Biogas purification by means of adsorption on pine sawdust-based activated carbon: Impact of water vapor

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HIGHLIGHTS

- Biogas upgrading by PSA on a lignocellulosic-based activated carbon is studied.
- Pine sawdust carbon best performs in the lower pressure range to separate CO_2/CH_4.
- The effect of water vapor on the adsorption of CO_2 and CH_4 is evaluated.
- Water vapor reduces the CO_2 uptake of the pine sawdust carbon due to co-adsorption.
- Pre-adsorbed water reduces adsorption capacity but facilitates selectivity to CO_2.

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ABSTRACT

Biogas main components besides methane are carbon dioxide and water that often have to be removed to increase the calorific value of the gas. In this study the effect that the presence of water vapor has on CO_2 separation from a biogas stream by means of adsorption on a lignocellulosic-based activated carbon is addressed.

Binary CO_2/CH_4 breakthrough experiments at 30 °C to account for competitive adsorption under dry conditions were conducted at several feed compositions and adsorption pressures in a fixed-bed lab set-up. An adsorption selectivity factor was selected for analysis of the different cases. The results indicated that CO_2/CH_4 separation by adsorption on this material could be most promising at lower pressures.

Humid gas mixtures were then evaluated in the fixed-bed set-up purposely adapted. The effect of water vapor co-adsorption on the separation of CO_2 and CH_4 was studied for different CO_2/CH_4 ratios, at 30 °C and atmospheric pressure. Under humid conditions the CO_2 uptake was reduced but the CH_4 uptake showed negligible influence of water vapor co-adsorption. Results also indicated that the presence of pre-adsorbed water vapor (saturated bed) reduced the capacity of the bed to adsorb CO_2 and CH_4 but it prompted CO_2 adsorption over CH_4 and hence facilitated the selectivity towards CO_2 with respect to the dry case.

1. Introduction

Biogas is produced during anaerobic digestion of organic substrates, such as the organic fractions of household and industry waste, manure, sewage sludge and agriculture residues. The exact composition of biogas depends on the type of feedstock being digested. Biogas is also produced during anaerobic degradation in landfills and is then referred to as landfill gas. Although, under EU policy, landfilling is the last option to be considered, it still remains the most common form of municipal waste disposal in the majority of member states [1].

Biogas from anaerobic digestion and landfills consists primarily of CH_4 (35–70%) and CO_2 (30–65%). Trace components that are often present in biogas are water vapor, hydrogen sulfide, siloxanes,

hydrocarbons, ammonia, oxygen, carbon monoxide and nitrogen [2,3]. The carbon dioxide content of biogas must be reduced in order to increase the heating value and to avoid pipeline and equipment corrosion in the presence of water.

There are several methods for biogas upgrading, such as absorption processes, membrane separation, cryogenic distillation and adsorption [4,5]. Among these technologies, adsorption-based processes such as Pressure Swing Adsorption (PSA) are promising because of their low cost and high energy efficiency [6,7]. A variety of microporous materials, such as activated carbons, zeolites [8], and metal-organic frameworks (MOFs) have been considered to carry out CO_2 separation [9,10]. The utilization of activated carbons offers advantages due to their high adsorption capacity at ambient conditions, low regeneration cost, long-
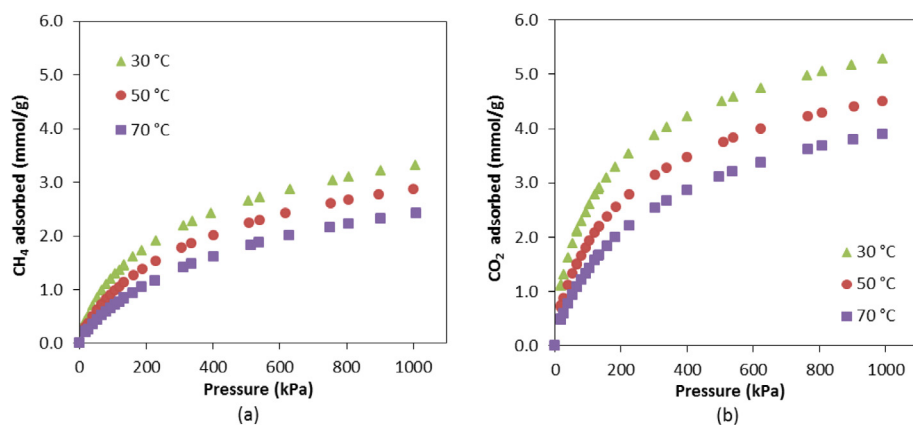
Fig. 1. CH_4 (a) and CO_2 (b) adsorption isotherms for the pine sawdust carbon.

term stability and fast kinetics.

Raw biogas is usually saturated with water [11] and the water content depends on temperature. For example, at 30 °C it is approximately 4% [5]. Hence, the effect of water vapor on the separation of CO_2 from biogas arises relevant as topic of research.

