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Mass spectrometry study of lignocellulosic biomass combustion and pyrolysis with NO_x removal

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Mass spectrometry study of lignocellulosic biomass combustion and pyrolysis with NO_x removal

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Abstract

Herein, a study of the thermal combustion/pyrolysis behaviour of three lignocellulosic biomass materials was tested. Alongside this an investigation on the reduction of the subsequently produced pollution emissions was carried out. The lignocellulosic biomasses (*miscanthus* × *giganteus*, orange peel waste (OPW) and potato peel waste (PPW)) were physiochemically characterized, along with in-situ gas detection from the combustion/pyrolysis processes. XRD and EDX results showed high level of inorganic salts in the bulk and surface of the samples tested which had an impact on the combustion/pyrolysis behaviour. Among the three lignocellulosic biomasses tested, OPW showed the highest higher heating value of 17.88 MJ.Kg^{-1} , where potato ash was the best candidate as a potential source of potassium (23.8 wt.%) to be used in the fertiliser industry. The EDX results showed that *miscanthus* was the only lignocellulosic biomass to show high % Si in the surface composition. This was the reason for the low-temperature melting due to the formation of low fusion-temperature silicate as a result of SiO_2 , K, Cl and S. Pyrolysis experiments were conducted under pure nitrogen atmosphere, where hydrogen gas was observed in the temperature range of $580\text{-}700^\circ\text{C}$. Combustion experiments were run under air where NO_x emissions are generated during the combustion process. To mitigate those emissions, coupling the De NO_x catalyst with urea to construct in-situ NH_3 -SCR system during the combustion achieved low levels of NO_x emissions.

Keywords: Lignocellulosic biomass, Combustion, Mass spectrometer, NO_x emissions.

Graphical Abstract:

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1. Introduction

Lignocellulosic biomass is considered one of the most promising energy sources due to being an environmentally friendly fuel. For instance, one tonne of lignocellulosic biomass (miscanthus) can produce 30 gallons of fuel [1]. When processed by steam gasification, it produces around 1.1 m³.Kg⁻¹ of gas containing more than 40% H₂ and CO with H₂/CO ratio of 1.7 ~2 as well as a low yield of tar, char, CO₂ and CH₄. This composition makes it suitable for the production of biofuels such as methyl alcohol, dimethyl ether (DME) or through Fischer–Tropsch (FT) processes for the production of heavier hydrocarbons including biodiesel [2-5].

However, a comparison study of combustion efficiency between eight different biomass fuels (pine, spruce, brash, three different willow species, miscanthus and wood pellets) in a small multi-fuel boiler was carried out by Forbes et al.[6] who reported that the standard wood pellet showed the best overall performance with the highest output of energy per unit mass (4.11 kWh.Kg⁻¹) as an energy crop. Of the range tested miscanthus was the lowest (3.7 kWh.Kg⁻¹). Moreover, a significant difference between these fuels was found in terms of energy output intensity, again with wood pellets being significantly higher than the miscanthus (126.9 and 83.6 kW.h⁻¹, respectively).

Biomass waste such as orange peel waste (OPW) and potato peel waste (PPW) could be of great interest as an energy carrier or other applications. Potatoes are the world's fourth-largest crop after corn, rice and wheat with 21.7 billion Kg produced in 2011. The peeling process in a potato processing plant can generate from up to 10% PPW along with additional 15% waste from trimming, defect removal and cutting processes. The four main components of PPW are nonstarch polysaccharide (30%), starch (25%), acid soluble and acid insoluble lignin (20%) and protein (18%) along with small amounts of ash and lipids with 6 and 1% composition, respectively [7]. On the other hand, the OPW is mainly composed of sugars, pectin, cellulose and hemicellulose along with a low content of lignin. More detailed chemical composition of the OPW was reported

by Ahmed et al.[8] with moisture (40.7%), sugars (28.48%), crude fiber (7.8%), ash (7.39%), pectin (7.0%), lignin (6.4%) and fat (1.85%).

Wu reported that there are 70,000-140,000 tonnes of PPW globally produced per annum which is commonly used for producing fertilizer, low-value animal feed or as a feedstock for the production of biogas via the anaerobic digestion process [9]. The PPW can also produce lactic acid or phenolic acid through extraction or in the ultrasonic extraction of steroidal alkaloids.

