



Fast pyrolysis processing of surfactant washed *Miscanthus*

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ARTICLE INFO

Article history:

Received 24 April 2014

Received in revised form 30 June 2014

Accepted 1 July 2014

Available online 23 July 2014

Keywords:

Miscanthus

Biomass pre-treatment

Ash

Fast pyrolysis

Bio-oil stability

ABSTRACT

Miscanthus × giganteus was subjected to pre-treatment with deionised water, hydrochloric acid or Triton X-100 surfactant, and subsequently fast pyrolysed in a fluidised bed reactor at 535 °C to obtain bio-oil. Triton X-100 surfactant was identified as a promising pre-treatment medium for removal of inorganic matter because its physicochemical nature was expected to mobilise inorganic matter in the biomass matrix. The influence of different concentrations of Triton X-100 pre-treatment solutions on the quality of bio-oil produced from fast pyrolysis was studied, as defined by a single phase bio-oil, viscosity index and water content index. The highest concentration of Triton X-100 surfactant produced the best quality bio-oil with high organic yield and low reaction water content. The calculated viscosity index from the accelerated ageing test showed that bio-oil stability improved as the concentration of Triton X-100 increased.

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1. Introduction

Renewable energy sources from biomass are a growing importance when considering trying to reduce the environmental concerns from fossil fuels. Certain processes have been developed to convert biomass into a product which has the potential to be used as a renewable fuel source. One of these approaches is fast pyrolysis which converts biomass, such as *Miscanthus × giganteus*, by rapid heating in the absence of oxygen and then rapid cooling of the vapours [1]. The products are bio-oil, non-condensable gases and char. The overall quality of the bio-oil as measured by stability was targeted for improvement by reducing the inorganic content (i.e. ash) in the initial biomass.

Different approaches have been used to pre-treat biomass including with water, surfactant and acid [2–7]. Water washes have been shown to be efficient in removing the majority of alkali metals such as potassium, sodium and chlorine from biomass [2] and are more efficient when the wash is agitated. Around 90% of alkali in biomass is present in water soluble form [8]. Water washing is more suited to high inorganic content biomass, as feedstock with lower inorganic contents (woody biomass) have a higher concentration of alkali metals bound to the organic structure which limits the effectiveness of water washing.

Tan and Wang [3] has shown that the metal ion content of biomass is decreased after hydrochloric acid (HCl) washing, resulting in an increased release rate of volatiles during pyrolysis. An increased volatile release rate leads to increased bio-oil yields and a decrease in secondary reactions of volatiles. A decrease in inorganic content after demineralisation with HCl was also observed by Mayer [4], but it was

found to change the primary polymer structure decreasing hemicellulose content. A change in the primary polymer structure from strong acid washes was also found by Tan and Wang [3]. Cellulose pyrolysis produces higher yields of bio-oil compared to hemicellulose and lignin, which produce char and gas in higher yields [9]. Strong acid washing decreases the amount of hemicellulose and cellulose in biomass due to hydrolysis, therefore increasing the proportion of lignin [4]. This leads to lower yields of bio-oil and increased char and gas yields. Weaker acid washes can either partially or fully hydrolyse hemicellulose and have little or no effect on cellulose content [5], but do not decrease metal ion content as much as a strong acid wash. Strong acid washing completely hydrolyses hemicellulose and cellulose increasing the porosity of the biomass due to their removal; weak acids only partially hydrolyse hemicellulose therefore the porosity is not increased as much. Research by Park [6] found that strong acid treatment of biomass caused mass losses; washing with nitric acid (HNO₃) and HCl caused 17% and 15% mass losses respectively. Park also found that alkali treatments resulted in greater mass losses; washing with sodium hydroxide (NaOH) and ammonium hydroxide (NH₄OH) caused 47% and 35% mass losses respectively. Work by Vamvuka [10] observed that carbonates, sulphates and alkali chloride minerals were dissolved when biomass was washed with HCl, when a weaker acid was used (e.g. acetic acid) the carbonates and sulphates were only partially removed.

Other compounds can be added to the washing solution to aid in inorganic reduction, such as surfactants. Surfactants are compounds that lower surface tension between two liquids or between a liquid and a solid. Surfactants are widely used in numerous commercial and industrial products including detergents, emulsifiers, wetting agents and dispersants [11]. Triton X-100 has been used for permeabilisation of microorganisms to determine enzyme activity [12], the treatment

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has been shown to make cells diffusible for macro molecules up to molecular weights around 70,000. It is thought that the addition of surfactant will promote further inorganic removal as it has been shown to increase cell permeability (ability to transmit fluids) [13]. Galabova et al. [14] showed that the permeability depended on the concentration of Triton X-100 and not the volume of solution. The main reason for adding a surfactant to the washing solution is to aid in inorganic material removal from biomass. Surfactant added to a water wash is a very useful technique as it helps to increase the efficiency of inorganic removal and should be considered when examining the economic merit, due to less water being retained by biomass; therefore reducing drying requirements.

There are two main problems with washing, the first being that the biomass has to be subsequently dried so that the moisture content is below 10% due to fast pyrolysis requirements. Secondly, if the biomass is acid washed the acid has to be separated and recovered or disposed, which increases the operational costs of pre-treatment. Acid washed biomass has to be rewashed with deionised water to remove remaining acid ions, such as chlorine ions from a hydrochloric acid wash. If chlorine ions were to remain in pre-treated biomass they can lead to adverse effects on bio-oil yield and quality due to catalytic cracking of the fast pyrolysis vapours. This increased washing water requirement increases water demand which can increase operational costs dramatically. Triton X-100 is biodegradable [15] and relatively large amounts of the surfactant and its biodegraded by-products are currently released into the environment. Thus it can be used in a washing solution without having to be separated and recovered or disposed of after use, which saves on operational costs.

The objectives of this study were to explore the extent of inorganic matter removal under different washing regimes as well as the impact on bio-oil quality. Two sets of experiments were conducted. The first was to identify which washing medium solution (deionised water, 1.00% HCl and 0.10% Triton X-100) removed the most inorganic matter. The second set explored the most promising washing medium (with varying solution concentrations) to identify the preferred pre-treatment to produce a high quality bio-oil (defined by composition and long-term stability).

2. Methodology

2.1. Feedstock

The biomass sample was selected as *Miscanthus × giganteus* (*Miscanthus*) because it has a consistently high inorganic content. The sample employed was grown at Woburn Experimental Farm (Bedfordshire, UK) on sandy soil. The crop was established in 2003 and from 2005 until 2007 the crop was part of a large agronomic experiment. The whole experimental site received 50 kg K ha⁻¹ (soluble potassium in an inorganic form) and 100 kg N ha⁻¹ fertiliser as *Nitram* (ammonium nitrate), in 2008 to unify the yield across the field. The *Miscanthus* for the work was harvested in February–March 2009 at this site.

2.2. Sample preparation

The *Miscanthus* samples were prepared before each set of experiments, by grinding (Retsch Ltd., Germany, Heavy-Duty Cutting Mill, Type SM2000) and sieving to a particle size fraction of 0.25–2.00 mm for pre-treatment experiments. After each pre-treatment the following particle size fractions were prepared for analysis: particle size 0.25–2.00 mm for fast pyrolysis processing and particle size 0.15–0.25 mm for pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) analysis. A biomass splitter was used to obtain a representative sample for Py–GC–MS characterisation.

2.3. Biomass pre-treatment

In this study two sets of different pre-treatment methods were used. Set 1 compared deionised water wash, 1.00% hydrochloric acid (used as in a mild-acid hydrolysis) wash and 0.10 wt.% Triton X-100 surfactant wash. Set 2 compared four different concentrations (0.10, 0.25, 0.50 and 1.00 wt.%) of Triton X-100.

Miscanthus batches of 500 g (ca. 10% of moisture) were washed with a 10 l solution whilst being agitated (300 rpm) for 4 h at room temperature. The solutions were made up on a weight percentage basis. After the batch had been washed it was filtered and then the HCl washed sample was washed with deionised water until the filtrate was Cl⁻ free. Silver nitrate was used to ensure that the filtrate was Cl⁻ free. The samples were left to stand for 24 h. Batches were dried in a Swallow oven at 60 °C ± 1 °C for 48 h. In order to accumulate sufficient raw material for a fast pyrolysis experiment, successive washings were carried out until approximately 1.5 kg of pre-treated *Miscanthus* was collected for each pre-treatment method.

