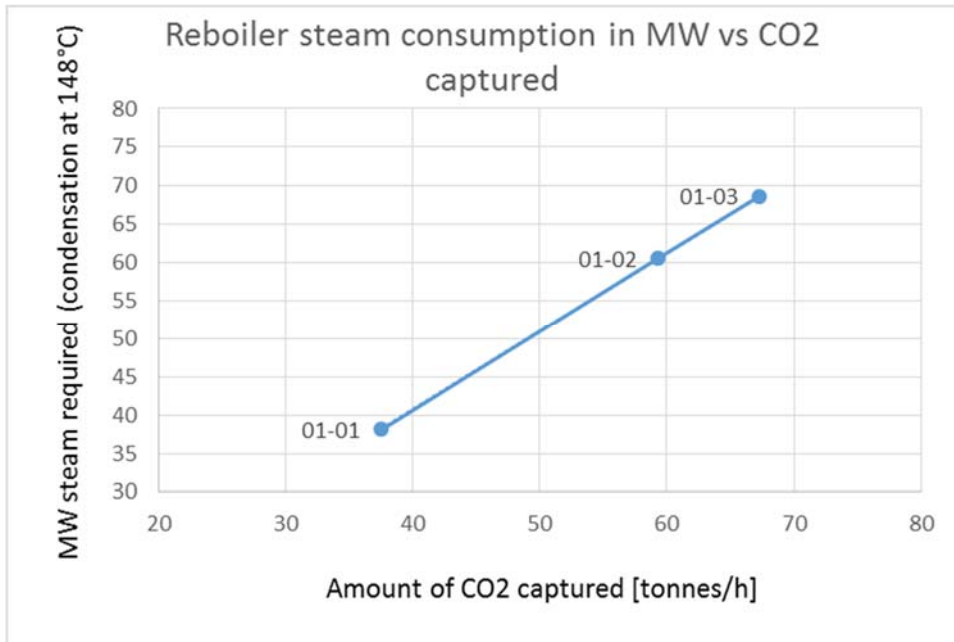
Figure 6. Amount of CO_2 captured as function of the amount of condensing steam for Base Case 1 capture cases.

4.2.3 Makeup water consumption

The total makeup water consumption for each case can be seen in **Figure 7**.

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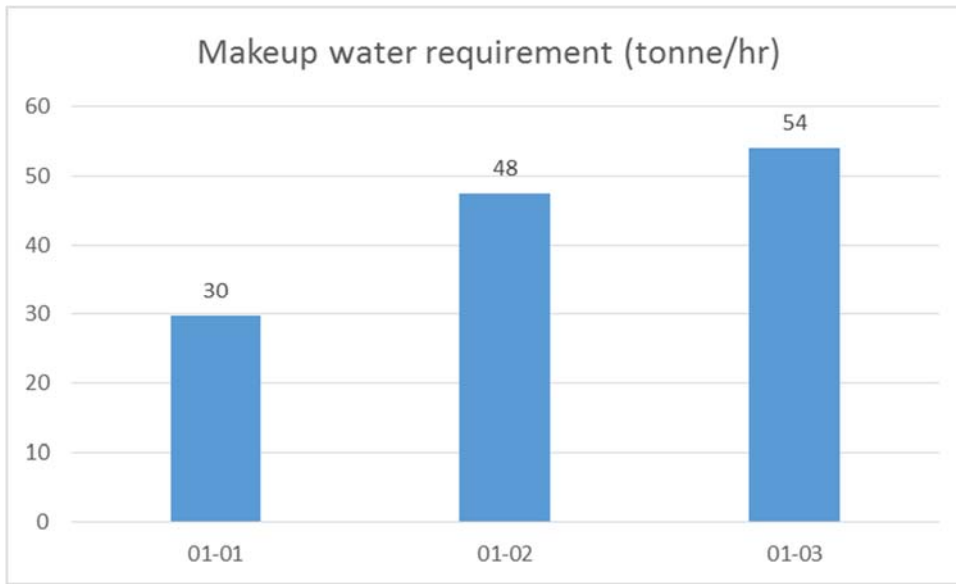
Figure 7. Makeup water consumption for the capture cases in Base Case 1.

### 4.2.4 Cooling water requirement

The cooling water consumption of the CO_2 capture plant can be seen in Figure 8. In comparison, the cooling water consumption of the refinery Base Case 1 without CO_2 capture is 9026 tonnes/hr (refer to table 5-6 in report *Performance analysis – Refinery reference plants*). This means that CO_2 capture will increase the cooling water consumption with 43-72%, depending on the capture case.
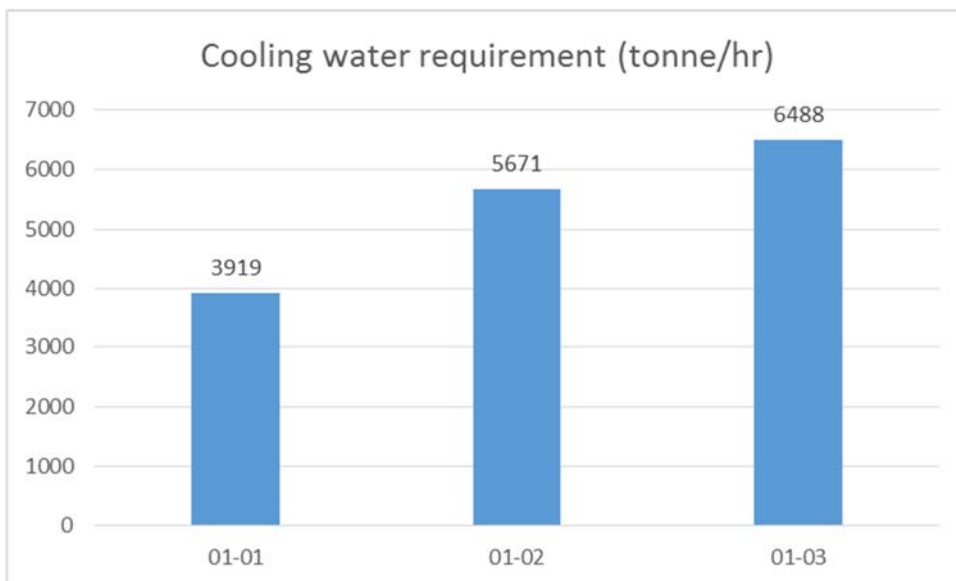
Figure 8. Cooling water requirement for the capture cases in Base Case 1.

4.2.5 Electric power consumption

The electric power consumption caused by the CO_2 capture can be seen in Figure 9. As can be seen, the main power consumers are CO_2 compression and flue gas fans, whereas the power consumption for the CO_2 pump and chiller is of smaller significance. In comparison, the power consumption for the refinery Base Case 1 without CO_2 capture is 28 MW (refer to table 5-6 in report *Performance analysis – Refinery reference plants*). This means that the power consumption increases with 20-35% depending on the capture case.
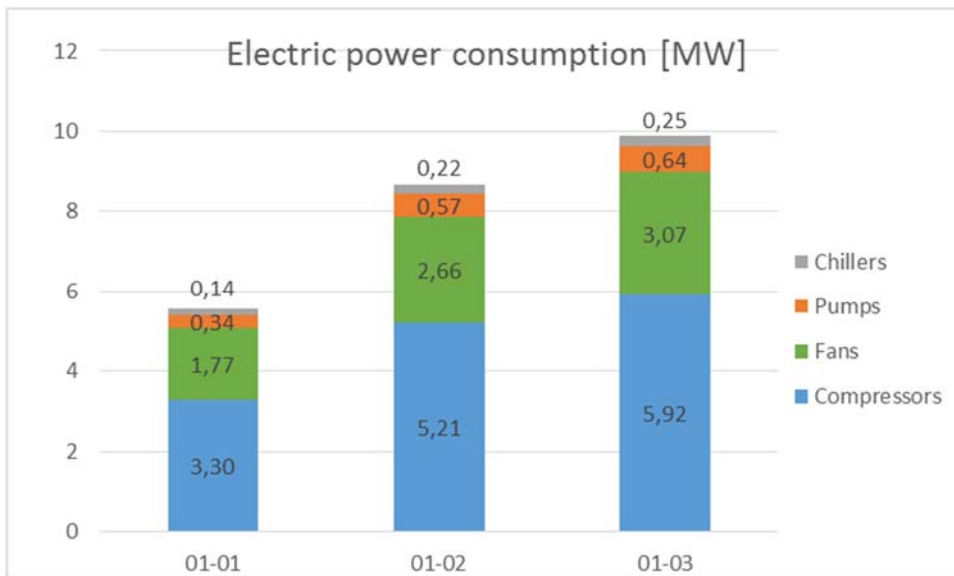
Figure 9. Electric power consumption for the capture cases in Base Case 1.

