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Fertiliser-catalysed suppression of the pyrolytic temperature for synthesis of nutrient-enriched biochar

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ABSTRACT

The catalytic suppression of the pyrolytic onset temperature of Eucalyptus grandis using three fertilising agents is presented. K_2CO_3 and K_3PO_4 successfully decreased the onset temperature with a maximum suppression of $-71 \,^{\circ}\text{C}$ (10.2 % K₂CO₃) and $-49 \,^{\circ}\text{C}$ $(10.5\% K_3PO_4)$. Higher loadings may achieve a temperature suppression maximum of $\Delta T_{K_2CO_3} = -94$ °C and $\Delta T_{K_2PO_4} = -55$ °C. This implies that substantial energy savings for the synthesis of biochar via pyrolysis are to be expected as a result of this considerable temperature suppression. BET surface area, porosity and ion exchange capacity may have also been enhanced in-situ but is yet to be evaluated.

Keywords: Catalytic pyrolysis, biochar, K_2CO_3 , K_3PO_4 , $Ca(NO_3)_2 \cdot 4H_2O$, TGA

NONMENCLATURE

Abbreviations		
TGA	Thermogravimetric analysis	
dTG	Derivative thermogravimetry	
Symbols		
A _i	Pre-exponential constant	
$E_{\mathbf{A}_i}$	Activation energy	
i	Component subscript	
k _i	Reaction rate constant	
n _i	Reaction order	
R	Universal gas constant	
Т	Temperature	
t	Time	
ω _i	Mass fraction	
ω_{0i}	Initial mass fraction	

1. INTRODUCTION

Biochar has been used for millennia as a source of heat and for soil remediation [1]. Its synthesis is *via* the pyrolysis of biomass in an oxygen-deplete environment at elevated temperatures of between 400 °C and 800 °C [2]. The parameters that affect pyrolysis are

temperature, pressure, residence time, particle size, and biomass composition [3].

Indigenous tribes of the Amazon introduced biochars to the otherwise nutrient-deplete soils of the region and so produced what is now the *terra preta* and *terra mulata* [4]. In general, *terra preta* soils are lower in acidity, and exhibit higher nutrient levels and fertility compared with their parent soils [5]. Biochar's ability to enhance agricultural soils [6] is observed through an increase in (i) specific growth rates of crops, (ii) soilspecific area, which leads to improved drainage and aeration, and (iii) soil porosity, which promotes the growth of mycorrhizal fungi and other soil microbiota [7].

As with fossil fuels, global pseudo-finite phosphorus reserves cannot support food production indefinitely using the current practises and has encouraged interest into sustainable alternatives [8]. It is estimated that the world's phosphate ore reserves currently stand at 71 billion metric tons [9]. With a world production of 0.22 billion metric tons in 2021 [10], and no substitution for phosphorus in agriculture, an increase in speciality fertilisers is expected.

The Haber-Bosch process, used to manufacture Nfertilisers, is thermodynamically unfavourable at elevated temperatures, which are otherwise required to increase reaction rates [11]. The Le Chatelier's principle is exploited in this regard to overcome these thermodynamic limitations through the use of very high pressures, resulting in an extremely energy intensive process. [12]. It is estimated that only half of the applied fertilisers are utilised by crops [13]. The application of fertilisers to agricultural soils are prone to leaching [13] and causes many issues such as eutrophication of water bodies and disruption of soil microbiology [14].

Adoption of biochar in agriculture is perpetuated primary through the production costs and cost price demanded of biochar [15]. Large applications of neat biochar are required to offset fertiliser utilisation [16].

It is known that alkali compounds in ash promote selective biochar synthesis catalytically [17]. It may be

possible to use this aspect to lessen the energy requirements by decreasing the pyrolytic onset temperature. The use of fertiliser agents in the production of nutrient-enriched biochars are investigated to (i) decrease the onset temperature required for pyrolysis and (ii) mitigate inefficient adsorption by biochars when applied neat in the field prior to fertiliser applications.

The catalytic suppression of the pyrolytic onset temperature for *Eucalyptus grandis* is assessed using thermogravimetric analysis (TGA). Three fertiliser agents, namely potassium carbonate (K_2CO_3), calcium nitrate tetrahydrate ($Ca[NO_3]_2 \cdot 4H_2O$), and tripotassium phosphate(K_3PO_4), are investigated for their catalytic potential.

2. MATERIALS AND METHODS

2.1 Selection of candidate fertilisers

Four criteria were used in the selection of prospective fertilising agents, namely mass fractions, ω_i , of fertiliser elements NPK, price per total mass fraction of fertiliser elements, thermal stability & heat of fusion, and toxicity. In total 79 prospective compounds were assessed and K_2CO_3 , $Ca(NO_3)_2\cdot 4H_2O$ and K_3PO_4 were selected.

