Carbon capture in biomass combustion plants using promoted potassium carbonate solutions

A cost and safety evaluation

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Abstract

Biomass combustion can be seen as CO₂ neutral, thereby biomass combustion plants can have negative CO₂ emissions if retrofitted with post combustion capture (PCC) technology using liquid absorbents. Monoethanolamine (MEA) has been used for carbon capture in coal combustion plants but are not suitable for use in biomass combustion plants due to corrosion and high solvent regeneration cost. Instead, the hot potassium carbonate (HPC) process using potassium carbonate (K₂CO₃) as absorbent show better attributes in these aspects. Although, K₂CO₃ has slow reaction kinetics with CO₂ which need to be improved using promoters. Piperazine is the most tested promoter but are hazardous to humans. Recent research has revealed promising alternatives, among these different amino acid salts such as glycine, proline, and isonipecotic acid which are chemically benign. Biomass flue gas composition vary depending on the biomass fuel characteristics. How this affects the degradation and potential formation of hazardous substances need to be studied further. Biomass combustion plants are generally equipped with flue gas condensation systems, making retrofitting more feasible due to increased system flexibility and energy recovery options. The operation costs of carbon capture and sequestration (CCS) in biomass combustion plants need to be monitored to optimize the plant revenue. To make implementation of HPC in biomass combustion plants a reality, piperazine should be used as promoter. Meanwhile, research should focus on improving the absorption rate in HPC process with more chemically safe promoters.
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1 Introduction

Biomass combustion can be seen as carbon neutral since all biomass on earth originates from the photosynthesis, where carbon dioxide (CO₂) from the atmosphere reacts with water to produce carbohydrates and oxygen with the use of energy from the sun. These carbohydrates are stored within the complex biomass structure and later released to the atmosphere in the form of CO₂ trough either combustion or decay. This biogenic CO₂ is then absorbed into new biomass and the circle is complete. [1]

The idea of biomass combustion is that no additional CO₂ is introduced to the biosphere as is the case with fossil fuel combustion, which is one of the driving forces causing the climate change. Consequently, biomass combustion plants have potential for negative CO₂ emissions if combined with carbon capture and sequestration (CCS) technology. When the captured CO₂ is biogenic the method is called bioenergy with carbon capture and storage (BECCS). The pulp- and paper industry and biomass fuelled combined heat and power (CHP) plants give rise to large point emissions of CO₂. The pulp factories are generally energy self-sufficient since the biomass biproducts from the process are reused as fuel in heat and power production within the process. Often the pulp factories can deliver heat and electricity to the national grid since they convert more energy than the process requires [2].

Biomass fuels have many differences from fossil fuels both in terms of fuel characteristics and the flue gases produced. In general, biomass has a higher humidity content than coal which lowers its effective heat value due to the vaporisation energy needed for drying the fuel in the furnace [1]. This vaporisation energy is lost with the flue gas but can be recovered to a high extent as useful heat in a flue gas condensation system (FGC), increasing the overall plant efficiency.

For combustion processes there are three main technologies for CO₂ capture from flue gases, pre-combustion-, oxy-fuel-combustion and post-combustion. Out of these, post combustion capture (PCC) has the greatest potential for retrofitting in existing biomass combustion plants, making a wide implementation of BECCS possible, enabling active withdrawal of CO₂ from the atmosphere. [3]

Up to recently, mainly chemical absorption of CO₂ into liquid solvents like Monoethanolamine (MEA) have been used for PCC in coal combustion plants. MEA has proven to have rapid reaction rates and more than
90% CO₂ removal rates. This method utilizes a temperature swing to shift the vapor/liquid equilibrium (VLE) between the absorber and desorber. However, this method requires large amounts of heat for the solvent regeneration [4]. This heat is supplied by steam extracted from the steam turbine, resulting in a substantial energy penalty, reducing the overall efficiency of the power plant [5].

This is the main reason for the MEA technology not being implemented in biomass combustion plants despite the technological maturity of the MEA absorption process. Adding to this, MEA carries with it some other disadvantages as high degradation and corrosivity, requiring more expensive materials in the system to withstand the corrosion [6].

1.1 The HPC process

There are other approaches to PCC that do not share these negative aspects, the most known being the hot potassium capture (HPC) process, also known as the Benfield process. The Benfield process has been used in gas purifying processes since the 1950s, therefore its chemical properties for CO₂ absorption are well known. [5] This method utilizes a pressure swing between the absorber and desorber, making the HPC process mainly dependent on electricity to pressurize the flue gas before entering the absorber. Although heat is required for the reboiler connected to the stripper. This heat can be supplied by a low-pressure steam flow from the turbine or steam generated by an electric heater. [7]

Figure 1 shows a basic illustration of the process. The flue gas enters the absorber after being pressurised in the compressor. The lean solvent is injected at the top of the absorber and flows through the packing material while absorbing CO₂ from the flue gas. The purpose of the packing material is to enlarge the liquid surface area exposed to the flue gas, thereby increasing the CO₂ absorption rate. The CO₂ rich solvent is then led from the bottom of the absorber to the top of the stripper where the pressure is lower, releasing CO₂ on the way down. The CO₂ is extracted at the top of the desorber and led to the liquification process, and the lean solvent is pumped back to the absorber.
Figure 1: A basic illustration of the HPC process, the absorber and desorber are in upright position. (Own figure)

The HPC process has 17% lower cost for CO₂ capture and liquefaction compared to amine absorption techniques since the energy used for compression partly can be recovered as useful heat [5]. Adding to this, potassium carbonate (K₂CO₃) as absorbent generally has comparatively low regeneration energy demand, low degradation, low toxicity and low corrosivity. On the downside, potassium carbonate has slow reaction kinetics with CO₂, lowering the absorption rate, particularly in PCC applications due to the low CO₂ partial pressure in the flue gas. In compensation the absorber needs to be scaled up in size for a given cyclic capacity, increasing the investment and operation cost. [6] This is the reason for the HPC process not yet being implemented in PCC despite all its favourable properties.