4.2.6 CO₂ avoided

As mentioned above, it has been assumed in this report that an additional natural gas-fired CHP plant is constructed on the refinery site to respond to increased steam and power requirements. CO_2 capture from this CHP plant has not been included in the study. Hence, although the CO_2 capture from the stacks in the investigated cases is 90%, the net CO_2 avoided from these emission sources is lower. This is illustrated in Figure 10.
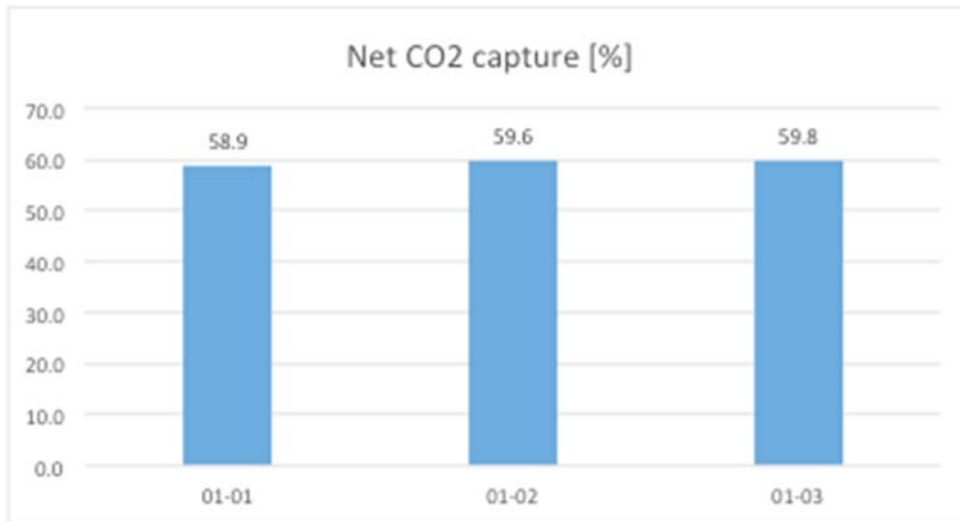
Figure 10. CO₂ avoided in % for the different capture cases for Base Case 1.

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5 Base Case 2

It should be noted that all results provided for CO_2 capture from this and the other Base Cases in this report are for the refinery *operating point*, as determined in the report *Performance analysis – Refinery reference plants.* Sizing and costing in the subsequent report *Cost estimation and economic evaluation of CO_2 capture options* is done for the *design point*.

5.1 Capture case descriptions

The five largest emission sources in the refinery Base Case 2, the power plant (B1), the fluid catalytic cracking unit (B2), the crude and vacuum distillation units train B (B3), the crude distillation unit train A (B4) and the steam methane reformer (B5), were selected as candidates for CO_2 capture (refer to Table 12). The emissions from the power plant (B1) are from natural gas and refinery fuel gas combustion in gas boilers. The emissions from the fluid catalytic cracking unit (B2) come from burning coke desposited on the catalysts in the cracking process and regeneration of the deactivated catalyst. The emissions from the crude and vacuum distillation units train B and the crude distillation unit train A (B3 and B4) come from fuel oil combustion in the fired heater related to the process. The steam methane reformer (B5) converts natural gas to syngas that mainly contains hydrogen and carbon dioxide. The syngas stream contains 15.7 t/h of CO_2 as shown in Table 12 with a concentration of 24.2 vol% (35.2 wt%). H_2 is separated from CO_2 in a PSA and the resulting tail gas that mainly contains CO_2, some H_2 and unreacted methane are sent to the furnace as supplementary fuel. Refinery fuel gas is used as the primary fuel in the furnace to provide heat to the endothermic reforming reaction. The combustion of refinery fuel gas results in 3.7 t/h of CO_2. Thus the total CO_2 emitted in the furnace exhaust is the sum of these two sources with a concentration of 17.7 vol% (26.7 wt%).

Table 12. Emission sources selected for capture in refinery Base Case 2.

		CO_2 [t/h] @ operating point	% of total CO_2 emissions	CO_2 %vol	CO_2 %wt	Flue gas [t/h] @ operating point
B1	POW[1]	92.2	35.9%	8.3	13.2	697.5
B2	FCC	44.3	17.2%	16.6	24.6	180.1
B3	CDU-B/VDU-B	33.2	12.9%	11.3	17.2	193.7
B4	CDU-A	23.6	9.2%	11.3	17.2	137.4
B5	SMR	3.7	7.5%	17.7	26.4	72.4
		15.7				

[1]Reference should be made to section 1.1.2 in report *Performance analysis – Refinery reference plants* for explanation of abbreviations POW, FCC, CDU, VDU, SMR.

Based on the emission sources listed in Table 12, four CO_2 capture cases were defined for Base Case 2. First, cases 02-01, 02-02 and 02-03 were selected according to the principle to have three cases of varying size. Thereafter case 02-04 was added. Approximately the same amount of CO_2 is capture from cases 02-01 and 02-04, but the difference is that the flue gases in case 02-04 require desulfurization before CO_2 capture while case 02-01 does not, and the difference in cost between these two options is interesting to investigate. The capture cases are described in Table 13.

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Table 13. The four selected capture cases for refinery Base Case 2. Refer to Table 12Table 9 for definition of emission sources B1-B5.

		CO_2 emissions [t/h] @ operating point	% of total CO_2 emissions	Avg CO_2 vol%
02-01	B1	92.3	35.9%	8.3
02-02	B1+B2	136.5	53.1%	9.9
02-03	B1+B2+B3+B4+B5	212.7	82.7%	10.7
02-04	B2+B3+B4	101.1	39.3%	13.1

The refinery Base Case 2 without CO_2 capture is self-sustained with power. To cover the additional power consumption caused by the CO_2 capture and compression, an additional natural gas-fired CHP plant is included (see appendix B). CO_2 is not captured from this CHP plant in the present study.

5.2 Results

Key results from the CO_2 capture simulations, with capture of 90% of CO_2 from selected emission sources are presented below. All simulations and results presented are for the refinery operating point. Further results from the simulations, as well as process flow diagrams can be found in Appendix A. Results are presented without utilities unless specified otherwise. In the diagrams, the cases are presented in ascending order with respect to amount of CO_2 captured, i.e. case 02-04 is presented between case 02-10 and case 02-02. Further results from the simulations can be found in Appendix A.

5.2.1 Specific utilities consumption

A summary of the specific utilities consumption for the capture plant at the operating point is provided in Table 14. Further details can be found in appendix A. Note that the specific electricity and cooling water demands provided in appendix A are per process unit, i.e. per absorber, stripper and for the compression unit, whereas the total numbers are provided below. The CO_2 avoided for all capture cases is lower than the CO_2 captured, due to the additional CO_2 emissions from the utilities CHP plant (see appendix B).

**Table 14. Specific utilities consumption for Base Case 2 capture cases.**

	02-01	02-02	02-03	02-04
CO_2 captured [t/hr][1]	82.8	122.5	191.1	91.0
Net CO_2 avoided [t/hr][2]	54.9	81.4	127.2	60.6
Steam demand [GJ / t CO_2 captured]	3.68	3.66	3.65	3.64
Electricity demand [kWh / t CO_2 captured]	155.2	144.2	142.1	139.8
Cooling water demand [t / t CO_2 captured]	101.5	96.9	92.1	86.6
Makeup of water [t / t CO_2 captured]	0.93	0.95	0.98	1.19

[1]Excluding dissolved water in CO_2 stream. [2]Including CO_2 emissions from utilities CHP plant.

5.2.2 Steam consumption

The very small variation in specific reboiler steam consumption gives a linear correlation between the amount of steam consumed (in MW) and the amount of CO_2 captured, as can be seen in

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Figure 11. It should be recalled that the heat released from condensing steam varies with varying condensation temperature and pressure, i.e. is valid for steam condensing at 147.7°C with the corresponding heat of condensation being 2121.37 kJ/kg steam (a temperature approach of 20°C was selected in the CO_2 capture process simulations).
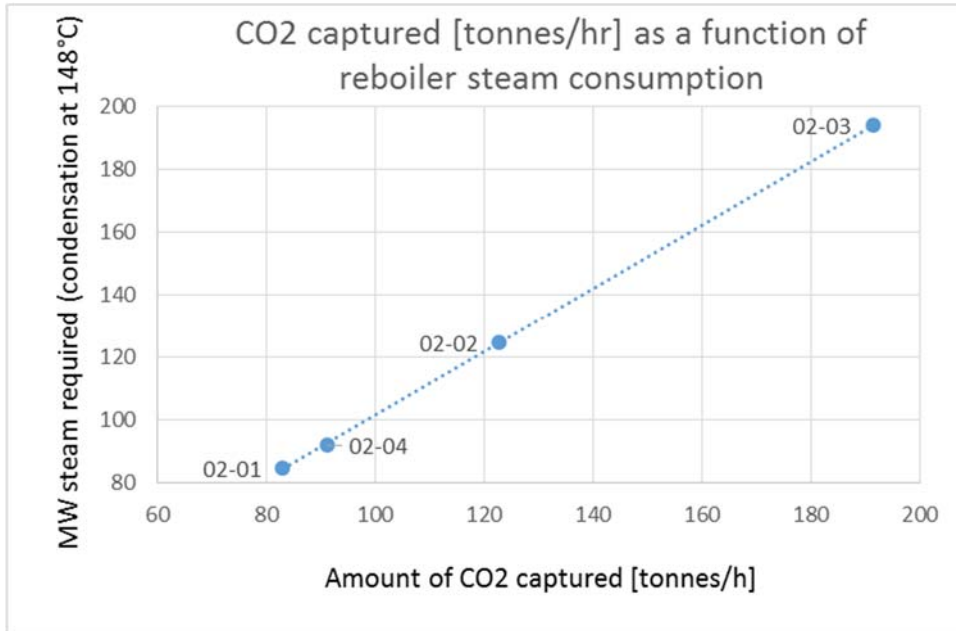
Figure 11. Amount of CO_2 captured as function of the amount of condensing steam for Base Case 2 capture cases.

