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**Rapid, simple and sustainable synthesis of ultra-microporous carbons with high performance for CO<sub>2</sub> uptake, via microwave heating**

Gabriela Durán-Jiménez<sup>\*1</sup>, Lee A. Stevens<sup>1</sup>, Emily T. Kostas<sup>2</sup>, Virginia Hernández-Montoya<sup>3</sup>, John P. Robinson<sup>1</sup>, Eleanor R. Binner<sup>1</sup>

<sup>1</sup>Faculty of Engineering, the University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

<sup>2</sup>Department of Biochemical Engineering, The Advanced Centre of Biochemical Engineering, Bernard Katz Building, University College London, Gower Street, London, WC1H 6BT, U.K.

<sup>3</sup>TecNM/Instituto Tecnológico de Aguascalientes, Av. Adolfo López Mateos No. 1801 Ote. C.P. 20256, Aguascalientes, México.

\* Corresponding author

e-mail: gaby\_231105@yahoo.com.mx/gabriela.duranjimenez@nottingham.ac.uk

Tel: +44 (0)77 2793 4248

**Abstract**

A one step microwave pyrolysis-activation method has been developed for the preparation of activated carbons from biomass with high CO<sub>2</sub> capture efficiency (5.3 mmol g<sup>-1</sup>) by employing a low impregnation ratio (1) of KOH and K<sub>2</sub>CO<sub>3</sub>. The high microwave susceptibility identified by the dielectric properties enabled the preparation of a series of activated carbons in short processing times (<6 min), and the pyrolysis-activation simultaneously enhanced the formation of ultra-micropores leading to high CO<sub>2</sub> uptake at 15 and 100% CO<sub>2</sub> in the temperature range of 0-100 °C. The high CO<sub>2</sub>/N<sub>2</sub> selectivity of up to 36 the adsorptive capacities were directly correlated to a pore size of ~0.7 nm, which favoured CO<sub>2</sub> uptake up to 5.3 and 4.5 mmol g<sup>-1</sup> at 1.1 bar and 0 °C and an uptake of 3.7 and 3.3 at 25 °C for activated samples with KOH and K<sub>2</sub>CO<sub>3</sub>, respectively. The activated carbons presented in this study are the first examples of samples that have been prepared by this simple and rapid method, which represents a 96.66% reduction in the processing times in comparison to conventional heating routes, and the CO<sub>2</sub> uptake is comparable to the largest reported in literature for activated carbons. The outstanding uptake and selectivity, the simple synthesis using microwave technology in addition to the utilisation of a waste biomass as a carbon precursor, satisfy the requirements for the development of new and more sustainable energy environmental processes.

**KEYWORDS:** CO<sub>2</sub> capture, Ultra-microporous adsorbents, Microwave, Selective uptake, Regeneration, Rapid sustainable preparation of activated carbons.

## 1 Introduction

It has been estimated that over two-thirds of the globally produced anthropogenic greenhouse gas emissions are generated by the burning of fossil fuels to produce energy [1]. From 1970 until 2004 the annual global emissions of Carbon Dioxide (CO<sub>2</sub>) have increased by 80% [2] and the current air concentration (>400 ppm) exceeds the maximum permissible limit for climate safety (350 ppm) [3]. Consequently, an increase in global temperature from 1.8 to 4 °C is expected by the year 2100 as a result of global warming [4-6]. Although other greenhouse gases such as water vapour, methane (CH<sub>4</sub>), and nitrous oxide (NO<sub>x</sub>) contribute to global warming, 90% of the emissions are attributed to CO<sub>2</sub> [7]. In view of this, large-scale CO<sub>2</sub> control is essential to minimize the global impacts associated with climate change [8].

Cryogenic processes, membrane separation, chemical absorption and adsorption have been investigated for CO<sub>2</sub> capture and storage. In particular, chemical absorption with ammonia based absorbents (wet scrubbing) is currently being implemented on an industrial scale for CO<sub>2</sub> capture. This process commonly utilizes alkanolamine-functional groups such as monoethanol amine (MEA) which react with CO<sub>2</sub> from the flue gas in an absorber column. Despite the fact that absorption technologies can achieve efficiencies of up to 90%, there are several issues such as limited surface utilization, corrosion, volatilization/degradation and a significant energy penalty associated with material regeneration [9-11]. Due to the shortcomings of the conventional amine scrubbing process in CO<sub>2</sub> removal from flue gas, solid adsorption processes have been proposed as an alternative. In particular, gas adsorption on solids represents a well-developed technology used in many industries and offers several advantages for CO<sub>2</sub> capture applications compared to CO<sub>2</sub> absorption. These include no liquid wastes being produced and a wider temperature range application (25–700 °C) [12]. It has been found that porous materials have great potential as excellent inorganic solid adsorbents for CO<sub>2</sub> uptake

due to their high surface area and large pore volume. Zeolites, [13, 14] activated carbons, [15, 16] calcium and magnesium oxides, [17, 18] and metal organic frameworks, [15, 19] are some of the adsorbents extensively tested on the CO<sub>2</sub> capture. Activated carbon is one of the most utilized adsorbents due to its high surface area and chemical properties such as its hydrophobicity, which prevents an additional step for moisture removal prior to CO<sub>2</sub> adsorption. Furthermore, the 'green' credentials of activated carbons can be further enhanced if they are prepared from sustainable biomass resources that would normally be considered as waste residues [20].

To increase the CO<sub>2</sub> adsorption capacity of porous carbons, much attention has focussed on surface functionalisation with inorganic bases for the incorporation of basic sites, by generally preparing N-doped activated carbons. The carbon materials are treated with urea or NH<sub>3</sub> at high temperatures to incorporate N in the carbon matrix. Further activation of N-doped carbons is used to increase the surface area [21]. Traditionally, physical and chemical activation has been achieved using conventional furnaces. The physical activation consists of the gasification of a carbon precursor with oxidizing gases such as steam or air at high temperature (800-1100 °C). In the case of chemical activation, the precursor is first thermally treated (~700 °C) under inert conditions to obtain a carbon-rich material, which is later mixed with an activating agent such as H<sub>3</sub>PO<sub>4</sub>, ZnCl<sub>2</sub>, KOH and K<sub>2</sub>CO<sub>3</sub> and subsequently activated at high temperatures (800-1100 °C) [22, 23].

It has been found that the incorporation of N atoms in the carbon matrix coupled with chemical activation by KOH or K<sub>2</sub>CO<sub>3</sub> results in a significant improvement in the adsorption of CO<sub>2</sub> [24]. Fujiki *et al.* [25] reported the enhanced CO<sub>2</sub> adsorption of chitosan derived activated carbon with N-doping and found the CO<sub>2</sub> adsorption to be 4.9 mmol g<sup>-1</sup> at 1 bar and 25 °C. Zhang *et al.* [26] employed a NH<sub>3</sub> solution during carbonization to incorporate N-containing functional groups on the surface of synthesized activated carbons. A three-step procedure was

used where black locust biomass was first carbonized at 650 °C, then the resultant carbon was activated with a 6 times impregnation ratio of KOH:carbon at 830 °C, followed by modification with NH<sub>3</sub> solution at 600 °C. The CO<sub>2</sub> uptake at 25 °C was 5.5 mmol g<sup>-1</sup> [26]. Although the aforementioned results are impressive, the preparation of N-doped carbons by functionalisation and an activation method requires high amounts of expensive and hazardous chemicals in a complex process, which may ultimately also damage the structure and properties of the porous carbon materials [27].

On the contrary, activated carbons using hydrochar as a precursor has also been reported. Sevilla *et al.* [28] demonstrated that by using an impregnation ratio of 2 (KOH/hydrochar), an activated carbon with a CO<sub>2</sub> uptake of 4.8 mmol/g was generated. However, the preparation of this carbon was relatively laborious as the synthesis of the hydrochar was firstly required, followed by an impregnation step and lastly the activation of the material. Furthermore, the high temperature step, undertaken by conventional heating is extremely energy intensive. Therefore, in order for activated carbons (for CO<sub>2</sub> capture) to become environmentally sustainable and economically viable, new manufacturing processes which utilise less energy and hazardous chemicals and fewer unit operations, are required.

In recent years, microwave heating has gained attention as a promising heating method, due to its characteristics of instantaneous and volumetric heating, which overcome the limitations of conventional heat transfer [29]. Microwave heating has been shown to offer significant benefits such as exceptionally rapid processing times and selectivity [30].

There are a few reports on single pyrolysis-activation of biomass via conventional heating, and the majority of the studies that do employ microwaves focused on the use of microwave heating for the activation stage of a carbon-rich material that has been pre-pyrolysed in conventional furnaces [31]. In the search for sustainable and more economically viable methods of activated

carbons preparation, it is desirable to simplify the synthesis process and in particular to negate the need for carbonisation prior to activation. In this paper, for first time a rapid method for the synthesis of ultra-microporous activated carbons in one step used for CO<sub>2</sub> capture is described. This route negates the requirement of high amount of activating agent (often 2:1 or even higher), the pre-carbonization step and also a significant reduction in processing times compared to the 4 – 6 h durations required in conventional processes, whilst delivering sustainable activated carbons with good properties for CO<sub>2</sub> capture. This represents a novel production route that could transfer the microwave preparation of activated carbons from laboratory novelty to industrial application, leading to significant reductions in capital and operating costs as well as environmental impact.

## 2 Experimental

### 2.1 Materials

Pecan nutshell (PNS) is a lignocellulosic agricultural co-product that was used as an activated carbon precursor in these studies. It was collected from an agro-food company in Aguascalientes, México. The composition of PNS was determined to be 47.27% C, 6.41% H, 0.18% N and 46.14% O. The activating agents used in this work, potassium hydroxide (KOH) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) were of analytical grade and purchased from Sigma-Aldrich and used without any further purification.

The precursor was firstly crushed and sieved to obtain a particle size ~1 mm, washed with deionised water and dried in an oven at 80 °C for 24 h, then physically mixed with the chemical agent (i.e. KOH or K<sub>2</sub>CO<sub>3</sub>) at mass ratio 1:1 (KOH: PNS and K<sub>2</sub>CO<sub>3</sub>:PNS).

