INVESTIGATION OF THE CO2 ADSORPTION CAPACITY OF CHARS PRODUCED BY PYROLYSIS OF MACRO-COMPONENTS OF DIGESTED MANURE AND THEIR BLENDS

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ABSTRACT: Cellulose, lignin, soybean protein and calcium carbonate are used as representative macro compounds for bio-degraded manure. Chars from the pyrolysis of these components and mixtures thereof at 750oC in the ceramic reactor of a thermogravimetric analyzer are tested for their capability to adsorb CO2. Adsorption isotherms are measured at 25oC and the temperature dependence of CO2 adsorption is studied between 25oC and 120oC. The results lead to the following conclusions: First, the chars from cellulose and lignin show quite good CO2 adsorption but the char yields from lignin are more than two times higher. Second, soybean protein pyrolysis produces little char which hardly adsorbs CO2. CaO from CaCO3 calcination only adsorbs CO2 slowly but irreversibly. Third, char production and quality of mixtures can in most cases be rationalized by additive contributions from the pure components, meaning that no positive synergetic effects from the protein or calcium carbonate are observed. Fourth, the adsorption isotherms are in line with Dubinin’s theory of volume filling of micropores (TVFM). Also in agreement with TVMF is the small enthalpy of adsorption deduced from the temperature dependent data. Finally, the char properties obtained with organosolv lignin differ substantially from those with Kraft lignin. Based on the current work, it seems unlikely that manure can be valorized by pyrolyzing it at 750oC to a profitable CO2-adsorbing char.

*Keywords: Thermogravimetry, Organic waste valorization, Pyrolysis, CO2 adsorption capacity, Adsorption isotherms*

1. INTRODUCTION

Utilization of waste materials is an increasingly important task of the society to achieve a sustainable life style, and to address climate change issues and the limits of natural resources. In this context the reduction of the carbon footprint e.g. by reducing the use of plastics and by increasing the recycling efficiency is probably one the most well-known current goals. Another area of importance is to find an environmentally friendly utilization for manure and similar residues to protect ground water reservoirs, lakes and rivers.

Manure is the most abundant residue from intensive livestock areas. There are a number of different manures such as liquid manure, solid manure or litter-based farmyard manures. These are usually mixed with bedding materials such as straw or wood shavings. In 2011, the production of pig, cattle and poultry manure in the EU27 was estimated to be around 1.4 billion tons. On average only about 7.8% of manure produced in Europe has been further processed in the past years while the remainder was mainly spread on arable or grassland. Excessive spreading of manure causes air, soil and water pollution and therefore alternative options to use manure are needed. The most common utilization of manure is its anaerobic digestion to produce biogas. EU plans support biogas production from manure and lignocellulosic residues as decentral valorization technologies ([Scarlat et al., 2018](#_ENREF_3)). One challenge of this application is that biogas contains, apart from methane, rather high concentrations of CO2, H2S and other pollutants ([Sun et al., 2015](#_ENREF_5)). Environmentally friendly ways to clean biogas are needed to improve the process efficiency and economy ([Sun, Li, Yan, Liu, Yu, & Yu, 2015](#_ENREF_5)). The purification of the biogas with a cheap solid adsorbent obtained by pyrolysis of the digestate could alleviate the barriers for a wider implementation of this process.

Digested manure is a carbonaceous solid which upon pyrolysis is known to yield char which adsorbs CO2 ([Xu et al., 2016](#_ENREF_8); [Zhang et al., 2019](#_ENREF_9)). However, very disperse adsorption capacities have been reported in the literature. Furthermore, the ash content of manure can be very high, which at first glance should be an argument against the use of manure for CO2-adsorbing char production. However, it is well known that CO2 and water can activate char at high temperatures ([Rodríguez-Reinoso et al., 1995](#_ENREF_2)), hence the calcination of minerals might actually have a beneficial effect. A thorough understanding of the factors and pyrolysis conditions that produce a cheap char with good CO2-adsorbing properties would allow the optimization of the biogas production process from manure and improve its economics. This need leads to the main objective of this work: To systematically study the CO2 adsorption capacity of chars produced via pyrolysis of the main macro-components of digested manure as well as their mixtures. Due to its origin, the main macro-components of digested manure are cellulose and lignin from the bedding materials and the lignocellulosic residues, proteins originating from the excrements and also from the microorganisms implied in the anaerobic digestion, and lastly CaCO3 which is found in the excrements, since it is usually used in animal feeding composition.

In order to meet this objective, this work reports on pyrolysis and CO2 adsorption tests of the manure macro-components and their blends performed in a thermobalance (TGA). Char characterization is used to explain the results. CO2 adsorption isotherms and temperature dependent CO2 adsorption results are used to deduce the strength of CO2 adsorption (adsorption energy) and to distinguish between physisorption and chemisorption. The results allow to identify which major components mainly contribute to the production of CO2-adsorbing material and to identify the role of interactions between these components during the pyrolysis step.

