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Demonstrating a Refinery-adapted cluster-integrated strategy
to enable full-chain CCUS implementation - REALISE

D 3.2. Integration of CO_2 capture plant in refineries

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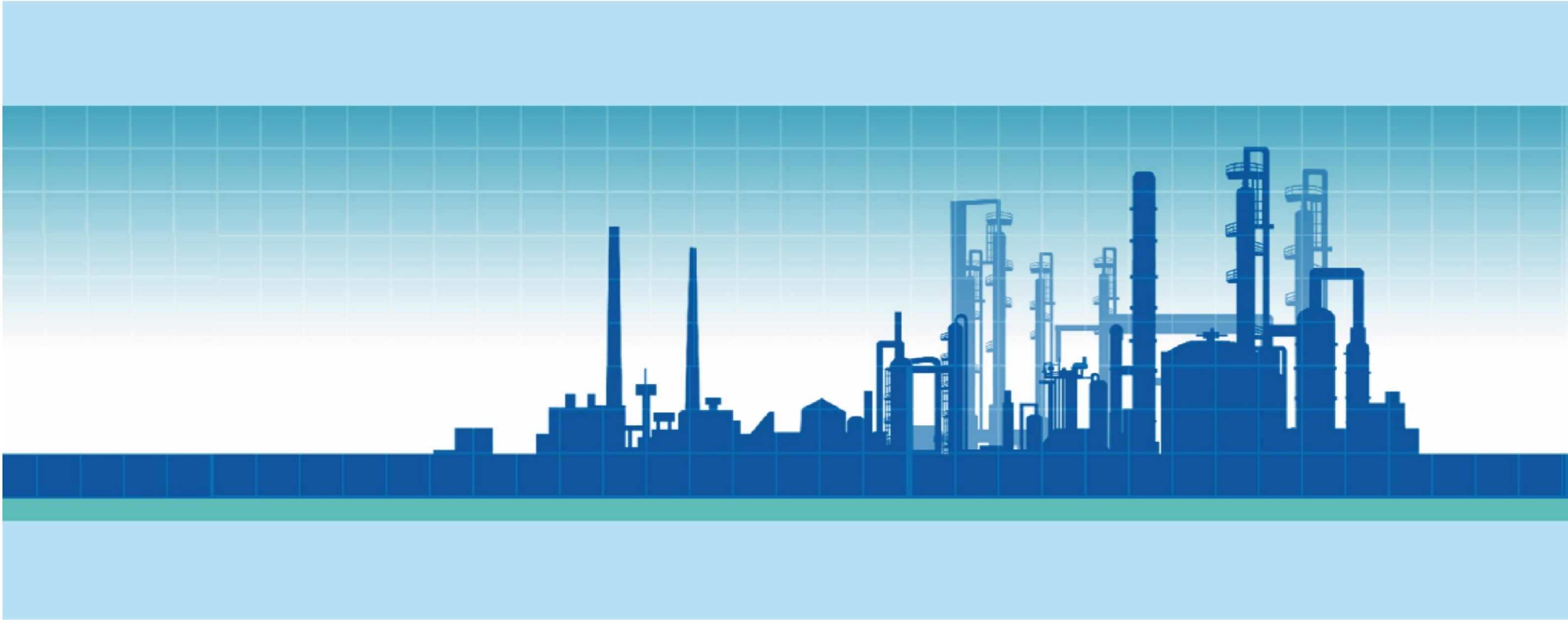

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Document History

Revision History

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Authorisation

This document requires the following approvals:

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Disclaimer

Executive summary

This report aims at illustrating the procedure followed for the design and optimization of a CO_2 capture plant for the treatment of the fluegas generated at Irving Oil Whitegatel Refinery (Cork, Ireland) and possible energy and gas treatment integrations with two power plants located at short distance from the refinery site, namely the ESB Aghada NGCC and the BGE Whitegate power stations.

More specifically, this work deals with:

- A preliminary assessment for the feasibility of CO2 capture from the mentioned oil refinery according to the impurity content in the stacks to be treated.
- The definition of the most reasonable layout for the plant design; more specifically, both a single absorber and a double-absorber configuration are proposed and qualitatively compared consideing MEA 30 wt% as reference solvent.
- The simulation and optimization of a multiple-stack CO_2 capture plant for the treatment of flue gas generated by the Irving Oil Whitegate refinery. The comprehensive Aspen Plus VLE model for the HS3 solvent disclosed in deliverable D1.3 (WP1) is exploited as modelling tool. MEA 30 wt% is selected as benchmark solvent for comparative purposes. To this aim, the same plant simulations have been carried out also using default AspenTech model for MEA 30 wt%.
- A discussion on specific strategies for heat recovery within the plant in order to minimize the duty (steam) to be provided by an external heat source. Since internal heat recovery can only part of the steam required for solvent regeneration, the residual steam is supposed to be generated on-site by means of a natural gas fed boiler.
- A sensitivity analysis for the optimization of process operating conditions such as the lean loading, the stripper pressure and the columns’ packing heights.
- The sizing of the main unit operations in the plant flowsheet as well as the estimation of steam, electricity and cooling water requirements.
- A discussion on strategies for energy integration between the refinery and two power plants located at short distance. To this aim, the capture plant is simulated again considering that the power plant provides the required missing steam for the reboiler of the solvent regeneration tower. In this way, there is no need for extra flue gas treatment, thus both the total gas and solvent circulating flows will be lower at the expense of a reduction in the power plant electricity output efficiency that needs to be assessed.
- The comparison between the performances of HS3 with respect to the benchmark MEA solvent in terms of equipment sizing, energy requirements and other key performnace indicators (KPIs) in all the analyzed case-studies.
- In the last section, the possibility of a fluegas treatment integration in addition to the already assessed steam integration between the oil refinery and one of the power plants is investigated. Different process schemes are proposed. Advantages and disadvantages of the available options are discussed based on simulation results.

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1 CO_2 capture from Irving Oil Whitegate refinery

1.1 Introduction

This report describes the testing of the Aspen Plus® VLE model developed and validated in WP1 on a large-scale application to test its reliability for the industrial scale-up purposes of interest for the project. Before getting into the details of the modelling, it is worth introducing the context of CO_2 capture from refineries.

Oil refineries are included in the range of the most attractive CO_2 sources for carbon capture due to their relevant impact in terms of global greenhouse gas emissions, which are reported by (Lei et al., 2021) and (Ma et al., 2022) to be close to 4% of the annual worldwide carbon emissions.

The peculiarity of this carbon capture application is the fact that refineries are complex plants, with several CO_2 emitters. In particular, the main emission sources in large conversion refineries can be classified as follows (Sunny et al., 2022):

- the power station (≈30% of total emissions);
- fluid catalytic cracking unit (≈20%);
- topping column for atmospheric oil distillation (≈20%)
- steam methane reformer for hydrogen production (≈10%)
- heaters, boilers, and gas turbines are also powered by fuel (i.e. oil, natural gas). These sources are generally small emitters singularly, but they may emit large quantities of CO_2 altogether.

This complexity leads to the generation of CO_2 sources with high variation in their CO_2 concentration. In turn, this results in a different carbon capture efficiency, being the most concentrated streams the ones who guarantee the highest capture efficiency. Based on these considerations, two main strategies should be adopted to select which streams are worth conveying to the capture plant. First, only streams responsible for an appreciable percentage of the global refinery emissions should be considered: to this aim, in this work a threshold of 2 vol% contribution to the total emissions has been chosen as a threshold value. Secondly, it is worth prioritizing the streams with the highest CO_2 concentration for the sake of minimizing the energy consumption per unit of captured CO_2. The possibility to split the stacks into two separated absorption units, one dealing with the most concentrated streams providing a higher capture rate and another plant treating to a lower extent the low-concentrated stacks is also discussed for a preliminary qualitative choice on the most effective process configuration to be adopted.

The content of this chapter can be summarized as follows: the first sections describe the Irving Oil Whitegate refinery, the characterization of its flue gas stacks, the reasons for the choice on single or split capture plant and a specific configuration proposed as preliminary heat recovery to minimize the requirement for extra-steam generation. The following paragraphs are focused on the development of a dedicated flowsheet for the proposed application and a sensitivity analysis to optimize some key operating parameters. Finally, the last section includes the simulation results and a preliminary estimation of the energy requirements. For the sake of comparison, the same process is simulated under consistent conditions using both HS3 solvent and MEA 30wt%, which is chosen as reference benchmark for comparative techno-economic assessment.

1.2 The Irving Oil Whitegate refinery

Irving Oil is a privately owned, Canadian energy company founded in 1924 with a history of long-term partnerships and relationships. In 2016, Irving Oil expanded operations to Ireland at the Whitegate Refinery, situated on a scenic 330-acre site on the outskirts of Whitegate village. Since opening in 1959, the Whitegate Refinery has played a critical role in Ireland's energy infrastructure. With a capacity of 75,000 barrels a day, Whitegate is Ireland's sole refinery, serving commercial and wholesale customers.

1.2.1 Refinery flue gas characterization

Ten continuous flow flue gas streams characterized by different CO_2 content, temperature and flowrate are generated at the Irving Oil Whitegate refinery site (Deliverable D2.1) Discontinuous flows are disregarded in this analysis. For simplicity, each stack is assumed to contain only of CO_2, H_2O, O_2 and N_2, while impurities such as NO_x and SO_x are present is small amounts and can be neglected for the purpose of this study (please see the next section for more details on a preliminary feasibility study). The average flue gas composition monitored at the Irving Oil site is listed in Table 1**Errore. L'origine riferimento non è stata trovata.**. Being only the CO_2 content known precisely for each stack, molar fractions of the other three components have been rescaled starting from the average composition data reported in the refinery site documentation.

Table 1. Average Irving Oil Refinery flue gas composition (REALISE project documentation).

Component	Mole content [%]
CO_2	8
H_2O	14
N_2	74
O_2	4

The average CO_2 concentration is ranging from 6 to 10 mol%, thus intermediate with respect to the typical CO_2 content of a natural-gas fired power plant (close to 4 mol%) and a coal-fired power plant (10-12 mol%).

1.3 Effect of impurities on capture plant feasibility

According to the documentation released by Irving Oil Whitegate Refinery in deliverable D2.1 of the REALISE project concerning the characterization of the refinery flue gas stacks, quantitative information on NO_x and SO_x impurity content is available for the eight stacks to be treated in the CO_2 capture plant The NO_x content ranges from a minimum of 83 mg/Nm^3 to a maximum of 190.6 mg/Nm^3 (corresponding to 134 ppmv), while the SO_x content is between 5.1 and 32.5 mg/Nm^3 (corresponding to 14 ppmv). A preliminary feasibility study is carried out to investigate potential issues arising from the presence of the mentioned impurities in the flue gas to be treated.

In general. the presence of NO_x. SO_2. HF. HCl e O_2 in the *flue gas* can potentially affect amine-based CO_2 capture processes because these compounds are known as agents responsible for increased degradation and corrosion. Thus, the higher is the concentration of the mentioned compounds, the higher is the degradation observed in the reactive system. Amine degradation is un undesired phenomenon to be limited to the lowest possible extent due to the following main reasons:

- the CO_2 uptake performance decreases due to the formation of stable chemicals such as the *heat stable salts*, which circulate and continuously accumulate in the solvent flow;
- it leads to the formation of undesired and toxic volatile compounds;
- it enhances corrosion phenomena. leading to potential degradation of the process equipment (unit construction materials).

It is possible to distinguish between two main degradation paths: the thermal one, favoured by high temperatures, and the oxidative one, which is favoured by the presence of oxidising agents (i.e. O_2 and SO_2).

(Zhou et al., 2012) show that thermal degradation enhanced by the presence of acidic compounds such as SO_2 in the flue gas becomes relevant at temperatures higher than 130°C (see Figure 1), while the operating temperature of CO_2 capture process do not overcome 122-123°C (maximum process temperature at the bottom of the stripper considering both MEA and HS3 as solvents). Even if this study refers to MEA, a similar behaviour can be expected for the two amine constituents of HS3 blend. This consideration leads to the conclusion that further increasing the stripper pressure to reduce the process energy requirements would result in a significant increase in the thermal degradation potential, but, under the process conditions selected for the Irving Oil case-study presented in this work (see section 1.4), it is reasonable to disregard the thermal effect on solvent decomposition.

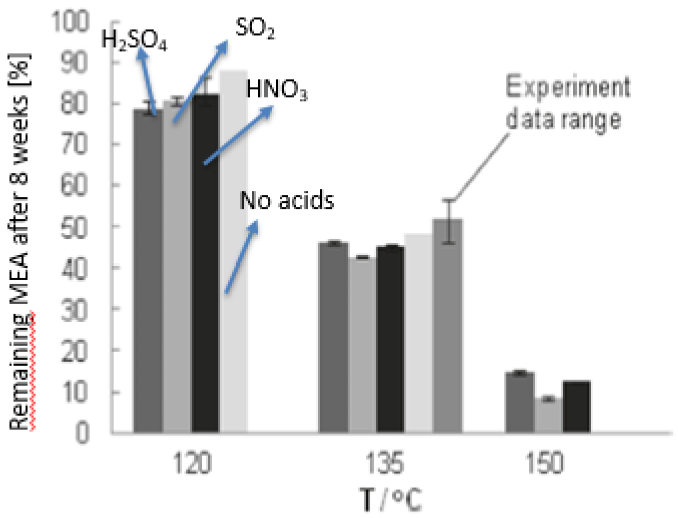


Figure 1. Effect of the presence of acidic compounds in the *flue gas* on MEA thermal degradation at 120°C. 135°C and 150°C (Zhou et al.. 2011).

The oxidative degradation path is instead more critical, being NO_x and SO_x responsible for the formation of toxic degradation products. More specifically, NO_2 enhances the formation of nitramines and nitrosamines, while SO_2 leads preferentially to the formation of sulfamates. The following paragraphs describe more in detail the potential issues arising from the presence of the concentrations of NOx and SO_x measured in the Irving refinery flue gas. respectively.

1.3.1 SO_x

A study by (Uyanga & Idem, 2007) estimated the impact of SO_2 content on MEA degradation (Figure 2) in a SO_2 concentration range in the *flue gas* between 6 and 196 ppm. The collected experimental data show that the observed degradation after at least 100 hours of plant operation cannot be disregarded when the SO_2 content overcomes the order of magnitude of ppm.

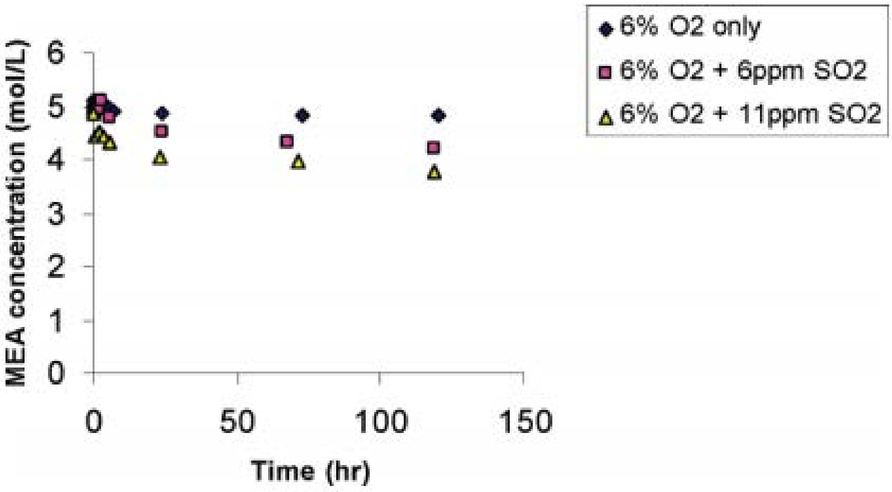


Figure 2. MEA concentration reduction in time due to oxidative degradation at variable SO_2 content in the flue gas to be treated (Uyanga & Idem, 2007).

Guidelines published by (Davison, 2007) report an order of magnitude threshold value of 10 ppm of SO_2 as limiting content above which a De-SO_x system should be installed for a preliminary flue gas treatment prior to carbon capture. This threshold value refers to an oxygen concentration in the flue gas of 6 vol%. Therefore, it can be assumed as a conservative value for the case-study discussed in this work, since the average flue gas oxygen concentration is in the order of 4 vol%, and a lower degradation extent is expected in presence of a lower oxygen volume fraction. None of the eight Irving Oil stacks presents a SO_x content above 15 ppm. Based on the abovementioned guidelines, no specific treatment for additional SO_x abatement is required for the Irving Oil Whitegate gas upstream carbon capture.

1.3.2 NO_x

NO_x may lead to the formation of nitramines and nitrosamines (Fostås et al., 2011). Even if the degradation reaction path is extremely complex and hundreds of components may form, nitrosediethanolamine is among the compounds forming in more significant amounts and can be considered a relevant example to describe the overall NO_x effect on degradation. Figure 3 shows that the formation of these degradation compounds increases with a direct second-order proportionality with the NO_x concentration.

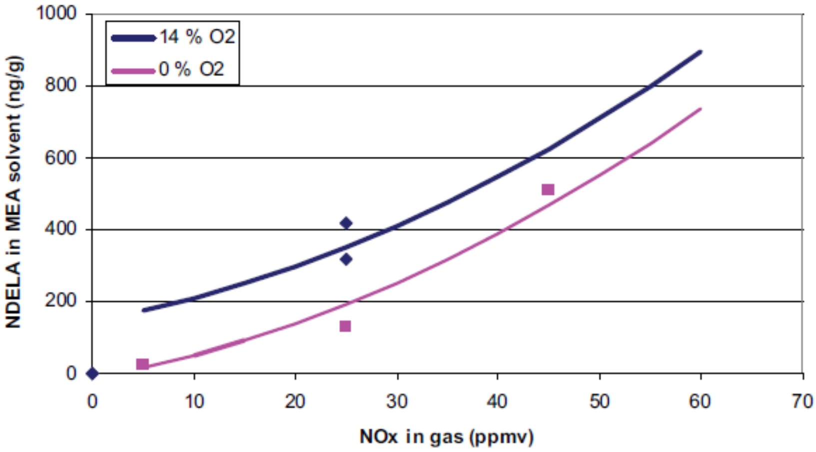


Figure 3. Nitrosediethanolamine (NDELA) formation (in ng/g) due to MEA degradation as a function of the NO_x content (in ppm) in the flue gas treated in a CO_2 capture plant (Fostås et al., 2011).

(Bosoaga et al., 2009) report a threshold value of 20 ppm of NOx at 6% oxygen concentration as a safe limit for a stream to be treated in a capture plant without a strong enhancement effect of corrosion and degradation phenomena. Even if Irving Oil flue gas is characterized by a lower oxygen concentration on average, the data reported in **Errore. L'origine riferimento non è stata trovata.** show that NO_x concentrations are one order of magnitude higher for the majority of the eight stacks. Therefore, an upstream NO_x abatement step (for example with SCR technology) is recommended, or in any case proper corrosion inhibitors must be considered. As for the HS3 solvent. amine degradation tests have already been carried out successfully within the REALISE project (refer to dedicated project deliverables): the collected data show that the degradation extent is comparable or slightly lower with respect to the observations collected for benchmark MEA. For these reasons, the guidelines reported for MEA can be considered a conservative criterion to be adopted also when operating with the HS3 solvent.

1.3.3 Conclusions of the feasibility study

Based on flue gas impurities concentration data measured at the Irving Oil site and considering the guidelines reported in the literature in terms of maximum recommended levels of acceptable SO_x and NO_x content. it is possible to state that SO_x content is not a concern, while potential issues may arise from the presence of stacks characterized by NO_x content, which is in the order of magnitude of 100 ppm. With the NOx content of the same order of magnitude for all stacks (from 75 to 133 ppmv), there is no particular reason for preventing some of the stacks from being treated in the capture plant due to a significantly higher impurity content. Therefore, the plant will be designed considering the treatment of all the eight stacks considered from the preliminary screening based on CO_2 concentration (see section 1.4).

Treating the Irving Oil stacks in an amine-based CO_2 capture plant is feasible provided that reliable corrosion inhibitors are used when running the plant. Due to the presence of significant NO_x contents, the solvent make-up flowrates could be higher with respect to the ones that must be provided in CO_2 capture plants currently in operation for the treatment of flue gases generated by power plants (lower NO_x content). If possible, further abatement of NO_x concentration by means of dedicated NO_x burners to be placed upstream the CO_2 capture plant is strongly recommended to reduce at the lowest possible extent any operating issue related to corrosion and degradation.

Due to lack of specific information to quantify degradation, the CO_2 capture plant designed for the Irving Oil case-study and described in the next secrtion does not take into account the effect of impurities. In other words, only the four main flue gas constituents (nitrogen, oxygen, water, and carbon dioxide) are considered for modelling in Aspen Plus®. It is remarkable that, apart from amine degradation, no other appreciable effects are associated with the flue gas impurities on the CO_2 capture plant performance.

1.4 Capture plant simulation: methods

1.4.1 Single versus multiple absorber design

The efficiency of amine-based carbon capture is known to depend on the CO_2 concentration in the gas flow to be treated. In particular, very poor removal efficiency and high costs per unit of removed CO_2 are expected for streams having a poor CO_2 concentration (i.e. air itself), while the energy requirements progressively lower at increasing concentrations (González Díaz et al., 2016). This concept can be exploited for a smart design of a multi-stack capture plant, like the one to be designed for the Irving Oil Whitegate refinery. In fact, it is possible to split the stacks into two separated absorption units, one dealing with the most concentrated streams (equal or higher than 8 mol%) providing a higher capture rate (i.e. 95%) and another plant treating to a lower extent (i.e. 85% capture) the low-concentrated stacks (<8 mol%). The CO_2-enriched solvent coming from the two absorbers can be then conveyed to a common stripper (REG), since the regeneration duty depends only on the total solvent flow to be regenerated. The single and the two-absorber configuration layout are conceptually reproduced in Figure 4.

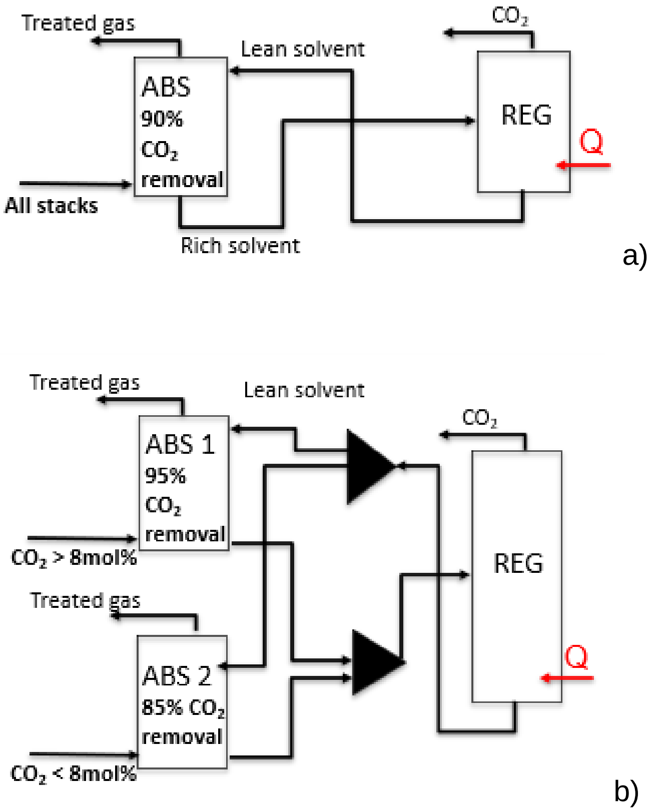


Figure 4. Conceptual design of a CO_2 capture plant for the treatment of the Irving oil refinery flue gas: single (a) versus split (b) plant configuration.

The two presented process schemes are qualitatively analysed by comparing the expected total CO_2 capture duty in the different scenarios with the benchmark solvent (MEA 30 wt%). A final selection on the best option is made considering a trade-off between the qualitatively estimated expected reduction in the energy requirements obtained by decoupling the streams and the corresponding increase in the investment costs due to the need to double or triplicate the number of absorbers in the process flowsheet. To proceed with this qualitative comparison, it is necessary to reasonably estimate the rate of variation of the specific reboiler duty (SRD) for MEA solvent regeneration as a function of both the CO_2 capture rate and the CO_2 concentration in the gas. At the state of the art:

- a 5% increase in the capture rate from 85% to 90% or from 90% to 95% at constant flue gas composition generated an average SRD increase of 2%, corresponding to about 0.07 MJ/kg CO_2 captured (Duan et al., 2012; Soltani et al., 2017);
- for the treatment of a NGCC (Natural Gas Combined Cycle) plant flue gas, which is characterized by an average CO_2 concentration of 4 vol%, the reported SRD for MEA is close to 4 MJ/kg CO_2 captured (Subramanian et al., 2017);
- for high-concentrated flue gas, under optimal operating conditions the SRD can be lowered down to 3.4-3.5 MJ/kg CO_2 captured (Biermann et al., 2022).

Based on the abovementioned information, an approximate SRD has been defined for all the capture rates and CO_2 gas contents of interest for this qualitative comparison (see Table 2).

Table 2. Approximate SRD values in [MJ/kg CO_2 captured] at different CO_2 concentrations in the flue gas and different CO_2 capture rates according to the literature.

CO_2 vol% content	**90% capture**	**95% capture**	**85% capture**
4% CO_2	4	4.07	3.93
6% CO_2	3.8	3.88	3.73
7% CO_2	3.7	3.77	3.63
9% CO_2	3.5	3.55	3.43
10% CO_2	3.4	3.47	3.33

A rough estimate of the absorber diameter in the two configurations is considered as an indicator of the CAPEX variation determined by the splitting of the flue gas stacks into two separate columns for CO_2 capture. The diameter is estimated according to expression (1), where v_{gas} is the flue gas velocity (set equal to 2 m/s). The diameter of the single column calculated for the configuration without stream splitting is compared with the sum of the two absorbers diameters estimated for the configuration with splitting.

$$D_{abs} = \sqrt{\frac{4 \cdot Volume\ flow\ to\ be\ treated}{\pi \cdot v_{gas}}} \tag{1}$$

The reboiler duty for solvent regeneration is instead considered as representative of the OPEX of the plant. It is simply obtained by expression ((2), thus multiplying the SRD times the CO_2 mass flow entering the capture plant times the fraction of CO_2 which has to be captured (85%, 90% or 95%). For the multi-absorber configuration, the total duty will be the sum of two contributions accounting for the two different capture rates, both estimated with expression ((2).

$$Duty = SRD \cdot CO_2\,inlet\,mass\,flow \cdot \frac{CO_2\,captured}{CO_2\,inlet\,mass\,flow} = SRD \cdot CO_2\,captured \tag{2}$$

Results show that the expected reduction in the energy requirements allowed by the streams splitting is too limited to justify the CAPEX increase given by the design of a double unit, thus the single absorber configuration is adopted to proceed with the complete flowsheet design and simulation in Aspen Plus®. For details on the single versus double-absorber qualitative comparison results. see section 1.7.1.

1.4.2 CO_2 capture plant: base layout

Eight stacks from the Irving Oil Whitegate refinery flue gas were chosen according to the criteria presented in section 1.2.1 (overall CO_2 concentration of 7.65 mol% on a wet basis) and are routed to the CO_2 capture plant. A schematic representation of the base process flowsheet designed for this application is depicted in Figure 5. The same flowsheet is adopted both for the HS3 and the MEA-based process, to guarantee consistency for the sake of comparison between the two solvents. In other words, the number and type of unit operation is unchanged.