### 2.2 Dielectric properties measurements

The loss tangent ( $\tan \delta = \varepsilon''/\varepsilon'$ ) is an estimation of the material's ability to convert electromagnetic energy into heat at a specific temperature and frequency. Dielectric properties

and the temperature dependence of impregnated PNS (KOH:PNS and  $K_2CO_3$ :PNS) were obtained using the cavity perturbation technique for a temperature range of 20–500 °C at 2450 MHz. The system consisted of a furnace and cylindrical  $TM_{0n0}$  mode cavity. An automated step-motor was used to rapidly move the sample from the furnace to the cavity, where the dielectric properties are measured by a HP 8753 vector network analyser (VNA). The sample was placed in a quartz tube of 3 mm (ID) and the dielectric properties were calculated using the cavity response between a load and empty tube. The results presented in this work are the averages of three replications.

### 2.3 In-situ Microwave Pyrolysis-Activation of biomass

The innovative direct pyrolysis-activation by microwave was conducted using a single mode cavity that operated at a frequency of  $2450 \pm 25$  MHz and includes a generator with 2 kW maximum output power, an automatic three-stub tuner (S-TEAM STHD v1.5) connected to a rectangular WR430 waveguide and a sliding short. The automatic tuner and the sliding short were used for impedance matching, to maximise the absorbed power and to log the absorbed power over time so that an energy balance can be calculated. A cylindrical single mode  $TE_{010}$  cavity was connected by WR430 waveguide to the sliding short and the incident, absorbed and reflected powers were recorded. The pyrolysis-activation reactor consisted of a quartz tube (30 mm ID) with a sintered plate where the mixture (KOH:PNS or  $K_2CO_3$ :PNS) was placed. The mixture was pyrolysed-activated in a single step at incident powers of 300 and 400 W and times of 2 – 6 minutes (Table 1). The incident powers and treatment times were selected based on previously published work using the same single mode cavity [32]. All the experiments were carried out in an inert atmosphere of nitrogen ( $N_2$ ) at a flow rate of  $1 \text{ L min}^{-1}$ . Once the target time was reached, the sample was maintained in the inert atmosphere for 5 min to cool down.



The surface temperature of the sample was measured with a thermocouple RS K-type 1319A immediately after each treatment. It should be noted that the temperature values are an indication of a single-point temperature reached by the sample surface during the pyrolysis-activation process, however a representative average temperature measurement is not possible due to the volumetric and instantaneous nature of the microwave heating process.

The percent of absorbed and reflected power was calculated from the signals of incident power, absorbed power and reflected power. The specific absorbed energy ( $E$ ) was determined by numerical integration of the absorbed power, ( $P_a$ ), according to the following equation:

$$E = \frac{\int P_a dt}{M} \quad (1)$$

Where  $E$  is the specific absorbed energy ( $\text{kJ g}^{-1}$ ),  $t$  is time differential (sec), and  $M$  is the initial mass of the sample (g).

To calculate the yield, the final carbon was repeatedly washed with 0.1 M HCl and deionised water until a neutral pH was obtained and then dried at 105 °C overnight. It was found the yields ranged from 22 and 25% for both activated carbons prepared with KOH and  $\text{K}_2\text{CO}_3$ .

For convenience, the activated carbons were labelled as  $x$ - $y$ -KOH and  $x$ - $y$ - $\text{K}_2\text{CO}_3$  where  $x$  is the incident power (W) and  $y$  is the pyrolysis-activation time (min).

Table 1. Processing conditions of activated carbons preparation in one step of pyrolysis-activation by microwave

<b>Sample name</b>	<b>Incident Power (W)</b>	<b>Time (min)</b>	<b>Absorbed energy (kJ/g)</b>	<b>*Temperature (°C)</b>
300-3-KOH	300	3	4.52	312
300-4-KOH	300	4	6.35	392
300-5-KOH	300	5	8.07	405
300-6-KOH	300	6	11.32	451

400-2-KOH	400	2	4.28	353
400-3-KOH	400	3	6.36	422
400-4-KOH	400	4	6.74	446
300-3-K <sub>2</sub> CO <sub>3</sub>	300	3	6.45	224
300-4-K <sub>2</sub> CO <sub>3</sub>	300	4	8.16	296
300-5-K <sub>2</sub> CO <sub>3</sub>	300	5	10.67	305
300-6-K <sub>2</sub> CO <sub>3</sub>	300	6	13.49	375
400-2-K <sub>2</sub> CO <sub>3</sub>	400	2	4.26	263
400-3-K <sub>2</sub> CO <sub>3</sub>	400	3	5.20	292
400-4-K <sub>2</sub> CO <sub>3</sub>	400	4	6.93	283

\*Measured with a thermocouple after microwave treatment

## 2.4 Characterisation techniques

The textural properties of the activated carbons were calculated from the sorption isotherms of N<sub>2</sub> at -196 °C using a Micromeritics ASAP 2420 apparatus from 0.00005 to 0.99 relative pressure (P/P<sub>0</sub>). Approximately, 250 mg of samples was weighed into a sample tube and degassed for 15 h at 120 °C. The surface area was calculated using the Brunauer–Emmett–Teller (BET) theory, based on adsorption data in the range of 0.01–0.1 P/P<sub>0</sub> to give positive BET ‘C’ parameters. The narrow micropore, micropore and total pore volumes and size distributions were determined by Non-Local Density Functional Theory (NLDFT) on carbon slit pores by combining a CO<sub>2</sub> adsorption isotherm at 0 °C to a N<sub>2</sub> adsorption isotherm beginning at 0.0005 P/P<sub>0</sub> using Microactive Software V5.0.

XRD analysis was performed on a Bruker D8 Advance Da Vinci diffractometer, with 0.02 ° step size and step time of 10 sec in the 2θ range 10 - 80 °. The morphology of the samples was examined by Scanning Electron Microscopy (SEM) using a Philips XL 30 microscope.

Thermogravimetric analysis (TGA) was performed in alumina pans using a TA Instruments SDT Q600 analyzer. Samples were heated up to 950 °C at 15 °C min<sup>-1</sup> under a flow of nitrogen at 25 ml min<sup>-1</sup>.

## 2.5 CO<sub>2</sub> capture experiments

The CO<sub>2</sub> uptake was determined using volumetric and thermogravimetric analysers by a Micromeritics ASAP 2420 and TGA Q500 TA Instrument. The CO<sub>2</sub> uptake isotherms were obtained at 0 and 25 °C on a volumetric analyser. Prior the measurements the samples were degassed at 120 °C for 15 h. The adsorption capacity was investigated in terms of adsorbed amount (CO<sub>2</sub> 99.99%) per gram in the pressure range of 0.001–1.2 bar.

The thermogravimetric CO<sub>2</sub> uptake was carried out using a Q500 TA instrument. The carbon samples were dried at 120 °C in N<sub>2</sub> (100 ml min<sup>-1</sup>, 1 bar) for 30 min before being cooled to the set CO<sub>2</sub> adsorption temperature to remove any physisorbed moisture. The CO<sub>2</sub> uptake was obtained at a variety of temperatures between 25 and 100 °C, at an atmospheric pressure of 1 bar. At adsorption temperature the gas was switched at 15% CO<sub>2</sub> and 100% CO<sub>2</sub>. Once the adsorption reached equilibrium at a given temperature, the adsorbed amount of CO<sub>2</sub> was recorded vs time for 60 min, then the sample was heated up to 120 °C in N<sub>2</sub> for 15 min to complete the CO<sub>2</sub> desorption. Cyclic adsorption and desorption tests were also conducted to study the stability and reusability of the samples. This procedure was repeated three times and the main of replications is presented.

The N<sub>2</sub> gas adsorption (for CO<sub>2</sub> and N<sub>2</sub> selectivity) was measured using a thermogravimetric analysis. Both set of experiments were conducted at 25 °C. The sample was degassed under Ar at 120 °C and the gas was switched from Ar to N<sub>2</sub>. The isosteric heat of adsorption ( $Q_{st}$ ) was calculated using CO<sub>2</sub> adsorption isotherms measured at different temperatures based on the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{Q_{st}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (2)$$

where  $P_i$  is pressure for isotherm  $i$ ;  $T_i$  is temperature for isotherm  $i$ ;  $R$  is the universal gas constant  $8.315 \text{ J K}^{-1}\text{mol}^{-1}$ . In this study, the  $Q_{st}$  was calculated using  $\text{CO}_2$  adsorption isotherms measured at 0 and 25 °C.

All experiments were conducted in triplicate and the data presented were obtained from the mean calculated. In general, standard deviations were below 5 % of average values.

### 3 Results and Discussion

#### 3.1 Dielectric properties of impregnated PNS

Fig. 1 shows the loss factor,  $\epsilon''$ , against temperature in the temperature range of 20 - 500 °C for the impregnated PNS samples, along with previously reported values for raw PNS measured using the same method [33]. Materials with  $\epsilon'' < 0.01$  require a very high electric field strength in order to attain a reasonable heating rate, whereas heating materials with  $\epsilon'' > 5$  may be problematic due to the low penetration depth causing non-uniformities of heating. Materials with loss factors within the range  $0.01 < \epsilon'' < 5$  are therefore considered to be good candidates for microwave heating applications [34].

The results in Fig. 1 show that the  $\epsilon''$  of the raw PNS is within the range 0.1 - 0.2 from 20-300 °C, but drops to close to the lower processing threshold (0.01) from 350 - 500 °C. Similar results have been reported previously for biomass such as switchgrass [35], rice husk [36], corn stover [37], oil palm shell [38], wood biomass [39], empty fruit bunch [40]. The findings highlighted biomass is low loss dielectric materials, and are essentially transparent to microwaves from room temperature to 500 °C. However, when the biomass samples are subjected to higher temperatures, the structures become essentially char, which is known to be a high microwave absorbing material due to the Maxwell–Wagner effect, which causes a very

high displacement of  $\pi$ -electrons on carbonized structures [41, 42]. Materials with  $\epsilon'' < 0.01$  require a very high electric field strength in order to attain a reasonable heating rate, whereas heating materials with  $\epsilon'' > 5$  may be problematic due to the low penetration depth causing non-uniformities of heating. Materials with loss factors within the range  $0.01 < \epsilon'' < 5$  are therefore considered to be good candidates for microwave heating applications [34].