1. EXPERIMENTAL METHOD AND MATERIALS

The first part describes the equipment and procedures of the measurements and the second part lists the sources and characteristics of the materials that have been used for making residuals to remove CO2.

2.1 Experimental method

2.1.1 Thermogravimetry

A Netzsch STA 449 Jupiter® thermobalance was used to study the pyrolysis profiles of the macro-components, mixtures and manure, and to measure the CO2 adsorption characteristics of the produced residual solids (“chars” or CaO in case of CaCO3 calcination). All materials were used as powders or thin needles. Initial tests were performed to test the influence of different particle size ranges on the CO2 adsorption results but no pronounced impact was observed. Therefore, neither the materials used in the final pyrolysis experiments reported, nor the chars used for the reported CO2 adsorption tests were size selected. Almost all measurements reported here were done with large crucibles of 3.4 ml volume. Argon was used as carrier and protective gas, pure CO2 for the adsorption tests and synthetic air for decoking purposes.

The procedure used to convert a char precursor to char and subsequently determine its CO2 adsorption capacity includes: i) the heating of the TGA with the selected material, at approximately 10ºC/min, up to 750ºC in argon (200 cm3·min-1 (STP)). Once the target temperature is reached (a temperature overshoot of around 20ºC exists) it is held for 2 hours before cool-down begins, which takes about four hours; ii) when the TGA is at around 25ºC, Ar is replaced by CO2 and for chars with significant adsorption capacity, a weight increase due to CO2 adsorption is detected and recorded.

The procedure used to measure CO2 adsorption isotherms at 25ºC starts with degassing the sample at 250 oC. After cool down to 25ºC the sample is exposed to various CO2/Ar mixtures and the change in sample weight is measured. Halfway through the set of measurements, the sample was again degassed at 150oC to test for chemisorption.

CO2 adsorption as a function of temperature is measured for three CO2 mole fractions. First, char is degassed before exposing it at 25 oC to 100% CO2 carrier gas (50 cm3·min-1 (STP)). The actual CO2 mole fraction is diluted to 0.71 by the use of 20 cm3·min-1 (STP) Ar to protect the balance. CO2 adsorption increases the weight. Then the temperature is raised by 2 oC/min up to 120 oC (desorption branch) and afterwards lowered to 25 oC (adsorption branch). The weight change is monitored as function of temperature. The degassing, desorption and adsorption steps are repeated for two other CO2 mole fractions (0.57 and 0.43). The total pressure in the TGA is assumed to be always close to 1 atm – a pressure gauge is not available.

2.1.2 Surface area measurement

The specific surface areas of the samples were determined through N2 adsorption isotherms which were measured with a Quantachrome Autosorb® 6 Surface Area and Pore Size Analyzer. The samples were degassed at 523 K for 8 h prior to each analysis. Specific surface area and micropore volume were calculated using the Dubinin-Radushkevich (DR) equation.

2.1.3 ATR-FTIR

IR spectra of the starting materials and chars were recorded with an Agilent Cary 600 Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectrometer. The stated resolution is 4 cm-1 in the wavelength range of 4000 - 400 cm-1 (medium IR region).

2.1.4 Data analysis

The results from the pyrolysis experiments are analyzed in terms of CO2 uptake (eq. 1) and total CO2 uptake (eq. 2).

; units eq.1

; units eq.2

“” is the weight change upon CO2 addition, and “” are the total amount of biomass pyrolyzed to produce the char that is subsequently used to adsorb the CO2.

The error bars shown in several figures are standard deviations calculated as:

eq.3

with being the number of data points, , and is the average value. All pyrolysis experiments have been repeated at least once, and for materials yielding low amounts of char up to four experiments were carried out.

An approximate value for the enthalpy of adsorption can be obtained from the temperature-dependent adsorption measurements at constant CO2 partial pressure assuming that the entropy difference between gas phase and surface species remains constant within the temperature range, that the activity coefficient of CO2 on the surface, , is proportional to the amount (W) of CO2 adsorbed while that for the gas phase, is constant. The enthalpy difference between surface and gas phase, , is the enthalpy of adsorption, which can be determined from the slope of a ln(W) versus 1/T plot (eq. 6).

eq.4

eq.5

eq.6

The Dubinin-Radushkevich equation

eq.7

relates the volume *W* filled at temperature T and relative pressure to the total available volume of the micropores. *β*, the affinity coefficient, is characteristic for the adsorbate and the parameter *B* is related to the pore size. From the straight line of an *ln(W)* vs plot the total volume of the micropores can be extrapolated. Deviation of linearity in a D-R plot indicates contributions from non-microporous surface areas ([Stoeckli, 1990](#_ENREF_4)).