Ledesma et al.[10] reported the release of hydrogen cyanide (HCN), ammonia (NH₃), and isocyanic acid (HNCO) from the thermal gas-phase cracking of coal pyrolysis tars, using a two stage set up. Firstly, with a fluidised bed reactor to generate the tar, followed by a tubular flow reactor in the temperature range of 600-1000°C to decompose the formed tars with a rapid heating rate in the first stage of 10⁴ K.s⁻¹. It was found that HNCO evolved first at a temperature above 600°C, where HCN and NH₃ released in the temperature range of 700-1000°C, with NH₃ evolution reached a maximum at 850°C [10]. Hansson et al. studied the Formation of HNCO, HCN, and NH₃ from the pyrolysis of bark at a temperature range of 700-1000°C and reported that cracking of the cyclic amides is suggested to be the main reaction leading to HCN and HNCO [11]. Bark pyrolysis showed that quantification of HCN and NH₃ was unreliable at temperature up to 800 °C due to low concentrations [11]. Other studies showed that pyrolysis of biomass N over 300°C releases NH₃ and HCN which can be detected easily via online-FTIR or offline-spectrophotometry [12-14]. Although the release of HCN may occur at higher temperatures. However, due to the various types of small molecular gases in the pyrolysis gases and the limitations of mass spectrometry, it may not be the best technique to directly detect NH₃ and HCN.

One of the major challenges of using biomass as an energy carrier is the treatment of such emissions during the thermal process (combustion/pyrolysis). Nitrogen oxides (NO_x) are considered one of the main gas emissions during the thermal processes of biomass [6]. Therefore, this kind of emissions needs to be controlled, as they have an impact on the environment and human health. NO_x family gases are often recognised to cause acid rain. They consist of seven oxides; nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), dinitrogen dioxide (N_2O_2), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4) and dinitrogen pentoxide (N_2O_5) with the first three oxides considered to be the most abundant NO_x emissions in the air. Moreover, N_2O which is mainly produced from biogenic sources such as plants, is considered a potent greenhouse gas with a global warming potential of 298 times that of CO_2 with a long half-life time in the atmosphere (100-150 years) [15]. Furthermore, N_2O is an ozone depleting substance and it is being produced and treated the same way as the rest of the NO_x gases [15]. Recently, the UK government reported that NO_x gases are the only air emissions that have not met the agreed governmental regulations thus far [16].

There are seven main ways to mitigate NO_x emissions during fuel combustion. Firstly, by reducing the peak temperature using a catalytic combustion system, reduced air preheat, air staging, natural gas reburning, injecting water (steam) or using low NO_x burner. The second method is to reduce residence time at peak temperature by injecting air, fuel or steam. The third method is a chemical reduction of NO_x by using selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR). The fourth method is NO_x oxidation with subsequent absorption using nonthermal plasma reactor or injects oxidant. The fifth method is the removal of nitrogen by using oxygen instead of air or using ultra-low nitrogen fuel. The sixth method is using a sorbent in the combustion chamber, while the last method is combining two or more of the last six methods in order to achieve a low level of NO_x emission. The most common chemical method is either

HC-SCR using hydrocarbon over Ag/Al₂O₃ catalyst or NH₃-SCR over noble metals catalyst at low temperature (urea can be used to provide the ammonia needed for this particular method).

Miscanthus has attracted considerable attention as an alternative candidate for a wide range of applications. Currently, it is grown to some degree as a biomass energy crop for use in power plants and heating combustion units. However, high ash and mineral contents in the composition of miscanthus make its use as an energy source a challenge. Moreover, these minerals can have the effect of lowering the melting point of miscanthus ash, causing a series of problems within many combustion systems. There are ever-increasing necessities to study the thermal combustion behaviour of the lignocellulosic biomass along with reducing the subsequent related pollution emissions from the air.

The above discussion leads to the conclusion that this research area needs further investigation in order to understand the gas emissions and the combustion/ pyrolysis behaviour of biomass using *in-situ* mass spectrometry technique along with the mitigation of NO_x emissions by using the *in-situ* after-treatment catalytic system. Herein, a correlation between the chemical analysis and the combustion/pyrolysis behaviour of the three different lignocellulosic biomasses (*miscanthus* × *giganteus*, orange peel waste and potato peel waste) was drawn via *in-situ* gas detection using Mass spectrometer (MS) technique. To the best of the author's knowledge, this is the first detailed study to correlate and understand the lignocellulosic biomass of miscanthus, OPW and PPW emissions behaviour during combustion and pyrolysis along with mitigating the NO_x emissions using *in-situ* NH₃-SCR system.

2. Materials and methods

2.1 Lignocellulosic biomass Material Preparation

The miscanthus was harvested from a 10-yr-old energy crop grown at the Agri-Food and Biosciences Institute (AFBI), Environment & Renewable Energy Centre, Hillsborough, Northern

Ireland (54.453077, -6.086162) [17]. The peel wastes (OPW and PPW) were dried at 110 °C until complete dryness, then crushed into a form of powder for the characterization tests and sieved to obtain particles of 110- 300 µm size for the thermal decomposition tests.

