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

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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 CO₂ separation from a biogas stream by means of adsorption on a lignocellulosic-based activated carbon is addressed.

Binary CO₂/CH₄ 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 CO₂/CH₄ 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 CO₂ and CH₄ was studied for different CO₂/CH₄ ratios, at 30 °C and atmospheric pressure. Under humid conditions the CO₂ uptake reduced but the CH₄ 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 CO₂ and CH₄ but it prompted CO₂ adsorption over CH₄ and hence facilitated the selectivity towards CO₂ with respect to the dry case.

Keywords: activated carbon; biogas; CO₂ separation; water vapor adsorption

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.

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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 carbon, 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-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 carbon due to their wide availability and low cost that makes industrial-scale production relatively affordable. Different precursors and their suitability to separate CO₂ from CO₂/CH₄ 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 CO₂/CH₄ 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 CO₂ and CH₄ on an activated carbon in the presence of different amounts of water; they observed a remarkable differentiated behavior in the CO₂ and CH₄ 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 CO₂/CH₄ feed gas mixture) and wet conditions (binary N₂/H₂O and quaternary CO₂/CH₄/H₂O/N₂ 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 CO₂ 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 CO₂ and CH₄ adsorption isotherms

CO₂ and CH₄ 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 minutes.

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 CO₂ and CH₄ adsorbed were then estimated following the procedure described elsewhere [29]. Figure 1 shows the high pressure adsorption isotherms of CH₄ and CO₂ (absolute amounts) on the pine sawdust carbon.

Figure 1. CH₄ (a) and CO₂ (b) adsorption isotherms for the pine sawdust carbon.

As expected, the adsorbed amounts of CH₄ and CO₂ 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 Figure 1, it stands out that under selected conditions of pressure and temperature, CO₂ is preferentially adsorbed over CH₄ on the pine sawdust carbon. It has been previously reported that the larger quadrupole moment of CO₂ (CH₄ does not hold a quadrupole moment) produces a stronger attraction to the adsorbent surface that results in enhanced CO₂ uptake [20,30].

2.2. Water vapor adsorption isotherms

The adsorption isotherms of H₂O_(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. Figure 2 displays the collected data for H₂O_(v) adsorption. As expected, isotherms show *S-shape* pattern, common to carbon materials. In Figure 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 [31].

Figure 2. Water vapor adsorption isotherms for the pine sawdust carbon at 30, 50 and 70 °C up to the corresponding saturation pressure (full symbols correspond to the adsorption branch and empty symbols to the desorption branch): (a) absolute pressure and (b) relative pressure.

According to the data in Figure 1 and Figure 2 adsorption capacities for pure components under similar pressure and temperature conditions follow $\text{H}_2\text{O}_{(\text{v})} > \text{CO}_2 > \text{CH}_4$.

2.3. Isostatic heats of adsorption

Isostatic heats of adsorption for the pure components were estimated by means of the Clausius–Clapeyron equation [32]. The calculated values remained fairly constant with surface loading (see Figure 3) indicating a balance between the strength of cooperative gas–gas interactions and the degree of heterogeneity of gas–solid interactions [33]. The average values obtained were 19.9 J/mmol for CH_4 and 24.2 J/mmol for CO_2 , as estimated from the high pressure adsorption isotherms, and 43.9 J/mmol for water vapor adsorption up to atmospheric pressure. The magnitude of the heats of adsorption for the three components is indicative of the different adsorption strength.

Figure 3. Isosteric heats of adsorption of H₂O_(v), CO₂, and CH₄ on the pine sawdust carbon, as estimated by the Clausius-Clapeyron equation.

2.4. Dynamic column breakthrough experiments

Cyclic adsorption-desorption experiments were conducted in a fixed-bed set-up (see Figure 4). The adsorber column is a stainless steel reactor 13 cm in height and 1.30 cm in diameter that is equipped with a porous plate located 4.7 cm from the bottom of the column. A K-type thermocouple is used to continuously monitor the column temperature with an accuracy of ± 1.5 °C. The temperature is controlled by coupling the heating element coiled around the reactor to an air-cooling device. The bed pressure is controlled by means of a back-pressure regulator, with a pressure range of 0-4000 kPa, located in the outlet pipe. The system is also equipped with a semi-continuous gas analyzer, a dual channel micro-gas chromatograph (micro-GC) CP 4900 from Varian, fitted with a thermal conductive detector (TCD). The detailed description of the system can be found elsewhere [34].

