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CO₂ Capture and Purification for Use in the Molten Carbonate Electrolysis Cell

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The Molten Carbonate Fuel Cell (MCFC) is a technology that provides clean electricity and requires carbon dioxide to operate due to its carbonate electrolyte environment. This characteristic offers it an advantage as a technique for carbon capture during fuel cell operation and re-use of captured CO₂ during electrolysis mode operation in the Molten Carbonate Electrolysis Cell (MCEC). In both cases, the cell's feeds must be inspected for any impurities since MCFC/MCEC is highly sensitive to sulfur. Since CO₂ as a feed for the cell is captured from the flue gases that contain impurities like SO_x, NO_x, and others, it is necessary to purify it to reach the MCFC's tolerance limit. The purpose of this study is to simulate a full process for capturing CO₂ and purifying it to fulfill impurity constraints of 1 ppm sulfur for use in MCEC. For this purpose, the conventional MEA-based absorption carbon capture method was created with a real flue gas composition input from a coal-fired power station and associated with two distinct desulfurization processes: wet limestone and cryogenic. According to this study, the wet limestone desulfurization process eliminates almost 100 % of the sulfur; however, the standard cryogenic process couldn't attain a 1 ppm sulfur limit, promoting for studying a newly optimized cryogenic process with yielded 100 % of sulfur removal. As for the MEA-based absorption process, it captures around 95% of the CO₂. The economic assessment revealed that the desulfurization process based on the optimized cryogenic process combined with the MEA capture system provides a lower total cost than the one based on the wet limestone. The latter's high expenses contribute to the requirement of an excessive amount of raw material to attain the threshold of 1 ppm sulfur. This overall analysis demonstrates that the cryogenic approach appears to be the best option for this target, whereas the limestone process requires more improvements to reduce its costs.

1. Introduction

In the context of increasing attention to global warming, several countries, such as Germany, signed the Paris Agreement on April 22, 2016. The main goal of this agreement is to reach carbon neutrality in the second half of the century, to limit the environmental and social consequences of an excessive increase in the earth's temperature. To achieve this goal, the German government has put in place the Climate Action Plan 2050. Among the several objectives set by the German government to achieve carbon neutrality by 2050, the industrial sector must reduce its emissions from 49 % to 41 % by 2030, compared to 1990. To achieve this, one of the measures put forward by the German government is the establishment of a research and development program to reduce greenhouse gas emissions from traditional industrial processes. It is in this context, that the capture of CO₂ from the flue gases of certain fossil fuels seems necessary. Given that Germany is still a major user of coal, ranking seventh in the list of countries with the most coal-fired power plants in operation in 2021, it seems interesting to consider a method for capturing CO₂ from such power plants. However, this issue of CO₂ cannot be addressed without thinking of its future use. The most relevant way to valorize the CO₂ captured from flue gases would be the use of MCFCs, a cell that requires CO₂ with its feed for operation to produce and store clean electricity. Indeed, by using CO₂ as a reagent, this cell allows the production of electricity when used in fuel cell mode, and produces, when used in electrolysis mode (MCEC), synthesis gases which allow the storage of electricity produced by renewable energy. The detailed operation of the MCEC is fully described in prior publication by Monzer et al. (2021).

However, the CO₂ captured from flue gases that will be used as a feed for the cell contains impurities including SO_x, NO_x and others to which the MCFC has been reported to be highly sensitive. This implies the necessity to purify the feed stream in order for it to reach the MCFC's tolerance limit which remains quite unclear for now. Indeed, although sulfur has been recognized as the most harmful impurity in the flue gas for the MCFC (Di Giulio et al., 2012), operating conditions such as temperature or pressure seem likely to modify the influence of sulfur on the cell degradation and the tolerance limit of the cell. A broader look at all the impurities that are likely to be found in flue gas is needed to avoid cell deterioration.

Given that the purpose of the work reported in this research paper study is to simulate a full process for capturing CO₂ and purifying it to fulfill impurity constraints for use in the MCEC cell, it is necessary to find an appropriate desulfurization mode for this situation. A thorough literature review carried by Li et al. (2022) led to the selection of two desulfurisation methods, which had already been implemented on the ASPEN Plus software: cryogenic desulfurization and desulfurization using limestone. However, none of these simulations were focused on reducing the sulfur concentration to 1 ppm, nor were they combined with a CO₂ capture system. As a result, for the method of capturing CO₂ from the flue gas, it was decided to investigate a chemical absorption method using MEA as a solvent. This process; however, is sensitive to sulfur with a tolerance limit of 10 ppm. So, it seemed appropriate to perform the desulfurization to 1 ppm before capturing CO₂ for its final use in the MCEC cell. Several models of the MEA capture process have already been set up using ASPEN Plus (Alie, 2004), but in each of these models, it was assumed that the incoming gas no longer contained any sulfur.