5.2.3 Makeup water consumption

The makeup water consumption for each case can be seen in **Figure 12**.
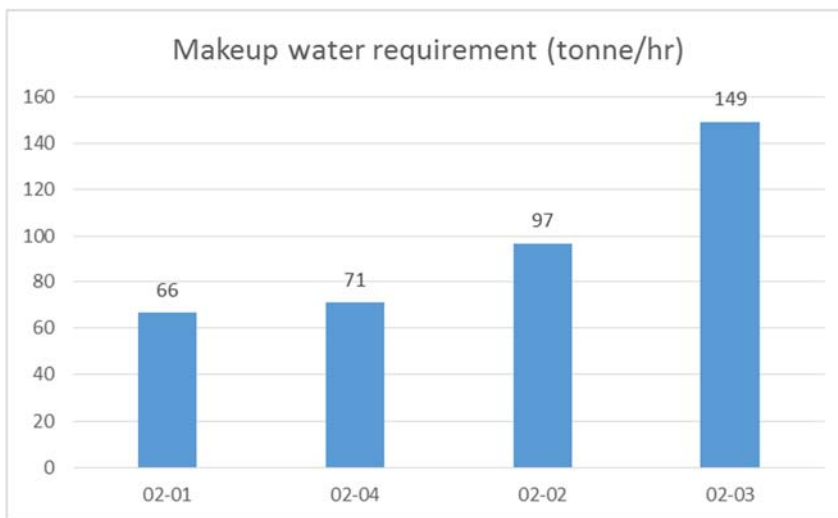
Figure 12. Makeup water consumption for the capture cases in Base Case 2.

5.2.4 Cooling water requirement

The cooling water consumption of the CO_2 capture plant and can be seen in Figure 13. In comparison, the cooling water consumption of the refinery Base Case 2 without CO_2 capture is 25122 tonnes/hr (refer to table 6-6 in report *Performance analysis – Refinery reference plants*). This means that the CO_2 capture will increase the cooling water consumption with 31-70%, depending on the capture case.
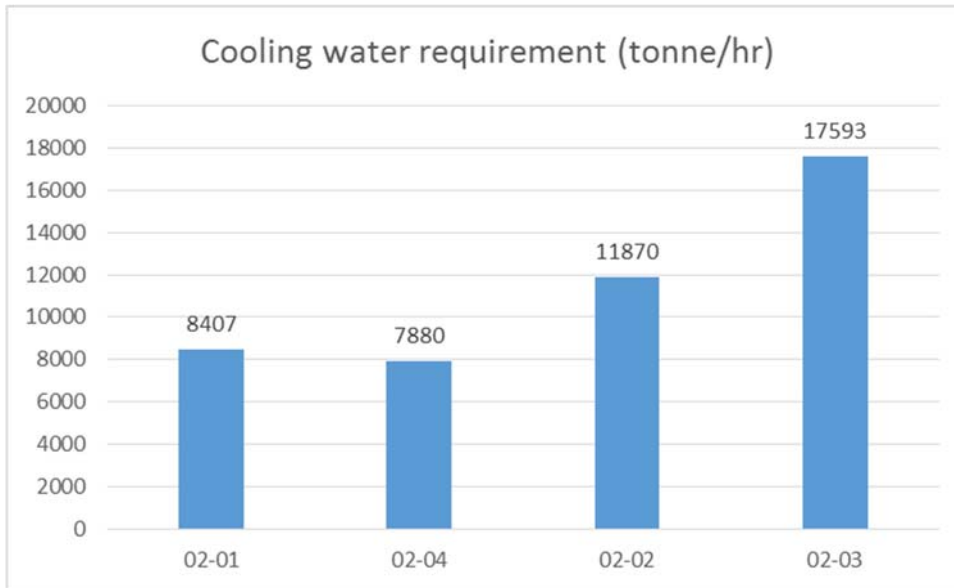
Figure 13. Cooling water requirement for the capture cases in Base Case 2.

5.2.5 Electric power consumption

The electric power consumption caused by the CO_2 capture can be seen in Figure 14. As can be seen, the main power consumers are CO_2 compression and flue gas fans, whereas the power consumption for the CO_2 pump and chiller is of smaller significance. In comparison, the power consumption for the refinery Base Case 2 without CO_2 capture is 60.4 MW (refer to table 6-6 in report *Performance analysis – Refinery reference plants*). This means that the power consumption increases with 21-45% depending on the capture case.

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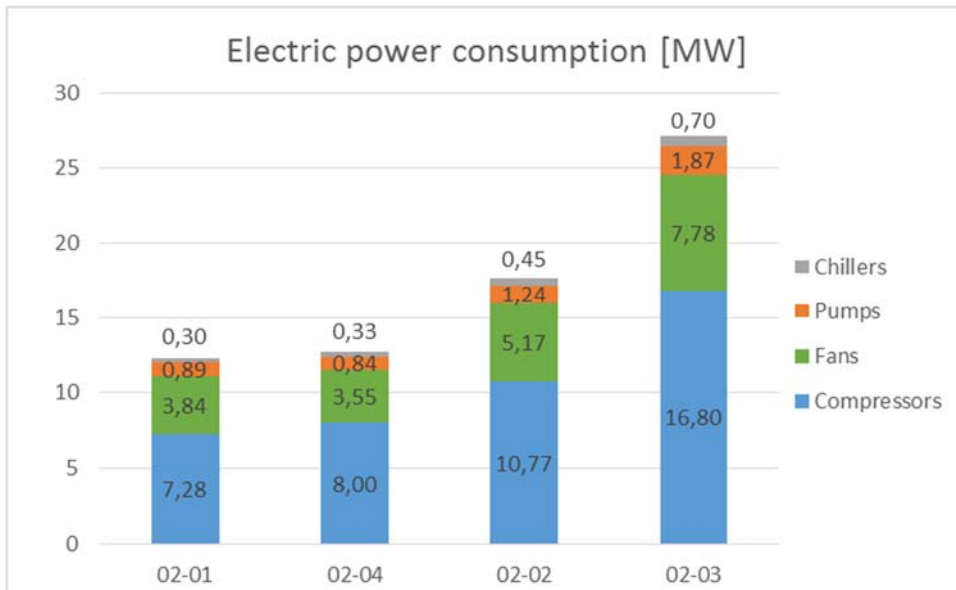
Figure 14. Electric power consumption for the capture cases in Base Case 2.

5.2.6 CO_2 avoided

As mentioned above, it has been assumed in this report that an additional natural gas-fired CHP plant is constructed on the refinery site to respond to increased steam and power requirements. CO_2 capture from this CHP plant has not been included in the study. Hence, although the CO_2 capture from the stacks in the investigated cases is 90%, the net CO_2 avoided from these emission sources is lower. This is illustrated in **Figure 15**.
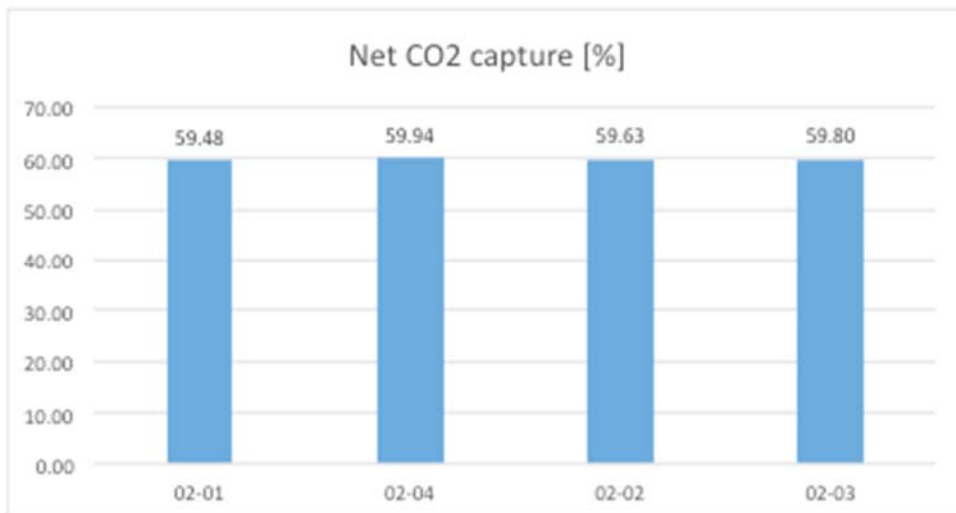
Figure 15. CO_2 avoided in % for the different capture cases for Base Case 2.

6 Base Case 3

It should be noted that all results provided for CO_2 capture from this and the other Base Cases in this report are for the refinery *operating point*, as determined in the report *Performance analysis – Refinery reference plants.* Sizing and costing in the subsequent report *Cost estimation and economic evaluation of CO_2 capture options* is done for the *design point*.

