

Differences on Capturing CO₂ from the Combustion of Biomass and Coal by using Chemical Absorption

Worrada Nookuea¹, Beibei Dong^{1,2}, Kåre Gustafsson³, Hailong Li^{1*}, Jinyue Yan¹, Eva Thorin¹

¹ School of Business, Society and Technology, Mälardalens University, Sweden

² Tianjin University of Commerce, China

³ Strategig development manager, Stockholm Exergi

ABSTRACT

Even though all capture technologies developed for capturing CO₂ from the utilization of fossil fuels can be applied to capture CO₂ from the utilization of biomass, due to the obvious different properties, the performance can also be quite different. This work investigates the differences when using chemical absorption to capture CO₂ from the combustion of recycled woods and coal, in order to provide suggestions on the integration of CO₂ capture in the utilization of bioenergy and promote the application of bioenergy with CO₂ capture and storage (BECCS). Two solvents, Monoethanolamine (MEA) and hot potassium carbonate (HPC), have been included. The results show that the flue gas (FG) from the combustion of recycled wood (RW) has a higher CO₂ content, but lower O₂, SO_x and NO_x content compared to the coal fired FG. In comparison to the coal fired FG, capturing CO₂ from the RW fired FG requires less energy for both solvents, due to its higher CO₂ content. The estimated oxidative and acid gas degradations are higher for FFCCS compared to BECCS, due to the higher O₂, SO_x and NO_x contents in coal fired FG compared to those in the RW fired FG. For HPC process, FG compression work account for the largest part of the total energy consumption. Even though, the reboiler duty of the HPC process is lower than that of the MEA process, the total energy penalty is higher.

Keywords: BECCS, Monoethanolamine, Hot potassium carbonate, Energy penalty, Degradation, Gas composition

NOMENCLATURE

Abbreviations

BECCS	Bioenergy with CO ₂ capture and storage
CHP	Combined heat and power plant
CO	Carbon monoxide
CO ₂	Carbon dioxide
DEA	Diethylamine
ENRTL	Electrolyte nonrandom two liquid
ESP	Electrostatic precipitator
FFCCS	Fossil fuel with CO ₂ capture and storage
FG	Flue gas
FGD	Flue Gas Desulfurization
H ₂ O	Water
HCl	Hydrochloric acid
HF	Hydrogen fluoride
Hg	Mercury
HPC	Hot potassium carbonate
HPC–CA	HPC based chemical absorption
K	Kelvin
K ₂ CO ₃	Potassium carbonate
K ₂ CO ₃ .1.5H ₂ O	Sesquihydrate potassium carbonate crystal
MEA	Monoethanolamine
MMEA	2–methyl–methanolamine
M–CA	MEA based chemical absorption
N/A	Not available
NH ₃	Ammonia
NO _x	Nitrogen oxides
O ₂	Oxygen

ppmv	Parts per million by volume
RW	Recycled wood
SCR	Selective catalytic reduction
SNCR	Selective non-catalytic reduction
SOx	Sulfur oxides

1. INTRODUCTION

In 2017, Sweden has passed legislation which legally binds the country to reach net-zero emissions by the year 2045 and net-negative emissions beyond that year. In order to achieve the goal of carbon-neutrality, residual emissions need to be offset and therefore, Negative emissions have been targeted, which mean that greenhouse gas emissions from activities should be less than the amount of carbon dioxide absorbed by nature. The Swedish Energy Agency has evaluated four scenarios for the future of the Swedish energy system. The only one that would achieve climate neutrality within the timeframe set by the new act is to realize negative emissions through bioenergy with CO₂ capture and storage (BECCS). According to Statistics Sweden, the greenhouse gas emission is 63.7 Mton CO₂ equivalent in 2018 [1], and CO₂ emission from the utilization of bioenergy is about 35.3 Mton. For the ideal scenario, if all bio-CO₂ can be captured, it can offset all emissions from fossil fuel and achieve net zero emission.

The most common way to use biomass is combustion. For post combustion capture, chemical absorption is the only commercialized technology for CO₂ capture [2,3]. In order to reduce the energy penalty, different solvents have been proposed for chemical absorption, of which Monoethanolamine (MEA) and hot potassium carbonate (HPC) have received most of attention [4].