In order to adapt this set-up to the evaluation of the adsorptive separation of CO₂ in wet biogas streams, a controlled evaporator mixer (CEM) equipped with a liquid delivery system (LDS) to feed liquid H₂O (LIQUI-FLOW type, from Bronkhorst High-Tech) was installed. Nitrogen was used to pressurize the water tank and to carry the water vapor into the adsorber.

Figure 4. Schematic diagram of the experimental setup for the cyclic adsorption-desorption experiments.

Breakthrough adsorption experiments were conducted with representative biogas streams under dry and wet conditions. The methodology followed in each set of experiments is described in the sections below.

2.4.1. Dry experiments

The adsorption of binary mixtures of CO_2 and CH_4 with compositions ranging from 35 to 70% in CH_4 , which can be considered representative of dry biogas streams, was assessed through breakthrough studies carried out in the fixed-bed adsorption unit at different pressures and feed flowrates. Figure 5 shows the complete breakthrough adsorption experiment for a 30/70 vol.% CO_2/CH_4 binary gas mixture that consists of six consecutive adsorption–desorption cycles. Before each run the adsorbent was regenerated in an initial drying step at 180 °C under inert gas flow (Helium). The first step (1) of each cycle corresponds to the pre-conditioning of the adsorbent bed characterized by a decrease in temperature down to the adsorption temperature (30 °C) under inert gas atmosphere. The second step (2) is the adsorption stage in which the gas mixture is fed. The breakthrough experiments were conducted until saturation was reached, i.e., until the outlet CO_2 concentration equals that of the inlet stream, in order to

assess the maximum dynamic adsorption capacity of the adsorbent as well as the breakthrough time. During the third step (3) the bed is heated up to 180 °C under inert gas flow to achieve complete regeneration of the adsorbent bed.

Figure 5. Complete breakthrough experiment consisting of six consecutive cycles for a mixture of 30/70 vol.% CO₂/CH₄ at 30 °C, 120 kPa and a feed flowrate of 30 mL/min.

The amount of CO₂ and CH₄ adsorbed was estimated from the experimental breakthrough curves by making a component mass balance to the adsorber unit and discounting the hold up in the gas phase. More details about the calculation procedure can be found in Gil et al. [34]. Breakthrough times were taken at a relative concentration ($C_{i,outlet}/C_{i,feed}$) of 0.05.

The efficiency of the CO₂/CH₄ separation was assessed by means of the separation factor or selectivity (Eq. 1). Thus, the selectivity of the activated carbon to separate CO₂ from CO₂/CH₄ mixtures can be estimated from the following expression:

$$S_{CO_2/CH_4} = \frac{q_{CO_2}/q_{CH_4}}{p_{CO_2}/p_{CH_4}} \quad (1)$$

where q_i is the uptake and p_i is the partial pressure of each component (i represents CO_2 or CH_4).

2.4.2. Wet experiments

With the aim of performing the wet experiments, dynamic tests were conducted in the fixed-bed adsorption unit with mixtures of CH_4 , CO_2 , N_2 and $\text{H}_2\text{O}_{(\text{v})}$. In all cases, the adsorbent was initially fully regenerated by heating the adsorber up to $180\text{ }^\circ\text{C}$ in He flow for at least 1 h and then cooling it down to the temperature of the adsorption step ($30\text{ }^\circ\text{C}$). The total pressure was set at 135 kPa and the total feed flowrate of the dry gas mixture (CO_2 , CH_4 and N_2) was kept at 100 mL/min to which 0.11 g/h of water vapor (which implies a relative humidity of approximately 55% at the experiment temperature) were added by means of the LDS-CEM system.

The effect of water vapor on the adsorption of CO_2 and CH_4 was studied for different feed gas compositions. The ratio of the partial pressures of CO_2 and CH_4 was kept equal to the dry experiments, i.e., feed compositions including 35 to 70% of CH_4 with respect to CO_2 .

To address not only the effect of water vapor on CO_2 and CH_4 adsorption performance, but also the effect of CO_2 and CH_4 on $\text{H}_2\text{O}_{(\text{v})}$ adsorption, the quaternary $\text{N}_2/\text{CO}_2/\text{CH}_4/\text{H}_2\text{O}_{(\text{v})}$ breakthrough curve was compared to a binary $\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ breakthrough curve obtained in the absence of CH_4 and CO_2 . Moreover, the most adverse conditions for CO_2 and CH_4 adsorption were evaluated: quaternary $\text{N}_2/\text{CO}_2/\text{CH}_4/\text{H}_2\text{O}_{(\text{v})}$ breakthrough curves were obtained departing from a bed initially saturated with $\text{H}_2\text{O}_{(\text{v})}$ and N_2 .