1.2 Absorption rate enhancement

The absorption rate of CO₂ into the potassium carbonate solvent can be greatly improved by adding chemical promoters to the solution. Higher absorption rates reduce the required absorber dimensions, lowering both the investment as well as operation cost. [6] Promoters for enhanced reaction kinetics in K₂CO₃ solutions for CO₂ capture have been the subject of many studies.

In the selection of a suitable promoter not only the increase in absorption rate is of importance, but several other aspects must also be considered with regards to implementation in PCC. Potassium carbonate has low
toxicity. Therefore, it is contraintuitive to add a highly toxic promoter, from a health and safety as well as environmental point of view. Furthermore, the promoter should be stable, non-corrosive, effective, recyclable, not too expensive and have low vapor pressure [3].

There are many articles to be found concerning this matter, but articles about promoters in $\text{K}_2\text{CO}_3$ solutions for PCC applications in biomass combustion plants are scarce. Since there is an opportunity for making biomass combustion plants carbon sinks with retrofitting of PCC systems, efforts are necessary to adapt the technology making retrofitting feasible.

Since MEA brings a substantial energy penalty as well as other negative aspects, the potassium carbonate process is a promising alternative that needs further exploration. With promoters in the $\text{K}_2\text{CO}_3$ solution the absorption rate can be enhanced, reducing the investment cost.

However, to make wide implementation a reality in the near future there is a need for compromise between finding the optimal solution from an economic perspective and the environmental benefits of negative $\text{CO}_2$ emissions. The focus should be on getting the equipment in place in biomass combustion plants, stripping $\text{CO}_2$ from the atmosphere as soon as possible, not waiting for the optimal solution. Consequently, future research should be focused on enhancing the processes while in use.

1.3 Health and safety

Personal health and safety must be of highest priority when considering retrofitting of PCC in biomass combustion plants. Aside from regular workplace safety standards and regulations, potential health hazards must be addressed.

One complication that stands out among other is the potential formation of carcinogenic nitrosamines. These are formed in the reaction between amines and nitrous oxides (NOx), which occur both in the absorber and stripper as well as in the atmosphere when solvent molecules escape with the flue gas. NOx- species present in the flue gas must be expected to cause formation of nitrosamines from any amine and are greatly influenced by the quality of the flue gas delivered to the $\text{CO}_2$ capture process. Nitrosamines can be destroyed at the high temperatures of the stripper, but there is a potential of accumulation of nitrosamines in the PCC system. This can be hazardous for workers in maintenance operations or in the event of leakage from the equipment. [8]
Introduction

Even though the potassium carbonate process could include smaller fractions of amines as promoters this issue must be kept in mind when developing PCC systems and in promoter selection. Biomass combustion plants often use a mix of different biomass fuels that varies in moisture and ash content depending on heat demand and availability of different fuel fractions. This makes the moisture levels and composition of the flue gas more fluctuating compared to coal fired combustion plants, occasionally leading to increased NOx levels in the flue gas.

Modern biomass combustion plants generally have highly effective flue gas cleaning systems. Although, research in the form of measurements of nitrosamines in PCC equipped biomass combustion plants or in lab scale experiments including representative biomass flue gases is needed.

1.4 Author’s remarks

The purpose of this study is to provide a new perspective to the field of CCS research. The aim is to highlight the potential for biomass combustion plants to become carbon sinks, discuss the possible complications and contribute with suggestions for further research. Another goal is to contribute with a method for calculating the costs for a HPC process. This study is limited to promoters for $\text{K}_2\text{CO}_3$ solutions for use in the HPC process.

The main problem is that the cost for implementing HPC in biomass combustion plants is too high, therefore different measures need to be taken to lower the costs, one being increasing the $\text{CO}_2$ absorption rate.

The main question to be answered in this study is which promoter would be the best alternative for implementation of the potassium carbonate CCS process in a biomass combustion plant?

The author’s contribution is a safety and economic analysis of promoters based on a previous screening test of twelve promoters. Also, a new method is proposed for calculating the actual operation cost based on type of biomass fuel used for a HPC process used in a biomass combustion plant. Furthermore, possible complications and energy recovery opportunities when implementing the HPC process in a biomass combustion plant is discussed throughout the article. Where a piece of text is not referenced, it is the author’s own discussion. The most suitable promoter for use in biomass combustion plants is chosen based on analysis made in the study, and suggestions are made on further research in this perspective.
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Introduction