The results in Fig. 1 show that the  $\epsilon''$  of the raw PNS is within the range 0.1 - 0.2 from 20-300 °C, but drops to close to the lower processing threshold (0.01) from 350 - 500 °C. Up to 200 °C, chemical impregnation of PNS with  $K_2CO_3$  has little or no effect on the dielectric response;  $\epsilon''$  remains  $< 0.2$ . The loss factor of PNS impregnated with KOH on the other hand increased from 0.5 at room temperature to 7.6 at 150 °C, and then reduced to 1.1 by 250 °C. This suggests that all three samples are adequate candidates for microwave heating up to 200 °C, however KOH:PNS is likely to heat more efficiently and this may be related to the moisture in the sample. From 250 to 450 °C, the  $\epsilon''$  of both of the impregnated samples stabilised around 0.3 - 1.2 (with KOH:PNS being slightly higher), which is higher than the virgin PNS. At 500 °C,  $\epsilon''$  increased to 1.0 and 1.8 for  $K_2CO_3$  and KOH respectively, indicating that although the heating rate would increase if heated to 500 °C, thermal runaway should not be a problem if processing within this temperature range. The dielectric characterisation therefore indicates that both impregnated materials would be expected to heat with microwaves at temperatures of 250 °C and above, and that they should heat more readily than raw PNS within that range.

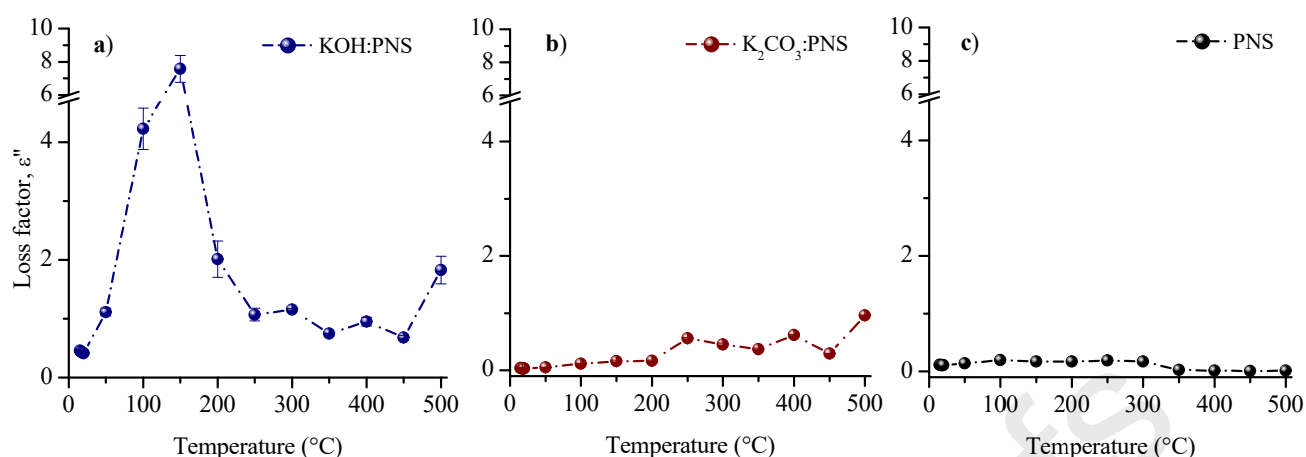


Fig. 1. Dielectric loss ( $\epsilon''$ ) at 2450 MHz against temperature of (a) PNS:KOH, (b) PNS:K<sub>2</sub>CO<sub>3</sub> and (c) PNS.

The impregnation of PNS with KOH and K<sub>2</sub>CO<sub>3</sub> affected the dielectric loss of the material. Both impregnated materials have dielectric loss within the range that is considered amenable to microwave processing. Up to 250 °C, the dielectric loss of KOH:PNS is higher than K<sub>2</sub>CO<sub>3</sub>:PNS, suggesting good selectivity and heating rates during the microwave activation experiments.

### 3.2 Effect of processing time and micropore size of activated carbons

A significant amount of research has focussed on increasing the surface area of activated carbons, as it is generally assumed that higher surface areas and greater pore volumes generate more desirable adsorbents for greater gas uptake [4]. The N<sub>2</sub> sorption isotherms and pore size distribution of the carbons prepared via single pyrolysis-activation at a mass ratio (KOH:PNS, K<sub>2</sub>CO<sub>3</sub>:PNS) of 1 are presented in Fig. 2 and the corresponding textural properties are summarized in Table 2. The two set of samples are generally similar, showing a type I-N<sub>2</sub> isotherm, according to the IUPAC classification, indicating the predominance of micropores in the activated carbons [43]. At lower pressures, there is evidence of a well-defined micropore filling stage, which suggests the presence of very small pores <1 nm which is corroborated in

the pore size distribution. The hysteresis loop shown in some samples suggest the presence of mesopores. The H4 loops are often found with aggregated crystals of zeolites, some mesoporous zeolites, and micro-mesoporous carbons [44].

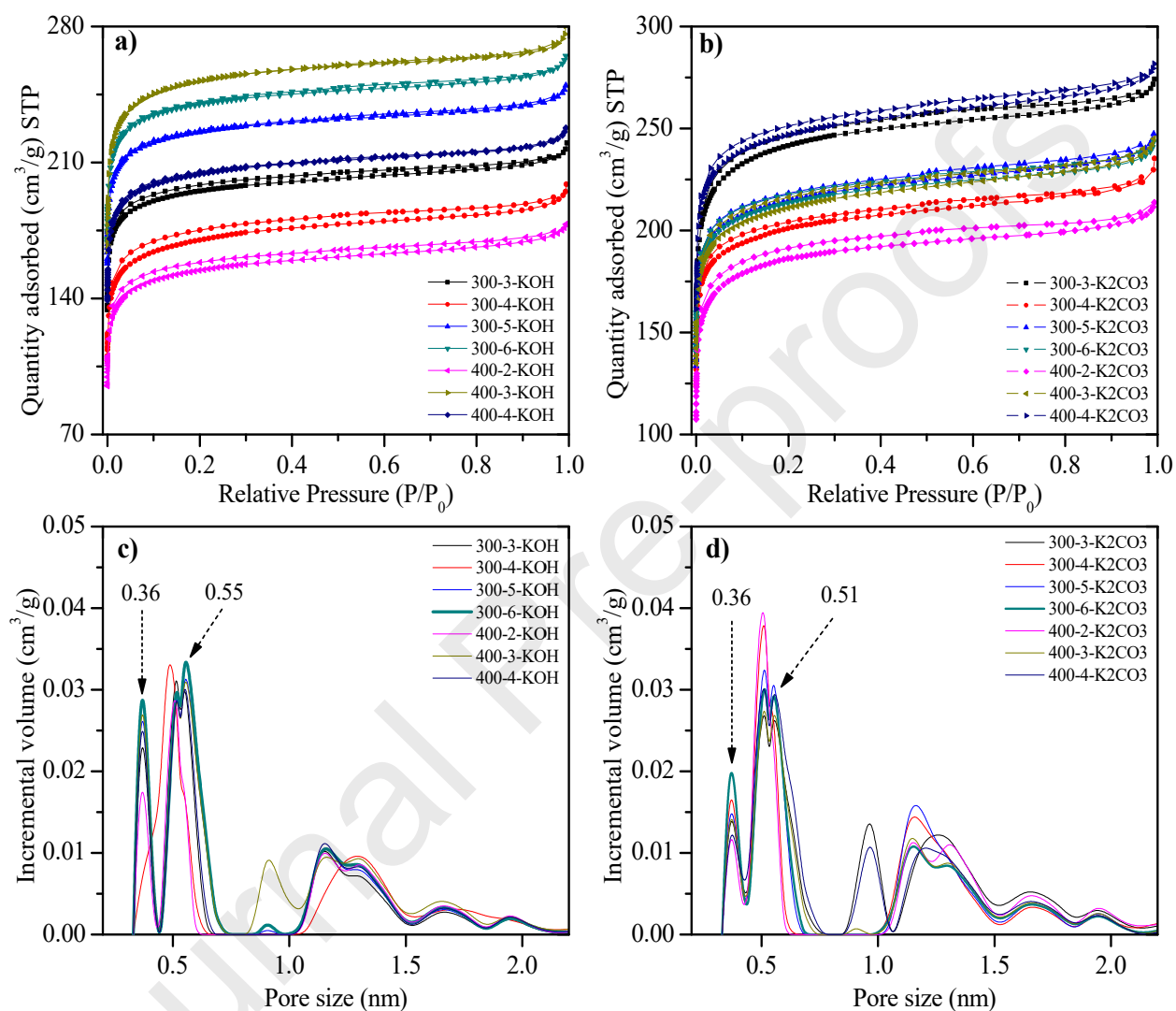


Fig. 2. N<sub>2</sub> adsorption-desorption isotherms at -196 (N<sub>2</sub>) (a-b) and pore size distribution from combined N<sub>2</sub> (-196 °C) and CO<sub>2</sub> (0 °C) adsorption isotherms using NLDFT carbon slit model (c-d) of activated carbon prepared in single pyrolysis-activation by microwave

As summarized in Table 1 and 2, changing the power and time (energy) appeared to have an effect on the surface area and pore volume. The surface areas ranged from 608-1000 m<sup>2</sup> g<sup>-1</sup> and 842-974 m<sup>2</sup> g<sup>-1</sup> and pore volumes ranged from 0.25-0.39 cm<sup>3</sup> g<sup>-1</sup> and 0.31-0.40 cm<sup>3</sup> g<sup>-1</sup> for the

KOH and  $K_2CO_3$  carbon samples, respectively. These results validate the applicability of a direct activation of biomass using low processing time with microwaves. Interestingly, Fig. S1 showed that in general the percent of pore volume ( $V_{<0.8nm}$ ) for samples  $K_2CO_3$  are comparable in the range of energies from 4.26 to 10.67  $\text{kJ g}^{-1}$ , with a volume pore percent ( $V_{<0.8nm}$ ) of 60.51 - 63.93%. However, for the KOH prepared samples, a more remarkable effect is presented which may be associated with the dielectric properties previously discussed. At an energy of 4.52  $\text{kJ g}^{-1}$  the ( $V_{<0.8nm}$ ) percent is 60.93% which increased up to 73.49% at 11.32  $\text{kJ g}^{-1}$ . It should be noted, however, that 300-6-KOH possessed more abundant ultra-micropores (73.49%) than the other carbons, as displayed in Fig. 2 and Table 2.

Despite the fact that the samples were prepared in rapid processing times (6 min), the activated carbons possessed a considerable micropore percent and surface area. In general, the surface area and pore volume of the activated carbons prepared in a single pyrolysis-activation are comparable or even higher to those of equivalent agent ratios prepared with more processing steps, by carbonisation followed by activation using conventional heating [45-47]. In certain cases, the surface area is also comparable to those prepared with higher amounts of agent: carbon ratio (i.e., 2:1 and 4:1) and conventional carbonisation and activation [48, 49]. This finding is of high importance, which confirms that the porosity is not compromised when microwave pyrolysis-activation is performed via the faster and more environmentally friendly processing route detailed in this work.