The composition of streams, from which CO₂ is captured, can clearly affect the performance of the capture technology. Biomass has quite different characteristics from fossil fuels, and hence, after combustion, using biomass can result in quite different compositions in the FG. The performance of BECCS may be different compared to fossil fuel with CO₂ capture and storage (FFCCS) in an energy efficient and cost-effective way. Therefore, it is important to know the difference between BECCS and FFCCS.

The objective of this work is to identify the differences in energy consumption and solvent degradation in chemical absorption for BECCS and FFCCS. The performance of MEA based chemical absorption (M-CA) and HPC based chemical absorption (HPC-CA) to

capture CO₂ from the combustion of biomass and coal were also analyzed.

2. METHODOLOGY

2.1 Model descriptions

To evaluate the performance of chemical absorption, simulation models are developed and validated in Aspen Plus for M-CA and HPC-CA, as shown in Fig 1(a) and 1(b), respectively. Both M-CA and HPC-CA were simulated by rate-based models using RADFRAC distillation columns for the absorber and desorber. Based on the previous literatures, the Electrolyte nonrandom two liquid (ELECNRTL) method was chosen for modeling the properties of M-CA and HPC-CA [5]. For both systems, the mass transfer coefficient models and interfacial area model were taken from [6]. For the absorber and desorber, the V-plug was chosen as a stage flow option [7].

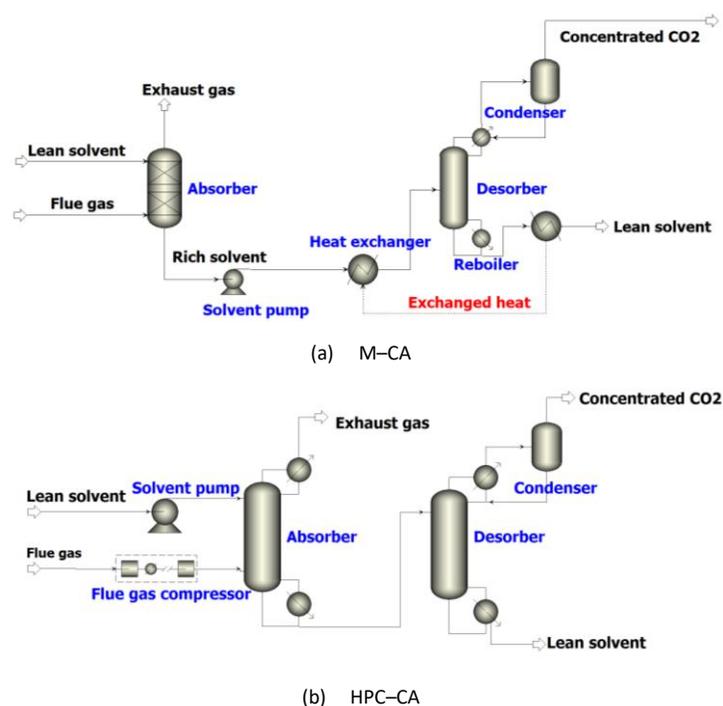


Fig 1. Process configuration of chemical absorption

2.2 Inputs and validations

For M-CA process, the input data and column internals were taken from [8]. For HPC-CA, the input data and column internals were taken from [9], which are listed in Table 1.

Table 1. Input data for model validations [8,9].

Parameter	Input data of M-CA [8]
CO ₂ content in FG (mol%)	13.3
Solvent (30wt% MEA)	
Lean loading	0.24
Solvent flow rate (m ³ /tonCO ₂)	20
Lean solvent temperature (K)	313
Parameter	Input data of HPC-CA [9]
CO ₂ content in FG (mol%)	13.0
Solvent (30wt% K₂CO₃)	
Lean loading	0.17
Solvent flow rate (kg/s)	11.1–12.5
Lean solvent temperature (K)	316.8–321.8

For M-CA, the simulation model was validated by comparing with the simulation results from [8], as plotted in Fig 2, good agreement can be observed. The average deviation of the desorber temperature and the reboiler duty are $\pm 0.1\%$ and $\pm 8.9\%$, respectively.