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List of abbreviations

\( m_{CO_2} \) \( x \) Mass of captured CO\(_2\) from the flue gas
AAS Amino acid salts
BECCS Bioenergy carbon capture and storage
\( C_{bf} \) Biomass fuel price
CCS Carbon capture and sequestration
CHP Combined heat and power
\( C_h \) Hourly HPC process cost
\( C_{hpc} \) Actual HPC process cost
\( C_{h,mix} \) Hourly HPC process cost using biomass fuel mix
\( C_{mix} \) Actual HPC cost using a biomass fuel mix
CO\(_2\) Carbon dioxide
\( E_d \) HPC process energy duty
\( E_{hpc} \) HPC energy use
EDA Ethylenediamine
\( E_{df} \) Energy duty in terms of heat input
FGC Flue gas condensation
\( H_{cal} \) Calorific heat value
\( H_{eff} \) Effective heat value
\( H_{mix} \) Biomass fuel mix effective heat value
HPC Hot potassium carbonate
\( \lambda \) Excess air ratio
\( m \) molal (concentration, mol/kg)
\( M \) molar (concentration, mol/l)
MEA Monoethanolamine
\( \dot{m}_{fuel} \) Biomass fuel mass flow
\( \dot{m}_{mix} \) Biomass fuel mix mass flow
MSW Municipal solid waste
NO\(_x\) Nitrous oxides
PCC Post combustion capture
\( P_{el} \) Electric load
\( P_{fuel} \) Fuel input power
\( P_{heat} \) Heat load
PZ Piperazine
TETA Triethylenetetramine
VLE Vapor/liquid equilibrium
\( y_i \) Mass fraction of component i
\( \eta_{cap} \) CO\(_2\) capture efficiency
\( \eta_{el} \) Electricity production efficiency
Promoters for rate enhancement in K$_2$CO$_3$ solutions

To make retrofitting feasible in biomass combustion plants, the chemical reaction kinetics of CO$_2$ into the K$_2$CO$_3$ solvent need to be enhanced with promoters to lower the investment cost. There are three main types of promoters: organic, inorganic, and enzymatic.

The 2021 review article by Ochedi et al. [3] includes a comprehensive overview of the latest findings, briefly referred to in the following section. Addition of amines as promoters have been studied extensively with primary and secondary amines seeming to be more effective than tertiary amines. Monoethanolamine (MEA), Diethanolamine (DEA) and Pipera-\text{azine} (PZ) are well tested and have high absorption rates and good CO$_2$ selectivity. On the downside amine activators also bring their negative aspects to the K$_2$CO$_3$ solution, such as increased corrosion, evaporation, toxicity, and degradation. [3]

Amino acid salt (AAS) as promoters do not share some of those disadvantages, having low toxicity and volatility, higher solubility and surface tension and faster absorption rate than amines. Among the commonly tested amino acid salts are glycine, arginine, lysine, and proline, with glycine promoted K$_2$CO$_3$ solutions showing highest absorption rates of these. However, AAS tends to form stable carbamates requiring increased regeneration energy. [3]

Enzymatic promoters have more recently been introduced as a promising alternative, although showing low stability, reuse problem and reduced activity after the required immobilization. If these challenges can be overcome, enzymatic promoters can be a highly effective alternative, with carbonic anhydrase being the most researched enzyme. [3]

Lately, mixtures of multiple promoter types have been tested. Blends of different cyclic amines and cyclic amines with aliphatic have shown synergetic effects. Furthermore, Ochedi et al. (2021) suggests research into kinetics and crystallization equilibria of potassium bicarbonate, potassium sulphate, and potassium nitrate in the presence of flue gas to prevent formation of these salts causing blockage in absorption systems. More effort is required for deeper knowledge of thermodynamics and kinetics of potassium carbonate CO$_2$ absorption processes. [3]
2.1 Research on promoters

Beiron et al (2022) studied the cost of implementing BECCS in Swedish CHP plants with the main focus on MEA processes in different configurations of PCC applications. Alternative CO₂ capture processes were also discussed, one being the HPC process. Further research into the degradation of solution components when the HPC process is used in municipal solid waste (MSW) combustion processes were suggested, to better understand the operating costs. [9]

Ramezani et al (2021) studied the promotion of 2 M K₂CO₃ in solution with 0.2-0.5 M diethylenetriamine (DETA) in a laboratory scale experiment. Density, viscosity, diffusivity, and CO₂ absorption rate from a mixture of N₂O, N₂ and CO₂ gas were measured at 30, 40 and 50 °C. The results showed an increase in both solubility and diffusivity with temperature, and that the absorption rate increases with temperature and promoter solvent concentration. In terms of reaction rate the distribution of promoters were DETA > proline > ethylaminoethanol (EAE) > arginine > MEA > taurine > histidine > alanine. [10]

Borhani et al (2022) studied the effect on absorption rate in a column with two different packing types and two different mixtures in a steady state modelling study in MATLAB. One mixture consisted of 5 m K₂CO₃ + 2.5 m PZ and the other of 6.4 m K₂CO₃ + 1.6 m PZ. They found a presence of water vapour throughout the column, indicating that water evaporates from the aggregated solution in the bottom of the column. The study also generated a model framework useful for the modelling of complex mixtures for CO₂ absorption. [11]

Ayittey et al. (2020) investigated the lean solvent concentrations impact on the reboiler duty with combinations of 30 and 40 wt% K₂CO₃ + 2, 3 and 6 wt% boric acid in solution. Then found that a higher lean solvent concentration lowered the reboiler duty, albeit at a higher chemical supply cost and increased risk for salt precipitation in the column. Therefore techno- economic analyses were suggested to investigate the optimum lean solvent concentration. [12]