2.4. ASTM ash content analysis

Feedstock and bio-oil ash content were calculated on a moisture free basis. Prior to analysis the feedstock was dried at 60 °C ± 2 °C for 24 h. Ash content was calculated using E 1755 ASTM method [16]. Crucibles and lids (8–10) were put in a Carbolite AAF1100 furnace and heated to 575 °C for 3 h; crucibles were then removed from the furnace and cooled in a desiccator. A desiccator was used to ensure that the samples remained dry. The crucible weight was recorded and then replaced in the furnace at 575 °C for a further hour, cooled and re weighed until the weights are within 0.1 mg. Approximately 0.5 to 1.0 g of dried feedstock or bio-oil were weighed into each crucible. The crucible, lid and sample were placed in a furnace and heated to 250 °C at 10 °C min⁻¹ and held for 30 min, then increased to 575 °C for 3 h (crucible lids placed slightly off so not fully sealed). After 3 h the crucibles were removed and cooled in a desiccator. Each crucible was weighed to the nearest 0.1 mg. Crucibles were replaced in a furnace and heated at 575 °C for 1 h periods until the crucible weight was constant to within 0.3 mg.

2.5. Elemental analysis and heating values

A Carlo-Erba 1108 elemental analyser EA1108 was used to determine the elemental analysis for carbon, hydrogen and nitrogen. Carbon, hydrogen and nitrogen content (wt.% on dry basis) were analysed in duplicate and average values were taken.

The higher heating value (HHV) was calculated using Eqs. (1) and (2) [17] on the basis of elemental carbon, nitrogen and hydrogen concentrations; the first is an ordinary least squares regression (OLS) and the second is a partial least squares regression (PLS), and an average taken of the two values. The lower heating value (LHV) was obtained using Eq. (3) [18].

$$\text{HHV}_{\text{Dry}}(\text{OLS}) = 1.87\text{C}^2 - 144\text{C} - 2802\text{H} + 63.8\text{CH} + 129\text{N} + 20147 \quad (1)$$

$$\text{HHV}_{\text{Dry}}(\text{PLS}) = 5.22\text{E}^2 - 319\text{C} - 1647\text{H} + 38.6\text{E} + 133\text{E} + 21028 \quad (2)$$

$$\text{LHV}_{\text{Dry}} = \text{HHV}_{\text{Dry}} - 2.442 * (8.936 \text{ H}/100). \quad (3)$$

2.6. Pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS)

Untreated and Triton X-100 pre-treated *Miscanthus* samples (3 mg) were pyrolysed using a CDS 5200 pyrolyser close-coupled to a

PerkinElmer Clarus 680 gas chromatograph (GC) and Clarus 600S mass spectrometer (MS), to a pyrolysis temperature of 550 °C (held for 15.0 s at 550 °C) at a heating rate of 20 °C ms⁻¹. The separation was carried out using a PerkinElmer Elite-1701 column (cross-bond: 14% cyanopropylphenyl and 85% dimethyl polysiloxane; 30 m, 0.25 mm i.d., 0.25 mm df). The GC oven was held at 45 °C for 5 min, then heated at 5 °C min⁻¹ to 250 °C and held at this temperature for 5 min. Proposed assignments ($m/z = 45\text{--}300$) were made from mass spectra detection using the NIST 2011 MS library and from assignments in the literature [19–21].

2.7. Fast pyrolysis processing

The fast pyrolysis experiments were carried out in a 1 kg h⁻¹ continuous bubbling fluidised bed reactor (#4) shown in Fig. 1. There are three flow regimes in which the reactor can be operated, bubbling, turbulent or fast fluidisation [22]. To maintain a consistent bed material weight a bubbling fluidisation flow regime was used to ensure that no bed material was removed from the reactor. The rig is composed of three sections: the feeding system, the fast pyrolysis reactor and product collection. The feeding system consists of an air-tight hopper (#1) with a nitrogen purge with speed regulated twin metering screws to supply up to 1 kg h⁻¹ of feedstock to the high speed feed screw (#2) which is water cooled at the feed point to minimise pre-pyrolysis. The biomass was fed into the lower part of the fluid bed reactor, 10.16 cm above the distributor plate. The reactor bed material is 1 kg of sieved quartz sand with a particle size between 600 and 710 µm. The reactor was fluidised with three times the minimum fluidising velocity (17 dm³ min⁻¹) [23] using pre-heated nitrogen on a single pass basis. A single pass basis was used so that the gas stream (nitrogen and product gas) can be analysed every 150 s, therefore the product gas composition can be studied at any point during a fast pyrolysis experiment. The nitrogen was pre-heated (#3) electrically in a chamber below the fluid bed reactor. All experiments were carried out with the aim of achieving an average pyrolysis bed temperature of 535 ± 5 °C. The residence time of the

vapours in the reactor and associated hot pipework and cyclones was calculated to be below 1.1 s [23]. As the vapour and gas stream left the reactor it passed through two heated cyclones in series (#5 and 6) where the char was separated. Following the cyclones the vapours were condensed in a cooled quench column (#8) directly contacted with ISOPAR™ (ISOPAR V. CAS number: 64742-46-7. Supplier: Multisol Limited) as the quenching media are controlled between 20 and 25 °C, by a water jacket surrounding the quench column. The aerosols were coalesced in a wet walled electrostatic precipitator (ESP, #9), working at 20 kV and 0.2 mA, flushed with ISOPAR™. The bio-oil was periodically run-off from the collection tank and collected in the bottom of the tank.

Following the electrostatic precipitator the gas passed through a water cooled condenser (#11) at 0–15 °C, two dry ice–acetone condensers (#12) in series at –70 °C and finally a cotton wool filter (#13), followed by 250 g of silica gel (silica gel orange, Sigma Aldrich, reference: 13767, CAS number: 112926-00-8, particle size 2–5 mm). An on-line Varian CP 4900 Micro-GC microgas chromatograph with a thermal conductivity detector (TCD) and two columns (Varian CP-5A Molsieve and CP-PortaPLOT) were used for interval analysis (every 150 s) of the non-condensable gases for each fast pyrolysis run. Any excess gas was vented to the fume hoods. Temperatures were measured and recorded using K-type thermocouples joined to a Microlink 751 ADC unit using Windmill data logging software. System pressures were measured by analogue instrumentation at varying points, so that any blockages or leaks could be identified. The fluidised bed was also monitored to ensure that it was operating suitably. Mass balances (wt.% on dry basis) were calculated based on mass of biomass processed and final fast pyrolysis products of bio-oil, char and non-condensable gases.

2.8. Bio-oil characterisation

2.8.1. Whole sample analysis of fast pyrolysis liquids (bio-oils)

All bio-oil samples were subjected to volatilisation at 250 °C (without any solvent addition) in order to identify all GC-detectable compounds using CDS 5200 pyrolyser close-coupled to a PerkinElmer Clarus 680 gas

