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# Reactivity during bench-scale combustion of biomass fuels for carbon capture and storage applications

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## HIGHLIGHTS

- 16 • Combustion reactivity of 4 biomasses investigated with TGA.
- 17 • Conventional and CCS combustion environments analysed.
- 18 • Willow and grassy energy crops well characterised by modified Coats-Redfern method.
- 19 • Oxygen enrichment increases reactivity of volatiles and char.
- Substituting N<sub>2</sub> with CO<sub>2</sub> has complex effect on reactivity. 20
- 21

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## ABSTRACT

Reactivities of four biomass samples were investigated in four combustion atmospheres using non-isothermal thermogravimetric analysis (TGA) under two heating rates. The chosen combustion atmospheres reflect carbon capture and storage (CCS) applications and include O2 and CO2-enrichment. Application of the Coats-Redfern method assessed changes in reactivity. Reactivity varied due to heating rate: the reactivity of char oxidation was lower at higher heating rates while devolatilisation reactions were less affected. In general, and particularly at the higher heating rate, increasing [O<sub>2</sub>] increased combustion reactivity. A lesser effect was observed when substituting  $N_2$  for  $CO_2$  as the comburent; in unenriched conditions this tended to reduce char oxidation reactivity while in O2-enriched conditions the reactivity marginally increased. Combustion in a typical, dry oxyfuel environment (30% O<sub>2</sub>, 70% CO<sub>2</sub>) was more reactive than in air in TGA experiments. These biomass results should interest researchers seeking to understand phenomena occurring in larger scale CCS-relevant experiments.

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### 1. Introduction

53 Combatting anthropogenic climate change and satisfying the 54 forecast growth in global energy demand requires novel solutions for many established industries. Increasing pressure to limit and 55 reduce greenhouse gas (GHG) emissions – particularly CO<sub>2</sub> – from 56 power generation are widely understood to present a need to move 57 58 away from unabated fossil fuel use. Reducing the emissions of CO<sub>2</sub> while maintaining a fleet of flexible thermal plant - required to 59 balance and mitigate the variability of renewables generation 60 against the inflexibility of nuclear generation - is seen as impor-61 62 tant by many nations. Two leading options to achieve this goal are to replace some or all of the fossil fuels with sustainably 63

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http://dx.doi.org/10.1016/j.fuel.2014.05.050 0016-2361/© 2014 Published by Elsevier Ltd. sourced carbonaceous fuels such as biomass or to capture and permanently store the CO<sub>2</sub> resulting from the combustion process. While neither biomass cofiring nor carbon capture and storage (CCS) are truly sustainable in the long-term (only dedicated biomass firing without CCS could be envisioned as such) they represent one of the strongest options developed nations possess to reduce their GHG emissions while largely maintaining the quality of life of their citizens in the coming decades. Indeed, "[w]ithout CCS, overall costs to halve CO<sub>2</sub> emission levels by 2050 increase by 70%" [1]. Separately these processes could ideally offer substantial reductions in the emissions of CO<sub>2</sub> from electricity generation, but combined Bio-CCS projects could represent a net removal of CO<sub>2</sub> from the atmosphere. A net reduction of atmospheric CO<sub>2</sub> during Bio-CCS occurs as the CO<sub>2</sub> absorbed by plants during their photosynthetic growth stage is ultimately prevented from returning to the atmosphere being stored instead in deep geological formations.

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80 This is important since Bio-CCS is claimed to be "the only large-81 scale technology that can remove  $CO_2$  from the atmosphere" [2] 82 and with sustainably sourced fuels is able to produce power with 83 lower GHG emissions than all other low-carbon generation tech-84 nologies [3].

85 In the UK, early decarbonisation of the electricity system is seen 86 as a priority in meeting the 2050 80% reduction targets since other 87 sectors (e.g. transport and domestic heating) will require low-carbon electricity in order to reduce their sector's carbon intensity [4]. 88 Many technology roadmaps for the UK and globally strengthen the 89 90 view that Bio-CCS is a necessary technology option for combatting 91 climate change in the UK and around the world [1,2,5,6].

#### 92 1.1. Knowledge to date

93 Conventional combustion of 100% biomass and cofiring with 94 fossil fuels is widely practised on an industrial scale. However, 95 CCS is still a developing technology which contains a wide range of configurational options and areas requiring further research 96 97 [7]. A leading CCS technology option is oxyfuel combustion where, 98 instead of selectively extracting CO<sub>2</sub> from a relatively dilute flue 99 gas, the fuel is burnt in an environment that largely comprises of 100 oxygen diluted by recycled flue gas (predominantly CO<sub>2</sub>) which 101 acts as a thermal diluent to match adiabatic flame temperatures 102 to those seen in air-firing [8]. Through removing the largely inert 103 nitrogen from the combustion process oxyfuel combustion is able 104 to produce a flue gas far richer in CO<sub>2</sub> than conventional combus-105 tion processes requiring more conventional and economic gas 106 clean up systems than envisioned for other CCS systems [9,10].