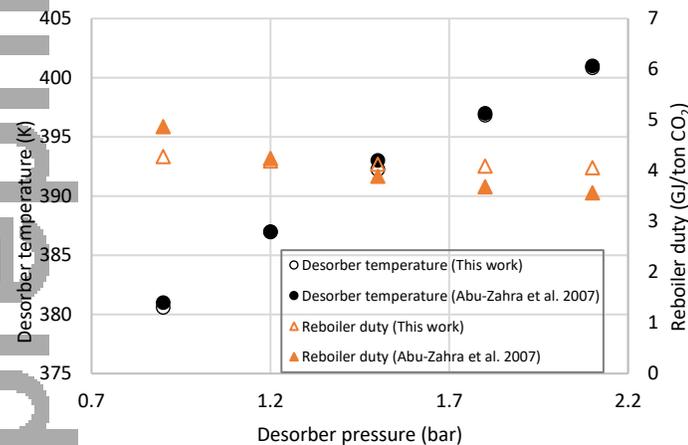


Fig 2. Validation of desorber temperature and reboiler duty at different desorber pressures for M-CA.

In the case of HPC-CA, the simulation model was validated by comparing with the plant operating data reported in [9]. As plotted in Fig 3, the average deviation of the CO₂ recovery and the reboiler duty are $\pm 12.9\%$ and $\pm 1.6\%$, respectively, which are in good agreement as well.

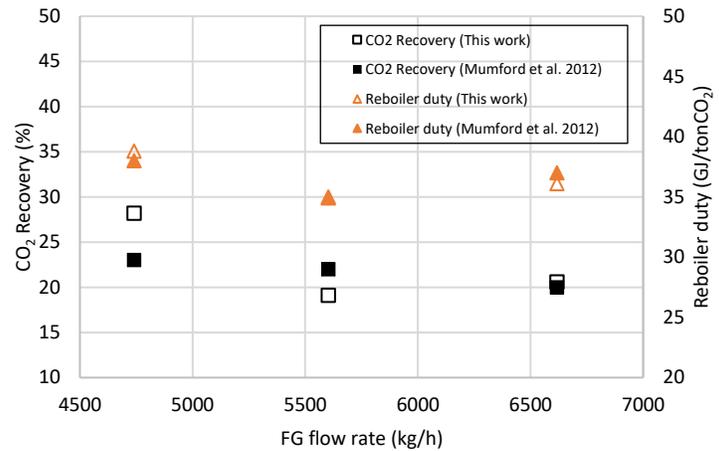


Fig 3. Validation of CO₂ recovery and reboiler duty at different FG flow rates for HPC-CA.

To improve the performance of HPC-CA, the operating pressure of the absorber was changed. Following [4], for HPC, reboiler duty can be reduced by the formation of the sesquihydrate potassium carbonate crystal (K₂CO₃·1.5H₂O) in the HPC-CA. The formation of this crystal only occurs when the absorber is operated at high pressure (10–20 bar) and high temperature (382–488K). The operating condition of the absorber were adapted to be operated at 15.2 bar and 383.15 K in this work. Therefore, the FG compressor and the lean solvent pump are required to increase the FG and lean solvent pressures.

3 DIFFERENT PERFORMANCES OF CHEMICAL ABSORPTION

3.1 composition of CO₂ stream

Biomass can be divided into different groups, such as agricultural waste, forest residual, recycled wood, industrial and municipal waste, and sewage sludge. In this work, attention is mainly paid to the feedstock of recycled wood (RW), which is one of the common fuels for CHP plants.

In addition, after combustion, FG needs to be cleaned before going into the subsystem of CO₂ capture. Different technologies are used for FG cleaning in biomass fired CHP plants and coal fired power plants, which can also affect the FG composition. As biomass contains less nitrogen, the content of NO_x is usually lower compared to using coal as fuel. Therefore, selective non-catalytic reduction (SNCR) is normally used instead of selective catalytic reduction (SCR). It is similar for the content of sulfur. Since biomass, except waste, usually has a lower content, dry FG desulfurization is

commonly used instead of wet desulfurization [10]. For the removal of particles, due to the relatively small scale of bio-CHP plants, baghouse filter is more economical than electrostatic precipitator (ESP). In addition, different regulations may be adopted regarding the emissions of pollutants [11,12].