3. Results and discussion

3.1. Dry experiments

A simulated biogas binary CO_2/CH_4 mixture (50/50 vol.%) was fed (30 mL/min) to the fixed-bed adsorption unit and the adsorption performance of the sample was evaluated at $30\text{ }^\circ\text{C}$ and at four different pressures (120, 300, 500 and 1000 kPa). For each pressure six consecutive adsorption-desorption cycles were conducted to test the reproducibility of the system, where

adsorption proceeded until saturation and desorption was extended to full regeneration of the carbon. The main characteristics of the adsorbent bed are summarized in Table 1.

Table 1. Bed characteristics for the fixed-bed experiments.

Pine sawdust carbon	
Mass of adsorbent (g)	≈ 4
Total porosity (ϵ_T)	0.87
Bed diameter (cm)	1.30
Bed height (cm)	11.85
Bed density (g/cm^3)	0.265

The resulting CH_4 and CO_2 breakthrough curves are displayed in Figure 6. The adsorption pressure affects the shape of the breakthrough curve as well as the breakthrough time. Longer breakthrough times are observed at higher adsorption pressures for both CO_2 and CH_4 . Independently of the pressure, the less adsorbed component of the gas mixture, CH_4 , always breaks first than the strongest adsorbate, CO_2 ; additionally, a so-called roll-up effect is exhibited in the corresponding breakthrough curves, where the concentration of CH_4 at the column exit temporarily exceeds the feed concentration. This is due to the displacement of initially adsorbed CH_4 by incoming CO_2 . It can be noticed that as the total pressure increases, the height of the roll-up decreases but it becomes wider. This behavior has also been reported for other biomass based carbons intended for CO_2/CH_4 separation [35].

Figure 6. CO₂ (blue) and CH₄ (red) breakthrough curves of a mixture with 50/50 vol.% CO₂/CH₄ at different pressures: (a) 120, (b) 300, (c) 500 and (d) 1000 kPa.

Comparing the CO₂ breakthrough curves, as pressure increases more distended mass transfer zone is observed between the breakthrough point and saturation. At the different pressures, the slopes of the CO₂ curves are remarkably disparate. However, in the case of CH₄, all the breakthrough curves present similar slopes.

Table 2 summarizes the main parameters calculated from the binary breakthrough experiments. It should be mentioned here that selectivity calculations were carried out using the experimental partial pressures instead of the theoretical values corresponding to a 50/50 vol.% gas mixture. Feed gas composition fluctuated between 50 and 51 vol.% for CO₂ and 48 and 49 vol.% for CH₄.

Table 2. Comparison of the CO₂ and CH₄ adsorption capacities, breakthrough times and selectivities of the dynamic experiments at 30 °C and at different pressures feeding a binary CO₂/CH₄ (50/50 vol.%) mixture.

Pressure (kPa)	Uptake (mmol/g)		Breakthrough time (min)		S_{CO_2/CH_4}
	CO ₂	CH ₄	CO ₂	CH ₄	
120	2.00	0.37	9.57	5.56	5.23
300	3.09	0.68	14.76	10.22	4.31
500	3.91	0.96	15.59	13.20	3.93
1000	5.24	1.47	19.47	17.27	3.42

The adsorptive performance is influenced by the gas mixture firstly because of the reduction in the partial pressures of the components when mixed. However, the adsorption of CH₄ from a binary mixture with 50/50 vol.% CO₂/CH₄ seems to be more affected than that of CO₂. The CH₄ uptake is considerably lower than that predicted by the pure component adsorption isotherm at the same partial pressure (see Figure 1), whereas CO₂ uptake is in agreement with the pure component experimental adsorption data at the corresponding pressure. As can be seen in Table 2, selectivity towards CO₂ is inversely proportional to pressure. The highest selectivity is attained at the lowest pressure, 120 kPa.

In addition, the dynamic behavior of the pine sawdust carbon was studied at 120 kPa in two additional binary CO₂/CH₄ gas compositions (30/70 and 65/35 vol.%, respectively), to cover the concentration range of CO₂ that can be encountered in biogas depending on its source of origin. Therefore, the activated carbon was tested in both extreme scenarios. Figure 7 shows the breakthrough curves of CO₂ and CH₄ at 30 °C and at 120 kPa as a function of the feed composition. Table 3 summarizes the main results.