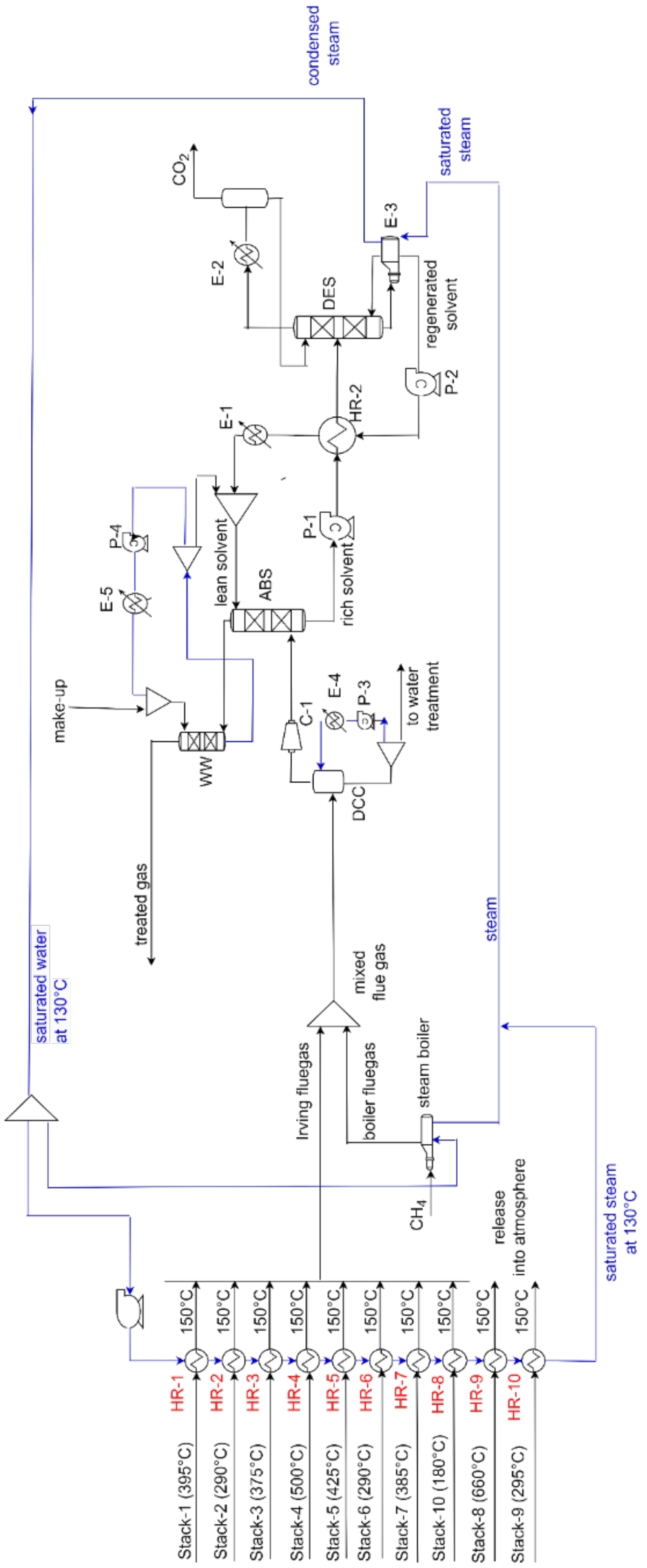


Figure 5. Schematic flowsheet of the plant designed for CO_2 capture from the Irving oil refinery.

The stacks (available at high temperatures ranging from 250°C to 600°C) are cooled down to 150°C in a train of process-process heat exchangers (HR-1 to HR-10). It is remarkable that the choice to simulate one heat recovery for each stack is due to both flexibility reasons and the need to locate HR as close as possible to the stack emission points. Details on the criteria adopted for this preliminary heat integration are presented in the following subsection. The pressure drop on the flue gas side for these heat exchangers is close to 0.09 bar. This is a result from detailed design of HR-1 to HR-10 assuming flat-plate technology in Aspen EDR. For details, see the dedicated section MM.

The precooled flue gas is further cooled down in a direct contact cooler (DCC). Since the cooling water circuit is assumed to provide cooling water at an inlet temperature of 20°C, the process water flow circulating inside the DCC loop can be available at 25°C. This assumption on cooling water temperature is based on the available data for the average temperature of the air (17°C, National Centres for Environmental Information (National Centres for Environmental Information, accessed March 2023) and of the sea water (15°C, seatemperature.info) in summer (the most critical condition) in the Cork area. Furthermore, a 3°C temperature approach is considered for the DCC, so that the flue gas leaves the top of the DCC at 28°C. The column is simulated using a rate-based approach; the packing height is set to 3 m, while the diameter is calculated so that the unit works at 70% of the flooding velocity. This higher margin with respect to the default 80% flooding velocity criterion proposed as default by Aspen Tech (Aspen Plus®, 2019) allows to reduce the pressure drops inside the column. Part of the water present in the flue gas condenses inside the DCC, reaching saturation conditions. For this reason, the cooling water loop circulating in the DCC is provided with a splitter to discharge this excess water content. This extra-water must be sent to water treatment.

A fan (C-1) allows overcoming the total pressure drops occurring inside the preliminary heat exchangers (HR-1 to HR-10), inside the DCC, the absorber (ABS) and the water-wash (WW). Since the absorption column is much more complex than the packing itself, the pressure drops estimated by the process simulator by means of rate-based modeling, which refer only to the specified packing height, are doubled for the sake of conservativeness to consider in a rough estimate also the additional expected pressure losses due to injection system, effective column height and possible split into multiple packing beds. The fan is modelled assuming an efficiency equal to 80%. The total pressure drop to be overcome is also a function of the total absorber packing height, but it is in any case included between 0.2 and 0.23 bar for both solvents.

CO_2 is removed inside an absorber (ABS), which is packed with Mellapak 250x (Sulzer). The solvent flow to be fed to ABS is determined in such a way that the 90% of the total entering CO_2 can be removed inside the column. The interactive sizing tool available in Aspen Plus V11 has been exploited to estimate the design diameter for the absorber and the stripper: to this aim, as abovementioned 70% flooding velocity has been adopted as design basis. This procedure is carried out by means of a temporary Calculations Type switch from rate-based to equilibrium, since the mentioned tool cannot be used in rate-based mode. After the sizing, the simulation is switched again to the rate-based mode, which is necessary to properly account for mass-transfer limitations in the system. For the estimation of pressure drop associated to the elevation gain, the total columns height is assumed to be twice the packing height as a rule of thumb (S. Zhang & Lu, 2015).

The treated gas is routed to a water wash (WW) to lower the residual amine content in the gas to less than 5 ppm. This threshold is chosen on the basis of current legislations on amine emission tolerance: for example, 6 ppmv is the maximum daily average total amine concentration limit according to the Norwegian environmental authority (Shah et al., 2018) released for medium-scale demonstration plant, while other permits for larger-scale demonstration systems such as ROAD permit (2012) allow amine emissions up to 23 mg/Nm^3 (Sepa, 2015).

The diameter of the water-wash is supposed to be equal to the one of the absorber. The water-wash packing height is selected as the minimum height required to reach the specification on the residual amine content in the treated gas using a circulating water rate such that 70% flooding velocity is not overcome inside the washing section. The washing water circulates in a close-loop to avoid the need for continuously integrating large amounts of fresh water to the plant. This water loop includes a water circulation pump and cooling water is exploited as utility to bring the circulating water in the DCC back to the original feed temperature. The pressure drop inside cooling water loops is set to 2 bar (adwatec.com). A makeup freshwater stream is also included to close the water balance of the plant.

The rich-solvent is pumped in P-1 to a pressure that must be sufficient to reach the stripper operating pressure and to overcome at the same time the pressure drops in the lean-rich heat recovery exchanger (HR-11) and the pressure drops required to feed the solvent to the stripper at its upper stage. To this purpose, the pressure drop in HR-11 is set to 0.35 bar in accordance with the rules of thumb proposed by Seider et al. (Seider et al., 2016), while in terms of elevation gain a pressure drop of 1 bar per 10m of vertical elevation is assumed. A temperature approach of 10°C is imposed as specification in HR-11.

The rich solvent is then sent to the regenerator (DES), which is provided with a top condenser (E-2) working at a temperature of 30°C. CO_2 is recovered from the top, while lean solvent is recovered from the bottom and redirected towards the absorber after heat integration in HR-11 with the rich solvent to be regenerated. Also the stripper is modelled as a rate-based unit, but kinetics is disregarded since it is based on experimental data collected at much lower temperatures (25-40°C) with respect to the ones observed inside this column. This assumption is often adopted since desorption reactions are fast enough so that mass transfer becomes the limiting step (Van Wagener & Rochelle, 2011). The column has one degree of freedom which is saturated by imposing that the regenerated solvent must have a lean loading equal to the one of the initial solvent fed to the absorber. This specification allows closing the CO_2 mass balance and it considerably speed up the convergence of the unit with respect to alternative specifications such as the bottom temperature, especially while working with the HS3 model.

The regenerated solvent is pumped in P-2 to guarantee a sufficient pressure to overcome the elevation gain to reach the top of the absorber, and it is further cooled in E-1 and recycled back to the absorber. Heat exchangers E-1, E-2 E-4 and E-5 have been modelled simply as coolers; cooling water entering at 20°C and discharged at 35°C is exploited as utility. In addition, a pump for water circulation inside the DCC and WW loops is included (P-3 and P-4, respectively).

Since the amount of heat recovered in HR-1 to HR-10 is not enough to provide the entire reboiler duty to E-3, the inlet stacks are mixed-up together with an additional stream representing the flue gas generated by a natural gas-fed steam boiler, which is required to generate the additional steam required to meet the overall energy requirements of the CO_2 capture plant. The amount of methane (assumed pure) to be fired in the steam boiler to generate the required duty for the solvent regeneration is calculated according to expression

(3), where LHV stands for the lower heating value of methane (50 MJ/kg) and η for the efficiency of the boiler. assumed equal to 0.8 (Pellegrini et al., 2015). Methane is supposed to be fully converted according to its combustion reaction. and a standard 15 mol% excess air is considered for the calculation of the generated flue gas composition (Schiffhauer, 2009).

$$F_{CH_4} = \frac{Q}{LHV_{CH_4} \cdot \eta} \tag{3}$$

The molar flowrate of the steam boiler flue gas to be fed to the CO_2 capture unit is calculated according to expression (4), where MW is the molecular weight, Q_{reb} is the total regeneration column's reboiler duty and $_{Qrec.stacks}$ is the amount of heat recovered by cooling each refinery stack down to 150°C in the abovementioned heat recovery section.

$$F_{boiler,\,fluegas} = \frac{Q_{reb} - Q_{rec,stacks}}{LHV_{CH_4} \cdot \eta \cdot MW_{CH_4}} \tag{4}$$

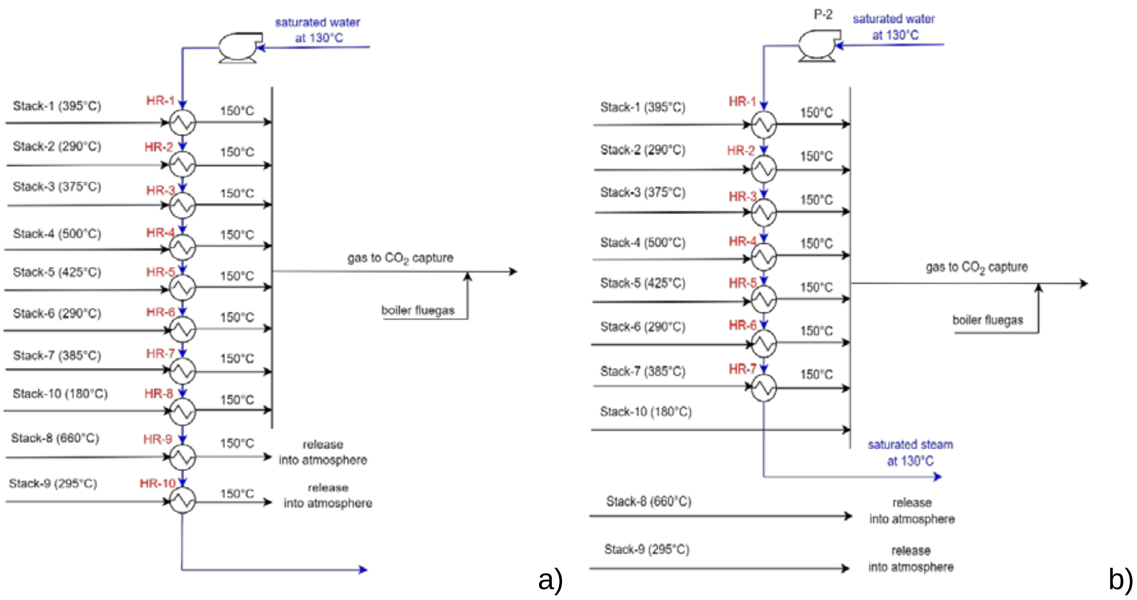
1.4.3 Preliminary heat recovery: hot flue gas – steam generation thermal coupling

The utility considered as the source of thermal duty for solvent regeneration is saturated steam at 130°C; such saturation temperature is selected to guarantee a minimum approach temperature of 10°C in the reboiler. being the temperature at the bottom of the desorber close to 120°C. The steam condenses inside the reboiler and is recovered in the form saturated water, thus it needs to be vaporized back before being recirculated to the reboiler (E-3). The major heat input to the process is given by the amount of heat required to re-vaporize the steam for the reboiler. Minimizing this heat duty is crucial for the economical sustainability of the proposed plant.

To this purpose. a network of recovery heat exchangers distributed in parallel configuration in which each single refinery stack gets cooled down by exchanging heat with the utility used in the CO_2 capture process for solvent regeneration has been designed. In fact, the Irving Oil refinery flue gas stacks are available at temperatures ranging from 180 up to 660°C, as shown in the data reported in **Errore. L'origine riferimento non è stata trovata.**. Since the CO_2 capture process operates at much lower temperatures (30-50°C), this residual heat could be exploited for some energy integrations within the capture plant to reduce to the lowest extent the need for external steam generation to meet the carbon capture plant energy requirements for amine solvent regeneration. This work will prove that a substantial portion of the heat required for saturated water vaporization can be provided by the hot refinery stacks (please refer to results section). In this way. flue gas cooling is thermally coupled with the reboiler of the regeneration column. Remarkably. the flue gas outlet temperature is set to 150°C to keep a 20°C approach temperature between the process fluid and the utility side.

As the ten Irving Oil stacks are characterized by different flowrates and temperatures, it is straightforward that there will be streams from which heat recovery is much more efficient than others. Moreover, the addition of ten process-process heat exchangers in the carbon capture plant flowsheet is expected to provide a significant impact on the investment costs, meaning that a trade-off between the number of heat exchange units and the total amount of heat recovered in this section to limit steam generation should be found for a smart plant design. To this aim, two scenarios are considered: in the first case-study (CS1). all the flue gas streams are routed to heat recovery (Figure 6a). In the second case-study (CS2), instead, the two streams which are not treated in the capture plant as well as stack-10, which provides a very limited heat recovery, are excluded from heat integration (Figure 6b). It is important to remark that the specific configuration selected for heat exchange (i.e. exchangers in series or in parallel) does not have any impact on the energy requirements since the temperature remains constant from the inlet to the outlet of each heat exchanger on the utility-side. The two investigated scenarios are compared through preliminary costs estimate carried out according to the methodology proposed in section 1.6 dedicated to the economic assessment. This comparison is carried out considering MEA as solvent and considering a baseline set of operating conditions assumed as starting values before performing the sensitivity analysis, which is then performed directly on the best scenario. The baseline values assumed for packing heights, stripper pressures, solvent and gas feed temperatures can be found in section 1.5 (sensitivity analysis).

The heat exchangers have been first added in the process flowsheet as short-cut process-process exchangers in order to estimate how much total duty could be recovered from each refinery stack and the corresponding impact in terms of reduction of the overall energy requirements of the CO_2 capture process. In a second step. the single heat recovery units have been optimally designed by means of Aspen EDR (Exchanger Design and Rating), considering flat plate heat exchangers type in counter-current configuration. Detailed results concerning the optimal sizing of the heat recovery exchangers as well as pressure drops estimation are described in the results section.



a) b)

Figure 6. Designed network of heat recovery exchangers (HR-1 to HR-10) for the hot flue gas – steam thermal coupling: a) heat recovery from each stack (CS1), and b) heat recovery from seven streams only (CS2).

1.5 Sensitivity analysis on process operating conditions

1.5.1 Setting of the baseline layout

The optimal operating conditions for the CO_2 capture plant have been determined by means of a sensitivity analysis both for MEA and for HS3. A baseline case is defined as follows:

- Inlet solvent temperatures is set to 43°C;

- a CO_2 capture rate of 90% is assumed;
- the stripper pressure is set to 1.8 bar.
- For MEA solvent, the minimum absorber and stripper packing heights are set to 6 m and 8 m, respectively, based on the results of a previous CO_2 capture plant optimization work for a similar flue gas composition (Ghilardi, 2020). For HS3, 16 m is set as a conservative starting absorber and stripper packing height, since experimental pilot scale campaigns have pointed out that under comparable operating conditions and desired capture performances HS3 is a considerably slower solvent from a kinetics point of view. The baseline simulation considers top stage for the rich solvent feeding to the stripper column.
- Finally, the total amine lean loading is set to 0.27 for MEA (based on a previous optimization work with the same default MEA Aspen framework by Ghilardi, 2020) and 0.07 for HS3 (the optimal loading according to the experimental observations collected at Tiller pilot plant). No water wash is considered for the baseline process, since it has no impact on the energy requirements, thus on the SRD which is the parameter to be minimized.

1.5.2 Procedure

The aim of the sensitivity analysis is to minimize the operating costs. A key indicator of the energy consumption is given by the specific reboiler duty (SRD), defined as the duty consumed in the desorber per unit of captured CO_2 (MJ/kg CO_2). Starting from the presented baseline simulation, the following parameters are optimized in line with the methodology proposed by AbuZahra (Abu-Zahra et al., 2007):

- lean loading (α): the trend of the SRD as a function of α is monitored in a range between 0.18 and 0.36 for MEA and between 0.05 and 0.12 for HS3;
- desorber pressure: a range between 1.5 bar and 2.2 bar (0.1 bar step) is considered. At increasing pressure the SRD lowers, but the temperature at the bottom of the column increases. The optimal pressure is defined as the highest pressure for which the reboiler temperature does not overcome 122°C: this condition is important to maintain a sufficient approach temperature with respect to the utility side (saturated steam at 130°C);
- lean solvent temperature: a reduction in the solvent temperature does not modify appreciably the SRD. On the one hand a higher solvent temperature allows reducing the cooling water consumption, but on the other hand amine and water losses inside the absorber increase. 43°C is therefore selected for both solvents as a trade-off.

In addition, a further optimization of absorber and stripper packing heights was added, based on the following criteria:

- absorber packing height: the SRD trend versus α is investigated at different packing heights, with a discretization step of 2m. The optimal height is selected as the minimum height for which an increment in the SRD lower than 1% is observed with respect to the previous case study (2 m higher column);
- stripper feed stage: selected as the one for which the SRD is minimized;

- desorber packing height: SRD has been calculated at different heights, with a discretization step of 2 m. The optimal height is selected according to the same criteria adopted for the absorber;

Considering the lack of a standardized procedure to be followed for this kind of optimization, this threshold value of 1% is adopted since the main scope in this work is the minimization of the total costs rather than finding the minimum of operating costs only (Aromada et al., 2021).

1.6 Preliminary costs estimate

The present paragraph describes the methodology followed and the assumptions adopted for the comparative economic analysis between two proposed heat recovery case-studies (CS1 and CS2).

1.6.1 Investment cost

The fixed investment costs have been calculated following the approach proposed by Guthrie (Guthrie, 1974), Ulrich (Ulrich, 1984) and Navarrete (Navarrete, 1995), according to which the effective costs can be estimated starting from equipment purchase costs under standard pressure conditions and construction material (C_P^0). This method is included in the third estimate class (preliminary cost estimate) and is characterized by a 10-40% reliability in terms of absolute values returned for the estimated costs (Christensen et al., 2005); however, the method is sufficiently accurate for the sake of a comparative economic analysis between the two proposed scenarios.

The purchase cost under standard condition (C_P^0) can be defined using expression (5), where A represents the characteristic dimension of the specific unit and K_1, K_2 and K_3 are coefficients depending on the considered unit operation.

$$\log_{10}(c_P^0) = K_1 + K_2 \cdot \log_{10}(A) + K_3 \cdot (\log_{10}(A))^2 \tag{5}$$

Coefficients K_i for each of the unit operation of interest were taken directly from Turton (Turton, 2012). Flat type solution has been chosen for the flue gas-condensing steam heat exchangers (HR-1 to HR-10), while the water-coolers as well as the lean-rich heat recovery exchangers have been modelled as shell and tubes with floating head. The global heat transfer coefficients adopted for the estimation of the heat exchange surfaces according to the type of circulating fluids are taken from Perrys Chemical Engineering Handbook (Green & Perry, 2007).

For unit operations exceeding the range size of validity for the applications of expression (5), the purchase cost is determined using the method by Hill. Indeed, expression (5) is adopted to estimate the purchase cost under base conditions ($Cost_{lim}$) of an equipment having the maximum allowable size (A_{lim}) according to the limit values for K_i coefficients reported by Turton (Turton, 2012).Then, the cost of the real equipment at its actual size ($Cost_{real}$) is defined according to expression (6), where A_{real} is the real dimension of the unit, A_{lim} is the maximum allowable size, and n is an exponent which is typically set to 0.6 (Rodríguez et al., 2011).

$$Cost_{real} = Cost_{\lim} \cdot \left(\frac{A_{real}}{A_{lim}}\right)^n \tag{6}$$

The C_P^0 for each unit must be actualized taking into account a factor which describes the effect of costs variation in time, mainly due to inflation. The factor adopted in this work for costs updating is the *Chemical Engineering Plant Cost Index* (CEPCI).

More specifically, equation (7) can be used to calculate the current equipment cost C_2 given the equipment cost referred to a certain year in the past (C_1).

$$C_2 = C_1\left(\frac{Index_2}{Index_1}\right) \tag{7}$$

In this expression, C represents the cost, while *$Index_1$ and $Index_2$* indicate the value of CEPCI index in the year in which the equipment cost is known and in the year for which the new costs estimation is desired, respectively. In this work, the costs have been referred to the CEPCI index for 2022.

The bare module cost refereed to standard material and pressure (C_{BM}^0) and the bare module cost accounting for the effective operating conditions (C_{BM}) are defined according to expressions (8) and (9), respectively, where B_1 and B_2 are coefficients, whose values depend on the specific unit under consideration and F_M and F_P are two correction factors accounting for the effective construction material and system pressure, respectively.

$$C_{BM}^0 = C_P^0 \cdot (B_1 + B_2) \tag{8}$$

$$C_{BM} = C_P^0 \cdot (B_1 + B_2 \cdot F_M \cdot F_P) = C_P^0 \cdot F_{BM} \tag{9}$$

For estimating K_i and B_i coefficients for the generic i-th equipment, as well as F_M and F_P, values reported by Turton (Turton, 2012) and by Guthrie (Guthrie, 1974) have been exploited. Since the maximum operating pressure in the designed CO_2 capture process never overcomes 5 bar (< 19 barg), it is reasonable to set the pressure adaptative parameter F_P equal to 1 for heat exchangers, pumps and compressor.

The Total Module Costs (CTM) can be determined by means of equation (10) summing the contributions of all the equipment (N_{eq}) accounted for.

$$CTM = 1.18 \cdot \sum_{i=1}^{N_{eq}} C_{BM,i} \tag{10}$$

Remarkably, the value of CTM represents the total investment cost for making small to moderate changes or expansions to an existing facility, such as revamping. In the case-study developed in this work, even if the site can be considered ready for construction, the CO_2 capture plant needs to be built from ground. Therefore, for the sake of conservativeness, the Grass Root Costs (CGR) are assumed as representative for the total CAPEX. These costs include the additional expected costs for auxiliary buildings, site development, off-sites and utilities, which are estimated as half of the total purchased cost under base conditions (equation (11)).

$$CGR = CTM + 0.5 \cdot \sum_{i=1}^{N_{eq}} C_{BM,i}^0 \tag{11}$$

The total plant fixed investment costs (FCI) are finally calculated by summing the CGR to the initial solvent cost (ISC), which is calculated according to the following expression (12), where

F_{solv} stands for the total circulating solvent mass flow, w_{amine} is the weight fraction of amine in the unloaded solvent (namely 55 wt% for HS3 and 30 wt% for MEA), while amine and water costs are expressed per unit of mass ($/kg).

$$ISC = F_{solv} \cdot w_{amine} \cdot [Amine\_cost] + (1 - w_{amine}) \cdot [Water\_cost] \tag{12}$$

The actual MEA price is close to 1.5 $/kg, while for HS3 solvent it is difficult at present to estimate a precise cost, since at the moment the two amine constituents are specialty chemicals with very small rate of production. For calculations, the price has been set to three times MEA solvent cost; this is an estimate of the price that the solvent could have as it starts being produced in large amounts. It is remarkable that, in any case, the ISC contribution does not strongly affect the total investment cost of the capture plant.

1.6.2 Operating cost

The operating costs are estimated as the sum of direct operating costs, fixed operating costs and general operating expenses in compliance with the methodology proposed by Turton (Turton, 2012). For what concerns the direct operating costs, the contribution associated to waste treatment has been neglected for simplicity, whereas the contributions of utilities, operating labor, direct supervisory and clerical labor, maintenance and repair, operating supplies and laboratory charges are all included. The fixed operating costs include local taxes and insurance as well as the so-called plant overhead costs and the effect of depreciation due to equipment deterioration in time. Administration and distribution costs are included in the general expenses. The single contributions to the overall operating costs and the expression used for their estimation are gathered in Table 3. Noticeably, many operating costs contributions are function of the total fixed investment costs (FCI).

The total operating costs (referred to as costs of manufacturing (COM) according to Turton (2012)) obtained summing all the listed contribution is further increased accounting for extra expenses associated to patents and royalties, selling costs and a contribution related to research and development. These contributions are calculated as function of the COM themselves according to the expressions highlighted in Table 3. The total operating costs including all the mentioned contributions is referred to as COM_{tot} and represents the final estimation of the operating costs of the CO_2 capture plant.

Table 3. Expressions for direct, indirect and general operating costs estimation (Turton, 2012).

Direct operating costs	
Raw materials	Cost of amine make-up + water make-up
Utilities	Cost of natural gas + electricity + cooling water
Operating labor (C_{OL})	$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5}$
Direct Supervisory and clerical labor	$0.18 \cdot C_{OL}$
Mantainace and repair	$0.07 \cdot FCI$
Opearating supplies	$0.009 \cdot FCI$
Laboratory charges	$0.15 \cdot C_{OL}$
Fixed operating costs	
Depreciation	$0.1 \cdot FCI$
Local taxes and insurance	$0.03 \cdot FCI + 0.01 \cdot FCI$
Plant overhead costs	$0.708 \cdot C_{OL} + 0.036 \cdot FCI$
General expenses	
Administrative costs	$0.177 \cdot C_{OL} + 0.009 \cdot FCI$

Table 4. Contributions to the operating costs that are function of the cost of manufacturing - COM (Turton, 2012).

Extra operating costs	
Patents and royalties	$0.03 \cdot COM$
Distribution and selling	$0.1 \cdot COM$
Research and development	$0.05 \cdot COM$
Contingency	$0.05 \cdot COM$

The contribution of the operating labor is calculated starting from expression (13), where N_{OL} stands for the number of workers required per shift, P is the number of process stages handling solid matter (none for the specific case-studies of interest) and N_{np} is the number of process stages that are not handling any solid matter. Pumps and vessels are not included in the number of unit computation, according to Turton et al.