Data of gas compositions have been collected from the literature for both coal fired power plants and RW fired CHP plants and results are summarized in Table 2 [13–18]. The RW fired FG has more CO₂ and H₂O contents but less O₂ and N₂ contents than coal fired FG. For the minor components, NO_x, SO_x and CO contents are higher in the coal fired FG compared to RW fired FG. Regarding the trace components, HCl, HF and Hg present in the coal fired FG. For the RW fired FG, HCl and NH₃ present in the gas stream.

Table 2. FG components from coal and RW fired power plants after cleaning.

Components	FG of coal combustion	FG of RW combustion
CO ₂ (mol%)	12.2	14.9
H ₂ O (mol%)	10.5	14.5
O ₂ (mol%)	5.2	2.7
N ₂ (mol%)	72.1	67.9
NO _x (ppmv)	99.1	65.3
SO _x (ppmv)	74.3	16.3
CO (ppmv)	41.3	23.2
HCl (ppmv)	4.9	4.6
HF (ppmv)	0.1	N/A
NH ₃ (ppmv)	N/A	2.8
Hg (ug/Nm ³)	1.9	N/A

3.2 Energy performance

The energy consumption of M-CA mainly includes the electricity consumed by pump to transfer the rich solvent to the desorber and the heat needed in reboiler for the regeneration of solvent. For HPC-CA, the energy consumption mainly consists of the work of lean solvent pump and the FG compressor and the heat of reboiler. The detailed results about energy consumption are compared in Table 3.

For M-CA, the required pump work and reboiler duty to capture 90% CO₂ recovery at 99 mol% CO₂ purity from coal fired FG are 0.003 and 4.25 GJ/tonCO₂, respectively. For RW fired FG, the required pump work and reboiler duty are 0.002 and 3.97 GJ/tonCO₂, respectively. Therefore, the total energy penalty to capture CO₂ from the coal fired FG by M-CA is higher than that for the RW fired FG.

Similar result was observed for HPC-CA. For HPC-CA, the required compression work, pump work and reboiler duty to capture 20% CO₂ recovery at 94 mol% CO₂ purity

from coal fired FG are 10.9, 0.4 and 3.03 GJ/tonCO₂, respectively. For RW fired FG, the required compression work, pump work and reboiler duty to are 7.1, 0.34 and 2.56 GJ/tonCO₂, respectively. Hence, the total energy penalty to capture CO₂ from the coal fired FG by HPC-CA is higher than that for the RW fired FG.

Regarding the results of different capture processes, the CO₂ recovery for M-CA is around 90%. However, the CO₂ recovery in HPC-CA is only around 20% due to its slow reaction with CO₂. This limitation can be overcome by adding the rate activator agents. The captured CO₂ purity from M-CA is higher compared to that from HPC-CA, which is 99mol% for both CO₂ from coal fired FG and RW fired FG. The captured CO₂ purity from HPC-CA from coal fired FG and RW fired FG are 94 mol%.

The FG compression work for HPC-CA is the highest compared to the pump work and the reboiler duty. To compress the coal fired FG and the RW fired FG, the required compression works are 10.9 and 7.1 GJ/tonCO₂, respectively. The pump work for M-CA is lower compared to the pump work for HPC-CA due to the lower discharge pressure of the solvents. For M-CA the required pump works are 0.003 and 0.002 GJ/tonCO₂ for the coal fired and the RW fired FG, respectively. For HPC-CA, the required pump works are 0.40 and 0.34 GJ/tonCO₂ for the coal fired and the RW fired FG, respectively.

The reboiler duty for M-CA is higher compared to that for HPC-CA. To regenerate the captured CO₂ from coal fired FG, the required reboiler duty for M-CA and HPC-CA are 4.25 and 3.03 GJ/tonCO₂, respectively. The required reboiler duty for M-CA and HPC-CA to regenerate the captured CO₂ from coal fired FG are 3.97 and 2.56 GJ/tonCO₂, respectively. Even though, the reboiler duty of M-CA is higher than that of the HPC-CA, its total energy penalty is lower. This is due to the large FG compression work for the HPC absorption.

Table 3. Simulation results of M-CA and HPC-CA.