2.2 Lignocellulosic biomass Characterization

Powder X-ray diffraction (XRD) was carried out using a PANalytical X'Pert Pro X-ray diffractometer. This diffractometer was equipped with a CuK_α X-ray source with a wavelength of 1.5405 Å. The diffractograms were collected up to $2\theta = 80^\circ$. The X-ray tube was set at 40 kV and 40 mA.

Scanning Electron Microscopy (SEM) was carried out on a FEI Quanta 250 FEG MKII with a high-resolution environmental microscope (ESEM) using XT Microscope Control software and linked to an energy-dispersive X-ray (EDX) detector. Two types of detectors were used in SEM analysis; the Everhart-Thornley Detector (ETD) which is used to detect secondary electrons emitted from the sample and Back-Scattered Electron Detector (BSED). The EDX used was a 10 mm² silicon drift detector (SDD)-x-act from Oxford Instruments which utilizes Aztec® EDS analysis software. Both systems used the same chamber.

Brunauer-Emmett-Teller (BET) analysis was performed using a Micromeritics ASAP 2020 system. BET surface area and pore volume were measured by N₂ adsorption and desorption isotherms at liquid nitrogen temperature (-196 °C).

Compositions of the three lignocellulosic biomass samples were characterized by means of proximate and ultimate analyses. Elemental (C, H and N) Analysis was performed using a Perkin Elmer PE2400 CHNS/O Elemental Analyzer. The oxygen content was calculated by difference from the data obtained by a Perkin Elmer PE2400 CHNS/O Elemental Analyzer machine.

TGA was performed from 50 to 900 °C with different heating rates of 2.5, 10, 20 and 30 °C.min⁻¹, in a stream of dry N₂ flowing at 20 cm³.min⁻¹, using a simultaneous thermal analysis Mettler Toledo (TGA/DSC) Thermogravimetric analyzer Pyris TGA/DSC1. Changes in mass of the sample were recorded during the ramping operation. Differential Scanning Calorimetry (DSC) was used to determine the heat liberated in watts per gram.

2.3 *In-situ gas detection of lignocellulosic biomass combustion/pyrolysis*

The combustion/pyrolysis of the three lignocellulosic biomass experiments was conducted in a fixed bed reactor, where the output of the reactor is coupled with a mass spectrometer (MS) through a heated quartz capillary tube. In order to prevent any condensation, dissolution or adsorption on the tube wall, all of the lines were heated to 150 °C, where the evolved gas mixtures were then directly fed to the mass spectrometer. The MS (Hiden Analytical instrument) performed under vacuum and *in-situ* detecting the characteristic fragment ion intensity of the evolved gas according to its mass to charge ratio (m/z) qualitatively. The selected ion recording mode was used to detect the MS signals of certain molecular ions marked accurately for the representative gas species such as $m/z = 84$ (Krypton), $m/z = 16$ (oxygen), $m/z = 43$ (acetic acid), $m/z = 78$ (benzene), $m/z = 44$ (carbon dioxide), $m/z = 27$ (ethane), $m/z = 2$ (hydrogen), $m/z = 13$ (methane), $m/z = 31$ (methyl alcohol), $m/z = 64$ (sulphur dioxide), $m/z = 76$ (carbon disulphide), $m/z = 26$ (propane), $m/z = 30$ (nitrogen dioxide, nitric oxide), $m/z = 45$ (nitrous oxide), $m/z = 94$ (phenol), $m/z = 91$ (toluene), $m/z = 18$ (water), $m/z = 29$ (acetaldehyde), $m/z = 57$ (hexane) and $m/z = 42$ (pentane). In fact the molecular ion of both N₂O and CO₂ is 44, however, their ion peaks are different where N₂O is 44, 30 and 28 and CO₂ is 44, 28 and 16.

3. Results and Discussion

3.1 *Lignocellulosic biomass characterisation*

3.1.1 XRD analysis

The XRD diffractogram patterns of the orange peel waste (OPW) and potato peel waste (PPW) are shown in Figure 1 (a) along with their ashes in Figure 1 (b). The OPW and PPW diffractograms showed two different phases; amorphous and crystalline cellulose. In previous work [18], miscanthus showed mainly crystalline cellulose (JCPDS data 03-0289) with diffraction lines at $2\theta = 22^\circ$ corresponding to the crystallographic plane (002). It is obvious from Figure 1 (a) that the crystalline cellulose is much lower in the case of OPW and PPW compared to the miscanthus. The crystallinity index gives the measure of crystalline cellulose for amorphous regions. The % CRI was given according to equation 1

$$\%CRI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad \text{(Equation 1)}$$

Where: I_{002} : is the highest peak (002) intensity of the crystalline fraction at $2\theta = 22^\circ$

I_{am} : is the low-intensity peak of the amorphous region at $2\theta = 18^\circ$

The % CRI values calculated for miscanthus, OPW and PPW according to equation 1 were 77.1, 46.0 and 24.1 %, respectively. Bicu and Mustata calculated the % CRI for orange peel which showed 43.7% and this is in line with our results [19]. They attributed the low cellulose crystallinity to the high amorphous portion and consequently greater permeability to water and chemicals for the orange peel. PPW showed the lowest crystalline cellulose among the series of the three lignocellulosic samples with 24.1% CRI.