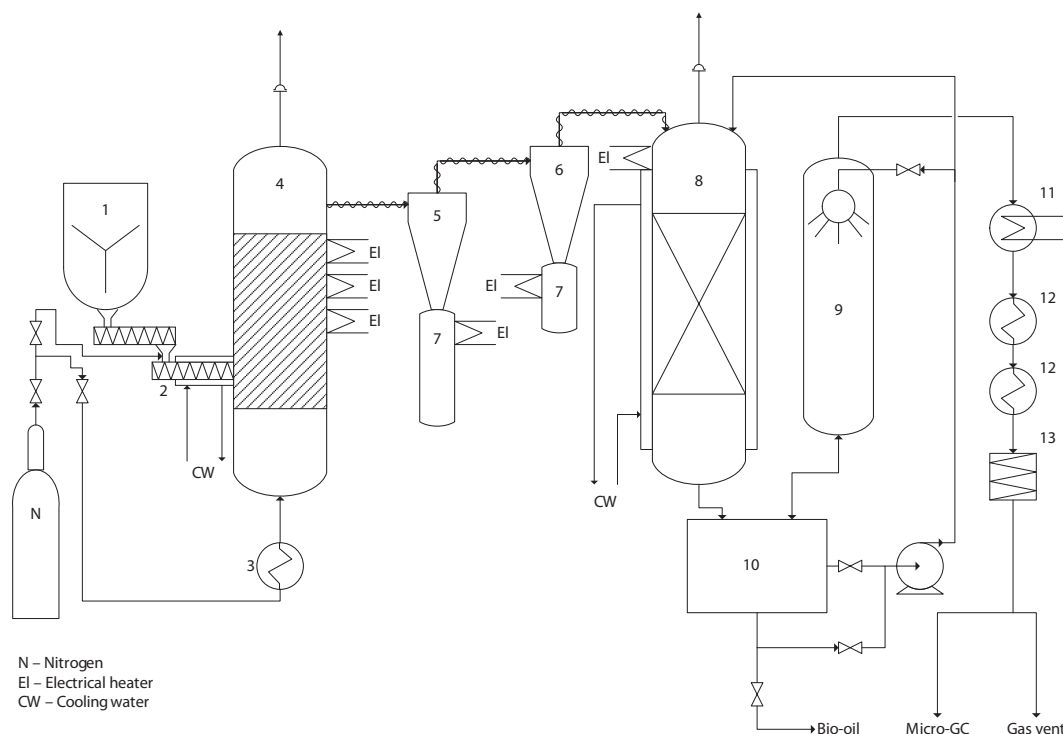


Fig. 1. 1 kg h⁻¹ fast pyrolysis rig set-up. 1 – feed hopper, 2 – fast screw, 3 – nitrogen pre-heater, 4 – bubbling fluidised bed reactor, 5 – cyclone one, 6 – cyclone two, 7 – char pot, 8 – quench column, 9 – electrostatic precipitator, 10 – collection tank, 11 – water cooled condenser, 12 – dry ice/acetone condenser, 13 – cotton wool filter.

chromatograph (GC) and Clarus 600S mass spectrometer (MS) with flame ionisation detector (FID). For each analysis 2 µl of bio-oil was injected onto the pyroprobe quartz tube and volatilised at 250 °C (heating rate: 250 °C min⁻¹/dwell time 30 s). Devolatilised compounds were immediately trapped on cold Tenax®-TA adsorbent trap (to avoid secondary/recombination reactions). Tenax®-TA adsorbent trap was then heated up to 275 °C and bio-oil compounds were transferred on to the GC column via a heated transfer line kept at 280 °C. Helium was used as the carrier gas. A PerkinElmer Elite-1701 (cross-bond: 14% cyanopropylphenyl and 85% dimethyl polysiloxane; 30 m, 0.25 mm i.d., 0.25 mm df) was used to separate bio-oil components. The GC injection port was kept at 275 °C and a 1:125 split ratio was used. The GC oven heated at 5 °C min⁻¹ from 45 °C to 280 °C. FID detector was held at 275 °C with hydrogen–air combustion mixture (with constant flows of 45 ml min⁻¹ and 450 ml min⁻¹ for hydrogen and air respectively). Proposed peak assignments (m/z = 45–300) were made from mass spectra detection using the NIST 2011 MS library and from assignments in the literature [20,21].

2.8.2. Dynamic viscosity

A Brookfield Viscometer model DV-II + pro rotational viscometer was used to measure the dynamic viscosity of bio-oil samples. Prior to use, the viscometer (accuracy, ±1% full-scale range; repeatability, 0.2% full-scale range) was calibrated with 4.7 cP Brookfield silicone viscosity calibration standard. Specific spindles (CS4–18 and CS4–34) were used depending on how viscous the sample appeared. A computer programme was used to set an initial speed resulting in a 10% torque reading, then after every minute the speed was increased by 0.5 rpm for 120 min. A temperature controlled water bath (temperature 40 ± 0.1 °C) was used.

2.8.3. Water content

Volumetric Karl–Fischer (KF) titration was used to determine the water content of all the fast pyrolysis liquid products. A Mettler Toledo V20 KF titrator with Hydranal (R) K as a working medium and Hydranal (R) Composite 5 K as a titrant. Prior to analysis, the KF instrument was calibrated with HPLC–grade water and the system was flushed with the working medium between different samples. All analyses were performed in triplicate with the water content reported visually after being calculated automatically by the KF, based on the weight of bio-oil sample used.

To find out if a bio-oil sample was single phase the water content has to be measured at three separate points (33, 50 and 66% from the top of the sample). The bio-oil can be classed as a single phase if the difference between two consecutive points was lower than 1 wt.% [24]. If any one of the three readings falls outside of the 4 wt.% range then the bio-oil sample was classed as separated.

2.8.4. pH analysis

A Sartorius PB-11 pH metre was used to measure the acidity of the bio-oils. Prior to each measurement the pH metre was calibrated with pH buffers (pH = 2, 4, 7 and 10) which were provided by Sartorius. Calibrations were repeated for each sample to ensure that exact readings were recorded and the probe was cleaned between sample analyses to ensure that no cross contamination occurred.

2.9. Bio-oil accelerated storage experiment

Each bio-oil sample was centrifuged (10 min at 4200 rpm) to remove all the ISOPAR™. A maximum of 96 ml (8 × 12 ml samples) of bio-oil could be centrifuged at a single time; therefore after the ISOPAR™ was removed each sample was poured into a single glass vial and left to stand until air bubbles dissipated. 75 ml of each bio-oil was placed in a 100 ml glass bottle which had been dried at 105 °C for 4 h to remove all moisture. The lids were replaced on the bottles and then placed in an oven at 80 °C for 24 h, as this is claimed to simulate

one year degradation at ambient temperature [25]. After the first 10 min the bottle lids were re-tightened. After 24 h the bio-oil was removed from the oven and left to cool to ambient temperature. The viscosity and water content were re-measured so a viscosity and water content index could be calculated (Eqs. (4) and (5)). An index of 1.00 indicates a perfectly stable liquid in which the viscosity or water content does not change with heating or time. Most applications for bio-oil require the bio-oil to retain its initial physical properties during storage, transport and use.

Viscosity index (v_i)

$$v_i = 1 + \frac{v_1 - v_0}{v_0} \quad (4)$$

v_0 viscosity before the accelerated storage experiment (0 h)
 v_1 viscosity after the accelerated storage experiment (24 h)

Water content index (w_i)

$$w_i = 1 + \frac{w_1 - w_0}{w_0} \quad (5)$$

w_0 water content before the accelerated storage experiment (0 h)

w_1 water content after the accelerated storage experiment (24 h)

3. Results and discussion

3.1. Characterisation of pre-treated samples

3.1.1. Pre-treated *Miscanthus* characterisation (set 1)

This first set of experiments compared different washing agents. The carbon (C), hydrogen (H) and nitrogen (N) analyses for the untreated *Miscanthus* were as follows: 49.06% C; 6.10% H; 1.07% N. The C, H and N analyses for the pre-treated *Miscanthus* were all similar with a range of: 46.42–49.53% C; 5.73–6.01% H; 0.71–1.03% N. This shows approximately the same carbon and hydrogen, and a slight decrease in nitrogen compared to the untreated sample. Specific values can be found in Table 1. Accuracy is ±0.30% absolute. No major changes to the chemical structure of *Miscanthus* due to pre-treated washing occurred. However it was observed that HCl pre-treatment resulted in partial hydrolysis of hemicellulose which was shown by TGA analysis (results not shown).

3.1.2. Surfactant pre-treated *Miscanthus* characterisation (set 2)

This second set of experiments compared different concentrations of surfactant. The ultimate C, H and N analyses for the untreated *Miscanthus* were as follows: 48.63% C; 5.98% H; <0.10% N. The C, H and N analyses for the Triton X-100 treated *Miscanthus* were all similar with a range of: 48.65–49.23% C; 5.89–6.18% H; <0.10% N. The surfactant washes had very little effect on carbon, hydrogen and nitrogen contents

Table 1
Elemental analysis of pre-treated *Miscanthus*.

| Measurement | Untreated <i>Miscanthus</i> | Deionised water | 1.00% HCl | 0.10% Triton X-100 |
|-----------------------------|-----------------------------|-----------------|-----------|--------------------|
| ASTM ash content (%) | 3.68 | 1.92 | 3.52 | 1.53 |
| C (wt.% ^{d.a.f.}) | 49.06 | 46.42 | 49.53 | 48.71 |
| H | 6.10 | 5.73 | 6.01 | 5.99 |
| N | 1.07 | 1.03 | 0.81 | 0.71 |
| O* | 43.77 | 46.82 | 43.65 | 44.59 |
| HHV (MJ kg ⁻¹) | 19.66 | 18.49 | 19.80 | 19.43 |
| LHV | 18.32 | 17.24 | 18.48 | 18.12 |

d.a.f. – dry ash free.