2. Methods

2.1 Flue gas composition

To begin, as the main goal of the research is to simulate the whole purification and capture process, as close to reality as possible, the real composition of the feeding flue gas needs to be found. However, since the biggest impacts are related to CO₂ and impurity concentration, finding a complete composition that did not compromise the precision of the concentration of impurities was impossible. This led to the selection of the volumetric percentages of most components such as CO₂ and all impurities from Lee et al. (2009) experiments, taking classic concentrations of O₂ and H₂O from various sources in literature such as Song et al. (2004) and Di Giulio et al. (2012) and using N₂ as balance, as it is an inert gas.

Table 1: Flue gas composition and Simulation Parameters

Parameters	Value	Chemical species	Volumetric percentage
Inlet Flue Gas Parameters		CO ₂	12
Temperature (°C)	52	SO ₂	0.3
Pressure (MPa)	0.1	SO ₃	0.006
Volumetric flow rate (m ³ /h)	2.55x10 ⁶	NO ₂	0.004
Process Parameters		HCl	0.01
MEA inlet mass fraction	0.3	H ₂ O	10
Lean MEA purge loss (%)	15	O ₂	5
CaCO ₃ inlet mass fraction	0.0007	N ₂	72.68

2.2 Tolerance limit for impurities

In relation to the composition that has been chosen to simulate a flue gas from a coal-fired power plant, it seems important to look at the impact that different impurities have on the cell, in order to set a limit to be respected thanks to a prior purification of the gases. Since MCEC and MCFC cells have the same chemical composition but simply a different electrochemical functioning, it will be adequate to look at the impact of the distinct species on one of these two cells: the MCFC. Di Giulio et al. (2012) took up the existing body of work, recognized that sulfur is the most dangerous impurity in the flue gas for the MCFC and studied the impact of operating conditions on the tolerance limit of this cell to sulfur. Sulfur interacts with the cell in the following way: SO_{x(g)} contained in flue gas is readily uptake by the molten carbonate electrolyte. The molecules Na₂SO₄ and Li₂SO₄ formed are highly soluble in the molten carbonate, and migrate within the electrolyte. At the anode, these species are reduced and eliminated from the electrolyte in the form of H₂S_(g), where it may interact with the anode.

The results of their work showed that the temperature has a major impact on the degradation of the cell due to sulfur and that such degradation can occur from 1 ppm H₂S. Subsequently, Milewski and Lewandowski (2012) investigated the impact of sulfur in high concentrations up to 680 ppm, closer to the concentrations found in the flue gases. They concluded that even for concentrations lower than 100 ppm, a voltage drop across the cell of 2 % is observed after 48 h. It can be deduced that such concentrations would seriously damage the cell very quickly, severely reducing its operational life. Marina (2014) takes a broader look at all types of impurities,

including sulfur, that are likely to be found in combustion flue gases. This paper states that negligible performance losses are observed for sulfur concentrations up to 1 ppm.

By studying the other impurities such as mercury, chlorine, fluorine and selenium (Marina, 2014), it can be concluded that only chlorine could poison the cell. Chlorides are favored to displace carbonate from the molten salt electrolyte. Chlorides are then eliminated from the electrolyte through volatilization of alkali chlorides, which could lead to substantial electrolyte loss. Chlorine can be found at concentrations up to 0.1 ppm $\text{HCl}_{(g)}$: from this limit, 5 % electrolyte loss would be observed during the cell's operating time. It will only be necessary, given the above composition, to desulfurize the smoke from the thermal power plant.

2.3 Desulfurization process

Li et al. (2022) in their paper, provided a state of the art of desulfurization. He highlighted the fact that among dry, wet, and semi-dry desulfurization, wet desulfurization is the most efficient. In addition, Gutiérrez Ortiz et al. (2006) argue that desulfurization using limestone is the most suitable for the current study's purpose due to its low installation cost. Figure 1 shows a scheme of the wet limestone desulfurization process. The flue gas desulfurization happens in the absorber tower where the slurry – a calcium carbonate mixture – reacts with the SO_x and removes it by chemical absorption. A filter is added after the absorber tower to remove the precipitated gypsum and recycle the liquid outlet through a loop. In order to reach the goal of 1 ppm sulfur at the outlet, an optimal calcium carbonate to sulfur ratio needed to be found. A sensitivity analysis on ASPEN Plus demonstrated that the more slurry entering, the more efficient the desulfurization. However, the Economic Analysis module revealed that the most costly component of this process is the raw material (CaCO_3) contained in this slurry leading to the selection of the lowest mass flow, allowing it to reach the objective of 1 ppm.