Figure 1 (b) shows the XRD pattern of orange and potato ash. Like the miscanthus ash in the previous study, both orange and potato ash showed mainly potassium hydrogen disilicate (KHSi_2O_5 at $2\theta = 28.4$ and 32.2) and potassium chloride (KCl at $2\theta = 40.6, 50.25, 58.6$ and 66.5) phases. Orange ash showed more CaCO_3 ($2\theta = 33.8$) than that of potato ash [20]. Both samples showed also diffraction lines corresponding to K_2SO_4 ($2\theta = 21.6$), $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$ ($2\theta = 21.6, 23.8, 30.8, 36.8$ and 45.03), crystalline silica (SiO_2 at $2\theta = 26.2$) and KHCO_3 ($2\theta = 29.4$) [21].

Figure 1: XRD patterns of orange and potato peel waste (OPW and PPW) (a) and orange and potato ash (b) samples.

3.1.2 SEM-EDX analysis

The SEM images of OPW and PPW along with their ashes using the backscattered electron detector (BSED) are shown in Figure 2. The BSED is used to measure the backscattered electrons from the sample, where the elements of higher atomic number appear brighter in the image due to emitting a large number of back-scattered electrons (BSE). OPW and PPW samples showed few lighter spots as those samples are mainly carbon and oxygen only with traces of heavy elements. It is obvious that orange and potato ash images (Figure 2 (c, d) showed more lighter spots than that of OPW and PPW (Figure 2 (a, b) which indicates the presence of inorganic salts (heavier element than carbon) such as KHSi_2O_5 and KCl as shown from the XRD analysis of the ash samples.

269 **Figure 2:** SEM images of OPW (a), PPW (b), orange ash (c) and potato ash (d).

The EDX analysis revealed the chemical composition of OPW and PPW as shown in Figure 3 and Table 1. It is obvious that both samples are mainly composed of carbon (~ 60 wt.%) and oxygen (~40 wt.%) with traces of potassium (0.7-2.3 wt.%), calcium (0.3 wt.%) and sulphur (0.2 wt.%). Interestingly, miscanthus is the only lignocellulosic biomass in this study to show high silicon (0.6 wt.%) in the composition which is six times higher than the other biomass samples as shown in Table 1. The highest percentage compositions of the inorganic salts in the OPW were observed for potassium and calcium with a K/Ca % ratio of 2.33, which is in agreement with the ratio reported by Santos et al.[22] of 2.15.

Figure 3: EDX data of orange peel (a), potato peel (b) samples.

The EDX data of the orange and potato ashes are shown in Figure 4. It is obvious that the inorganic salts are dramatically increased compared to the wt.% composition shown in Figure 3. For example, the potassium and calcium % composition in orange ash showed 17.5 and 7.6 wt.%, respectively. While in potato ash potassium and chloride % composition showed 26.6 and 3.3

wt.%, respectively. It is worth noting that the potassium % composition in dry miscanthus plant was 0.9 wt.%, while in the miscanthus ash, it increased to reach 23.8 wt.%. The inference being that potato ash is the best candidate among that the three lignocellulosic biomass of being used as a potential source of potassium in the fertilizer industry with 23.8 wt.% of its composition is potassium. The EDX results are in agreement with the SEM and XRD results that showed the presence of inorganic salts in the ash samples.

Figure 4: EDX data of orange ash (a), potato ash (b) samples.