Table 2 Textural parameters of the series of activated carbons prepared in a single pyrolysis activation step using microwaves.

Sample	<sup>a</sup> S <sub>BET</sub> (m <sup>2</sup> /g)	<sup>b</sup> V <sub>p</sub> (cm <sup>3</sup> /g)	<sup>c</sup> V <sub>&lt;2nm</sub> (cm <sup>3</sup> /g)	<sup>d</sup> V <sub>&lt;0.8nm</sub> (cm <sup>3</sup> /g)	% (V <sub>&lt;0.8nm</sub> )
300-3-KOH	778	0.314	0.287	0.225	71.63
300-4-KOH	667	0.289	0.253	0.190	65.69
300-5-KOH	902	0.356	0.329	0.261	73.13
300-6-KOH	959	0.377	0.349	0.277	73.49
400-2-KOH	608	0.259	0.227	0.158	60.93
400-3-KOH	1000	0.394	0.365	0.260	66.13
400-4-KOH	811	0.327	0.296	0.228	69.92
300-3-K <sub>2</sub> CO <sub>3</sub>	947	0.389	0.346	0.226	58.22
300-4-K <sub>2</sub> CO <sub>3</sub>	789	0.334	0.294	0.209	62.53
300-5-K <sub>2</sub> CO <sub>3</sub>	844	0.357	0.312	0.224	62.83
300-6-K <sub>2</sub> CO <sub>3</sub>	842	0.351	0.310	0.234	66.89
400-2-K <sub>2</sub> CO <sub>3</sub>	728	0.312	0.275	0.189	60.51
400-3-K <sub>2</sub> CO <sub>3</sub>	827	0.351	0.303	0.222	63.31
400-4-K <sub>2</sub> CO <sub>3</sub>	974	0.401	0.354	0.257	63.93

<sup>a</sup> Specific surface area calculated by the BET method.

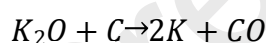
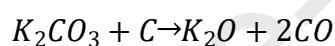
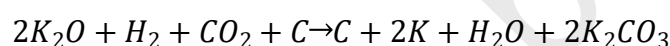
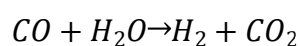
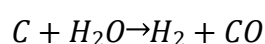
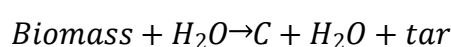
<sup>b</sup> Total pore volume recorded at 100 nm on cumulative pore volume by NLDFT carbon slit pore model.

<sup>c</sup> Micropore volume obtained at 2 nm on cumulative pore volume by NLDFT carbon slit pore model.

<sup>d</sup> Ultra-micropore volume obtained at 0.8 nm on cumulative pore volume by NLDFT carbon slit pore model

The development of larger pore sizes is due to gasification effects associated with the decomposition of potassium salts. The reaction between biomass carbon and KOH starts at low temperatures which leads to oxidation of carbon, resulting in the formation of K<sub>2</sub>CO<sub>3</sub> and the hydroxide itself gets reduced to metallic potassium and hydrogen [50]. KOH dehydrates to

transform into  $K_2O$  at  $400\text{ }^\circ\text{C}$ , then the carbon is consumed by the reaction of carbon and  $H_2O$  with the emission of  $H_2$ .  $K_2CO_3$  formed as a result of redox reactions can further react with biomass carbon to generate  $K_2O$ , metallic potassium and volatiles. Previous studies indicate  $K_2CO_3$  is formed at about  $400\text{ }^\circ\text{C}$  and at  $600\text{ }^\circ\text{C}$   $KOH$  is completely consumed.  $K_2CO_3$  is decomposed into  $CO$  and  $K_2O$  at temperatures higher than  $700\text{ }^\circ\text{C}$  and disappears at temperatures around  $800\text{ }^\circ\text{C}$  [51].



Potassium metal (K) is produced during  $K_2O$  activation at high temperatures and it was found that the formation of pores was due to the loss of carbon (C). The activation involves the etching of the carbon framework via the redox reactions (listed above). The potassium vapour that is produced may penetrate between the carbon layers and induce swelling and disintegration of the carbon microstructure, thereby resulting in the framework expansion and generation of a porous network [4, 45, 46]. The potassium compounds formed during the process are subsequent removed using acid wash.

### 3.2.1 Morphology and chemical structure of activated carbons

Powder X-ray diffraction was used to analyse the nature of the inorganic species present in the materials after the microwave treatment and to corroborate the complete removal of K species after the washing. Fig. 3 shows the patterns of sample 300-6-KOH and 300-6- $K_2CO_3$ , respectively. It is observed that the only species remaining after the microwave pyrolysis-

activation is the calcium carbonate ( $\text{CaCO}_3$ ) in sample 300-6-KOH, which is confirmed in EDX (Fig. 3 c). The XRD pattern of the carbon materials are characteristic of activated carbons with amorphous structures showing broad and diffused peaks at  $2\theta = 30^\circ$ , which corresponds to the (002) set of planes related to the interlayer spacing, and at  $43^\circ$  (100), corresponding to the microcrystallinity

lateral dimension of (100) planes, respectively [46, 48, 52]. Sample 300-6-KOH additionally shows distinctive peaks for  $\text{CaCO}_3$ , which results from the transformation of the initial inorganic compound previously reported in the PNS biomass (calcium oxalate) [33].

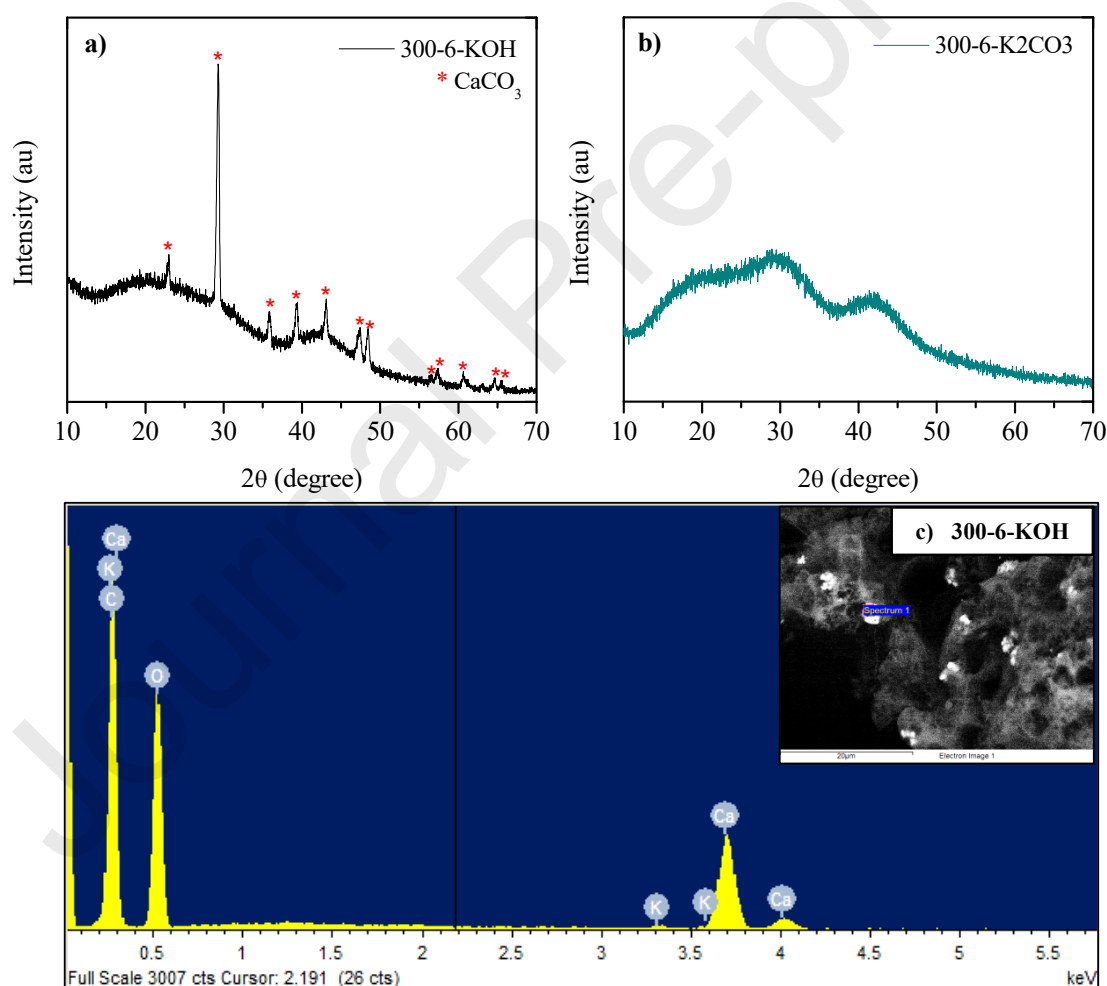


Fig. 3. XRD pattern of (a) 300-6-KOH and (b) 300-6-K<sub>2</sub>CO<sub>3</sub> activated carbons, and (c) EDX analysis of 300-6-KOH carbon

The morphologies of the selected activated carbons prepared using KOH and  $K_2CO_3$  were analysed by SEM, and the images are shown in Fig. 4. Additional morphologies of PNS biochar prepared at 300 W and 6 min without chemical impregnation is presented for comparison. Distinctive morphologies between char and activated carbons are illustrated. In both cases of activated carbons, the morphologies are dominated by particles with large conchoidal cavities, which are consistent with what has previously been reported for activated carbons. The morphology of KOH (Fig. 4 a, b) shows microsheets and possession of a large number of interconnected pores [53]. The SEM images of  $K_2CO_3$  activated carbon (Fig. 4 c, d) show a material of irregular shapes and a rough topography. The SEM images indicate that the activated carbons are porous structures and the electron diffraction illustrates that the white deposit are composed of  $CaCO_3$ ; validated in the XRD data (Fig. 3a, c). The surface morphology also depicts microcracks, which suggests possible swelling and subsequent shrinkage of carbon during the pyrolysis-activation.