Ahmed et al. (2020), studied the desorption and absorption rate enhancement with solutions of 1 M K₂CO₃ and 10 wt% of different AAS as promoters. This with bench scales experiment using a mix of N₂ and CO₂ and small-scale packed columns at an absorption temperature of 25 °C and atmospheric pressure. The results showed an increase in CO₂ loading and
regeneration efficiency for each promoter tested, with methionine showing the best performance and glutamine having the highest regeneration efficiency. The AAS tested were glutamine, glutamic acid, tyrosine, methionine and tryptophane. [13]

Harja et al. (2020) studied the effect on viscosity in 25 wt% $\text{K}_2\text{CO}_3$ solutions promoted with 3, 5 and 7 wt% ethylenediamine (EDA) or 3, 5 wt% triethylenetetramine (TETA) at temperatures between 25 – 70 °C. This resulted in a polynomial equation with three coefficients useful for predicting the viscosity of EDA promoted $\text{K}_2\text{CO}_3$ solutions at different temperatures. The study showed increased viscosity with increased concentrations of EDA or TETA in the solution. [14]

Niknam et al. (2020), studied the $\text{CO}_2$ absorption performance with L-proline promoted $\text{K}_2\text{CO}_3$ solution using hollow fibre membrane contactor (HFMC). 0.05 mol/l L-proline with 4 wt% $\text{K}_2\text{CO}_3$ increased $\text{CO}_2$ capture more than 1.2 times, thus showing it to be a promising absorbent alternative for CCS using HFMC. [15]

### 2.2 Promoter cost and safety analysis

Most studies of the promoting effect are bench scale experiments with a mixture of pure gases such as nitrogen mixed with fraction of $\text{CO}_2$ that represents the amount in flue gas.

Park et al. (2014), performed a bench scale screening test of twelve different amines and amino acid salts as promoters at 70°C and 1 atm with 30 wt% $\text{K}_2\text{CO}_3$ and 3 wt% promoter in solution. The promoters were compared in terms of increase in cyclic capacity versus the unpromoted solution. [16]

In this work, these screening test results are further analysed in terms of price and chemical safety, see table 1.

In the screening test the addition of promoters increases the cyclic capacity up to 8.7 times compared to the unpromoted solution, clearly showing the benefits of using promoters. The prices were obtained from a vendor’s homepage and are not representative for large scale operations as chemicals in that case are acquired at bulk prices. Although, the prices are relevant for smaller scale experiments and can give a sense of the price distribution between the promoters even for large scale operations. Screening tests of this magnitude are very useful since they can be further analysed as all promoters are tested at the same conditions.
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Table 1: Comparison of promoters in solution with 30 wt% K2CO3 and 3 wt% promoter at 70°C and atmospheric pressure. [16] Prices were obtained from www.tcichemicals.com [17] and chemical safety information from www.pubchem.com [18] (Own table)

<table>
<thead>
<tr>
<th>Promoter</th>
<th>Cyclic capacity [g CO2/l sol]</th>
<th>Increase [promoted/unprom.]</th>
<th>Price [€/kg]</th>
<th>Corrosive [O]</th>
<th>Irritant [∆]</th>
<th>Health hazard [X]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium carbonate (unpromoted)</td>
<td>6.6</td>
<td>77</td>
<td>∆</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pipecolic acid</td>
<td>58.0</td>
<td>8.7</td>
<td>180</td>
<td>∆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piperazine</td>
<td>52.1</td>
<td>7.8</td>
<td>62</td>
<td>O</td>
<td>∆∆</td>
<td>XXX</td>
</tr>
<tr>
<td>Isonipecotic acid</td>
<td>47.7</td>
<td>7.2</td>
<td>218</td>
<td>∆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sarcosine</td>
<td>46.1</td>
<td>6.9</td>
<td>236</td>
<td>O</td>
<td>∆∆</td>
<td></td>
</tr>
<tr>
<td>1-aminocyclohexane carboxylic acid</td>
<td>45.8</td>
<td>6.9</td>
<td>6070</td>
<td>O</td>
<td>∆∆</td>
<td></td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>44.8</td>
<td>6.7</td>
<td>48</td>
<td>O</td>
<td>∆∆</td>
<td>XX</td>
</tr>
<tr>
<td>Proline</td>
<td>39.0</td>
<td>5.9</td>
<td>264</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alanine</td>
<td>37.2</td>
<td>5.6</td>
<td>448</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-aminoisobutyric acid</td>
<td>33.6</td>
<td>5.1</td>
<td>504</td>
<td>∆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycine</td>
<td>31.1</td>
<td>4.7</td>
<td>48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Histidine</td>
<td>28.7</td>
<td>4.3</td>
<td>384</td>
<td>∆∆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arginine</td>
<td>19.5</td>
<td>2.9</td>
<td>214</td>
<td>∆</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Description of hazard level labelling with symbols (i) of respective category, (authors own grading based on LCSS)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Causes irritation to eyes, skin or respiratory systems, harmful if inhaled or swallowed</td>
</tr>
<tr>
<td>ii</td>
<td>Causes serious damage to eyes or skin</td>
</tr>
<tr>
<td>iii</td>
<td>Causes severe damage to eyes or skin, suspected damage to fertility and unborn child</td>
</tr>
</tbody>
</table>

Each promoter are graded in terms of how hazardous they are to humans with up to three symbols based on information from laboratory chemical safety summary (LCSS) sheets for each promoter, see description in table 2 [18]. Each level builds upon the previous. Of most concern is piperazine, which is suspected to cause damage to fertility and damage to the unborn child and thereby was given the highest hazard level.

