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Impact of vegetation type and pre-processing on product yields and properties following hydrothermal conversion of conservation biomass

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Highlights

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Biomass is generated during management of low input high diversity (LIHD) vegetation.

LIHD biomass was subjected to hydrothermal carbonisation and liquefaction.

Pre-processing had little impact on related product yields and composition.

Vegetation type had a greater effect on product chemistry.

Utilising this type of unwanted biomass supports ecosystem service delivery.

Abstract

Changes in agricultural practices and land abandonment across less favoured areas have led to an increase in land management for nature conservation. Substantial areas of vegetation are cut annually for habitat management, but the conservation biomass generated is generally discarded. Samples of two types of conservation biomass harvested from marginal sites dominated by rushes (*Juncus* spp) or bracken (*Pteridium aquilinum*) were washed and pressed to generate fluid and fibrous process streams using the Integrated Generation of Solid Fuel and Biogas from Biomass (IFBB) process. Previous work established the fluid from the IFBB process could be anaerobically digested to generate enough energy for the washing and pressing stages. The current study focussed on the fibrous process stream, subjecting material to hydrothermal conversion and investigated the extent to which i) vegetation type, ii) the impact of pre-treatment by hot water washing and pressing (partial demineralisation) and iii) hydrothermal conversion route (hydrothermal carbonisation or hydrothermal liquefaction) affected the yields, relative proportions, and characteristics of products generated. Feedstock source had substantially more effect on product chemistry than product yields. The most effective process route for combustion fuel production was based on hydrothermal carbonisation of pre-processed feedstock. However, if bio-oil production was to be the priority product in a biorefinery, then biomass pre-processing would not be required.

Keywords

Conservation biomass, Habitat management, Hydrothermal carbonisation, Hydrothermal liquefaction, Bioenergy, Ecosystem services

1. Introduction

Natural resources are limited and there is a need to maximise available biomass types to help mitigate climate change. A key challenge of our time is to deliver a bioeconomy sustainably without jeopardising food security and whilst maximising environmental benefits. One bioenergy feedstock which addresses this challenge is conservation biomass [1,2]. By using the waste created from habitat management to generate bioenergy and bioproducts many additional benefits can be leveraged including the safeguarding of broader ecosystem services such as biodiversity, flood prevention and preservation of existing carbon stocks. However, this potential is currently curtailed by a lack of knowledge of the ways in which these novel feedstocks respond to different processing options, and the yields and properties of product streams produced.

Different native vegetation communities consist of mixtures of different plant species with different chemical properties, yet they frequently share common characteristics. The type of low input high diversity (LIHD) biomass harvested from semi-natural vegetation types [3] typically contains a mixture of species that are comparatively low in water-soluble carbohydrates and high in minerals. This biomass is therefore considered unsuitable as a feedstock for anaerobic digestion due to low availability of sugars [4], and unsuitable as a solid fuel feedstock because the mineral composition is damaging to combustion chambers and leads to high emissions [5]. A green biorefinery platform represents an alternative processing route for such feedstocks [6], and would generally incorporate a screw press to provide an initial fractionation of the feedstock into fluid and fibrous sub-fractions. The Integrated Generation of Solid Fuel and Biogas from Biomass (IFBB) process employs such a procedure [7,8]. During the IFBB process partial demineralisation of biomass is achieved by washing and pressing, i.e. through hydrothermal pre-treatment followed by mechanical dehydration (HPMD). This produces a fibrous fraction (press cake) that can be employed as a solid fuel, and a fluid that can be anaerobically digested to generate biogas. This gas can be scrubbed and used for generating the energy needed for processing. Following the IFBB process the primary product for entry onto the general market is currently a solid fuel briquette. The current study was the first to explore alternative, and potentially complementary, hydrothermal conversion routes for LIHD generated from habitat management.

Hydrothermal (HT) conversion is a method of processing biomass to obtain products for energy generation, carbon sequestration or chemical production. Under these conditions the biomass is converted into a multiple product mix comprised of an aqueous solution, oil, gas and hydrochar [9]. The proportions of these products can be varied by altering the reactor temperature, and consequently the pressure. Oil production is favoured at temperatures of 280–370 °C and pressures ranging from 10 to 25 MPa [10] (hydrothermal liquefaction: HTL). Hydrochar production is instead favoured at temperatures of 180–250 °C and pressures of between 2 and 10 MPa [11] (hydrothermal carbonisation: HTC). A feedstock does not need to be dried prior to efficient conversion via HTC or HTL whereas if a biomass feedstock has a moisture composition of 70% or more, dry pyrolysis becomes prohibitively expensive energetically because there is no waste heat and/or product gas produced from the process [12]. Ensiled LIHD derived from semi-natural landscape and habitat management typically has moisture contents of 50–80% and would therefore be expected to be more suitable for HT conversion. Furthermore, since HT conversion is not reliant upon the presence of water-soluble carbohydrates it is an option for biomass low in sugars, such as LIHD.

To date, research relating to the hydrothermal processing of biological wastes has focussed on sewage sludge and manures [[13], [14], [15], [16]], plus some work with crop by-products such as straws and husks [17]. There has also been a concerted research effort centred around the potential of microalgae [[18], [19], [20], [21]]. However, the potential of biomass arising from grasslands and rangelands, which are among the largest ecosystems globally, has to date been largely overlooked. This is despite potential for LIHD mixtures of native grassland perennials to achieve greater greenhouse gas reductions and lower levels of agrichemical pollution than energy crops [3], and exploitation of waste grassland offering an answer to concern as to whether or not there is not enough land on which to grow energy given the increasing world population [22].