* Calculated by difference.

Table 2
Elemental analysis of surfactant pre-treated *Miscanthus*.

| Measurement | Triton X-100 pre-treatments | | | | |
|-----------------------------|-----------------------------|-------|-------|-------|-------|
| | 0% | 0.10% | 0.25% | 0.50% | 1.00% |
| ASTM ash content (%) | 1.78 | 1.11 | 0.95 | 0.85 | 0.68 |
| C (wt.% ^{d.a.f.}) | 48.63 | 48.65 | 48.65 | 48.92 | 49.23 |
| H | 5.98 | 5.89 | 6.01 | 6.10 | 6.18 |
| N | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| O* | 45.29 | 45.36 | 45.24 | 44.88 | 44.49 |
| HHV (MJ kg ⁻¹) | 19.31 | 19.08 | 19.33 | 19.47 | 19.63 |
| LHV | 18.01 | 17.80 | 18.02 | 18.14 | 18.28 |

^{d.a.f.} – dry ash free.

* Calculated by difference.

of the *Miscanthus*. Specific values can be found in Table 2. Accuracy is $\pm 0.30\%$ absolute. The pre-treatment methods slightly increase both the HHV and LHV. Increasing concentrations of Triton X-100 resulted in reducing the ash content from 1.78% (untreated *Miscanthus*) to 0.68% (1.00% Triton X-100). Triton X-100 speeds up the wetting of the biomass permitting water to pass quicker through the biomass structure, also promotes swelling of the capillaries allowing water to wash the biomass more [13,14]; therefore higher concentrations improve ash removal.

Pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) analysis was also applied to study the generation of heavier hydrocarbons produced during pyrolysis of untreated and Triton X-100 pre-treated *Miscanthus*. Untreated *Miscanthus*, 0.10%, 0.25% and 0.50% Triton X-100 washed *Miscanthus* gave very similar results. Identified structures for low molecular weight components (acetic acid, acetic acid propenyl ester, propanol), alkyl-, methoxy- and ethoxy-phenols, furfural as well as levoglucosan and sugar derivatives originate from the lignocellulosic material. The major identified volatile products were: acetic acid (3.10 min), 3-furaldehyde (7.08 min), 2-hexene (11.87 min), pentanol (17.67 min), 4-methyl-benzaldehyde (21.53 min),

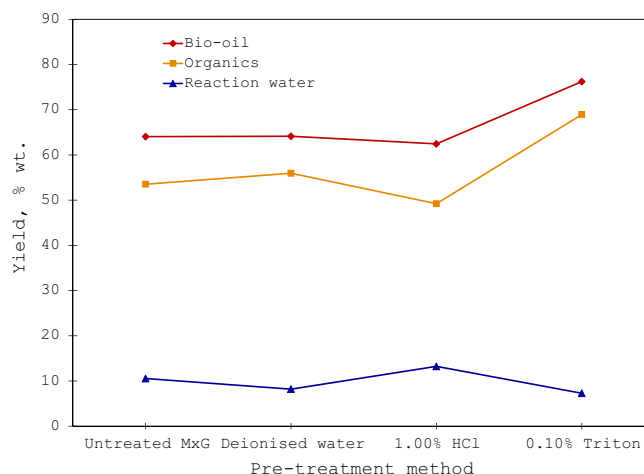


Fig. 2. Yields of fast pyrolysis liquids for different pre-treatment methods.

2,6-dimethoxyphenol (syringol) (22.80 min) and 2-methoxy-4-(2-propenyl)phenol (eugenol) (24.77 min). 1.00% Triton X-100 had a significant effect on the pyrolytic decomposition profile of *Miscanthus*. The major volatile products were: acetic acid (3.53 min), trimethyl-2-cyclohexen-1-one (17.60 min), pentanol (18.13 min), 4-methyl-benzaldehyde (21.59 min), 3-methyl-benzaldehyde (21.69 min), 2,6-dimethoxy-phenol (syringol) (22.92 min), 2-methoxy-4-(2-propenyl)phenol (eugenol) (24.87 min) and 4-hydroxy-3-methoxybenzaldehyde (vanillin) (25.25 min). The abundance of acetic acid (3.53 min), pentanol (18.13 min) and 4-methyl-benzaldehyde (21.59 min) all increased. Additional major volatile peaks of trimethyl-2-cyclohexen-1-one (17.60 min) and 3-methyl-benzaldehyde (21.69 min) occurred due to increased Triton X-100 washing solution. It was observed that increased concentrations of Triton X-100 promoted the removal and/or partial decomposition of hemicellulose, which explains the

Table 3
Pre-treated *Miscanthus* fast pyrolysis mass balances and product properties.

| | Pre-treatment experiments | | | |
|---------------------------------------|-----------------------------|-----------------|-----------|--------------------|
| | Untreated <i>Miscanthus</i> | Deionised water | 1.00% HCl | 0.10% Triton X-100 |
| <i>Yield (wt.% on dry feed basis)</i> | | | | |
| Char | 13.70 | 12.97 | 10.69 | 9.77 |
| Bio-oil | 64.05 | 64.13 | 62.44 | 76.21 |
| Phase | Single | Single | Single | Single |
| Organics | 53.52 | 55.94 | 49.21 | 68.93 |
| Reaction water | 10.53 | 8.19 | 13.23 | 7.29 |
| Gas | 12.33 | 11.01 | 15.16 | 8.25 |
| Mass balance closure | 90.08 | 88.11 | 88.29 | 94.24 |
| <i>Char properties</i> | | | | |
| Ash (wt.% ^{d.b.}) | 13.77 | 14.86 | 15.82 | 17.65 |
| C (wt.% ^{d.a.f.}) | 82.88 | 75.76 | 79.79 | 84.99 |
| H | 3.47 | 3.72 | 3.22 | 4.00 |
| N | 0.12 | 1.37 | 2.38 | 0.12 |
| O* | 13.53 | 19.15 | 14.61 | 10.89 |
| HHV (MJ kg ⁻¹) | 32.77 | 29.73 | 30.09 | 35.04 |
| LHV | 32.02 | 28.90 | 30.29 | 34.17 |
| <i>Bio-oil properties</i> | | | | |
| C (wt.% ^{d.a.f.}) | 55.70 | 52.02 | 50.58 | 54.95 |
| H | 11.18 | 8.54 | 7.50 | 8.79 |
| N | 0.15 | 0.81 | 0.63 | 0.56 |
| O* | 28.97 | 38.63 | 41.29 | 35.70 |
| HHV (MJ kg ⁻¹) | 25.72 | 21.99 | 20.77 | 23.82 |
| LHV | 23.28 | 20.13 | 19.13 | 21.90 |
| pH | 2.43 | 3.11 | 3.35 | 2.96 |

^{d.b.} – dry basis.

^{d.a.f.} – dry ash free.

n/a – not analysed.

* By difference.