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \tag{13}$$

The total number of operators required by the plant at different times shift (N_{op}) is calculated as the ratio between the yearly shifts required by the plant ($N_{shitft,tot}$) and the yearly shifts of each operator ($N_{shift,op}$), which in turn are given by the ratio between the operability of the plant and the time duration assumed for each shift (expression (14)).

$$N_{OP} = \frac{N_{shift,tot}}{N_{shift,OP}} = \frac{N_{shift,tot}}{operability} \cdot time\_per\_shift \tag{14}$$

The total number of operators required by the plant (N_{tot}) is then calculated as the product of the number of operators required per shift (N_{OL}) times the total number of operators required by the plant at different times shift (N_{op}).

$$N_{tot} = N_{OL} \cdot N_{OP} \tag{15}$$

Finally, the Cost of Operating Labor (C_{OL}) is given by expression (16), namely by the product of the average yearly salary of an operator and N_{tot}.

$$C_{OL} = salary\left[\frac{\$}{year \cdot operator}\right] \cdot N_{tot} \tag{16}$$

Further assumptions for C_{OL} calculations are listed in Table 5.

Table 5. List of assumptions for Operating Lobar cost estimation.

Assumption	**Value**
Plant operability (h/year)	8000
Time per shift (h)	8
Shifts per year ($N_{shift,tot}$)	1000
Salary (€/year/operator)	40000

As concerns utilities, natural gas for the steam boiler, electricity for pumps and compressor as well as cooling water are included. The utilities costs considered for this economic analysis are gathered in Table 6. It is remarkable that the natural gas and electricity prices refer to the average price reported for March 2023 by GME (Gestione Mercato Elettrico - GME, accessed March 2023). The cooling water price is estimated considering a circuit provided with an air cooling tower working with 10°C to 15°C temperature difference on the cooling water side (Turton, 2012).

Table 6. Costs of utilities adopted for the preliminary costs estimate in this work.

Utility	**Cost [$/GJ]**
Natural gas	12.50
Electricity	27.78
Cooling water	0.354

For the cases-studies in which steam from a power plant is exploited to meet the energy requirements instead of generating steam by natural gas boiler, a steam price of 14.05 $/GJ is used for calculations. This estimate is provided by Turton (Turton, 2012) and refers to low-pressure steam (maximum 5 barg) without credit for power production.

The costs of raw materials must include water and amine make-up to compensate the solvent losses occurring while running the capture plant. Moreover, the amine make-up cost is multiplied times a factor of 1.2 to take into account the additional costs due to the need for using corrosion inhibitors in the plant. The water make-up is set to 1.8 $/ton (Turton, 2012), while the amine make-up cost cannot be calculated just considering the amine mass balance in the capture plant, due to degradation issues. For this reason, amine make-up costs are expressed as a function of the amount of captured CO_2 based on the degradation extent observed in MEA-based plants in operation (1.55 \$/ton CO_2) (ref). Considering that a comparable degradation is expected for HS3 and the higher solvent cost, a three times higher value is considered for HS3 also for make-up costs estimation.

Finally, total costs (C_{tot}) are calculated as the sum of the costs of manufacturing and the fixed investment costs, according to expression (17).

$$Ctot = \frac{FCI}{UL} + COM_{tot} \tag{17}$$

In expression (17), the FCI have been referred for simplicity to the whole expected useful life of the capture plant, assumed equal to 25 years.

1.7 Results

1.7.1 Single versus double absorber configuration

The absorber diameters and the reboiler duties estimated for the single and for the double absorber configuration as a result of a qualitative comparison carried out following the methodology described in section 1.4.1 are gathered in

Table 7.

Table 7. Sizing and key performance indicators for single and double absorber configurations, respectively.

Parameter	**SINGLE ABSORBER**	**DOUBLE ABSORBER**	
		1 (CO_2-rich)	**2 (CO_2-poor)**
Gas flow (m^3/s)	91.81	36.24	55.57
CO_2 average conc. [mol/mol]	7.4	8.9	5.9
Capture rate [%]	90	95	85
Diameter [m]	7.65	4.80	5.95
SRD [MJ/kg CO_2]	3.7	3.55	3.73
Regeneration duty [MW]	22.79	22.39	

Summing the contributions of the two absorbers and strippers in the split configuration, a total absorber diameter and regeneration duty of 10.75 m and 22.39 MW are obtained, respectively. On the one hand, a 40% higher absorber section is required by phase splitting; on the other hand, the beneficial effect on the regeneration duty given by the lower average SRD is very limited: indeed, the estimated duty lowers by only 0.4 MW, corresponding to only 1.7% of the duty. Considering the limited expected benefit from an energy requirements point of view, the single absorber configuration is adopted for the following steps in this work.

1.7.2 Preliminary heat recovery section

The amount of heat recoverable in each of the ten modelled flue gas-condensing steam process-process heat exchangers is gathered in Table 8. Considering that all the stacks are included in heat recovery (CS1), it is possible to save 18.17 MW summing all the single heat exchangers duties. If only the first seven stacks are conveyed to this preliminary heat recovery section (CS2), the recovered duty lowers to 16.21 MW (decrease of 10.8%), but only seven heat exchangers are required instead of ten.

Table 8. Amount of heat recovered in each of the designed preliminary heat recovery exchangers (HR-1 to HR-10) for hot flue gas – condensing steam thermal coupling.

Heat recovery exchanger	Recovered duty [kW]
HR-1	1034.97
HR-2	1221.71
HR-3	2548.07
HR-4	1525.73
HR-5	2228.08
HR-6	4230.88
HR-7	3418.53
HR-8	1507.20
HR-9	246.21
HR-10	206.18

A T-Q diagram for the single heat exchangers is available in Figure 7. On the utility-side (steam) the temperature remains constant (130°C) along the heat exchanger due to phase transition.

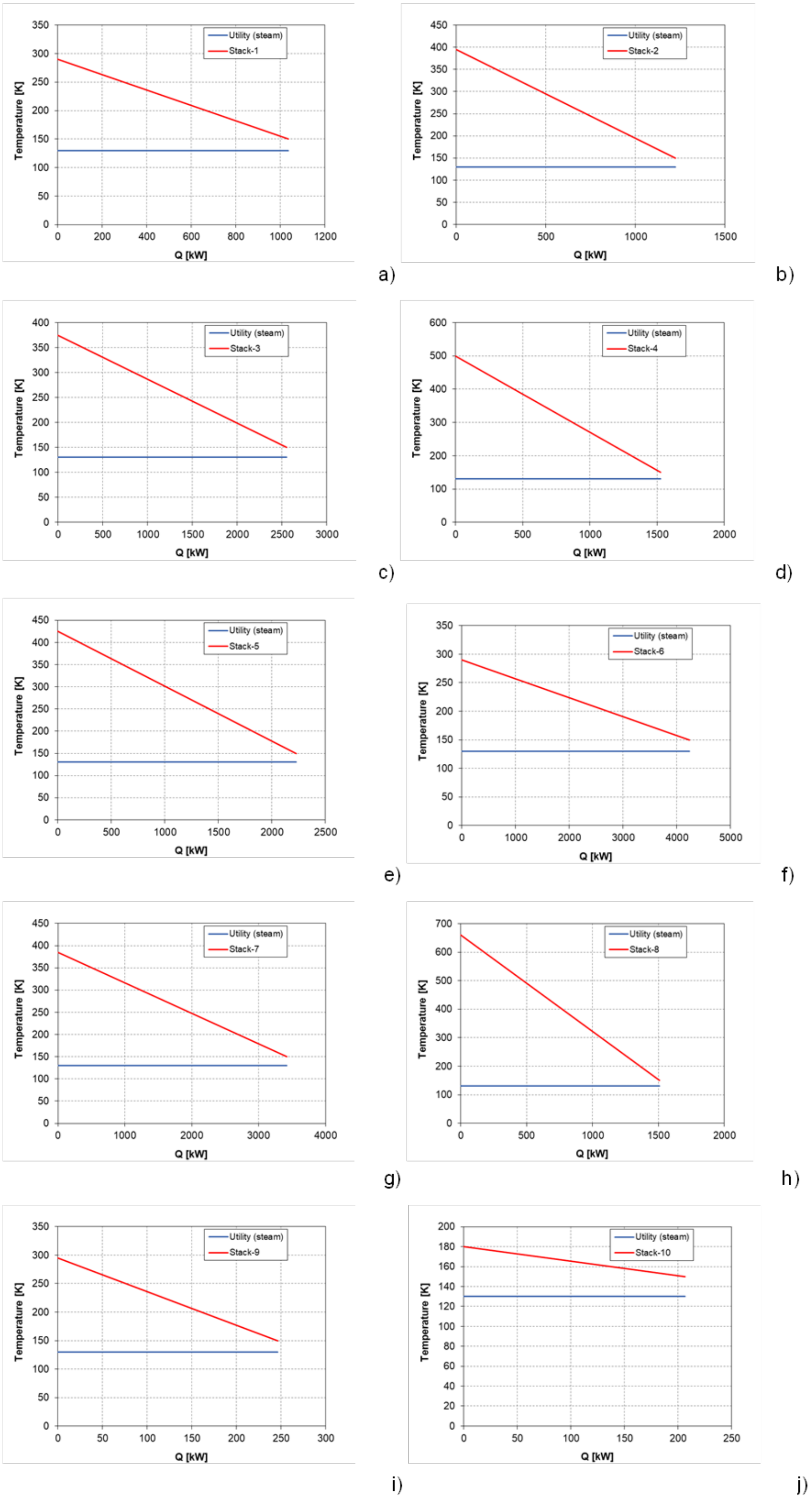


Figure 7. T-Q profiles for the flue gas-phase transition water preliminary heat recovery exchangers (HR-1 to HR-10): utility (cold fluid, blue) and flue gas stacks (hot fluid, red): a) HR1; b) HR-2; c) HR-3; d) HR-4; e) HR-5; f) HR-6; g) HR-7; h) HR-8; i) HR-9; j) HR-10.

The two heat recovery options (CS1 and CS2) have been compared buy means of a preliminary costs estimate on the baseline plant (not yet optimized through sensitivity analysis) for the benchmark solvent. Table 9 compares the column and heat exchanger sizes as well as the steam and electricity demand for the two case-studies, while Table 10 and Table 11 gather the results of the preliminary cost estimate.

Table 9. Comparison between the CS1 and CS2 scenarios in terms of equipment size and energy requirements.

Indicator	**CS1**	**CS2**	**CS2 versus CS1[%]**
Absorber diameter [m]	6.15	6.20	+0.8%
Stripper diameter [m]	3.25	3.27	+0.6%
Solvent flow [ton/h]	493.4	503.4	+2.0%
Heat recovered [MW]	18.17	16.21	-10.8%
Reboiler duty [MW]	35.69	36.40	+2.0%
Heat recovered fraction [%]	50.91	44.53	-12.5%
Electric power [MW]	2.25	2.28	+1.3%

Table 10. Comparison between the CS1 and CS2 scenarios in terms of investment costs.

Investment costs (CBM) in Million $	**CS1**	**CS2**	**CS2 versus CS1[%]**
Absorption tower	9.88	10.37	+5%
Absorber internals	1.97	2.05	+4%
DCC	3.75	3.75	=
DCC internals	0.68	0.68	=
HR-1 to HR-10	11.04	8.50	-23%
HR-11	7.01	7.08	+1%
Regeneration tower	2.55	2.60	+2%
Regeneration internals	0.47	0.48	+2%
Coolers (E-1, E-4, E-5)	11.81	11.81	=
Condenser (E-2)	1.14	1.15	+1%
Reboiler (E-3)	5.55	5.72	+3%
Pumps (P-1 to P-6)	0.55	0.55	=
Fan	0.20	0.20	=
Steam boiler	12.41	12.79	+3%
Total costs (CGR)	**69.04**	**67.75**	**-1.86%**

Table 11. Comparison between the CS1 and CS2 scenarios in terms of operating costs.

Operating costs [Million $/year]	**CS1**	**CS2**	**CS2 versus CS1[%]**
Natural gas for steam generation	6.27	7.09	13.0%
Electricity	1.00	1.00	=
Cooling water	0.26	0.27	3.6%
Total COM	**29.20**	**29.98**	**+2.7%**

As expected, reducing the number of process-process heat recovery exchangers from ten to seven units results in a relevant decrease in the associated investment cost (-23%). However, the recovered duty reduces almost by 11%, which results in the need for an increased external steam generation in the steam boiler. A bigger amount of steam to be produced in the boiler leads in turn to increase total flue gas flowrates to be treated in the capture plant. Remarkably, this increase in the total gas circulating flow is responsible for the increase in the dimensions required for all the main unit operations, thus in the associated investment cost (from +1% to +5%). This effect reduces the benefit given by the costs saved for units HR-8 to HR-10 on the total investment cost, which in the end is just less than 2% lower in CS2 with respect to CS1.

For what concerns the operating costs, the increased steam consumption for solvent regeneration requires a 13% higher natural gas flow to be burnt in the steam boiler. This has a relevant impact on the utility costs of the plant. As expected, no relevant variations occur for the other utilities consumption (cooling water and electricity). Moreover, being several indirect and general expenses contributions function of the total Costs of Manufacturing (COM) themselves, the increased utility cost is associated with a corresponding increment also on other operating costs terms (see the methodology section related to the costs estimation). As a result, the total COM in CS2 is about 3% higher with the one calculated for CS1.

The final aim of this analysis is to compare the two configurations in terms of total costs. Assuming to refer the investment costs to the entire useful lifetime of the plant (25 years), the total costs is 31.96 M$ for CS1 and 32.69 M$ for CS2. It is demonstrated that considering the complete set of recovery exchanger is still the best option to minimize the total costs, thus all exchangers from HR-1 to HR-10 have been considered to proceed with the sizing in Aspen EDR, the sensitivity analysis on CO_2 capture plant operating conditions, plant optimization and the final estimation of energy requirements and costs.

1.7.2.1 Sizing with Aspen EDR

The set of heat recovery exchangers (HR-1 tp HR-10) has been designed in Aspen Exchanger Design and Rating (Aspen EDR®) considering flat-plate geometry. The aim of this design is to characterize the geometry of these units to get a rough estimate of the expected space requirements for their effective implementation on the Irving Oil Whitegate rRefinery site. The Aspen EDR tool searches for different possible designs which are all potentially applicable to reach the set specification and finally proposes as the best solution the one which minimizes the cost. It is worth remarking again that the specification set in this work is the hot fluid (flue gas) outlet temperature, which cannot overcome 150°C to maintain a 20°C approach temperature with the utility (steam under phase transition at 130°C). Table 12 summarizes the most relevant outcomes of this design analysis for each heat exchanger. While flowing from HR-1 to HR-10, the utility entering the train of heat exchangers as saturated water is fully vaporized until it reaches saturated steam conditions at the outlet of HR-10. To guarantee the exact shift from saturated water to saturated steam conditions, the flowrate of water fed to this heat recovery section is regulated by means of a design spec in Aspen Plus®. It is remarkable that the pressure drops occurring under the optimal proposed configuration is on average equal to 0.088 bar on the flue gas side (outlet pressure of 0.912 bar), while the total pressure drop on the utility side across the train of exchangers is 0.18 bar. For this reason, the saturated water available at 130°C and saturation pressure (2.66 bar) needs to be slightly pumped to 2.84 bar before entering HR-1 in order to guarantee that the saturated steam exiting HR-10 is available at the desired temperature (130°C). No appreciable variations can be noticed in the flue gas outlet pressures between the different stacks, except for stacks 8 and 9 which cannot reach vacuum conditions because they are directly discharged to the atmosphere after this heat integration rather then being fed to the capture plant.

Table 12. Results of preliminary heat recovery (HR-1 to HR-10) sizing by means of Aspen EDR considering flat type technology.

Exchanger	Vapor fraction	Outlet P cold side [bar]	Outlet P hot side [bar]	Plate area [m^2]	N° plates	N° channels
HR-1	0.0568	2.8436	0.9134	2.79	195	97
HR-2	0.1226	2.84	0.9126	2.79	858	214
HR-3	0.2621	2.8355	0.9129	2.79	534	133
HR-4	0.3437	2.8047	0.9124	2.79	211	105
HR-5	0.4697	2.788	0.9136	2.79	382	95
HR-6	0.7021	2.7849	0.9121	2.79	1500	187
HR-7	0.8897	2.7707	0.9123	2.79	762	190
HR-8	0.9725	2.6882	1.0210	2.79	283	141
HR-9	0.9860	2.6779	1.0120	2.79	945	157
HR-10	1.0000	2.6676	0.9100	2.79	945	157

A graphical representation of the plate geometry for all the sized exchangers is shown in Figure 2.

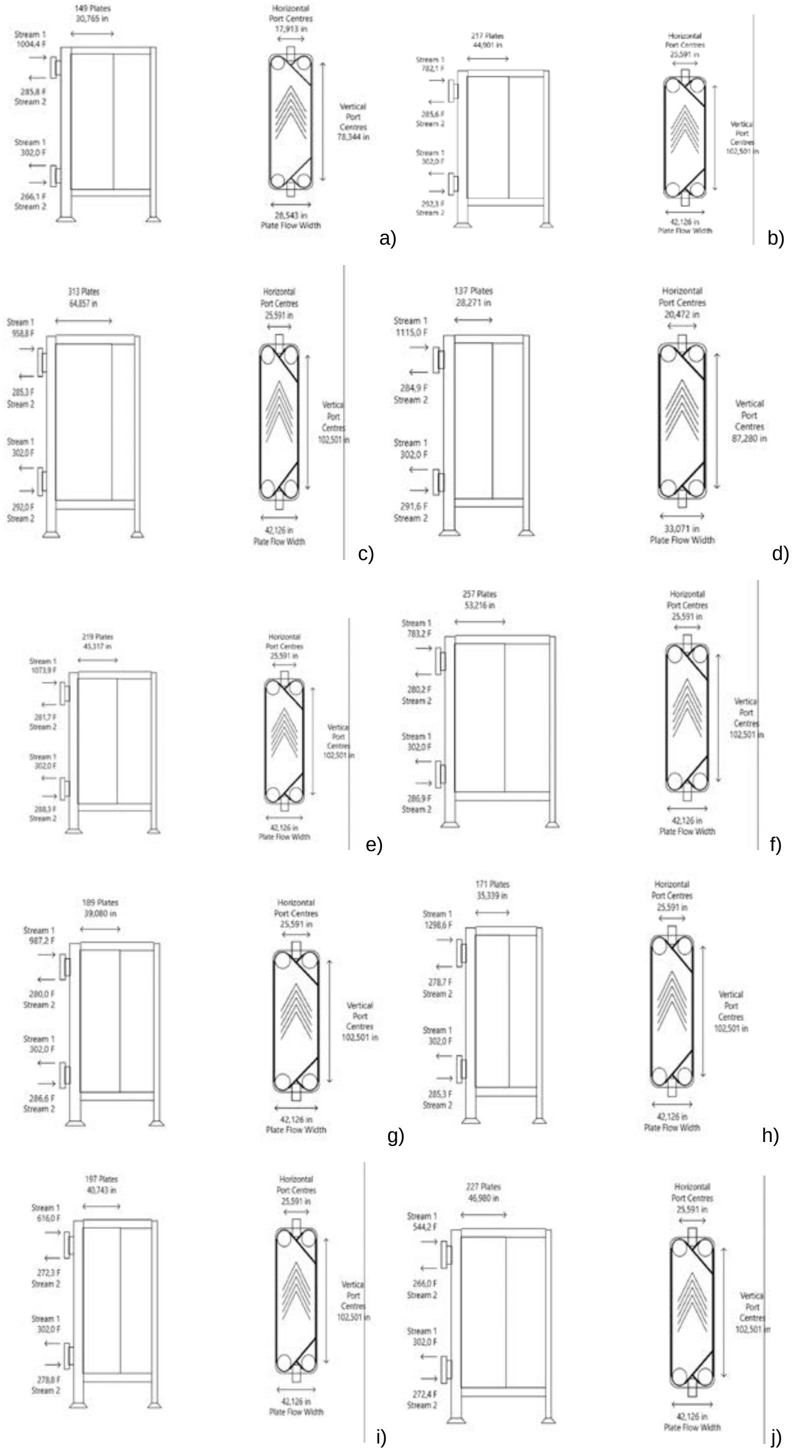


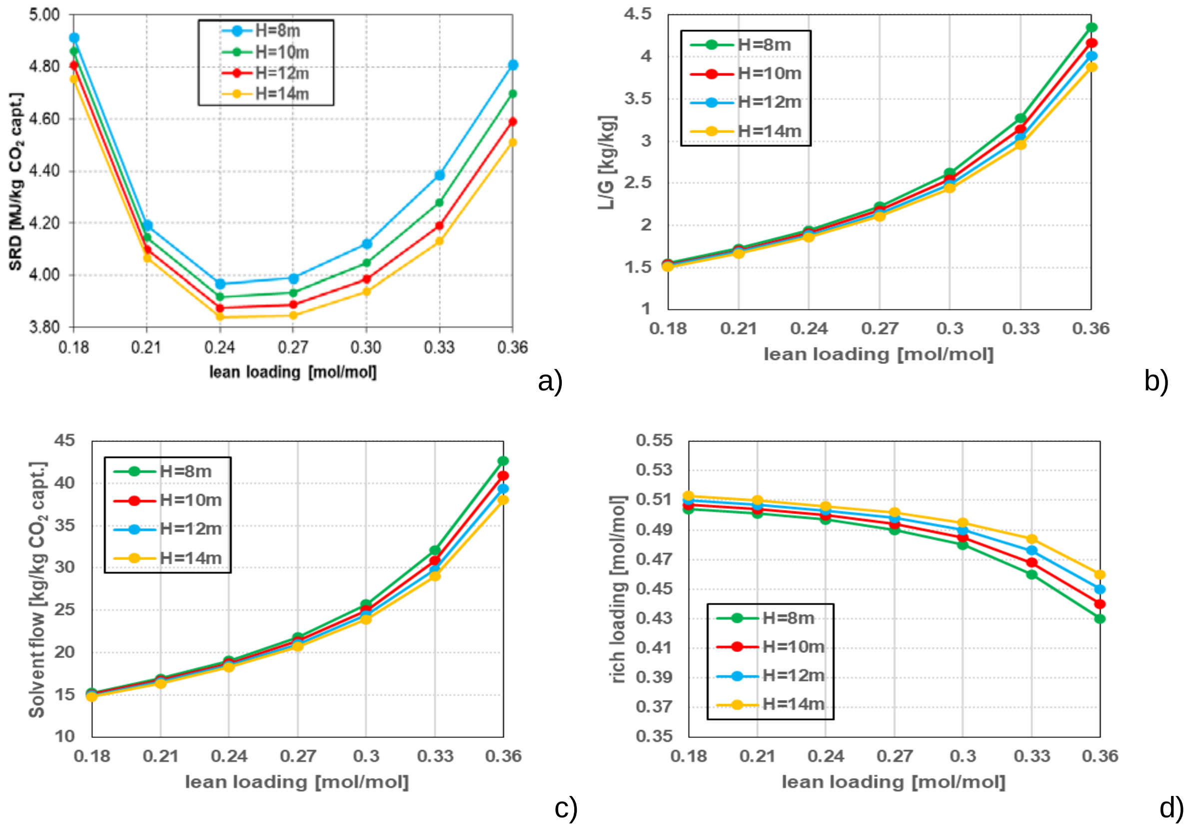
Figure 8. Schematic geometrical representation and size details for the recovery exchangers HR-1 to HR-10 as a result of optimal design carried out using Aspen EDR®.

1.7.3 Sensitivity analysis

This section presents the results of the sensitivity analysis for the optimization of absorber and stripper packing heights, stripper feed stage, lean loading, gas and solvent inlet temperatures for both HS3 and the reference solvent made up of MEA 30 wt%.

1.7.3.1 Absorber packing height and lean loading

Figure 9 and Figure 10 show the trend of the SRD, of the L/G ratio, of the specific solvent flow (kg/kg CO_2 captured) and of the rich loading as a function of the loading at different packing heights for the benchmark and the new HS3 solvent, respectively. The optimal lean loading for MEA is 0.24. The corresponding cycling capacity in molar terms for the optimal case is close to 0.27. These values are in line with pilot scale data collected during a campaign carried out at Technology Centre Mongstad (Norway) and reported by Brigman et al. (Brigman et al., 2014), as well as with other modelling works under comparable operating conditions (Raynal et al., 2011). The minimum packing height needed to limit the SRD increase below 1% with respect to a 2 m higher column is 12 m, which is selected as the final packing height to be adopted for simulations with MEA 30 wt%.



a)

b)

c)

d)

Figure 9. SRD (a), L/G ratio (b), specific solvent flow per unit of CO_2 captured (c) and rich loading (d) as a function of the lean loading for MEA solvent evaluated at different packing heights: 8m (light blue), 10m (green), 12m (red), and 14m (orange).

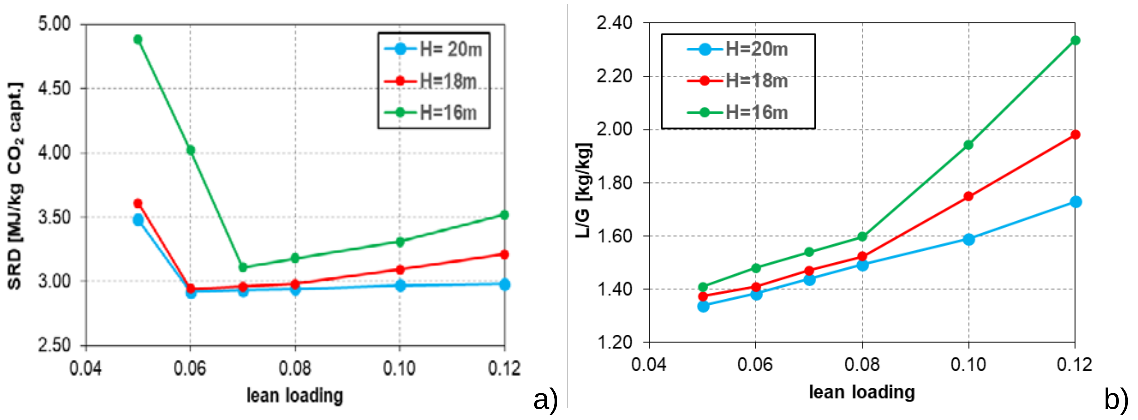


Figure 10. SRD as a function of the lean loading for HS3 solvent evaluated at different packing heights: 20m (light blue), 18m (red), 16m (green), and 14m (orange).

Similarly, HS3 performances are optimized at significantly lower loadings, in compliance with the fact that this solvent has a higher total amine concentration (55 wt% versus 30 wt%). It is remarkable that the energy requirements remain almost flat in a range of loadings between 0.06 and 0.08, whereas they rapidly increase if the loading is slightly reduced from 0.06 to 0.05. This peculiarity is confirmed by pilot plant observations collected at Tiller (confidential data). Based on these considerations, 0.07 has been selected as the final optimal lean loading, in order to maintain a sufficient safety margin from the critical loading below which rapid SRD increase starts without increasing appreciably the reboiler duty itself. Concerning the packing height, results show that adopting the same criteria for the sensitivity analysis a 50% higher packing height is required for HS3. This result is somehow expected, since it is proved knowledge that the new blend is kinetically hindered with respect to the benchmark.

1.7.3.2 Stripper packing height

Simulations of the CO_2 capture plant at variable stripper packing height (2m discretization step) are run after having already set the absorber packing height and the lean loading to their optimal values presented in the previous section. The resulting plots are shown in Figure 11

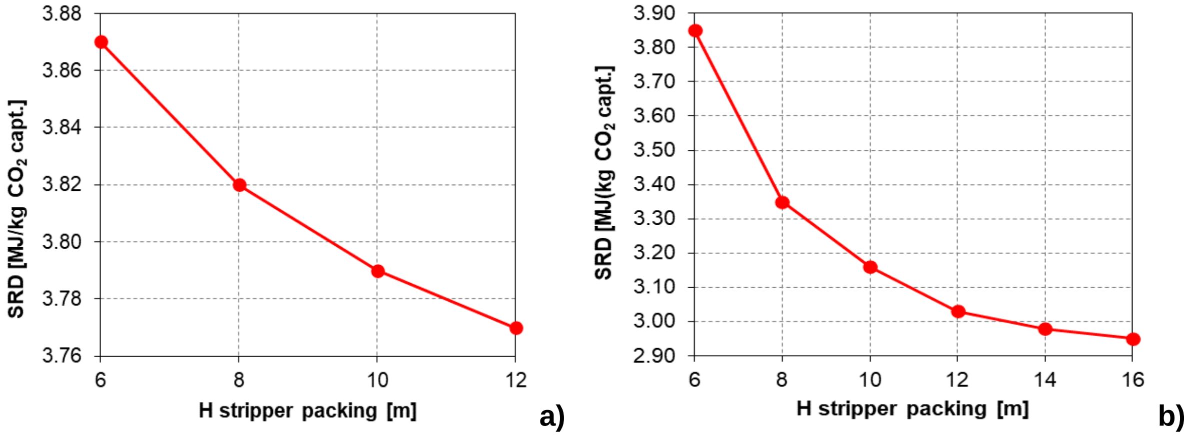


Figure 11. SRD profiles as a function of the stripper packing height for a) MEA and b) HS3 solvents. Absorber packing height and lean loading are already set at the optimal values.