Figure 7. Effect of the feed composition on the CO₂ and CH₄ breakthrough curves at 30 °C and 120 kPa:

(a) 30/70 vol.% CO₂/CH₄; (b) 60/35 vol.% CO₂/CH₄.

Analyzing the breakthrough curves of CO₂ and CH₄, it can be noticed that CH₄ breaks first even when the concentration of CO₂ in the feed is larger. The time gap between CH₄ and CO₂ breakthroughs shortens when the partial pressure of CO₂ increases (Figure 7b), indicating a less effective separation. It can also be observed that the CH₄ roll-up phenomenon is higher but narrower in this case, meaning that a greater quantity of CH₄ is displaced by CO₂.

Table 3. Comparison of the CO₂ and CH₄ adsorption capacities, breakthrough times and selectivities of the dynamic experiments at different feed composition, at 30 °C and 120 kPa.

Composition (vol.%)		Uptake (mmol/g)		Breakthrough time (min)		S_{CO_2/CH_4}
CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	
30	70	1.44	0.65	10.55	5.07	4.51
50	50	2.00	0.37	9.57	5.56	5.23
65	35	2.42	0.26	9.31	6.23	5.13

As expected, there is a decreasing trend in the CO₂ uptake with increasing mole fraction of CH₄ in the feed stream (Table 3).

The effect of the total feed flowrate in dry conditions has been studied as well. Experiments at 30 °C and 120 kPa for a simulated biogas CO₂/CH₄ mixture (50/50 vol.%) were carried out at 15 and 50 mL/min. Both experiments are also compared to the results presented in Figure 6a for a total flow of 30 mL/min. Table 4 shows the uptake capacities and breakthrough times .

Table 4. Comparison of the CO₂ and CH₄ adsorption capacities and breakthrough times of the dynamic experiments at different total flowrates at 30 °C and 120 kPa for a binary CO₂/CH₄ (50/50 vol.%) mixture.

Feed flowrate (mL/min)	Uptake (mmol/g)		Breakthrough time (min)	
	CO ₂	CH ₄	CO ₂	CH ₄
15	2.05	0.40	18.00	10.97
30	2.00	0.37	9.57	5.56
50	2.08	0.39	5.64	2.98

From the data in Table 4 it is corroborated that adsorption uptake of both CO₂ and CH₄ remained independent of the total flowrate, as would be expected since the equilibrium capacity is only affected by the partial pressure of the components in the feed gas which is identical in the three experiments. However, breakthrough times are longer for smaller flows. In addition, the concentration profile of both gases becomes steeper at higher feed flow rates as it can be observed in Figure 8.

Figure 8. Effect of the flow feed on CO₂ and CH₄ breakthrough curves at 30 °C and 120 kPa for a binary CO₂/CH₄ (50/50 vol.%) mixture: total flowrate of (a) 15 mL/min and (b) 50 mL/min.

Dynamic CO₂ uptakes of the activated carbon evaluated in this work are in good agreement with values reported in the literature for CO₂/CH₄ separation. Pine sawdust carbon outperforms some commercial activated carbon such as Calgon BPL and Norit C [34] that presented CO₂ adsorption capacities of 1.47 and 1.50 mmol/g, respectively, at 25 °C and 120 kPa for an equimolar CO₂/CH₄ mixture. Besides, an activated carbon produced from olive stones tested in breakthrough experiments feeding a CO₂/CH₄ mixture (50/50 vol.%) at 30 °C and pressures of 300 and 1000 kPa presented CO₂ uptakes between 2.53 and 5.12 mmol/g [36] while cherry stones-based activated carbon evaluated under similar conditions showed values of 2.80 and 5.14 mmol/g [35].

Other types of adsorbents used in biogas upgrading include zeolites and, more recently, also MOFs have been evaluated for this purpose. Mesoporous MIL-100 (Cr) MOF has reported a CO₂ uptake of 2.7 mmol/g at 30 °C and atmospheric pressure for an equimolar CO₂/CH₄ mixture [37]. García et al. [38] measured adsorption capacities for CO₂ up to 5.2 mmol/g at 30 °C and 500 kPa on zeolites also for equimolar CO₂/CH₄ mixtures and in the case of binderless beads of zeolite 13X evaluated at the same conditions, a CO₂ uptake of 4.7 mmol/g was estimated [39].