The current study complements findings from related work with conservation biomass determining the related potential for sustainable oil production via fast pyrolysis [23]. The research reported here was conducted using the same material, which had been harvested from two distinctive habitats containing multiple species common in the UK. One of the feedstocks was from upland grassland dominated by bracken (*Pteridium aquilinum*), and the other from an area dominated by rushes (*Juncus effusus*). These vegetation types were selected from a range of semi-natural communities following thermogravimetric analysis of related samples: the details of this selection process are described in Corton et al. [23]. The current study investigated the suitability of these novel LIHD feedstocks for HT conversion, and explored the extent to which 1) vegetation type, 2) biomass pre-treatment by hot water washing and pressing (partial demineralisation), and 3) HT conversion route (HTC or HTL) influence the yields and properties of related products.

2. Materials and methods

2.1. Feed-stock choice and preparation

The current study used two distinctive and contrasting multi-species feedstocks; one came from bracken-dominant vegetation (BRAC) and the other from rush-dominant vegetation (RUSH). Both bracken and rushes are considered invasive plant species in the UK and are routinely cut as part of management protocols under agri-environment initiatives. The material for processing was obtained by harvesting strips within triplicate 10 m × 10 m sites per vegetation community type using a fingerbar mower (Shank's Pony GC135, Honda, Slough, UK) during August. Individual samples from each site were then chopped to approximately 5 cm lengths using a forage chopper (Model BCS, 15kw; Electra, France). The chopped material was then stored as silage by compacting 25 kg of biomass into 60 l polyethylene barrels.

The two feedstock types were subjected to HT conversion in two forms: i) without additional processing (Control), and ii) after hydrothermal pre-treatment and mechanical dehydration (HPMD). During HPMD approximately half of the silage from each barrel was hydrothermally conditioned for 20 min using water at 25 °C applied by sprinklers on a moving conveyor, before being passed through an AV screw press (Anhydro Ltd., Kassel, Germany) and the fibrous press cake collected.

The ash content of the feedstocks was determined weighing a sample before and after incineration in a muffle furnace at 550 °C for 5 h. The carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) concentrations compositions of the samples were established using a FlashEA 1112 Elemental Analyzer (MEDAC Ltd, Surrey, UK). Oxygen composition was calculated by difference (100 - (Ash + C + H + N) = O). Neutral detergent fibre (NDF) and acid detergent fibre (ADF) were determined using the method of Van Soest et al. [24], adapted for the Gerhardt Fibrecap detergent system (FOSS UK Ltd, Warrington, UK).

2.2. Apparatus and experimental procedure

Conversions were performed in a 75 ml unstirred, bomb type batch reactor fitted with a temperature and pressure controller (Parr Instrument Company, Illinois 61265-1770 USA). The reactor was charged with 3 g of sample and 27 ml of distilled water, which were pre-mixed and added to the reactor as slurry prior to sealing and heating. To achieve HTC the reactor temperature was set to 250 °C and the residence time was 1 h. To achieve HTL the reactor temperature was set to 350 °C with a pressure of 170 bar, with the residence time again 1 h. The residence time was measured from the point at which the reactor reached 250 °C or 350 °C. The heating rate of the reactor was approximately 10 °C min^{-1} and the reactor was purged with N prior to processing.

Following HTC or HTL, the reactor contents were washed out of the reactor over pre-weighed filter paper into a 250 ml glass separator; the hydrochar fraction remaining on the filter paper. Washing was conducted with 50 ml of dichloromethane (DCM) and 50 ml of distilled water. The separator was shaken and any resulting gaseous build up was vented from the separator every 15 min before leaving the mixture for approximately 1 h to separate. Following separation, the DCM fraction was evaporated off in a flow cabinet at a flow rate of 0.58 m s^{-1}. The remaining residue – the bio-oil fraction – was sealed and refrigerated at 5 °C to await analysis. The fraction remaining in the separating funnel was filtered through pre-weighed filter paper and made up to 500 ml with distilled water. The residue remaining after filtering was weighed after drying in a fume cupboard for 48 h and the residue weight was added to the hydrochar yield. The diluted aqueous fraction was then sealed and stored at 5 °C to await characterisation.

The insoluble residue and filter paper were dried in a fume cupboard for 48 h and weighed. The filter paper weight was subtracted to obtain the hydrochar product weight and added to any residue weight established from filtering the aqueous fraction. The weight of the gaseous fraction was calculated from the ideal gas law using reactor pressure and temperature readings following a 24 h cooling and depressurising period post process. Measuring the composition of the gaseous fraction was outside the remit of this study and so the entire gaseous fraction was assumed to be composed of CO_2 in the subsequent yield calculations. Following the establishment of the hydrochar, oil and gas yields, the volume of the aqueous phase was determined by difference.

The gas yield was calculated using the equation $n = PV/RT$ (where n = moles of CO_2; P = pressure in the reactor when cold; V = volume in the top of the reactor above the content; R = the gas constant (0.082); T = temperature in reactor). Yields on a dry matter (DM) ash free (AF) basis were calculated using: yield (DM AF) = (fraction mass/feedstock mass x (100-H_2O-ash/100)) x 100.

2.3. Hydrochar characterisation

The hydrochar samples were analysed for K, Mg, Ca, P and Na concentration according to Hensgen et al. [25]. C, H, N and S concentrations were determined by combustion analysis as outlined previously, and O concentration again calculated by difference. Higher heating values (HHV), on a dry basis (HHV^{dry}), were calculated from CHNO composition using the equation [26]: $HHV^{dry} = 0.0355 \times C^2 - 23.2 \times C - 223 \times H + 0.512 \times C \times H + 13.1 \times N + 20600$ (KJ kg^{-1} DM). The lower heating values (LHV) were determined using the equation [27]: LHV^{dry} (Mj Kg^{-1}) = $HHV^{dry} - 2.442 \times (8.936H \div 100)$.