Piperazine and diethanolamine show good performance as promoters at relatively low prices but are also inferior in terms of chemical safety. Proline and alanine are chemically safe and show intermediate performance in this range but are comparably expensive, possibly because these also are human micronutrients sold as supplements. Glycine shows interesting properties as being safe and relatively cheap, although the cyclic capacity is lower. Pipecolic acid and isonipecotic acid show high cyclic capacities albeit at a higher price, but they are also relatively benign in terms of chemical safety. 1-aminocyclohexane butyric acid and 2-aminoisobutyric acid are too expensive to be considered for large scale PCC operation. However, the degradation and consumption of these promoters in
the presence of real biomass flue gases needs to be studied to make a comparison relevant for use in biomass combustion applications.

As piperazine and diethanolamine have low prices and high absorption rate enhancement properties, it is suggested that these should be tested with biomass flue gas to study the potential formation of nitrosamines, formation of corrosive compounds and degradation rate when used as promoters. Although chemically benign, glycine, proline and alanine need to be tested at the same terms, as the interactions between flue gas and absorber solutions are complex and hazardous compounds could be formed even though the solvents are safe to begin with. Pipecolic acid, isonipecotic acid and sarcosine have not been tested as often as the other promoters in previous studies but show interesting properties and decent performance.

As a result of this analysis, a screening test including piperazine, diethanolamine, glycine, proline, sarcosine, isonipecotic acid and pipecolic acid in the presence of flue gases from an operational biomass combustion plant is suggested. Important factors to study are degradation rate, consumption, corrosion, and the potential formation of hazardous substances such as nitrosamines.

This could be done using a small flue gas slip stream extracted downstream of the FGC and led into a small-scale laboratory inside e.g., a freight container located next to a biomass combustion plant. Keeping the experiment small scale make it possible to test a wide range of different promoters and absorber solvents under real conditions over time.

The interactions between solvents and biomass flue gases are very complex and the composition of biogenic flue gases vary over time depending on moisture level and the characteristics of the biomass combusted in the moment. It is possible that the promoter with the best properties in tests with pure gases is not suitable in real applications due to high degradation or formation of hazardous compounds in contact with biomass flue gas. The consumption of lower priced promoter could be higher, making use of a more expensive promoter more beneficial in the long run. Another aspect that needs to be studied is waste handling of used solvents but this falls outside the scope of this study.
3 Application in biomass combustion plants

There are several important design aspects that must be kept in mind when retrofitting PCC in biomass combustion plants as they have special properties bringing both challenges and opportunities.

Combustion of biomass is heavily influenced by feedstock properties and reaction conditions. The biomass structure is complex and has a significant influence on the combustion behaviour. [19]

3.1 Flue gas treatment

Knowledge of the inorganic fractions such as ash content and biomass characteristics is crucial to the design and operation of the biomass combustion plant as well as the PCC system. [19]

The flue gas treatment prior to the PCC system is critical to enable optimal performance and maintaining stable operation of the CO₂ capture process. Suboptimal conditioned flue gas accelerates absorbent degradation and consumption as well as increasing the risk for additional environmental impact through emission of compounds formed in the PCC system. Particulate matter may cause operational problems such as blockage or foaming in contact with the absorber solution. Therefore, the PCC system is preferably located downstream of the flue gas cleaning system to ensure maximum contaminant removal from the flue gases before entering the PCC section as described in figure 2. In liquid absorbent PCC, NO₂ and SOx reacts with amines, causing degradation and generating heat stable salts. [20]
Figure 2: Suggested placement of the HPC system in the flue gas stream of a biomass combustion plant. (Own figure)

Emissions from solid biomass combustion contains particulates in the form of an organic fraction of mainly soot and inorganic fraction of fly ash. The fly ash consists mostly of potassium (K), sulphur (S) and chlorine (Cl) which forms gaseous compounds in the flue gas. These gaseous compounds condensates on particle surfaces after nucleation. Medium scale biomass combustion plant from 0.5 MWth and larger often equipped with flue gas cleaning equipment such as cyclones, baghouse filters and electrostatic precipitators to reduce particulate emissions. The combination of these leads to a flue gas particulate reduction exceeding 99%. However, particles in the size range of 0.05-0.50 μm are not reduced efficiently in these systems. [21]

How these particles affect the degradation of the K₂CO₃ solution needs to be considered when designing a PCC system for a biomass combustion plant.

Because of the carbohydrate structure of biomass formed in photosynthesis and plant respiration, biomass fuels are generally highly oxygenated compared to fossil fuels with oxygen constituting 35-45 % of the dry mass. Nitrogen, sulphur, and chlorine are usually present in concentrations under 1 % but are in some cases much higher. This can lead to an escalation in the formation of NOx in the flue gases as well as increased corrosion, slagging, fouling and air pollution. [19]
In Sweden, biomass combustion plants most often use different types of wood fuel and forest residues with varying characteristics as fuel. Table 3 includes some biomass fuels commonly used in Swedish biomass combustion plants. These values were adopted from a Swedish handbook on biomass fuels in which median values for each biomass type has been calculated from a wide range of ultimate analyses [22]. As shown in table 3, the moisture and ash content of the biomass fuels on a as received basis vary to a notable degree, which affects the effective heat value, combustion behaviour and flue gas composition. Adding to the complexity, biomass combustion plants often use a mix of different wood fuels of which the composition depends on fuel availability and predicted heat load.

