CARBON DIOXIDE SEPARATION FROM CO-COMBUSTION PROCESS OF FOSSIL FUELS WITH BIOMASS

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Increase amounts of carbon dioxide emissions in the earth’s atmosphere enhance the greenhouse effect and thus contribute to global warming. Since the start of the world industrialization, the atmospheric CO₂ concentration has considerably increased. The use and combustion of fossil fuels by humans is the major source of the emitted CO₂. Currently, fossil fuels supply over 80% of all energy demands and will likely remain so, into the 21st century.

Capture of CO₂ from fossil fuel fired power plants is drawing increasing interest as a potential method for the control of greenhouse gases.

The paper aims to analyze the process of capturing CO₂ from the flue gas by means of a chemical absorption process. Aqueous monoethanolamine solution (40% wt.) was selected for the removal of CO₂. Moreover, in this paper, a flue gas desulphurization method is well studied and presented. All experiments have been performed on an experimental lab facility. Experimental test results have shown that the emissions of CO₂, SO₂ and NOx have been significantly reduced during the removal processes and have proved the viability of these systems. The combustion process of biomass with coal in fluidised bed has been not affected by the biomass supply.

Keywords: CO₂ capture, MEA, biomass, co-combustion, fluidised bed.

1. Introduction

The main source of CO₂ is the combustion of fossil fuels such as coal, oil and gas in the power generation, industrial, residential and transport sectors. Fossil fuels provide more than 80% of the world’s total energy demands. Currently power sector dominates global CO₂ emissions, accounting for about one-third of total emissions of CO₂. Future projections indicate that the share of these emissions from power generation will increase to around 40% of global CO₂ emissions by 2030, [1]. To reduce the dependency on fossil fuels and totally switch to other energy sources is quite difficult. Moreover, the conversion efficiency of other energy sources for power generation is mostly not as high as

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that of fossil fuels. A reduction of CO\textsubscript{2} emissions resulting from fossil fuels can be obtained by increasing the efficiency of power plants and production processes, switching to lower or zero-carbon fuels, combined with CO\textsubscript{2} capture and long term storage and developing alternative energy sources.

Coal, specifically lignite, is currently the dominant fuel in the power generation sector, in Romania. Coal-fired power plants provided 41% of electricity needs in 2004, Figure 1, [2].

Among the types of fossil fuel used, coal has the highest carbon content, resulting in coal-fired power plants having the highest output rate of CO\textsubscript{2} per kilowatt-hour produced. One question therefore arises how coal can be used further in a more environment-friendly way without its substitution. One of the solutions as a potential option for the control of CO\textsubscript{2} emissions is: (i) biomass co-combustion with coal into existing coal-fired power plants. This is because the use of biomass for energy production does not increase the CO\textsubscript{2} content of the atmosphere, and so, it is considered CO\textsubscript{2} neutral. Other main advantages of biomass are low sulphur and nitrogen concentrations, and higher the lower heating value than of lignite. Romania has a great biomass energy potential, evaluated at about 7600 thousands tones of oil equivalent a year, representing almost 19% from total energy consumption. Another mitigation option, already mentioned, is the application of post-combustion CO\textsubscript{2} capture technologies. In 2001, Romania has ratified the Kyoto protocol, engaging to reduce its emissions of CO\textsubscript{2} between 2008 and 2012 by 8%.

This paper is mainly focused on the analyses of the removal process of CO\textsubscript{2} from flue gases via chemical absorption in aqueous amine solution, and secondly, giving a better understanding of the proposed technology. Aqueous
monoethanolamine has been selected for CO$_2$ removing from the combustion gases, which selectively absorbs the CO$_2$ around ambient conditions. The tests were performed on an experimental installation of co-combustion biomass with coal in fluidised bed combustion. Fluidised bed has been chosen due to its uniform temperature distribution in the combustion zone during operation, and thus, we were expecting to higher combustion efficiency. For the co-combustion procedure, were chosen: for coal – lignite, from the Motru coal field (Romania), having a LHV of about 9,7 MJ/kg; and, for biomass – beech sawdust with a LHV of 14,6 MJ/kg. Because of the high contents of humidity, coal and biomass were dried prior to combustion.

Additional tasks were: since biomass-coal co-combustion generates other air pollutions such as oxides of nitrogen and sulphur, and other contaminants, particulate matters, it was highly desirable to remove all these pollutants prior to CO$_2$ capture. Because of two reasons (i) they can inhibit the ability of the solvent to absorb the CO$_2$ and secondly, (ii) to meet the Romanian legislation requirements. In order to retain these contaminants, the experimental installation was designed and equipped with upstream de-NOx and de-SOx facilities as well as with ash removal systems. Especially a flue gas desulphurization method is well described and presented. For the removal of sulphur dioxide and oxides of nitrogen have been chosen as solvents aqueous sodium hydroxide and ammonia.