6.1 Capture case descriptions

The five largest emission sources in the refinery Base Case 3, the power plant (C1), the fluid catalytic cracking unit (C2), the crude and vacuum distillation units train B (C3), the crude distillation unit train A (C4) and the steam methane reformer (C5), were selected as candidates for CO_2 capture (refer to Table 15). The emissions from the fluid catalytic cracking unit (C2) come from burning coke desposited on the catalysts in the cracking process and regeneration of the deactivated catalyst. The emissions from the crude and vacuum distillation units train B and the crude distillation unit train A (C3 and C4) come from fuel oil combustion in the fired heater related to the process. It should be noted that the power generation (C1) in Base case 3 is different from base case 2, since it also includes a gas turbine plant and thus has two emission sources as indicated in Table 15. The first, and smaller, emission source is the natural gas combined cycle (NGCC) plant where natural gas is burnt in the gas turbine combustor and refinery fuel gas used for supplementary firing in the heat recovery steam generator. The second power plant emission source is the set of three gas boiler power units that burn refinery fuel gas. The flue gas from the NGCC power plant is not combined with that from the boilers due to control constraints. The steam methane reformer (D5) converts natural gas to syngas that mainly contains hydrogen and carbon dioxide. The syngas stream contains 25.5 t/h of CO_2 as shown in Table 15 with a concentration of 24.2 vol% (35.2 wt%). H_2 is separated from CO_2 in a PSA and the resulting tail gas that mainly contains CO_2, some H_2 and unreacted methane are sent to the furnace as supplementary fuel. Refinery fuel gas is used as the primary fuel in the furnace to provide heat to the endothermic reforming reaction. The combustion of refinery fuel gas results in 5.8 t/h of CO_2. Thus the total CO_2 emitted in the furnace exhaust is the sum of these two sources with a concentration of 17.7 vol% (26.7 wt%).

Table 15. Emission sources selected for capture in refinery Base Case 3.

		CO_2 [t/h] @ operating point	% of total CO_2 emissions	CO_2 %vol	CO_2 %wt	Flue gas [t/h] @ operating point
C1	POW	28.0	28.6%	4.9	7.6	364.9
		51.3		8.1	12.9	397.0
C2	FCC	53.1	19.1%	16.6	24.6	225.4
C3	CDU-B/VDU-B	34.2	12.3%	11.3	17.2	199.2
C4	CDU-A	23.8	8.5%	11.3	17.2	138.6
C5	SMR	5.8	11.3%	17.7	26.7	108.8
		25.5				

Based on the emission sources listed in Table 15, three CO_2 capture cases were defined for Base Case 3. The capture cases selected in Base Case 3 are similar to that of Base Case 2. This will help identify the effect of the complexity of the refinery on the cost of CO_2 capture.

Table 16. The three selected capture cases for refinery Base Case 3. Refer to Table 15 for definition of emission sources C1-C5.

		CO_2 emissions [t/h] @ operating point	% of total CO_2 emissions	Avg CO_2 vol%
03-01	C1	79.3	28.6%	6.6
03-02	C1+C2	132.4	47.7%	8.7
03-03	C1+C2+C3+C4+C5	221.7	79.8%	10.0

The refinery Base Case 3 without CO_2 capture is self-sustained with power. To cover the additional power consumption caused by the CO_2 capture and compression, an additional natural gas-fired CHP plant is included (see appendix B). CO_2 is not captured from this CHP plant in the present study.

6.2 Results

Key results from the CO_2 capture simulations, with capture of 90% of CO_2 from selected emission sources are presented below. All simulations and results presented are for the refinery operating point. Further results from the simulations, as well as process flow diagrams can be found in Appendix A. Results are presented without utilities unless specified otherwise.

6.2.1 Specific utilities consumption

A summary of the specific utilities consumption for the capture plant at the operating point is provided in Table 17. Further details can be found in appendix A. Note that the specific electricity and cooling water demands provided in appendix A are per process unit, i.e. per absorber, stripper and for the compression unit, whereas the total numbers are provided below. The CO_2 avoided for all capture cases is lower than the CO_2 captured, due to the additional CO_2 emissions from the utilities CHP plant (see appendix B).

Table 17. Specific utilities consumption for Base Case 3 capture cases.

	03-01	03-02	03-03
CO_2 captured [t/hr][1]	71.5	119.6	199.6
Net CO_2 avoided [t/hr][2]	47.1	79.0	132.9
Specific reboiler duty [GJ / t CO_2 captured]	3.74	3.69	3.67
Electricity demand [kWh / t CO_2 captured]	159.1	149.0	144.7
Cooling water demand [t / t CO_2 captured]	96.5	93.1	92.3
Makeup of water [t / t CO_2 captured]	0.80	0.98	1.00

[1]Excluding dissolved water in CO_2 stream. [2]Including CO_2 emissions from utilities CHP plant.

6.2.2 Steam consumption

The very small variation in specific reboiler steam consumption gives a linear correlation between the amount of steam consumed and the amount of CO_2 captured, as can be seen in Figure 16. It should be recalled that the heat released from condensing steam varies with varying condensation temperature and pressure, i.e. Figure 16 is valid for steam condensing at 147.7°C (a temperature approach of 20°C was selected in the CO_2 capture process simulations).
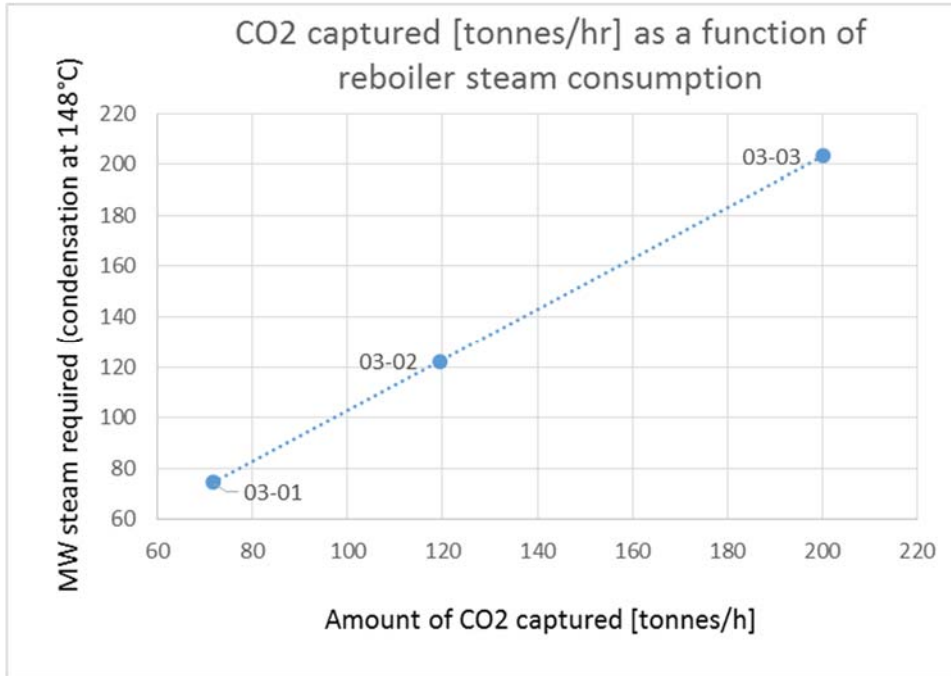
Figure 16. Amount of CO₂ captured as function of the amount of condensing steam for Base Case 3 capture cases.

6.2.3 Makeup water consumption

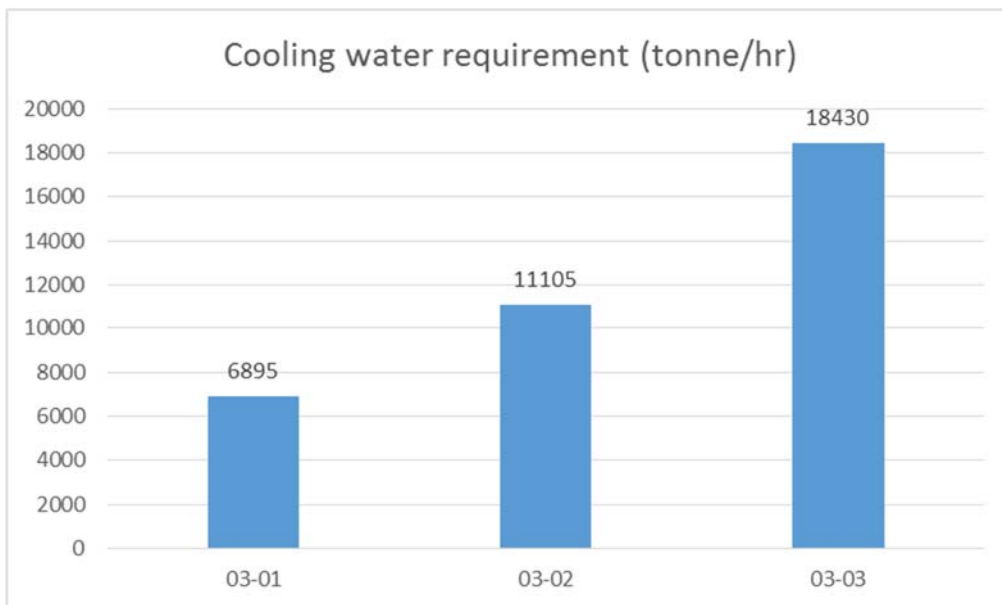The total makeup water consumption for each case can be seen in Figure 17.
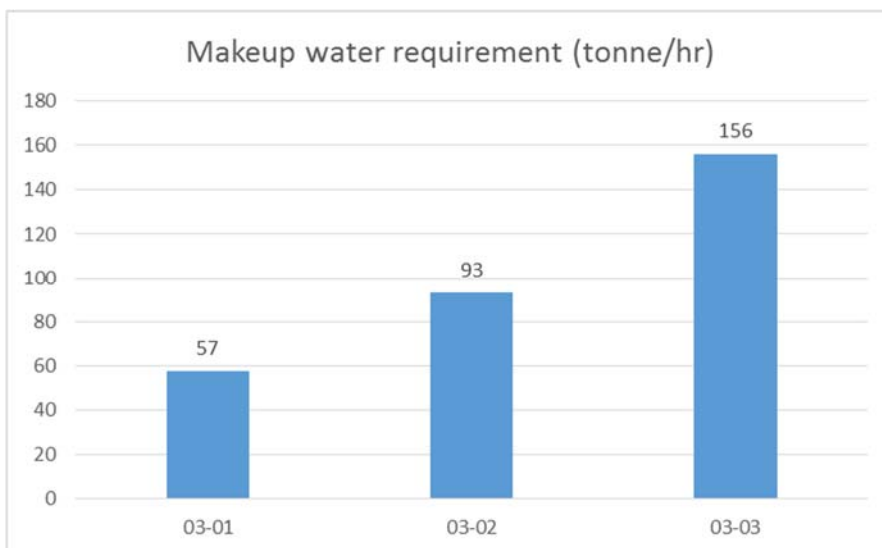
Figure 17. Makeup water consumption for the capture cases in Base Case 3.