Solvent	Fuel	CO ₂ Recovery (%)	CO ₂ purity (mol%)	Compression work (GJ/tonCO ₂)	Pump work (GJ/tonCO ₂)	Reboiler duty (GJ/tonCO ₂)	Total energy penalty (GJ/tonCO ₂)
MEA	Coal	90	99	–	0.003	4.25	4.25
	RW	90	99	–	0.002	3.97	3.97
HPC	Coal	20	94	10.9	0.40	3.03	14.33
	RW	20	94	7.1	0.34	2.56	10.0

3.3 Solvent degradation

3.3.1 MEA

The degradation of MEA is mainly affected by the oxidation of solvents and/or the formation of heat stable salts, which can clearly reduce CO₂ capture capability. Oxidative degradation is normally proportional to the O₂ content in the gas being captured [19,20]. When 30 wt% MEA is used for capture CO₂ from typical FG after post-combustion, it was found that 1% O₂ can result in 0.0135 kg/tCO₂ MEA loss and 0.028 mol NH₃ emission. Based on such results, oxidative degradation of MEA when capturing CO₂ from coal and RW is estimated according to different O₂ contents of FG. As shown in Table 4, the estimated MEA loss and NH₃ emission are higher for capturing CO₂ from FG of coal combustion due to the higher O₂ content compared to the FG of RW combustion. The MEA loss from the capture of coal fired FG and RW fired FG are 0.07 and 0.04 kg/tonCO₂, respectively. Regarding the based case of M-CA, the relative percentage of MEA loss was calculated from the captured CO₂ and the free MEA in the lean solvent. For the coal fired FG and RW fired FG, the relative percentage of MEA loss are 0.002 and 0.001%, respectively.

The acid gas, NO_x and SO_x, can react with solvent to form heat stable salts, such as nitrosamines, nitroimine, sulphate and sulphite, which also lead to MEA degradation. The accumulation of heat stable salts can also increase the pressure loss by increasing fluid viscosity and cause fouling resulting in a high resistance to heat transfer. However, the quantitative studies are scarce. Compared to the combustion of coal, due to the less sulfur content and lower combustion temperatures, FG from the combustion of RW has lower SO_x and NO_x. Therefore, the estimated MEA loss from heat stable salt formation is higher for capturing CO₂ from FG of coal combustion due to the higher SO_x and NO_x content compared those in the RW fired FG.

Table 4. Prediction of oxidative degradation

Solvent	Fuel	MEA loss		NH ₃ emission (mol/ tonCO ₂)
		kg/tonCO ₂	Relative loss (%)	
MEA	Coal	0.07	0.002	0.15
	RW	0.04	0.001	0.08

3.3.2 HPC

HPC has low cost and less toxic. It is also less prone to degradation at high temperature and with presence of O₂ and other minor gas components compared to amine-

based solvents. However, a challenge of using HPC is its slow reaction with CO₂. Activator agents such as MEA, diethylamine (DEA) and 2-methyl-methanolamine (MMEA) are usually added to the solvent to improve the mass transfer rate. The presence of O₂ and the acid gas in the FG causes oxidative degradation and the formation of heat stable salts of amine activator agents [21]. However, the concentration of the activator agents are quite low, which are around 2–5 wt% for DEA and 2–10% for MEA [22]. Therefore, the magnitude of oxidative degradation of the activator agents is expected to be lower for the case of HPC-CA compared to M-CA. Regarding O₂ content in the FG, the estimated activator agent loss and NH₃ emission are higher for capturing CO₂ from coal fired FG due to the higher O₂ content compared to RW fired FG. Moreover, the estimated activator agent loss from heat stable salt formation is higher for capturing CO₂ from coal fired FG due to the higher SO_x and NO_x content compared to RW fired FG.

4 CONCLUSIONS

The main finding of this work can be concluded into the following points:

- Due to the higher CO₂ content in the biomass fired FG, lower energy penalty is required in M-CA and HPC-CA for BECCS compared to FFCCS.
- For the oxidative degradation, the estimated amine loss and NH₃ emission are higher for the absorption of coal fired FG compared to RW fired FG. However, in general, biomass combustion normally needs more excess O₂ and therefore, the oxidative degradation of the amine and NH₃ emission can be worse in BECCS compared to FFCCS, except for natural gas.
- BECCS is less prone to acid gas degradation of the amine solvents and rate activator agents compared to FFCCS since burning biomass emits significantly lower SO_x and NO_x compared to burning fossil fuel.
- The reboiler duty of the HPC-CA is lower compared to the reboiler duty of M-CA. However, its total energy penalty is higher due to the large FG compression work for the HPC absorption.

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