107 As well as new power stations, the current fleet will continue to 108 emit CO<sub>2</sub> unless mitigating options are taken. While some plant will be suitable for total retrofitting of technologies such as oxyfu-109 110 el, in other situations alternative CCS options such as post-combus-111 tion capture (PCC) may be preferred. PCC typically uses a chemical 112 or physical agent to selectively remove CO<sub>2</sub> from the flue gas. How-113 ever, one drawback to this method is the magnitude of the cost and 114 size of a CO<sub>2</sub>-scrubbing plant that is necessarily large due to the 115 relatively dilute  $CO_2$  in conventional flue gas (typically ~10%). 116 One possibility for development in this area is to enrich the com-117 bustion air with oxygen, reducing the nitrogen content of the flue gas and hence concentrating CO<sub>2</sub> which could reduce the size and 118 119 cost of PCC components, albeit at the extra cost of supplying oxy-120 gen. However, in addition to the potential logistical benefits, this technology option has been demonstrated to enhance combustion 121 122 efficiency while simultaneously reduce nitrous oxide emissions 123 when oxidant staging with over-fired air is used [11,12].

#### 1.2. Experimental background 124

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125 While bench-scale combustion techniques differ from full-scale plant in a number of ways, thermogravimetric analysis is a useful 126 analogue for full-scale combustion that has been widely adopted 127 128 to assess trends in fuel reactivity in both air and oxyfuel combus-129 tion scenarios, for example [13-15]. As standalone technologies biomass combustion and CCS have received much attention. How-130 131 ever, a knowledge gap exists where little technical data has been published that concentrates on biomass combustion in situations 132 133 applicable to CCS. In this work the behaviour of four biomass fuels 134 in four combustion atmospheres which are useful to the develop-135 ment of CCS technologies are investigated to provide preliminary 136 indications of their behaviour in novel combinations of fuel and 137 combustion atmospheres. This work forms a part of a suite in 138 which the fuels and combustion environments investigated at 139 bench-scale are then used to inform the results of similar combus-140 tion tests carried out at pilot-scale [16].

Addressing climate change is a global challenge and the fuels 141 tested in this study, while typical in the UK energy mix, are com-142 mon outside of the UK so it is hoped the findings will be of wider 143 interest. 144

#### 2. Materials and methods

Three biomass resources – short rotation coppiced willow 146 (SRC), miscanthus (MC) and reed canary grass (RCG) – were grown 147 in the North of England by the BioReGen project [17]. Shea Meal 148 (SM) supplied by RWE NPower was also included to compare with 149 previous work [18]. Proximate analysis of the fuels was carried out 150 by TGA analysis of mass loss in a nitrogen atmosphere with a tem-151 perature ramp rate of 20 K min<sup>-1</sup>. Analysis of the lignocellulosic 152 contents of biomass was conducted by several wet chemistry 153 stages, as detailed in [19]. Results of analysis of the fuels are shown 154 in Table 1. The negative value for lignin derived using the acid 155 detergent lignin (ADL) method arises as the ADL measured value 156 is less than the ash content of the fuel which suggests some of 157 the ash components are solubilised by acid solutions. While this 158 is less apparent for the samples containing lower amounts of ash, 159 the negative value for RCG is thought to be due to the relatively 160 high ash content (8.1%) acid solubility of particularly Ca and Na 161 [20]. While the Klason and ADL methods for measuring lignin 162 appear similar, differences of the magnitude observed ineftab:fuels 163 are common, see for example [19]. 164

#### 2.1. Sample preparation

All of the UK-grown biomasses were harvested, dried and 166 milled to pass through a sieve of 0.5 mm. In an attempt to separate 167 experimental physical characteristics from those of a chemical nat-168 ure and to ensure homogeneity in small sample sizes, it was neces-169 sary to further reduce the size of the particles. Mass transfer effects 170 during thermal treatment have been shown to be largely mitigated 171 once particle size is reduced to approximately 200 µu [21]. To 172 avoid the escape of volatile species and/or waxy deposits, the bio-173 mass samples were milled using a SPEX 6770 Freezer Mill which 174 uses liquid nitrogen to ensure samples remain solid during milling 175 [22,23]. All samples were milled until they passed easily through a 176 212 µm sieve. 177

Table 1	l
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Combined results of fuel characterisation studies

Fuel	SRC	MC	RCG	SM			
Proximate analysis (%), ar							
Moisture	6.0	5.5	5.8	7.5			
Volatile matter (VM)	72.4	74	68.5	53.8			
Fixed carbon (FC)	18.7	17.3	17.6	31.9			
Ash	2.9	3.3	8.1	6.9			
Ultimate analysis (%), ar							
С	47.7	46.4	42.2	48.6 <sup>a</sup>			
Н	6.0	5.8	5.4	5.9 <sup>a</sup>			
N	0.4	0.3	1.4	2.9 <sup>a</sup>			
S	0.0	0.0	0.0	0.2 <sup>a</sup>			
O <sup>b</sup>	43.0	44.3	42.8	37.5 <sup>a</sup>			
C:H	8.0	8.0	7.8	8.3 <sup>a</sup>			
C:0	1.1	1.0	1.0	1.3 <sup>a</sup>			
Lignocellulosic content (%), ar							
Hemicellulose	11.7	22.4	27.5	10.9			
Cellulose	48.0	47.6	31.2	2.9			
Lignin (ADL)	14.0	6.0	-2.0	24.4			
Lignin (Klason)	27.2	23.0	20.0	41.6			

<sup>a</sup> Shea meal data from [11].

<sup>b</sup> By difference.

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