2.2 Materials

The co-digested manure (CDM) sample was supplied by the HTN Biogas Company located in Navarra (Spain) and was obtained by anaerobic co-digestion of cattle manure with agricultural residues. The anaerobically digested manure was separated in a decanter centrifuge and the solid fraction was dried at 105 ºC for 24 h until partial dryness. Ash and moisture contents were determined according to ISO-18122-2015 standard. The content of extractives was determined by Soxhlet extraction with methylene dichloride. The Van Soest method according to XP U44-162 and the Kjeldahl method according to EN-13342:2001 were applied to the CDM sample in order to determine the content of hemicellulose (HCELL), cellulose (CELL), lignin (LIG) and proteins.

Table 1. Main macro-components in manure.

|  |  |  |
| --- | --- | --- |
|  | **Actual composition of CDM** | **Relative contribution of the four selected representative constituents (wt.%) on dry basis** |
| Ash (wt.%) | 20 | 26 |
| Moisture (wt.%) | 13 | -- |
| Extractives (wt.%) | 1.0 | -- |
| Proteins (wt.%) | 12 | 15 |
| HCELL (wt.%) | 2.8 | -- |
| CELL (wt.%) | 30 | 38 |
| LIG (wt.%) | 16 | 21 |

Apart from moisture, the four most abundant constituents of CDM, ash, proteins, cellulose and lignin were selected as representative macro-components for CDM in order to shed light on the fundamental understanding that leads the CO2 adsorption over char. Cellulose as powder material with a quality level (MQ200) was purchased in Sigma Aldrich (Sigma Aldrich code C8002). There is a wide variety of lignin depending on the procedure used to isolate it from the biomass. Organosolv lignin was selected to represent organic waste, since its properties closely resemble natural lignin in biomass. Powder-like organosolv lignin with a purity higher than 85 wt.% was purchased in Hangzhou J & H Chemical Co., Ltd. To demonstrate the impact of choice of lignin, Kraft lignin (also known as “alkali” of “Kraft” lignin) was purchased from Sigma Aldrich (Sigma Aldrich code 471003). This lignin contains 4% sulfur impurity and is characterized by 3 wt-% of base (pH = 10.5). Powder-like edible soybean protein of high purity was obtained from a drugstore and used as is. A typical protein of plants, soybean protein, was chosen as model component for the proteic fraction of CDM. CaCO3 as a major constituent of the ash fraction in CDM was selected to represent the total ash content.

The elemental and proximate analyses of the organic macro-components and the CDM are presented in Table 2.

Table 2. Elemental and proximate analyses of the raw materials (moisture basis).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Soybean protein** | **Cellulose** | **Organosolv lignin** | **Kraft ligninc**  **(diff lot)** | **CDM** |
| C (wt. %) | 48.88 ± 0.07 | 39.52 ± 0.4 | 45.4 ± 0.2 | 50.13  (51.23) | 29.5 ± 0.5 |
| H (wt. %)a | 6.563 ± 0.008 | 6.1 ± 0.05 | 5.84 ± 0.07 | Not available  (5.04) | 4.1 ± 0.2 |
| N (wt. %) | 13.6319 ± 0.0003 | <0.284 ± 0.001 | 0.64 ± 0.2 | Not available | 2.05 ± 0.09 |
| S (wt. %) | 1.12 ± 0.02 | not detected | not detected | 3.33  (3.37) | 0.96 ± 0.03 |
| O (wt. %)b | 25.6 ± 0.1 | 54.38 ± 0.5 | 46.9 ± 0.5 | Not available | 26.0 ± 0.8 |
| Moisture (wt. %) | 5.9 ± 0.2 | 5.3 ± 0.3 | 21.8 ± 0.02 | Not available  (5.0) | 11.3 ± 0.9 |
| Volatiles (wt. %) | 80.8 ± 0.4 | 100 ± 0.04 | 67.90 ± 0.09 | Not available | 49.7 ± 0.7 |
| Ash (wt. %) | 4.2 ± 0.7 | not detected | 1.26 ± 0.1 | Not available  (Sodium: 5.4) | 37.4 ± 0.6 |
| Fixed carbon (wt. %) | 9.1 ± 0.5 | not detected | 9.0 ± 0.2 | Not available | 2 ± 1 |

a Hydrogen includes hydrogen from moisture.

b Oxygen was calculated by difference (O(wt.%)=100-Ash(wt.%)-C(wt.%)-H(wt.%)–N(wt.%)–S(wt.%)) and also includes oxygen from moisture.

C Sigma Aldrich certificate of analysis for LOT 04414PE, in parenthesis given are more complete LOT 09724CE results

*Mixture preparation*: Weighted amounts of the components were mixed by grinding with a mortar and pestle until the mixture appeared homogenous in color and grain size. In *Table 3*, the mixtures used in this study are listed.