Hydrochars produced via HTC also underwent surface area and pore analysis. A single representative sample from each of the duplicated HTC runs was randomly chosen for surface area analysis. Out-gassing was carried out prior to adsorption to remove adsorbed gases from atmospheric exposure. This was conducted for 2 h at a temperature of 105 °C. Sample weights in the range of 0.0776–0.141 g were used. Nitrogen adsorption measurements were performed at 77 K using a Quantachrome adsorption system running NovaWin v10.01 software (Quantachrome Instruments, Florida, USA). The Brunauer, Emmett and Teller (BET) [28] method was used to calculate the specific surface areas using adsorption data. The pore size distribution and the mesoporous range were derived by means of the Barrett, Joyner and Halenda (BJH) [29] model, again using the NovaWin software. Total pore volume (V_t) was also established using the BJH method. Imaging of hydrochars was also undertaken using a Zeiss Evo MA15 scanning electron microscope (Oxford Instruments, Abingdon, UK) in conjunction with Zeiss SmartSEM processing software (Oxford Instruments, Abingdon, UK). The apparatus used a Tungsten electron donor. Prior to analysis samples were mounted and coated with 20 nm of platinum in a vacuum environment using a sputter coater. Magnification ranges between ×59 and x 15,000 were explored.

2.4. Bio-oil characterisation

The C, H, N, O and S concentrations of the bio-oils were determined following the same procedure as outlined above for the feedstocks and hydrochars. The HHVs and LHVs of the bio-oils, on a wet basis (HHV^{wet}/LHV^{wet}), were established using the following equations: HHV^{wet} (MJ/kg^{-1}) = $HHV^{dry} \times (1-H_2O/100)$ & LHV^{wet} (MJ/kg^{-1}) = $LHV^{dry} (1-H2O/100) - 2.442 \times (H2O/100)$ respectively.

2.5. Data analysis

The hydrothermal experiments were replicated enabling statistical analyses to be conducted. Where appropriate data were subjected to a general analysis of variance (ANOVA) (Genstat 16; VSN International Ltd, Hemel Hempstead, UK), with the interactive treatment effects of vegetation type (RUSH vs BRAC), biomass pre-treatment (HPMD vs NON) and hydrothermal conversion route (HTC vs HTL) explored.

3. Results

Both vegetation types produced feedstock which was high in C and fibre, and low in N (Table 1). Subjecting the biomass to HPMD pre-processing reduced the ash content and concentrations of plant cell structural components.

Table 1. Composition of the experimental feedstocks used in the study, prepared by ensiling rush-dominated (RUSH) and bracken-dominated (BRAC) semi-natural vegetation. Biomass was left untreated (NON) or subjected to hydrothermal washing followed by mechanical dehydration (HPMD) (all values g/kg dry matter).

	RUSH		**BRAC**	
	NON	**HPMD**	**NON**	**HPMD**
Ash	34.6	29.3	86.0	54.0
C	456.7	466.4	425.2	450.3
H	60.5	58.6	53.5	56.4
N	15.2	11.5	21.0	19.2
S	<1.0	<1.0	4.0	<1.0
Neutral-detergent fibre	782.1	643.5	763.3	628.1
Acid-detergent fibre	413.2	349.5	505.1	314.5

3.1. Impact of vegetation type, pre-processing and HT conversion route on product yields

There was no overall effect of vegetation type on percentage hydrochar yield following conversion, but the bio-oil yield was significantly lower in the product stream from the BRAC biomass (Table 2). Given that the gaseous fraction was also numerically lower from conversion of BRAC, the lower oil volume in the BRAC derived product stream was not explained by mass being transferred to the gaseous fraction instead of the oil. There was no significant impact of HPMD processing upon the product yields.

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Table 2. Impact of vegetation type, biomass processing and hydrothermal conversion route on the percentage composition of products produced from ensiled biomass harvested from rush-dominated (RUSH) and bracken-dominated (BRAC) semi-natural vegetation. The feedstock converted without pre-processing (NON) or after receiving a hydrothermal pre-treatment followed by mechanical dehydration (HPMD) and was subjected to hydrothermal (HT) conversion via hydrothermal carbonisation (HTC) or hydrothermal liquefaction (HTL).

	Main treatment effects											
Product fraction yield (DM ash free)	**Vegetation type**				**Pre-processing**				**HT conversion route**			
	RUSH	**BRAC**	**s.e.d.**	***F* prob**	**NON**	**HPMD**	**s.e.d.**	***F* prob**	**HTC**	**HTL**	**s.e.d.**	***F* prob**
Hydrochar	43.5	43.5	9.21	ns	41.7	45.3	4.53	ns	58.8	28.2	4.53	<0.001
Oil	11.5	6.8	2.01	<0.05	9.6	8.7	2.01	ns	1.7	16.6	2.01	<0.001
Gas	13.9	9.2	2.19	ns	10.7	12.5	2.19	ns	8.3	14.8	2.19	<0.05
Aqueous	31.1	40.5	5.15	ns	38.1	33.6	5.15	ns	31.2	40.4	5.15	ns

Where s. e.d. = standard error of the difference; HTC was undertaken at 250 °C; HTL was undertaken at 350 °C.

The percentage hydrochar yield from conversion was significantly affected by the conversion route, with HTC producing greater percentage yields (Table 2). Conversely, the percentage yields for bio-oil and gas were substantially higher following HTL. Overall, there was no treatment effect for HT conversion route on percentage yield of the aqueous fraction, but a significant interaction effect between vegetation type, pre-processing and HT conversion route was identified ($P < 0.01$). There were no other significant treatment interaction effects.