6.2.4 Cooling water requirement

The cooling water consumption of the CO_2 capture plant can be seen in **Figure 18**. In comparison, the cooling water consumption of the refinery Base Case 3 without CO_2 capture is 28362 tonnes/hr (refer to table 7-6 in report *Performance analysis – Refinery reference plants*). This means that the required cooling water for CO_2 capture will increase the cooling water consumption with 24-65%, depending on the capture case.

Figure 18. Cooling water requirement for the capture cases in Base Case 3.

6.2.5 Electric power consumption

The electric power consumption caused by the CO_2 capture can be seen in Figure 19. As can be seen, the main power consumers are CO_2 compression and flue gas fans, whereas the power consumption for the CO_2 pump and chiller is of smaller significance. In comparison, the power consumption for the refinery Base Case 3 without CO_2 capture is 68.6 MW (refer to table 7-6 in report *Performance analysis – Refinery reference plants*). This means that the power consumption increases with 17-42% depending on the capture case.
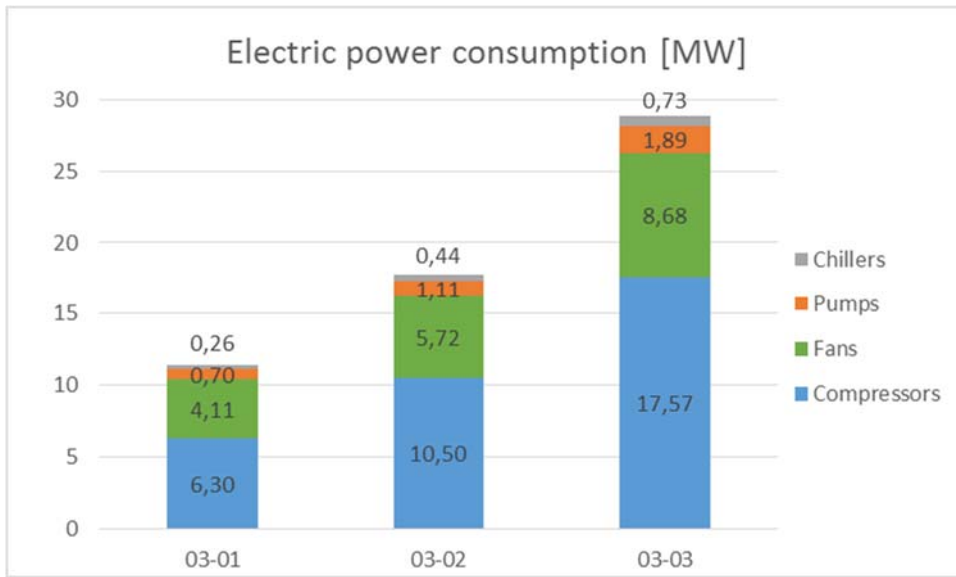
Figure 19. Electric power consumption for the capture cases in Base Case 3.

6.2.6 CO₂ avoided

As mentioned above, it has been assumed in this report that an additional natural gas-fired CHP plant is constructed on the refinery site to respond to increased steam and power requirements. CO_2 capture from this CHP plant has not been included in the study. Hence, although the CO_2 capture from the stacks in the investigated cases is 90%, the net CO_2 avoided from these emission sources is lower. This is illustrated in Figure 20.
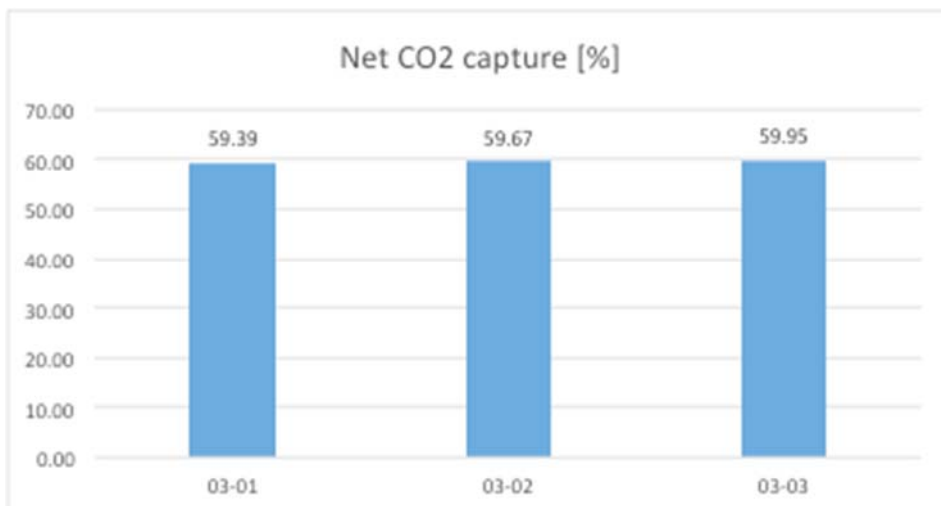
Figure 20. CO₂ avoided in % for the different capture cases for Base Case 3.

7 Base Case 4

It should be noted that all results provided for CO_2 capture from this and the other Base Cases in this report are for the refinery *operating point*, as determined in the report *Performance analysis – Refinery reference plants*. Sizing and costing in the subsequent report *Cost estimation and economic evaluation of CO_2 capture options* is done for the *design point*.

7.1 Capture case descriptions

The five largest emission sources in the refinery Base Case 4, the power plant (D1), the fluid catalytic cracking unit (D2), the crude and vaccum distillation units trains A&B (D3 and D4 respectively) and steam methane reforming unit (D5), were selected as candidates for CO_2 capture (see Table 18). The emissions from the fluid catalytic cracking unit (D2) come from burning coke desposited on the catalysts in the cracking process and regenration of the deactivated catalyst. The emissions from the crude and vacuum distillation units A & B (D3 and D4) come from fuel oil combustion in the fired heater related to the process. The power plant (D1) has two emission sources as shown in Table 18. The first, and larger, emission source is the natural gas combined cycle (NGCC) plant where natural gas is burnt in the gas turbine combustor and refinery fuel gas used for supplementary firing in the heat recovery steam generator. The second power plant emission source is the gas boiler power unit that burns refinery fuel gas. The flue gas from the NGCC power plant is not combined with that from the boiler due to control constraints. The steam methane reformer (D5) converts natural gas to syngas that mainly contains hydrogen and carbon dioxide. The syngas stream contains 97.5 t/h of CO_2 as shown in Table 18 with a concentration of 24.2 vol% (35.2 wt%). H_2 is separated from CO_2 in a PSA and the resulting tail gas that mainly contains CO_2, some H_2 and unreacted methane are sent to the furnace as supplementary fuel. Refinery fuel gas is used as the primary fuel in the furnace to provide heat to the endothermic reforming reaction. The combustion of refinery fuel gas results in 19.8 t/h of CO_2. Thus the total CO_2 emitted in the furnace exhaust is the sum of these two sources with a concentration of 17.7 vol% (26.7 wt%).

Table 18: Emission sources selected for capture in refinery Base Case 4.

		CO_2 [t/h] @ operating point	% of total CO_2 emissions	CO_2 %vol	CO_2 %wt	Flue gas [t/h] @ operating point
D1	POW[1]	76.0	20.9%	4.23	6.6	1160.5
		21.4		8.1	12.9	165.5
D2	FCC	53.1	11.4%	16.6	24.6	215.9
D3	CDU-A/VDU-A	49.2	10.5%	11.3	17.2	286.5
D4	CDU-B/VDU-B	49.2	10.5%	11.3	17.2	286.5
D5	SMR	19.8	25.1%	17.7	26.7	438.6
		97.5				

[1]Reference should be made to section 1.1.4 in report *Performance analysis – Refinery reference plants* for explanation of abbreviations POW, FCC, CDU, VDU, SMR.