Table 4
Surfactant fast pyrolysis mass balances and product properties.

| | Triton X-100 pre-treatments | | | | |
|---------------------------------------|-----------------------------|--------|--------|--------|--------|
| | 0% | 0.10% | 0.25% | 0.50% | 1.00% |
| <i>Yield (wt.% on dry feed basis)</i> | | | | | |
| Char | 14.56 | 10.78 | 12.74 | 10.87 | 10.43 |
| Bio-oil | 56.86 | 57.34 | 56.34 | 63.59 | 64.54 |
| Phase | Single | Single | Single | Single | Single |
| Organics | 43.03 | 41.00 | 46.31 | 52.56 | 55.28 |
| Reaction water | 13.83 | 11.33 | 10.03 | 11.03 | 9.26 |
| Gas | 18.75 | 17.58 | 15.68 | 12.82 | 12.73 |
| Mass balance closure | 90.17 | 85.70 | 84.76 | 87.28 | 87.87 |
| <i>Char properties</i> | | | | | |
| Ash (wt.% ^{d.b.}) | 13.51 | 13.81 | 20.57 | 22.99 | 14.34 |
| C (wt.% ^{d.a.f.}) | 82.89 | 81.74 | 89.41 | 90.95 | 84.38 |
| H | 3.60 | 3.76 | 4.20 | 4.13 | 3.93 |
| N | 0.12 | 0.20 | 0.28 | 0.35 | 0.12 |
| O* | 13.39 | 14.30 | 6.11 | 4.57 | 11.57 |
| HHV (MJ kg ⁻¹) | 33.04 | 32.75 | 38.15 | 38.95 | 34.55 |
| LHV | 32.26 | 31.93 | 37.23 | 38.05 | 33.69 |
| <i>Bio-oil properties</i> | | | | | |
| C (wt.% ^{d.a.f.}) | 52.56 | 52.03 | 56.57 | 52.96 | 50.76 |
| H | 7.42 | 6.65 | 7.98 | 7.16 | 7.04 |
| N | 0.19 | 0.10 | 0.10 | 0.10 | 0.10 |
| O* | 39.83 | 41.22 | 35.35 | 39.78 | 42.10 |
| HHV (MJ kg ⁻¹) | 21.70 | 21.07 | 24.21 | 21.77 | 20.62 |
| LHV | 20.08 | 19.60 | 22.47 | 20.21 | 19.08 |
| pH | 2.87 | 2.95 | 2.76 | 3.09 | 2.46 |

^{d.b.} – dry basis.

^{d.a.f.} – dry ash free.

n/a – not analysed.

* By difference.

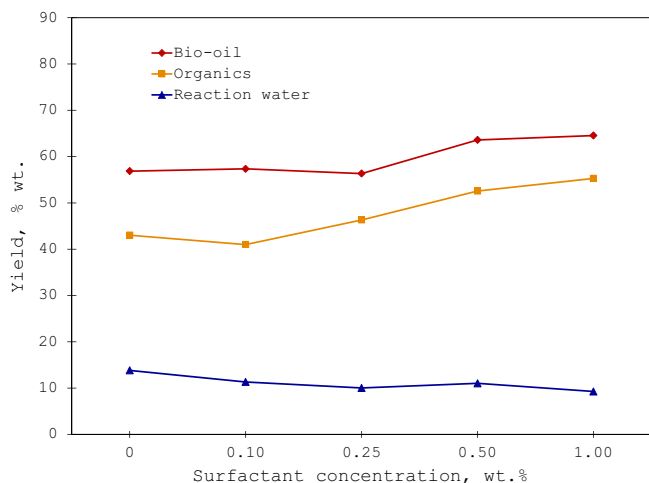


Fig. 3. Yields of fast pyrolysis liquids for different surfactant concentrations.

decrease in yield of lighter volatile compounds. All key markers for Py–GC–MS analysis of set 2 samples are given in Appendix A.

3.2. Fast pyrolysis processing and products characterisation

3.2.1. Fast pyrolysis experiments for pre-treated *Miscanthus* (set 1)

The fast pyrolysis mass balances for pre-treated *Miscanthus* are summarised in Table 3. Acceptable mass balance closures were achieved for all four feedstock's (>88%). The total bio-oil yield obtained from pre-treated *Miscanthus* stayed stable for demineralised water and HCl washes (62.44 and 64.13 wt.% respectively) when compared to untreated *Miscanthus* (64.05 wt.%) which suggests that these washes have no benefit in terms of bio-oil yield. Triton X-100 washed *Miscanthus* increased the bio-oil yield to 76.21 wt.% due to reduced cracking of organics to water and carbon dioxide as a result of a lowered ash content (refer Table 1). Untreated and demineralised water washed *Miscanthus* also had similar organic (53.32 and 55.94 wt.% respectively) and reaction water yields (10.53 and 8.19 wt.% respectively). HCl washed *Miscanthus* had decreased yields of organics (49.21 wt.%) and increased yields of reaction water (13.23 wt.%). This could be due to increased cracking of organics to water and carbon dioxide [26] as the second deionised water wash may not have removed all of the chlorine (as a result of HCl wash). Triton X-100 washed *Miscanthus* had higher yields of organics (68.93 wt.%) compared to raw and other pre-treated *Miscanthus* samples, also reaction water yields were the lowest (7.29 wt.%). Triton X-100 can increase cell permeability [13] allowing for the washing solution to wash a larger proportion of the biomass sample removing increased quantities of inorganics therefore reducing organic cracking. Yields of fast pyrolysis liquids for different pre-treatment methods are compared in Fig. 2.

Char yields decreased for all pre-treated *Miscanthus* samples, with Triton X-100 having the lowest char yield (9.77 wt.%) when compared to untreated *Miscanthus* (13.70 wt.%). As Triton X-100 pre-treatment lowered the inorganic content of *Miscanthus* the greatest (assumed from *Miscanthus* ash content, refer to Table 2) it was observed that lower char yields were obtained due to reduced catalysis of char forming reactions. Gas yields decrease for deionised and Triton X-100 washed *Miscanthus* (11.01 and 8.25 wt.%) when compared to untreated *Miscanthus* (12.33 wt.%), but HCl washed *Miscanthus* results in higher gas yields (15.16 wt.%). As mentioned previously increased reaction water and gas yields can be due to cracking of organics to water and carbon dioxide. All bio-oil produced was single phase.

Char higher heating values decreased for deionised and HCl washed *Miscanthus* (29.73 and 30.09 MJ kg⁻¹ respectively) but increased for Triton X-100 washed *Miscanthus* (35.04 MJ kg⁻¹) when compared to