3.2. Impact **of** *vegetation type, pre-processing and HT conversion route on* **hydrochar properties**

Vegetation type significantly affected the composition of the hydrochar produced by HT conversion (Table 3). The hydrochars prepared from the RUSH biomass had a higher C concentration, and higher HHVs and LHVs than those prepared from BRAC. In contrast, the hydrochars made from BRAC biomass had higher N concentrations. Overall, pre-processing by HPMD reduced the N concentration compared to the NON treatment, although there was an interaction effect with HT conversion route. There was also a main treatment effect of HT conversion route on most parameters. Concentrations of C and N, and the corresponding LHVs and HHVs, were significantly higher in hydrochars produced by HTL compared to HTC.

Significantly higher Mg concentrations were found in the hydrochars made from biomass derived from RUSH compared to BRAC. In contrast, hydrochars from BRAC had higher concentrations of ash, Ca and P (Table 4). Pre-processing by HPMD reduced the concentrations of Mg and P in the hydrochars produced but did not affect the concentrations of other minerals. Only Ca was influenced by conversion route, with concentrations higher in hydrochars produced by HTL, although interaction effects between HT route and vegetation type, and HT route and processing were noted for ash.

The hydrochars produced via HTC from the BRAC feedstock appeared to have higher surface areas than those produced from the RUSH feedstock, which could be linked to greater pore volumes for the former (Table 5). In contrast, pore radius was similar for the hydrochars derived from the different biomass types. The hydrochars derived from feedstock which received no pre-processing were observed as having lower surface areas, similar pore volumes and higher pore radius measurements compared to hydrochars from feedstock that had undergone HMPD. Inspection of the hydrochars by SEM also highlighted differences between hydrochars made from biomass derived from the different vegetation types. The hydrochars made from biomass from the RUSH feedstock showed a high frequency of ladder-like structures (Fig. 1). In contrast, a feature of the SEM images of the hydrochars from the BRAC feedstock was the presence of well-defined micro spheres and a high frequency of particles with microtubules (Fig. 2).

Table 3. Impact of vegetation type, biomass processing and hydrothermal (HT) conversion route on the C, H, N and O concentrations (% DM), and associated higher heating values (HHV) and lower heating values (LHV) (MJ/kg) of hydrochars produced by hydrothermal carbonisation (HTC) and hydrothermal liquefaction (HTL) of ensiled biomass harvested from rush-dominated (RUSH) and bracken-dominated (BRAC) semi-natural vegetation. The feedstock was converted without pre-processing (NON) or after receiving a hydrothermal pre-treatment followed by mechanical dehydration (HPMD).

	Main treatment effects												**Interactive effects**		
	Vegetation type (VT)				**Pre-processing (PP)**				**HT conversion route**				**VT × PP**	**VT × HTR**	**PP × HTR**
	RUSH	**BRAC**	**s.e.d.**	***F* prob**	**NON**	**HPMD**	**s.e.d.**	***F* prob**	**HTC**	**HTL**	**s.e.d.**	***F* prob**	***F* prob**	***F* prob**	***F* prob**
C	71.2	65.3	0.49	<0.001	67.9	68.6	0.49	ns	65.2	71.3	0.49	<0.001	<0.05	<0.05	ns
H	4.9	4.8	0.08	ns	5.0	4.8	0.08	n	5.3	4.5	0.08	<0.001	<0.05	ns	ns
N	2.0	2.2	0.04	<0.001	2.2	1.9	0.04	<0.001	1.8	2.3	0.04	<0.001	ns	ns	<0.05
O	14.1	18.7	0.36	<0.001	16.1	16.6	0.36	ns	19.9	12.8	0.36	<0.001	<0.01	<0.05	ns
HHV	29.3	26.2	0.18	<0.001	27.8	27.8	0.17	ns	26.7	28.9	0.17	<0.001	<0.001	<0.05	<0.01
LHV	28.3	25.2	0.17	<0.001	26.7	26.8	0.17	ns	25.5	27.9	0.17	<0.001	<.0001	<0.01	<0.01

Where s. e.d. = standard error of the difference; HTC was undertaken at 250 °C; HTL was undertaken at 350 °C. There were no VT × PP × HTR treatment interactive effects.

Table 4. Impact of vegetation type, biomass processing and hydrothermal conversion route on the mineral composition (% DM) of hydrochars produced by hydrothermal carbonisation (HTC) and hydrothermal liquefaction (HTL) of ensiled biomass harvested from rush-dominated (RUSH) and bracken-dominated (BRAC) semi-natural vegetation. The feedstock was converted without pre-processing (NON) or after receiving a hydrothermal pre-treatment followed by mechanical dehydration (HPMD).

	Main treatment effects												**Interactive effects**	
	Vegetation type (VT)				**Pre-processing (PP)**				**HT conversion route (HTR)**				**VT × HTR**	**PP × HTR**
	RUSH	**BRAC**	**s.e.d.**	***F* prob**	**NON**	**HPMD**	**s.e.d.**	***F* prob**	**HTC**	**HTL**	**s.e.d.**	***F* prob**	***F* prob**	***F* prob**
Ash	7.15	7.91	0.249	<0.01	7.41	7.65	0.249	Ns	7.32	7.62	0.249	ns	<0.01	<0.05
Ca	0.15	0.39	0.058	<0.01	0.33	0.22	0.058	Ns	0.17	0.38	0.058	<0.01	ns	ns
K	0.03	0.06	0.012	ns	0.06	0.04	0.012	Ns	0.03	0.06	0.012	ns	ns	ns
Mg	0.04	0.00	0.006	<0.001	0.03	0.01	0.006	<0.05	0.01	0.03	0.006	ns	ns	ns
Na	0.03	0.04	0.008	ns	0.04	0.03	0.008	ns	0.03	0.04	0.008	ns	ns	ns
P	0.09	0.22	0.034	<0.01	0.21	0.10	0.033	<0.05	0.12	0.19	0.033	ns	ns	ns
S	0.42	0.58	0.162	ns	0.59	0.41	0.162	ns	0.53	0.47	0.162	ns	ns	ns

Where s. e.d. = standard error of the difference; HTC was undertaken at 250 °C; HTL was undertaken at 350 °C.