3.1.3 TGA/DSC analyses

The TGA (a, c) and DSC (b, d) curves of OPW and PPW under nitrogen and air atmosphere, respectively, are shown in Figure 5. The TGA curves of the thermal pyrolysis (under N₂ atmosphere) of OPW and PPW showed % weight loss of 74.75 and 72.81%, respectively, which is slightly lower than that of miscanthus in previous work (72.5%) [18]. The rate of the % weight loss in OPW is slower than that of PPW as shown in Figure 5 (a, c). The DSC curves of the thermal combustion (under an air atmosphere) of OPW and PPW showed in Figure 5 (b, d) with two combustion stages at temperature ranges of 220-370°C and 410-650°C. It is not surprising the two combustion peaks were shifted toward higher temperatures with increasing the heating rate. The calculated ignition and burnout temperatures along with the heat released by the combustion of the three studied lignocellulosic biomass are shown in Table 1, which again all dramatically increased with increasing the heating rates. For instance, the ignition temperatures of miscanthus, OPW and PPW were slightly increased by 24, 25 and 23°C, respectively, with increasing the heating rates from 2.5 to 30 °C.min⁻¹ as shown in Figure S1 and Table 1. On the other hand, the burnout temperature of miscanthus, OPW and PPW was significantly increased by 112, 157 and 160°C, respectively with increasing the heating rates by the same value as shown in Figure S2 and Table 1. Similarly, the heat liberated in W.g⁻¹ of miscanthus, OPW and PPW was dramatically increased by approximately ten times with increasing the heating rates by the same value in the three lignocellulosic biomass samples from around 500 to 5000 W.g⁻¹ as shown in Table 1 and Figure S3. The elemental (C, H and N) analysis is shown in Table 1, which revealed that the % C, H, N and O were in the range of 41 – 45 %, 5.7 - 5.9 %, 1.2 - 1.8 % and 47 – 50 %, respectively along with minor contribution of sulphur ~0.2%, this is agreement with the previous publication [18]. The surface area measurement the three lignocellulosic biomass is shown in Table 1. It is obvious that they showed low surface areas of approximately 17 m².g⁻¹ with a pore size of 16 Å°.

Figure 5: TGA curves of OPW (a) and PPW (c) under nitrogen atmosphere (20 ml.min⁻¹) along with the DSC curves of OPW (b) and PPW (d) under air atmosphere (20 ml.min⁻¹).

332 Table 1: Physicochemical characterisations of miscanthus, OPW and PPW samples.

samples		Miscanthus	Orange peel waste	Potato peel waste
Elemental composition (wt% on dry and ash free basis)	% C	42.85	45.36	41.52
	% H	5.83	5.96	5.71
	% N	1.21	1.32	1.86
	% S	0.1	0.2	0.2
	% O	50.01	47.16	50.71
Proximate analysis (wt% on dry and ash free basis)	Moisture	2.9	7.38	3.85
	Volatile	72.5	74.75	72.81
	Char	27.5	25.25	27.19
	Fixed carbon	21.22	13.5	12.16
	Ash	3.38	4.37	11.18
	HHV ^a	16.58	17.88	15.73
	LHV ^b	15.37	16.07	14.02
EDX analysis (wt% on dry and ash free basis)	C	61.7	60.2	56.5
	O	35.8	38.6	40.3
	K	0.9	0.7	2.3
	Si	0.6	0.1	--
	Ca	0.3	0.3	0.3
	P	0.1	--	0.2
	Mg	0.1	--	--
	Cl	0.1	--	0.2
	S	0.2	0.2	0.2
DSC results (Different heating rates)	Ignition Temp. (°C)	2.5 °C min ⁻¹	242	250
		10 °C min ⁻¹	252	260
		20 °C min ⁻¹	262	269
		30 °C min ⁻¹	266	275
	Burnout Temp. (°C)	2.5 °C min ⁻¹	488	475
		10 °C min ⁻¹	563	529
		20 °C min ⁻¹	587	572
		30 °C min ⁻¹	600	632
	Heat liberated (W/g)	2.5 °C min ⁻¹	291.9	565.5
		10 °C min ⁻¹	1352	1828.6
		20 °C min ⁻¹	2916.2	3294.1
		30 °C min ⁻¹	4916.3	3881.2
SBET results	S _{BET} (m ² /g)		1.89	
	Pore volume (cm ³ /g)		0.0018	0.002
	Pore size (Å)		18.9	15.7

333 ^a High heating value (kJ. g⁻¹ dry feedstock) in MJ.kg⁻¹334 ^b Low heating value (kJ. g⁻¹ dry feedstock) in MJ.kg⁻¹

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3.2 Mass spectrometer analysis of lignocellulosic combustion/pyrolysis:

3.2.1 Miscanthus combustion under air atmosphere:

The *in-situ* MS profile for the gases evolved during the combustion of miscanthus under air atmosphere is shown in Figure 6. As mentioned in the introduction, that there are seven nitrogen oxides species, however, N_2O , NO and NO_2 are the most abundant nitrogen oxide species in the air. It is obvious that nitrous oxide shows the highest level of gas emissions during miscanthus combustion as shown in Figure 6. It is well known that nitrous oxide is mainly produced through biogenic sources such as plants [15], so it is not surprising that nitrous oxide showed the highest level of emissions, followed by water (H_2O) and carbon dioxide (CO_2). Forbes et al.[6] studied the combustion of miscanthus and reported that NO_x is one of the two main gases emissions. The low level of gas emissions is shown in the inset, where it showed the presence of nitric oxide (NO), nitrogen dioxide (NO_2), oxygen (O_2), Acetaldehyde (CH_3CHO), acetic acid (CH_3COOH) and hydrogen (H_2) emissions with traces of benzene. Miscanthus was the only lignocellulosic sample to melt during the combustion, this is in agreement with the the EDX results that showed miscanthus was the only lignocellulosic biomass to show % Si in the surface composition. This was the reason for the low temperature melting behaviour of miscanthus herein.