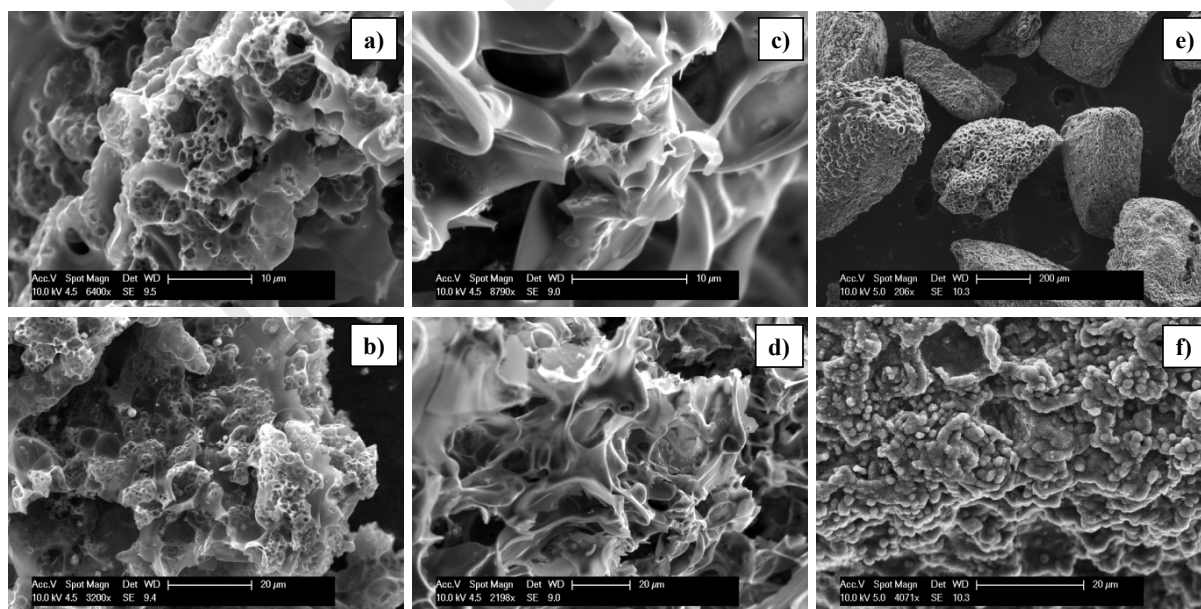


Fig. 4. SEM images of activated carbons prepared by direct pyrolysis-activation in microwave heating, 300-6-KOH (a,b) and 300-6- $K_2CO_3$  (c,d). PNS biochar 300-6 without chemical activation for comparison (e,f).

Thermogravimetric analysis (TGA) was used to characterise the thermal stability of the prepared activated carbons. As shown in Fig. S2, both activated carbons 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> show an initial mass loss below 100 °C, due to removal of water, followed by a mass loss after 700 and 500 °C for 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub>, respectively. According to the TGA curves, the activated carbon 300-6-KOH shows better thermal stability (as indicated by the carbon burn off maxima at 700 °C) compared to 300-6-K<sub>2</sub>CO<sub>3</sub> with the burn off maxima at 500 °C. It appears that sample 300-6-KOH is more thermally stable and this may be related to the increase in level of graphitisation due to a better microwave absorption when KOH is the activating agent, as discussed in section 3.1 (dielectric properties).

### 3.3 CO<sub>2</sub> adsorption studies

#### 3.3.1 Relevance of ultra-micropores for CO<sub>2</sub> uptake

The CO<sub>2</sub> uptake capacity of the activated carbons was investigated at 0 and 25 °C using volumetric and gravimetric analysis. The CO<sub>2</sub> uptake isotherms for all materials prepared via microwave pyrolysis-activation are shown in Fig. 5 and the samples with better CO<sub>2</sub> uptake performance are summarised in Table 3. The highest CO<sub>2</sub> uptake at 1.1 bar was 5.3 and 4.58 mmol g<sup>-1</sup> for 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> at 0 °C and 3.7 and 3.3 mmol g<sup>-1</sup> for 300-6-KOH and 300-K<sub>2</sub>CO<sub>3</sub> at 25 °C. The CO<sub>2</sub> uptake clearly indicates that it is not the total surface area, but the pore size that actually determined the CO<sub>2</sub> uptake. As evidenced by XRD, sample 300-6-KOH appears to have calcium carbonate. In order to explore its potential effect on CO<sub>2</sub> capture performance, an additional experiment was performed using the calcium of sample 300-6-KOH (obtained from the ash). The results are presented in Fig. S3 b), and reveal a CO<sub>2</sub> adsorption of 0.05 mmol/g. This suggests that the calcium on the sample proposes minimal contribution to the overall performance of sample 300-6-KOH (at 25 °C and 1 bar) and may

clog some porosity. This confirms the results reported in literature, the micropores are in fact, a main key parameter in the uptake of CO<sub>2</sub>.

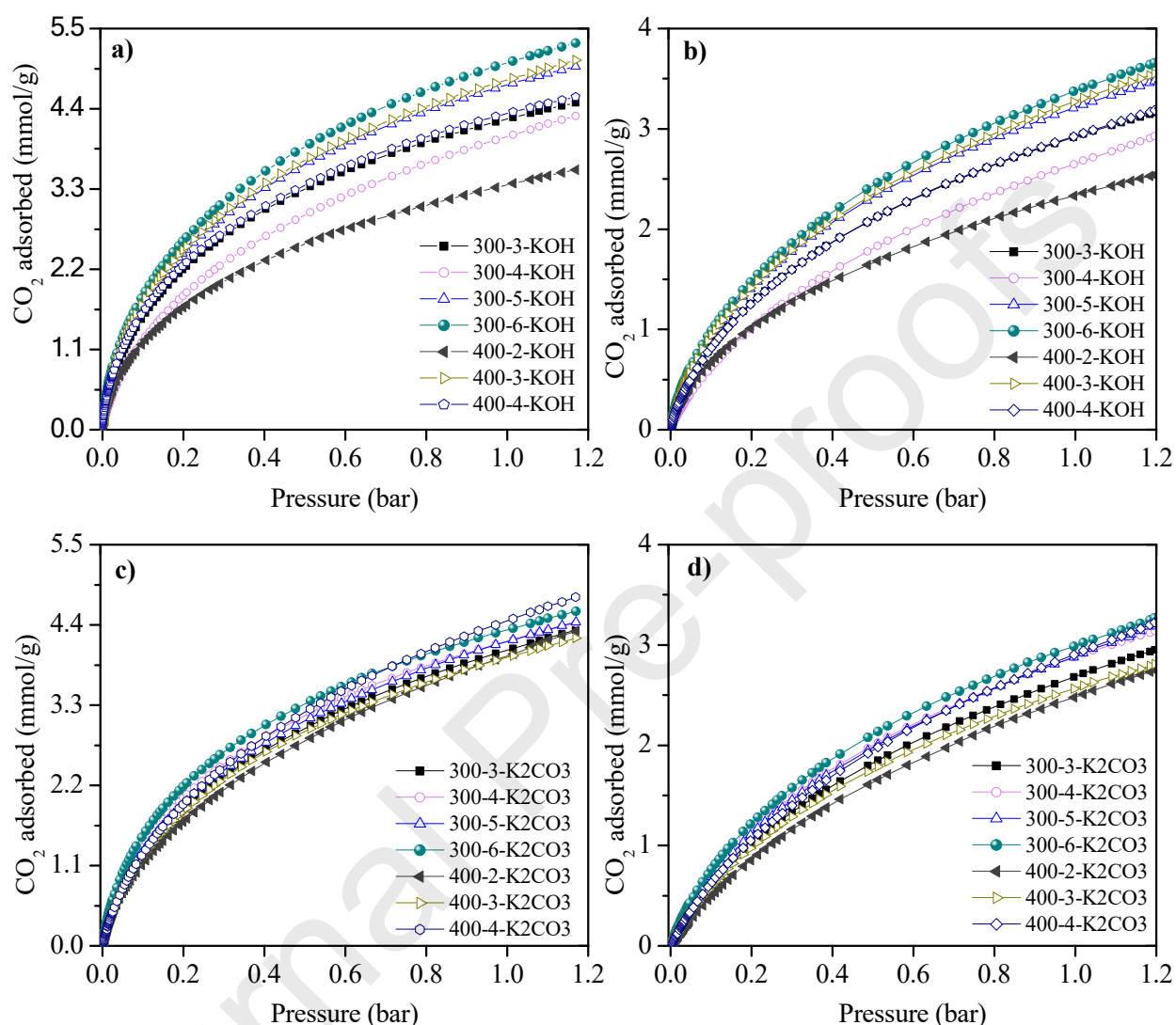


Fig. 5. CO<sub>2</sub> adsorption profiles at 0 °C and 25 °C for all KOH (a, b) and K<sub>2</sub>CO<sub>3</sub> carbons (c, d) from the microwave pyrolysis-activation at different powers and times. Conditions: 100% CO<sub>2</sub>

The surface area of 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> carbons are 959 and 842 m<sup>2</sup> g<sup>-1</sup>, however 300-6-KOH possess 73.49% of ultra-micropores with a size of <0.8 nm, compared to 66.89% in sample 300-6-K<sub>2</sub>CO<sub>3</sub>. Previously, it has been demonstrated that at pressures of 0-1 bar and temperatures of 0-25 °C, the enhancement of CO<sub>2</sub> uptake is negligible for micropores widths

larger than around two to three times the molecular diameter ( $\text{CO}_2$  diameter  $\sim 0.33$  nm) [16, 54]. This important finding is also in agreement with the results obtained in this study. To better understand the adsorption mechanism and reveal the significant effect of pore size, the fraction of ultra-micropore filling by  $\text{CO}_2$  ( $f_{\text{CO}_2}$ ) was calculated [54] and is shown in Fig. 6. This parameter describes the relationship between the pore size and the pore filled by  $\text{CO}_2$  and is defined as  $f_{\text{CO}_2} = q / (V_{<0.7\text{nm}} \cdot \rho_{\text{CO}_2})$ , where  $q$  is the  $\text{CO}_2$  uptake,  $V_{<0.7\text{nm}}$  is the ultra-micropore volume and  $\rho_{\text{CO}_2}$  is the density of liquid  $\text{CO}_2$  ( $1.03 \text{ g cm}^{-3}$  at  $0^\circ \text{C}$ ).

