Pretreatment of lignocellulosic agricultural residues using coal fly ash to enhance methane production by anaerobic digestion

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Lignocellulosic agricultural residues are plant biomass that are rich in fibre and predominantly consist of cellulose, hemicellulose and lignin. These residues, such as straw from cereal crop production, represent a valuable source of renewable bioenergy, which is currently untapped in many economically developing countries, that could offer and improve long-term energy security. In Indonesia, for example, approximately 73% of agricultural crop residues are disposed by *in situ* burning (Yevich and Logan, 2003) causing serious air pollution with major negative impacts on human health and climate change.

One of the approaches to convert lignocellulosic agricultural residues to bioenergy is by methane (CH_4) production from the anaerobic digestion (AD) process. However, the residues, are recalcitrant to AD, and CH_4 conversion rates are limited because the lignin is strongly bound to the cellulose and hemicellulose fractions and provides a protective barrier to microbial attack (Shetty *et al*., 2017). Alkaline pretreatment of lignocellulosic agricultural residues using pure chemicals such as sodium hydroxide (NaOH) and calcium oxide (CaO), prior to AD, breaks down the lignin structure to increase the accessibility of cellulose and hemicellulose to enzymatic attack and is an effective method to increase biodegradability and CH_4 production (Dai *et al*., 2018; Guan *et al.*, 2018; Shetty *et al.*, 2017). The use of pure chemicals for large-scale pretreatment, however, is not cost-effective or environmentally sustainable due to high chemical cost and the use of new resources in chemical production.

Significant opportunities exist to identify secondary materials as suitable alternatives for alkaline pretreatment, and this would also provide major economic and environmental advantages compared to pure chemicals. Coal fly ash (CFA), for example, represents a significant global disposal issue and is also particularly problematic in Indonesia (Sukandar, 2018). The presence of calcium oxide (CaO) in CFA could provide an alternative source of alkali that is suitable as a pretreatment of lignocellulosic waste for AD. However, CFA and lignocellulosic agricultural residues are both very low in nitrogen, which is an essential nutrient requirement for the AD process. For example, lignocellulosic agricultural residues typically have a high carbon-to-nitrogen (C/N) ratio (43.4-81.45) compared to the optimum ratio required for bacterial growth (25-30). The imbalance in C/N ratio can be rectified by the addition of other N-rich waste materials (Yang *et al*., 2014; Yong *et al*., 2015), such as food waste, which is also a major polluting waste stream in Indonesia. In addition to providing alkalinity for pretreatment, CFA contains trace elements such as iron, zinc, nickel, cobalt, molybdenum, selenium and tungsten, that are essential to methanogenesis and other important microbial transformations in AD, and trace element supplementation can further increase CH_4 production (Huiliñir *et al.*, 2017).

The integrated use of CFA as an alkali pretreatment of lignocellulosic agricultural residues combined with food waste processed simultaneously in AD (co-digestion) has not been previously investigated. The first phase of this research therefore aims to determine the effects of CFA on the biodegradability of lignocellulosic agricultural residues to enhance CH_4 production during AD. Barley straw was used as a standard, consistent and representative type of lignocellulosic agricultural residue. Coal fly ash was supplied from the largest power plant in the UK, situated in North Yorkshire. The effects of CFA pretreatment on CH_4 production and biodegradability rates from straw were evaluated by mixing CFA at rates of 0.1, 0.25 and 0.5 g CFA/g barley straw with deionised water to obtain a solid to liquid ratio of 1:7 to saturate the barley straw. The mixtures were shaken for 12 hours and blended with barley straw that was ground and sieved into 1 mm particle size. The control condition only included deionized water, without CFA amendment. The duration of the pretreatment period was 7 days, and the incubation temperature was maintained at 30ºC, representative of ambient conditions in Indonesia. The effect of the pretreatment conditions on the properties of the barley straw was determined by measuring the cellulose, hemicellulose and lignin (fibre) contents, according to Van Soest *et al*. (1991). Anaerobic digestion tests were conducted in 1 L glass microcosms with a working volume of 600 mL as batch experiments. The anaerobic biomass inoculum source was digested sludge, which would also supplied major nutrients, such as nitrogen and phosphorus. Biogas volume measurements were taken daily using a novel water displacement system adapted from Song *et al*. (2013).