2. Co-combustion test facility

Experimental lab facility for biomass co-firing with coal in a fluidised bed combustion system is schematically illustrated in Figure 2, in which the main components of the system are presented. Also, the scheme shows the process flow diagram for CO$_2$ removal via chemical absorption, and the reduction procedures of SO$_2$ and NOx with ammonia/sodium based solvents. Last two and the process of ash removing were applied before CO$_2$ absorption in order to minimize their concentration in the flue gas. During co-combustion were used dried lignite and sawdust, <2 mm in size and <4 mm respectively. The main fuel characteristics are given in Table 1.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Coal (lignite)</th>
<th>Biomass (beech sawdust)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Heating Value</td>
<td>9689</td>
<td>14607</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>26,42</td>
<td>72,50</td>
</tr>
<tr>
<td>Ash content</td>
<td>32,0</td>
<td>1,6</td>
</tr>
<tr>
<td>Water content</td>
<td>24,3</td>
<td>19,24</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>0,54</td>
<td>0,17</td>
</tr>
</tbody>
</table>

Table 1
3. Experimental

The chamber of combustion consists of a vessel with a grate at the bottom through which air was introduced. Before combustion, in an air pre-heater, air is being heated up. When the inlet-bed temperature in the combustor reaches almost 400°C, the fuel mixture of sawdust and lignite ignites.

During the process of combustion, the coarse ash was removed from the combustor by means of a screw, located at the bottom. From the top of the combustion chamber, the hot combustion gases with temperatures up to 1000°C are passed through a heat exchanger where they are cooled down to the temperature levels required for the removal processes, specified earlier. Afterwards, the flue gas enters tangentially a cyclone where particles of the fly ash are separated and removed from the bottom of the unit, while the treated flue gas leaves the top. The amount of fly ash depends mainly on ash content of the fuel as well as on combustion system used. After leaving the cyclone, the flue gas with low ash content flows through a desorber. Flue gases with still high temperatures, around 255°C, come into contact counter-currently with rich monoethanolamine.

In Table 2, there are indicated the main operating conditions of the system.
During the first test for the removal of NOx was selected ammonia, which was injected into the gas stream before the cyclone. Once injected, ammonia converts the NOx to nitrogen and water. The following reaction takes place:

$$6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$$ \hspace{1cm} (1)

To reduce emissions of sulphur dioxide, the co-combustion test installation has been equipped with a flue gas desulphurization system, in which an aqueous solution of sodium hydroxide was selected as washing fluid. Prior to be introduced, sodium hydroxide was dissolved in water, forming a strongly alkaline solution. Flue gases come into direct contact with aqueous solution of NaOH, which is pumped to the scrubber with 2 l/h. Sulphur dioxide reacts with sodium hydroxide and forms a mixture of sodium sulfite (Na$_2$SO$_3$) and water. After that, sodium sulfite absorbs additionally sulphur dioxide, resulting in a chemical compound of sodium hydrogen sulfite (NaHSO$_3$). It is important to note that, the solution of sodium hydroxide also reacts with other acid gases. For example, carbon dioxide reacts with aqueous sodium hydroxide to yield sodium carbonate (Na$_2$CO$_3$). The absorption process of SO2 is as follows:

$$4\text{NaOH} + 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$$ \hspace{1cm} (2)

After the removal of sulphur dioxide, the flue gas is sent to the CO$_2$ absorption unit. The CO$_2$-gas is separated from the flue gases by means of a chemical solvent. As a solvent, there was selected an aqueous solution of monoethanolamine, of which concentration was 40%.
The flue gases with low sulphur content enter the CO₂ absorption tower and come into contact counter-currently with lean solution of MEA, which chemically absorbs the CO₂-gas. The fundamental reaction between carbon dioxide, a weak acid, and monoethanolamine, a weak base, is reversible under specific thermal conditions. So that, if aqueous MEA is cooled to the temperature levels of 40-60°C, then CO₂ is retained by the chemical solvent. Opposite to this procedure, when MEA is heated up to 120-140°C, it releases the CO₂-gas and the regeneration of the chemical solvent takes place. Especially in these operational levels, the MEA can absorb and release the largest amount of CO₂. Also, it is of great interest to emphasize that, the MEA solution was widely used in the petrochemical industries for the removal of CO₂ and H₂S.

The principal chemical reaction is:

\[ \text{HOC}_2\text{H}_4\text{NH}_2 + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{HOC}_2\text{H}_4\text{NH}_3^+ + \text{HCO}_3^- \] (3)

During the absorption process, the reaction proceeds from left to right. From the bottom of the column, the rich MEA solution, which contains the chemically bound CO₂, is passed through a cooling phase. After that, it is pumped to the desorption tower where, it is heated counter-currently by the flue gas stream up to 140°C to release almost pure CO₂. During regeneration, the reaction proceeds from right to left, CO₂ and H₂O evolve from the amine solution and are separated. The CO₂, having been liberated from the MEA, leaves through the top of the separation unit. It is then compressed and stored. The lean solution of monoethanolamine, containing far less CO₂ is cooled down to 40°C, in a cooler, and recycled back to the absorber for additional CO₂ capture.