Based on the emission sources in Table 18, six post-combustion capture cases were defined for refinery Base Case 4. The first three cases selected were 04-01 to 04-03 that cover a wide range of capture ratios as seen in Table 19. Case 04-04 was thereafter added to compare CO_2 capture from end-of-pipe flue gases and capture from synthesis gas stream in an SMR. The SMR and the FCC are relatively small emission sources – they each represent less than 15% of the total Base Case 4 CO_2 emissions (but still emit more than 0.4 Mtonnes CO_2/y). Therefore, Cases 04-05 and 04-06 are included to investigate the addition of the SMR and FCC

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emission sources to the larger sources (D1-POW and D3/D4-CDU/VDU A&B). This enables identifying the effect of adding a relatively small emission source. Note that there is a common regenerator/stripper for all the capture cases. From an energy penalty perspective, the increase in energy consumption is rather linear in terms of GJ/tonne CO_2 as can be seen in the results section below, whereas the results from an economy of scale perspective are not obvious but need further investigation (see report *Economic evaluation of CO_2 capture options*).

Table 19: The six selected capture cases for refinery Base Case 4. Refer to Table 18 for definition of emission sources D1-D5.

		CO_2 emissions [t/h] @ operating point	% of total CO_2 emissions	Avg CO_2 vol%
04-01	D1	97.4	20.9	4.7
04-02	D1+D3+D4	195.8	42.0	6.7
04-03	D1+D2+D3+D4+D5	366.2	78.5	9.4
04-04	D5	117.3	25.1	17.7
04-05	D1+D3+D4+D5	313.1	67.1	8.7
04-06	D1+D2+D3+D4	248.9	53.3	7.7

The refinery Base Case 4 without CO_2 capture is self-sustained with power. To cover the additional power consumption caused by the CO_2 capture and compression, an additional natural gas-fired CHP plant is included (see appendix B). CO_2 is not captured from this CHP plant in the present study.

7.2 Results

Key results from the CO_2 capture simulations, with capture of 90% of CO_2 from selected emission sources are presented below. All simulations and results presented are for the refinery operating point. Further results from the simulations, as well as process flow diagrams can be found in Appendix A. Results are presented without utilities unless specified otherwise.

7.2.1 Specific utilities consumption

A summary of the specific utilities consumption for the capture plant at the operating point is provided in Table 20. Further details can be found in appendix A. Note that the specific electricity and cooling water demands provided in appendix A are per process unit, i.e. per absorber, stripper and for the compression unit, whereas the total numbers are provided below. The CO_2 avoided for all capture cases is lower than the CO_2 captured, due to the additional CO_2 emissions from the utilities CHP plant (see appendix B).

Table 20. Specific utilities consumption for Base Case 4 capture cases.

	04-01	04-02	04-03	04-04	04-05	04-06
CO_2 captured [t/hr][1]	87.7	176.0	329.7	105.5	282.0	223.8
Net CO_2 avoided [t/hr][2]	57.2	116.1	219.9	71.4	188.0	148.0
Specific reboiler duty [GJ / t CO_2 captured]	3.85	3.76	3.68	3.57	3.69	3.72
Electricity demand [kWh / t CO_2 captured]	182.7	164.2	146.5	122.2	148.6	157.6
Cooling water demand [t / t CO_2 captured]	84.6	87.0	84.8	77.3	84.1	87.3
Makeup of water [t / t CO_2 captured]	0.80	0.99	0.95	0.73	0.89	1.00

[1]Excluding dissolved water in CO_2 stream. [2]Including CO_2 emissions from utilities CHP plant.

7.2.2 Steam consumption

The relatively moderate variation in specific reboiler steam consumption gives a rather linear correlation between the amount of steam consumed and the amount of CO_2 captured, as can be seen in Figure 21. Case 04-04 has the lowest specific steam consumption, since CO_2 is only captured from the stream that has the highest CO_2 concentration. It should be recalled that the heat released from condensing steam varies with varying condensation temperature and pressure, i.e. Figure 21 is valid for steam condensing at 147.7°C (a temperature approach of 20°C was selected in the CO_2 capture process simulations).
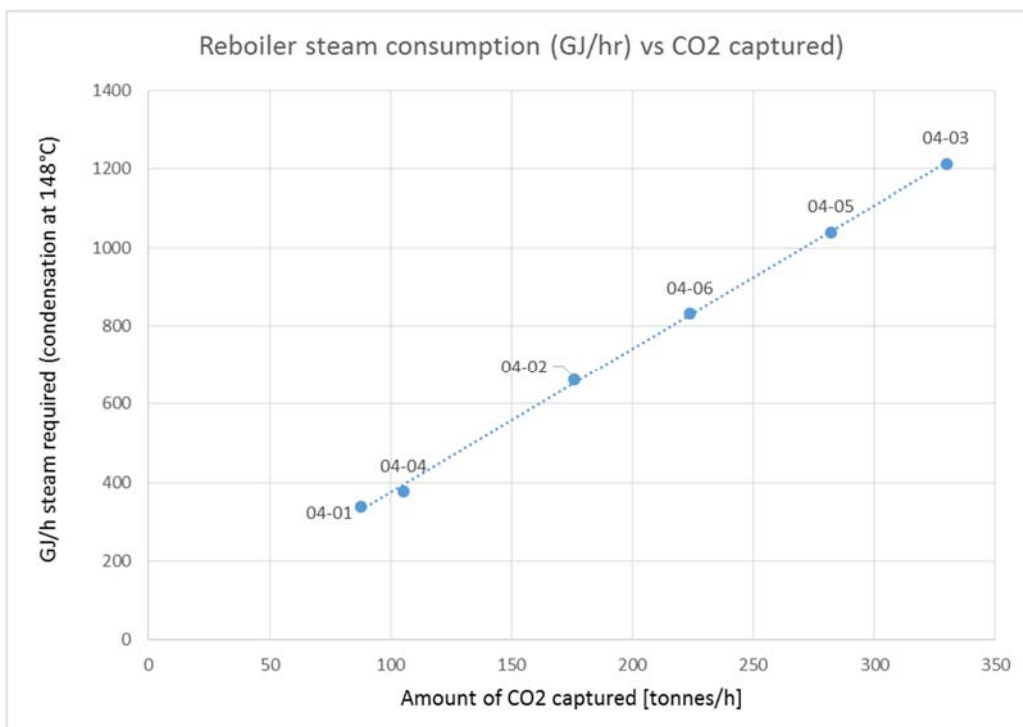
Figure 21. Amount of CO_2 captured as function of the amount of condensing steam for Base Case 4 capture cases.

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7.2.3 Makeup water consumption

The make-up water consumption for CO_2 capture unit in base case 4 can be seen in Figure 22. Please note that this is the make-up water for the capture unit only and does not include the utility section. The raw water requirement for the cases, which includes water for the utility section, varies from 282.6 t/h for Case 04-01 to 1107.5 t/h for Case 04-03. In comparison the raw water requirement for the Base Case 4 refinery is 2790 t/h.
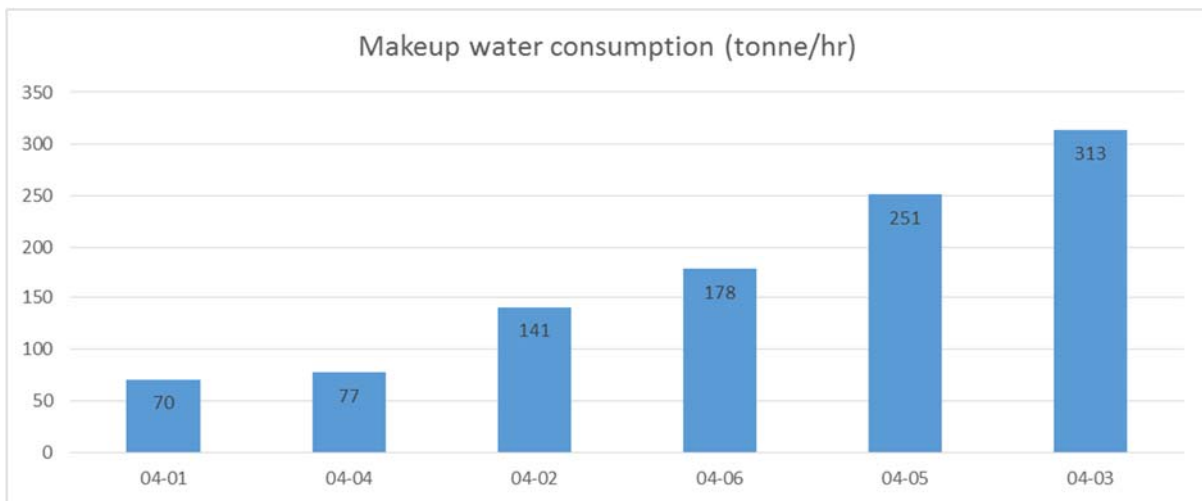
Figure 22. Makeup water consumption for the capture cases in Base Case 4.

### 7.2.4 Cooling water requirement

The cooling water consumption of the CO_2 capture plant can be seen in Figure 23. In comparison, the Cooling water consumption of the refinery Base Case 4 without CO_2 capture is 35364 tonnes/hr (refer to table 8-6 in report *Performance analysis – Refinery reference plants*). This means that the required cooling water for CO_2 capture will increase the cooling water consumption with 20-79%, depending on the capture case.