Table 3: Compositions of the mixtures used in this work. (CELL= Cellulose, LIGO = organosolv lignin, LIGA = Kraft lignin, SOY = soybean protein, CaCO3 = calcium carbonate.

|  |  |
| --- | --- |
| **Mixture**1 | **Composition in wt-%** |
| *Binary mixtures* | |
| Cellulose : Organosolv lignin | 53.0 CELL : 47.0 LIGO |
| Cellulose : Kraft lignin | 49.6 CELL : 50.4 LIGA |
| Cellulose : Soybean protein | 80.0 CELL : 20.0 SOY |
| Organosolv lignin : Soybean protein | 78.8 LIGO : 21.2 SOY |
| *Multi component mixtures* | |
| Cell.:OrgSolv\_lig : Soy\_Prot. | 37.8 CELL : 42.9 LIGO : 19.4 SOY |
| Cell.: OrgSolv\_lig : CaCO3 | 40.3 CELL : 39.6 SIGO : 20.1 CaCO3 |
| Cell.: OrgSolv\_lig : CaCO3 : Soy\_Prot. | 39.5 CELL : 30.2 LIGO : 20.2 CaCO3 : 10.1 SOY |
| Cell.: Kraft\_lig : CaCO3 : Soy\_Prot. | 40.2 CELL : 29.0 LIGA : 20.1 CaCO3 : 10.7 SOY |

1 Names as used in the respective figures

1. RESULTS

The results will be presented in four separate sections starting with the formation of chars (or residuals in the case of CaCO3) and their CO2 adsorption capacity at 25ºC, followed by char characterization data. Afterwards the CO2 adsorption properties are tested in terms of 25ºC isotherms and finally as function of temperature to determine an approximate enthalpy of adsorption value.

3.1 Char production and CO2 uptake at 25ºC

Chars have been produced from pure macro-compounds, binary mixtures of those and multicomponent materials, and their CO2 adsorption capacity at 25ºC in 100 cm3·min-1 (STP) CO2 and 20 cm3·min-1 (STP) Ar (protective gas) has been measured directly after the pyrolysis stage. Figure 1 shows an example of the conditions and the general weight change profile in TGA for char production from a precursor material and its subsequent interaction with CO2.

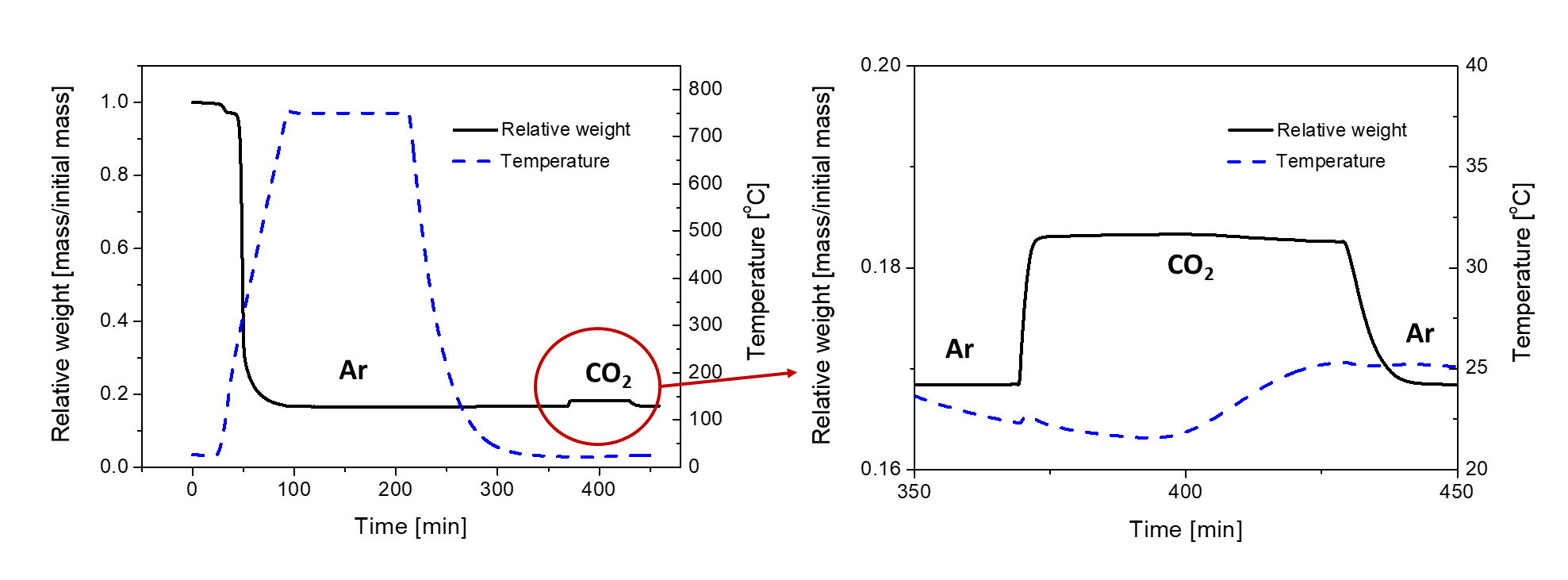


Figure 1: Conditions and example profile for char production from a precursor material (here cellulose) and its subsequent interaction with CO2. The positions of the labels ‘Ar’ and ‘CO2’ indicate the carriers gas composition at that stage of the experiment. Right part: blow-up of the CO2 adsorption-desorption test.