Table 5. Influence of vegetation type and biomass processing upon the surface structure of hydrochars produced by hydrothermal carbonisation.

Vegetation type	Biomass processing	BET surface area (m^2 g^{-1})	BJH pore volume (cc g^{-1})	BJH pore radius (Å)
RUSH	NON	3.57	0.014	21.33
RUSH	HPMD	5.49	0.015	18.57
BRAC	NON	13.60	0.070	18.99
BRAC	HPMD	14.36	0.054	15.07

Where BET = Brunauer, Emmet and Teller [27] model; BJH = Barrett Joyner and Halenda [28] model.

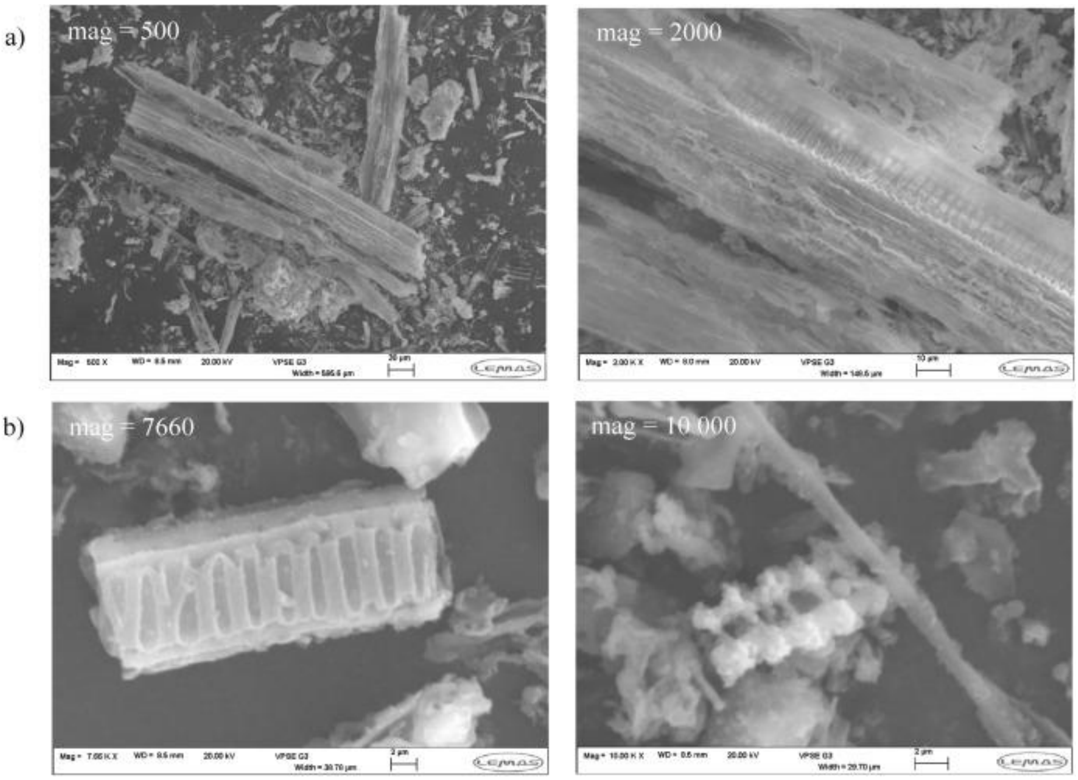

Fig. 1. Scanning electron micrographs of hydrochars created by subjecting ensiled biomass from rush-dominated vegetation to hydrothermal carbonisation at 250 °C, with (a) and without (b) hydrothermal pre-treatment and mechanical dehydration (where mag = magnification).