Table 3: Comparison of biomass fuels commonly used in biomass combustion plants. [22] (daf = dry ash free, ar = as received) (Own table)

<table>
<thead>
<tr>
<th></th>
<th>Wood pellets</th>
<th>Conifer bark</th>
<th>Birch bark</th>
<th>Forest residues</th>
<th>Recycled wood</th>
<th>Straw</th>
<th>Crop residues</th>
<th>Peat</th>
</tr>
</thead>
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<td>moisture [w%]</td>
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<td>57.20</td>
<td>50.00</td>
<td>43.95</td>
<td>33.70</td>
<td>12.40</td>
<td>11.90</td>
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<tr>
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<td>2.65</td>
<td>4.60</td>
<td>4.95</td>
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<tr>
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<td>8.60</td>
<td>17.40</td>
<td>10.50</td>
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<td>16.42</td>
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<td>17.36</td>
<td>6.90</td>
<td>15.80</td>
<td>8.60</td>
<td>11.50</td>
<td>14.51</td>
<td>14.94</td>
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</tr>
<tr>
<td>C [w%] daf</td>
<td>50.90</td>
<td>53.80</td>
<td>55.80</td>
<td>51.00</td>
<td>45.60</td>
<td>48.32</td>
<td>48.80</td>
<td>56.80</td>
</tr>
<tr>
<td>H [w%] daf</td>
<td>6.14</td>
<td>6.10</td>
<td>6.90</td>
<td>6.10</td>
<td>6.30</td>
<td>5.93</td>
<td>6.75</td>
<td>5.80</td>
</tr>
<tr>
<td>O [w%] daf</td>
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<td>39.80</td>
<td>36.90</td>
<td>40.00</td>
<td>39.90</td>
<td>44.89</td>
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</tr>
<tr>
<td>S [w%] daf</td>
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<td>0.04</td>
<td>0.04</td>
<td>0.17</td>
<td>0.08</td>
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<td>Cl [w%] daf</td>
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<td>0.02</td>
<td>0.08</td>
<td>0.12</td>
<td>0.11</td>
<td>0.05</td>
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### 3.2 Flue gas condensation

Since biomass fuels in general have relatively high moisture content compared to fossil fuels, biomass combustion plants often are equipped with flue gas condensation (FGC) systems for recovery of the vaporization heat used in drying the fuel in the furnace. With FGC, the boiler efficiency can be improved by up to 15% depending on the heat sink temperature, excess air, and moisture content. The heat recovered from the FGC can be used in a district heating system (DH), or in the process itself [9].

There are two main types of FGC, the condensing heat exchanger, and the scrubber type. The condensing heat exchanger are made of ceramics, carbon steel or stainless steel inserted into the flue gas stream. The water vapor condensates on the heat exchanger surface as the flue gas is cooled below the dew point temperature and is then removed from the system. Close to the heat exchanger surface there is a zone of supersaturated steam where flue gas particles act as condensation nuclei for the water. Thereby, the FGC also has a cleansing effect, removing some of the 0.05-
0.50 μm particles not captured in the upstream flue gas cleaning system. [21] In a scrubber type FGC water droplets are injected vertically into the flue gas stream and rapid mass- and heat transfer between the gas and liquid occurs, condensing the flue gas water vapour. Here as well the flue gas particles act as condensation nuclei and are thereby trapped in the condensate. The scrubber type is also less prone for corrosion since the inside walls of the quench unit is constantly wetted. [23]

3.3 System implementation

When implementing PCC in a biomass combustion plant, the special attributes of biomass combustion gives an opportunity for various heat recovery options between the PCC system and the combustion plant. The absorber in a HPC process works in a temperature range of 60-120 °C and pressure in the absorber can be between 6-12 bar. The lower temperature is set to avoid unwanted precipitation of potassium bicarbonate in the absorber. Because of this, no further cooling after the FGC is needed and the flue gases can be led directly to the flue gas compressor. Depending on the partial pressure of the water vapour in the flue gases which determines the water condensation temperature, the flue gases are generally cooled below 60 °C, adding to the required compressor work. A higher pressure increases the absorption rate in the absorber because of the VLE shift with the cost of additional compressor work. [9] As the type of motor used also affects the optimal pressure level, the system should be optimized with regards to the optimal pressure level for the absorbent-promoter combination used.

Biomass combustion plants used for DH purposes compete with other heating technologies such as heat pumps on the market. Therefore, the flexibility in production is crucial for the business viability. Most of the DH producers are CHP plants, where the balance between electricity and heat production is adjusted depending on electricity price and DH load to optimize the revenues. Implementation of BECCS under these circumstances can add to the production flexibility.

If a FGC is not fitted prior to the PCC installation it would be beneficial to install a FGC unit simultaneously. Existing FGC units are often used to heat the DH system but when retrofitted, the recovered heat can be used in the PCC process instead, depending on which configuration gives the best economic value. A study on different process modifications have shown that cooling the flue gas from 110-70 °C increased the capture efficiency by 11.46 %, albeit at a higher reboiler duty [24]. In this case the
reboiler duty could be lowered if the heat recovered in the FGC is transferred to the reboiler.