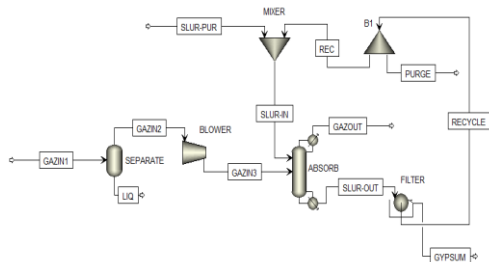


Figure 1: ASPEN Plus implementation of limestone desulfurization

In addition, recent research led by Zhang et al. (2021) has focused on the use of a new process: cryogenic desulfurization. Their simulation results demonstrate that this process, which is based on the liquefaction of sulfur in the flue gas, provides a desulfurization efficiency of 73.2 % at a low temperature of $-45\text{ }^\circ\text{C}$ and pressure of 0.5 MPa where this efficiency can reach 90.2 % with a pressure increase to 2.5 MPa. Based on this study, the cryogenic process was adapted and modified to desulfurize the flue gas to a target of 1 ppm. However, CO_2 liquefies with sulfur at high pressures based on phase diagram data which were the condition cases addressed by Zhang et al. (2021). As a result, the process's working pressure has been reduced to 0.1 - 0.2 MPa to avoid CO_2 liquefaction with sulfur. The standard cryogenic desulfurization process was studied at low pressure as well as an optimized process was proposed and studied. The latter consists of an additional pre-reactor that was added to shift SO_2 into SO_3 since SO_3 has a higher boiling point than that of SO_2 , as illustrated in Figure 2.

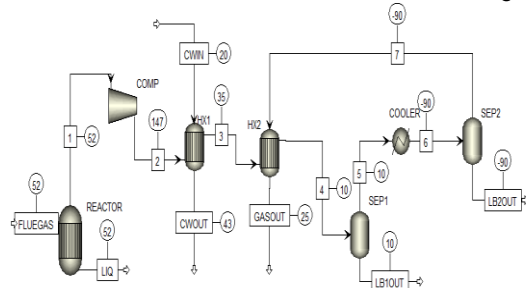


Figure 2: ASPEN Plus implementation of cryogenic desulfurization

The general operation of the current process is to primarily cool down the gas stream to remove the excess water stream as the subsequent temperature will be very low and would freeze the water, which would probably

couldn't achieve a sulfur level of 1 ppm where the SO₂ outlet mass fraction is 230 ppm. A pressure increase to 3 MPa improved the desulfurization process to 1 ppm sulfur. This condition, however, results in a massive loss of CO₂ with sulfur in the form of liquid. As a result, the standard cryogenic technique appears ineffective for desulfurization to 1 ppm sulfur. On the contrary, the addition of the pre-reactor has improved the cryogenic desulfurization where it can be found in Table 2 that the sulfur mass fraction in the outgoing flue gas is below 1 ppm. In a comparison of both desulfurization processes, the wet limestone process achieved almost 100 % yield of both SO₂ and SO₃ removal, whereas the standard cryogenic one (without reactor) yielded 72 % and almost 100 % of SO₂ and SO₃ removal. Nevertheless, the optimized cryogenic process (with reactor) proves almost 100 % yield of both SO₂ and SO₃ removal which could be competitive with the conventional wet limestone process. However, a 31 % CO₂ loss was obtained in the optimized cryogenic process which requires further studies to reduce or avoid it.

For MEA, both simulations, whose flue gas composition can be found in Table 2, also reach their goals which are on one hand to capture a large part of the CO₂ from the flue gas to release carbon-free fumes into the atmosphere, and on the other hand, concentrate the CO₂ to have an outlet flow close to purity to use as feed for the cell. The post-limestone MEA process yielded a 94.5 % and 94.7 % CO₂ capture for the process without and with recovery heat exchangers (HeatX), respectively. On the other hand, the post-cryogenic MEA process achieved a 94.8 % CO₂ capture yield with both processes. Besides, the reboiler duty proved a decrease of 20 % with the recovery heat exchangers (HeatX) optimized process for the post-limestone MEA process and a decrease of 36 % for the post-cryogenic MEA process.

