TOWARDS NEGATIVE CARBON DIOXIDE EMISSIONS: CAPTURE OF CARBON IN BIOSYNGAS BY AQUEOUS PENTAETHYLENEHEXAMINE

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ABSTRACT

In this work, aqueous pentaethylenehexamine (PEHA) was studied as a solvent for CO_2 removal to produce purified bio-syngas from biomass gasification, but also as a first step towards negative carbon emissions applying carbon capture and storage (CCS) technologies. Capture of CO_2 was tested both with synthetic gas (lab-scale) and real syngases from the pilot-scale gasifier fed with a wide range of forest-based biomasses. The results showed that the effects of the components other than CO_2 and the impurities from the real syngas on the performance of PEHA for CO_2 removal are negligible. Combined with previous research results from lab-testing with pure CO_2 absorption, the aqueous PEHA was shown to be a promising solvent for CO_2 removal from syngas. PEHA was also tested as a biomass pre-treatment agent to improve gasification behavior, however, no significant improvement could be identified during the tests performed in this study.

Keywords: pentaethylenehexamine, CO_2 removal, biomass pretreatment, gasification, bio-syngas, carbon capture and storage, bio-CCS

NONMENCLATURE

Abbreviations	
BW	Birch wood
CCS	Carbon capture and storage
MEA	Monoethanolamine
PEHA	Pentaethylenehexamine
SB	Spruce bark
SN	Spruce needle
Symbols	
λ	Oxygen stoichiometric ratio

1. INTRODUCTION

Global climate change is underway because of increasing greenhouse gas emissions dominated by CO_2 [1], calling for use of climate-neutral renewables and decarbonization of energy conversion processes as well as a better balance between positive and negative CO_2 emissions, for example, by applying carbon capture and storage (CCS) in bio-based processes. Biomass gasification has been proposed as an important solution to upgrade low-grade and heterogeneous lignocellulosic resources (forest and agricultural residues, by-products, wastes etc.) as well as black liquor from pulp mills into biosyngas as a feedstock for biofuels and biochemicals besides the co-generation of heat and power. The produced syngas from gasification is a mix of mainly H_2, H_2O, CO, CO_2, CH_4 and C_2H_4/C_2H_6 and it contains up to 1/3

of CO_2. If the syngas is intended for downstream synthesis of fuels or chemicals, the syngas must be conditioned in order to have an efficient synthesis. This often requires some extent of CO_2 removal. Current methods for CO_2 removal from biosyngas are energy consuming, cause equipment corrosion (e.g. amine-based technology) or usually require large-scale operations, which justifies the efforts for new developments [2]. Considering high-efficiency and continuity, developing effective technologies for CO_2 removal with new solvents is highly desirable.

Polyamines have received great attention due to the existence of multiple reactive sites for CO_2 capture, and pentaethylenehexamine (PEHA) is one kind of polyamines with two primary and four secondary amine groups with the merits of high thermal stability and low toxicity. In our previous work, aqueous PEHA has been used as an absorbent for CO_2 capture. In comparison with monoethanolamine (MEA), PEHA showed higher absorption rate and capacity, higher stability as well as lower volatility [3]. However, the research was only conducted for pure CO_2 at the ambient temperature and pressure. While for CO_2 removal from biosyngas, the gas is also composed of other gaseous components like CO, H_2, CH_4 as well as other trace components such as H_2S, NH_3. In addition, it is common to have other impurities such as particulate matter in the form of ash and soot particles. However, it is still unclear how the syngas components other than CO_2 and the impurities will affect the performance of PEHA. Besides, to achieve a high performance of gasification, biomass needs to be milled into fine powders, consuming considerable amount of electrical energy. Chemical method has been proposed for biomass pretreatment,[4] however, there is still a great challenge to find solvents that are efficient under the mild pretreatment conditions.