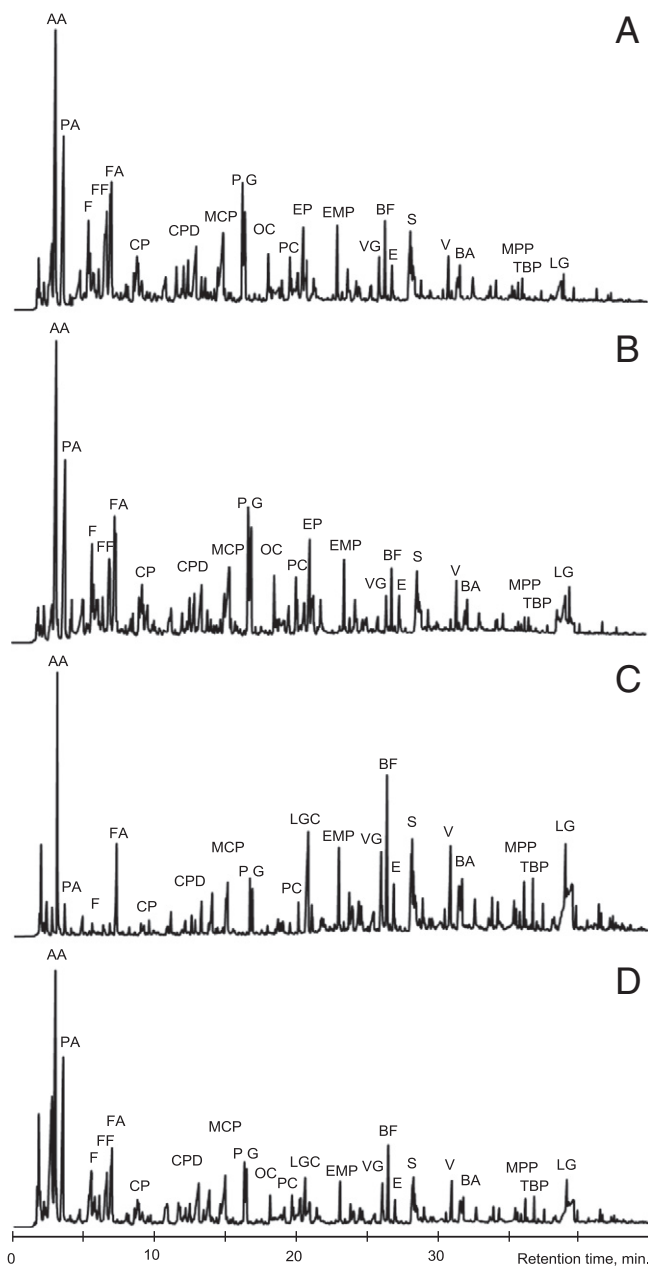


Fig. 4. GC–FID chromatograms of bio-oils produced from (A) untreated, (B) deionised water washed, (C) HCl washed and (D) 1.00% Triton X-100 washed *Miscanthus* × *giganteus*. Peak assignments and retention times: acetic acid (AA, 2.83 min); propionic acid (PA, 3.37 min); furan (F, 5.30 min); furfural (FF, 5.85 min); 2-furanmethanol (FA, furfuryl alcohol, 6.74 min); 2-cyclopenten-1-one (CP, 8.28 min); cyclopenten derivatives (CPD): 1-(2-furanyl)-ethanone (9.02 min); 2-hydroxy-2-cyclopenten-1-one (10.12 min); 5-methyl-2-furan-carboxyaldehyde (11.13 min); 3-methyl-2-cyclopenten-1-one (12.23 min); 2(5H)-furanone (12.64 min); 3-methyl-1,2-cyclopentane-dione (13.65 min); 2-hydroxy-3-methyl-2-cyclopenten-1-one (14.46 min); phenol (P; 15.78 min); 2-methoxyphenol (G; guaiacol, 15.94 min); 2-methylphenol (OC, o-cresol, 17.55 min); 4-methylphenol (PC, p-cresol, 19.79 min); levoglucosenone (LGC, 20.27 min); 4-ethylphenol (EP, 21.13 min); 4-ethyl-2-methoxyphenol (EMP, 23.05 min); 2-methoxy-4-vinylphenol (VG, 4-vinylguaiacol; 25.94 min); 2,3-dihydrobenzofuran (BF, 25.63 min); 2-methoxy-4-(2-propenyl)phenol (E, eugenol, 26.38 min); 2,6-dimethoxyphenol (S, syringol, 27.49 min); 4-hydroxy-3-methoxybenzaldehyde (V, vanillin, 30.11 min); 4-hydroxybenzaldehyde (BA, 32.94 min); 1-(2,5-dimethoxyphenyl)-ethanone (34.33 min); 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (34.92 min); 2,6-dimethoxy-4-(2-propenyl)-phenol (MPP, 35.14 min); 4-(tert-butyl)phenol (TBP, 36.21 min); levoglucosan (LG, 38.51 min).

Table 5
Results for the stability of bio-oils derived from pre-treatment experiments (set 1).

| Analysis | Pre-treatment experiments | | | | | | | |
|--|---------------------------|-------|-----------------|-------|-----------|-------|--------------------|-------|
| | Untreated Miscanthus | | Deionised water | | 1.00% HCl | | 0.10% Triton X-100 | |
| | 0 h | 24 h | 0 h | 24 h | 0 h | 24 h | 0 h | 24 h |
| Viscosity (cP) | 12.1 | 38.1 | 339.5 | 555.0 | 125.1 | 175.7 | 65.6 | 94.2 |
| Stability index based on viscosity | 3.15 | | 1.63 | | 1.40 | | 1.44 | |
| Water content increase (%) | 24.35 | 32.70 | 17.67 | 20.80 | 15.16 | 18.27 | 29.02 | 30.63 |
| Stability index based on water content | 1.34 | | 1.18 | | 1.21 | | 1.06 | |
| pH | 2.43 | 2.31 | 3.11 | 3.01 | 3.35 | 3.13 | 2.96 | 2.85 |

untreated *Miscanthus* (32.77 MJ kg⁻¹). Bio-oil higher heating values decreased for deionised, HCl and Triton X-100 washed *Miscanthus* (21.99, 20.77 and 23.82 MJ kg⁻¹ respectively) when compared to untreated *Miscanthus* (25.72 MJ kg⁻¹).

3.2.2. Fast pyrolysis experiments for surfactant pre-treated *Miscanthus* (set 2)

The fast pyrolysis mass balance for the surfactant demineralised *Miscanthus* are summarised in Table 4. Acceptable mass balance closures were achieved for all feedstocks (>84%). The total bio-oil yield obtained from Triton X-100 washed *Miscanthus* stayed stable for low concentrations of Triton X-100 from 56.34 to 57.43 wt.% (0.25% and 0.10% Triton X-100 respectively) compared to an untreated *Miscanthus* yield of 56.86 wt.%. As the concentrations of Triton X-100 increased so did the bio-oil yields to 63.59 and 64.54 wt.% (0.50% and 1.00% Triton X-1000 respectively) suggesting that increased concentrations of Triton X-100 result in more effective removal of inorganic matter due to reduced catalytic cracking of fast pyrolysis vapours. The organic content of bio-oil was increased from 43.03 wt.% (untreated *Miscanthus*) to 55.28 wt.% (1.00% Triton X-100). Triton X-100 decreases char and water produced whilst increasing liquid phase organics. Reaction water yields a decrease from 13.83 wt.% (untreated *Miscanthus*) down to 9.26 wt.% (1.00% Triton X-100), due to the decreased amount of cracking of organics to water and carbon dioxide. Fig. 3 compares yields of fast pyrolysis liquids for different pre-treatment surfactant concentrations.

Char yields decreased with increased concentrations of Triton X-100 from 14.56 wt.% (untreated *Miscanthus*) to 10.43 wt.% (1.00% Triton X-100). The char yields seemed to become stable as the concentration of Triton X-100 goes above 0.50% suggesting that further concentration increases would result in no improved reductions on char yields. Gas yields decrease with increased Triton X-100 concentrations from 17.58 wt.% (0.10% Triton X-100) to 12.73 wt.% (1.00% Triton X-100), but when the concentrations of Triton X-100 reached 0.50% the gas

yield stabilised at 12.82–12.73 wt.% (0.50% and 1.00% Triton X-100 respectively). All bio-oil produced was single phase.

Char higher heating values increased as Triton X-100 concentration increased from 32.75 to 38.95 MJ kg⁻¹ (0.10 and 0.50% Triton X-100 respectively), apart from 1.00% Triton X-100. The heating value was expected to be above 38.95 MJ kg⁻¹ but dropped to 34.55 MJ kg⁻¹, this could be due to the removal and/or partial decomposition of hemicellulose at higher concentrations of Triton X-100. Bio-oil higher heating values were similar for untreated *Miscanthus*, 0.10%, 0.50% and 1.00% Triton X-100 (21.66, 21.04, 21.73 and 20.58 MJ kg⁻¹ respectively), but when the concentration of Triton X-100 was at 0.25% the heating value increased to 24.17 MJ kg⁻¹.

The main compounds identified in the bio-oils are reported in Appendix A. All GC–MS chromatograms were similar for the main bio-oil samples produced from Triton X-100 pre-treated *Miscanthus* (chromatograms not shown). This identifies that Triton X-100 pre-treatment does not affect the biomass composition, apart from reducing the inorganic content.

3.2.3. GC–MS characterisation of pyrolysis liquids (bio-oils)

GC–FID chromatograms of bio-oils produced from untreated, deionised water washed, HCl washed and 1.00% Triton X-100 washed *Miscanthus* are shown in Fig. 4A, B, C and D respectively; with particular peak assignments and retention times. All key markers for GC–MS analysis of produced bio-oils are given in Appendix A.

Acetic acid was found as a major carboxylic acid in all bio-oils. This acid is an end-product of pyrolytic reactions of acetyl group removal from hemicelluloses (with xylose and glucuronic acid as main building blocks) [27]. A very short residence time of hot vapours seen at high heating rates (fast pyrolysis) favours formation of levoglucosan from cellulose. Levoglucosan is formed by depolymerisation reaction through transglycosylation and its further pyrolytic decomposition produces small amounts of acids and furans such as: acetic acid, propionic acid, furfural, 2- or 3-furaldehydes [28]. If levoglucosan undergoes further dehydration reactions levoglucosenone is also produced [29]. Furfural was observed in all bio-oils except the bio-oil produced from the HCl-treated *Miscanthus* sample. Subsequent proton addition, to the final furfural product results in the formation of 2-furanmethanol (furfuryl alcohol) [30], and this marker was predominant in acid washed sample. In bio-oil produced from untreated *Miscanthus* (with the highest concentration of ash/metals) and in bio-oils from deionised water and 1.00% Triton X-100 washed *Miscanthus* (with partially removed ash/metals) propionic acid as well as furan and cyclopentene derivatives such as: 1-(2-furanyl)-ethanone; 2-hydroxy-2-cyclopenten-1-one; 5-methyl-2-furan-carboxyaldehyde; 3-methyl-2-cyclopenten-1-one; 2(5H)-furanone; 3-methyl-1,2-cyclopentanedione; 2-hydroxy-3-methyl-2-cyclopenten-1-one were observed with much higher abundance compared to the bio-oil from HCl treated *Miscanthus*. This is due to the catalytic effect of the most abundant inorganic components of biomass (particularly Na, K, Mg, and Ca) which promote pyrolytic decomposition of cellulose and levoglucosan [26]. Demineralisation was shown to increase the yield of levoglucosan, levoglucosenone and 2,3-dihydrobenzofuran.