Figure 6: Mass spectrum profile of the gases released during miscanthus combustion under air atmosphere with a temperature ramp of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature is shown in a dashed line.

3.2.2 Miscanthus pyrolysis under nitrogen atmosphere:

Similarly, miscanthus pyrolysis using nitrogen atmosphere (Figure 7) showed again the main gasemissions are N_2O and H_2O . On the other hand, traces of CO_2 was detected under the pyrolysis conditions and two large H_2 peaks were observed at a temperature of 580 and 700°C . The low level of gas emissions (the inset) showed the presence of CO_2 , hydrocarbons (methane and ethane), acetic acid, methyl alcohol and hydrogen with traces of nitrogen oxides (NO and NO_2).

Figure 7: Mass spectrum profile of the gases released during miscanthus pyrolysis under nitrogen with a temperature ramp of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature is shown in a dashed line.

3.2.3 *Miscanthus combustion under oxygen atmosphere:*

Miscanthus combustion under an oxygen atmosphere (Figure 8) showed similar emissions behaviour as in the combustion under air atmosphere with the main emissions being N_2O , H_2O and CO_2 with two stages of combustion at a temperature of 282 and 349 $^{\circ}\text{C}$ and this is in agreement with the DSC results in Figure 5. The low level of gas emissions (the inset) showed the presence of acetic acid, methane, acetaldehyde and hydrogen with traces of nitrogen oxides (NO and NO_2).

Figure 8: Mass spectrum profile of the gases released during miscanthus combustion under oxygen atmosphere with a temperature ramp of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature is shown in a dashed line.

3.2.4 *Miscanthus* biochar combustion under air atmosphere:

The MS profile for the gas emissions during the combustion of miscanthus biochar is shown in Figure 9. Again, the highest level of gas emissions was shown for N_2O . However, it was followed by CO_2 and O_2 gases with traces of H_2O , CH_3CHO and H_2 emissions.

Figure 9: Mass spectrum profile of the gases released during miscanthus biochar combustion under an air atmosphere with a temperature ramp of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature is shown in a dashed line.

3.2.5 Orange peel waste combustion under air atmosphere:

The *in-situ* MS profile for the gases evolved during the combustion of OPW under air atmosphere is shown in Figure 10. It is obvious that the combustion occurred in two stages at a temperature range of 160-370°C and 440-600°C. The MS profile showed that with the main emissions are N₂O, H₂O, CO₂ and O₂. The low level of gases emission (the inset) showed the presence of CH₄, H₂ and ethane with traces of CH₃CHO and nitrogen oxides (NO and NO₂). Zapata et al. [23] reported that the thermal degradation firstly started by the depolymerization and thermal cracking of the functional groups of hemicellulose in the temperature range of 150-250°C, followed by the defunctionalization, depolymerization and chain breaking of cellulose in the temperature range of 250-360°C. Finally, lignin degradation occurred at the temperature range of 380-585°C.

Figure 10: Mass spectrum profile of the gas released during orange peel waste combustion under an air atmosphere with a temperature ramp of 10 °C.min⁻¹. The temperature is shown in a dashed line.

3.2.6 Potato peel waste combustion under air atmosphere:

The in situ MS profile for the gases evolved during the combustion of PPW under air atmosphere is shown in Figure 11. Unlike the OPW combustion which occurred in two stages, the combustion of PPW showed two main combustion stages at temperature ranges of 200-300°C and 400-500°C along with a small combustion peak at high temperature (>700°C). Again, the MS profile showed that with the main emissions are N₂O, H₂O, CO₂ and O₂, while The low level of gas emissions (the inset) showed the presence of CH₃CHO, CH₃COOH, CH₄, H₂ and C₂H₆ with traces of and nitrogen oxides (NO and NO₂). The results are in agreement with the work done by Liang et al. [7] who reported the presence of CH₃CHO and CH₃COOH with a relative abundance of 2.89 and 14% during the pyrolysis of PPW using GC-MS technique. It is worth noting that the total combustion of the OPW was observed at 600°C, wherein the PPW there was an extra small combustion peak at a temperature of >700°C. This is attributed to the high lignin content (decomposes at high temperature) in the PPW compared to OPW which are 20 and 6.4%, respectively [7].

