



Intrinsic activation: The relationship between biomass inorganic content and porosity formation during pyrolysis



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HIGHLIGHTS

- The inorganic content of biomass predicts the porosity of the resulting pyrolytic carbon.
- Specific surface areas of up to 1500 m²/g can be achieved with this method using macro-algae.
- Using widely available oilseed rape straw a specific surface area of 950 m²/g can be obtained.
- These properties are comparable to commercially available activated carbons.
- Porosity formation is intrinsic and does not require the addition of chemical activating agents.

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ABSTRACT

The utility of pyrolytic carbons is closely related to their porosity and surface area, there is a clear benefit to the development of biomass pyrolysis processes which produce highly porous carbons. The results presented in this work demonstrate that by using biomass precursors with high inorganic content along with specified process conditions, carbons can be consistently produced with specific surface areas between 900 and 1600 m²/g. Results from 12 different source materials show that the formation of increased porosity in pyrolytic carbons is strongly associated with the presence of inorganic elements in the precursors including: magnesium, potassium and sulfur. It was found that pyrolysis of macro-algae can produce especially high specific surface area carbons (mean: 1500 m²/g), without externally applied activating agents. Using cheap readily available agricultural residues such as oilseed rape straw, pyrolytic carbons can be produced with specific surface areas of around 950 m²/g.

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1. Introduction

It has been established that bioenergy generally offers advantages over non-renewable energy sources not least of all its neutrality with respect to carbon dioxide emissions. This is due to the process fuel being derived from plant matter which in turn is produced photosynthetically from carbon dioxide in the atmosphere (Cherubini et al., 2011).

Pyrolysis can also be used as a means of disposal of organic waste (Zheng, 2008; Islam et al., 2011). In addition to energy, pyrolysis (and gasification) produce a carbon-rich residue or char (Zhang et al., 2010). This material is the left over carbon and inorganic matter after thermal decomposition is largely complete. This char can be used as a fuel, adsorbent or as a soil amendment. As the

adsorption capacity of carbon is limited by its porosity and the related property of specific surface area, it is possible for subsequent physical or chemical activation to increase the potential utility of pyrolytic carbons (Marsh and Rodriguez-Reinoso, 2006). This approach has the drawback of requiring extrinsic activation agents such as potassium carbonate or zinc chloride and an additional energy intensive treatment step. Chemical activating agents are often used in 1:1 to 2:1 ratios (by mass) of activating agent to precursor using zinc chloride (Acharya et al., 2009) or potassium carbonate (Gurten et al., 2012) respectively.

A great deal of research has been published on the subject of producing activated carbons from biomass (Acharya et al., 2009; Azargohar and Dalai, 2008; Bagheri and Abedi, 2009; Kalderis et al., 2008; Tsai et al., 2001). These studies involve the addition of activating agents to a novel biomass precursor and an examination of the resulting carbon's physical or adsorptive properties.

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Some high specific surface area biochars of 186–450 m²/g have been directly produced from sugar cane bagasse, chicken litter and other agricultural wastes (Carrier et al., 2012; Cantrell et al., 2012). Pyrolysis of grass and wood have been shown to produce materials with specific surface areas of 8–20 m²/g using pyrolysis temperatures between 250–500 °C and between 371–605 m²/g using pyrolysis temperatures of 850 °C (Bornemann et al., 2007).

For this investigation it was hypothesised that the inorganic compounds present in source materials could function as activation agents. Relationships are shown between variations in the pyrolysis process, inorganic elemental composition of the feedstock and the textural properties of the carbons produced from 12 different source materials. Emphasis is placed on the residual biomass of common agricultural crops as well as potential bioenergy feedstocks such as macro-algae and straws. While macroalgae are discussed in the context of their hypothetical use as a feedstock, they are already harvested on a modest scale in Western Europe (Roberts and Upham, 2012) suggesting very real potential for their use.

2. Methods

2.1. Materials used for the batch pyrolysis process

Non-woody plants used were: leaves of sea beet (*Beta vulgaris*), stems and leaves of stinging nettle (*Urtica dioica*), oilseed rape straw (*Brassica napus*), alfalfa straw (*Medicago sativa*) and barley straw (*Hordeum vulgare*). Seabeet was collected from Littlehampton and Goring beach, Stinging nettles were collected from common land around the town of Arundel (UK), oilseed rape straw was collected from a farm in Northchapel (UK), alfalfa was purchased from an agricultural supplier (Rokers, UK) and barley straw was sourced from a domestic pet shop (Petsmart, UK). Woods used were: shavings of Sweet chestnut (*Castanea sativa*), eucalyptus (*Eucalyptus gunnii*) and scots pine (*Pinus sylvestrus*). Sweet chestnut and eucalyptus were collected from coppices in Petworth (UK) and the Forestry commission's Alice Holt site respectively, pine shavings were sourced from Petsmart, UK. Macroalgae used were: Sea sorrel (*Desmarestia ligulata*), oarweed (*Laminaria digitata*), bladderwrack (*Fucus vesiculosus*) and the serrated wrack (*Fucus serratus*). All macroalgae were sourced from Littlehampton Beach. Materials were shredded to a size less than 2 cm and dried at 40 °C for 24 h before use in pyrolysis reactions.