The profile shows a first decline at 60-120ºC due to the loss of adsorbed molecules including water, and a second decline above 200ºC, attributed to decomposition chemistry of the carbonaceous material. The char from the precursor material (in this case cellulose) rapidly adsorb CO2 once the carrier gas composition has changed. Finally, when Ar replaces CO2 again in the carrier gas, CO2 desorbs rapidly from the cellulose char and the final weight is similar to that prior to the CO2 adsorption test. This points to a weak physisorption process.

3.1.1 Pure components

The temperature at which the material mainly decomposes depends on the char precursor used. Cellulose and soybean protein degrade earlier than lignin, whereas CaCO3 is stable up to 700ºC and decomposes slowly even at 750ºC. The final weight of the char or residual varies drastically depending on the given pure component considered. After decomposition at 750ºC in Ar, CaCO3 retains 57% of its initial weight (the theoretical value for complete decomposition to CaO and CO2 is 56%), lignin produces around 50 % char, soybean about 30% and cellulose about 20% (Figure 2, left part).



Figure 2: Char (residual) yield (left) and CO2 uptakes (right) after pyrolysis of macro-components: cellulose, organosolv lignin, Kraft lignin, soybean protein and CaCO3. Conditions: Pyrolysis peak temperature: 750ºC, carrier gas: Ar; CO2 adsorption at 25ºC in 83% CO2/17% Ar.

The chars produced from cellulose and organosolv lignin adsorb notable amounts of CO2, while only small levels of CO2 are adsorbed by soybean char, CaO (residual from CaCO3 calcination) and Kraft lignin (Figure 2, right part).

Note the superior total CO2 uptake value for organosolv lignin char. It reflects that this lignin yields large amounts of well CO2-adsorbing char. Cellulose follows as second best starting material because its char yields are much lower. All other components are much worse sources for CO2-adsorbing char. Surprisingly this includes Kraft lignin suggesting that the lignin extraction process has a severe impact on the chemical properties of the product. Future work could address the question if the high sulfur content and pH in Kraft lignin might cause it to form poorly CO2-adsorbing char.

3.1.2 Binary mixtures

Binary mixtures prepared from the macro-components cellulose, organosolv lignin, Kraft lignin and soybean protein have been prepared and pyrolyzed. The cellulose/lignin samples contain approximately equal amounts of both ingredients, while samples containing soybean protein contain about 20% of it. Although varying mixing ratios would lead to improved data sets, time constraints limited this study to just one composition per macro component combination. For the same reason, CaCO3 is not used in this part of the work. Figure 3 shows the char yield and CO2 uptake results from all experiments.



Figure 3: Char yield and CO2 uptakes after pyrolysis of binary mixtures of cellulose, organosolv lignin, Kraft lignin and soybean protein. Char produced from binary mixtures pyrolysis at 750ºC in Ar; CO2 adsorption test at 25ºC in 83% CO2/17% Ar.

The order of char yields follows expectations as the lignin/soybean mixture contains about 80% of lignin, which produces more char than the other components (Figure 3 left part), while the cellulose/soybean mixture combines two macro-components that each produces little char. The largest amounts of CO2 adsorbed per gram of solid correspond to chars from cellulose/organosolv lignin (1:1) and organosolv lignin/soybean protein (4:1) mixtures as their weight gains demonstrate. Char from the cellulose/soybean protein mixture also adsorbs CO2 but at a lower level. Surprisingly, very little CO2 uptake capacity is found for char produced from an almost 1:1 mixture of cellulose/Kraft lignin even though pure cellulose produces a highly adsorbing char.

The observed char yields and CO2 adsorption capacities are compared to those calculated from contributions of the individual components assuming that no cross-chemistry exists. The CO2 uptake relative to the amount of initial material (total CO2 uptake) is also compared to predicted values. For the cellulose/organosolv lignin mixture, the actual char yields fall short of the expected ones but the adsorption quality of this char is as good as expected. The opposite is true for the cellulose/alkali lignin mixture: in this case the char yields follow expectations but this char hardly adsorbs any CO2. Regarding the mixtures of cellulose/soybean protein and organosolv lignin/soybean protein, the results are in line with expectations.

3.1.3 Multicomponent mixtures and manure

Multicomponent mixtures prepared from the macro-components cellulose, organosolv lignin, Kraft lignin, calcium carbonate and soybean protein have been prepared and pyrolyzed. The cellulose/lignin/soybean\_protein or CaCO3 samples contain approximately 2:2:1 amounts of ingredients while for samples containing all four macro-components (cellulose/lignin (organosolv or Kraft) /CaCO3/soybean\_protein) the ratio is 4:3:2:1, respectively. The results obtained with these mixtures and with manure are compared in Figure 4.