3.2. Wet experiments

The ability of the adsorbent to separate CO₂ from humid biogas streams was addressed by means of three types of experiments. Firstly, a quaternary CO₂/CH₄/N₂/H₂O_(v) gas mixture was fed to a fresh bed of pine sawdust adsorbent to assess co-adsorption of CO₂, CH₄ and H₂O_(v) on the solid bed. Secondly, a binary N₂/H₂O_(v) gas mixture was fed to a fresh bed to evaluate the adsorption of water vapor solely. Finally, a quaternary CO₂/CH₄/N₂/H₂O_(v) gas mixture was fed to a bed previously saturated with water vapor to picture the most adverse scenario.

3.2.1. Experiments I: quaternary CO₂/CH₄/N₂/H₂O_(v) gas mixture to a fresh bed

A quaternary mixture of CO₂/CH₄/N₂/H₂O_(v) was fed to a regenerated bed and the adsorption performance of the pine sawdust carbon was evaluated at 30 °C and 135 kPa. The flowrates of the different gases were set as follows: 50 mL/min of N₂, 0.11 g/h of H₂O_(v) and 50 mL/min of CO₂/CH₄ mixture. Different CO₂/CH₄ compositions (30/70, 50/50 and 65/35 vol.%, respectively) were evaluated.

Figure 9. Breakthrough curves for CH₄ and CO₂ (a) and water vapor (b) over a regenerated bed feeding a wet gas stream (Experiments I). See Table 5 for experiments nomenclature.

The breakthrough curves obtained for the quaternary CO₂/CH₄/N₂/H₂O_(v) gas mixtures are shown in Figure 9 for the tested activated carbon. The CH₄ breakthrough curves show the same characteristic roll-up as in the dry experiments; it is higher with increasing partial

pressure of CO₂ in the feed gas. Nevertheless, a slight roll-up pattern can also be perceived in the CO₂ breakthrough curves due to H₂O_(v) co-adsorption (see inset in Figure 9a).

Table 5 summarizes the CO₂ and CH₄ uptakes, breakthrough times and selectivities for the different feed compositions tested (real compositions are given in parentheses). For calculation purposes of the dynamic adsorption capacity of CO₂ and CH₄, a final integration time of 60 minutes was considered (the same time as in the dry experiments at atmospheric pressure) although the wet experiments were extended over longer time. Based on the results, there is a decreasing trend in CO₂ uptake and an increasing trend in CO₂ breakthrough time with increasing CH₄ mole fraction in the feed, consistent with the behavior observed in the dry experiments (see Table 3).

Table 5. Comparison of the CH₄ and CO₂ adsorption capacities, breakthrough times and selectivities of the dynamic experiments under wet conditions (Experiments I).

Composition ratio CO ₂ /CH ₄ (vol.%)		Uptake		Breakthrough		S _{CO₂/CH₄}
		(mmol/g)		time (min)		
		CO ₂	CH ₄	CO ₂	CH ₄	
Exp I A	30/70 (31/69)	0.96	0.72	5.17	2.31	2.97
Exp I B	50/50 (49/51)	1.39	0.43	4.51	2.60	3.36
Exp I C	65/35 (63/37)	1.64	0.32	4.36	2.85	3.09

From the breakthrough curves in Figure 9, it is inferred that water vapor adsorption is extremely slow, particularly when compared to the adsorption of CO₂ or CH₄.

The H₂O_(v) adsorption capacities, breakthrough times and partial pressures for the experiments at different feed compositions are listed in Table 6. As can be seen, similar H₂O_(v) breakthrough times were obtained for the three experiments with wet feed gas to the fixed-bed, independently of the CO₂ and CH₄ concentrations.

After extending the experiments for more than 28 hours, an average partial pressure for water vapor at the exit of the adsorber of around 2.16 kPa was reached. This value is slightly lower than expected, most likely because adsorption equilibrium has not been completely achieved. Therefore, the water uptake estimates from the breakthrough experiments are somewhat reduced when compared to the theoretical values predicted from the pure component $\text{H}_2\text{O}_{(v)}$ adsorption isotherm (see Figure 2). But even then, water uptake in these experiments ranged from 4 to more than 7 times the CO_2 uptake. Water vapor adsorption is further analyzed and discussed in section 3.3.1.

Table 6. Comparison of the water vapor uptakes, breakthrough times and partial pressures at the end of the adsorption step in dynamic wet experiments (2 vol.% of $\text{H}_2\text{O}_{(v)}$) with different CO_2/CH_4 feed composition ratios, at 30 °C and 135kPa (Experiments I).