2.2. Materials used for fed batch pyrolysis process

The following source materials were used in the fed batch pyrolysis processes: straw from non-Woody vascular plants; oilseed rape (*B. napus*), alfalfa (*M. sativa*).

The only wood used was scots pine (*P. sylvestrus*). Macroalgae used were: oarweed (*L. digitata*) and bladderwrack (*F. vesiculosus*). All materials were from the same sources as described in Section 2.1.

2.3. Pyrolysis

2.3.1. Batch pyrolysis

A muffle furnace (Carbolite, UK) was used to supply the heat for pyrolysis, pyrolysis reactions proceeded for 1 h at the required temperature, excluding time required for ramp up and cooling; no carrier gas was used. Batch pyrolysis was followed by acid washing in dilute HCl (0.1 M) for 48 h at room temperature to remove residual inorganic content from the carbon. Chars were produced by placing 25 g of the source material inside a hollow cylindrical stainless steel container of 25 cm in length and 9 cm in diameter with one end sealed and a stainless steel lid secured

on the other end by two bolts. With the lid fitted a 4 mm hole remained in the side of the container, this was to allow gases to exhaust during pyrolysis. A carbon wadding produced from pyrolysed paper was placed between the source material and the lid of the reaction vessel to act as an oxygen scavenger; the wadding was inspected for deterioration due to combustion after each run and this was not observed in any experiments. Ramping of the temperature in the furnace was carried out at an approximate rate of 100 °C per 15 min until the final pyrolysis temperature was reached. This temperature was maintained for one hour, after which the furnace was switched off and left until cool. Observation of temperature ramp rate was facilitated by an infrared heat sensor (RayTemp 38, UK) which was directed at the container. Infrared temperature measurement was used to confirm temperature readings displayed by the furnace temperature gauge. This confirmation was carried out in test runs using both the empty vessel and the vessel charged with source material. The furnace was not opened during pyrolysis runs where the resulting material was to be used for subsequent analysis.

2.3.2. Fed batch pyrolysis

Porosity formation rates for each precursor were determined by pyrolysing 50 g of a given source material at 800 °C for, 10, 30 and 60 min in a sealed rotary tube furnace (Carbolite, UK) rotating at 10 RPM. The apparatus consisted of a rotary tube furnace at an angle of 15° with sealed, water-cooled steel housings around the exit and entrance of the hot zone of the furnace. A hopper contained the biomass at the elevated end and a vibration feeder dispersed material downwards into the pre-heated furnace. At the opposite end another stainless steel hopper was present to collect the now-carbonised biomass. Both hoppers were sealed and nitrogen fed into them from a cylinder (BOC) and flow meter ensuring the process was maintained in an atmosphere which was, at all stages, as free of oxygen as possible. An exhaust flu was attached to the sealed housing at the elevated end of the furnace and this was vented to an adjacent fume hood via a flexible stainless steel exhaust hose. The pyrolysis took place either in a flowing nitrogen atmosphere (10 l/min) or within a stationary atmosphere following a nitrogen purge. The nitrogen purge was carried out at a rate of 10 l/min for 20 mins prior to the introduction of precursor to the pre-heated furnace tube. After pyrolysis the char was acid washed in dilute HCl (0.1 M) for 48 h to remove soluble inorganic content from the carbon. Following pyrolysis and acid washing samples were dried at 40 °C for 24 h and analysed by N₂ BET as in 2.9. Reaction rates were calculated for each precursor in cm³ g⁻¹ min⁻¹ by subtracting the carbon specific pore volume produced during shorter pyrolysis runs (e.g. 10 min) from that formed from the same precursor pyrolysed for longer time intervals (e.g. 30 min or 1 h). This gave an estimate of the specific pore volume formation rate during each time interval as well as the total formed during the full 1 h reaction for a given source material. In addition, a pyrolysis reaction was carried out at 500 °C and 300 °C for each precursor to provide material for use in XRD analysis and in determination of the amount of inorganic carbon (carbonate) formed during pyrolysis. A temperature of 500 °C was chosen as this temperature was high enough for thermal decomposition of the source material but not high enough to cause decomposition of carbonate compounds. To facilitate comparison of chemical compositions of the source materials and intermediate pyrolysis products, yields by weight were measured after pyrolysis at 500 °C before washing. A similar procedure was followed for materials produced at 300 °C.

2.4. ICP-OES

The inorganic composition of the biomass feedstocks and chars was determined using ICP-OES analysis (Alexander et al., 2006).

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