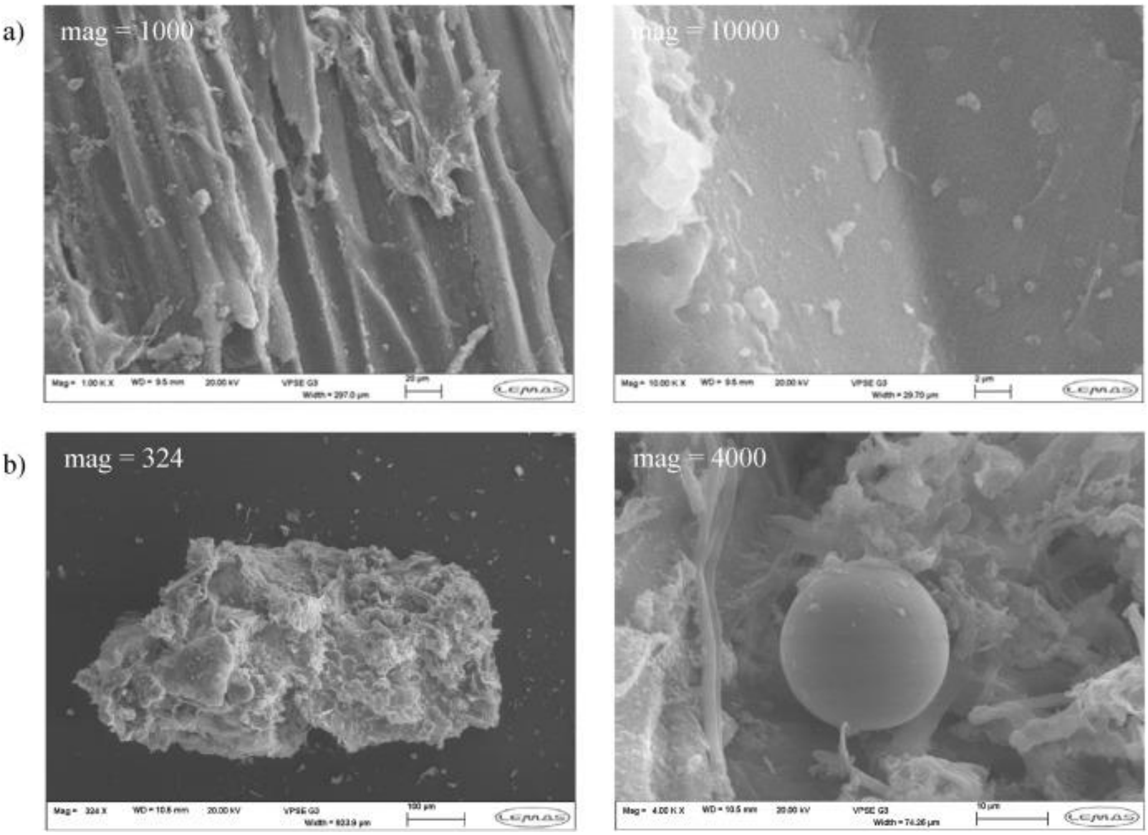

Fig. 2. Scanning electron micrographs of hydrochars created by subjecting ensiled biomass from bracken-dominated vegetation to hydrothermal carbonisation at 250 °C, with (a) and without (b) hydrothermal pre-treatment and mechanical dehydration (where mag = magnification).

3.3. *Impact of vegetation type, pre-processing and HT conversion route* on bio-oil properties

Since ash concentrations could not be measured (due to the low sample volume) the O concentration of the bio-oils could not be calculated. The C, H and N concentrations and associated HHV and LHV values of the oils were all significantly influenced by feedstock source. Bio-oil made from BRAC biomass had higher concentrations of C, H and N, and higher HHV and LHV values (Table 6). Biomass pre-processing did not influence the ultimate composition, nor HHV and LHV values (Table 6). Bio-oils produced via HTL had significantly higher concentrations of C and H compared to those produced via HTC, and thus significantly higher HHVs and LHVs. Both the H and N compositions of the bio-oils were significantly influenced by interaction effects between vegetation type and the HT conversion route.

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Table 6. Impact of low-input high-density vegetation type, biomass processing and hydrothermal conversion route on the C, H, and N concentrations (% DM), and associated higher heating values (HHV) and lower heating values (LHV) (MJ/kg) of bio-oils produced by hydrothermal carbonisation (HTC) and hydrothermal liquefaction (HTL) of ensiled biomass harvested from rush-dominated (RUSH) and bracken-dominated (BRAC) semi-natural vegetation. The feedstock was converted without pre-processing (NON) or after receiving a hydrothermal pre-treatment followed by mechanical dehydration (HPMD)

	Main treatment effects												**Interactive effects**
	Vegetation type (VT)				**Pre-processing (PP)**				**HT conversion route (HTR)**				**VT × HCP**
	RUSH	**BRAC**	**s.e.d**	***F* prob**	**NON**	**HPMD**	**s.e.d.**	***F* prob**	**HTC**	**HTL**	**s.e.d**	***F* prob**	***F* prob**
C	69.1	70.7	0.70	<0.05	70.1	70.0	0.70	ns	65.8	74.0	0.70	<.001	ns
H	7.4	8.0	0.14	<0.001	7.7	7.7	0.14	ns	7.3	8.1	0.14	<.001	<0.05
N	1.4	2.5	0.16	<0.001	2.1	1.9	0.16	ns	2.1	1.9	0.16	ns	<0.05
HHV$^{(wet)}$	31.5	33.6	0.56	<0.001	32.7	32.4	0.56	ns	29.3	35.7	0.56	<.001	ns
LHV$^{(wet)}$	29.9	31.8	0.53	<0.001	31.0	30.7	0.53	ns	27.7	34.0	0.53	<.001	ns

Where s. e.d. = standard error of the difference. There were no VT × PP, PP × HTR or VT × PP × HTR treatment interactive effects.

4. Discussion

Conservation biomass is potentially a highly abundant natural resource. A conservative estimate predicted that 1 million tonnes of biomass could be harvested per annum in Wales alone [1]. Globally this could be a significant and largely untapped resource at a time when we need to find feedstocks for developing the bioeconomy without jeopardising food security or the environment. By expanding the choice of conversion technologies available for such LIHD feedstocks new value chains can be created. The data in this paper are the first to be reported following hydrothermal conversion of such feedstocks and make a substantial contribution to the evidence base required to ensure these resources are used as effectively and efficiently as possible.

The process of HTC is simple, cheap and easily scalable. The feedstock does not need to be dry before the process begins and the hydrochar can be easily filtered from the product mix. These attributes make the process attractive for large-scale commercial development [30]. In contrast, HTL is an alternative to fast pyrolysis for producing oil from biomass. The oils derived from HTL typically have more desirable qualities compared to fast pyrolysis oils, and the energetic efficiency of the process is generally greater [31]. In contrast, oils produced via fast pyrolysis contain more oxygen and have higher moisture contents compared to HTL derived oils (both undesirable characteristics). A lower O concentration in bio-oils means they become more stable, less reactive and higher in calorific value, and is key to making them miscible with conventional oil [32].