	$\text{H}_2\text{O}_{(v)}$		
	Uptake (mmol/g)	Breakthrough time (min)	Partial pressure (kPa)
Exp I A	7.37	71.3	2.15
Exp I B	7.11	66.4	2.15
Exp I C	6.90	67.8	2.17

3.2.2. Experiments II: binary $\text{N}_2/\text{H}_2\text{O}_{(v)}$ gas mixture to a fresh bed

A breakthrough curve for a binary mixture with 98/2 vol.% $\text{N}_2/\text{H}_2\text{O}_{(v)}$ was obtained at 30 °C and 135 kPa, which means that the relative humidity of the inlet gas was around 55%. Water vapor adsorption presents very slow kinetics and therefore saturation was reached after approximately 24 hours. Three replicas were conducted as shown in Table 7 where good repeatability is observed (standard deviation of 0.14). The final water vapor partial pressure at the exit gas stream is practically the same as in the feed what ensures equilibrium conditions.

Table 7. Water vapor uptake, breakthrough times and partial pressure of the dynamic wet experiments for a binary $\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ mixture, at 30 °C and 135 kPa (Experiments II).

	$\text{H}_2\text{O}_{(\text{v})}$		
	Uptake (mmol/g)	Breakthrough time (min)	Partial pressure (kPa)
Exp II A	8.43	90.4	2.37
Exp II B	8.45	86.7	2.40
Exp II C	8.68	89.1	2.38

As expected, the $\text{H}_2\text{O}_{(\text{v})}$ breakthrough time of the binary $\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ mixture is higher than that of the quaternary mixtures (see Table 6); the water vapor uptake is also enhanced due to the lack of competition with CO_2 and CH_4 and practically reaches the value forecasted from the adsorption isotherm (Figure 2).

Figure 10. Water vapor breakthrough curves at 30 °C and at 135 kPa for a binary $\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ feed gas mixture.

The breakthrough curve of $\text{H}_2\text{O}_{(\text{v})}$, shown in Figure 10, presents two uptake zones with an intermediate plateau. Comparing the shape of the breakthrough curve of $\text{H}_2\text{O}_{(\text{v})}$ for a binary $\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ mixture with the ones obtained for quaternary $\text{CO}_2/\text{CH}_4/\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ mixtures fed to a fresh bed (see Figure 9b), it is clearly observed that $\text{H}_2\text{O}_{(\text{v})}$ adsorption is affected by CH_4 and

CO₂ co-adsorption. It seems that the CH₄ and CO₂ adsorbed on the sample would hinder the last step of water vapor adsorption observed in the binary experiment.

3.2.3. Experiments III: quaternary CO₂/CH₄/N₂/H₂O_(v) gas mixture to a saturated bed

In order to study the separation of biogas in the least favorable conditions, the adsorbent bed was initially saturated with a mixture of water vapor and N₂ of similar composition to that in the set of Experiments II. Subsequently, several quaternary mixtures containing N₂, H₂O_(v), CO₂ and CH₄ with different compositions were fed to the adsorbent bed. Same CO₂/CH₄ composition ratios as in Experiments I were employed (i.e., 30/70, 50/50 and 65/35 vol.%, respectively).

Figure 11 shows the breakthrough curves of CO₂ and CH₄ for the experiments over a saturated bed. Curves practically overlap for each component regardless of the feed gas composition and, accordingly, breakthrough for the different compositions of CO₂ and CH₄ occurs at similar times. These results differ from those obtained when biogas was fed to a regenerated bed.

Figure 11. Breakthrough curves of CO₂ and CH₄ for all the experiments in wet conditions when the bed is initially saturated with a binary N₂/H₂O_(v) mixture (Experiments III).

According to results in Figure 11, higher CO₂ partial pressures in the feed lift the roll-up in the CH₄ profile but it becomes narrower. In this case, as opposed to the quaternary mixture in the

set of Experiments I, no roll-up effect on CO₂ is observed as water vapor is already in the saturation phase and so CO₂ is not displaced by other stronger adsorbing component.

As can be seen in Table 8, breakthrough times and adsorption uptakes for CH₄ and CO₂ are considerably reduced when compared to the results obtained with a fresh bed (Table 5). Referring these results to the values from the pure component adsorption isotherms (see Figure 1), the amounts of CH₄ and CO₂ adsorbed are approximately 85 and 60% lower, respectively. However, in relation to the dry experiments a reduction of up to 50% in uptake for both gases is observed (Table 3). Adsorption of the two gases is affected to a similar extent due to the fact that microporosity in the pine sawdust carbon bed is already filled with water.