Figure 11: Mass spectrum profile of the gas released during potato peel waste combustion under air atmosphere with a temperature ramp of $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$. The temperature is shown in a dashed line.

3.3 NO_x Abatement Systems SCR with and without urea:

The selective catalytic reduction (SCR) of NO_x during the combustion of miscanthus in an air atmosphere using an only DeNO_x catalyst which is Pt/TiO₂/ZSM-5 is shown in Figure 12. The preparation of the DeNO_x catalyst is shown elsewhere [24]. Interestingly, the MS profile showed that the highest gas emission is water i.e. the DeNO_x catalyst did reduce the N₂O emissions into H₂O and N₂. However, the emission level of N₂O still observable as shown in Figure 12.

Figure 12: Mass spectrum profile of the gas released during miscanthus combustion under air atmosphere with a temperature ramp of 10 °C.min⁻¹ along with the addition of the DeNOx catalyst. The temperature is shown in a dashed line.

To check the efficiency of the NH₃-SCR system, the combustion test (miscanthus in air) was performed with the addition of DeNOx catalyst along with urea as shown in Figure 13. It is obvious that the emission level of the N₂O was dramatically reduced with water is the highest level of emission i.e. most of the N₂O emissions were converted into water according to the Equation 2 or Equation 3.

447 So by adding urea that decomposes to ammonia during the reaction along with the DeNO_x
 448 catalyst showed better efficiency in mitigating the NO_x emissions than using only the DeNO_x
 449 catalyst.

451 **Figure 13:** Mass spectrum profile of the gas release during miscanthus combustion under air
 452 atmosphere with a temperature ramp of 10 °C.min⁻¹ along with the addition of the
 453 DeNO_x catalyst and urea. The temperature is shown in a dashed line.

4. Conclusions

Herein, three different lignocellulosic biomasses (*miscanthus* $\times$ *giganteus*, orange peel (OPW) and potato peel (PPW) waste) were characterized using XRD, SEM-EDX, S_{BET} , CHNS, TGA and DCS techniques. The crystalline cellulose in *miscanthus* is much higher than that of OPW and PPW with % crystallinity index values of 77.1, 46.0 and 24.1%, respectively. Potato ash was the best candidate among the three lignocellulosic biomasses of being used as a potential source of potassium in the fertilizer industry with 23.8 wt.% of its composition is potassium, where OPW showing the highest HHV (higher heating value) of 17.88 MJ.Kg⁻¹ among the three samples. XRD results showed that all the three biomass feedstock ashes composed of mainly potassium hydrogen disilicate and potassium chloride phases which has an impact on the combustion/pyrolysis performance. *In-situ* gas detection from combustion/pyrolysis of those lignocellulosic biomass samples with NO_x removal were studied using Mass spectrometer (MS) technique. The combustion experiments were performed under pure air or oxygen while pyrolysis under nitrogen along with the combustion of the produced biochar under air atmosphere. Unlike *miscanthus* and OPW combustion which occurred in two stages, the combustion of PPW showed two main combustion stages at temperature ranges of 200-300°C and 400-500°C along with a small combustion peak at high temperature (>700°C) due to the higher lignin content herein. The results revealed that NO_x gases are the main gases emission during the combustion/pyrolysis processes. During the combustion of the three samples, different emissions were released such as nitrous oxide (N₂O), water (H₂O), carbon dioxide (CO₂), nitric oxide (NO), nitrogen dioxide (NO₂), oxygen (O₂), acetaldehyde (CH₃CHO), acetic acid (CH₃COOH) and hydrogen (H₂) emissions with traces of benzene. While under pyrolysis conditions, emissions such as N₂O, H₂O, traces of CO₂, two large H₂ peaks (at a temperature of 580 and 700°C), hydrocarbons (methane

and ethane), acetic acid, methyl alcohol and hydrogen with traces of nitrogen oxides (NO and NO₂).

The *in-situ* mass spectrometer technique showed that by adding a DeNO_x catalyst (Pt/TiO₂/ZSM-5) during the combustion, it reduced the N₂O (NO_x) emissions by converting such emissions into H₂O and N₂, however, the emission level of NO_x still observable. Thus, by coupling the DeNO_x catalyst with urea to construct an *in-situ* NH₃-SCR catalytic system during the combustion, it effectively reduces the NO_x emissions.

Supporting Information:

Figure S1: Ignition temperatures of miscanthus, OPW and PPW samples derived from the DSC curves at different heating rates under air atmosphere.

Figure S2: Burnout temperatures of miscanthus, OPW and PPW samples derived from the DSC curves at different heating rates under air atmosphere.

Figure S3: Heat liberated from miscanthus, OPW and PPW samples derived from the DSC curves at different heating rates under air atmosphere.