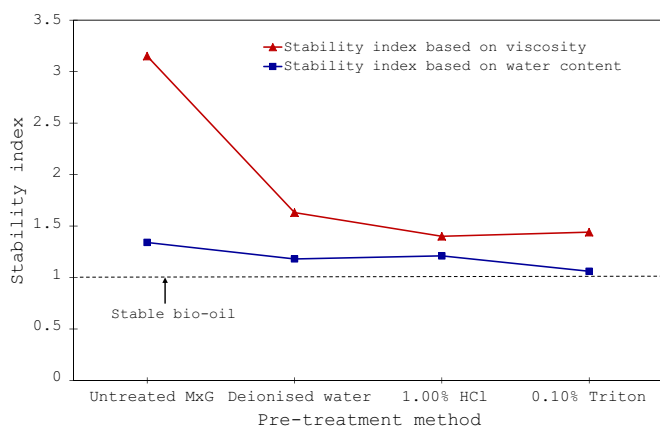


Fig. 5. Comparison of viscosity and water content stability indexes for different pre-treatment methods.

Table 6
Results for the stability of bio-oils derived from *Miscanthus* pre-treated with varying concentrations of Triton X-100 (set 2).

| Analysis | Triton X-100 washes | | | | | | | | | |
|--|---------------------|-------|-------|--------|-------|-------|-------|-------|-------|-------|
| | 0% | | 0.10% | | 0.25% | | 0.50% | | 1.00% | |
| | 0 h | 24 h | 0 h | 24 h | 0 h | 24 h | 0 h | 24 h | 0 h | 24 h |
| Viscosity (cP) | 110.7 | 298.5 | 684.5 | 1758.5 | 311.5 | 785.3 | 165.5 | 420.5 | 154.1 | 375.0 |
| Stability index based on viscosity | 2.69 | | 2.57 | | 2.52 | | 2.54 | | 2.43 | |
| Water content increase (%) | 16.22 | 21.67 | 5.17 | 5.55 | 7.35 | 7.75 | 8.73 | 9.26 | 8.21 | 8.32 |
| Stability index based on water content | 1.34 | | 1.07 | | 1.05 | | 1.06 | | 1.01 | |
| pH | 2.87 | 2.65 | 2.95 | 2.81 | 2.76 | 2.64 | 3.09 | 2.89 | 2.46 | 2.32 |

Acid and surfactant treatment decreased the yield of reaction water with no major impact on the abundance of key lignin markers such as: 2-methoxyphenol (guaiacol); 4-ethyl-2-methoxyphenol; 2-methoxy-4-(2-propenyl)phenol (eugenol); 2,6-dimethoxyphenol (syringol); 4-hydroxy-3-methoxybenzaldehyde (vanillin) and 4-hydroxybenzaldehyde.

3.3. Bio-oil quality and stability

The bio-oil stability experiments (set 1) for untreated *Miscanthus* and pre-treated *Miscanthus* are summarised in Table 5. Fig. 5 compares viscosity and water content stability indexes. As expected viscosity of all bio-oil samples placed in accelerated storage increased. The viscosity index shows that each different washing solution had a positive effect by reducing the index (towards one) compared to untreated *Miscanthus*. As the demineralisation washes have reduced the ash content of the feedstock results in a lower inorganic content of the char, which small amounts of char can be entrained in the fast pyrolysis vapours and therefore inorganic material may end up in the bio-oil. Reduced inorganic content in the bio-oil reduces ageing reactions, therefore the viscosity and water content indexes are closer to one (entirely stable). HCl and Triton X-100 washed *Miscanthus* have the lowest viscosity index (1.40 and 1.44 respectively) with deionised water washed *Miscanthus* having a slightly higher index (1.63). The water content index shows that Triton X-100 washed *Miscanthus* produces the most stable bio-oil (1.06), compared to deionised and HCl washed *Miscanthus* (1.18 and 1.21 respectively). Overall Triton X-100 washed *Miscanthus* bio-oil samples are more stable in both viscosity and water content indexes compared to the other large scale washings. This could be because the char that is entrained in

the bio-oil contains less inorganics (such as potassium and phosphorous) therefore reducing any further catalytic cracking or ageing reactions.

The pH of the bio-oil reduced after accelerated storage (Table 5) indicating decomposition of bio-oil organic constituents to low molecular weight products such as carboxylic acid, acetic acid and propanoic acid. Ortega et al. [31] proposed that organic constituents undergo oxidation reactions during storage forming alcohols, then ketones or aldehydes, followed by acids increasing the acidity of the bio-oil.

The bio-oil stability experiments (set 2) for untreated *Miscanthus* and Triton X-100 treated *Miscanthus* are summarised in Table 6. Fig. 6 compares viscosity and water content stability indexes for different surfactant concentrations. Viscosity of all bio-oil samples placed in accelerated storage increased. The viscosity index and water content index show that 1.00% Triton X-100 produces the most stable bio-oil (2.43 and 1.01 respectively), compared to untreated *Miscanthus* bio-oil (2.69 and 1.34 respectively). The viscosity index decreases slightly as the concentration of Triton X-100 increases. Varying concentrations of Triton X-100 have been studied to identify a specific concentration at which the stability of bio-oil becomes consistent. The water content index decreases as the concentration of Triton X-100 increases, 1.00% Triton X-100 produces a bio-oil with a water content index close to 1 (indicating a perfectly stable bio-oil). An increased concentration of Triton X-100 was expected to improve the stability of bio-oil in both viscosity and water content due to the more effective removal of inorganic content prior to fast pyrolysis processing (refer to Table 2). Overall 1.00% Triton X-100 *Miscanthus* bio-oil samples are the most stable in terms of viscosity and water content indexes.

4. Conclusions

Triton X-100 was identified to have the greatest effect on demineralisation of *Miscanthus* compared to deionised water and hydrochloric acid pre-treatments. This was identified by maximum yields of bio-oil (76.21 wt.%) as well as minimum yields of char (9.77 wt.%), reaction water (7.29 wt.%) and non-condensable gases (8.25 wt.%). Bio-oil stability was improved by all pre-treatment methods. Triton X-100 pre-treated *Miscanthus* bio-oil samples are more stable in both viscosity and water content indexes compared to the other pre-treatments. This is due to the entrained char in the bio-oil containing less inorganics (such as potassium, sodium and phosphorous) therefore reducing any further catalytic cracking or ageing reactions.

The influence of different concentrations of Triton X-100 pre-treatment solutions on the quality of bio-oil produced from fast pyrolysis was studied, as defined by a single phase bio-oil, viscosity index and water content index. By increasing the concentration of Triton X-100 to 1.00% resulted in the highest total liquid yield (64.54 wt.%) and the lowest char and reaction water yields (10.43 and 12.73 wt.% respectively). As the concentration of Triton X-100 reached 0.50% and above, the increase in bio-oil yield and decrease in char and reaction water yields began to become stable, indicating that concentrations above 1.00% would have no or little effect on mass balance yields. All concentrations of Triton X-100 give similar stability indexes.