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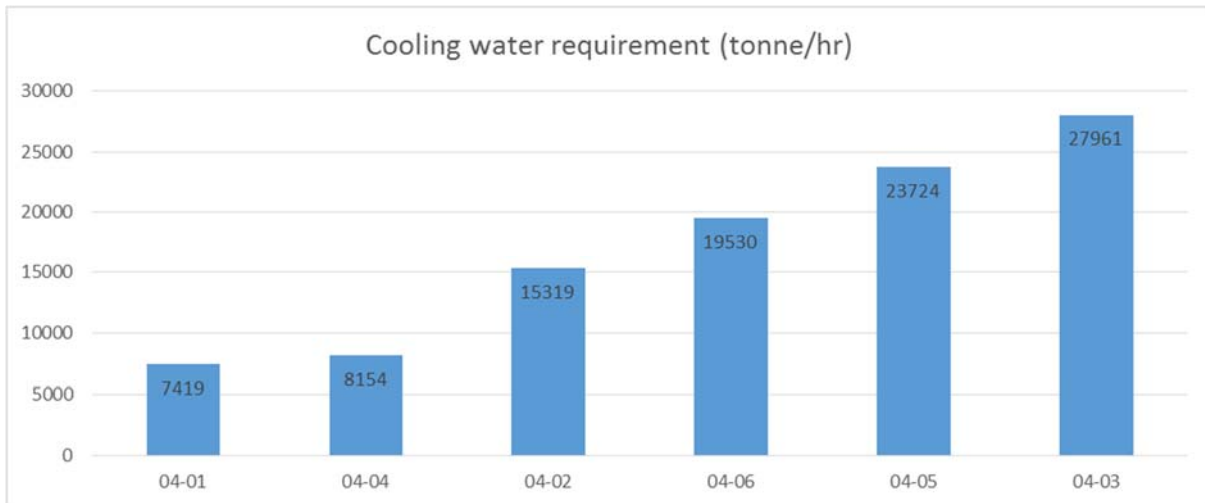
Figure 23. Cooling water requirement for the capture cases in Base Case 4.

### 7.2.5 Electric power consumption

The electric power consumption caused by the CO_2 capture can be seen in Figure 24. The refinery Base Case 4 without CO_2 capture is self-sustained with power. To cover the additional power consumption caused by the CO_2 capture and compression, an additional natural gas-fired power plant is included. As can be seen, the main power consumers are CO_2 compression and flue gas fans, whereas the power consumption for the CO_2 pump and chiller is of smaller significance. In comparison, the power consumption for the refinery Base Case 4 without CO_2 capture is 119 MW (refer to table 8-6 in report *Performance analysis – Refinery reference plants*). This means that the power consumption increases with 5-34% depending on the capture case.
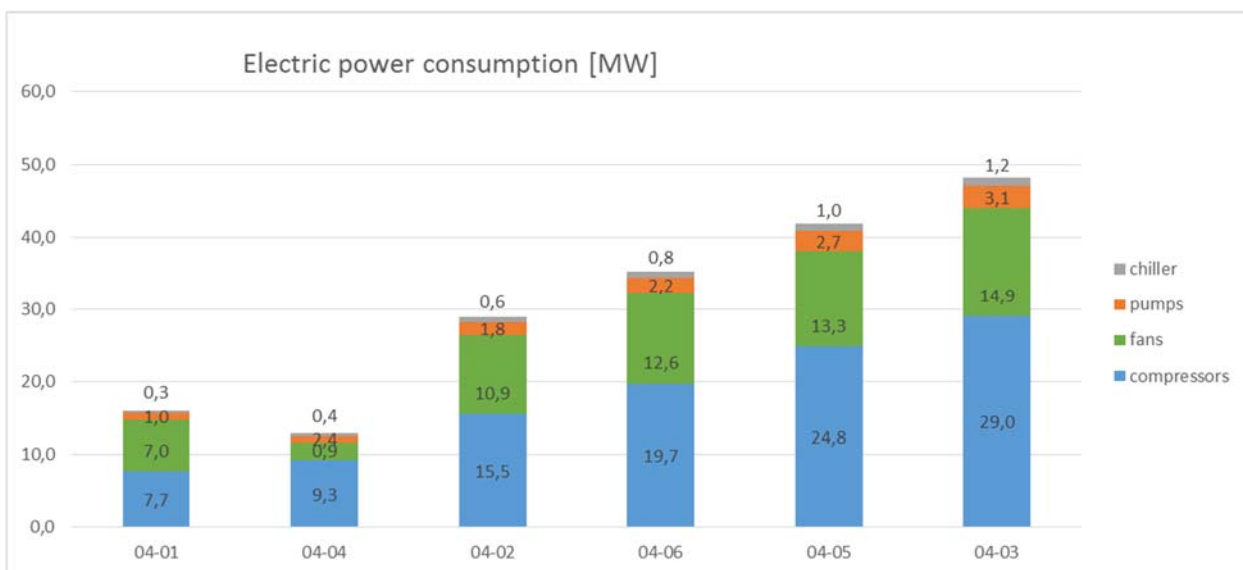
Figure 24. Electric power consumption for the capture cases in Base Case 4.

7.2.6 CO₂ avoided

As mentioned in section 1.1, it has been assumed in this report that an additional natural gas-fired CHP plant is constructed on the refinery site to respond to increased steam and power requirements. CO_2 capture from this CHP plant has not been included in the study. Hence, although the CO_2 capture from the stacks in the investigated cases is 90%, less CO_2 emissions to the atmosphere are avoided, since the additional energy required for CO_2 capture and compression will generate CO_2 emissions. The net CO_2 avoided in % for Base Case 4 capture cases can be seen in Figure 25. It can be seen that it is considerably lower than the CO_2 capture rate from the stacks, around 60%.
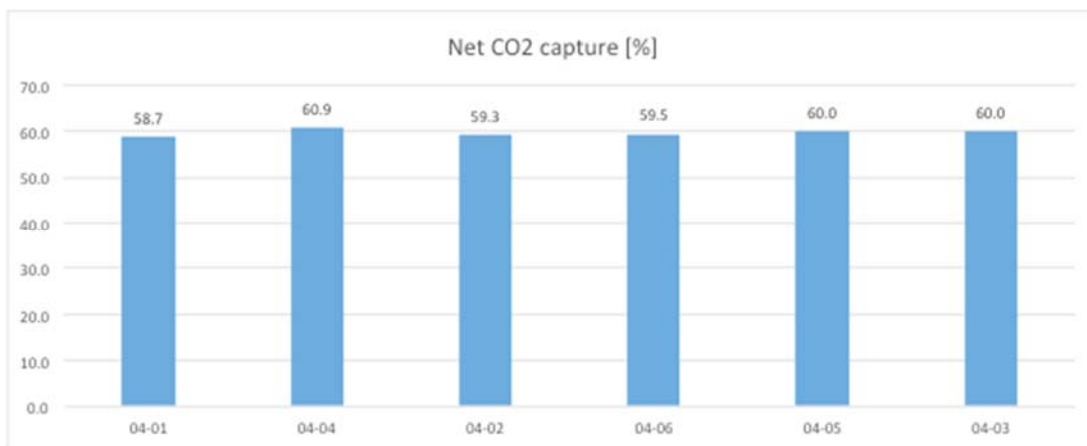
Figure 25. CO₂ avoided in % for the different capture cases for Base Case 4.

8 CO₂ capture from SMRs in refineries

IEAGHG has recently released a report[3] that evaluates steam methane reformer (SMR) for hydrogen production with CCS through a techno-economic analysis. The study evaluates the design, performance and cost of a "greenfield" state-of-the-art SMR plant producing 100,000 Nm^3/h of hydrogen using natural gas as feedstock and fuel. The work looked at different options for CO_2 capture within the H_2 plant with overall capture rate ranging between 50 and 90%. The different CO_2 capture cases considered are:

- Case 1A: SMR with CO_2 capture from shifted syngas using MDEA
- Case 1B: SMR with burners firing H_2 rich fuel and capture of CO_2 from the shifted syngas using MDEA
- Case 2A: SMR with CO_2 capture from PSA tailgas using MDEA
- Case 2B: SMR with CO_2 capture from PSA tail gas using cryogenic and membrane separation
- Case 03: SMR with capture of CO_2 from the flue has using MEA.

The cases of specific interest to this report are Cases 1A and Case 03 as they are the most "mature" options for capturing CO_2 from SMR process and have been demonstrated on industrial units. The performance parameters for these two cases compared with the base case SMR with no CO_2 capture are provided in the table below.

Table 21: Comparison of process performance of base case SMR with no CO₂ capture and two capture options[4]

	Base Case (no capture)	Case 1A	Case 3
Total energy input (as NG) [MWth]	394.77	407.68	433.72
Total energy in product (as H_2) [MWth]	299.70	299.70	299.70
Net power exported to grid [MWe]	9.918	1.492	0.426
Specific NG consumption [MJ/Nm³ H_2]	14.21	14.68	15.61
Specific CO₂ emissions [kg/Nm³ H_2]	0.8091	0.3704	0.0888
CO₂ capture rate [%]	-	55.7	90
CO₂ avoided [%]	-	54.2	89
SPECCA [MJ/kg CO₂]	-	2.44	2.90

Note that the SMR plant is a net exporter of power without CCS. The net power exported to the grid shown in Table 21 is from the hydrogen plant and not a separate combined heat and power plant.

It is clear from Table 21 that Case 3 where CO_2 is captured from flue gas at atmospheric conditions has a greater thermal energy input and lower net power output compared to Case 1A where CO_2 is captured from shifted syngas prior to H_2 purification in the PSA. However, Case 3 has a greater CO_2 capture rate and CO_2 avoided compared to Case 1A.