Activated carbons seem promising materials for adsorption under humid conditions because of their significant low cost and their lower hydrophilic character; in fact, they present low affinity toward water vapor at low relative humidity [12]. Thus, the use of activated carbons could avoid the preliminary drying step. In addition, they present remarkable stability and easiness to regeneration; the adsorption capacity remains unaltered after being cyclically exposed to high levels of humidity.

The use of activated carbons for biogas upgrading is extensive [13–16]. The production of carbon adsorbents from biomass feedstocks can involve physical or chemical activation to develop the porosity. Agricultural and forest residues are attractive precursors for activated carbons due to their wide availability and low cost that makes industrial-scale production relatively affordable. Different precursors and their suitability to separate CO_2 from CO_2/CH_4 mixtures have been studied by several authors, such as coconut shells [17,18], wood, empty fruit bunch [19], cherry stones [20] or starch [21]. Results have shown competition for active adsorption sites and preferential adsorption of carbon dioxide over methane [22]. Nonetheless, references in the literature about the impact of water vapor adsorption are very limited. These authors have identified three studies that addressed the effect of water vapor on CO_2/CH_4 separation with carbon nanotubes [23], zeolite [24] and MOFs [25]. Regarding the particular application of activated carbons, only Wang et al. studied equilibrium sorption data of CO_2 and CH_4 on an activated carbon in the presence of different amounts of water; they observed a remarkable differentiated behavior in the CO_2 and CH_4 sorption on wet samples but the study was limited to static measurements of equilibrium of adsorption [26].

In the present work a biomass-based activated carbon, previously synthesized in our laboratory, has been selected to address the impact of water vapor on biogas purification by means of adsorption. Competitive adsorption has been evaluated by means of dynamic breakthrough experiments under dry (binary CO_2/CH_4 feed gas mixture) and wet conditions (binary N_2/H_2O and quaternary $CO_2/CH_4/H_2O/N_2$ feed gas mixture) at 30 °C in a lab-scale fixed-bed set-up purposely adapted. An adsorption selectivity factor was selected to account for the separation efficiency of the biomass-based carbon under the evaluated scenarios.

2. Materials and methods

The selected adsorbent material is a biomass-based activated carbon produced in our laboratory from a low cost biomass precursor, pine

sawdust. The raw pine sawdust was conformed into pellets of 4.1 mm in diameter and activated with CO_2 at 800 °C for 1 h in a single step procedure. The preparation protocol has been thoroughly described in a previous work [27] and a detailed textural characterization of the activated carbon can be found elsewhere [28]. Besides the description of the experimental protocol, in this section the results from the equilibrium of adsorption of the gas components on the pine sawdust activated carbon are also reported so as to define the benchmark scenario.

2.1. High pressure CO_2 and CH_4 adsorption isotherms

CO_2 and CH_4 adsorption isotherms at 30, 50 and 70 °C and up to 1000 kPa were determined in a high- pressure magnetic suspension balance (Rubotherm-VTI). This instrument allows the elimination of most of the disadvantages of the gravimetric technique by physically separating the sample and the high resolution balance by means of a magnetic suspension coupling. The sample is exposed to the measuring conditions while the balance is at ambient temperature. Prior to adsorption measurements, the sample was dried *in situ* under vacuum at 100 °C for 120 min.

In the high-pressure magnetic suspension balance, absolute adsorption cannot be measured directly from the mass profile; the excess mass adsorbed is delivered instead. The absolute amounts of CO_2 and CH_4 adsorbed were then estimated following the procedure described elsewhere [29]. Fig. 1 shows the high pressure adsorption isotherms of CH_4 and CO_2 (absolute amounts) on the pine sawdust carbon.

As expected, the adsorbed amounts of CH_4 and CO_2 at equilibrium increase with pressure and decrease with temperature. At higher pressures there is a reduction in the slope of the isotherm due to the fact that the adsorption sites are close to saturation.

Comparing the adsorption isotherms in Fig. 1, it stands out that under selected conditions of pressure and temperature, CO_2 is preferentially adsorbed over CH_4 on the pine sawdust carbon. It has been previously reported that the larger quadrupole moment of CO_2 (CH_4 does not hold a quadrupole moment) produces a stronger attraction to the adsorbent surface that results in enhanced CO_2 uptake [20,30].

2.2. Water vapor adsorption isotherms

The adsorption isotherms of $H_2O_{(v)}$ at 30, 50, and 70 °C were measured up to the corresponding saturation pressure using a water vapor sorption analyzer (Hydrosorb 1000 HT, Quantachrome). Prior to the adsorption measurements, the sample was outgassed overnight under vacuum at 100 °C. Fig. 2 displays the collected data for $H_2O_{(v)}$ adsorption. As expected, isotherms show *S-shape* pattern, common to carbon materials. In Fig. 2b, data at 30 and 50 °C overlap and at 70 °C there is similar uptake up to a relative pressure of 0.4–0.5. This behavior has been previously reported in biomass based carbon materials