The hydrochar yields from the conversion of both RUSH and BRAC feedstocks were similar. The consistency of the hydrochar yield across a broader range of conservation wastes from semi-natural vegetation communities should now be determined to confirm that the impact of source is minimal. From a commercial perspective, the predictability of hydrochar yield would be advantageous to downstream processing. This would enable processing plants to be able to generalise potential hydrochar productivity across semi-natural landscapes and related resources. However, although vegetation type had no effect on the percentage yield of hydrochar, the bio-oil yield was significantly higher in the product stream from the RUSH biomass. This had been predicted by TGA of the feedstocks [23]. A positive correlation between volatile composition and the proportion of oil in the product mix had been reported previously [33] and these results corroborate those findings.

There was no significant impact of pre-processing upon the product yields. One of the primary compositional differences between feedstock that has and hasn't undergone HPMD is that the press cake from HPMD is predicted to have a significantly lower metal composition, including alkali metals such as potassium [25]. Alkali metals can be used to catalyse hydrothermal reactions; for example, potassium catalysis can be used during hydrothermal gasification to increase reaction rate [34]. The addition of potassium catalysts also results in higher H concentrations in the gas produced [34]. This is attractive for H fuel production via hydrothermal conversion. However, in the current study, the significantly higher concentrations of potassium detected in the NON biomass compared to the HPMD biomass had no impact upon the subsequent fraction yields. This is in keeping with the findings of Ross et al. [35], who concluded that alkali metals did not impact upon fraction yields following hydrothermal processing of algal biomass. However, in the current study there was no attempt to measure or calculate reaction rate and the gaseous phase composition was not analysed. Based only on the current results, and considering the time and energy expended in a HPMD pre-treatment regime, hydrothermal yields would appear to be insufficiently increased to render it worthwhile when bio-oil production is the main objective. Both HTC and HTL produced substantially lower percentage yields of oil than fast pyrolysis from similar material [23]. However, the yields of hydrochar were similar (HTL) or substantially higher (HTC) than those obtained through fast pyrolysis.

While the HT conversion route significantly affected relative hydrochar and bio-oils yields as predicted, there was no impact upon the percentage aqueous yield. There is consensus across the literature that HT conversion conducted within the parameters relating to HTL will produce more oil and gas compared to those conversions conducted within the parameters relating to HTC [12], as reflected in the current study. The stability of the aqueous yield in relation to the HT conversion process renders the fraction a candidate for investigation as a potentially useful by-product in a biorefinery system. Although the productivity of the aqueous fraction appeared to be a parameter on which downstream processes could depend, yield was influenced by an interaction between vegetation type, pre-processing and conversion process. Further multivariate studies would be helpful to elucidate this complex range of influences to optimise the yield of the fraction. The utilisation of the aqueous fraction for microbial culture could add further biorefinery products [36].

Hydrochars typically have HHVs of 24–30 MJ kg^{-1} [37]. The HHV of the RUSH derived hydrochars was in the higher end of the range and thus has potential as a high calorie hydrochar fuel. The higher C concentration (and thus higher HHVs and LHVs) for RUSH derived hydrochar compared to BRAC derived hydrochar likely reflected differences in the C contents of the original vegetation [25]. It may also be due to C being differently distributed amongst the product fractions during conversion, with the pattern of distribution mirroring the TGA results reported previously [23]. Bio-oil derived from the BRAC feedstock had higher C concentrations than bio-oil from the RUSH feedstock, indicating that reaction routes contributed to the distribution of C. Thus, a factor associated with vegetation type impacted upon the fate of C during conversion, and C in turn had an impact upon the calorific value of the hydrochar or bio-oil fractions produced. If this influence could be identified and simulated the calorific value could be increased. Work by Lu et al. [38] demonstrated that carbonisation can be increased in the hydrochar fraction by prolonging the conversion process, although this was not found for all feedstock types examined in that work.

The focus of the current study was on exploring the impact of vegetation type and pre-processing, and conversions were carried out at temperatures and pressures expected to give favourable results given the underlying chemical composition of the materials being tested. Further research is now needed to explore the influence of HT reaction parameters and duration for LIHD feedstocks to determine the impact of these upon carbonisation and resultant calorific content, in order to optimise the overall conversion process. The use of catalysts during HTL plus interactions between these and process temperature should also be investigated. Previous research has shown that the yield of different forms of bio-oil can be influenced by both these factors [39], and that the optimum combination can differ between plant species [40,41]. This will likely make selection of an appropriate catalyst for biomass from mixed-species grassland that may vary in floristic and chemical composition across the growing season more challenging, but potential improvements in product yields and related conversion efficiencies should be explored.

Concentrations of C and N, and the corresponding LHVs and HHVs, were significantly higher in hydrochar produced by HTL compared to HTC. Conversely, the H and O concentrations were higher in hydrochar following HTC compared to HTL. Despite the excess water inherent in the conversion process, dehydration reactions occur at the pressure and temperatures employed. Increased reaction rates at higher temperatures and pressures would have resulted in higher dehydration levels during HTL compared to HTC (since the duration times were identical), and this explains the lower H and O compositions of the HTL hydrochars. This tendency is well documented [42]. Decarboxylation is another mechanism whereby O is removed from the hydrochar during HT conversion. The reaction involves the removal of carboxyl (R–COOH) and carbonyl groups (C═O), generating gaseous CO_2 and CO respectively [43].