With respect to the char yields, the most relevant observation is manure pyrolysis produces more char than expected from its composition. However, the composition of manure might not be very well known as coarse entries without uncertainty information in *Table 1* indicate. The experimental char yields of the mixtures are in good agreement. Among these, the Kraft lignin containing mixture produces somewhat less char than expected but this deviation is much smaller as that seen in the case of manure

Char produced from the Kraft lignin containing mixture adsorbs less CO2 than expected while char yields from the three other mixtures are in line with the sum of additive contributions from its components. Char from manure is also less strongly adsorbing C O2 as expected. Looking at the CO2 adsorption capability per gram biomass, good agreement between experimental and predicted values is seen except for the Kraft lignin containing mixture.



Figure 4: Char yield and CO2 uptake values from pyrolysis of multicomponent mixtures and manure. Pyrolysis conditions: peak temperature 750ºC in Ar. CO2 adsorption tests: 25ºC in 83% CO2 / 17% Ar.

3.2 Char characterization

3.2.1 Surface area

Some results from nitrogen adsorption isotherm measurement are shown in Figure 5. The selected plots correspond to chars from the two lignins (organosolv and Kraft) used in this study, Figure 5 (left), and the 4-components mixtures containing those, Figure 5 (right). The isotherms were recorded using standard setting for the p/po range, which is 0.01 to 0.99. This pressure range does not allow to probe the full isotherms but only the high pressure part.

Chars produced from organosolv lignin show much more pronounced hysteresis indicating that the adsorption and/or desorption branches are far from the equilibrium state. These hysteresis loops at the high relative pressure point to the presence of mesopores and/or macropores and a qualitative interpretation would be that such meso and macropores are more dominant in chars from organosolv lignin containing material.



Figure 5: N2 adsorption isotherms for chars from organosolv lignin (filled symbols) and Kraft lignin (open symbols) (left part), and for chars from the 4-component mixtures containing either organosolv lignin (filled symbol) or Kraft lignin (open symbol) as ingredient (right part).

Normally the standard p/po range covers the region (p/po = 0.05 – 0.3) in which BET plots are linear. Linear fits can be used to extract the BET parameter C and the surface volume (which is used to calculate the surface area). One criteria to ensure that such fits are physically meaning is that C must be positive. Multi-point BET analyses of the plots shown in Figure 5 resulted in positive C values only when the analysis was restricted to the three lowest p/po. For the char from the organosolv lignin containing mixture and from the alkali lignin containing mixture, the surface areas, 82.5 m2/g and 46.0 m2/g, respectively, are very small and their ratio does not reflect the huge difference in CO2 adsorption capacities seen experimentally. Extended N2 adsorption isotherms are required to verify this data.

Another analysis attempt made was to use of non-linear density functional theory (NLDFT) to this data. This analysis consistently produced results that showed that micropores are responsible for N2 adsorption on all chars tested (last column in Table 4). Also encouraging is that experimental CO2 uptake values follow the same order as the NLDFT surface areas. A further in-depth analysis has not been done because of the limited pressure range of the N2 isotherms.

Table 4. BET and NLDFT surface area results for the N2 isotherms shown in Figure 5. Mixture details are given in Table 3.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Char source (see Table 3) | CO2 uptake  (mg/g char) | Surface area from BET analysis  (m2/g) | Surface area from NLDFT  (m2/g) | NLDFT  Pore width  (nm) |
| Organosolv lignin | 80.0 | 31.5 | 135.2 | 1.410 |
| Kraft lignin | 1.0 | 16.6 | 14.0 | 1.410 |
| Cell.: OrgSolv\_lig : CaCO3 : Soy\_Prot. | 51.0 | 82.5 | 125.8 | 1.410 |
| Cell.: Kraft\_lig : CaCO3 : Soy\_Prot. | 6.0 | 46.0 | 41.1 | 1.474 |

3.2.2 FTIR

FTIR analyses have been performed for selected samples, including the char precursors and the chars produced from their pyrolysis at 750ºC. Figure 6 shows the FTIR spectra for cellulose, organosolv lignin and soybean protein, and for their respective chars.



Figure 6: FTIR spectra for cellulose, organosolv lignin and soybean protein, and for their respective chars.

The FTIR spectra of cellulose and lignin (organosolv) look very different. However, once pyrolyzed at 750ºC the residual chars look very similar. In contrast, the FTIR spectra of soybean protein and its char look quite similar – the soybean protein char still retains features from the unpyrolyzed material -, but very different to the chars from the other macro-components (cellulose and organosolv lignin). These results correlate with the CO2 adsorption capacities shown in the previous section, where char from cellulose and organosolv lignin showed good CO2 adsorption capacity and char from soybean protein poor capacity.