In this work, the performance of PEHA for CO_2 removal in a real fixed bed gasifier was studied. The procedure included systematic variation of the feedstock for gasification and the gasifier operating conditions. The stem wood, spruce bark and needles from typical softwood and hardwood species in boreal forests were chosen for the feedstock of gasification. Furthermore, the gasifier was operated varying the fuel feeding rate, O_2 feeding rate and stoichiometric ratio, simultaneously measuring the production of biosyngas and the CO_2 removal rate. In addition, the CO_2 absorption capacity up to 20 bars and the performance of aqueous PEHA solution for CO_2 removal from the synthetic syngas were conducted in lab-scale for comparison and discussion.

Besides, PEHA was tested as a biomass pre-treatment agent to study the effect on the gasification behavior.

2. MATERIAL AND METHODS

2.1 Materials

PEHA (technical grade) and D_2O (99.9 atom % D) were purchased from Sigma-Aldrich. Deionized water was used throughout the experiments. CO_2 (mole fraction ≥ 99.9%) was received from AGA AB (Linde group). The synthetic syngas was purchased from AGA AB (Linde group). The real biosyngas was generated from a real fixed-bed gasifier.

The softwood species Norway spruce (*Picea abies* Karst. (L.)) and Scots pine (*Pinus sylvestris* L.) and the hard wood species birch (*Betula ssp.*) that characterize boreal forests were chosen as model species. The tree components tested as biomass models were stem wood (sawdust) from birch, as well as spruce bark and spruce needles representing various parts of the above-ground forest-based biomass to widen the experimental base of the feedstock. Bark and birch sawdust were collected from Rundvik sawmill at SCA Timber, Husum papermill at Metsä Board. Spruce needles (SNs) were sampled from fresh branches spruce trees grown in Umeå, Sweden, and dried overnight drying at 60˚C. The materials were finally dried to about 9% moisture content and ground using a hammer mill fitted with a 4 mm sieve before pelletizing. Production of pellets was done using a SPC PP 150 pelletizer (Sweden Power Chippers, Borås, Sweden) at the pilot facility, Swedish University of Agricultural Sciences, Sweden, and the press channel length and diameter were 55 mm and 8 mm, respectively.

2.2 Characterization

Pellet moisture and ash content as well as bulk density and mechanical durability were determined according to ISO standards (18134-2:2015, 18122:2015, 17828:2015 and 17831-1:2015). Proximate and ultimate analysis of the pelletized materials were done by the accredited laboratory Eurofins Environment Testing Sweden AB, Lidköping, Sweden, including gross calorific value (EN ISO 18125:17), volatile matter content (SS-EN 15148), contents of carbon, hydrogen, nitrogen, sulphur (SS-EN ISO 16948:2015), oxygen (EN ISO 18125:17), and Cl (SS-EN ISO 16994:2016). Ash forming elements Al, Ba, P, Fe, Ca, K and Mg were determined according to EN ISO 16967:2015 whereas Sb, As, Be, Pb, B, Cd, Co, Cu, Cr, Mn, Mo and Ni according to EN ISO 16968:2015. Hg and Na were analyzed using EN 16277:2012 and NMKL No 161 1998 mod./ICP-AES, respectively.

The structure of chemicals was characterized using Bruker Avance 600 MHz Nuclear magnetic resonance (NMR) instrument. Bruker's Topspin (3.5 pl7) was used to process NMR spectra. D_2O was used as a solvent in NMR analysis. The gaseous composition was detected by a micro-GC (Varian 490 GC, equipped with molecular sieve 5A and PoraPlot U columns and TCD detectors). The micro-GC continuously monitored the syngas composition (of He, H_2, N_2, CH_4, CO, CO_2, C_2H_2, C_2H_4/C_2H_6) approximately every 4 min.