2.2 Sample preparation

E. grandis as sawdust (particle size distribution < 90 µm) with a moisture content of 7.1 % (±0.25 %) and ash content of 0.705 % (±0.025 %) was dried in an oven at 105 °C for 4 h. K_2CO_3 , $Ca(NO_3)_2 \cdot 4H_2O$ and K_3PO_4 were sourced from Merck & Co., Inc. Deionised water was used in all experiments.

2.2.1 <u>Heterogeneous mixing preparation</u>

The fertiliser agents were pounded and ground together with the *E. grandis* sawdust at concentrations of 1%, 2%, 5% and 10% on a mass basis using a mortar and pestle for 5 min. Processed samples were stored in a desiccator prior to TGA runs.

2.2.2 <u>Pseudo-homogenous mixing preparation</u>

Solutions of K_2CO_3 , $Ca(NO_3)_2\cdot 4H_2O$ and K_3PO_4 were prepared in 250 mL volumetric flasks. The solutions were prepared such that volumes of 5 mL of fertiliser agents in mass percentages of approximately 1~%, 2~%, 5~% and 10~% were added to biomass samples. The samples were mixed thoroughly and dried in an oven at $105~^\circ\text{C}$ for 24~h to ensure the removal of moisture from the processed samples. The final ash contents for K_2CO_3 , $Ca(NO_3)_2\cdot 4H_2O$ and K_3PO_4 were determined by ashing the processed samples at $825~^\circ\text{C}$ for 24~h in a muffle furnace (Table 1).

Tab. 1 Ash contents of processed samples.

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Target %	K ₂ CO ₃	K ₃ PO ₄	$Ca(NO_3)_2$
1 %	1.7 %	1.7 %	2.7 %
2 %	2.6 %	2.7 %	2.8 %
5 %	5.4 %	5.6 %	3.1 %
10 %	10.2~%	10.5~%	3.7 %

2.3 Thermogravimetric analysis

TGA was performed using a Hitachi STA7300 horizontal-beam TGA-DTA system, and alumina crucibles (5 mm height \times 6 mm outer diameter). Nitrogen gas flow was kept constant at a volumetric rate of 80 mL min⁻¹. Samples of 5.5 mg \pm 0.5 mg were preheated to 30 °C and a heating rate of 5 °C min⁻¹ up to an isothermal temperature of 750 °C was used throughout the analyses.

The dTG data for neat biomass (Fig. 1) presents 3 characteristic peaks associated with water loss at T = 44.0 °C, degradation of hemicellulose at T = 261 °C; and two convoluted peaks associated with cellulose-lignin degradation at T = 325 °C and maximum weight loss.



Fig. 1 TG and dTG analysis for neat biomass.

2.4 Deconvolution model of TG and dTG data

The deconvolution of the peaks associated with the chemical constituents of biomass was necessary to obtain the reaction kinetics used to confirm whether fertilising agents had a catalytic effect on pyrolysis or not. The change in component i with respect to time is assumed to have a characteristic rate of reaction described by

$$-\frac{\mathrm{d}\omega_i}{\mathrm{d}t} = k_i \omega_i^{n_i} \tag{1}$$

where k_i is the reaction rate constant, n_i is the reaction order, and ω_i is the mass fraction of the chemical constituents, namely cellulose, hemicellulose and lignin. The mass fractions as a function of time, t, are described by

$$\omega_i = \left(\omega_0_i^{1-n_i} - [1-n_i]kt\right)^{(1-n_i)^{-1}}$$
(2)

with ω_{0_i} the initial mass fraction of each component. Python programming language and Microsoft Excel (365) were used to determine the reaction orders, n_i , mass fractions for the aforementioned equations, as well as the activation energies, E_{A_i} , and pre-exponential factor, A_i (Fig. 2), for the equation

$$k_i(T) = A_i \mathrm{e}^{-E_{\mathrm{A}i}/RT} \tag{3}$$

The reaction orders, activation energies, preexponential factors and the mass fractions were estimated for cellulose ($n_{\rm C} = 1.13$; $E_{\rm A_C} =$ 254 MJ kmol⁻¹; $A_{\rm C} = 3.06 \times 10^{18} \, {\rm s}^{-1}$; $\omega_{\rm C} = 0.48$), hemicellulose ($n_{\rm H} = 0.78$; $E_{\rm A_{\rm H}} = 112 \, {\rm MJ \, kmol^{-1}}$; $A_{\rm H} = 5.85 \times 10^7 \, {\rm s}^{-1}$; $\omega_{\rm C} = 0.17$) and lignin ($n_{\rm C} =$ 0.78; $E_{\rm A_{\rm L}} = 116 \, {\rm MJ \, kmol^{-1}}$; $A_{\rm L} = 2.19 \times 10^7 \, {\rm s}^{-1}$; $\omega_{\rm L} = 0.27$) on a wet basis with a moisture content of $\omega_{\rm H_2O} = 0.07$ (Fig. 2).



