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Characterisation of lignocellulosic sugars from municipal solid waste residue

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ABSTRACT

Municipal solid waste (MSW) contains significant quantities of plant-derived carbohydrates which have the potential to be exploited as a biomass source. This study evaluated the chemical composition and fractionation of MSW water-insoluble organic matter remaining after recycling of other components (MSWR). The organic matter was prepared as a dry, alcohol insoluble residue (MSWR-AIR, comprising $w = 6\%$ of original MSW) and size fractionated into fractions A, B, C & D. Carbohydrates were present in all the sub-fractions, comprising up to $w = 54\%$; their complexity was also assessed by FT-IR spectroscopy. The lignin content in the samples ranged from $w = 11\text{--}22\%$. The most carbohydrate-rich subfraction (C; $w = 4\%$ original MSW) was sequentially extracted to provide information on the likely constituent cell wall-derived polymers, sugar compositions and uronic acid content. The results indicate that approximately $w = 25\%$ of the MSWR-AIR comprises glucose, which appears to be mostly cellulosic in origin. The results are discussed in relation to the potential for exploitation.

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1. Introduction

Production of liquid fuels such as ethanol from renewable and waste materials (which may contain cellulosic material) has the potential to reduce the growing world dependence on petroleum [1]. There is a great need for renewable energy supplies that do not cause significant environmental harm and do not compete with food supplies. Ethanol from such municipal waste is likely to have a lower carbon footprint than that produced from energy crops or simple sugars because of its waste status. Furthermore, the production of such ethanol is likely to have lower greenhouse gas emissions than landfilling [2].

According to the Zero Waste Scotland 2010 final report [3], the main components of MSW in Scotland are paper and card (21%) and food/kitchen waste (18%); which between them represent approximately 39% by weight of total MSW arisings. The overall composition of MSW in Scotland is similar to both that determined in a study in Wales in 2002/03 and the composition determined by the Defra review of compositional analyses (mostly conducted in England) published in 2009 [4]. It is clear that there is a drive to recycle the municipal waste in the UK to significantly reduce the amount currently sent to landfill.

A large proportion of MSW, including dry paper and card, metal and plastic, can be readily recovered for recycling.

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However, a significant proportion of (usually wet) residual material rich in organic material may remain. An extensive understanding of the overall composition and carbohydrate constituents of such material is lacking. Such knowledge is required for the generation of potentially valuable fractions or exploitation for example in ethanol production. The aim of this study was to evaluate the chemical compositions of alcohol-insoluble residues (AIR) prepared from an organic-rich mass fraction of MSW. The AIR was also size-fractionated, and the main fibre-based fraction (Fraction C) sequentially extracted in order to separate the main polysaccharide components and to characterise their carbohydrate and phenolic compositions.

2. Materials and methods

2.1. Sample

Municipal solid waste residue (MSWR) was provided by BIFFA Limited (Leicester, England). The process involved the use of industrial fractionation to remove the bulk of metal, plastic (including bags), bulk card/paper and water soluble components. The material was collected from the area around Leicester during 2008–9. The MSWR had a moisture content of $w = 64.5\%$ and the dry matter component comprised approximately $w = 7\%$ of the original MSW, although was subject to some seasonal variation. Prior to evaluation, three batches of MSWR were prepared as an alcohol-insoluble residue (MSWR-AIR) [5], in order to sterilize the material, after which it was washed in acetone, and air-dried overnight. The dried MSWR-AIR was then size-fractionated into four fractions using Laboratory Test Sieves (Endecotts Ltd., London, England; brass bodied, stainless steel mesh, aperture sizes 4 mm, 2 mm and 1 mm).

2.2. Composition evaluation of MSWR-AIR fractions

All the sample fractions were observed by microscopy for their physical content and analysed for neutral sugars, uronic acids, phenolic acids, lignin and ash compositions using standard methods. Samples were analysed in triplicate and the data is presented as means with standard deviations.

2.3. Light microscopy

To visually evaluate the main component structures of the size-fractionated sub-fractions A–D, they were examined at low power with a stereo microscope (Wild, Heerbrugg, Switzerland). Sub-fractions were mounted in water, light paraffin oil, or dilute iodine/potassium iodide (I/KI) and observed and recorded using the higher magnification of the bright field or polarising optics of an Olympus BX60 (Japan) with ProgRes® Capture Pro 2.1 software (Jenoptik, Germany). The presence of yeast and molds in the fractions were observed by Cotton Blue acid dye that stains the chitin in cell walls of fungi. Lignified components in the fractions were identified by their pink colouration after staining with phloroglucinol-HCl. Autofluorescence of the fibrous material was recorded at neutral

and alkaline pH using the UV filter cube (U-MWU, exciter filter BP330-385, barrier filter BA420) of the microscope.

2.4. Neutral sugars analysis

Analysis of neutral sugars released from MSWR-AIR was carried out by suspending 2 mg into 200 mm³ of $w = 72\%$ sulphuric acid (H₂SO₄) for 3 h at room temperature followed by dilution to 1 mol L⁻¹ and hydrolysis at 100 °C for a total of 2.5 h. Sugars were reduced with NaBH₄ and acetylated by the method of Blakeney et al. [6] using 2-deoxyglucose (200 mm³, 1 g L⁻¹) as an internal standard. Alditol acetates were quantified by gas chromatography (Perkin Elmer, P.E. Auto system XL Gas Chromatograph) using P.E. TotalChrom Workstation software, version 6.2.1 to process the data. Each sample (2 mm³) was injected onto a RESTEK rtx-225 (15 m 320 μm i.d.) column under helium gas. The flow rate was 2 cm³ min⁻¹; the injection temperature was 250 °C; the run time was 50 min. A flame ionisation detector (FID) was used for detection. Samples were analysed in triplicate.

2.5. Uronic acid analysis

Total uronic acid content was determined colorimetrically by the method of Blumenkranz and Asboe-Hansen [7] after dispersal in 200 cm³ of 72% H₂SO₄, dilution to 1 mol L⁻¹ and hydrolysis for 1 h at 100 °C. Samples were analysed in triplicate.

2.6. Phenolic acid analysis

The total alkali-extractable hydroxycinnamate content of fractions was determined by hydrolysis with 4 mol L⁻¹ sodium hydroxide (NaOH) for 24 h at room temperature. Samples were centrifuged, neutralised and partitioned into ethyl acetate by liquid–liquid solvent extraction before being reduced to dryness and resuspended in MeOH:H₂O (50/50, v/v). Samples were then injected onto a LUNA (2) 5C18 reverse phase HPLC column (Phenomenex, Macclesfield, UK) and eluted with a programmed gradient [8]. Ferulic and *p*-coumaric acid levels were quantified against standard curves. Ferulic acid dehydromers were quantified according to the method of Waldron et al. [8]. Samples were analysed in triplicate.

2.7. Klason lignin analysis

Klason lignin was quantified gravimetrically by a modification of the method of Theander and Westerlund [9]. Samples of approximately 100 mg were dispersed into 0.75 cm³ of 72% H₂SO₄ and incubated at room temperature for 3 h shaking frequently. The samples were further incubated for 2.5 h after diluting with 9.0 ml water, in a temperature-controlled oven set at 100 °C. The residues were recovered by filtration through pre-weighed sintered glass funnels (10 mm diameter, Fisher Scientific) under vacuum. The insoluble material was washed with warm water until the residue was free of acid. The glass filters were dried at 50 °C in a temperature-controlled oven overnight or until a constant weight was obtained and Klason lignin calculated gravimetrically (Eq. (1)). Samples were analysed in triplicate.

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