4. Results and discussions

A number of measurements were taken during the experiments of co-combustion of biomass with coal. The main object of the tests was to separate the emissions of CO₂ using an aqueous monoethanolamine solution with a concentration of 40%. Additionally, during the tests were reduced the pollutant emissions such as sulphur dioxide and oxides of nitrogen. There were selected ammonia (used in TR1) and sodium hydroxide (TR2) for their removal. In Table 3 the main results of the tests are given, representing an average of all data mapped for each test run.
Table 3

<table>
<thead>
<tr>
<th>Test Nr.</th>
<th>TR1</th>
<th>TR2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide (%)</td>
<td>10.61</td>
<td>12.83</td>
</tr>
<tr>
<td></td>
<td>1.73</td>
<td>6.44</td>
</tr>
<tr>
<td>Sulphur Dioxide mg/m³</td>
<td>4382.46</td>
<td>2386.43</td>
</tr>
<tr>
<td></td>
<td>160.05</td>
<td>44.29</td>
</tr>
<tr>
<td>Oxides of Nitrogen mg/m³</td>
<td>576.75</td>
<td>302.74</td>
</tr>
<tr>
<td></td>
<td>270.11</td>
<td>82.10</td>
</tr>
<tr>
<td>Flue Gas Temperature °C</td>
<td>271.50</td>
<td>253.80</td>
</tr>
<tr>
<td></td>
<td>264.80</td>
<td>50.85</td>
</tr>
</tbody>
</table>

1,II – before and after removing

As mentioned early, for the removal of NOx and SO₂, there were selected: TR1, - direct injection of ammonia in the flue gas and for the TR2, - the separation was achieved using aqueous sodium hydroxide. To be noted, these chemical solvents are active both for nitrogen as well as for sulphur dioxide. The concentration of CO₂ was measured after the cyclone and after absorption of CO₂, in the exhaust stack.

The absorption efficiency of CO₂ with monoethanolamine during the first test was higher than in the second one. This is because of:

- TR1: the concentration of CO₂ in the flue gas during the whole test was almost the same, varying between 10-14%, after absorption its content was significantly decreased, reaching 1.73% of CO₂. This represents an efficiency of separation of 85%. It must be said that, although the content of other gases was reduced, ash was removed before the process, the solvent of MEA has partially reacted with some of them, has absorbed some particulates, which finally lead to degradation of it. If in case of CO₂, it can be released from MEA, then other chemical compounds received cannot be evolved.

- TR2: having the same target “CO₂ mitigation” via chemical absorption, the previous solution of MEA has been used. Achieving an absorption efficiency of 50%. Actually it was higher most of the time, but during operation for a moment the fuel supply has been stopped. In that time the CO₂ has decreased from 15 to 4%. One of the reasons why this procedure has been done is to see the absorption capacity of MEA when the CO₂ concentration is very low, e.g. reduction of 1%.

Moreover, during the tests one has been clearly noticed, which is very import when such system is applied to. Even if the flue gas contains very low levels of oxides of nitrogen and sulphur before CO₂ absorption, they can still inhibit the ability of the solvent. Generally speaking, it was the second reason why in some cases the absorption capacity decreased. This is because SO₂ and NOx react with the MEA to form stable, non-regenerable salts, and so cause a steady
loss of the MEA. Low content of ash in the flue gases can lead to the same problems. Mixture received cannot be used further and MEA cannot be regenerated.

Measures for reducing SO$_2$ and NOx have also been taken. To bring down the level of these emissions as much as possible was done in order to (i) minimizing the amine loses, and (ii) meeting the Romanian legislation requirements. The maximal limits are: for the NOx emissions 400 mg/m$^3_N$, for SO$_2$ less than 200 mg/m$^3_N$. Using both aqueous sodium hydroxide and ammonia can reduce the sulphur content in the flue gas by almost 95%. The reduction efficiency of NOx via ammonia injection was around 50%, and reaching over 70% using sodium hydroxide. Chemical analysis of the received solution after the scrubber contains not only sulphur, but also carbon and nitrogen. With regard to sulphur and nitrogen, the conclusion of the study is that, that the biomass co-combustion with coal will definitely decrease the amount of sulphur dioxide emitted in the atmosphere. Although the nitrogen content of biomass is low as well, main control of NOx is by suppressing its formation during the combustion process. This involves operating at low excess air and reducing peak temperatures. If this can be realized only partially, a post-combustion control of NOx is necessary. Using both solvents a reduction of NOx can be achieved.

5. Conclusions

This study explains and analyzes how amine based solutions, namely monoethanolamine, is used for the removal of CO$_2$ from flue gases. Reduction processes of air emission pollutants such as SO$_2$ and NOx with sodium hydroxide and ammonia were investigated. All tests were carried out on an experimental test facility of co-combustion biomass with coal in fluidised bed.

Main findings of the study are: CO$_2$ - over 85% absorption efficiency using MEA; SO$_2$ - reduction of 95%, using both NaOH and NH$_3$; NOx - reduction over 36% when ammonia is injected and over 50% with NaOH.

General conclusion of the study is that, the co-combustion of biomass together with coal is a viable option that promises reduction in the emissions of CO$_2$, SO$_2$ and NOx. Moreover, it represents probably at the moment one of the most feasible energy options. Applying CO$_2$ capture technologies as well as, de-SOx and de-NOx facilities to power plants these emissions can be definitely mitigated.

REFERENCES