2.3 Pretreatment of birch wood

The birch wood (BW) was pretreated with aqueous PEHA solution. Typically, about 0.6 kg of BW was mixed with 5 L of aqueous PEHA (20 vol% of PEHA) in the pressure cooker equipped with thermocouple and the temperature controller box. The pretreatment was performed at 110 °C for 2 h. After that, the mixture was filtered and the solid material was washed with hot water, then was air-dried overnight in fume hood and finally was oven-dried at 100 °C for 5 h. The procedure was performed several times to get enough dry pretreated material for gasification experiment.

2.4 Gasification

The fixed bed gasifier used for the experiments was described in detail by Wiinikka et al. [5]. The gasification experiments were designed to give a realistic spread in the syngas composition resulting from gasification of Scandinavian woody biomass, and to evaluate the effect in the downstream CO_2 capture apparatus. The gasifier was operated for more than 1 h, usually up to 2 h, at each individual operating condition. Generally, the process temperature was above 1000 °C during the experiments.

3. RESULTS AND DISCUSSION

3.1 Gasification performance

Four different feedstocks (birch wood, spruce bark, spruce needles and pretreated birch wood) were gasified at different operating conditions (i.e. different oxygen stoichiometric ratio, λ). The process temperature during gasification is a result of the heat generated by the chemical reactions and the corresponding heat losses from the gasifier. Increasing λ results in an elevated process temperature, which in turn results in cracking of methane and higher hydrocarbons into CO and H_2.

Fig. 1 shows an example of syngas concentration over the experiment time using Spruce needles (SN). Gasification of SN was performed at three operating conditions (λ=0.47, 0.42 and 0.34). Fig 1 shows that the
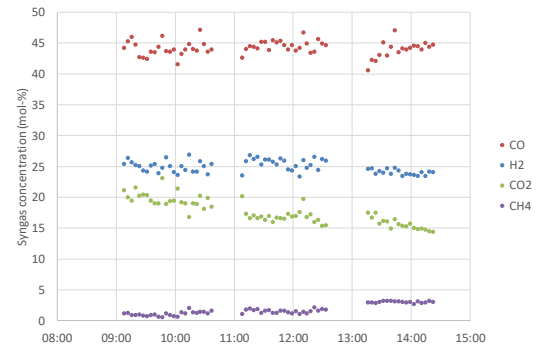

Fig 1. Syngas composition over time (Spruce needles, SN)

syngas composition was quite stable within each λ-set point, and the concentration of CO_2 decreased while that of CH_4 increased when λ was reduced. The concentrations of CO and H_2 seemed rather unaffected by the λ variation. This was also the general trend for all the fuels of this study, see Fig 2. Worth mentioning here is that the syngas concentration seemed to be unaffected by the birch wood pretreatment.
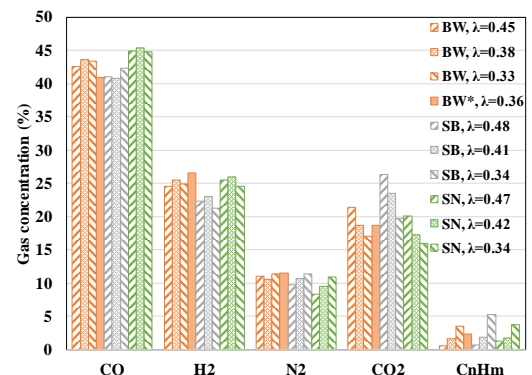

Fig 2. Syngas composition with diffent feedstocks and operating conditions

3.2 CO_2 removal performance

The CO_2 absorption capacities in aqueous PEHA solution with different water contents were detected at room temperature and at pressures up to 20 bars, and those at MEA were also measured for comparison. It was observed that using 30 wt% of PEHA in water had the same CO_2 loading (g-CO_2/g-solvent) as MEA solution, while 20 wt% of PEHA in water had lower CO_2 loading which was around 0.11 g-CO_2/g-solvent. However, the CO_2 capacity per kg-amine of 20 wt% of PEHA in water was higher than those of MEA (30 & 20 wt%) with values of 17 and 15 mol-CO_2/kg-amine, respectively. According to our previous work [3], the viscosity of aqueous PEHA solution decreased with the increase of water amount. For the solution of 20 wt% of PEHA in water, its viscosity was 2.75 cp [4]. When it was saturated with CO_2, its viscosity increased to 3.65 cp, which still has the

potential to be used in a traditional mass transfer unit. Therefore, 20 wt% PEHA in water was used in the gas purification of syngas from real gasifier.