3.2.3 CO2 adsorption isotherms

The CO2 adsorption capacity of various chars produced in the TGA has been measured at constant temperature (25 oC) as a function of CO2 partial pressure. Selected results are shown in Figure 7. The adsorption profiles for chars from cellulose, organosolv lignin and from a 1:1 mixture of these two agree within experimental error with each other. The char from the mixture containing 20% CaCO3 and 10% soybean protein clearly adsorbs less CO2. This has already been discussed before but it is nicely confirmed in these measurements. Char from manure adsorbs less CO2 than this 4-component mixture. Very little CO2 adsorption is seen for char from soybean protein. Interestingly, all profiles are equally well represented by Langmuir isotherms suggesting that the surface area of the chars might be an important parameter. However, such an interpretation would contradict the results from the N2 isotherms presented above. It should be noted that for each CO2 mole fraction, 30 min time was allocated to establish equilibrium between CO2 in the gas phase and on the surface. For cellulose and lignin based chars this time is sufficient but char from soybean protein adsorbs CO2 very slowly and the weight was still increasing after 30 min. The final CO2 adsorption capacities for soybean protein char and to a lesser extent for the char from manure will be somewhat higher than measured here. CaO, which is present in the char from the 4-component mixture also absorbs CO2 very slowly and irreversibly.



Figure 7: Experimental CO2 isotherm and Langmuir fits at 25ºC for selected chars produced in the TGA apparatus.

3.2.4 Adsorption energies

CO2 adsorption-desorption cycles have been measured by varying the temperature between 25 oC and 120 oC while keeping the CO2 partial pressure constant. These measurements were done for three CO2 mole fractions (71%, 57 and 43 % CO2 in Ar). The results for five selected chars (from cellulose, organosolv lignin, soybean protein, the 4-component mixture with organosolv lignin, and manure) have been used to determine an approximate overall enthalpy of CO2 adsorption (eq.6). The slope of the linear part of plots is a measure of the enthalpy of adsorption (Table 5) if the assumption of approximately constant ∆Sads holds for this temperature range.

Table 5: Approximate enthalpy of adsorption values, ∆Hads [kcal/mol], for selected chars and three CO2 mole fractions.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Char from:** | | | | |
| **CO2 mole fraction in the gas phase (%)** | **Cellulose** | **Organosolv lignin** | **Soybean protein** | **4-component mixture (Cell.:OrgSolv\_Lig.:CaCO3:Soy\_Prot.)** | **Manure** |
| 71 | 3.5 | 3.6 +/- 0.2 | 2.0 | 3.2 | 3.1 |
| 57 | 3.7 | 3.8 +/- 0.2 | 1.4 | 3.6 | 3.1 |
| 43 | 4.2 | 4.3 +/- 0.2 | 1.1 | 3.9 | 3.3 |

In all cases except for char from soybean protein the results for 43% CO2 yield the largest slopes and those for 71% CO2 yield the shallowest ones. The enthalpy of adsorption is in the range of 3-4 kcal/mol, which is reasonable for physisorption, and the gradual decrease of the average enthalpy of adsorption with increasing CO2 mole fraction (and therefore larger total amount of adsorbed CO2) reflects the fact that the strongest binding sites are occupied first.

1. DISCUSSION

The aim of this study is to address two main questions. First, is it reasonable to use organic waste material with appreciable protein and ash (CaCO3) content to produce CO2-adsorbing char? Second, how do individual macro-components contribute to the CO2 adsorption capacity?

The results of this study show that CO2-adsorbing char is largely formed from the cellulosic and ligninic (organosolv) organic fractions. No notable synergetic contributions from the protein fractions are observed. CaO chemisorbs CO2 on a long time scale and the calcination step at 750oC did not display an activating effect. The adsorption enthalpies are small making the CO2 adsorption process very sensitive to the temperature. For example, char from cellulose adsorbs about 82 mg/g char at 25oC but only 70 mg/g char at 30oC. Furthermore, the adsorption capability reduces drastically if CO2 is only present at small concentrations (see Figure 1) meaning these chars might be able to reduce CO2 from gas mixtures but not to completely remove them. If the drastic changes seen when replacing organosolv lignin with Kraft lignin are caused by sulfur or base impurities, then one needs to be concerned that in a similar way minor ingredients present in organic waste could strongly impact the char quality produced from such waste streams. Lignocellulosic waste material with high lignin and low ash content seems to be the most promising candidate for the production of CO2-adsorbing char.

The BET analyses of the N2 adsorption isotherms suggest that the char surface area is not a critical factor for the CO2 uptake capability of char. This negates the idea that functionalization of the char surface with nitrogen containing groups may yield chars with higher CO2 adsorption capacity. The results for mixtures containing soybean protein agree with this conclusion.