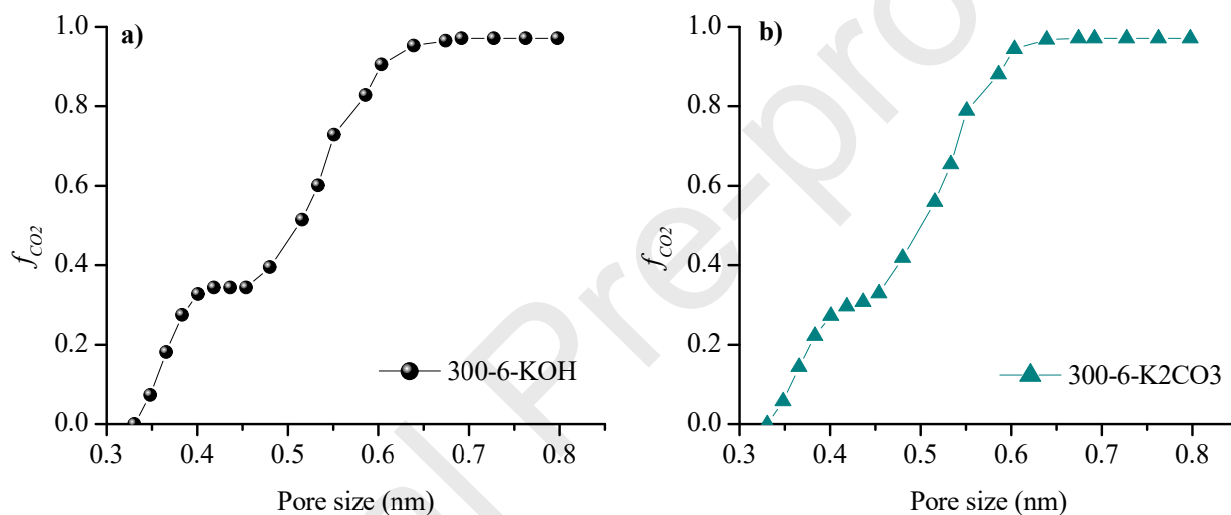


Fig. 6. Pore filled by  $\text{CO}_2$  with average micropore size of sample 300-6-KOH (a) and 300-6- $\text{K}_2\text{CO}_3$  (b), deduced by applying the NLDFT model to  $\text{CO}_2$  isotherms at  $0^\circ \text{C}$ .

The results presented in Fig. 6 reveal that at pressures of 0-1 bar, the  $\text{CO}_2$  adsorption is mainly determined by the ultra-micropores with a size below 0.8 nm. The results indicate the highest fraction of pore filled occurs in pores of size of 0.7 nm, whereas other pores such as super-micropores (0.8-2 nm) are not relevant for  $\text{CO}_2$  capture at this given conditions (0-1 bar). The results confirm that the adsorption mechanisms consist of volume-pore filling rather than surface cover, which is typically observed in mesoporous materials. This validates the lack of a correlation between the  $\text{CO}_2$  uptake and specific surface area ( $S_{\text{BET}}$ ) and total pore volume



( $V_T$ ); indicating that the interaction between adsorbents and  $\text{CO}_2$  becomes stronger when the pore size decreases and the ideal pore size is around 0.7 nm. It is important to mention that the  $\text{CO}_2$  adsorption at higher pressures (30-70 bar) could be enhanced by the super-micropores (0.8-2 nm) and as results of coverage adsorption mechanism [16].

It is worth to note that the  $\text{CO}_2$  uptake of sample 300-6-KOH at 0 and 25 ° C (5.3 & 3.7 mmol  $\text{g}^{-1}$ ) is comparable or even higher to activated carbons with good performance for  $\text{CO}_2$  uptake at 1.1 bar [45-47, 53, 55-57]. (See Table 3). Furthermore, all materials previously generated and tested for  $\text{CO}_2$  uptake were prepared in two or three step processes that typically utilised a material that was already carbonised, which was then subsequently activated at a high impregnation ratio and temperature for longer processing times. Huang *et al.* [55] reported for first time the direct activation by microwaves of oil palm shell using an impregnation ratio of 2.5:1 of KOH:Oil palm shell and a microwave power of 750 W for 30 min. The maximum  $\text{CO}_2$  uptake reported was 1.7 mmol  $\text{g}^{-1}$ , significantly lower than what was achieved herein. Also a comparable performance was achieved to the best templated activated carbons impregnated (KOH:hydrochar) with a ratio of 2:1 [49] and 6:1, [26] respectively. The  $\text{CO}_2$  capture is only slightly exceeded by activated carbons derived from sawdust (4.9 mmol  $\text{g}^{-1}$ ) [28] and examples of N-doped activated carbons (4.7-4.9 mmol  $\text{g}^{-1}$ ) or composites [25, 58, 59]. However, it is important to highlight that the materials prepared in the present work have the advantage of a low impregnation ratio (1:1), which essentially circumvents a doping step. Furthermore, the short processing times represents a novel and energy-effective pathway for the development of such materials for a range of industrial applications.



Table 3. Comparative evaluation of CO<sub>2</sub> adsorption capacities and textural parameters of activated carbons prepared from different biomass.

Raw material	Carbonization (C) & Activation (A) (Temp. °C)/Residence time. min)	Agent	Agent:Biomass Agent:Char ratio	Microwave power/time (W/min)	CO <sub>2</sub> uptake at 1 bar (mmol g <sup>-1</sup> )/T (°C)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>tot</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>micro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	Ref.
*PNS	n/a	KOH	1:1	300/6	5.3/0	959	0.377	0.35	This work
*PNS	n/a	KOH	1:1	300/6	3.7/25	959	0.377	0.35	This work
*PNS	n/a	K <sub>2</sub> CO <sub>3</sub>	1:1	300/6	4.5 /0	974	0.401	0.35	This work
*PNS	n/a	K <sub>2</sub> CO <sub>3</sub>	1:1	300/6	3.3/25	974	0.401	0.35	This work
Oil palm shell	n/a	KOH	2.5:1	750/30	1.7/25	1069	0.52	0.42	[60]
Rice straw	-	-	-	200/20	1.75/25	122	0.08	0.03	[55]
Pitch	A-800/120	KOH	1:1	n/a	1.93/25	1012	0.422	0.374	[45]
Rice husk	A-600/60	KOH	1:1	n/a	3.25/25	536	0.24	0.19	[46]
Chestnut	C-600/120 A-800/120	NH <sub>3</sub>	1.25:1	n/a	2.3/25	747	-	-	[47]
Corncob	C-800/180 A-800/180	NH <sub>3</sub> -KOH	4:1	n/a	2.81/25	1154	0.57	-	[53]
Rice husk	C-900/60 A-100/60	K <sub>2</sub> CO <sub>3</sub> -CO <sub>2</sub>	5:1	n/a	3.1/25	-	-	-	[56]
Empty fruit bunch	C-350/20 A-800/30	KOH	5:1	n/a	3.4/25	1322	0.78	0.23	[57]
Arundo donax	C+A-600/120	KOH	2:1	n/a	3.6/25	1122	0.59	0.50	[49]
Chitosan	A-600/60	K <sub>2</sub> CO <sub>3</sub> -NH <sub>3</sub>	4:1	n/a	4.9/25	1355	0.60	0.47	[25]
Sawdust	C-250/120 A-600/60	KOH	2:1	n/a	4.9/25	1260	0.62	0.55	[28]
Black locust	C-650/180 A-800/90	KOH	6:1	n/a	3.75/25	2064	0.98	0.87	[26]
Pine cone	C-600/60 A-800/60	KOH-NH <sub>3</sub>	3:1	n/a	4.7/25	1680	0.61	0.53	[58]

\*Single step pyrolysis-activation

### 3.3.2 Adsorption kinetics and selectivity

An effective CO<sub>2</sub> carbon adsorbent should not only possess desirable characteristics such as a large surface area, high micropore volume and high CO<sub>2</sub> uptake capacity, but also have fast adsorption kinetics and suitability for use in swing cycles. The CO<sub>2</sub> adsorption kinetics for all materials and the selectivity of selected carbons against N<sub>2</sub> are shown in Fig. 7. The kinetics and selectivity curves for all materials were carried out in a thermogravimetric system at 25 °C, as described in section 2.5. It can be seen the rate of adsorption was exponential and the equilibrium uptake was achieved for samples 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> in less than 3 min (Fig. 7a-b). This can be observed with detail in Fig. S4 and Fig. S5. It can be observed that the materials exhibit a short breakthrough time, in accordance with their equilibrium capacity, suggesting a low mass transfer resistance over the activated carbons. The low time required to reach the equilibrium, may be associated to the optimum pore size of the adsorbent which has been reported is two or three times the diameter of the adsorbate. Given the kinetic diameter of CO<sub>2</sub> is 0.33 nm, the optimum pore size is between 0.7 and 0.9 nm [43]. Therefore, the porosity and pore size in the activated carbons may play a crucial role in the CO<sub>2</sub> diffusion in the porous network. These results indicate that CO<sub>2</sub> can be separated effectively in short adsorption cycle times, which is of significant importance for practical industrial applications.

The selectivity of activated carbons was highlighted by comparing the CO<sub>2</sub> uptake with N<sub>2</sub> sorption at 25 °C and 1 bar for representative samples (300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub>). The CO<sub>2</sub> and N<sub>2</sub> uptake are compared in Fig. 7 (c-d). The CO<sub>2</sub> uptake for both samples is far higher than that of N<sub>2</sub>, which only reached 0.09 mmol g<sup>-1</sup> and 0.14 mmol g<sup>-1</sup> for samples 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub>, respectively. The  $\alpha$  (CO<sub>2</sub>/N<sub>2</sub>) ratio measured at equilibrium conditions was 36.6 and 19.5 for both selected activated carbons. The selectivity of the materials prepared in this work was found to be very high and even higher than N-doped activated carbons ( $\alpha$  (CO<sub>2</sub>/N<sub>2</sub>) = 6.5) [61, 62]. The results indicate the development of CO<sub>2</sub> selective adsorbents,

which are preferable and economically feasible since pure CO<sub>2</sub> can be extracted from the adsorbent and utilized as another carbon source for industry. The selectivity may depend on the different physical properties of the gas molecules such as polarizability or quadrupole moment. The results indicate the Van der Waals forces between N<sub>2</sub> molecules and the micropore carbon are weaker than that of CO<sub>2</sub>, which is expected due to the higher polarizability of CO<sub>2</sub> that has a greater affinity to carbon. In this sense the polarizability of CO<sub>2</sub> and N<sub>2</sub> is  $29.1 \times 10^{-25} \text{ cm}^3$  and  $17.4 \times 10^{-25} \text{ cm}^3$  respectively, [57] and leads to achieve higher CO<sub>2</sub> selectivity.