In order to study the effect of the component other than CO_2 on the CO_2 absorption capacity, the gas with 35.10 mol% H_2, 18.30 mol% CO, 31.80 mol% CO_2, 4.990 mol% CH_4, and 9.810 mol% N_2 was selected as a synthetic syngas to study the performance of aqueous PEHA (30 wt.%) at 293.15 K and 1 atm. The investigation showed that the CO_2 concentration in the aqueous PEHA solution increased from 8 to 31.8% at the first 60 minutes and then kept constant, which meant that the solvent reached equilibrium after 60 minutes. H_2 was an inert gas to the solution. The saturated gas absorption amounts of CO_2, CH_4, and CO were 76.92, 2.24 and 0.355 mg/g-solvent, respectively. This implies that the solubility of CO is within the tolerance, while the CH_4 solubility can be neglected compared to the high CO_2 solubility. Thus, H_2, CH_4 and CO have a slight effect on the performance of aqueous PEHA solution for CO_2 removal.

The performance of 20 wt.% PEHA solution was further tested with the real biosyngas generated from a real fixed-bed gasifier with the set up illustrated in Fig 3.
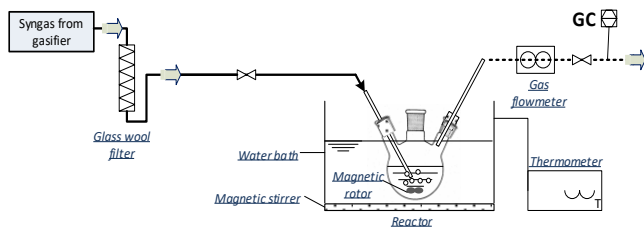

Fig 3. Flowsheet of the set-up of CO2 capture from bio-syngas generated from pilot-scale gasifier

In experiment, once the gas composition from the gasifier kept stable, the raw bio-syngas was introduced into the set-up. The gas composition of outlet gas stream was recorded by Micro-GC every 140s. In general, the gas composition of CO_2 decreased first and then increased to the same value as the inlet gas, which meant that the solvent was saturated by CO_2. While the composition of other gases showed the opposite trend compared to CO_2. After inserting gas around 20 minutes, CO_2 composition began increasing to the same as the inlet gas stream.

The comparison of the experimental results with the raw syngas from the real gasifier with different feedstsocks and operating conditions showed that the performance of aqueous PEHA solution is almost the same as for different cases. The comparison with the result from the synthesized syngas also shows similar results. All this implies that the impurities in the raw syngas from the real gasifier do not affect the CO_2 removal for the aqueous PEHA solutions.

The PEHA solutions after the absorption with different gas streams (pure CO_2, synthetic syngas, real raw syngas) were analyzed with NMR. It reveals that all the nitrogen atoms were effectively interacted with CO_2 molecule, and a variety of different carbamate species were formed after being saturated with CO_2.

4. CONCLUSION

The investigation of aqueous (PEHA) as a solvent for CO_2 removal to produce purified bio-syngas from biomass gasification as a first step towards negative carbon emissions applying carbon capture and storage technologies showed that the effects of the components other than CO_2 and the impurities from the real syngas on the performance of PEHA for CO_2 removal were negligible. Combined with previous research results from lab-testing with pure CO_2 absorption, the aqueous PEHA is a promising solvent. The study of PEHA as a biomass pre-treatment agent showed that no significant improvement on gasification could be identified within the tests performed in this study.

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