The minimum packing height necessary to keep the SRD increase lower than 1% is 10 m and 14 m for MEA and HS3, respectively.

1.7.3.3 Stripper feed stage

Variations in the SRD as a function of the stage considered for feeding the rich solvent to the stripper are recorded in Figure 12. Indeed, even if the column is of packed type, a certain height of packing corresponds to an ideal height of a theoretical stage in trayed columns. The feed stage associated to the minimum SRD is selected as the best solution, thus the upper stage for HS3 and the second ideal stage for the benchmark.

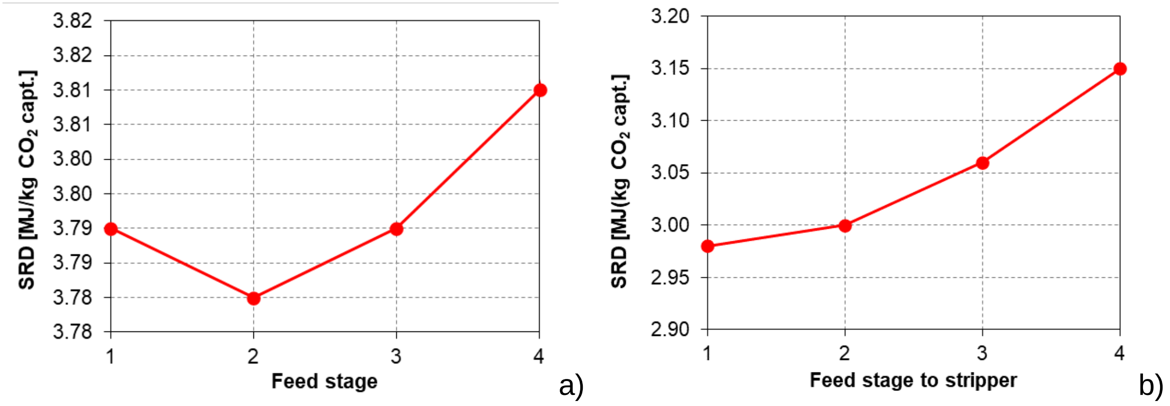


Figure 12. SRD variation as a function of the rich solvent feed stage to the stripper. Absorber, stripper packing height and lean loading are already set at the optimal values.

1.7.3.4 Stripper pressure

The SRD as well as the temperature reached in the stripper reboiler (maximum temperature reached process side in the CO_2 capture process) are gathered at different stripper operating pressures in a range between 1.6 and 2.2 bar. The results are available in Figure 13 and Figure 14 for MEA and HS3, respectively. As expected, the higher the stripper pressure the lower the SRD, but the higher the corresponding reboiler temperature. The maximum operating pressure that allows not to overcome the selected temperature threshold of 123°C in the reboiler is equal to 1.9 and 1.8 for MEA and HS3, respectively.

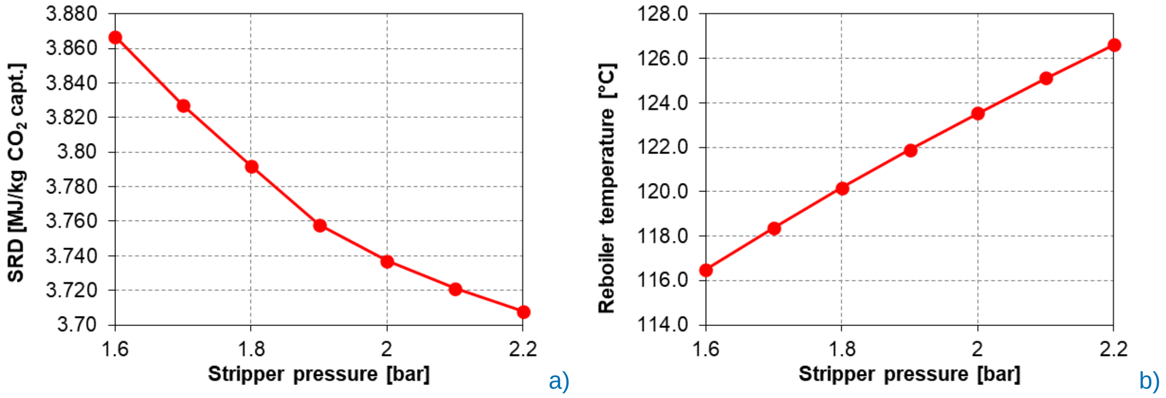


Figure 13. Plot of a) SRD and b) reboiler temperature as a function of the stripper operating pressure for MEA solvent. Packing heights, lean loading and feed stage to regeneration are set to the optimal values.

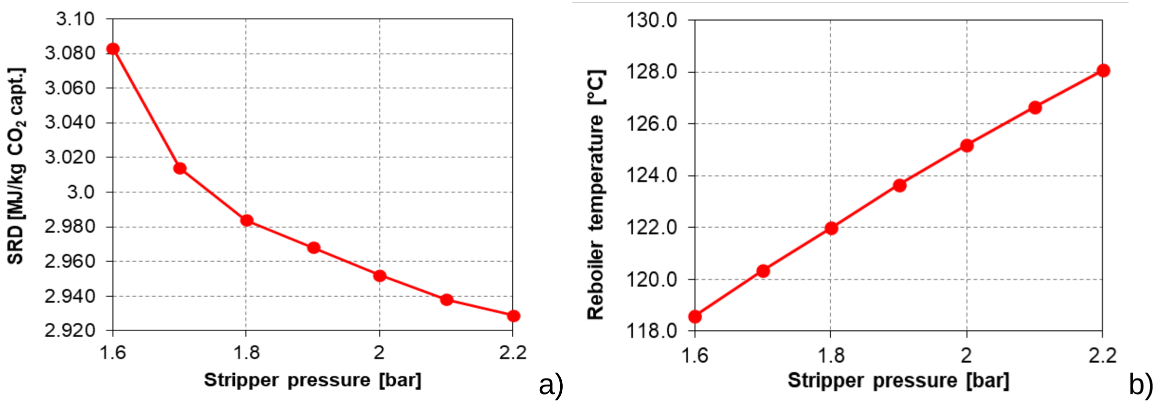


Figure 14. Plot of a) SRD and b) reboiler temperature as a function of the stripper operating pressure for HS3 solvent. Packing heights, lean loading and feed stage to regeneration are set to the optimal values.

1.7.3.5 Solvent feed temperature

SRD does not show variations above 1% if the lean solvent temperature is varied in a range between 35°C and 50°C, which is the typical solvent inlet temperature range considered for these applications (Adu et al., 2020; Li et al., 2016). On the other hand, it is anyway important to analyze the effect of the lean solvent temperature on other performance indicators, in particular the cooling water consumption in cooler E-1 and the volatile amine emissions, or in other words the residual amine content in the treated flue gas. It is remarkable that the other cooling water duties do not vary in a detectable way changing the lean solvent temperature. The residual amine content here reported refer to the gas immediately exiting the top of the absorber, since the estimation of the water-wash packing height required to meet the amine emission requirement will be carried out in a second step directly on the optimized plant configuration resulting from this sensitivity analysis.

For what concerns amine emissions, it is possible to notice that AP emissions are comparable to the MEA ones, while the amount of PRLD present in the treated flue gas is one order of magnitude higher concentration with respect to benchmark MEA. It is important to remark that the reported amine concentrations have a significant impact on the design of the water wash section, which is the reason why they should be limited as much as possible. Based on these considerations, the lean solvent temperature must be chosen to find a compromise between the cooling water consumption and the amine emissions, which are both linked to a potentially relevant increase in both investment and operating costs.

Results are reported Figure 15 and Figure 16. It is evident that the cooling water requirements start increasing much more rapidly if the set solvent inlet temperature is below 43°C. On the other hand, amine emissions grow almost linearly. Therefore, 43°C is kept as optimal feed solvent temperature.

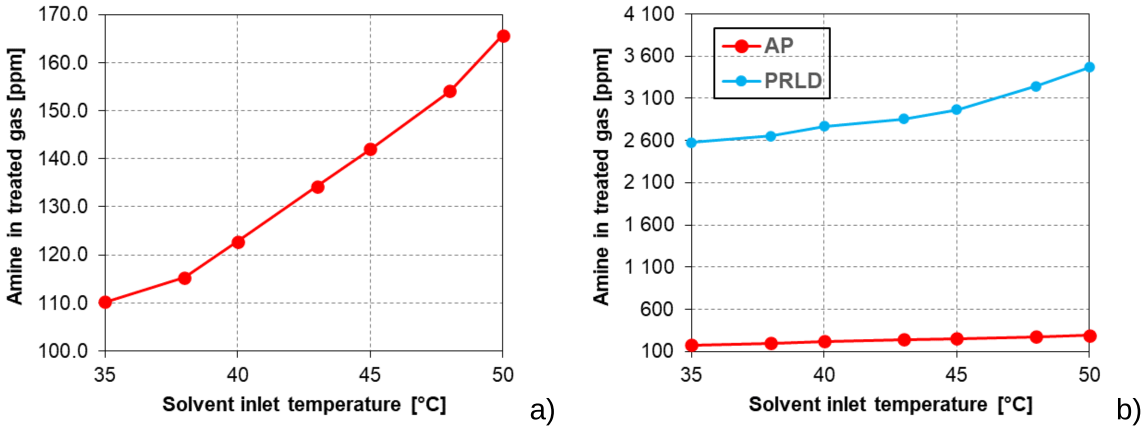


Figure 15. Residual amine concentration (in ppm vol) in the treated gas at different solvent inlet temperatures using a) MEA and b) HS3 solvent.

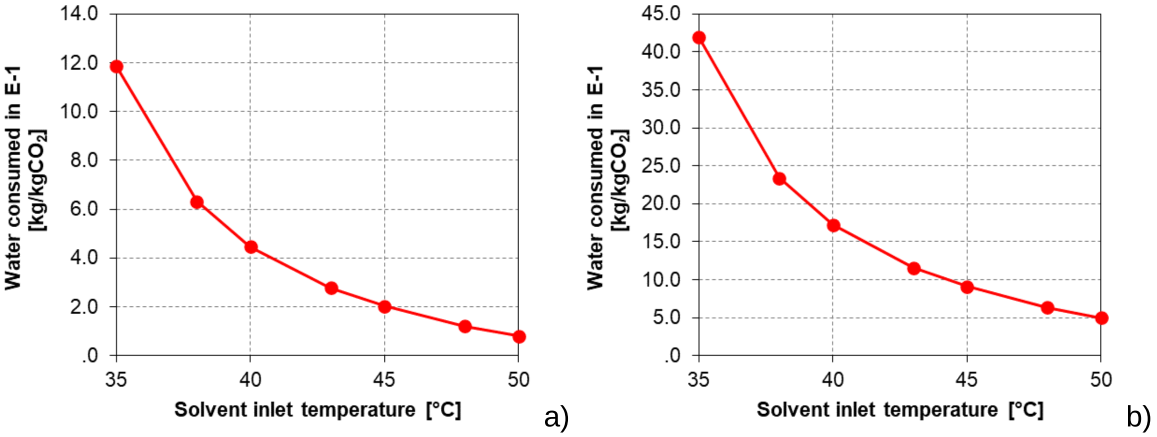


Figure 16. Cooling water consumption in solvent cooler (E-1) at different solvent inlet temperatures using a) MEA and b) HS3 solvent.

1.7.3.6 Summary

The optimal operating parameters and the key performance indicators (KPI) resulting from the sensitivity analysis are summarized in Table 10 for both HS3 and MEA. It is remarkable that, due to a slower kinetics, higher packing heights are necessary for HS3 solvent. On the other hand, the specific reboiler duty (SRD) and the solvent/gas (L/G) ratio (kg/kg) required to reach 90% capture for the optimal selected case are 23% lower using HS3. Moreover, the specific steam requirement (SSR), defined as the reboiler duty minus the heat recovered in the preliminary heat recovery section per unit of captured CO_2, can be reduced by over 57% using HS3.

Table 13. Results of the sensitivity analysis for the optimization of MEA and HS3-based CO_2 capture process for the treatment of the Irving oil refinery flue gas.

Optimal parameters	MEA	HS3	KPI	MEA	HS3
Lean loading [mol/mol]	0.24	0.07	L/G [kg/kg]	1.91	1.47
Absorber packing height [m]	10	18	SRD [MJ/kg CO_2]	3.77	2.98
Stripper packing height [m]	8	12	SSR [MJ/kg CO_2]	1.59	0.68
Desorber feed stage	2	1			
Desorber pressure [bar]	1.9	1.8			
Lean solvent temperature [°C]	43	43			

1.7.4 Capture plant performances and energy requirements: HS3 versus MEA

1.7.4.1 MEA

This section reports the results of the simulations of the CO_2 capture plant for the treatment of the Irving Oil flue gas in Aspen Plus, carried out adopting the optimal operating conditions resulting from the sensitivity analysis. In particular, the focus is on the estimation of the main equipment size and on the energy requirements. The collected results refer to both MEA and HS3 solvents, and a comparison between the two solvents based on energy requirements is also available.

The plant treats 280.31 ton/h of Irving Oil flue gas and an additional flow of 27.72 ton/h representing the flue gas generated by the steam boiler to meet the plant energy requirements. In other words, the increase in the total gas flow determined by the boiler contribution is 9.8%. The average flue gas CO_2 concentration prior (mixed stream) to saturation in the DCC is 7.2 mol%.

The amount of cooling water required to cool down the flue gas from 150°C assuming a 3°C approach temperature in the tower is 990.8 ton/h. This significant cooling water consumption is intrinsically determined by the high temperature gradient to be provided on the gas side. The column has a diameter of 6.8 m. The water stream recovered from the bottom of the unit reaches a temperature of 30°C, and it must be cooled back to 25°C by means of cooling water in E-4 before being recirculated back to the DCC. Being the flue gas water content higher with respect to the water saturation point, part of the water contained in the flue gas condenses inside the DCC. For this reason, the 0.5% of the water flow recovered at the bottom is purged from the cooling water loop. This purge corresponds to a flow of 21.22 ton/h, and it is made up almost by pure water, with only traces of condensed CO_2 (44 ppm), N_2 (9 ppm) and O_2 (0.9 ppm). Even if the purity level of this water could justify its use as make-up stream to avoid consuming fresh water as a make-up in the WW, this integration is not proposed in this work to avoid issues arising from the possible accumulation of impurities which can lead to a decreased efficiency of the washing section. Thanks to water condensation, the saturated flue gas has an increased CO_2 concentration of 7.98 mol%, which favors the capture efficiency.

The fan is designed to overcome the total pressure drop occurring on the flue gas side from the preliminary heat recovery until the top of the water-wash section. Indeed, it is essential to guarantee that the treated gas gets discharged to the atmosphere at a pressure at least equal to 1 atm. To consider a safety margin, the treated gas outlet pressure has been set to 1.05 bar.

As stated in the methodology section, the total pressure drops referred to the absorber and WW packing heights have been doubled to account for the fact that in the reality the column has much more complex layout and it is significantly higher with respect to the height simply referred to its packing. Based on the estimated pressure losses, the fan must compress the flue gas to 1.1 bar, with an electricity consumption of 1.845 MW. The outlet gas reaches a temperature of 50.41°C, which corresponds to the feed temperature to the absorber.

The solvent flow required to capture the 90% of the CO_2 content in the flue gas entering the absorber is 577.8 ton/h, corresponding to a L/G ratio equal to 2.01 and to a specific solvent flow of 18.39 ton solvent per each ton of captured CO_2.The solvent enriches in CO_2 along the column and reaches a rich loading of 0.506.Therefore, the available cycling is about 0.266 mol/mol amine (1.06 mol/kg solvent), which is compliant with the literature (Knuutila et al., 2019). The column has a packing height of 12 m, as stated from the sensitivity analysis, and a diameter of 5.86 m. Figure 17 shows the temperature profile and the variation of the CO_2 mole fraction in the vapor phase inside the column. The profile is in accordance with the theory of exothermic reactions and compliant with experimental observations on plants operating with MEA (Montañés et al., 2017; Nookuea et al., 2016). An irregular profile shape can be noticed for the very last few pacing meters: the vapor phase temperature reaches a minimum and then slightly increases again to comply with the vapor feed temperature. A possible explanation for this trend is the water evaporation taking place inside the column as a result of heat released by the reaction.

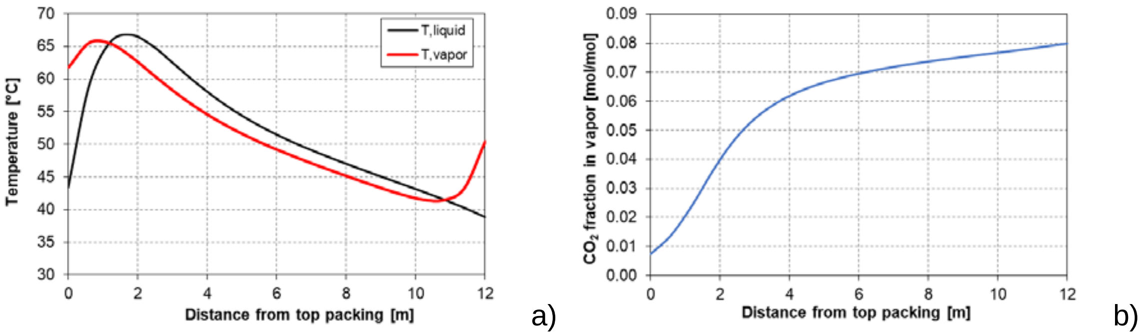


Figure 17. a) Temperature profile and b) CO_2 content in the vapor phase profile inside the absorber. Results from the simulation in Aspen Plus using MEA default model.

The maximum flowrate of circulating water inside the WW loop to fulfill the specified criterion on the flooding velocity approach percentage is 693 ton/h (22.1 ton/ton CO_2 captured). Under such operating conditions, a minimum packing height of 2.15 m is necessary to reach a residual MEA content in the treated gas of 5 pm. The chart in Figure 18 indicates how the mole fraction of MEA in the vapor phase reduces progressively along the WW packing height until it reaches the specified threshold.

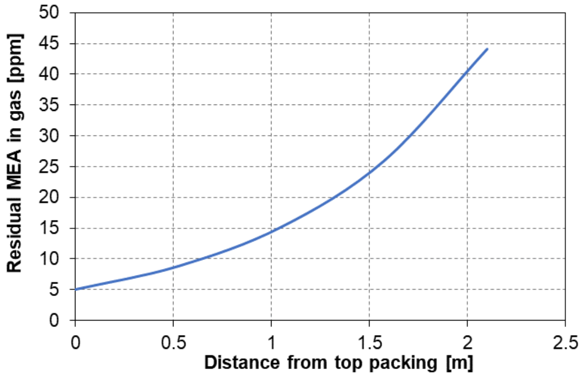


Figure 18. Progressive reduction of the residual MEA content in the treated flue gas at increasing water wash packing heigh. Results from the Aspen Plus simulation using MEA default package.

The CO_2 enriched solvent recovered from the bottom of the absorber is pumped to 4.25 to overcome the pressure drops of 0.35 bar in HR-11 and the 20 m of elevation gain required to feed the solvent to the stripper. Downstream of the pump, the solvent reaches a temperature of 38.97°C. This stream is preheated before entering the desorber in HR-11, by countercurrent heat exchange with the lean solvent recovered from the bottom of the stripper, which is available at 122°C. This technological solution allows to recover 38.19 MW of heat, thus significantly reducing the energy requirements inside the stripper itself. The preheated rich solvent stream reaches a temperature of 112.57°C, which is suitable for its feed to the stripper; at the same time, the lean solvent is cooled down to 49°C. This provides an additional beneficial effect on the overall cooling water consumption in the plant, since only a limited external duty still needs to be provided to further cool the lean solvent down to the absorber inlet temperature.

HR-11 has been designed in Aspen EDR® considering a shell and tube exchanger type. Details on the optimal geometry are reported in Table 14, together with a schematic design of the exchanger itself in Figure 19. In compliance with the sizing discussed for the preliminary heat recovery section, this analysis aims at providing an estimation of the space requirements for this heat exchanger.

Table 14. Geometry of the HR-11 exchanger for rich-lean solvent heat recovery sized using Aspen EDR®.

Sizing indicator	Value
Number of tubes	4723
Number of passes	1
Tube length [m]	6
Tube ext. diam. [mm]	19
Shell ext. diam. [m]	1.8
Specification	10°C approach temperature

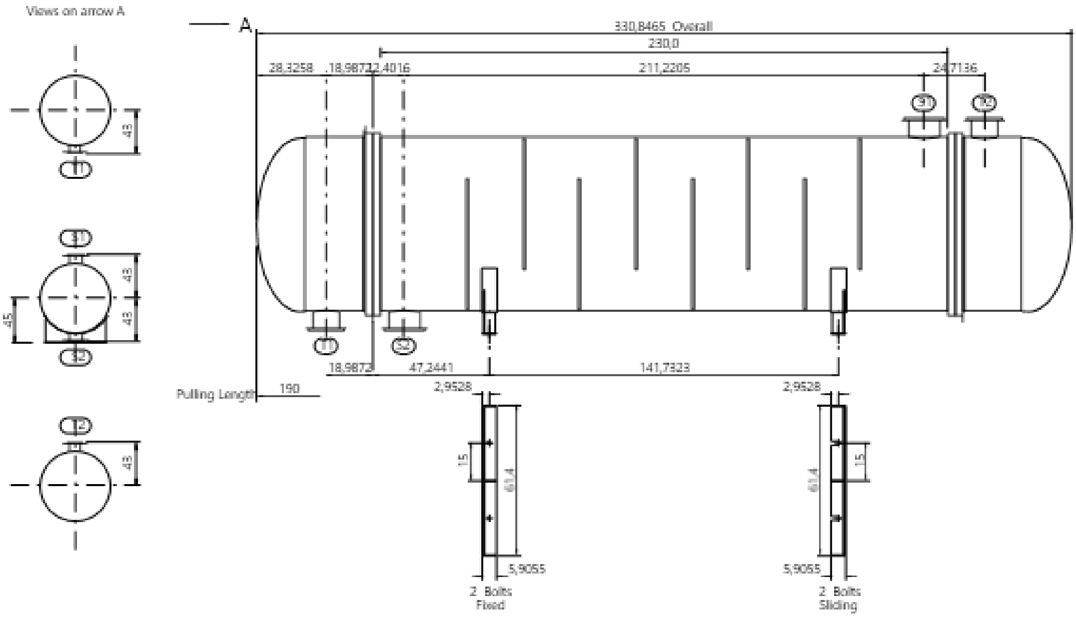


Figure 19. Schematic draw of the sizing of HR-11 with Aspen EDR®.

The stripper releases the CO_2 absorbed in the solvent so that the original lean loading of 0.24 is restored and the solvent is ready for recirculation. This column has a packing height of 10 m, while the estimated required diameter is 3.12 m. The condenser and reboiler duties are 10.51 and 33.05 MW, respectively. Therefore, the specific reboiler duty is 3.78 MJ/kg of captured CO_2. The temperature profiles inside the column as well as the variation of the CO_2 content (vol%) which is progressively released in the gaseous phase are shown in Figure 20.

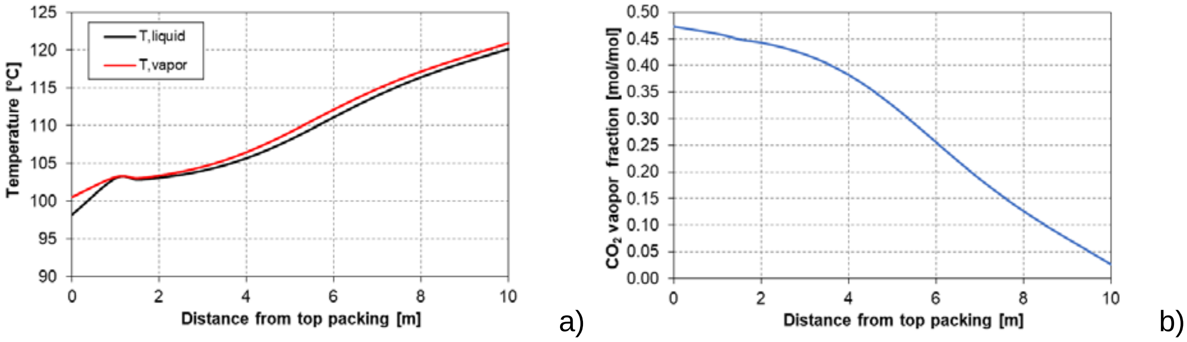


Figure 20. a) Temperature profile and b) CO_2 content in the vapor phase profile inside the desorber. Results from the simulation in Aspen Plus using MEA default model.

The released CO_2 flow is equal to 31.42 ton/h. It is important to underline that the CO_2-rich stream recovered from the stripper has a molar purity of 97.7%, with the remaining 2.3% which is made up of water. MEA's content is negligible (order of 10^{-11}), and only traces of dissolved nitrogen and oxygen in the order of ppm are present. However, the residual water can be easily separated when further reducing the stream temperature due to the huge difference in the boiling points. This means that the process allows the recovery of high-quality CO_2, whose purity already meets the requirements for the majority of applications, including transportation and storage in depleted oil and gas fields. For example, Ghaffar et al. (Ghaffar et al, 2016) indicate a CO_2 purity of 95.5% as specification for enhanced oil recovery applications. This value is in line with the guidelines provided by NETL (National Centres for Environmental Information, accessed April 2023) concerning CO_2 pipeline transportation, EOR or saline aquifer storage. Remarkably, the obtained CO_2 purity is another important index beside the energy requirements for a comprehensive comparison between MEA and HS3. We clarify that the design and costs estimation for the CO_2 compression and transportation systems is out of the scope of this contribution.

1.7.4.1.1 Materials and energy streams summary

With reference to the simplified process flow diagram drawn in Figure 21, the main process streams characterization in terms of temperature, pressure, molar and mass flowrate is available in Table 15AA. The streams molar composition is gathered in Table 15B.

It is remarkable that a consistent stream numbering and layout characterization will be also adopted by *Pentair* for the evaluation of the fixed, investment and total plant costs (D3.3) based on the outcomes of the Aspen Plus® simulations presented in this report.