Since the heat load for DH and electricity price fluctuate over time, a flexible system application can make retrofitting more feasible. Depending on DH load and electricity price, the heat flow from the FGC could be regulated between the DH system and PCC system, increasing the biomass combustion plant revenue by optimizing the production and carbon capture to the given circumstances.

Another option is to use a heat pump to cool the DH return prior to entering the FGC, using the heat for the PCC process. Thereby more heat is recovered from the flue gases increasing the overall efficiency of the biomass combustion plant, simultaneously lowering the energy penalty and PCC operation cost.

Considering that the FGC acts as an extra cleaner and that cooling the flue gases increases the capture efficiency, a $\text{K}_2\text{CO}_3$ PCC process unit is best placed after the FGC in a biomass combustion plant, as shown in figure 2.

Given the flexible nature of the biomass combustion plant there is a need for process simulations of biomass combustion plants with different configurations of heat recovery options to minimize the PCC energy penalty and operation cost, lowering the implementation threshold for investors.
4 Calculating the operating cost

4.1 Swedish financial support schemes

The Swedish government are investigating different types of state-led support schemes to make BECCS feasible for Swedish BECCS actors. The main financial support systems studied are a flat-tariff approach and reverse auction system. With flat-tariffs, companies are paid a fixed sum for each ton CO$_2$ captured. However, it is hard to estimate a fixed sum that is both suitable for BECCS actors and socioeconomically acceptable. The reversed auction system means that the government pre-buys an amount of captured CO$_2$ within a specified time frame at the lowest price offered. With this method, BECCS actors need to determine the total cost for their CCS operation to offer the lowest price in the reverse auction and still make a profit. The reverse auction system currently has the highest support among stakeholders. [25]

The reverse auction method also drives the BECCS actors to optimize their processes which in turn can be a driving force for further research into BECCS. The total cost for BECCS can be divided into the investment, capture process, transport, and storage cost [25]. To this cost a desired profit is added which results in the reverse auction price, see figure 3. The capture process cost is highlighted in green as this part is the focus of the following chapter.
4.2 Capture process cost calculation method

In this chapter, a method to calculate the operation costs for BECCS is proposed. The total cost for BECCS also includes investment, transport, and storage cost, but these parts falls outside the scope of this study. The calculation method is intended for a hypothetical HPC process in a CHP plant that uses wood fuels.

The profit of selling captured CO$_2$ with regards to the reverse auction system must be compared to the profit of selling the electricity otherwise used for the process. Therefore, the actual cost for the HPC process in terms of fuel costs to produce the electricity used by the process must be monitored. Also, it would be of interest to continuously lower the process energy duty to maximize the profit from the reverse auction, whereas the following calculation method could be useful as well.

The CHP plant simultaneously produces electricity and heat at varying fractions depending on the DH load and electricity price, and the biomass fuel mass flow is continuously adjusted to meet this power demand.

When a HPC system is incorporated is a CHP plant, the process energy duty would fluctuate depending on flue gas temperature, composition, mass flow and solvent degradation, affecting the absorption rate. On the other hand, the electrical energy for pumps, compressors, and the reboiler would be regulated more slowly, causing the actual energy duty to vary. By measuring the flue gas CO$_2$ content before and after the absorber, and
the total energy use for the process, the actual energy duty for the HPC system can be calculated, see figure 4.

![Diagram of HPC system](image)

**Figure 4: Mass and energy balance for the HPC system. (Own figure)**

The mean hourly value of energy use ($E_{\text{hpc}}$) divided by the difference in accumulated mass of CO$_2$ in the flue gas before and after the HPC system under one hour gives the actual energy duty for the HPC process ($E_d$).

$$E_d = \frac{E_{\text{hpc}}}{(m_{CO_2})_2 - (m_{CO_2})_1} \left[ \frac{MJ}{kg \ CO_2} \right]$$  \hspace{1cm} (1)

When measuring the mass of CO$_2$ in the flue gases the CO$_2$ capture efficiency can be calculated as

$$\eta_{\text{cap}} = 1 - \frac{(m_{CO_2})_2}{(m_{CO_2})_1}$$  \hspace{1cm} (2)

The energy for the HPC process is delivered by the CHP plant itself and the cost varies depending on the price of the combusted biomass fuel. For this model, it is assumed that the CHP plant continuously measure the heat output power ($P_{\text{heat}}$), the electric output power ($P_{\text{et}}$), and biomass fuel input mass flow ($\dot{m}_{\text{fuel}}$), as shown in figure 5. The required power input is held constant by adjusting the biomass fuel mass flow depending on the fuel effective heat value.
The biomass fuel input power \( P_{fuel} \) is calculated using the fuel input mass flow and the fuel effective heat value \( H_{eff} \).

\[
P_{fuel} = \dot{m}_{fuel} \times H_{eff} \quad [MW]
\]

Biomass combustion plants often use a mix of different fuels. In this case, the effective heat value for the fuel mix \( H_{mix} \) can be calculated given the mass fraction of each fuel \( y_i \) in the mix is known. From this the fuel input power when combusting a biomass fuel mix can be calculated.

\[
H_{mix} = \sum (y_i \times (H_{eff})_i) \quad [MJ/kg]
\]

The electricity production efficiency \( \eta_{el} \) for the CHP plant can be estimated with the following equation.

\[
\eta_{el} = \frac{P_{el}}{P_{fuel} - P_{heat}}
\]