The results showed that the alkalinity concentration of CFA solutions at the dose rates of 0.10, 0.25 and 0.50 g CFA/g barley straw were equivalent to 101, 206, and 394 mg/L $CaCO_3$, respectively, which were considerably smaller than has been previously reported for the pretreatment of lignocellulosic to reduce the fibre content (~1500 mg/L $CaCO_3$) (Xin *et al*., 2019). The low alkalinity of the CFA may be explained because the samples were collected from long-term storage stock-piles, which will reduce the alkaline reaction due to the hydrolysis of CaO and subsequent carbonation of calcium hydroxide ($Ca(OH)_2$) (You *et al.*, 2006). Fibre measurements of pretreated CFA also showed there were no significant change in the mass of fibre fractions compared to the untreated control. Thus, it is important to collect fresh CFA to maximise the effectiveness of the material as an alkaline pretreatment for AD. Therefore, the experiment was repeated by the direct addition of supplemental CaO, which is predominant source of alkalinity in fresh CFA, to increase the alkalinity. The amount of CaO added to the UK CFA sample was adjusted to 15% to represent the CaO content found in CFA from a power plant in Indonesia (Risdanareni *et al.*, 2017). At this CaO content, the alkalinity concentrations provided by the dose rates of: 0.1, 0.25, and 0.50 g CFA/g barley straw were equivalent to approximately: 2,300, 6,000 and 12,000 mg/L (denoted as: S1, S2, and S3, respectively). Fibre measurements for the experimental treatments, including the water control, are shown in Figure 1. The reduction in hemicellulose content of straw increased with dose rate and a maximum loss of 37% was recorded for S3 compared to the control. The lignin content also decreased by up to 19.4% with increasing alkalinity dose, compared to the control, however, no significant change in cellulose content was observed. The results suggested that the overall biodegradability of fibres may be improved by the delignification of the straw, by increasing access of anaerobic microorganisms to cellulose and remaining and solubilised hemicellulose fractions as carbon sources.

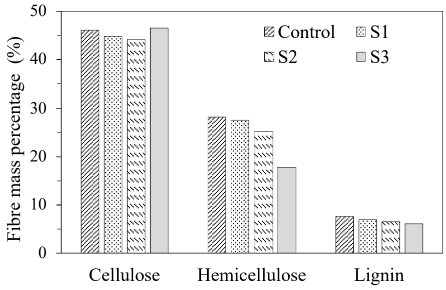

Fig 1. Effect of alkaline pretreatment by CFA and supplemental CaO on the fibre contents of barley straw (S1, 2,300; S2, 6,000; S3, 12,000 mg $CaCO_3$ /l; Control was pretreated with water)

Batch AD experiments were carried out on the S2 and S3 pretreated straw materials; S1 was omitted due to the relatively small reduction in hemicellulose (3.3%) observed in the pretreatment experiment. However, additional pretreatment conditions were included in the AD experiment to specifically examine the contribution of CFA to the AD process. Therefore, treatments analogous to S2 and S3 were prepared, but without CFA, denoted as S4 and S5 (approximately 6,000 mg/L and 12,000 mg/L $CaCO_3$, respectively). A modified Gompertz model was used to represent the patterns in experimental cumulative specific biogas yield data (Figure 2), which provided an exceptionally high degree of statistical confidence with coefficient of determination (R^2) values above 0.99, except for the control, which was 0.97.

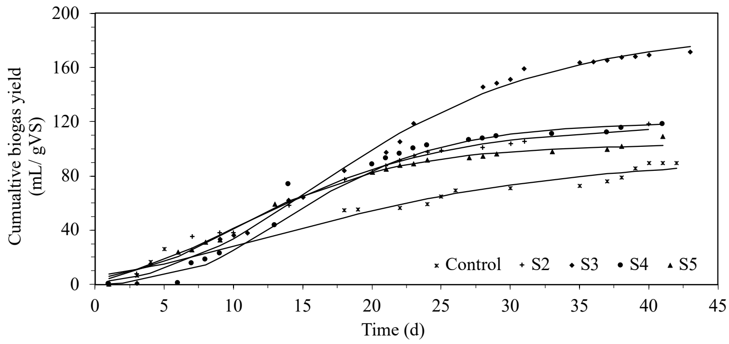

Fig 2. Modified Gompertz model fitted to cumulative biogas yield from anaerobic digestion of barley straw, pretreated with different CFA dose rates supplemented with CaO (S2, 6000; S3,12,000 mg $CaCO_3$/l) and analogous treatments to S2 (S4) and S3 (S5) without CFA.

The largest cumulative specific biogas yield (171.4 mL biogas/g VS) was observed for treatment S3 (CFA+CaO) at the largest alkalinity dose rate, which increased the specific biogas yield compared to S2 and the control by 45% and 92%, respectively. Interestingly, the biogas yield of S3 was also increased by 57% compared to S5 (109.2 mL biogas/g VS), strongly indicating that CFA has other beneficial effects in enhancing the AD of lignocellulosic waste in addition to supplying alkalinity, for example, trace element supplementation. This potential contribution will also be tested in the next phase of the research, using fresh samples of CFA to maximise the alkaline pretreatment potential of the material. The digestate residue by-product will also be examined for its potential fertiliser value, and soil contamination constraints with heavy metals will be investigated, to assess whether CFA pretreatment of lignocellulosic agricultural wastes is a practical and sustainable option for resource recovery and renewable energy production.

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