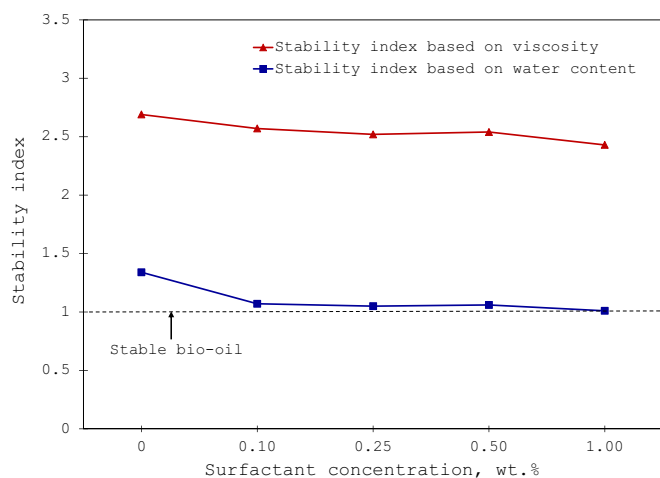





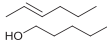
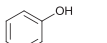
























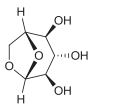
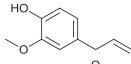
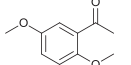
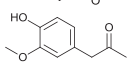
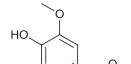
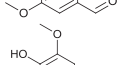
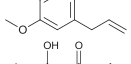
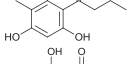
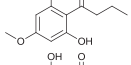


Fig. 6. Comparison of viscosity and water content stability indexes for different surfactant concentrations.

**Appendix A. Key marker assignment for Py–GC–MS analysis of biomass samples and GC–MS characterisation of produced bio-oils
(Markers ordered by increasing molecular weight)**

| Compound | Chemical structure | Chemical formula | Molecular weight | m/z |
|--|---|---|------------------|---------------------------------|
| Acetic acid |  | C ₂ H ₄ O ₂ | 60.05 | 60.02 (100.0%), 61.02 (2.2%) |
| Furan |  | C ₄ H ₄ O | 68.07 | 68.03 (100.0%), 69.03 (4.4%) |
| Propionic acid |  | C ₃ H ₆ O ₂ | 70.08 | 74.04 (100.0%), 75.04 (3.4%) |
| 1-Hydroxy-2-propanone |  | C ₃ H ₆ O ₂ | 74.08 | 74.04 (100.0%), 75.04 (3.4%) |
| 2(5H)-furanone |  | C ₄ H ₄ O ₂ | 84.07 | 84.02 (100.0%), 85.02 (4.3%) |
| 2-Hexene |  | C ₆ H ₁₂ | 84.16 | 84.09 (100.0%), 85.10 (6.6%) |
| Pentanol |  | C ₅ H ₁₂ O | 88.15 | 88.09 (100.0%), 89.09 (5.4%) |
| Phenol |  | C ₆ H ₆ O | 94.11 | 94.04 (100.0%), 95.05 (6.6%) |
| 3-Furaldehyde |  | C ₅ H ₄ O ₂ | 96.08 | 96.02 (100.0%), 97.02 (5.4%) |
| Furfural |  | C ₅ H ₄ O ₂ | 96.08 | 96.02 (100.0%), 97.02 (5.4%) |
| 2H-pyran-2-one |  | C ₅ H ₄ O ₂ | 96.08 | 96.02 (100.0%), 97.02 (5.4%) |
| 2-Furanmethanol |  | C ₅ H ₆ O | 98.10 | 98.04 (100.0%), 99.04 (5.6%) |
| 2-Hydroxy-2-cyclopenten-1-one |  | C ₅ H ₆ O ₂ | 98.10 | 98.04 (100.0%), 99.04 (5.6%) |
| 2-Methylphenol (o-cresol) |  | C ₇ H ₈ O | 108.14 | 108.06 (100.0%), 109.06 (7.7%) |
| 4-Methylphenol (p-cresol) |  | C ₇ H ₈ O | 108.14 | 108.06 (100.0%), 109.06 (7.7%) |
| 1-(2-furyl)-ethanone |  | C ₆ H ₆ O ₂ | 110.11 | 110.04 (100.0%), 111.04 (6.6%) |
| 1,2-Dihydroxybenzene (catechol) |  | C ₆ H ₆ O ₂ | 110.11 | 110.04 (100.0%), 111.04 (6.6%) |
| 3-Methyl-1,2-cyclopentane-dione |  | C ₆ H ₈ O ₂ | 112.13 | 112.05 (100.0%), 113.06 (6.7%) |
| 2-Hydroxy-3-methyl-2-cyclopenten-1-one |  | C ₆ H ₈ O ₂ | 112.13 | 112.05 (100.0%), 113.06 (6.7%) |
| 4-Methyl-benzaldehyde |  | C ₈ H ₈ O | 120.15 | 120.06 (100.0%), 121.06 (8.8%) |
| 3-Methyl-benzaldehyde |  | C ₈ H ₈ O | 120.15 | 120.06 (100.0%), 121.06 (8.8%) |
| 2,3-Dihydrobenzofuran |  | C ₈ H ₈ O | 120.15 | 120.06 (100.0%), 121.06 (8.8%) |
| 4-Hydroxybenzaldehyde |  | C ₇ H ₆ O ₂ | 122.12 | 122.04 (100.0%), 123.04 (7.7%) |
| 4-Ethylphenol |  | C ₈ H ₁₀ O | 122.16 | 122.07 (100.0%), 123.08 (8.8%) |
| 2-Methoxyphenol (guaiacol) |  | C ₇ H ₈ O ₂ | 124.14 | 124.05 (100.0%), 125.06 (7.7%) |
| Levogluconenone |  | C ₆ H ₆ O ₃ | 126.11 | 126.03 (100.0%), 127.04 (6.7%) |
| 2-Methoxy-4-vinylphenol |  | C ₉ H ₁₀ O ₂ | 150.17 | 150.07 (100.0%), 151.07 (9.9%) |
| 4-(tert-butyl)phenol |  | C ₁₀ H ₁₄ O | 150.22 | 150.10 (100.0%), 151.11 (11.0%) |
| 4-Hydroxy-3-methoxybenzaldehyde (vanillin) |  | C ₈ H ₈ O ₃ | 152.15 | 152.05 (100.0%), 153.05 (8.9%) |
| 4-Ethyl-2-methoxyphenol |  | C ₉ H ₁₂ O ₂ | 152.19 | 152.08 (100.0%), 153.09 (9.9%) |
| 2,6-Dimethoxyphenol (syringol) |  | C ₈ H ₁₀ O ₃ | 154.16 | 154.06 (100.0%), 155.07 (8.9%) |

Appendix A. (continued)

| Compound | Chemical structure | Chemical formula | Molecular weight | m/z |
|--|---|--|------------------|--|
| Levoglucofan |  | C ₆ H ₁₀ O ₅ | 162.14 | 162.05 (100.0%), 163.06 (6.8%), 164.06 (1.2%) |
| 2-Methoxy-4-(2-propenyl)phenol (eugenol) |  | C ₁₀ H ₁₂ O ₂ | 164.20 | 164.08 (100.0%), 165.09 (11.0%) |
| 1-(2,5-Dimethoxyphenyl)-ethanone |  | C ₁₀ H ₁₂ O ₃ | 180.20 | 180.08 (100.0%), 181.08 (11.1%) |
| 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone |  | C ₁₀ H ₁₂ O ₃ | 180.20 | 180.08 (100.0%), 181.08 (11.1%) |
| 4-Hydroxy-3,5-dimethoxybenzaldehyde |  | C ₉ H ₁₀ O ₄ | 182.17 | 182.06 (100.0%), 183.06 (10.0%), 184.06 (1.2%) |
| 2,6-Dimethoxy-4-(2-propenyl)-phenol |  | C ₁₁ H ₁₄ O ₃ | 194.23 | 194.09 (100.0%), 195.10 (12.2%), 196.10 (1.3%) |
| 1-(2,4,6-Trihydroxy-3-methylphenyl)-1-butanone |  | C ₁₁ H ₁₄ O ₄ | 210.23 | 210.09 (100.0%), 211.09 (12.0%) |
| Desaspidinol |  | C ₁₁ H ₁₄ O ₄ | 210.23 | 210.09 (100.0%), 211.09 (12.0%) |
| Aspidinol |  | C ₁₂ H ₁₆ O ₄ | 224.25 | 224.10 (100.0%), 225.11 (13.3%), 226.11 (1.6%) |

Acknowledgments

The authors are grateful for the financial support from the SUPERGEN Bioenergy II Consortium under the Engineering and Physical Sciences Research Council, UK (EPSRC) grant no. EP/E039995/1: SUPERGEN Biomass Biofuels and Energy Crops II Core.

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