Paint it Blue (Part II): CO$_2$ Removal in Steam-Methane Reforming

In order to be properly stored, CO$_2$ from Steam-Methane Reforming (SMR) needs to be separated and conditioned. One important parameter for transport and storing CO$_2$ is the degree of purity of the CO$_2$-rich stream. In the Northern-Lights project, for example, the CO$_2$ must be delivered nearly pure with ppm levels of contaminants such as: < 30 ppm H$_2$O, < 10 ppm for O$_2$ and < 50 ppm for H$_2$ [1].

Although several processes can be applied to remove CO$_2$ from the SMR H$_2$-rich stream, not all processes can produce a CO$_2$-rich stream that can be sent to standard liquefaction units. This is the case with the often-used PSA which produces a tail-gas with several components in large concentrations. Thus, a process that can be selective to CO$_2$ removal would be advantageous for the purpose of separating and storing it. Chemical absorption provides such characteristics and will be explored further here.

In part I of this series, the Steam-Methane Reforming (SMR) process was modelled in OGT | ProTreat® and a sensibility analysis was done to investigate the effect of reformer temperature and pressure on the process performance. Three possibilities were also identified for applying a CO$_2$ removal process, namely: (i) at the outlet of the shift reactors; (ii) at the tail-gas of the PSA; and (iii) at the exhaust gas of the reformer.

In this Part 2 of the series, we will explore the possibilities of implementing the CO$_2$ capture process at a SMR facility using an aqueous amine solution as the absorption solvent.

Case Study

For the case study, we arbitrarily selected to work with the reforming operating at 20 bar and 870°C. The inlet temperature of the high- and low-temperature water gas shift were set to 350°C and 200°C, respectively. The natural gas flow fed to the reactor was set to 56 KNCMH and the water/natural gas molar flow ratio was set to 3.5.

At the exit of the low-temperature shift reactor, the gas is cooled to 35°C. The PSA unit is modelled as a simple component splitter and is set to recover 90% of the H$_2$.

For simplicity, we assume 100% selectivity, so the H$_2$ stream is composed of 100% H$_2$. The tail-gas from the PSA is returned to the reformer burner and is combusted with extra natural gas to provide the energy required by the reformer. The air flow is adjusted so that the O$_2$ concentration in the flue gas is 2%. The exhaust gas temperature was set to 1025°C, and it is also assumed that after heat recovery the flue gas will be available at 150°C.

The alternatives to place the CO$_2$ capture plant provide different gas conditions, and the selection of the optimal process (and solvent) will depend on that. Table 1 summarizes the stream characteristics.

Table 1: Possible streams to be sent to CO$_2$ removal.: after the water gas shift condenser (WGS), the tail-gas of the PSA (TG), and the flue gas of the reformer (FG)

	WGS	TG	FG
T (°C)	35	35	150
P (bara)	18.3	1	1
Flow (kNm³/h)	264.6	80.4	439.1
%CO$_2$ (mol)	19.3	63.7	17.8
CO$_2$ Flow (t/h)	100.5	100.5	153.4
% Total CO$_2$ Emissions	65.6	65.6	100

Based on the CO$_2$ concentration in the gas streams, the most suitable places for installing a CO$_2$ capture plant using amine-based solvents would be either at the WGS or at the FG. OGT | ProTreat® was used to simulate a CO$_2$ capture plant at both locations. For the WGS, we take advantage of the high pressure and the lack of O$_2$ and NOx and use a blend of MDEA/PZ as the solvent. For the flue gas case (FG) we selected the benchmark 30% MEA as the solvent. The standard capture process was applied in both cases, i.e., no extra operations such as intercooler, lean-rich split, etc. were included in the design.

Results

The processes simulated could potentially be further optimized, for example by adding an intercooler. However, the intention of this issue is to show the difference of the process when different streams are considered for CO$_2$ capture. Table 2 shows a comparison between the two

simulated processes.

The absorber in the WGS case is much more compact than the FG case. This is because of the lower inlet gas volumetric flow, through its operation at higher pressure.

Table 2: Results of the CO_2 capture plant applied at the end of the water gas shift condenser (WGS) and at the reformer flue gas (FG).

	WGS	FG
Absorber		
Packing Height (m)	6	15
Diameter (m)	3.6	9.2
Max Temperature (˚C)	76	82
Stripper		
Packing Height (m)	4	10
Diameter (m)	4.5	6.0
SRD (MJ/kg$_{CO2}$)	2.01	3.30
Reboiler Duty (MW)	53.7	126.3
Removal (%)	95	90
Treated Gas CO_2 (mol%)	0.98	1.91
CO_2 Removed (tonne/h)	96	138
Emission Avoided (%)	62.6	90
Produced CO_2 (%mol, dry)	99.96	99.98

In addition to the differences shown in Table 1, the two gas sources also differ in component slate. The flue gas will unavoidably contain NO_X and O_2 which will play an important role in solvent management. These components will react with the solvent to form degradation products (which can themselves react creating additional degradation compounds) plus heat stable salts. For example, secondary amines can react with NO_X to form toxic nitrosamines. Therefore, a proper choice of the solvent is very important.

In traditional SMR processes, natural gas is also used to provide the thermal energy required by the reformer. Hence, placing the capture plant at the WGS location will only remove a part of total CO_2 emitted (in the simulated case (62.6%). There are some R&D activities developing processes that could minimize the carbon footprint of SMR. For instance, the use of electrified reformers avoiding the necessity to combust natural gas to provide energy and generating CO_2 has been proposed [2].

Conclusions

Hydrogen is considered a promising fuel to decarbonize several energy consuming sectors. Although hydrogen production through water electrolysis has been extensively discussed, it is not yet economically competitive with current production pathways. The state-of-the-art steam the SMR process which is heavily based on relatively inexpensive fossil fuels and which intrinsically contributes to anthropogenic CO_2 emissions.

Despite the consideration of H_2 as an energy vector, it already has an important role as a prime feedstock, *e.g.*, for ammonia production. Current climate targets require the reduction of carbon emissions in all sectors, including H_2 production.

In the case of SMR, carbon capture and storage (CCS) seems the most straightforward way to reduce carbon emissions as it can be easily retrofitted to existing plants and still produce cost competitive H_2 (when comparing to emerging technologies). To understand how CCS can be incorporated in the SMR process, we have used ProTreat to simulate some capture options. Due to the differences in the gas characteristics (temperature, pressure, flow rate and compositions), the optimal process will vary.

References

[1] Quality specification for liquified CO_2. Northern Lights. https://norlights.com/wp-content/uploads/2021/12/Quality-specification-for-liquified-c02.pdf. Accessed on 02/11/2022.
[2] Natrella et al, 2021. How to give a renewed chance to natural gas as feed for the production of hydrogen: Electric MSR coupled with CO_2 mineralization. https://doi.org/10.1016/j.clet.2021.100280

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