Fig. 2 Deconvolution of dTG for neat biomass.

3. RESULTS AND DISCUSSION

The data produced for the heterogeneous mixing approach was unreliable as weak alterations of peaks were observed for 1%, 2%, and 5%, respectively, while much stronger catalytic suppression of the pyrolytic temperature was observed for 10% (Fig. 3). It is possible that inadequate mixing of the fertilising agents and biomass was responsible for these results. However, these data suggest that some catalytic suppression of the pyrolytic temperature may be possible if the mixing procedure is enhanced. An alternative method of introducing fertiliser agents was formulated according to the pseudo-homogeneous mixing approach, whereby fertiliser agents are introduced into the biomass in solution.



Fig. 3 dTG data for heterogeneous mixing approach.

Suppression of the pyrolytic temperature in the case of K_2CO_3 and K_3PO_4 is observed to be dosagedependent (Fig. 4) with shifts in the cellulose-lignin peak: Fig. 5B $\Delta T_{K_2CO_3} = -11 \,^{\circ}C (1.7 \,\%), -25 \,^{\circ}C (2.6 \,\%),$ $-48 \,^{\circ}\text{C}$ (5.4 %), and $-71 \,^{\circ}\text{C}$ (10.2 %); Fig. 5D: $\Delta T_{\text{K}_2\text{PO}_4} = -2 \text{ °C} (1.7 \text{ \%}), -10 \text{ °C} (2.7 \text{ \%}), -33 \text{ °C}$ (5.6%), and -49 °C (10.5%). The effect of $Ca(NO_3)_2$ on the pyrolytic temperature associated with the cellulose-lignin peak is negligible (Fig. 5F). Furthermore, the TGA data provides insight into the ash content of the samples. Fig. 5A & 5C confirm that an increase in fertilising loading leads to a higher ash content and therefore resulting in a larger final mass, as expected. This observation is not as pronounced for $Ca(NO_3)_2 \cdot 4H_2O$ (Fig. 5E) as with the other cases. This might suggest denaturing of the compound in question and the possible inactivation of catalysis prior to pyrolysis. A model was used to estimate the maximum temperature suppression by utilising the pyrolytic temperature of a control sample to extrapolate the data. Using the trendlines of K_2CO_3 and K_3PO_4 plotted in Fig. 4, the maximum suppression in the pyrolytic onset temperature was determined to be $\Delta T = -94$ °C and $\Delta T = -55$ °C, respectively.

Both K_2CO_3 and K_3PO_4 are alkaline, whereas $Ca(NO_3)_2 \cdot 4H_2O$ is netrual when dissolved in deionised water. This is due to K_2CO_3 and K_3PO_4 being produced from a weak acid and strong base, while $Ca(NO_3)_2 \cdot 4H_2O$ is generated by a strong acid and base. Saccharides are susceptible to both acid- and alkaline-hydrolysis. Furthermore, the close proximity of the acetyl groups to the xylan polymer ensures that lysis occurs before alkaline hydrolysis can take place [18]. The presence of pyrolytic vapours, including water (as a result of hemicellulose pyrolysis), in tandem with alkaline compounds, is the possible reason for the suppression of pyrolytic temperature with respect to cellulose.



Fig. 4 Modelled temperature suppression of major pyrolysis peak as a function of fertiliser content.

4. CONCLUSION AND RECOMMENDATIONS

 $\rm K_2CO_3$ and $\rm K_3PO_4$ both achieved a reduction in the pyrolytic onset temperature of *E. grandis*. With a loading of 10.2 % $\rm K_2CO_3$ and 10.5 % $\rm K_3PO_4$, a suppression temperature of $\Delta T=-71\,^{\rm o}C$ and $\Delta T=-49\,^{\rm o}C$ was observed. $\rm Ca(\rm NO_3)_2\cdot 4H_2O$ did not produce as pronounced catalytic temperature

suppression as K_2CO_3 and K_3PO_4 . A maximum suppression of -94 °C (10.2 %) and -55 °C (10.5 %) was calculated for K_2CO_3 and K_3PO_4 , respectively. More experimental work on the relationship between pH and pyrolytic suppression should be conducted. A technoeconomic impact of fertiliser-catalysed suppression of the pyrolytic temperature should be assessed to determine how this technology could decrease the cost price of biochar. The effect that preloading fertiliser agents has on the physical morphology (*i.e.*, BET surface area, porosity, *etc.*) and adsorptivity needs to be investigated.

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Fig. 5 TG and dTG analyses for Eucalyptus grandis pre-loaded with K_2CO_3 (A & B), K_3PO_4 (C & D), and $Ca(NO_3)_2$ (E & F), respectively. The modulus is used for all dTG data sets.

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