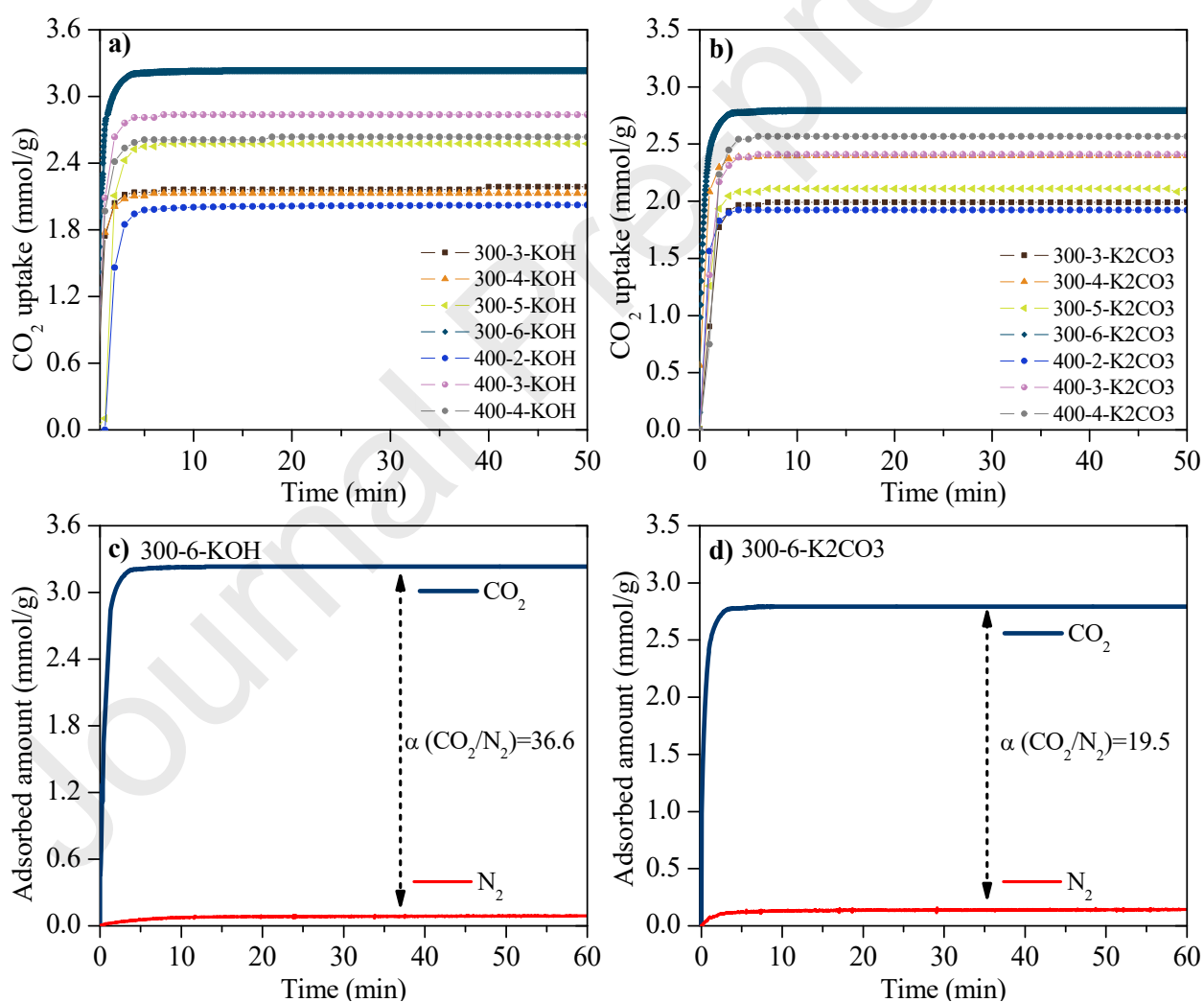


Fig. 7. Adsorption kinetics of CO<sub>2</sub> for all KOH (a) and K<sub>2</sub>CO<sub>3</sub> (b) carbons from the microwave pyrolysis-activation at different conditions. Adsorption kinetics and selectivity of CO<sub>2</sub> and N<sub>2</sub> for sample 300-6-KOH (c) and 300-6-K<sub>2</sub>CO<sub>3</sub> (d) Conditions: 1 bar, 25 °C.

### 3.3.3 High temperature CO<sub>2</sub> uptake

In order to evaluate the commercial application of the materials prepared in this work, the CO<sub>2</sub> capture uptake was explored at higher temperatures (25 – 100 °C) to simulate their performance in post-combustion capture. The results of 100% CO<sub>2</sub> and 15% CO<sub>2</sub> at 1 bar are shown in Fig. 8. As expected, the CO<sub>2</sub> uptake decreased at higher temperatures. At 40 °C and 100% CO<sub>2</sub> the sample 300-6-KOH absorbed 2.47 mmol g<sup>-1</sup> and decreased to 0.62 mmol g<sup>-1</sup> at 100 °C. This is because at higher temperature the CO<sub>2</sub> have a higher molecular kinetic energy, which allows CO<sub>2</sub> to escape form the adsorbent. In many industrial processes, the CO<sub>2</sub> is produced as flue gas at 15% CO<sub>2</sub> and 1 bar, at these conditions, the CO<sub>2</sub> uptake is more challenging and decreases from 0.94 to 0.22 mmol g<sup>-1</sup> in the same range of temperature. The values are comparable to the values reported previously for hierarchical carbons [63]. The results indicate the adsorbents prepared in this work could be promising candidates for greater uptake at higher pressures.

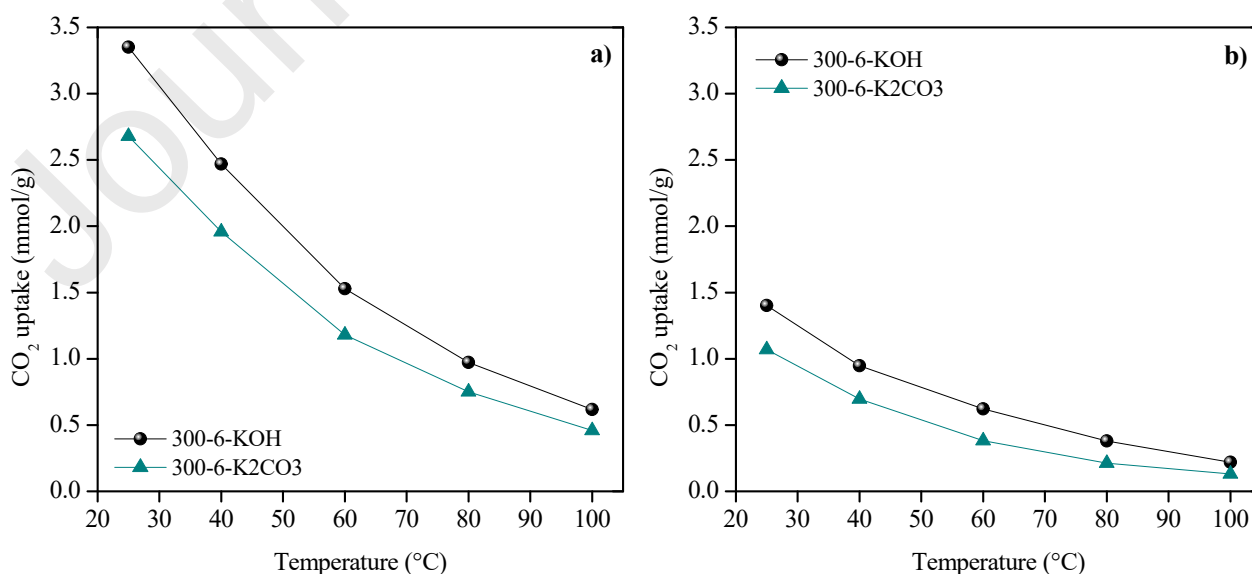


Fig. 8. CO<sub>2</sub> uptake of 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> in a 100% (a) and 15% (vol% CO<sub>2</sub>) gas flow at different temperatures

### 3.3.4 *Isosteric heat*

In order to investigate the interaction strength between the CO<sub>2</sub> and the adsorbents, the isosteric heats of adsorption ( $Q_{st}$ ) were calculated via the CO<sub>2</sub> adsorption isotherms at 0 and 25 °C and by applying the Clausius-Clapeyron equation. The adsorption data at different temperatures (Fig. 9a) and the relationship between the values of  $Q_{st}$  and CO<sub>2</sub> adsorption capacities are plotted in Fig. 9 (Fig. 9b). At the initial stage, 300-6-KOH exhibits a high  $Q_{st}$  of 37.4 kJ mol<sup>-1</sup> and at a steady stage of 28.2 kJ mol<sup>-1</sup>, which is even higher than previously reported values of porous carbons (e.g. 20.3-27.7 kJ mol<sup>-1</sup>, [64] 21.3–24.2 kJ mol<sup>-1</sup>, [65] 35.9-21.1 kJ mol<sup>-1</sup>, [66]). Sample 300-6-K<sub>2</sub>CO<sub>3</sub> exhibited a lower  $Q_{st}$  of 34.2-25.0 kJ mol<sup>-1</sup>. The higher  $Q_{st}$  value of 300-6-KOH in the initial adsorption stage is an indicator of the strong gas molecules interaction with the network of porous carbon, which can be explained by the quadrupolar interaction between CO<sub>2</sub> molecules and ultra-micropores with narrow pore size distribution (0.7 nm) [66]. At lower CO<sub>2</sub> uptake, the  $Q_{st}$  value of both samples are greater than the values reported for chemisorption (greater than 30 kJ mol<sup>-1</sup>) [67], however at higher CO<sub>2</sub> uptakes, the  $Q_{st}$  values are much smaller, indicating CO<sub>2</sub> adsorption involves mechanisms of physical adsorption and suggesting a reversible process that implies low energy in the regeneration process.

