

Influence of NH₃/CO₂ activation on the CO₂/H₂S adsorption capacity of cellulose char

África Navarro-Gil, Noemí Gil-Lalaguna, Isabel Fonts, Joaquín Ruiz, Jesús Ceamanos, Javier Ábrego, Gloria Gea

Afiliación: Grupo de Procesos Termoquímicos (GPT)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
Tel. +34-976762707, e-mail: africa@unizar.es

Abstract

This study examines the effect of NH₃ functionalization and/or CO₂ activation (at 700 °C) of cellulose pyrolysis chars (produced at 750 °C) on the adsorption of CO₂ and H₂S from a gas stream.

Introduction and objectives

Anaerobic co-digestion is an attractive opportunity for the energetic valorization of several organic residues generated in the livestock and agricultural sector. A combustible biogas is obtained, that could be used as a source of energy on the farm. The biogas is mainly composed of CH₄, CO₂ and trace amounts of other components such as H₂S. However, to reduce gas emissions and broaden the application of biogas as a fuel or as bio-methane, the concentration of CO₂ and H₂S must be decreased.

Materials and methods

Materials

Cellulose was chosen as raw material, because it is one of the main components in many agricultural and animal wastes, including manure and agricultural crop residues. Cellulose was purchased from Sigma Aldrich as a commercial product (CAS 8068-03-9).

Experimental Method

Adsorbent material preparation

The activated char used as adsorbent resulted from cellulose pyrolysis and subsequent activation with CO₂ and/or NH₃. The pyrolysis process was carried out in a fixed-bed reactor of around 10 g of capacity, using a heating rate of 10 °C/min from ambient temperature to 750 °C and maintaining during 1 h this final temperature. A flow of 45 mL_{STP}/min of N₂ was used as carrier gas to ensure an inert atmosphere in the reactor. During pyrolysis, a solid known as char is formed with appropriate qualities for gas

adsorption. The functionalization-activation process can be described as follows. A sample (~1.5 g) of char was heated up to 700 °C in a flow rate of 45 mL_{STP}/min of N₂. When the temperature was reached, N₂ was replaced by one of the following gases: (i) pure CO₂; (ii) 20 vol% NH₃ and 80 vol% Ar; (iii) two-sequential activation steps, using first pure CO₂ and next 20 vol% NH₃ and 80 vol% Ar. Each activation step lasted one hour.

Adsorption of CO₂ and H₂S

The adsorption experiments were carried out with two different gases, CO₂ and H₂S, at 25 °C and atmospheric pressure.

The CO₂ adsorption capacity of the char samples was examined by thermogravimetric analysis (TGA) with a Netzsch STA 449 Jupiter thermobalance. About 60 mg of char was first degassed at 150 °C with N₂ stream (120 mL_{STP}/min). After cooling to 25 °C, the char sample was exposed to various CO₂/N₂ mixtures, with CO₂ ranging from 2 vol% to 83 vol% to obtain its corresponding adsorption isotherm. The CO₂ adsorption capacity of the chars (mg CO₂/g char) for each %vol CO₂ was determined using the weight gain of the sample.

The H₂S adsorption capacities of the chars have been studied in a fixed-bed reactor equipped with a mass spectrometer to continuously monitor the effluent gas composition. In each experiment, 0.6 g of char was packed in the fixed-bed device. The concentration of H₂S in the gas was set at 1 vol% with a total flow rate of 65 mL_{STP}/min. These tests involved an adsorption step at 25 °C and a desorption step at 150 °C in Ar atmosphere. The H₂S adsorption capacity of the char (mg H₂S/g char) was calculated by adding the amount desorbed (determined by the integration of the area below the desorption curve expressed as mL_{STP}/min of H₂S leaving the reactor vs. desorption time) and the S retained in the chars (expressed as

H₂S) after adsorption-desorption cycle determined by an elemental analysis.

Char characterization

The concentration of nitrogen in the char samples, before and after chemical activation with NH₃, as well as the content of sulfur in the chars before and after the H₂S adsorption-desorption cycle were analyzed (elemental analyzer LECO CHN628 with sulfur analyzer module) to quantify N and S chemically retained in the char after the NH₃-activation step and after the H₂S adsorption-desorption process, respectively.

The specific surface area of the chars has been determined by adsorption-desorption tests with N₂ at 77 K. Data have been analyzed according to Brunauer-Emmett-Teller (BET) model and non-local density functional theory (NLDFE), by assuming slit pore geometry, to determine the pore size distribution.

Results and discussion

Char characterization

The N content of the NH₃-modified samples was higher than that of the unmodified char and CO₂-modified char (Table 1). These results show that either NH₃ or CO₂/NH₃ activation steps incorporated nitrogenous functional groups onto the char. The N content increased by 30 % during the two-steps activation process (CO₂-NH₃), whereas the functionalization with only NH₃ increased by up to 60 % regarding to the non-functionalized char.

The specific surface area (SS) of the prepared chars are shown in Table 1. The results of BET surface area show that the combined activation with CO₂ and subsequent NH₃ functionalization at 700 °C resulted in the greatest increase in the specific surface area (from 356-383 to 704 m²/g).