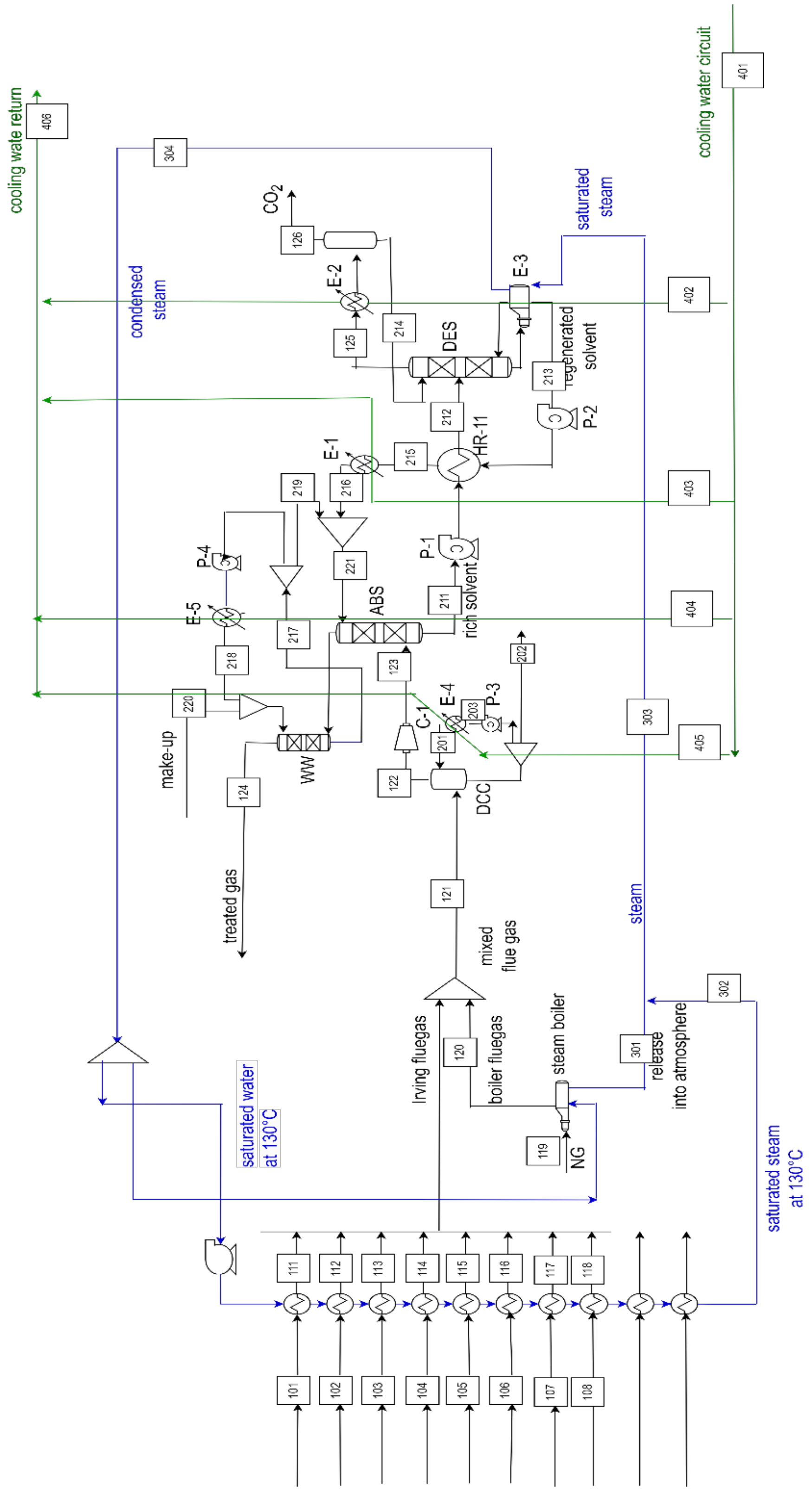


Figure 21. Process flow diagram for the CO_2 capture plant simulated in Aspen Plus for the treatment of the Irving oil refinery flue gas. All the main process streams are identified with a progressive number and a colour: material streams (black), steam circuit (blue) and cooling water circuit (green).

Table 15A. Streams characterization for the costs analysis: temperature, pressure, phase, mass and molar flows.

Stream	101	102	103	104	105	106	107	108	111
Temperature [°C]	290	395	375	500	425	290	385	180	150
Pressure [bar]	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	0.91
Mass flow [ton/h]	13.32	27.84	35.93	13.56	25.31	96.29	457.46	22.28	13.32
Mole flow [kmol/h]	474.6	995.8	1261.6	483.6	924.0	3462.4	1657.3	790.1	474.6
Stream	112	113	114	115	116	117	118	119	120
Temperature [°C]	150	150	150	150	150	150	150	25	150
Pressure [bar]	0.91	0.91	0.91	0.91	0.91	0.91	0.91	1.01	1.01
Mass flow [ton/h]	27.84	35.93	13.56	25.31	96.29	457.46	22.28	1.50	27.73
Mole flow [kmol/h]	995.8	1261.6	483.6	924.0	3462.4	1657.3	790.1	83.51	998.10
Stream	121	122	123	124	125	126	201	202	203
Temperature [°C]	150.00	28.00	50.41	32.17	100.54	30.00	25.00	47.07	47.07
Pressure [bar]	0.91	0.91	1.10	1.06	1.89	1.90	1.01	3.00	3.00
Mass flow [ton/h]	308.04	286.82	286.82	255.73	45.77	31.72	990.89	21.22	990.89
Mole flow [kmol/h]	11047.6	9872.26	9872.26	9178.58	1508.03	730.74	55002.76	1177.72	55000.33

Stream	211	212	213	214	215	216	217	218	219
Temperature [°C]	38.87	112.56	121.93	30.00	48.97	43.00	50.70	25.00	50.70
Pressure [bar]	1.10	3.90	1.90	1.90	1.55	1.10	1.06	1.06	1.06
Mass flow [ton/h]	581.19	581.19	549.48	14.04	549.48	549.48	720.66	692.35	28.31
Mole flow [kmol/h]	22490.56	22529.43	22473.26	776.99	22473.26	22473.26	39988.35	38417.22	1571.05
Stream	220	221	301	302	303	304	401	402	403
Temperature [°C]	25.00	43.49	130	130	130	130	20	20	20
Pressure [bar]	1.01	1.06	2.66	2.66	2.66	2.66	1.01	1.01	1.01
Mass flow [ton/h]	0.81	577.76	24.65	30.09	54.74	54.74	3414.9	602.6	176.7
Mole flow [kmol/h]	45.18	24039.86	1369.1	1671.7	3040.89	3040.89	1.90e5	3.35e4	9.82e3
Stream	404	405	406						
Temperature [°C]	20	20	35						
Pressure [bar]	1.01	1.01	1.01						
Mass flow [ton/h]	1181.1	1454.6	3414.9						
Mole flow [kmol/h]	6.56e4	8.08e4	1.90e5						

Table 15B. Streams characterization for the costs analysis: molar composition. For liquid streams, the apparent composition is reported. Data refer to MEA solvent.

Stream	101	102	103	104	105	106	107	108	111
H_2O	0.1398	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.1398
CO_2	0.0810	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0810
N_2	0.7392	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.7392
O_2	0.0400	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0400
Stream	112	113	114	115	116	117	118	119	120
H_2O	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.0000	0.1674
CO_2	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0000	0.0837
N_2	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.0000	0.7238
O_2	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0000	0.0251
CH_4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
Stream	121	122	123	124	125	126	201	202	203
H_2O	0.1437	0.0420	0.0420	0.0476	0.5256	0.0229	1.0000	1.0000	1.0000
CO_2	0.0720	0.0804	0.0804	0.0085	0.4741	0.9769	0.0E+00	2.46E-05	2.46E-05
N_2	0.7453	0.8340	0.8340	0.8970	0.0001	0.0002	0.0E+00	6.48E-06	6.48E-06
O_2	0.0390	0.0437	0.0437	0.0470	8.12E-06	1.68E-05	0.0E+00	6.31E-07	6.31E-07
MEA (trace)	0.0000	0.0000	0.0000	4.9E-06	0.0002	1.11E-11	3.57E-09	9.13E-07	9.13E-07
Stream	211	212	213	214	215	216	217	218	219
MEA	0.11323	0.11306	0.11662	0.00039	0.11668	0.11669	0.00010	0.00010	0.00010
H_2O	0.82959	0.82985	0.85537	0.99825	0.85530	0.85528	0.99985	0.99985	0.99985
CO_2	0.05717	0.05709	0.02801	0.00136	0.02802	0.02802	0.00005	0.00005	0.00005
Loading	0.505	0.505	0.240	3.524	0.240	0.240	0.541	0.541	0.541
Stream	220	221							
MEA	0.00000	0.10934							
H_2O	1.00000	0.86442							
CO_2	0.00000	0.02624							
Loading	-	0.240							

The duties of the plant including steam, electricity and cooling water are summarized in Table 16. Steam and cooling water are associated to the higher duties. The most impactful utility costs is the one associated to steam. To this aim, it is worth pointing out that the preliminary heat recovery section (18.17 MW heat recovery) allows to reduce the reboiler duty to be provided by an external utility by over 55% (see Table 17).

Table 17. Summary of total and specific reboiler duties and portion of the duty to be provided by an external heat source.

Reboiler duty [MW]	33.05
External duty [MW]	14.88
SRD [MJ/kg CO_2]	3.78
SSR [MJ/kg CO_2]	1.70

Therefore, even if the specific reboiler duty is 3.78 MJ/kg CO_2, the steam boiler must provide only 14.88 MW (1.70 MJ per every kg of carbon dioxide). In other words, considering that steam is supposed to e available at saturation conditions at 130°C, the steam generation requirement of the plant is 24.6 ton/h, corresponding to 0.78 ton/ton CO_2 captured.

For what concerns electricity consumption, the fan plays the key role, being responsible for the 91% of the overall electricity requirements. This result can be justified considering that, the pressure drops on the flue gas side are a significant contribution, even enhanced by the plant configuration adopted for this plant. Indeed, the preliminary heat recovery section allows a great steam saving, but at the expense of almost a 50% increase in the flue gas pressure drops.

Despite the high cooling duties of this plant, cooling water is a lower concern thanks to its low cost. As expected, the main cooling water consumption occurs inside the DCC and WW loops because of the high circulating flowrates on the process side.

Table 16. Summary of all the duties (in MW) of the MEA-based CO_2 capture plant.

Equipment	Utility	Duty [MW]
Reboiler (E-3)	Steam	33.05
Fan (C-1)	Electricity	1.845
Pump P-1	Electricity	0.05
Pump P-2	Electricity	0.03
Pump P-3	Electricity	0.06
Pump P-4	Electricity	0.04
Cooler E-1	Cooling water	3.08
Condenser E-2	Cooling water	10.51
Cooler E-4	Cooling water	25.37
Cooler E-5	Cooling water	20.61

Table 17. Summary of total and specific reboiler duties and portion of the duty to be provided by an external heat source.

Reboiler duty [MW]	33.05
External duty [MW]	14.88
SRD [MJ/kg CO_2]	3.78
SSR [MJ/kg CO_2]	1.70

1.7.4.2 HS3

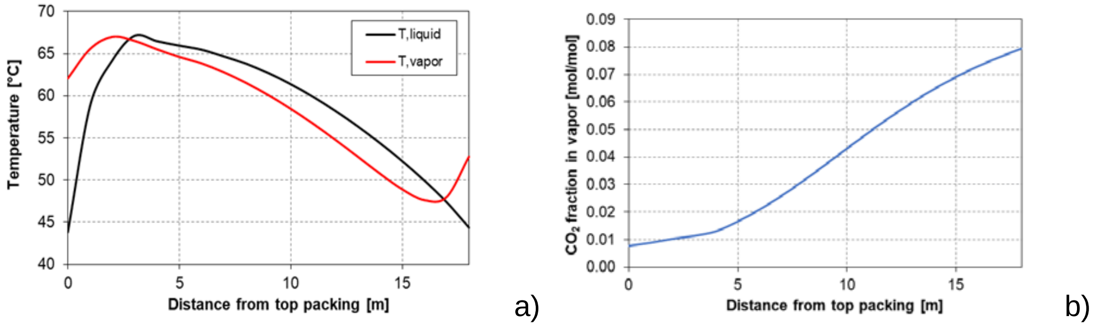
The plant treats the same Irving Oil flue gas flow which was considered for the MEA case study and an additional flow of 11.63 ton/h representing the flue gas generated by the steam boiler to meet the plant energy requirements. With respect to the MEA-based plant, the steam boiler flue gas flow is cut by 56%. This stream represents only the 4.27% of the total gas flow to be treated, and the 4.7% of the CO_2 fed to the capture plant.

The amount of cooling water required to cool the flue gas from 150°C down to 28°C is 934.8 ton/h. The column has a diameter of 6.5 m. Being the flue gas water content higher with respect to the water saturation condition at 28°C, also using HS3 solvent part of the water contained in the flue gas condenses inside the DCC. For this reason, the 2.1% of the water flow recovered at the bottom is purged from the cooling water loop. This purge corresponds to a flow of 19.9 ton/h (0.71 ton/ton CO_2 capt.), and it is made up almost by pure water, with only traces of condensed CO_2 (26 ppm mol), N_2 (7 ppm) and O_2 (26 ppm). The purge composition is comparable to the one obtained using MEA, and the same consideration on its exploitability still apply for the HS3 solvent.

The criteria adopted for the pressure drops estimation are compliant with the ones adopted for MEA for the sake of consistency. Based on the estimated pressure losses, the fan must compress the flue gas to 1.125 bar, with an electricity consumption of 1.93 MW. The increase in the pressure drop occurs both in the absorber and in the WW, and it is caused by the higher packing height. The outlet gas reaches a temperature of 52.76°C, which is close to the optimal feed temperature to the absorber for HS3 solvent.

The solvent flow required to capture the 90% of the CO_2 content in the flue gas entering the absorber is 438.3 ton/h, corresponding to a L/G ratio of 1.61 and to a specific solvent flow of 14.87 ton of solvent per each ton of captured CO_2. This means that the same capture rate for a given flue gas stream can be achieved with a 23% lower solvent circulating flow. The solvent enriches in CO_2 along the column and reaches a rich loading of 0.357. Therefore, the available cycling capacity is 0.287 mol/mol amine (1.08 mol/kg solvent), which is 8% higher with respect to the cycling capacity obtained for MEA. This observation is compliant with the reduction observed in the specific solvent flow requirement. The column has a packing height of 18m, as stated from the sensitivity analysis, and a diameter of 5.6 m.

Figure 22 shows the temperature profile and the variation of the CO_2 mole fraction in the vapor phase inside the column. The profile is qualitatively compliant with experimental observations collected on the Tiller plant. The temperature profile inside the column shows a peak temperature which is comparable to the one estimated for MEA. On the other hand, the temperature decrease towards the bottom of the column is definitely slower, which may be associates to the slower CO_2 absorption kinetics. Indeed, also the progressive reduction of the CO_2 content in the gas is slower and distributed more or less at the same extent throughout the whole column, whereas it is more rapid towards the top of the packing when MEA is used.



a) b)

Figure 22. a) Temperature profile and b) CO_2 content in the vapor phase profile inside the absorber. Results from the simulation in Aspen Plus using the HS3 model developed in this work.

A packing height of 4.9 m is necessary to reach a residual total amine content (AP + PRLD) in the treated gas of 5 pm. This is undoubtedly a disadvantage related to the innovative solvent, since a more than double WW packing height is expected to generate in a relevant increased capital cost. The reason for this relevant difference with respect to the benchmark is determined by the different volatility of the tested amines. Indeed, while AP and MEA have a similar vapor pressure at 60°C (representative of the operating conditions inside the column), PRLD has a significantly higher vapor pressure resulting in larger amine evaporation within the column and one order of magnitude higher residual PRLD content in the treated gas leaving the absorber itself. In fact, the vapor pressure obtained using the Antoine equation implemented in Aspen Plus® for the three amines is 1.52 mbar, 2.24 mbar and 8.1 mbar for MEA, AP and PRLD, respectively.

The chart in Figure 23 indicates how the mole fraction of MEA in the vapor phase reduces progressively along the WW packing height until it reaches the specified threshold. A discretization step of 1 m packing was considered for this analysis.

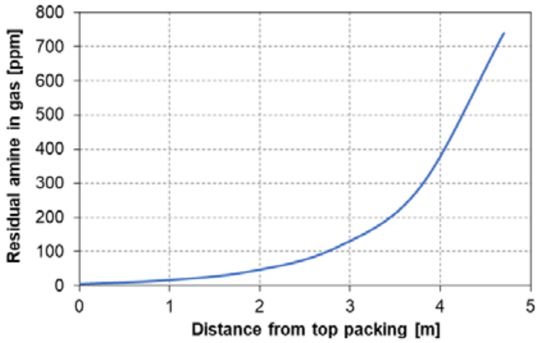


Figure 23. Progressive reduction of the residual total amines content in the treated flue gas at increasing water wash packing heigh. Results from the Aspen Plus simulation using the HS3 model developed in this work.

The CO_2 enriched solvent recovered from the bottom of the absorber is pumped to 4.95 bar. This pressure is 0.8 bar higher with respect to the one imposed for the simulation with MEA because of the higher elevation gain required to feed the solvent to the stripper, which has a 4 m higher packing height. The rich solvent is preheated to 109.2°C in HR-11before entering the desorber, by countercurrent heat exchange with the lean solvent recovered from the bottom of the stripper, which is available at 122°C and gets cooled down to 59.2°C. This technological solution allows to recover 23.81 MW of heat, thus significantly reducing the energy requirements inside the stripper itself. The heat recovery is lower than the one obtainable using MEA since the rich solvent leaves the absorber at a higher temperature (42.23°C). As a consequence, also the size of the heat exchanger is lower in terms of shell diameters and required number of tubes.

HR-11 has been designed in Aspen EDR® considering a shell and tube exchanger type. Details on the optimal geometry are reported in Table 18, together with a schematic design of the exchanger itself in Figure 24. In compliance with the sizing discussed for the MEA-based case-study, this analysis aims at providing an estimation of the space requirements for this heat exchanger.

Table 18. Geometry of the HR-11 exchanger for rich-lean solvent heat recovery with HS3 solvent sized using Aspen EDR®.

Sizing indicator	Value
Number of tubes	3956
Number of passes	1
Tube length [m]	5.4
Tube ext. diam. [mm]	19
Shell ext. diam. [m]	1.65
Specification	10°C approach temperature

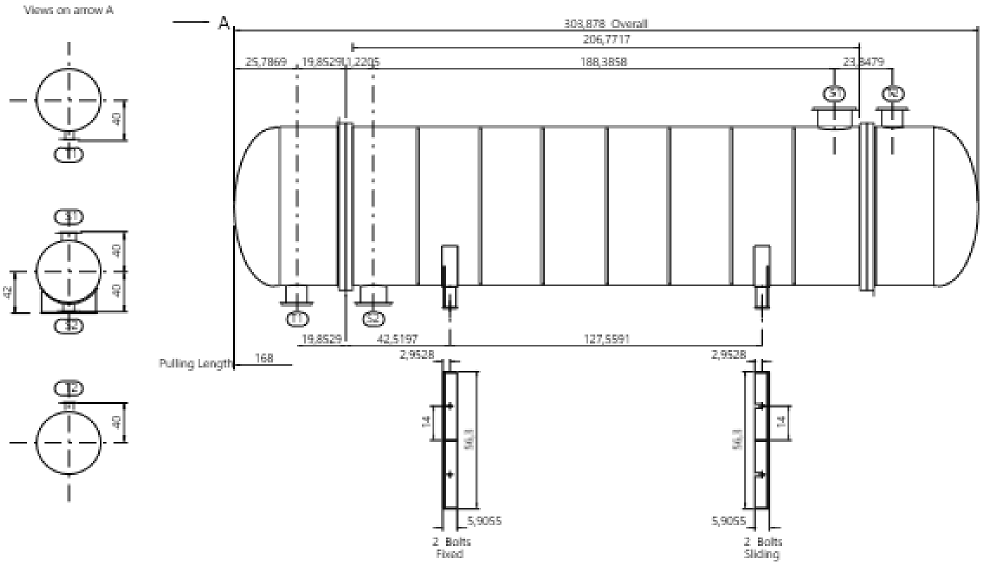


Figure 24. Schematic draw of the sizing of HR-11 for HS3 solvent with Aspen EDR®.

The stripper releases the CO_2 absorbed in the solvent so that the original lean loading of 0.07 is restored and the solvent is ready for recirculation. This column has a packing height of 14 m (4 m higher with respect to MEA), while the estimated required diameter is 2.69 m (-14%). The condenser and reboiler duties are 5.73 and 24.45 MW, respectively. Therefore, the specific reboiler duty is 2.984 MJ/kg of captured CO_2, with an appreciable reduction of 21%

with respect to the SRD calculated for MEA 30wt%. Details of the temperature profile inside the column as well as the variation of the CO_2 content (vol%) which is progressively released in the gaseous phase are drawn in Figure 25. The trends are comparable to the MEA ones and smooth: this is another evidence of the stability and reliability of the HS3 model proposed in this work.

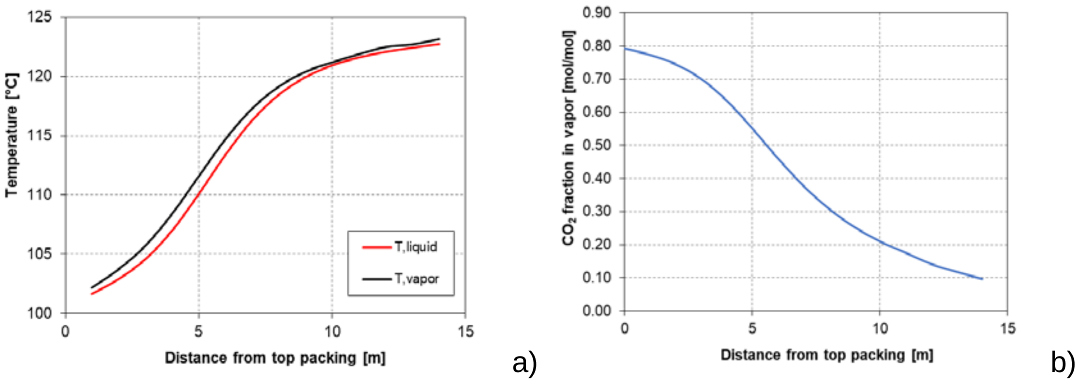


Figure 25. a) Temperature profile and b) CO_2 content in the vapor phase profile inside the desorber. Results from the simulation in Aspen Plus using the HS3 model developed in this work.

The released CO_2 flow is equal to 29.49 ton/h, lower with respect to total the CO_2 recovered in the simulation with the benchmark solvent due to the lower flue gas flow treated from the steam boiler. It is important to underline that the CO_2-rich stream recovered from the stripper has a molar purity of 97.6%, which is totally comparable to the purity associated with the benchmark operation. Thus, from the CO_2 product stream quality point of view the two solvents show the same features.

1.7.4.2.1 Material and energy streams summary

With reference to the simplified process flow diagram drawn in Figure 21, the main process streams characterization in terms of temperature, pressure, molar and mass flowrate is available in Table 19AA. The corresponding streams molar composition is gathered in Table 19B together with the CO_2 loading.

Table 19A. Streams characterization for the costs analysis: temperature, pressure, phase, mass and molar flows: data for the HS3 solvent.

Stream	101	102	103	104	105	106	107	108	111
Temperature [°C]	290	395	375	500	425	290	385	180	150
Pressure [bar]	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	0.91
Mass flow [ton/h]	13.32	27.84	35.93	13.56	25.31	96.29	457.46	0.64	13.32
Mole flow [kmol/h]	474.6	995.8	1261.6	483.6	924.0	3462.4	1657.3	39.80	474.6
Stream	112	113	114	115	116	117	118	119	120
Temperature [°C]	150	150	150	150	150	150	150	25	150
Pressure [bar]	0.91	0.91	0.91	0.91	0.91	0.91	0.91	1.01	1.01
Mass flow [ton/h]	27.84	35.93	13.56	25.31	96.29	457.46	22.28	1.27	11.63
Mole flow [kmol/h]	995.8	1261.6	483.6	924.0	3462.4	1657.3	790.1	79.07	418.62
Stream	121	122	123	124	125	126	201	202	203
Temperature [°C]	150.00	28.00	52.76	35.13	102.13	30.0	25.00	46.97	46.98
Pressure [bar]	0.91	0.91	1.12	1.06	1.79	1.8	1.01	3.00	3.00
Mass flow [ton/h]	291.95	272.06	272.06	242.69	37.56	29.79	934.84	19.88	934.84
Mole flow [kmol/h]	10468.3	9367.8	9367.8	8708.1	1085.07	686.7	51891.7	1013.6	51888.6

Stream	211	212	213	214	215	216	217	218	219
Temperature [°C]	44.36	109.22	124.00	30.00	59.23	43.00	52.24	25.00	52.24
Pressure [bar]	1.12	4.60	1.80	1.80	1.45	1.06	1.06	1.06	1.06
Mass flow [ton/h]	448.92	448.92	419.13	7.77	419.13	419.13	463.75	445.15	18.60
Mole flow [kmol/h]	12110.71	12115.72	12094.30	393.18	12094.03	12094.02	25637.13	24608.67	1028.43
Stream	220	221	301	302	303	304	401	402	403
Temperature [°C]	25.00	43.81	130	130	130	130	20	20	20
Pressure [bar]	1.01	1.06	2.66	2.66	2.66	2.66	1.01	1.01	1.01
Mass flow [ton/h]	0.65	437.73	10.40	30.10	40.50	40.50	2833.4	328.5	333.7
Mole flow [kmol/h]	36.18	13122.45	580	1672.2	2250.0	2250.0	1.57e5	1.83e4	1.85e4
Stream	404	405	406						
Temperature [°C]	20	20	35						
Pressure [bar]	1.01	1.01	1.01						
Mass flow [ton/h]	802.7	1368.6	2833.4						
Mole flow [kmol/h]	4.45e4	7.60e4	1.57e5						

Table 19B. Streams characterization for the costs analysis: molar composition. For liquid streams, the apparent composition is reported. Data refer to HS3 solvent

Stream	101	102	103	104	105	106	107	108	111
H_2O	0.1398	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.1398
CO_2	0.0810	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0810
N_2	0.7392	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.7392
O_2	0.0400	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0400
Stream	112	113	114	115	116	117	118	119	120
H_2O	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.0000	0.1674
CO_2	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0000	0.0837
N_2	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.0000	0.7238
O_2	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0000	0.0251
CH_4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000
Stream	121	122	123	124	125	126	201	202	203
N_2	0.7465	0.8341	0.8341	0.8973	3.03E-05	4.79E-05	0.0000	6.49E-06	6.49E-06
CO_2	0.0713	0.0795	0.0795	0.0083	0.6226	0.9757	0.0000	2.47E-05	2.47E-05
H_2O	0.1424	0.0420	0.0420	0.0467	0.3725	0.0240	1.0000	0.9999	0.9999
AP (traces)	0.0000	0.0000	0.0000	3.0E-07	0.001144	1.75E-11	0.0000	0.0000	0.0000
PRLD (traces)	0.0000	0.0000	0.0000	4.0E-06	0.003633	3.65E-09	0.0000	0.0000	0.0000
O_2	0.0398	0.0443	0.0443	0.0477	0.0001	0.0002	0	2.51E-05	2.51E-05
Stream	211	212	213	214	215	216	217	218	219
CO_2	0.06451	0.0645	0.01348	0.01378	0.01354	0.01355	0.00035	0.00035	0.00035
H_2O	0.75387	0.7537	0.79448	0.97321	0.79363	0.79342	0.99902	0.99902	0.99902
AP	0.06644	0.0665	0.07025	0.00312	0.07054	0.07061	0.00008	0.00008	0.00008
PRLD	0.11518	0.1153	0.12178	0.00990	0.12229	0.12241	0.00055	0.00055	0.00055
Loading	0.355	0.355	0.070	1.059	0.070	0.070	0.561	0.561	0.561
Stream	220	221							
MEA	0.0000	0.0125							
H_2O	0.99994	0.8090							
CO_2	3.00E-06	0.0652							
Loading	0.00006	0.1133							

The duties of the plant including steam, electricity and cooling water are summarized in Table 20 and Table 21. It is remarkable that the duty associated to external steam consumption for HS3 solvent regeneration is almost 58% lower with respect to the one calculated for MEA. Indeed, approximately 6 MW need to be provided by natural gas burning in the steam boiler, namely just 0.77 MJ per every kg of carbon dioxide. Considering that steam is supposed to be available at saturation conditions at 130°C, the steam generation requirement of the plant is limited to 10.4 ton/h, corresponding to 0.35 ton/ton CO_2 captured. The preliminary heat recovery exchangers network increases appreciably its beneficial impact on steam consumption containment: when HS3 is used, almost 75% of the total reboiler duty is in fact provided by means of heat recovery.