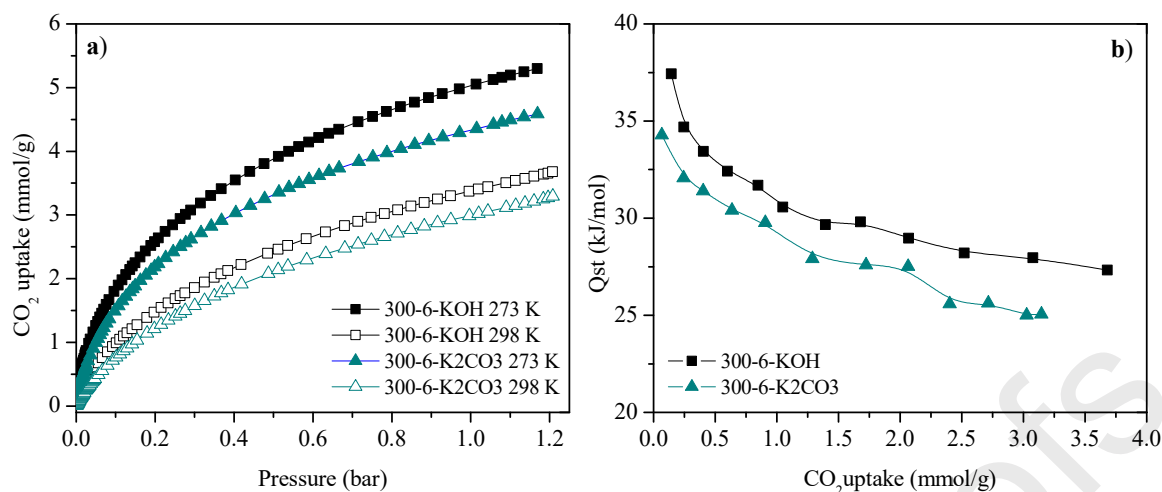


Fig. 9. CO<sub>2</sub> adsorption isotherms of 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> samples at 1 bar and 0 and 25 °C (a); Isosteric heat of CO<sub>2</sub> adsorption for 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> at different CO<sub>2</sub> uptakes (b).

The high  $Q_{st}$  value and the narrow micropores of sample 300-6-KOH (See Fig. 9b) predict stronger interactions between the carbon and CO<sub>2</sub> molecules. Indeed the results emphasise the importance of the pore size and surface, nevertheless 300-6-K<sub>2</sub>CO<sub>3</sub> possesses higher surface area and has lower  $Q_{st}$  compared to 300-6-KOH. Thus the ultra-micropores and high  $Q_{st}$  of 300-6-KOH emphasise the synergetic effects of textural parameters leading to superior CO<sub>2</sub> uptake. The high  $Q_{st}$  is ascribed to the optimal (with respect to CO<sub>2</sub> adsorption) pore size. It is envisaged that narrow micropores engender stronger interactions between adsorbents and CO<sub>2</sub> molecules than larger micropores or mesopores. Indeed, the importance of pore size is emphasised by the fact that sample 300-6-KOH possesses higher volume of ultra-micropores compared with 300-6-K<sub>2</sub>CO<sub>3</sub>, evidenced in Table 2 and Fig. 2.

It is important to highlight the materials prepared in the present work, were prepared using a waste precursor (PNS) using a low concentration of chemical agent, in a single step of pyrolysis-activation and in a very short time (6 min), allowing an easy, green and sustainable synthesis.

### 3.3.5 Adsorbents reuse and CO<sub>2</sub> adsorption cycles

Besides attaining a high uptake capacity and fast adsorption kinetics, an effective adsorbent that can be used within CO<sub>2</sub> capture systems must also exhibit high reusability properties, as this highlights the efficiency and economics of the CO<sub>2</sub> capture process. In this sense, the adsorption/desorption cycles of samples 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> at 100 and 15% CO<sub>2</sub> are shown in Fig. 10. The experiments were conducted at adsorption (CO<sub>2</sub>)-desorption (N<sub>2</sub>) pressure of 1 bar and 25 °C. The results showed that the CO<sub>2</sub> adsorbed can be easily desorbed after the carrier gas is switched from CO<sub>2</sub> to N<sub>2</sub>. These results indicate that after several adsorption-desorption cycles, the activated carbons maintain their adsorption capacity. Specifically the adsorption efficiency was maintained at 97-100% after the 20<sup>th</sup> cycle, which demonstrates high chemical and physical stability. Thus, CO<sub>2</sub> capture in both activated carbons is highly reversible and primarily based on physisorption. The simple and straight forward regeneration of 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> make them superior adsorbents compared to aqueous amine-adsorbents, which require large amounts of energy during the regeneration process [7]. This enables this technology to deliver high viability for scale-up and easy fabrication.

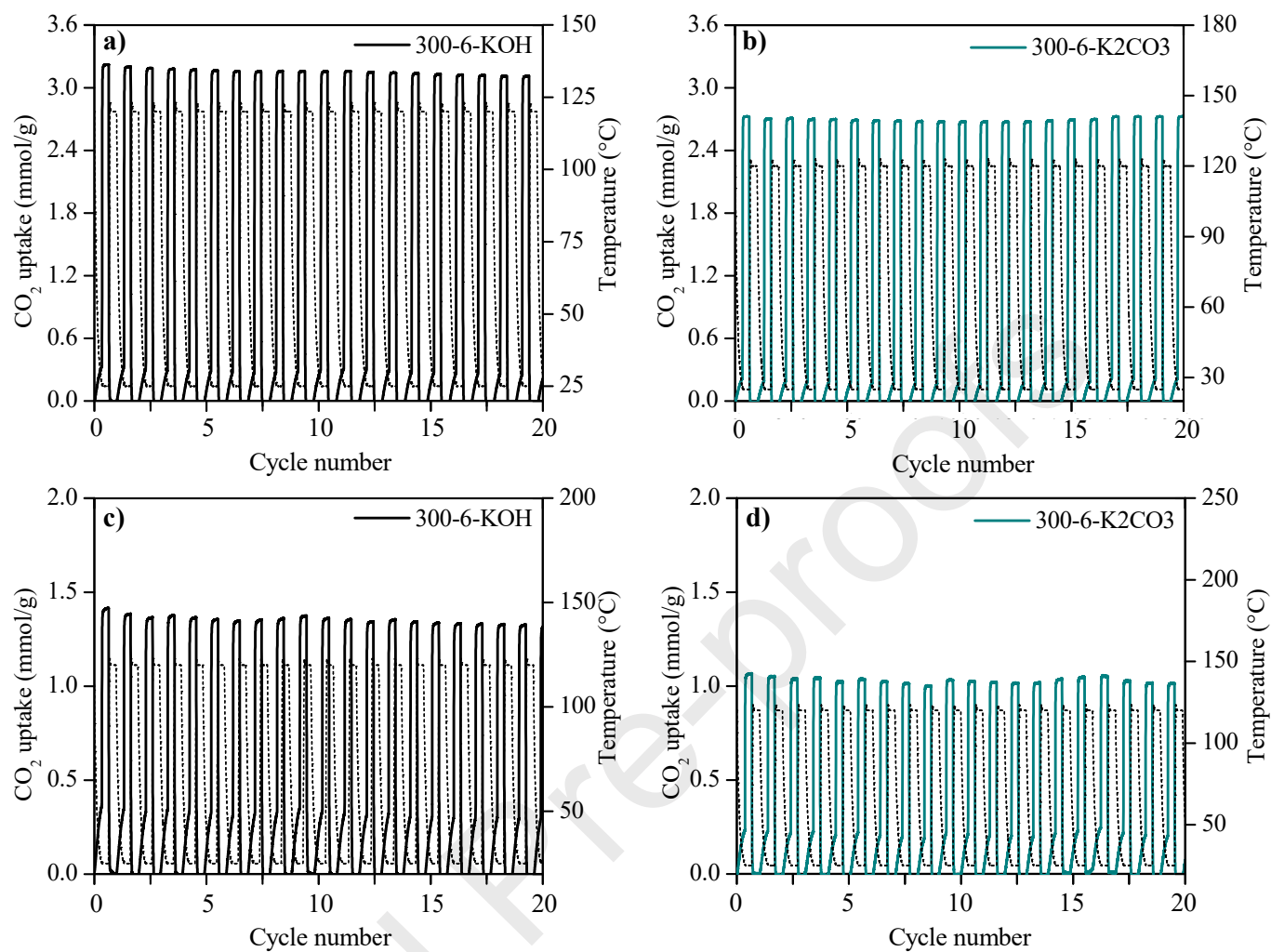


Fig. 10. CO<sub>2</sub> uptake of 300-6-KOH and 300-6-K<sub>2</sub>CO<sub>3</sub> (b, d) in a 100 % vol (a, b) and 15% vol (c, d) CO<sub>2</sub> gas flow at 25 °C in 20 five cycles of adsorption and desorption.



## 4 Conclusions

In summary, the work described herein has shown that a sustainable and a simple microwave thermal treatment can be implemented to prepare ultra-microporous activated carbons from a biomass waste feedstock in a direct pyrolysis-activation step by using low KOH and  $K_2CO_3$  impregnation ratio of 1. A rapid and simple route to synthesizing porous materials with high  $CO_2$  uptake and selectivity has been established. The highest  $CO_2$  uptake is  $5.3 \text{ mmol g}^{-1}$  at 1 bar and  $0 \text{ }^\circ\text{C}$ , which is one of the largest reported in literature for porous carbons using low agent ratio. Depending on the microwave heating conditions, the activated carbons have from a modest to high surface areas ranging from  $600$  to  $1000 \text{ m}^2 \text{ g}^{-1}$ , of which up to 73% of the surface area arises from ultra-micropores ( $<0.8\text{nm}$ ). The  $CO_2$  uptake capacity for the activated carbons is due to the narrow micropores ( $\sim 0.7 \text{ nm}$ ), enhancing its selectivity and simple regeneration after 20 cycles and in short adsorption cycle times, which is of significant importance for practical industrial applications. The present results suggest that an effective and green route with considerable energy savings can be implemented to prepare activated carbon porous materials for  $CO_2$  uptake and may be favourable for parallel applications such as liquid adsorption, catalysis and energy storage.

### Conflicts of interest

There are no conflicts to declare.

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## 1 Highlights

- 2 ● Simple and rapid (< 6 min) preparation of selective activated carbons by microwave
- 3 ● 96.66% reduction in the processing times compared with conventional heating
- 4 ● Large CO<sub>2</sub> uptake (5.3 mmol g<sup>-1</sup>) and high CO<sub>2</sub>/N<sub>2</sub> selectivity (36)
- 5 ● Ultra-micropore formation at low biomass/agent (KOH, K<sub>2</sub>CO<sub>3</sub>) impregnation ratio
- 6 ● Dielectric properties, kinetics and reusability of adsorbents

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