Adsorption performance

Figure 1 shows the CO₂ adsorption isotherms at 25 °C for both the activated and non-activated cellulose chars. There are no discrepancies between any of the displayed isotherms. The maximum capacity with an 83 vol% CO₂ concentration was 73 mg/g. Although the cellulose char functionalized with CO₂ and NH₃ exhibits a larger specific surface

area and higher N content, it maintains the same CO₂ adsorption capacity. However, the H₂S adsorption capacity at 25 °C has been enhanced, especially due to chemisorption contribution, which seems to be favored by NH₃ functionalization.

The potential of char to chemically retain H₂S increases as the content of N in the chars rises. The S content retained in the char functionalized with NH₃ was 1.5 wt%, compared to 0.32 wt% for untreated cellulose char. This highlights that H₂S adsorption on the chars treated with NH₃ (either with only NH₃ or CO₂/NH₃) mainly occurred by a chemical mechanism. However, H₂S uptake with the non-activated char or with the one activated only with CO₂ were lower and mainly physical in nature, which would allow for subsequent adsorption/desorption cycles.

Conclusion

The use of cellulose-rich waste chars could be an alternative for obtaining low-cost solid adsorbents for biogas cleaning.

Although the specific surface area of cellulose char increased significantly after activation with CO₂ and subsequent functionalization with NH₃, CO₂ adsorption capacity of the char was hardly affected. Significant improvements of the H₂S adsorption capacity have been obtained after the activation of cellulose pyrolysis chars with NH₃ or two activation steps, first with CO₂ and subsequent with functionalization with NH₃. However, H₂S chemical adsorption inhibits the use of chars for successive adsorption-desorption cycles, so subsequent uses of this spent material should be investigated.

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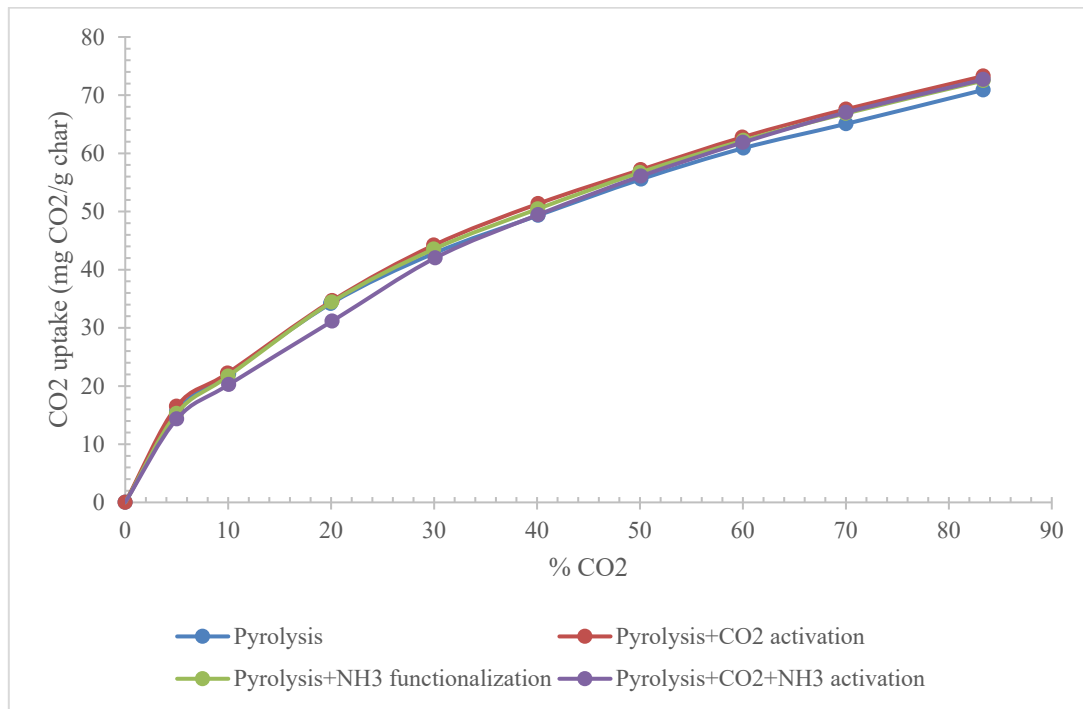


Figure 1. CO₂ adsorption isotherms at 25 °C and 1 atm for activated and non-activated cellulose chars

Table 1. Characterization of cellulose chars and results of CO₂ and H₂S adsorption

Treatment	N (%wt)	SS _{BET} (m ² /g)	CO ₂ adsorption 83 vol% (mg CO ₂ /g)	H ₂ S physisorption 1 vol% (mg H ₂ S/g)	H ₂ S chemisorption 1 vol% (mg H ₂ S/g)	S in char (wt%) after ads/des cycle
Pyrolysis	0.77	356	71 ± 2	19.5	3.4	0.32
Pyrolysis + CO ₂ activation	0.78	383	73 ± 2	18.0	5.8	0.54
Pyrolysis + NH ₃ functionalization	1.24	362	72.5 ± 0.6	15.4	15.9	1.50
Pyrolysis + CO ₂ +NH ₃ activation	1.00	704	73 ± 4	18.7	12.4	1.20