The energy duty in terms of biomass fuel input \( E_{df} \) can be calculated with regards to the electric production efficiency and the actual energy duty.

\[
E_{df} = E_d / \eta_{el} \quad [MJ/kg\ CO_2]
\]
In the next step the actual HPC process cost ($C_{hpc}$) is calculated using the biomass fuel energy duty and biomass fuel price ($C_{bf}$). The biomass is priced per MWh and thereby need to be converted to MJ.

$$C_{hpc} = E_{df} \cdot \frac{C_{bf}}{3.6} \left[ \frac{\varepsilon}{\text{ton CO}_2} \right]$$  \hspace{1cm} (7)

For a biomass fuel mix, the cost ($C_{mix}$) can be calculated with the following equation

$$C_{mix} = \Sigma \left( E_{df} \cdot \frac{C_{bf}}{3.6} \cdot y_i \right) \left[ \frac{\varepsilon}{\text{ton CO}_2} \right]$$ \hspace{1cm} (8)

To estimate the hourly cost of the HPC process using one type of biomass fuel, the following equation can be used with the mass fraction of moisture ($y_m$), ash ($y_a$), and carbon ($y_c$).

$$C_h = \eta_{cap} \cdot \dot{m}_{fuel} \cdot C_{hpc} \cdot \left( 3.6 \cdot \frac{M_{CO_2}}{M_C} \cdot ((1 - y_m - y_a) \cdot y_c) \right) \left[ \frac{\varepsilon}{h} \right]$$ \hspace{1cm} (9)

When using a biomass fuel mix, the hourly HPC process cost can be estimated as with the mass fractions for fuel ($y_i$) and the components of fuel ($i$).

$$C_{h, mix} = \eta_{cap} \cdot \dot{m}_{mix} \cdot C_{mix} \cdot \left( y_i \cdot \left( 3.6 \cdot \frac{M_{CO_2}}{M_C} \cdot ((1 - y_{m_i} - y_{a_i}) \cdot y_{c_i}) \right) \right) \left[ \frac{\varepsilon}{h} \right]$$ \hspace{1cm} (10)

### 4.3 Steady state HPC model

In this steady-state model, a HPC system installed in a CHP plant is considered for which the actual energy duty for the HPC process is assumed to be 1.21 MJ/kg CO$_2$ captured, including the liquification process. Transport and storage cost are not included. It is assumed that 50% of the energy used for the HPC process in the CHP plant is reusable, as described in Beiron et al (2021) [9]. The reboiler steam is produced by an electric heater, making the HPC process solely dependent on electricity. Performance data from CHP 8 in Stockholm were used as reference [5]. The CO$_2$ capture efficiency is here assumed to be 80%.

In this model, $P_{fuel}$, $P_{heat}$ and $P_{el}$ are fixed, and the fuel mass flow is adjusted to deliver the required heat input depending on the biomass fuel used, as would be the case in a real CHP plant. Required fuel mass flows and actual HPC operation costs when using each of the biomass fuels is calculated. The same is done for a fuel mix consisting of the three biomass fuels with assumed mass fractions for each fuel ($y_i$).
The biomass fuel prices were obtained from the Swedish Energy Agency and are mean values of all prices registered for the last quarter of 2021 [26]. The performance data, prices and calculation result are presented in table 4. The results show that the hourly cost for the HPC process in a biomass combustion plant varies in depending on the moisture, ash, and carbon content of the biomass fuels.

### Table 4: Results from the steady state HPC model. Prices are without taxes and obtained from the Swedish Energy Agency. [26] (Own table)

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<tr>
<th></th>
<th>CHP 8</th>
<th>Forest residues</th>
<th>Recycled wood</th>
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5 Discussion

Piperazine is the most tested promoter and should be used for implementation in biomass combustion plants today. Time is crucial in order to halt climate change, and in order to get BECCS going, compromise is inevitable. Under sizing the equipment, and using a well-tested promoter as piperazine, initially accepting a lower cyclic capacity could lower the implementation threshold. With the equipment in place, the focus would be on researching new promoters and absorbents with the possibility of full-scale testing, steadily improving both the cyclic capacity and chemical safety. Meanwhile, the HPC systems capture CO$_2$ from the atmosphere at an increasing rate.

The results from steady state model show that the calculation method can be used to calculate the operating costs in real life or in simulations of HPC processes in biomass combustion plants. This could be useful for BECCS actors participating in the proposed reverse auctions. The model in this work was simple with few parameters but served the purpose for this study and can be improved upon in future studies. The calculations of the hourly costs can only be seen as estimations, for accurate results the amount of flue gas CO$_2$ must be measured. The operation cost calculation method can also be useful when planning to retrofit HPC systems in existing biomass combustion plants.

Throughout this article, suggestions for energy recovery options has been made, although the flexible nature of biomass combustion plant make for many more energy recovery options. This should be studied further using modelling software, finding ways to lower the energy duty for the HPC systems already in place.

Several other aspects must come in place, such as transportation and storage options for the captured CO$_2$, but this falls outside the scope of this study. State-led economic support is necessary as well, a subject briefly discussed in this article.

With this study, the author hopes to contribute with a new perspective that inspire researchers to look into CCS for biomass combustion plants and make investors more prone to invest in research and technology related to BECCS.
6 References


Carbon capture in biomass combustion plants using promoted potassium carbonate solutions

Discussion

Håkan Bergman  2022-06-01


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2022-06-01

[Använd 16 05 2022].