The fan and pumps duties are comparable the ones calculated for MEA due to the compensation of two effects: the duty increase determined by the higher required compression ratio is partly compensated by the 6% decrease in the mass flowrate of the stream passing through the fan.

Also the cooling water consumption is reduced with respect to the benchmark solvent case-study. The main reason is the lower total gas and solvent circulating flowrates and, for what concerns the DCC, also the higher set approach temperature between the cooling water and the flue gas.

Table 20. Summary of all the duties (in MW) of the HS3-based CO_2 capture plant.

Equipment	Utility	Duty [MW]
Reboiler (E-3)	Steam	24.45
Fan (C-1)	Electricity	1.93
Pump P-1	Electricity	0.04
Pump P-2	Electricity	0.04
Pump P-3	Electricity	0.05
Pump P-4	Electricity	0.02
Cooler E-1	Cooling water	5.82
Condenser E-2	Cooling water	5.73
Cooler E-4	Cooling water	23.87
Cooler E-5	Cooling water	14.04

Table 21. Summary of total and specific reboiler duties and portion of the duty to be provided by an external heat source.

Reboiler duty [MW]	24.45
External duty [MW]	6.28
SRD [MJ/kg CO_2]	2.98
SSR [MJ/kg CO_2]	0.77

1.7.4.3 Summary: HS3 versus MEA

A list of the main advantages and disadvantages of HS3 with respect to the benchmark CO_2 capture solvent is reported in Table 22, summarizing the observations on the results presented in the last two sections. The comparison leads to the conclusion that HS3 allows a significant reduction in the energy requirements (both SRD and SSR), which is expected to impact appreciably on the operating costs. For what concerns the equipment sizing, which is a key indicator of the plant investment costs, it is necessary to balance two opposite effects: on the one hand, the lower circulating solvent flows guarantee the need for a lower diameters of the columns and heat exchange areas for the exchangers, but, on the other hands, a relevant increase in the packing heights of all the columns (absorber, water wash and stripper) must be taken into account.

A costs estimation is necessary to turn this qualitative comparison into a quantitative techno-economic assessment of the expected benefits arising from the implementation of the new HS3 solvent on a large-scale CO_2 capture application. However, this work limits the discussion to the equipment sizing and energy analysis. The comparative techno-economic assessment is not included in this report, since it will be the core of the following WP3 deliverable (D3.3), to be disclosed in the next months (July 2023). It is worth remarking that the TEA will exploit as a milestone the Aspen Plus MEA and HS3 simulations here presented, making directly reference to the proposed unit operation sizing and energy requirements. Thus, the two works are complementary, leading towards an optimal design solution for CO_2 capture at Irving Oil Whitegate refinery.

Table 22. Summary of the main advantages and disadvantages of HS3 solvent with respect to benchmark MEA according to the results of the equipment sizing and energy requirements analysis.

HS3 advantages	HS3 disadvantages	Equal performance
24% lower solvent flow and 19% lower L/G (1.62 vs 1.995)	Slower kinetics	Same capture rate
26% lower reboiler duty (24.45 MW vs 33.05 MW)	Higher column packing heights (+50% for absorber)	Purity of the product CO_2 stream (>97%)
Lower specific energy requirements (21% lower SRD)	Higher volatility (higher water wash section packing required)	Comparable pressure drops
Higher fraction of steam generated in the preliminary heat recovery section with respect to the total reboiler steam requirements (45% lower SSR)	Higher initial solvent cost	No need for water make-up according to the adopted configuration
Lower absorber and stripper diameters		Same plant layout (same number and type of unit operations)
Lower heat exchange surfaces due to both lower flue gas flow treated and lower solvent circulating flow.		

2 The Cork cluster: potential for integrated CO_2 capture

2.1 Introduction

The energy analysis carried out for the Irving Oil Whitegate refinery CO_2 capture plant has shown that the steam demand is responsible for a remarkable increase in the total costs. Internal heat recoveries have been considered to minimize the amount of steam to be produced on the Irving Oil site, but the residual heat available in process streams cannot be sufficient to meet the total steam needs of the capture plant. Even if the design of a steam boiler is an effective way to compensate this remaining steam demand, the preliminary cost estimate carried out to compare the two proposed different heat recovery schemes has shown that it considerably affects the total investment costs of the plant. Therefore, it is worth considering alternative energy integration options that could somehow eliminate the need to generate steam directly on the Irving Oil site just for the purpose of running the flue gas treatment plant, thus we no economic benefit arising from the production of a sellable product. A reasonable way to look into this problem is taking into account the geographical location of the plant, in order to investigate some potential steam providers located at short distance from the refinery.

Figure 26 shows an overhead view of the Irving Oil Whitegate Refinery area. The map shows the presence of two NGCC power station located at short distance from the oil refinery: The Aghada Generating Station run by ESB (ESB CCGT in the map) and the Whitegate Power Station run by BGE (BGE CCGT in the map). Google maps tool has been exploited to estimate the air distance between the Irving Oil refinery and the two power plants to investigate the feasibility of an energy integration between the sites (see Figure 27). As a matter of fact, the BGE and the Aghada ESB sites are located only at 900 m and 1540 m air distance from the Irving Oil refinery, respectively. For what concerns the Aghada site, also the road-distance is worth being estimated since the air distance covers a water surface. Considering road path, the distance is still limited to only 1.9 km. Based on these considerations, steam integrations between the sites is feasible. This means that part of the steam which is generated internally by the power plants in the steam cycle to generate electricity could be spilled from the steam cycle, transported and fed to the Irving Oil refinery CO_2 capture plant to meet its full steam requirements. At the same time, it is important to estimate how this steam spilling impacts in terms of electricity output loss from the power plants to assess the feasibility of the integration. These calculations require the availability of specific information about the configuration of the steam cycle in the NGCC plant, including how many and which levels of pressures are present (i.e high pressure, medium pressure and low-pressure steam circuits), temperature and pressure levels at the inlet and outlet of the turbine(s) and details on the design of the gas turbine flue gas heat recovery (HRSG).

Figure 26. Overhead view of the Cork industrial cluster: the Irving oil refinery, the BGE combined cycle power plant and the ESB Aghada combined cycle power plant.

Figure 27. Air (black) and road (blue) distance between a) Irving oil refinery and ESB Aghada power station, and b) Irving oil refinery and BGE Whitegate power station.

Unfortunately, there is lack of information to sufficiently characterize the BGE plant, while a quite detailed picture of the ESB Aghada site is available (Aghada ESB Documentation). This work investigates the integration between the refinery and the Aghada station as an example of refinery-power plant integration. It is remarkable that the CO_2 capture plant design, sizing and its related energy analysis are not influenced by which capture plant is considered. On the other hand, in principle the estimation of the power plant efficiency drop can change. However, considering that the two power plants are both NGCC plants (natural gas combined cycle), and they are characterized by a totally comparable nominal power capacity (435 MW versus 445 MW), same order of magnitude results can be expected for the alternative integration with the BGE site in terms of electricity output reduction and CO_2 capture costs. In any case, this analysis must be intended as a preliminary study to estimate the effects of an integrated CO_2 capture on the overall energy requirements and power plant efficiency production. The outcomes can be used for decision-making strategy to identify whether it is worth proceeding with a more detailed TEA for integrated CO_2 capture. Even if not explicitly required by the grant agreement, we believe this is an important step towards an optimal design of the CO_2 capture for the Cork cluster aiming at a maximization of the total capture rate at reduced specific costs. A more detailed economic analysis, including also transportation costs, will be necessary to identify the most convenient configuration, namely steam integration only or both capture plant and steam integration.

Combined CO_2 capture from the refinery and the power plant can be achieved either considering two separated plants, with steam integration but separate units for the flue gas treatment, or one single integrated facility that handles both the flue gases. This work proposes three different scenarios for the combined refinery and power plant flue gases CO_2 removal. A comparison in terms of energy requirements is finally provided.

2.2 The Aghada CO_2 power station

Aghada power station was built in 1980s and originally worked with a capacity of 577 MW, produced in a single conventional steam turbine with a capacity of 270 MW and three 85 MW open-cycle gas turbines. A significant upgrade to the site was finalized in 2010 through the realization of a natural gas combined cycle (NGCC), which provided a new base-load generating capacity to meet rising power demand in Ireland. With a capacity of 435 MW the new NGCC unit was able to increase the total capacity of the power plant from 528 MW to 963 MW. Nowadays, The station generates enough power to meet the electricity needs of around 450,000 homes. NGCC cycle is known to significantly improve the efficiency of electric power generation with respect to the single gas and steam turbine cycles. A simplified scheme representing how a combined cycle works and how CO_2 capture can be implemented in this kind of plants is reproduced in Figure 28. The flue gas generated by natural gas burning gets expanded inside the gas turbine leaves the cycle with an appreciable residual heat, which can be exploited to produce steam used to drive the steam turbine to generate additional electricity. This flue gas heat recovery takes place in a dedicated heat exchanger called HRSG (Heat-Recovery-Steam-Generator), where the gas turbine exhaust gas is cooled down to the lowest acceptable temperature to avoid acidic condensation in the stack (usually 100-120°C). Remarkably, the heat recovered in the HRSG is the only heat input to the steam cycle. In this way, the only heat provided by an external heat source is the natural gas burning in the gas cycle burner. The flue gas exiting the HRSG can be conveyed to a CO_2 capture unit to lower its CO_2 content before it is discharges through the stack to the atmosphere. To this aim, a portion of the steam circulating in the steam cycle can be spilled to meet the energy requirements of the capture plant, being then reintegrated in the steam cycle in the form of saturated water.

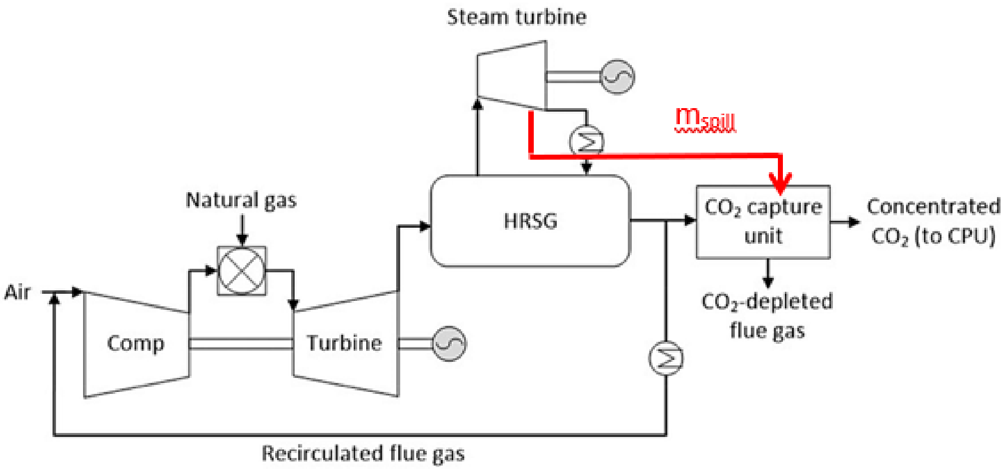


Figure 28. Schematic representation of a NGCC combined cycle power plant with the implementation of a CO_2 capture facility with steam spilling from the steam cycle.

The new 435 MW combined cycle is equipped with a single KA26 single-shaft gas turbine (CCGT) unit that houses Alstom's GT26B 2.2 dual-fuel model gas turbine (Aghada ESB Documentation). The plant is also installed with a reheat steam turbine and a hydrogen-cooled TOPGAS generator. Alstom's GT26B gas turbine guarantees excellent performances in terms of availability, efficiency, power output and reduction of the environmental emissions. Sequential combustion and a robust, maintenance-free welded rotor design are exploited for the design of these gas turbines. It is also provided with a low-NOx Environmental (EV) burner, a compact annular combustor and Egatrol GT controls. The gas turbine is rated at a nominal capacity of 288 MW, and it is characterized by a rotation pace of 3000 rpm. The flue gas generated by natural gas burning in the gas turbine leaves the cycle at an estimated temperature of 620°C, and this turbine's exhaust heat is used to produce steam used to drive the steam turbine. The additional electricity output generated in the steam cycle is equal to 147 MW. More details on the HRSG section and on the steam cycle are provided in the following subsections.

2.2.1 The steam turbine cycle in ESB Agbada power station

The Aghada ESB plant steam cycle operates at three different pressure levels (Aghada ESB steam turbine Documentation, accessed March 2023): a high-pressure cycle (HP - 138 bar), a medium pressure cycle (MP - 29 bar) and a low-pressure cycle (LP - 4.9 bar). A scratch of the cycle is drawn in Figure 29.

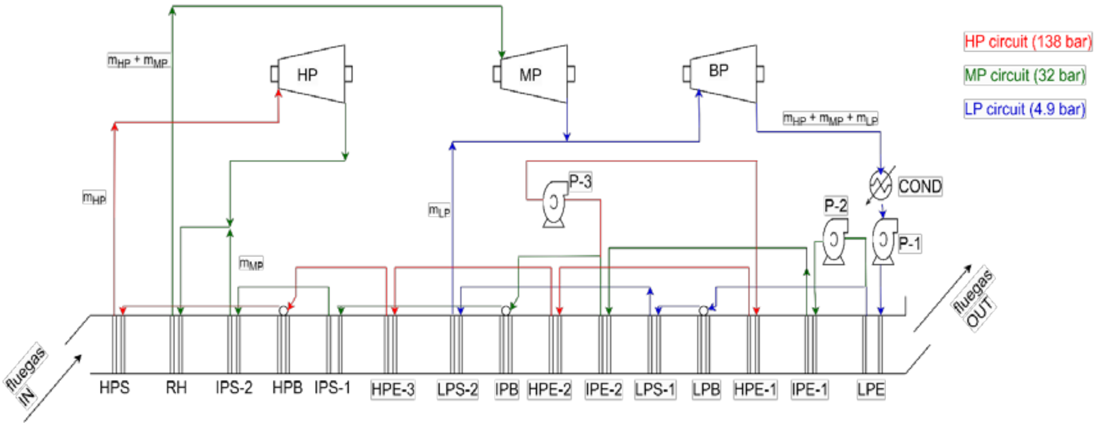


Figure 29. Schematization of the steam cycle in ESB Aghada power station with three different pressure level circuits: high pressure circuit (red), medium pressure circuit (green), and low pressure circuit (blue).

Each steam cycle is made up of four main units:

- a condenser, which collects the steam after expansion in the turbine and turns it back to saturated water at the lowest pressure level of the cycle;
- a pump, which increases the pressure of the liquid to the level of pressure required fir entering the turbine;
- the HRSG, where heat is provided to bring the water to its bubble point (economizer section), to generate saturated steam (boiler section) and finally overheated steam at the temperature required for entering the turbine;
- the turbine, where the steam is expanded to produce electricity.

In addition, the steam expanded in the HP turbine is mixed up with the overheated steam of the IP cycle and reheated back to the same temperature at which it was fed to the HP turbine (565°C) in a dedicated section of the HRSG called reheater (RH) before being conveyed to the intermediate pressure turbine. A pressure drop of 3 bar occurs during reheating.

The temperature and pressure conditions at the inlet and outlet of each of the three turbines are gathered in Table 23. The outlet temperature of the LP turbine also corresponds to the temperature at which water is condensed.

Table 23. Temperature and pressure at inlet and outlet of the three ESB Aghada plant turbines (Aghada ESB steam turbine Documentation).

	HP turbine	**MP turbine**	**LP turbine**
T, IN [°C]	565	565	284
P, IN [bar]	138	29	4.9
T, OUT [°C]	351	284	25.16
P, OUT [°C]	32	4.9	0.032

The electric power produced in the steam cycle can be calculated according to expression (18). Indeed, the total net power (P_{el}) is the one obtained summing up the work (W) generated inside the three turbines and subtracting the work consumed to run the pumps. For simplicity, due to lack of data the organo-electric efficiency is assume equal to 1.

$$P_{el} = W_{HP} + W_{MP} + W_{LP} - W_{P1} - W_{P2} - W_{P3} \tag{18}$$

The work generated in the three turbines is given by expressions set (19), where m stands for the steam mass flow circulating inside a specific steam cycle (HP, MP and LP) and Δh stands for the enthalpy change occurring across the turbine.

$$\begin{aligned} W_{HP} &= \dot{m}_{HP} \cdot \Delta h_{HP} \\ W_{MP} &= (\dot{m}_{HP} + \dot{m}_{HP}) \cdot \Delta h_{MP} \\ W_{LP} &= (\dot{m}_{HP} + \dot{m}_{HP} + \dot{m}_{LP}) \cdot \Delta h_{LP} \end{aligned} \tag{19}$$

The enthalpy difference across the turbines can be easily estimated since both inlet and outlet temperature and pressure levels are known. The amount of water/steam circulating in each of the three cycles has been estimated based on the information available on the steam cycle and on details concerning the operation of the HRSG section. Indeed, the Aghada site documentation states that a flue gas flowrate of 650 kg/s is generated by natural gas burning in the gas turbine under nominal power operation. This gas stream leaves the gas turbine at a temperature of 620°C and enters the HRSG section, where it cooled down to about 100°C. Thus, the temperature difference across the recovery section (ΔT_{HRSG}) on the gas side is known. The total heat duty exchanged in this recovery exchanger can be simply calculated by means of expression (20), where the specific heat capacity of the flue gas ($cP_{fluegas}$) has been assumed equal to 1.2 kJ/kg/K. The obtained total exchanged duty under the specified operating conditions is equal to 434.6 MW.

$$DutyHRSG = \dot{m}_{fluegas} \cdot cP_{fluegas} \cdot \Delta T_{HRSG} \tag{20}$$

Remarkably, this heat recovery occurs in multiple sections inside the HRSG. Typically, we refer to the section dedicated to water preheating till saturation as the economizer (E), to the HRSG section where evaporation occurs as the boiler (B), and to the HRSG section producing overheated steam as superheater (S). Each pressure cycle has its own dedicated E, B and S section: this multiple-section configuration allows to significantly improve the heat transfer efficiency, since each sub-section can be operated the closest possible to the pinch temperature.

The unknown steam flowrates circulating inside the low, medium and high-pressure cycles have been calculated by means of a multivariable optimization, imposing that the total net electricity produced by the three turbines (P_{tot}) must be equal to 147 MW under the constraints:

- the flue gas outlet temperature after the last HRSG section must be equal to 100°C;

- in each of the ten single identified sections of the HRSG a minimum temperature approach of 10°C must be provided for the feasibility of heat exchange.

Table 24 reports the resulting values of the calculated flows circulating in the three pressure circuits and the corresponding output works generated by the three turbines in absence of steam spilling.

Table 24. Steam flows circulating inside HP, MP and LP cycles and corresponding electric output of the three circuits.

Steam circuit	Circulating flowrate [kg/s]	Work output (MW)
LP	5.06	27.09
MP	43.03	64.54
HP	69.70	57.12

Considering the pressure levels on the plant and that the CO_2 capture plant requires a low-pressure steam (saturation temperature of 130°C), it is convenient to spill the amount of steam to be destined to the capture plant before entering the low-pressure turbine. Therefore, the steam flow conveyed to the capture plant is overheated steam at 4.9 bar and 284°C, corresponding to a specific enthalpy of 3031.82 kJ/kg. This steam flow can be expanded to 2.95 bar (wate saturation pressure at 133°C) and then enter the reboiler of the CO_2 capture plant as overheated steam to increase the exploitable enthalpy driving force. Indeed, the steam will be recovered at the outlet of the reboiler as saturated water at 133°C and 2.95 bar (559.21 kJ/kg), so that a total enthalpy difference (Δh_{steam}) of 2472 kJ/kg must be considered to estimate the amount of steam to be spilled to meet the reboiler duty requirements.

The amount of steam to be spilled can be calculated by means of expression (21), where $Q_{reb,eff}$ is the effective reboiler duty to be provided by external heat source. This contribution is equal to the total reboiler duty minus the heat recovered in the preliminary heat recovery section for the Irving Oil refinery capture plant.

$$\dot{m}_{spill} = \frac{Q_{reb,eff}}{\Delta h_{steam}} \tag{21}$$

Steam spilling generates a loss in the electricity production of the power plant, since a lower steam flow circulates in the last turbine, thus reducing the W_{LP} term. The new value of low-pressure turbine generated work in presence of steam spilling ($W_{LP,spill}$) is given by expression (22), and it represents a very important factor to quantify the power plant efficiency loss associated (ε_{loss}) to the steam spilling (equation (23)).

$$W_{LP,spill} = (\dot{m}_{HP} + \dot{m}_{HP} + \dot{m}_{LP} - \dot{m}_{spill}) \cdot \Delta h_{LP} \tag{22}$$

$$\varepsilon_{loss} = 1 - \frac{W_{LP,spill}}{W_{LP}} \tag{23}$$

2.3 CO_2 capture from Irving Oil refinery using power plant steam as utility

Considering the power plant steam as utility to meet the overall steam requirements of the CO_2 capture plant for the treatment of Irving Oil flue gas results only in a minor modification of the process layout. The new flowsheet is drawn in Figure 30. Basically, the only difference with respect to the configuration investigated in the previous chapter is that no natural gas fed steam boiler is present and, consequently, no flue gas streams in addition to the Irving Oil stacks are treated. Steam is spilled at the outlet of the medium pressure turbine at a pressure of 4.9 bar and a temperature of 284°C. This steam is expanded to 2.95 bar (to get a water saturation temperature of 130°C), then it is fed to the reboiler of the CO_2 desorber where it is cooled down to saturation point and fully condensed. Therefore, the spilled steam exits the DES column reboiler as saturated liquid at 130°C. This stream can be reintegrated inside the power plant after the condenser; in this way, the steam starts again circulating in the power plant steam loop, closing the steam cycle.

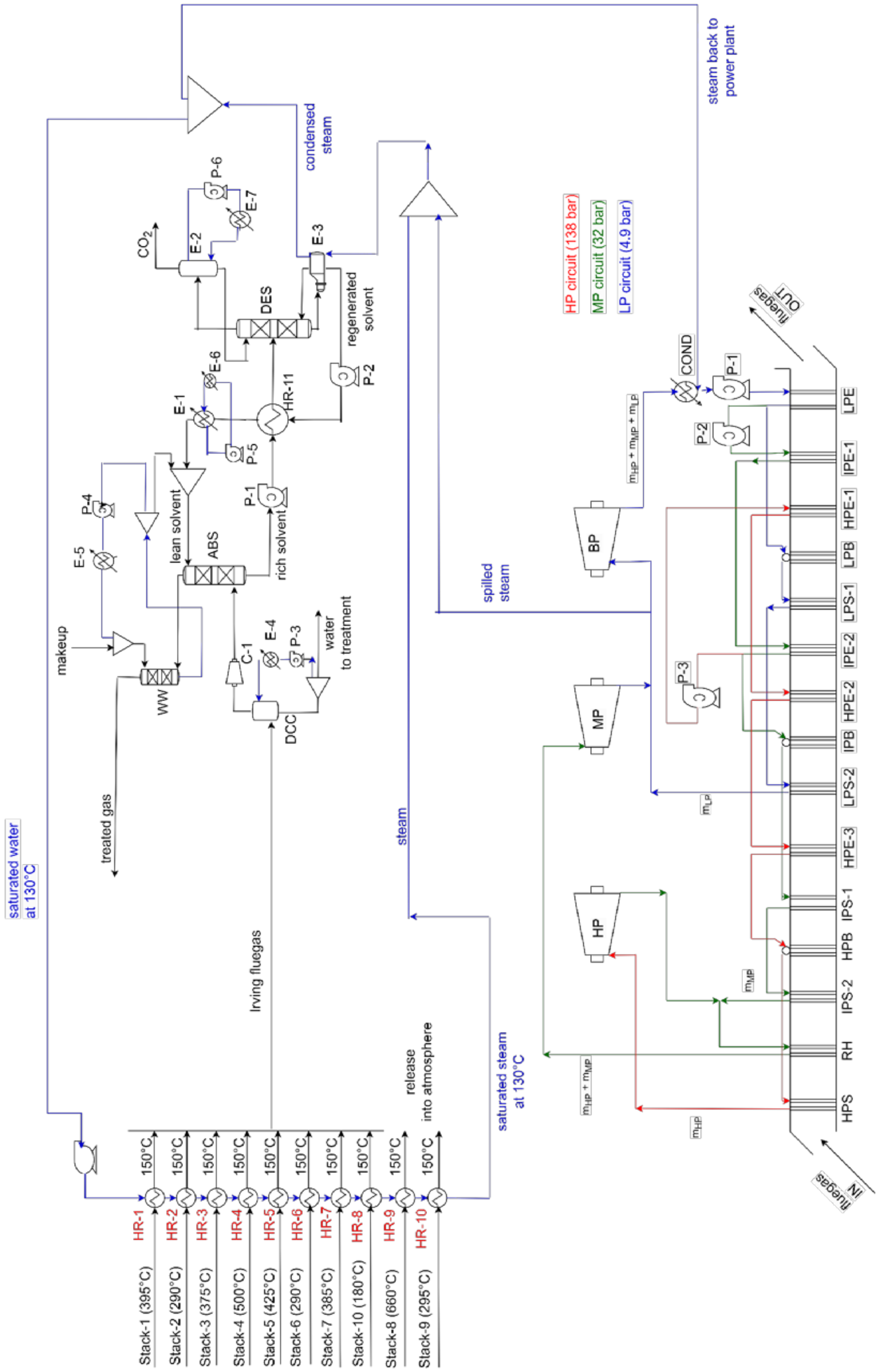


Figure 30. Flowsheet of the CO_2 capture plant designed for Irving oil gas treatment with steam integration from the Aghada ESB power station to meet the solvent regeneration energy requirements.

The new CO_2 capture plant is simulated in Aspen Plus® V11.0 and compared to the original configuration discussed in the previous section in terms of energy requirements, equipment sizing and costs. As for the power plant steam price, a value of 14.05 $/GJ of heating power is assumed (Turton, 2012).

The main aim is to quantify the impact of the reduction in the total treated flue gas flow on the sizing of the columns and heat exchangers.

2.3.1 Performance and energy requirements

This section reports the results of the simulations of the CO_2 capture plant for the treatment of the Irving Oil flue gas in Aspen Plus V11.0 with steam integration from the ESB Aghada power plant. The optimal operating conditions resulting from the sensitivity analysis carried out for the process configuration with the steam boiler are assumed to be still valid. The collected results refer to both MEA and HS3 solvents, and a comparison between the two solvents based on energy requirements is also available.

2.3.1.1 MEA

The plant treats 280.31 ton/h of flue gas, with an average CO_2 concentration prior (mixed stream) to saturation in the DCC of 7.07 mol%. This concentration is slightly lower with respect to the one of the gas treated in the configuration with steam boiler.

The amount of cooling water required to cool down the flue gas assuming a 3°C approach temperature is 896 ton/h, The column has a diameter of 6.45 m. Being the flue gas water content higher with respect to the water saturation condition, part of the water contained in the flue gas condenses inside the DCC. For this reason, the 2.05% of the water flow recovered at the bottom is purged from the cooling water loop. This purge corresponds to a flow of 18.85 ton/h, with the same composition obtained for the base case. The resulting saturated flue gas has an increased CO_2 concentration of 7.90 mol%.

No appreciable changes are noticed with respect to the base-case discussed for what concerns the pressure drops inside the columns. This is mainly due to the fact the no variation in the packing height occurs. The fan has an electricity consumption of 1.68 MW and the outlet gas reaches a temperature of 50.4°C, which corresponds to the feed temperature to the absorber.

The solvent flow required to capture the 90% of the CO_2 content in the flue gas entering the absorber is 517.8 ton/h, corresponding to a L/G ratio equal to 1.98 and to a specific solvent flow of 16.57 ton solvent per each ton of captured CO_2. The column has a packing height of 12 m, as stated from the sensitivity analysis, and a diameter of 5.65 m. As expected, the temperature profiles are substantially unchanged.