3.2 Cost Calculations

Another element to consider is the cost of these different processes which permits to compare them in terms of economic aspects. The cost is divided into two main categories. On one side, there is the initial investment (CAPEX) which includes the equipment and installation costs and on the other side there is the operating costs (OPEX) which include all ongoing costs such as the raw materials used and the electricity. The Economic Analyzer tool on ASPEN Plus calculates the equipment and installation costs of most blocks used in the different processes. However, it does not take all of them into account and needs to be completed using the data in Jones (2019). The operating costs can be of numerous forms, such as energy costs, raw material costs, and labor costs. The Energy Analyzer program estimates total energy expenses, while labor and raw material costs are determined based on market prices. In the current case, OPEX represents the sum of total utilities (energy expenses) and raw material costs. The raw material cost is calculated using Eq(1) based on the requirements of the raw materials of each process, where Δt is the operating time in hours (h), M is the molar mass in kg/kmol, $F(i)$ is the mole flow of the raw material stream(i) in kmol/h, and C is the cost in USD/kg.

$$\text{Raw material cost} = \sum F(i) \times x(i) \times \Delta t \times M(i) \times C(\text{USD}/\text{kg}_i) \quad (1)$$

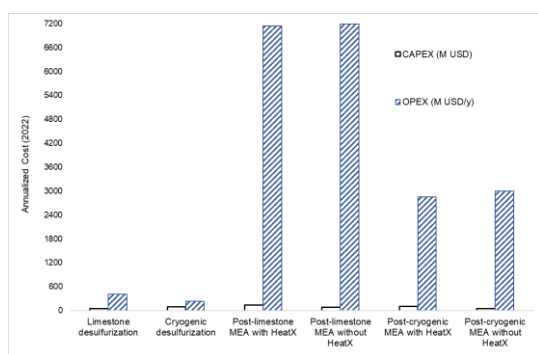


Figure 4: Total actualized cost of both desulfurization processes, along with the MEA-absorption process

3.3 Discussion

The yield calculations revealed that the desulfurization efficiency is analogous in the wet limestone and the modified cryogenic process. To compare the two techniques, the most relevant differentiating factors would be the total costs, so they were investigated, as shown in Figure 4. First, there is the cost specific to desulfurization. On the CAPEX side, the wet limestone desulfurization process investment is lower by 85 % than the optimized cryogenic process, where the investment cost of the cryogenic process is concentrated around the heat exchangers and the reactor. On the other side, both techniques have a significant operating expenses, with the wet limestone process being very demanding in raw materials in the entering slurry and the cryogenic process being very energy-consuming. Nevertheless, the optimized cryogenic process requires a lower operating cost

of 43 % than that of the wet limestone process due to the availability of heat integration in the cryogenic process that lowers the energy duty, but there is no way to reduce the raw material demand in the limestone process at the moment. Secondly, there is the cost related to CO₂ capture. The CAPEX in the capture post-limestone may be somewhat higher by an average of 29 % than in the capture post-cryogenic; however, the operational expenses in the capture post-limestone are far higher by an average of 40 %. This can be explained by two main factors. First, the entering flue gas needs to be compressed and cooled, which is not the case of post-cryogenic, and that adds an energy operating cost. Secondly, the flow of the MEA entering the absorption tower needed to reach the tolerance limit is much bigger, which adds a raw material cost. When considering the two different processes to capture CO₂ (with and without HeatX), it can be seen that while the process with heat exchangers has a higher installation cost, there is no significant improvement in the OPEX in the post-limestone case due to the large energy consumption for compression and cooling. However, the post-cryogenic proved a 4 % decrease in the OPEX when adding heat exchangers. Based on this economic study, the most viable option is to choose cryogenic desulfurization as the operating costs for the wet limestone are far too great. However, as the operating costs for the limestone process are mostly related to raw materials, more research on how to recycle the slurry and the MEA could improve the OPEX.

4. Conclusion

In this work, two different flue gas desulfurization and CO₂ capture processes were simulated using ASPEN Plus to obtain an acceptable CO₂ gas for the MCEC cell. Based on this research, it can be concluded that under the right operating conditions, both the wet limestone and optimized cryogenic desulfurization processes can produce flue gases containing less than 1 ppm of sulfur, whereas the standard cryogenic process was unable to achieve the 1 ppm target limit. While the wet limestone process is interesting relative to its maturity, the proposed cryogenic process provides comparable results with lower operating costs requirements. This cryogenic process combined with the MEA CO₂ capture process also led to a lower overall cost (CAPEX+OPEX) than the wet limestone process coupled with the MEA CO₂ capture. This assessment reveals that the cryogenic process seems the most suitable option coupled with MEA to have a CO₂ with less than 1 ppm sulfur.

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