The similarities in the FTIR spectra of the CO2-adsorbing chars, the almost identical shapes of the CO2 adsorption isotherms for all chars and the closely agreeing adsorption enthalpies suggest that all chars adsorb CO2 in a similar way. It is well established that micropores play an important role in CO2 adsorption by activated carbon ([Stoeckli, 1990](#_ENREF_4); [Wedler et al., 2021](#_ENREF_7)) and that the isotherms of many carbonaceous adsorbents are described as Type I isotherms ([Thommes et al., 2015](#_ENREF_6)). This contradicts the strong hysteresis features seen in the N2 adsorption isotherms are typical for Type IV isotherms, which therefore might not be describing CO2 adsorption well. Furthermore, the application of non-linear density functional theory (NLDFT) to these N2 adsorption isotherms strongly points to micropore adsorption, again suggesting that mesopores are not dominantly responsible for gas adsorption. According to Dubinin and coworkers micropore adsorption on carbonaceous material can well be described by the theory of volume filling of micropores (TVFM) ([Dubinin, 1989](#_ENREF_1)). In order to test if this theory also explains the current data, the results shown in Figure 7 are replotted as Dubinin-Radushkevich plot in Figure 8.



Figure 8: Dubinin-Radushkevich (DR) plots of the data shown in Figure 7.

The adsorption data for all chars follow straight lines with very similar slopes. The slopes correlate with the adsorption enthalpies and pore properties while the offsets are related to the adsorption volume *W0* at po The DR plots confirm the results for the enthalpies of adsorption extracted from the temperature-dependent adsorption measurements (Table 4). The good linearity over the entire pressure range is consistent with the micropore filling model for CO2 adsorption. Deviations from linearity in the D-R plot would indicate contributions from non-microporous surface areas ([Scarlat, Fahl, Dallemand, Monforti, & Motola, 2018](#_ENREF_3)). Since this is not the case one can conclude that the hysteresis features seen in the N2 isotherms are irrelevant for CO2 adsorption.

If according to the slit model these micropores are created by graphene sheets, it becomes clear that the molecular structure of the starting material is of little importance, as long as part of the carbon is converted to graphene sheets. Impurities in Kraft lignin or Kraft lignin itself either might prevent the formation of such graphene sheets or interfere with their packing in a way that prevents micropore formation. More experiments are needed to test this hypothesis. In any case, this interpretation is consistent with additive contributions from all carbon containing macro-components as long as they would not interfere with the stacking. In mixtures, co-pyrolysis with soybean protein might not be able to contribute much to the CO2 adsorption capacity because soybean protein might not be able to create aromatic ring structures. This explanation is supported by the FTIR spectrum of its char (Figure 6) which clearly differs from those from lignin or cellulose and which contains features retained from the original soybean protein spectrum. A structural change towards aromaticity is not obvious in this spectrum.

1. CONCLUSIONS

The potential for CO2 adsorption by chars produced from pyrolysis at 750ºC of macro-components of manure and their mixtures has been analyzed in a thermogravimetric analyzer (TGA). The CO2 adsorption capacities of the char samples at 25ºC have been determined, and the values obtained have been correlated with characterization results (BET and FTIR techniques) to improve the fundamental understanding of relation between composition and CO2 adsorption properties of final char material.

Results indicate that the char yield and the CO2 adsorption capacity of the chars produced from the macro-components of manure depends strongly on the given component considered. Cellulose and organosolv lignin produce char with good CO2 adsorption properties and similar FTIR spectra results. Among them, the char yield of lignin is higher than that of cellulose, and therefore it would be preferred as starting material. Kraft lignin, soybean protein and CaCO3 produce char or residual solid (in the case of CaCO3) with very poor CO2 adsorption properties.

The analysis of chars from mixtures of macro-components indicate in some cases additivity effects but not positive synergistic effects, highlighting that the higher the organosolv lignin content and, to a minor extent, the cellulose content, the better the char produced in terms of CO2 adsorption capacities. The low char yield and poor CO2 adsorption properties of manure char suggest that the idea of using it for adsorbent production is not profitable.

The overall adsorption enthalpy of the chars with potential for capturing CO2 shows values in the range of 3-4 kcal/mol, which is typical for weak physisorption process.

It is still not clear what is needed to produce an efficient CO2-adsorbing char (without further activation steps), pointing that more work is needed to study, among others, the effect of minerals and different char production temperatures.

ACKNOWLEDGEMENTS

Technical support with the TGA and BET experiments by Olga Marin, lab technician of the GPT, is highly appreciated. Without her help, this study would not have been possible.

The authors acknowledge funding received from the Aragón Government (Ref. T22\_17R), co-funded by FEDER 2014-2020 *"Construyendo Europa desde Aragón"* and from MICINN (RTI2018-098856-B-100 and ENE2017-85040-R). We also thank the Centro Universitario de la Defensa (CUD) (UZCUD2020-TEC-01) for financial support.

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