The maximum flowrate of circulating water inside the WW loop to fulfill the specified criterion on the flooding velocity approach percentage is 550 ton/h. Under such operating conditions, a minimum packing height of 2.15 m is still necessary to reach a residual MEA content in the treated gas of 5 pm. Indeed, the amine evaporation concentration is affected by the solvent volatility, and not by the reduced total gas and solvent circulating flowrates.

The rich-solvent pump must provide the same pressure gradient of the case with the steam boiler. Downstream of the pump, the solvent reaches a temperature of 38.8°C. This stream is preheated before entering the desorbed in HR-11, by countercurrent heat exchange with the lean solvent recovered from the bottom of the stripper, which is available at 122°C. This technological solution allows to recover 34.28 MW of heat. The preheated rich solvent stream reaches a temperature of 112.6°C, which is suitable for its feed to the stripper; at the same time, the lean solvent is cooled down to about 48.8°C.

The stripper column has the same packing height of 10m considered for the case study with the boiler, while the estimated required diameter reduces to 2.97 m. The condenser and reboiler duties are 9.43 MW and 29.61 MW, respectively. The specific reboiler duty is 3.79 MJ/kg of captured CO_2. The released CO_2 flow is equal to 28.13 ton/h.

The main process streams characterization in terms of temperature, pressure, molar and mass flowrate is available in Table 25AA, while the corresponding streams composition is gathered in Table 25B. The streams number refer to the bloc flow diagram developed for the case-study with the boiler drawn in Figure 21. The only differences in stream numbers are the following:

- streams 119 and 120 are not present since they referred to the natural gas boiler cycle; the same holds for stream 121, which simply represents the sum of the eight treated Irving Oil stacks flows at same temperature and pressure;
- Stream 301 represents the steam spilled from the power plant rather than the steam generated by the boiler.

Table 25A. Material and energy streams characterization for the costs analysis: temperature, pressure, phase, mass and molar flows: data for MEA solvent. Data refer to the process configuration with steam integration from the power plant.

Stream	101	102	103	104	105	106	107	108	111
Temperature [°C]	290	395	375	500	425	290	385	180	150
Pressure [bar]	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	0.91
Mass flow [ton/h]	13.32	27.84	35.93	13.56	25.31	96.29	457.46	22.28	13.32
Mole flow [kmol/h]	474.6	995.8	1261.6	483.6	924.0	3462.4	1657.3	790.1	474.6
Stream	112	113	114	115	116	117	118	122	123
Temperature [°C]	150	150	150	150	150	150	150	28.00	50.42
Pressure [bar]	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	1.10
Mass flow [ton/h]	27.84	35.93	13.56	25.31	96.29	457.46	22.28	261.46	261.46
Mole flow [kmol/h]	995.8	1261.6	483.6	924.0	3462.4	1657.3	790.1	9005.0	9005.00
Stream	124	125	126	201	202	203	211	212	213
Temperature [°C]	34.04	100.56	30.00	25.00	46.91	46.91	38.72	112.60	121.93
Pressure [bar]	1.06	1.89	1.90	1.01	2.00	2.00	1.10	3.90	1.90
Mass flow [ton/h]	234.52	41.00	28.40	896.34	18.85	896.34	520.66	520.66	492.26
Mole flow [kmol/h]	8433.28	1351.26	654.31	49754.37	1046.45	49752.37	20146.47	20180.79	20130.56

Stream	214	215	216	217	218	219	220	221	301
Temperature [°C]	30.00	48.82	43.00	53.02	25.00	53.02	25.00	43.63	284
Pressure [bar]	1.90	1.55	1.10	1.06	1.06	1.06	1.01	1.06	4.90
Mass flow [ton/h]	12.59	492.26	492.26	574.06	548.66	25.40	1.45	517.66	19.02
Mole flow [kmol/h]	696.69	20130.56	20130.56	31856.12	30446.48	1409.57	80.59	21540.13	1056.7
Stream	302	303	304	401	402	403	404	405	406
Temperature [°C]	130	189.64	130	20	20	20	20	20	35
Pressure [bar]	2.66	2.66	2.66	1.01	1.01	1.01	1.01	1.01	1.01
Mass flow [ton/h]	30.09	49.11	49.11	3022.65	1306.1	1021.7	154.2	540.7	3022.65
Mole flow [kmol/h]	1671.7	2728.3	2728.3	1.68e5	7.26e4	5.68e4	8.57e3	3.0e4	1.68e5

Table 25B. Streams characterization for the costs analysis: molar composition. For liquid streams, the apparent composition is reported. Data refer to MEA solvent the process configuration with steam integration from the power plant.

Stream	101	102	103	104	105	106	107	108	111
H_2O	0.1398	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.1398
CO_2	0.0810	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0810
N_2	0.7392	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.7392
O_2	0.0400	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0400
Stream	112	113	114	115	116	117	118	122	123
H_2O	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.0420	0.0420
CO_2	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0789	0.0789
N_2	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.8341	0.8341
O_2	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0451	0.0451
CH_4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Stream	124	125	126	201	202	203	211	212	213
H_2O	0.0529	0.5260	0.0229	1.0000	1.0000	1.0000	0.82955	0.82980	0.85531
CO_2	0.0083	0.4738	0.9769	0.0000	2.4E-05	2.4E-05	0.05717	0.05708	0.02801
N_2	0.8906	0.0001	0.0002	0.0000	6.5E-06	6.5E-06	-	-	-
O_2	0.0481	8.4E-06	1.7E-05	0.0000	6.5E-07	6.5E-07	-	-	-
MEA	4.88E-06	2.0E-04	1.1E-11	0.0000	0.0000	0.0000	0.11329	0.11312	0.11668
Loading	-	-	-	-	-	-	0.505	0.505	0.240
Stream	214	215	216	217	218	219	220	221	
MEA	0.00039	0.11674	0.11675	7.4E-05	7.42E-05	7.42E-05	3E-05	0.10934	
H_2O	0.99825	0.85524	0.85522	0.99988	0.99988	0.99988	0.99997	0.86442	
CO_2	0.00136	0.02802	0.02803	4.6E-05	4.6E-05	4.6E-05	0	0.02624	
Loading	3.522	0.240	0.240	0.620	0.620	0.620	0.000	0.240	

The duties of the plant including steam, electricity and cooling water are summarized in Table 26. The preliminary heat recovery section (18.17 MW heat recovery, as in the case study with the boiler) allows to reduce the reboiler duty to be provided by an external utility by 61% (see Table 27). Therefore, even if the specific reboiler duty is 3.79 MJ/kg CO_2, the steam boiler must provide only 11.44 MW (1.46 MJ per every kg of carbon dioxide). Thus, the steam generation requirement of the plant is 18.95 ton/h to be spilled from the power plant, corresponding to 0.67 ton/ton CO_2 captured.

Table 26. Summary of all the duties (in MW) of the MEA-based CO_2 capture plant. Data refer to the configuration with steam integration from the power plant.

Equipment	Utility	Duty [MW]
Reboiler (E-3)	Steam	29.65
Fan (C-1)	Electricity	1.68
Pump P-1	Electricity	0.03
Pump P-2	Electricity	0.03
Pump P-3	Electricity	0.05
Pump P-4	Electricity	0.05
Cooler E-1	Cooling water	2.69
Condenser E-2	Cooling water	9.43
Cooler E-4	Cooling water	22.79
Cooler E-5	Cooling water	17.82

Table 27. Summary of total and specific reboiler duties and portion of the duty to be provided by an external heat source using MEA solvent. Data refer to the configuration with steam integration from the power plant.

Reboiler duty [MW]	29.61
External duty [MW]	11.44
SRD [MJ/kg CO_2]	3.79
SSR [MJ/kg CO_2]	1.46

2.3.1.2 HS3

In this process configuration, the treated gas flow is the same independently from the solvent exploited for carbon capture. As a consequence, also the amount of cooling water required to cool down the flue gas assuming a 3°C approach temperature is unchanged, as well as the DCC diameter and the concentration of the flue gas leaving the DCC and entering the absorber.

No appreciable changes are noticed with respect to the base-case discussed for what concerns the pressure drops inside the columns. This is mainly due to the fact the no variation in the packing height occurs. The fan has an electricity consumption of 1.86 MW and the outlet gas reaches a temperature of 52.7°C, which corresponds to the feed temperature to the absorber.

The solvent flow required to capture the 90% of the CO_2 content in the flue gas entering the absorber is 416 ton/h, corresponding to a L/G ratio equal to 1.59 and to a specific solvent flow of 13.31 ton solvent per each ton of captured CO_2. The column has a packing height of 18 m, as stated from the sensitivity analysis, and a diameter of 5.5 m. As expected, the temperature profiles are substantially unchanged.

The maximum flowrate of circulating water inside the WW loop to fulfill the specified criterion on the flooding velocity approach percentage is equal to the one calculated for the MEA-based process. Under such operating conditions, a minimum packing height of 4.9 m is still necessary to reach a residual total amine content (AP + PRLD) in the treated gas of 5 pm. Indeed, the amine evaporation concentration is affected by the solvent volatility, and not by the reduced total gas and solvent circulating flowrates.

The rich-solvent pump must provide the same pressure gradient of the case with the steam boiler. Downstream of the pump, the solvent reaches a temperature of 49.1°C. This stream is preheated before entering the desorber in HR-11, by countercurrent heat exchange with the lean solvent recovered from the bottom of the stripper, which is available at 122°C. This technological solution allows to recover 22.65 MW of heat. The preheated rich solvent stream reaches a temperature of 109.1°C, which is suitable for its feed to the stripper; at the same time, the lean solvent is cooled down to about 59°C.

The stripper column has the same packing height of 14 m considered for the case study with the boiler, while the estimated required diameter reduces to 2.66 m. The condenser and reboiler duties are 5.46 MW and 23.31 MW, respectively. The specific reboiler duty is 2.98 MJ/kg of captured CO_2. The released CO_2 flow is equal to 28.17 ton/h.

The streams characterization summary reported here below (Table 28AA and Table 28B) refers to the same process scheme adopted for the MEA case study.

Table 28A. Material and energy streams characterization for the costs analysis: temperature, pressure, phase, mass and molar flows: data for the HS3 solvent. Data refer to the process configuration with steam integration from the power plant.

Stream	101	102	103	104	105	106	107	108	111
Temperature [°C]	290	395	375	500	425	290	385	180	150
Pressure [bar]	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	0.91
Mass flow [ton/h]	13.32	27.84	35.93	13.56	25.31	96.29	457.46	22.28	13.32
Mole flow [kmol/h]	474.6	995.8	1261.6	483.6	924.0	3462.4	1657.3	790.1	474.6
Stream	112	113	114	115	116	117	118	122	123
Temperature [°C]	150	150	150	150	150	150	150	28.00	52.74
Pressure [bar]	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	1.12
Mass flow [ton/h]	27.84	35.93	13.56	25.31	96.29	457.46	22.28	261.4	261.42
Mole flow [kmol/h]	995.8	1261.6	483.6	924.0	3462.4	1657.3	790.1	9004.0	9003.97
Stream	124	125	126	201	202	203	211	212	213
Temperature [°C]	33.91	102.09	30.00	25.00	46.91	46.91	44.15	109.10	124.01
Pressure [bar]	1.06	1.79	1.80	1.01	2.00	2.00	1.12	4.60	1.80
Mass flow [ton/h]	232.92	35.86	28.46	895.30	18.89	895.30	426.11	426.11	397.64
Mole flow [kmol/h]	8349.39	1035.18	656.14	49696.75	1048.69	49693.77	11489.36	11494.82	11473.68

Stream	214	215	216	217	218	219	220	221	301
Temperature [°C]	30.00	59.04	43.00	51.52	25.00	51.52	25.00	43.77	284
Pressure [bar]	1.80	1.45	1.20	1.06	1.06	1.06	1.01	1.06	4.90
Mass flow [ton/h]	7.40	397.64	397.64	467.40	449.70	17.70	0.17	415.34	8.51
Mole flow [kmol/h]	374.11	11473.42	11473.42	25862.81	24883.61	979.16	9.49	12452.58	472.8
Stream	302	303	304	401	402	403	404	405	406
Temperature [°C]	130	163.9	130	20	20	20	20	20	35
Pressure [bar]	2.66	2.66	2.66	1.01	1.01	1.01	1.01	1.01	1.01
Mass flow [ton/h]	30.09	38.60	38.60	2724.5	313.04	312.47	792.36	1306.64	Liquid
Mole flow [kmol/h]	1671.6	2144.4	2144.4	1.51e5	1.74e4	1.74e3	4.4e4	7.3e4	2724.5

Table 28B. Streams characterization for the costs analysis: molar composition. For liquid streams, the apparent composition is reported. Data refer to HS3 solvent and to the process configuration with steam integration from the power plant.

Stream	101	102	103	104	105	106	107	108	111
H_2O	0.1398	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.1398
CO_2	0.0810	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0810
N_2	0.7392	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.7392
O_2	0.0400	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0400
Stream	112	113	114	115	116	117	118	122	123
H_2O	0.1408	0.1362	0.1400	0.1458	0.1421	0.1440	0.1386	0.0420	0.0420
CO_2	0.0750	0.1050	0.0800	0.0420	0.0660	0.0540	0.0890	0.0789	0.0789
N_2	0.7440	0.7199	0.7400	0.7706	0.7513	0.7609	0.7328	0.8342	0.8342
O_2	0.0402	0.0389	0.0400	0.0417	0.0406	0.0411	0.0396	0.0449	0.0449
CH_4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Stream	124	125	126	201	202	203	211	212	213
N_2	0.8996	0.0000	0.0000	0.0000	6.50E-06	6.50E-06	-	-	-
CO_2	0.0081	0.6235	0.9757	0.0000	2.46E-05	2.46E-05	0.06481	0.06485	0.01343
H_2O	0.0439	0.3716	0.0240	1.0000	1.0E+00	1.0E+00	0.75357	0.75343	0.79447
AP	3.38E-07	1.1E-03	1.75E-11	0.0000	0.0000	0.0000	0.06645	0.06648	0.07028
PRLD	4.62E-06	3.6E-03	3.65E-09	0.0000	0.0000	0.0000	0.11517	0.11523	0.12182
O_2	0.0485	0.0001	0.0002	0.0000	2.55E-05	2.55E-05	-	-	-
Loading	-	-	-	-	-	-	0.357	0.357	0.070
Stream	214	215	216	217	218	219	220	221	
CO_2	0.01380	0.0135	0.01350	0.00028	0.00028	0.00028	0.00000	0.01249	
H_2O	0.97318	0.7936	0.79341	0.99924	0.99924	0.99924	1.00000	0.80902	
AP	0.00312	0.0706	0.07064	0.00005	0.00005	0.00005	0.00000	0.06516	
PRLD	0.00991	0.1223	0.12244	0.00042	0.00042	0.00042	0.00000	0.11332	
Loading	1.059	0.070	0.070	0.601	0.601	0.601	-	0.070	

The duties of the plant including steam, electricity and cooling water are summarized in Table 29. The preliminary heat recovery section (18.17 MW heat recovery, as in the case study with the boiler) allows to reduce the reboiler duty to be provided by an external utility by 61% (see Table 30). Therefore, even if the specific reboiler duty is 3.79 MJ/kg CO_2, the steam boiler must provide only 11.44 MW (1.46 MJ per every kg of carbon dioxide). Thus, the steam generation requirement of the plant is 18.95 ton/h to be spilled from the power plant, corresponding to 0.67 ton/ton CO_2 captured.

Table 29. Summary of all the duties (in MW) of the HS3-based CO_2 capture plant. Data refer to the configuration with steam integration from the power plant.

Equipment	Utility	Duty [MW]
Reboiler (E-3)	Steam	23.31
Fan (C-1)	Electricity	1.86
Pump P-1	Electricity	0.04
Pump P-2	Electricity	0.04
Pump P-3	Electricity	0.05
Pump P-4	Electricity	0.02
Cooler E-1	Cooling water	5.45
Condenser E-2	Cooling water	5.46
Cooler E-4	Cooling water	22.79
Cooler E-5	Cooling water	13.82

Table 30. Summary of total and specific reboiler duties and portion of the duty to be provided by an external heat source using HS3 solvent. Data refer to the configuration with steam integration from the power plant.

Reboiler duty [MW]	23.31
External duty [MW]	5.14
SRD [MJ/kg CO_2]	2.98
SSR [MJ/kg CO_2]	0.66

2.3.1.3 Comparison between the two solvents

While in the process configuration including steam generation via natural gas-fed boiler, this configuration that accounts for steam integration with the power plant is extremely interesting for the sake of an energy requirements comparison between MEA and HS3 since both processes treat the same gas flowrate, thus also the same amount of CO_2.

The main advantages and disadvantages associated to HS3 can be summarized as in Table 31. Remarkably, for all the main KPI (i.e., specific solvent flow and specific reboiler duty) there is no relevant change with respect to the conclusions drawn from the previous case-study.

Table 31. Summary of HS3 advantages and disadvantages over benchmark MEA for application in Irving oil carbon capture with steam integration from the power plant.

HS3 advantages	HS3 disadvantages
20% lower solvent flow and L/G (1.59 vs 1.98)	Slower kinetics
21% lower reboiler duty and SRD	Higher column packing heights (+50% for absorber)
55% lower SSR	Higher volatility (higher water wash section packing required)
2.6% lower absorber and WW diameter and 10% lower stripper diameter	Higher initial solvent cost
Lower heat exchange surfaces due to lower solvent circulating flows	

2.3.1.4 Energy consumption of the CO_2 capture plant with and without steam integration with the power plant

When comparing the process configuration with and without the steam boiler in terms of energy requirements, it is remarkable that the specific reboiler is only slightly increased for both solvents (2.98 versus 2.97 MJ/kg for HS3 and 2.79 versus 2.78 MJ/kg for MEA). This result is in line with expectations, considering that, at fixed capture rate, the SRD mainly depends on the CO_2 concentration in the flue gas. Indeed, in the case-study without steam boiler the CO_2 concentration is lower (7.9 vol% versus 8.04 mol%), which results in a 0.01 MJ/kg increase in the SRD. In conclusion, it is possible to state that the two configurations have comparable specific steam requirements. Also the specific solvent flowrates required to achieve 90% capture rate are unchanged.

2.4 Combined refinery and power plant flue gas treatment

This section discusses the option of extending CO_2 capture from the oil refinery only to the entire Cork cluster, thus including also at least one of the two NGCC power plant flue gas treatment.

2.4.1 Possible plant layouts

This section discussed different possible layouts for the design of a facility dealing with the treatment of both the Irving Oil refinery flue gas and the ESG Aghada power station flue gas. Even if the calculations proposed refer to this specific industrial cluster, the proposed approach can be considered general and is adaptable to different clusters characterized by two or multiple CO_2 emitting sources.

More specifically, three scenarios are hereby proposed:

- Scenario A: each site has its own independent CO_2 capture facility. Irving Oil refinery generates directly on-site the steam required for solvent regeneration in a methane-fed steam boiler. For what concerns the refinery flue gas treatment, this configuration is identical to the one already presented in section 1.4.2 for the refinery flue gas treatment. A new facility dedicated only to the power plant gas treatment must be designed.

- Scenario B: each site has its own CO_2 capture facility. The required steam and electricity is furnished by the power-plant located nearby the refinery. For what concerns the refinery flue gas treatment, this configuration is identical to the one already presented in section 2.3 for the refinery flue gas treatment. A new facility dedicated only to the power plant gas treatment must be designed; this further facility is identical to the one needed for scenario A.
- Scenario C: integrated capture plant treating both the flue gases. The required steam and electricity come from the power-plant.

A graphical representation of the three different options with the main material and energy stream connections within the proposed CO_2 capture clusters is drawn in Figure 31.

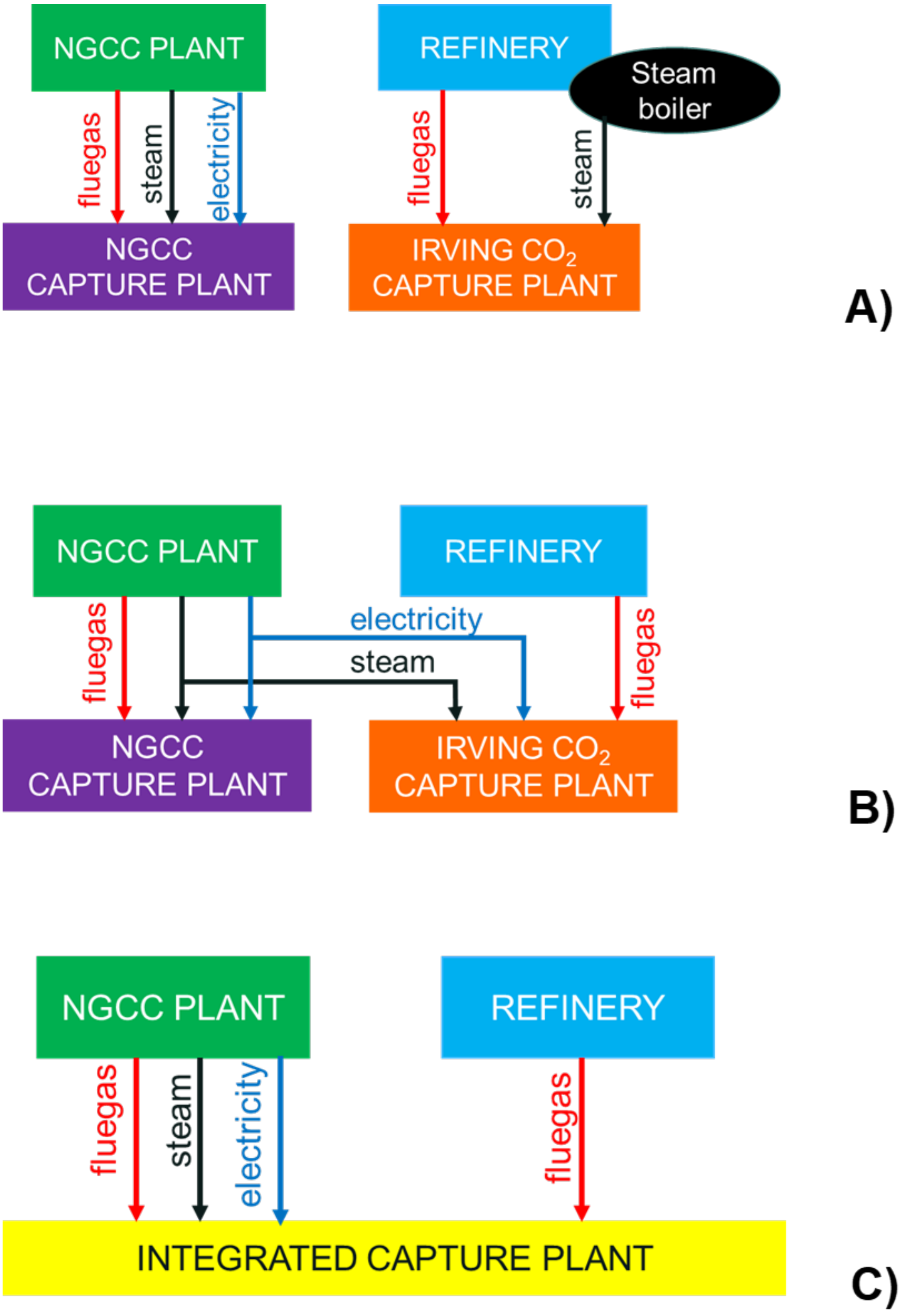


Figure 31. Schematic flowsheet for the three proposed scenarios for CO_2 capture from both the Irving oil refinery and the ESB Aghada power plant, including material and energy streams integrations: A) Scenario A; B) Scenario B; C) Scenario C.

The CO_2 capture plants to be designed for the sake of a comparison between the three proposed scenarios are the plant for the treatment of the power plant gas only and the plant for the combined treatment of both the refinery and the power plant gases together. The next paragraphs firstly present the assumptions, the plant design and the simulation results for these two additional plants together with the relative energy analysis and costs estimate. Assumptions and plant layout have been defined in accordance to the ones designed for the refinery gas treatment for the sake of consistency. Both MEA and HS3 have been considered in compliance with the approach followed for the Irving Oil Whitegate refinery.

2.4.2 Design of a capture plant for the treatment of the NGCC plant flue gas

A simplified process flowsheet for the treatment of the Aghada ESB flue gas only (required for scenarios A and B) has been designed in compliance with the plant designed for the Irving Oil gas treatment. For this analysis, operation at nominal power for the NGCC plant is assumed. The proposed process is represented in Figure 32. Remarkably, the only difference with respect to the capture plant proposed for the refinery is the absence of a preliminary flue gas heat recovery section. Indeed, the NGCC flue gas leaves the HRSG section at a residual temperature of 100°C and atmospheric pressure, thus it cannot be exploited for generating steam for the reboiler, which requires a saturation temperature of at least 130°C.

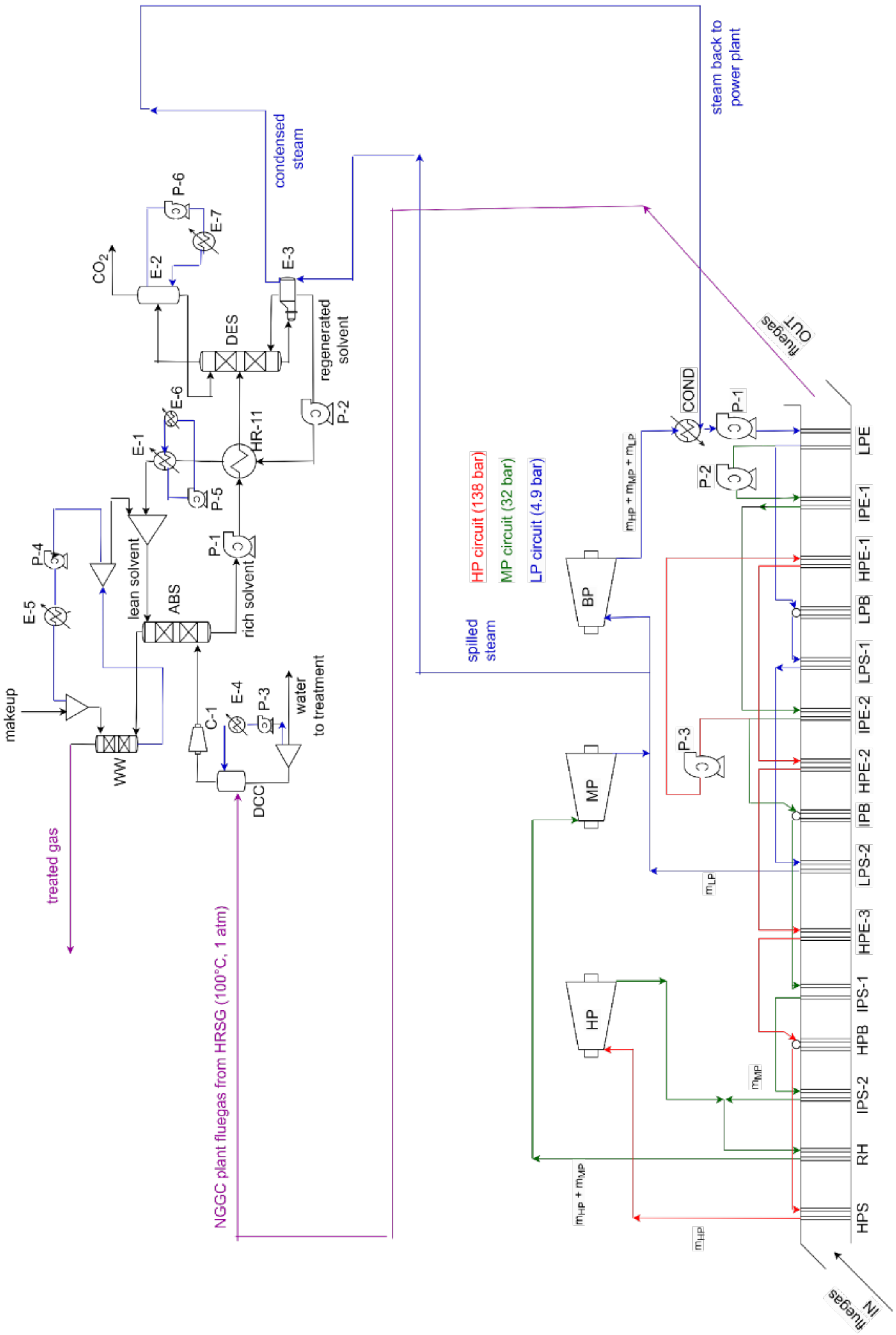


Figure 32. Process flowsheet designed for the treatment of the Aghada ESB power plant flue gas only.