Table 8. Comparison of the CH₄ and CO₂ adsorption capacities, breakthrough times and selectivities of the dynamic wet experiments at different feed compositions over a saturated bed (Experiments III).

	Composition ratio CO ₂ /CH ₄ (vol.%)	Uptake		Breakthrough		S _{CO₂/CH₄}
		(mmol/g)		time (min)		
		CO ₂	CH ₄	CO ₂	CH ₄	
Exp III A	30/70 (30/70)	0.42	0.15	2.12	0.43	6.33
Exp III B	50/50 (49/51)	0.65	0.11	1.95	0.39	6.20
Exp III C	65/35 (62/38)	0.78	0.08	1.92	0.44	5.89

3.3. Comparison between dry and wet experiments

Several parameters have been identified as critical in the study. These include the CO₂ and CH₄ adsorption capacities and the selectivity factor. In this section the results of all the conducted experiments are compared and conclusions on the effect that water vapor adsorption has on CO₂ separation from a biogas mixture are finally posed.

3.3.1. Adsorption isotherms of the pure components vs. breakthrough experiments

The cumulative amount of CH_4 and CO_2 adsorbed calculated from the breakthrough experiments at atmospheric pressure are compared to the adsorption data from the isotherms of the pure components (see Figure 12).

Figure 12. Comparison of CH_4 (a) and CO_2 (b) uptakes from breakthrough experiments and single component adsorption isotherms.

Figure 12 depicts a clear picture on the impact of co-adsorption on the CO_2 and CH_4 uptakes. The adsorbed amounts of CH_4 obtained from breakthrough experiments are clearly below those from the CH_4 adsorption isotherm that correspond to the maximum uptake at equilibrium. However, there is agreement between the adsorbed amounts of CO_2 from the breakthrough experiments and those from the CO_2 adsorption isotherm. The extent to which CO_2 and CH_4 adsorption is affected when mixing in binary and quaternary gas streams is completely apart: the presence of CO_2 (strongly adsorptive) significantly reduces the adsorption of CH_4 (weakly adsorptive). It is also noticed that when the breakthrough experiments are conducted in a pre-saturated bed, the adsorption of both components is drastically reduced.

Although it could stand out in Figure 12 that CH_4 uptake is higher in wet experiments over a regenerated bed than in dry experiments, it should be born in mind that the quantity of CO_2 present is in absolute terms smaller. Therefore, in Figure 13 uptake capacities are compared in terms of CO_2/CH_4 partial pressure ratio in the feed.

Figure 13. CH_4 (a) and CO_2 (b) adsorption capacities versus ratio of partial pressures in the feed gas.

For a given $p\text{CO}_2/p\text{CH}_4$ ratio, the partial pressures of CO_2 and CH_4 are greater in the dry than in the wet experiments. It can then be concluded that CO_2 uptake is mainly dependent on the partial pressure of CO_2 in the feed gas mixture since for a given ratio of CO_2/CH_4 partial pressures the highest uptake corresponds to the dry experiment. However, CH_4 adsorption is not only dependent on its partial pressure in the feed but also on the ratio of CO_2 and CH_4 partial pressures and so similar CH_4 uptakes are obtained for the dry and wet experiments for a given ratio of partial pressures, as shown in Figure 13.

From the experiments carried out in this study CO_2 uptake follows the next descending order: dry experiments > wet experiments over a regenerated bed > wet experiments over a saturated bed. Comparable values of CH_4 uptake are obtained for dry experiments and wet experiments over a regenerated bed, pointing out that methane is not affected by water vapor co-adsorption.

Regarding the adsorption capacity of $\text{H}_2\text{O}_{(\text{v})}$ at the relative humidity of the feed ($\text{RH} \approx 55\%$) for the binary $\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ mixture it is 17 times the adsorption capacity of N_2 (data not reported in this work). Meanwhile, for the quaternary $\text{CO}_2/\text{CH}_4/\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ gas mixture the adsorption capacity of $\text{H}_2\text{O}_{(\text{v})}$ is around 3.7 times the total sum of the adsorption capacities for the other gas components. This occurs despite the lower partial pressure of water vapor in the quaternary gas mixture.