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[3] IEAGHG, Techno-Economic Evaluation of SMR Based Standalone (Merchant) Plant with CCS, 2017/02, February, 2017
[4] All data from IEAGHG extracted from the above IEAGHG report except SPECCA

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In order to compare these different capture routes the SPECCA (Specific Primary Energy Consumption for Equivalent CO_2 avoided) index can be used. The SPECCA index is defined as the increased fuel consumption to avoid the emission of CO_2 in the SMR plant with CO_2 capture with respect to the reference SMR without capture (ref). It is evaluated using the following equation:

$$SPECCA \left[\frac{MJ_{LHV}}{kg_{CO2}} \right] = \frac{q_{SMR} - q_{SMR,ref}}{e_{SMR,ref} - e_{SMR}}$$

where q_{SMR} and $q_{SMR,ref}$ are the total thermal energy input to the SMR with CO_2 capture and the reference SMR without CO_2 capture respectively, and e_{SMR} and $e_{SMR,ref}$ are CO_2 emissions from SMR with CO_2 and SMR without CO_2 capture respectively.

SPECCA is calculated for Cases 1A and 3 and are reported in Table 21. To ensure a fair comparison, the reduction in power exported to the grid should also be taken into account. This lost power, in MWe, can be translated to fuel energy input, MWth, by assuming an efficiency for conversion. This efficiency is taken to be 60% and corresponds to the efficiency of a Natural Gas Combine Cycle for power production using an F class gas turbine. It can be seen from the SPECCA that Case 1A requires 2.44 MJ per kg of CO_2 avaoided compared to Case 3 that requires 2.90 MJ per kg of CO_2 avoided. It is clear from an energy perspective Case 1A is a more efficient route for capturing CO_2 in an SMR compared to Case 3.

The post-combustion capture from SMR is evaluated as Case 04-04 in this work. This is equivalent to Case 3 of the IEAGHG report. The performance of SMR with no CO_2 capture and post-combustion capture evaluated in this work is presented in Table 22 . The performance data show that while the base case SMR without capture has similar performance to the IEAGHG case, the post-combustion capture in this work has significantly worse performance.

There are a couple of reasons for this. The IEAGHG study uses an advanced split flow configuration for CO_2 capture compared to the simple configuration used in this study. This contributes to a larger energy requirement for CO_2 capture. Further, the utilities power consumption in the post-combustion capture case in this work is much larger than the IEAGHG case.

Another important reason for the difference is that, in the IEAGHG study, the hydrogen plant is a stand-alone merchant type unit that also exports power by expanding steam generated in the process. When post-combustion CO_2 capture is added to this plant, it is able to satisfy the steam and work requirements for the CO_2 capture process by reducing the net power exported. However, in this work, the steam generated by the SMR is used to satisfy refinery process requirements. As it is tightly integrated with the refinery, it does not produce any power. A separate NG boiler based CHP plant is required to satisfy the steam and work requirements for CO_2 capture. There is no CO_2 capture done on this CHP plant. Thus, although 90.2% of CO_2 is captured from the SMR, the CO_2 avoided is only 60.9% and thus has a higher specific CO_2 emissions compared to the IEAGHG case. This results in the significantly higher SPECCA for the post-combustion capture case in this work compared to the IEAGHG study.

The CO_2 capture from syngas case was not evaluated in this work. It is expected that the results would be higher than those evaluated in the IEAGHG study, given the constraints and assumptions in this work as discussed above. However, CO_2 capture from syngas is expected to perform better than post-combustion capture.

Table 22: Performance of SMR with no CO$_2$ capture and post-combustion capture evaluated as Case 04-04.

	Base Case (no capture)	Post-combustion capture Case 04-04
Total energy input (as NG) [MWth]	570.17	735.914
Total energy in product (as H$_2$) [MWth]	343.7	343.7
Net power exported to grid [MWe]	99.8	99.8
Specific NG consumption [MJ/Nm^3 H$_2$]	13.72	17.71
Specific CO$_2$ emissions [kg/Nm^3 H$_2$]	0.78	0.31
CO$_2$ capture rate [%]	-	90.2
CO$_2$ avoided [%]	-	60.9
SPECCA [MJ/kg CO$_2$]	-	8.50

9 Literature review of Oxy-combustion capture from FCCs in refineries

The fluid catalytic cracking (FCC) unit is responsible for 20-30% of total CO_2 emissions from a typical refinery (de Mello et al., 2013). Oxy-combustion, as one of the three well-known methods for CO_2 capture (i.e. post-, pre- and oxy-combustion), also enables the concentration and capture of CO_2 in the flue gas from FCC units. In an oxy-FCC process, pure O_2 is used instead of air for the burning of coke in the regeneration process of spent catalyst. As a result, dilution of CO_2 with N_2 is avoided.

A typical air fired FCC unit is shown in Figure 26(a). The oil feed is converted into the desired products with the help of catalyst in the riser reactor. Coke is an undesired by-product that is accumulated on the surface of the catalyst. As a result, the catalyst gets less active and needs to be regenerated. The coke on the spent catalyst is burned with air in the regenerator and CO_2 is thus produced. The CO_2 fraction is around 10-20 vol.% in the flue gas of the regenerator (de Mello et al., 2013). The CO_2 can be concentrated in the oxy-combustion case, as shown in Figure 26(b). An air separation unit is used to remove the N_2 from the O_2 prior to combustion. As a result, the CO_2 is concentrated in the flue gas due to the absence of N_2. A portion of the flue gas (known as Recycled Flue Gas- RFG), containing mainly CO_2 and H_2O, is recycled to the regenerator for temperature control. The CO_2 has a larger heat capacity than the N_2. The heat transfer characteristics and heat balance are thus different compared to the air-fired case.
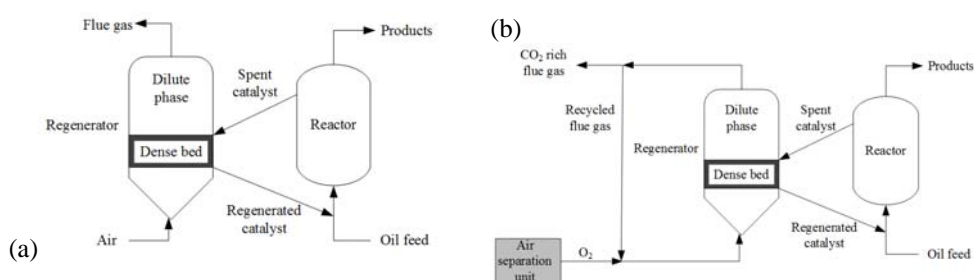
Figure 26. The FCC units: (a) the air fired case, (b) the oxy-combustion case

A pilot scale demonstration of the oxy-FCC process was performed in the CO_2 Capture Project - CCP (de Mello et al., 2013). The test shows that it is technically feasible to operate an oxy-FCC unit. The CO_2 can be concentrated to 95 vol.%. Two operating modes were tested in the pilot scale plant: the "same heat" mode (the same regenerator temperature as in the air fired case) and the "same inert" mode (the same volumetric flow of inerts as in the air fired case). Detailed testing results are presented in Table 23. The product yields and conversion rate in the "same heat" mode are very similar to the values obtained in the air-fired base case. A higher conversion rate (+3.4%) has been achieved when the "same inert" mode is used. The reason is that the regenerator temperature is lower (689 vs. 710 ^oC) due to a larger heat capacity of CO_2 compared to N_2. As a result, larger catalyst to oil ratio (7.9 vs. 6.7) should be used in order to maintain the reactor temperature. The conversion rate thus increases.

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Table 23. Main results from the pilot testing of the oxy-FCC processes (de Mello et al., 2013[5])

Testing mode	Air-fired base case	Oxy-fired same heat	Oxy-fired same inert
Reaction temperature, ^{o}C	540	540	540
Feed temperature, ^{o}C	350	349	348
Feed flow, kg/h	150	150	150
Catalyst to oil ratio (CTO)	6.7	6.8	7.9
Yields (mass basis), wt%		(% change relative to air-fired case)	
Dry gas	-	-1.9	-1.6
LPG	-	2.8	6.7
Gasoline	-	-0.8	2.4
Gasoline+LPG	-	0.1	3.4
LCO+Bottoms	-	-	-
Coke	-	0.8	9.0
Conversion	-	1.0	4.9
Regenerator dense phase temperature, ^{o}C	710	709	689
Air/oxidant temperature, ^{o}C	249	249	251
Excess O_2 in flue gas, mol%	2.7	2.6	2.5
%O_2 in oxidant gas, mol%	21	28.9	23.8
Inert flow rate, m^3/h	123	87	117
Flue gas composition, mol% (dry)			
CO_2	14.2	94.3	94.8
O_2	2.7	2.6	2.5
N_2	83.1	3.1	2.5
CO	0.00	0.06	0.11

[5] de Mello, L.F., Gobbo, R., Moure, G.T., Miracca, I., 2013. Oxy-combustion Technology Development for Fluid Catalytic Crackers (FCC) – Large Pilot Scale Demonstration. Energy Procedia 37, 7815–7824.

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A CO₂ capture process summary, stream data and PFDs

Separate document available at http://www.sintef.no/RECAP

B CO₂ capture integration and utilities

Separate document available at http://www.sintef.no/RECAP