Under nominal power operation, the capture plant must handle 650 kg/s of gas (Aghada ESB steam turbine Documentation), which corresponds to 2340 ton/h. Therefore, a big difference in the equipment size with respect to the capture plant designed for the refinery must be expected, since the overall gas flowrate to be treated is 8.35 times higher. The CO_2 concentration has been determined based on operation plant data referred to year 2019 provided by the power plant (confidential data). These data include the overall CO_2 emissions registered in the whole year (ton/year) as well as the effective obtained electricity output (MWh_{el}/year). The ratio between the real electricity output and the nominal power provides the capacity factor (CF) of the power plant (expression (24)).

$$CF = \frac{Actual\ electricity\ output\ \left[\frac{MWh_{el}}{year}\right]}{Elecrricity\ output\ at\ nominal\ power\ \left[\frac{MWh_{el}}{year}\right]} \tag{24}$$

Based on the estimated CF, the actual flue gas flowrate (AFF) emitted by the plant can be approximately defined according to equation (25), where NPFF stands for the flue gas flowrate under nominal power operation (650 kg/s).

$$AFF = CF \cdot NPFF \tag{25}$$

Finally, the CO_2 weight concentration is simply given by the ratio between the total CO_2 emitted and the AFF, both referred to the considered year of operation (expression (26)). The corresponding volume-basis concentration can be obtained just considering the flue gas average molecular weight.

$$CO_2(wt\%) = \frac{CO_2\,emissions\ \left[\frac{ton}{year}\right]}{AFF\ \left[\frac{ton}{year}\right]} \tag{26}$$

The resulting concentration for year 2019 is 4.02 vol%, thus a rounded value of 4 vol% has been adopted for simulation purposes in this work. This value is in line with the literature related to NGCC plants (Berstad et al., 2011; W. Zhang et al., 2017).

Differently from the refinery, which is a multiple-stack CO_2 source, for the power plant case-study all the CO_2 comes from a single stream. Therefore, there is no interest to investigate alternative multi-absorber configurations as for the refinery case-study.

The DCC, absorber, water wash and stripper diameters have been determined considering the same percentage of approach to the flooding velocity (70%) that was considered for the refinery plant.

For simplicity, the process operating conditions such as the lean loading, packing heights, stripper pressure and solvent feed temperature have been set to the same values adopted for the refinery gas treatment plant. This is a simplification, since in principle the optimal operating conditions for the power plant gas treatment may not coincide. However, the proposed assumption can be considered reasonable since the two flue gas CO_2 concentration differ only by 3% on a volume basis (4 vol% in power plant and 7.2 vol% in the refinery).

All the other assumptions, such as the capture rate, the maximum allowed residual amine content in the flue gas after water-wash treatment, temperature approach in the heat exchangers and criteria for pressure drops estimation are consistent with the plant designed for the refinery.

2.4.2.1 Results

The results of unit operation sizing, estimation of energy requirements and the main KPIs for the CO_2 capture plant dedicated to the ESB Aghada flue gas treatment simulated in Aspen Plus® V11.0 using both default MEA and the new developed HS3 models are summarized here below in the Table 32.

Table 32. Summary of equipment sizing, estimation of KPIs and energy requirements for the CO_2 capture plant designed for the treatment of the Aghada ESB power plant only with both MEA and HS3. Results from Aspen Plus simulations using default MEA and new developed HS3 models.

Unit operation	Parameter	MEA	HS3
DCC	Diameter (m) Water flowrate (ton/h)	17.85 5042	17.85 4997
Fan (C-1)	Duty (MW)	7.21	7.77
Absorber (ABS)	Diameter (m) Solvent flow (ton/h) L/G (kg/kg) Specific flow (ton/ton CO_2)	14.73 2501.6 1.100 17.23	14.34 2340 1.028 16.12
Pump (P-1)	Duty (kW)	224	217
Rich-lean exchanger (HR-1)	Recovered duty (MW)	169.27	133.17
Desorber (DES)	Diameter (m)	6.50	6.09
Condenser (E-2)	Duty (MW)	42.07	32.08
Reboiler (E-3)	Duty (MW) SRD (MJ/kg CO_2)	144.09 3.96	121.70 3.35
Cooler (E-1) Cooler (E-4) Cooler (E-5)	Duty (MW) Duty (MW) Duty (MW)	7.87 93.17 72.67	23.64 90.05 68.02

Looking at the reported results it is possible to draw the following main conclusions:

- The increased gas flow to be handled associates with a corresponding increase in the diameter of the columns of the order of 2 to 3 meters;
- The reduced CO_2 concentration in the flue gas decreases the efficiency of the HS3 solvent performance. Indeed, the L/G ratio is only 6.5% lower with respect to the MEA one, while for operation at 7.5 vol% CO2 concentration the L/G was almost 20% lower;
- This relative increase in the specific solvent flow demand also shows a corresponding effect on the SRD. As a matter of fact, when the CO_2 concentration is reduced from 7.5 vol% to 4 vol%, the MEA SRD increases from 3.79 to 3.96 MJ/kg (+4.5%), whereas the HS3 SRD increases from 2.98 to 3.35 MJ/kg (+12.4%);
- Despite the HS3 performances are decreasing at lower CO2 concentration, the reboiler duty and the associated SRD are still 15% lower with respect to the ones

obtained using the reference solvent. Therefore, this energy analysis proves that HS3 is worth consideration also for applications at lower carbon dioxide concentrations.

The steam requirement for the reboiler of the CO_2 capture plant designed for the NGCC plant gas treatment is 144.09 and 121.70 with MEA and HS3, respectively. Therefore, the resulting steam flow at medium pressure to be spilled from the power plant to meet such energy requirements calculated by means of equation (21) is equal to 58.27 kg/s and 49.22 kg/s, respectively. Thus, the total steam flow entering the low-pressure turbine reduces from 117.49 kg/s to 59.22 kg/s, lowering the electric output generated by the power station (originally 57 MW). Indeed, under these conditions the low-pressure turbine generates a work of 28.72 MW and 33.11 MW, respectively. In addition, it is necessary to consider that part of the generated work is consumed to provide the electricity input required by the fan and the pumps in the capture plant. The power plant electricity production from the steam cycle is 120.36 MW using a MEA-based capture plant and 124.75 MW if HS3 technology is considered, corresponding to a steam turbine efficiency decrease of 20.94% for HS3 and 23.55% for MEA. The results are summarized in Table 33: the overall combined cycle power output is 4 MW higher when HS3 is selected as a solvent.

Table 33. Assessment of steam spilling effects on the combined cycle power plant electricity production efficiency for both MEA and HS3 solvents. The analysis refers to the CO_2 capture plant designed for the treatment of the Aghada ESB flue gas only.

Performance indicator	MEA	HS3
Steam to be spilled (kg/s)	58.27	49.22
LP turbine work (MW)	28.72	33.11
Electricity consumption of capture plant	7.98	8.53
Steam cycle power output (MW)	112.38	116.22
Steam cycle efficiency drop	23.55	20.94
Combined cycle power output (MW)	400.38	404.22

2.4.3 Fully integrated CO_2 capture plant

The CO_2 capture plant designed for the combined treatment of both the refinery and the NGCC plant flue gas in a single absorber-stripper is drawn in Figure 33. For consistency the simulation is set up in accordance with all the previously modelled case-studies.

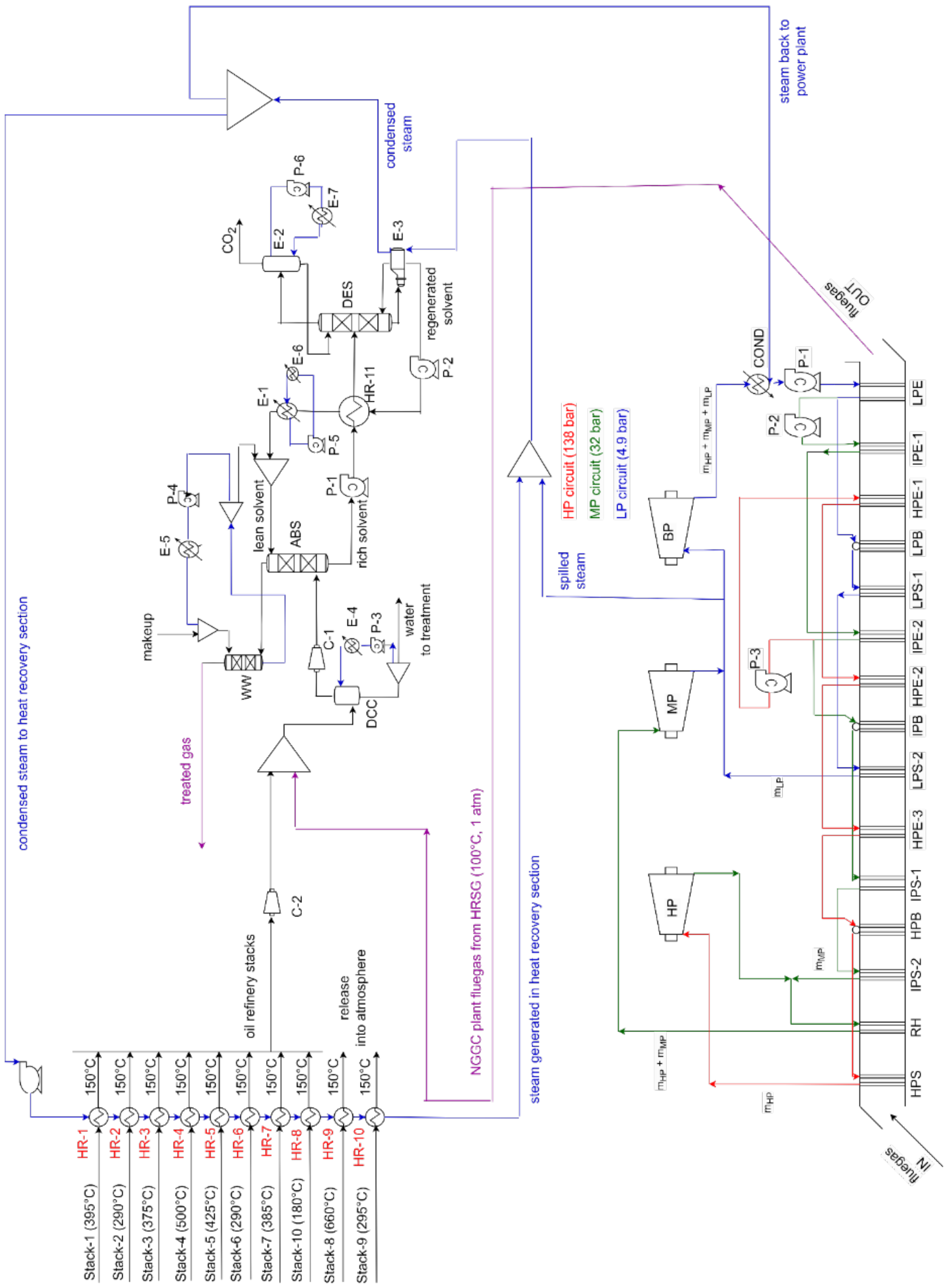


Figure 33. Process flowsheet designed for the integrated treatment of the Aghada ESB power plant flue gas and the Irving oil refinery flue gas in a single absorber-desorber.

The remarkable aspects of the plant design can be summarized as follows:

- it is still possible to recover heat from the refinery flue gas in order to reduce the amount of steam to be spilled from the power plant, thus enhancing the power plant productivity. Therefore, part of the steam to meet the energy requirements of the stripper reboiler comes from the heat recovery section (HR-1 to HR-10) and the remaining part comes from the power plant;

- the refinery flue gas after preliminary heat recovery has a pressure of 0.91 bar, while the NGCC plant gas is at atmospheric pressure. For this reason, a fan (C-2) is introduced to bring the refinery flue gas at the same pressure of the NGCC one before mixing the two;
- the mixing of the two flue gases occurs upstream the DCC, where the mixed gas is cooled down to 28°C before being sent to the main fan (C-1) and then directly to the absorber,
- despite the large overall flow of gas to be treated, the estimated diameters for the main towers are such that it is still reasonable to treat the whole gas in a single train of absorber and desorbed without splitting the streams into multiple columns.

2.4.3.1 Results

The results of unit operation sizing, estimation of energy requirements and the main KPIs for the CO_2 capture plant dedicated to the integrated ESB Aghada and Irving Oil refinery flue gas treatment simulated in Aspen Plus® V11.0 using both default MEA and the new developed HS3 models are summarized here below in Table 34.

Table 34. Summary of equipment sizing, estimation of KPIs and energy requirements for the CO_2 capture plant designed for the integrated treatment of the Aghada ESB power plant and Irving oil refinery flue gases in single absorber-desorber with both MEA and HS3. Results from Aspen Plus simulations using default MEA and new developed HS3 models.

Unit operation	Parameter	MEA	HS3
DCC	Diameter (m) Water flowrate (ton/h)	18.18 6003	18.18 5990
Fan (C-1) Fan (C-2)	Duty (MW) Duty (MW)	7.84 1.46	8.36 1.46
Absorber (ABS)	Diameter (m) Solvent flow (ton/h) L/G (kg/kg) Specific flow (ton/ton CO_2)	15.87 3025.1 1.19 17.15	15.23 2760.0 1.08 15.64
Pump (P-1)	Duty (kW)	271.93	254.17
Rich-lean exchanger (HR-1)	Recovered duty (MW)	213.88	157.101
Desorber (DES)	Diameter (m)	7.10	6.52
Condenser (E-2)	Duty (MW)	56.10	36.34
Reboiler (E-3)	Duty (MW) SRD (MJ/kg CO_2)	173.0 3.92	144.35 3.23
Cooler (E-1) Cooler (E-4) Cooler (E-5)	Duty (MW) Duty (MW) Duty (MW)	0.91 118.15 90.12	27.71 117.72 81.40

The plant sizing and energy requirement estimation leads to the following main comments:

- the energy benefit of using HS3 in terms of SRD and required solvent flowrates is more evident with respect to the case-study dealing with the power-plant only. This is due to the higher average concentration of the mixed gas entering the absorber (4.6 vol% versus 4 vol%);
- the reboiler duty increases only by 29 MW for MEA and by 22 MW for HS3 solvent with respect to the plant in which only the NGCC glue gas was treated; however, in the integrated plant configuration preliminary heat recovery from the refinery flue gas is possible, meaning that the net increase in the power plant steam consumption is limited to only 10.74 MW and 4.48 MW for MEA and HS3, respectively. This means that a 12% larger CO_2 overall uptake can be achieved with a very limited increase in the steam demand.
- almost 29 MW of thermal duty can be saved using HS3. The costs analysis will identify how this energy saving impact on the power plant power efficiency.

The amount of steam to be spilled is given by the steam flow required to generate a thermal duty equal to the reboiler duty minus the portion of the duty already recovered in preliminary heat recovery from the refinery flue gas in exchangers HR-1 to HR-10. For MEA, 62.62 of low-pressure steam must be spilled to provide 154.83 MW of thermal power, while using HS3 the spilled flowrate reduces to 51.03 kg/s. The relative ratio between the spilled steam for the two solvents is substantially equal to the one obtained for the power plant-only gas treatment. The electric power output which can be generated by the LP turbine if the proposed integrated capture plant is implemented is 26.75 MW for MEA and 32.37 MW for HS3. In addition, a further electric power loss must be considered for both solvents to compensate the capture plant electricity requirements. As a result, the efficiency drop of the steam cycle power generation is three percentage points lower for HS3, resulting in a 5 MW overall higher power plant nominal power output. For details, refer to Table 35.

Table 35. Assessment of steam spilling effects on the combined cycle power plant electricity production efficiency for both MEA and HS3 solvents. The analysis refers to the CO_2 capture plant designed for the integrated treatment of Aghada ESB power plant and Irving oil refinery flue gases in single absorber-desorber.

Performance indicator (KPI)	MEA	HS3
Steam to be spilled (kg/s)	62.62	51.03
LP turbine work (MW)	26.75	32.37
Electricity consumption of capture plant	8.77	9.39
Steam cycle power output (MW)	108.03	113.00
Steam cycle efficiency drop	26.51	23.13
Combined cycle power output (MW)	396.03	401.00

2.4.4 Comparison between the three proposed integration scenarios

2.4.4.1 Scenario A

Scenario A is combining the results of the following simulations:

- capture plant for the Irving Oil refinery gas treatment with steam generation by means of natural gas-fed boiler. Electricity is the only utility which is assumed to be transferred from the power plant to the refinery;
- capture plant for the treatment of the ESB station gas flue gas.

The spilled steam must provide only the energy requirements of the capture plant associated to the power plant, since the one handling the refinery gas has an independent steam generator (boiler). The corresponding overall electricity output that the steam cycle and the overall NGCC plant can guarantee at the specified conditions are gathered in Table 36, as well as the efficiency drop for power generation and the total effective electricity output of the power plant under scenario A conditions.

Table 36. Summary of steam spilling effects on the efficiency of the combined cycle power plant electricity output under the assumptions of scenario A. Both MEA and HS3 are considered as solvents for CO_2 removal.

Performance index	**MEA**	**HS3**
Steam spilled for the refinery capture plant (kg/s)	0	0
Steam spilled for the NGCC capture plant (kg/s)	58.24	49.22
LP turbine work (MW)	28.88	33.25
Total electric power from steam cycle (MW)	118.91	123.26
Steam cycle efficiency loss (%)	19.11	16.15
Electricity consumption for the refinery capture plant (MW)	2.02	2.16
Electricity consumption for the NGCC capture plant (MW)	7.98	8.54
NGCC cycle overall electricity production (MW)	396.91	400.56
NGCC cycle efficiency loss (%)	8.76	7.92
$E_{el,eff}$ (MWh/year)	3175312.27	3204507.66

2.4.4.2 Scenario B

Scenario B is combining the results of the following simulations:

- capture plant for the Irving Oil refinery gas treatment with both steam and electricity being provided by the power plant to the refinery;
- capture plant for the treatment of the ESB station gas flue gas.

Scenario B deals with two capture plants like scenario A, but there is no boiler. As demonstrated, this reduces the investment and total costs of the refinery capture plant, but at the expense of a further decrease in the power plant electricity output, which must be quantified. The total amount of steam to be spilled, the corresponding overall electricity output that the steam cycle and the overall NGCC plant can guarantee at the specified conditions are gathered in Table 37, as well as the efficiency drop for power generation and the total effective electricity output of the power plant under scenario B conditions.

Table 37. Summary of steam spilling effects on the efficiency of the combined cycle power plant electricity output under the assumptions of scenario B. Both MEA and HS3 are considered as solvents for CO_2 removal.

Performance index	MEA	HS3
Steam spilled for the refinery capture plant (kg/s)	4.63	2.08
Steam spilled for the NGCC capture plant (kg/s)	58.24	49.22
LP turbine work (MW)	26.64	33.25
Total electric power from steam cycle (MW)	116.68	122.26
Steam cycle efficiency loss (%)	20.62	16.83
Electricity consumption for the refinery capture plant (MW)	1.84	1.97
Electricity consumption for the NGCC capture plant (MW)	7.98	8.54
NGCC cycle overall electricity production (MW)	394.86	399.75
NGCC cycle efficiency loss (%)	9.23	8.10
$E_{el,eff}$ (MWh/year)	3158902.1	3198007.6

2.4.4.3 Scenario C

Scenario C considers only one single capture plant, which is treating a mixture of the refinery and power plant flue gases. Under this scenario, the steam and electricity requirements for the integrated capture plant are fully provided by the power plant, with no additional external energy requirements. This last scenario is worth special attention since a significant decrease in the investment cost per unit of captured CO_2 is expected, thanks to the fact that only one plant has to be designed instead of two. By reflex, tis can somehow also influence the overall combined cycle electricity production rate, thanks to a reduction in the total demand of steam.

The total amount of steam to be spilled, the corresponding overall electricity output that the steam cycle and the overall NGCC plant can guarantee at the specified conditions are gathered in Table 38, as well as the efficiency drop for power generation and the total effective electricity output of the power plant under scenario C conditions.

Table 38. Summary of steam spilling effects on the efficiency of the combined cycle power plant electricity output under the assumptions of scenario C. Both MEA and HS3 are considered as solvents for CO_2 removal.

Performance index	MEA	HS3
Steam spilled for the integrated capture plant (kg/s)	62.62	50.89
LP turbine work (MW)	26.75	32.44
Total electric power from steam cycle (MW)	116.80	122.46
Steam cycle efficiency loss (%)	20.54	16.70
Electricity consumption for the integrated capture plant (MW)	8.77	9.38
NGCC cycle overall electricity production (MW)	396.03	401.08
NGCC cycle efficiency loss (%)	8.96	7.80
$E_{el,eff}$ (MWh/year)	3168253.9	3208623.5

2.4.4.4 Comparison

Looking at the results of the capture plant costs estimation for the three proposed scenarios, the following main conclusions are reached:

- the design of a single integrated facility treating both the refinery flue gas and the power plant flue gas has a good economic potential in case an integrated CO_2 capture in a cluster is to be implemented;
- if two separated plants must be built either for safety issues or because flue gas transportation may not be feasible or convenient, it is in any case better to privilege a solution in which steam is taken from an external source rather than producing it directly on the carbon capture site by means of a steam boiler;
- it is important to underline that the assessment performed in this work is a simplification of the reality since it is not considering some additional issues which can potentially affect the final decision on the most convenient configuration to be adopted, not necessarily for the additional costs, but mainly from practical feasibility or safety point of view. The main additional factors are the costs for steam transportation from the power plant to the refinery carbon capture site and also the transportation of flue gas at least from one of the two sites if a single integrated facility is the chosen option. These contributions are more difficult to be quantified, and can substantially vary from one example of industrial cluster to another one;
- everything considered, the performances of MEA and HS3 are comparable for the integrated capture plant scenarios, with differences in the cost per MWhel of electric power within 3%;
- these results are somehow general and can be considered as a starting point also for the investigation of carbon capture from other clusters.

3 Conclusions

This report describes the procedure followed for the design of an optimized multi-stack CO_2 capture plant for the treatment of the Irving Oil Whitegate refinery flue gas with the HS3 solvent. In compliance with the deliverable task, different plant configurations have been proposed, accounting for different possible energy integration option. For each of the analysed scenarios, a preliminary sizing of the main unit operations and an energy analysis have been carried out. For the columns diameter estimation, 70% flooding velocity has been adopted as design basis. The reported results have to be primarily intended as a milestone for the technoeconomic assessment, which would lead to the final choice on the best capture plant configuration for the Cork cluster case-study.

The Aspen Plus V11.0 HS3 model developed within WP1 and released in D1.3 has been used as modelling tool. Therefore, this report can be also considered as a first successful testing of the new solvent model for a large-scale application. For the sake of comparison of the performances of the new solvent with a benchmark, the same simulations have also been run using the default MEA 30 wt% model proposed by AspenTech.

The work shows that a single-absorber configuration is preferential for this specific application, given the flowrates and composition of the stacks to be treated. A detailed sensitivity analysis has also been proposed following a standardized methodology to define the optimal operating conditions for the CO_2 capture process in terms of CO_2 lean loading, the columns' packing heights and the stripper pressure. For consistency, the same criteria have been adopted for both HS3 and the reference solvent.

The core of the report is the assessment of energy integration options, including both heat recovery with internal sources (refinery gas stacks available at high temperatures), and eternal utilities available within the Cork industrial cluster. This work demonstrates that up to 55% and 74% of the steam required for solvent regeneration when the capture plant is run with MEA and HS3, respectively, can be produced by means of a thermal coupling between the hot flue gas from the refinery and saturated water at 130°C to be vaporized for steam generation to be exploited as reboiler utility. A train of heat recovery exchangers has been designed for this heat integration by means of Aspen EDR. A preliminary costs estimate has been done to demonstrate that, despite the increase in the total investment cost, considering a dedicated heat recovery for each of the stacks to be treated in the capture plant is convenient in terms of total costs reduction, thanks to the great potential in steam requirements reduction Remarkably, the final proposed process configuration allows to maximize internal heat recovery.

Two different scenarios have been proposed for the remaining heat duty to meet the total energy requirements: the refinery could either generate steam onsite in a burning consuming a fuel (natural gas) or exploit part of the steam generated by one of the two NGCC power plants located at short distance from the oil treatment site. For the first scenario, the flue gas generated by the natural gas fed boiler is considered as an additional stack to be treated, in order to still reach a 90% overall capture rate. A comparison between the two alternatives is presented in terms of columns and heat exchanger size as well as energy consumption. Results show that steam integration has the potential to reduce the gas and solvent flowrates circulating in the plant, which results also in an appreciable decrease in the total duties, thus is a lower steam and cooling water requirement. Indeed, when steam integration is accounted for, the steam demand is cut by 18% and 23% if HS3 or MEA are used as solvents, respectively. For the integrated scenario, an estimation of the corresponding decrease in the power plant electricity output production capacity due to steam spilling for the Irving Oil Whitegate capture plant has been also carried out considering the ESB Aghada power station. This analysis points out that steam spilling would result in a decrease in the electricity output of the steam cycle in the combined cycle power plant of only 1.52% and 0.68% when using MEA and HS3 as solvents, respectively.

Concerning HS3 solvent assessment for the proposed application, it is remarkable that the new solvent is associated with a specific reboiler duty of only 2.98 MJ/kg CO_2 captured, when for the benchmark a corresponding value of 3.78 M/kg CO_2 is estimated when considering for both solvents the optimized configurations for the Irving Oil Whitegate CO_2 capture plant (average CO_2 initial concentration of 7.6 vol%). Moreover, the solvent flowrate required to reach the specified capture rate lowers from 1.91 to 1.47 kg per kg of treated gas. The reduced steam demand is expected to provide a sensible cut of the plant utility costs, and, as a reflex, of the total operating costs. The only drawbacks for HS3 are the lower kinetics and the higher volatility of the tertiary amine constituent. These result in a higher packing height in the absorber (and stripper) to reach the same capture rate and in a higher water wash section packing needed to comply with amine emissions legislation. In turn, this also affects the electricity consumption due to the higher pressure drops to be overcome as well as the higher elevation gains to be achieved by circulation pumps. A total costs assessment is required to quantify the economic benefit obtainable with HS3 solvent. This will be the core of the next WP3 deliverable (D3.3).

Finally, the potential for extending CO_2 capture to the entire Cork cluster, also including the treatment of at least one of the two power plant flue gases, is assessed. To this aim, both two separated capture plants handling only the refinery and the power plant flue gases separately and a single integrated facility treating both the flue gas flows have been proposed and compared in terms of energy requirements and equipment sizing. It is remarkable that the energy benefit associated to HS3 is lower when a low-concentrated flue gas is considered (such as the gas from a NGCC plant), but the energy requirements are still appreciably lower with respect to the benchmark. Indeed, the calculated SRDs are 3.96 and 3.35 MJ/kg CO2 for a 4 CO_2 vol% gas.

The main outcome of the comparative assessment between the separated and the integrated capture plants is that the fully integrated facility could guarantee the same overall CO_2 capture rate observed for the two separated facility, a comparable electricity output and a slightly reduced overall steam consumption (-0.3%), but a significantly lower investment cost should be expected for the realization of one single plant. The real potential for the fully integrated scenario must be determined based on total costs and considering an assessment of flue gas and steam transport feasibility.

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