Figure 14 represents the amount of water vapor adsorbed after 1500 min of adsorption for all the experiments conducted under wet conditions.

Figure 14. Comparison of water vapor uptake with the pure water adsorption isotherm at 30 °C.

As mentioned before, water vapor uptakes for the $\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ mixture (Experiments II A, B and C) are in good agreement with the reported data from the $\text{H}_2\text{O}_{(\text{v})}$ adsorption isotherm at 30 °C. In comparison, water vapor adsorbed in the quaternary experiments (Experiments I A, B and C) is considerably lower than the maximum adsorption capacity in equilibrium (isotherm). First of all, it should be taken into account that for the $\text{CO}_2/\text{CH}_4/\text{N}_2/\text{H}_2\text{O}_{(\text{v})}$ mixture, after 1500 minutes of adsorption, equilibrium is not fully reached due to the slow kinetics of water vapor adsorption. In addition, co-adsorption of the other gas components should be considered: CO_2 and CH_4 competitively adsorb onto the activated carbon taking over part of the available adsorption volume and reducing the availability for water vapor adsorption.

3.3.2. Selectivity factor

In order to compare all the results from the different experiments, the values of the selectivity factor calculated for the set of Experiments I, II and III are compiled in Figure 15.

Figure 15. Selectivity factor vs CO_2/CH_4 partial pressure ratio: (a) dry experiments at different total pressures, (b) comparison between dry (red color) and wet biogas experiments over a regenerated (green color) and a saturated bed (blue color).

Selectivity factors for the dry experiments at different conditions are displayed in Figure 15a. Selectivity towards CO_2 decreases with increasing adsorption pressure but variation of feed gas composition does not have a significant influence.

Evaluating the selectivity of the dry and wet experiments in Figure 15b, the highest values correspond to the wet experiments over a saturated bed. This could be ascribed to the reduced adsorption capacities of CO_2 and CH_4 at these conditions that favor CO_2 over CH_4 . Selectivity follows an almost constant pattern with the ratio of partial pressures of CO_2 and CH_4 in all the experiments conducted under dry and wet conditions.

The selectivity of the pine sawdust adsorbent for CO_2/CH_4 separation was found to be within the range of the values reported in the literature for other activated carbons. For instance, cherry-stones-derived activated carbons showed selectivities between 3.2 and 4 depending on the adsorption conditions [20]. Selectivity values of 3.6 were obtained using Sips-based Ideal

Adsorbed Solution Theory (IAST) model with experimental results from different CO_2/CH_4 mixtures for pitch-based activated carbon at 30°C [15]. CO_2 selectivities of BPL, a commercial activated carbon, predicted with IAST at 100 kPa and 25°C varied from 3.8 to 4 [40]. Ferella et al. reported a separation factor between 3.6 and 4.2 for a commercial granular activated carbon [8].

Humid biogas separation has been scarcely studied. Therefore, specific data on selectivity of activated carbon under wet conditions are barely available. However, an enhanced selectivity towards CO_2 in the presence of pre-adsorbed water has been also reported by Liu et al. [23] using GCMC simulations on carbon nanotubes (up to 9.2 for the highest water content evaluated at 100 kPa) and on one of the MOFs studied by Xian et al. [25] reaching a selectivity value of 16.3.

4. Conclusions

This study has shown the potential application of a pine sawdust activated carbon to the separation of CO_2 from biogas streams. Breakthrough experiments were conducted at different conditions covering a wide range of biogas compositions (dry and wet) and adsorption pressures. Results indicated that this material performed best in CO_2/CH_4 separation at atmospheric pressures.

Under humid conditions the CO_2 uptake on a regenerated bed decreases as its partial pressure in the quaternary mixture is reduced in comparison with the dry experiments; however, CH_4 adsorption remains practically unaltered for a given $p\text{CO}_2/p\text{CH}_4$ ratio. On the other hand, the presence of pre-adsorbed water vapor on the bed reduces the adsorption of both CO_2 and CH_4 but it prompts CO_2 adsorption over CH_4 and hence facilitates the CO_2/CH_4 separation with respect to the dry case. Therefore, despite the reduction in gas uptake, the pine sawdust activated carbon shows great potential in CO_2 separation from biogas saturated with water vapor. An operational window exists to carry out the CO_2/CH_4 separation under saturated conditions effectively.

It can be concluded that the CO₂ separation from biogas could be achieved on the pine sawdust carbon bed without the need of water removal prior to the adsorption unit.

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