Dehydration and decarboxylation, in combination with polymerisation and aromatization, are currently accepted as the primary reactions of hydrothermal conversion [31,42,44]. These reactions decrease H and O compositions in the resultant hydrochar (some C loss also occurs). Loss of O is particularly important in order to decrease the H:C and O:C ratios [44]. A low H:C ratio is generally indicative of a higher quality fuel [31] and HT conversion aims to produce hydrochars and oils with lower H:C ratios. It has been reported that a large proportion of O is removed as CO_2 under liquefaction conditions but not during carbonisation [45]. This results in a difference in the concentration of C, a lower O:C ratio and consequently a higher HHV and LHV is created in the resultant hydrochar or oil. In addition, the higher temperatures during HTL encourage carbonisation by 'further driving off' H and O [46]. This increased energy densification explains the higher C composition, and increased energy densification seen in the HTL derived hydrochars compared to the HTC derived hydrochars.

The N concentration of the BRAC derived feedstock was approximately double that of the RUSH feedstock and is linked to the relative concentrations of N found in the hydrochars and bio-oils produced. The current work therefore illustrates the impact of feedstock chemistry upon the product composition following HT conversion. Another example was the higher ash composition of the hydrochar made from BRAC compared to that from RUSH, which reflected the different ash contents of the two feedstocks. The fate of the minerals during any potential fuel production process is important because the mineral composition relates specifically to the ash softening temperature and emission profile [47]. Plant species composition, stage of maturity, seasonality and growing conditions all have potential to strongly impact upon the chemical composition of LIHD feedstocks such as semi-natural grasslands. Given that the current study and confirmed that such feedstocks do indeed have potential for generating hydrochars and bio-oils via HT conversion, further research should be conducted to better define these relationships in order to shape related resource management guidelines. Results for feedstocks derived from grassland in the USA have suggested liquefaction yields are influenced by heating rate, time under HTL, and process temperature [48].

As resources were limited hydrochar structural analyses were only conducted on hydrochars generated by HTC. This was because HTC yields more hydrochar compared to HTL and would therefore be the favoured conversion route for hydrochar production, and thus hydrochar characterisation would be more applicable to HTC derived hydrochars in an applied setting. The BRAC derived hydrochars had higher surface areas compared to the RUSH derived chars. This appears to relate to the pore volume (BJH) rather than the pore radius. There was a highly significant difference in the P composition of the hydrochars from the two different sites, with the BRAC chars having higher concentrations. Work by Wang et al. [49] found carbon activation using phosphoric acid to significantly increase the surface area of hydrochars, and it is possible there was a degree of phosphoric acid activation during

HTC of the BRAC derived feedstock. This may explain why the BRAC hydrochars had significantly higher surface areas compared to the RUSH hydrochars. The hydrochars derived from NON had generally lower surface areas (BET), similar pore volumes but lower pore radius measurements compare to the HPMD chars.

Scanning electron microscopy of material derived from a mixed species source is inevitably problematic with regards to sample representation, and only fragments of hydrochar could be highlighted in the images produced. However, sufficient differences in structure were apparent during this observational study to indicate further research is required into the specific properties of hydrochars produced from different grassland components and their related potential as high value compounds. For example, the hydrochars made from RUSH showed ladder-like structures. Similar 'scaffold like' structures have been found in *Juncus maritimus* following thermal decomposition [50]. Following infiltration with molten silicon these structures were deemed to be viable scaffolds for tissue engineering. If *J. effuses* (the dominant species from the RUSH site) can provide a scaffold for tissue engineering, then a plentiful and economic source would be available for this purpose. In contrast, the micrographs from the BRAC hydrochars indicate the presence of microspheres. Work by Sevilla et al. [51] has shown that the shell of such spheres may contain functional groups that include oxygen (hydroxyl, carbonyl and carboxyl) and are hydrophilic, and it was established through X-ray photoelectron spectroscopy and fourier-transform infrared spectroscopy that the nuclei are highly aromatic and hydrophobic. Further work is required to explore the extent to which the properties of hydrochars produced from different LIHD feedstocks are influenced by different pyrolysis parameters in order to design biochars for a desired purpose [52], and add to the range of high-value products produced.

Almost all the conservation waste created through habitat management across Europe is currently being discarded. This financially limits the extent of the land management activities possible. Using this feedstock to generate bioenergy and bioproducts would turn material which has been a problematic waste into a resource with an economic value. This could act as an alternative income source for rural communities in marginal areas struggling to maintain agricultural viability, especially if the associated carbon and biodiversity gains were rewarded through revised land use policies and support payments. Further developmental work is now required to scale up the proof-of-principle research of the current study and explore the production potential identified in greater detail.

5. Conclusions

This study has demonstrated that LIHD feedstocks derived as a by-product of land management for nature conservation are suitable for conversion via hydrothermal carbonisation or hydrothermal liquefaction. The most effective process route for combustion fuel production was HTC of HPMD-processed RUSH feedstock, based on the comparatively low mineral composition, high hydrochar yield and high HHV value. If bio-oil production was to be the priority product, then biomass processing through HPMD would not be required and biomass from RUSH would provide the highest yield. If the goal was a product mix of both hydrochar and bio-oil for refining, HTL would again be the most suitable HT conversion route.

CRediT authorship contribution statement

J. Corton: Investigation, Writing - original draft. **I.S. Donnison:** Conceptualisation, Supervision, Funding acquisition. **A.B. Ross:** Methodology, Resources. **A.R. Lea-Langton:** Methodology, Resources. **M. Wachendorf:** Conceptualisation, Funding acquisition. **M.D. Fraser:** Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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