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5. References

- [1] SEIL, Miscanthus, a revolutionary biomass crop, <http://www.recrops.com/miscanthus>, accessed at 4pm 19-07-2016, 2016. <http://www.recrops.com/miscanthus>. 2016).
- [2] N. Brosse, A. Dufour, X. Meng, Q. Sun, A. Ragauskas, Miscanthus: a fast-growing crop for biofuels and chemicals production, *Biofuels, Bioproducts and Biorefining* 6(5) (2012) 580-598.
- [3] A.I. Osman, J.K. Abu-Dahrieh, D.W. Rooney, J. Thompson, S.A. Halawy, M.A. Mohamed, Surface hydrophobicity and acidity effect on alumina catalyst in catalytic methanol dehydration reaction, *J Chem Technol Biot* 92(12) (2017) 2952-2962.
- [4] A.I. Osman, J.K. Abu-Dahrieh, M. McLaren, F. Laffir, P. Nockemann, D. Rooney, A Facile Green Synthetic Route for the Preparation of Highly Active γ -Al₂O₃ from Aluminum Foil Waste, *Nature Scientific Reports* 7(1) (2017) 3593.
- [5] A.I. Osman, J.K. Abu-Dahrieh, A. Abdelkader, N.M. Hassan, F. Laffir, M. McLaren, D. Rooney, Silver-Modified η -Al₂O₃ Catalyst for DME Production, *The Journal of Physical Chemistry C* 121(45) (2017) 25018-25032.
- [6] E.G.A. Forbes, D.L. Easson, G.A. Lyons, W.C. McRoberts, Physico-chemical characteristics of eight different biomass fuels and comparison of combustion and emission results in a small scale multi-fuel boiler, *Energy Conversion and Management* 87 (2014) 1162-1169.
- [7] S. Liang, A.G. McDonald, Chemical and Thermal Characterization of Potato Peel Waste and Its Fermentation Residue as Potential Resources for Biofuel and Bioproducts Production, *Journal of Agricultural and Food Chemistry* 62(33) (2014) 8421-8429.
- [8] I. Ahmed, M.A. Zia, M.A. Hussain, Z. Akram, M.T. Naveed, A. Nowrouzi, Bioprocessing of citrus waste peel for induced pectinase production by *Aspergillus niger*; its purification and characterization, *Journal of Radiation Research and Applied Sciences* 9(2) (2016) 148-154.
- [9] D. Wu, Recycle Technology for Potato Peel Waste Processing: A Review, *Procedia Environmental Sciences* 31(Supplement C) (2016) 103-107.
- [10] E.B. Ledesma, C.-Z. Li, P.F. Nelson, J.C. Mackie, Release of HCN, NH₃, and HNCO from the Thermal Gas-Phase Cracking of Coal Pyrolysis Tars, *Energy & Fuels* 12(3) (1998) 536-541.
- [11] K.-M. Hansson, J. Samuelsson, C. Tullin, L.-E. Åmand, Formation of HNCO, HCN, and NH₃ from the pyrolysis of bark and nitrogen-containing model compounds, *Combustion and Flame* 137(3) (2004) 265-277.
- [12] A. Anca-Couce, P. Sommersacher, N. Evic, R. Mehrabian, R. Scharler, Experiments and modelling of NO_x precursors release (NH₃ and HCN) in fixed-bed biomass combustion conditions, *Fuel* 222 (2018) 529-537.
- [13] H. Zhan, X. Zhuang, Y. Song, X. Yin, C. Wu, Insights into the evolution of fuel-N to NO_x precursors during pyrolysis of N-rich nonlignocellulosic biomass, *Applied Energy* 219 (2018) 20-33.
- [14] P. Glarborg, A.D. Jensen, J.E. Johnsson, Fuel nitrogen conversion in solid fuel fired systems, *Progress in Energy and Combustion Science* 29(2) (2003) 89-113.
- [15] I.T.a.P.I.D.O.o.A.Q.P.a.S.U.S.E.P.A. Clean Air Technology Center (MD-12), Nitrogen Oxides (NO_x), Why and How They Are Controlled, (1999).

- [16] Department for Environment, Food and Rural Affairs & Department for Transport, Improving air quality: national plan for tackling nitrogen dioxide in our towns and cities, accessed at 7/9/2017 10 am., <https://consult.defra.gov.uk/airquality/air-quality-plan-for-tackling-nitrogen-dioxide/> (5 May 2017).
- [17] A.I. Osman, A. Abdelkader, C.R. Johnston, K. Morgan, D.W. Rooney, Thermal Investigation and Kinetic Modeling of Lignocellulosic Biomass Combustion for Energy Production and Other Applications, *Industrial & Engineering Chemistry Research* 56(42) (2017) 12119-12130.
- [18] A.I. Osman, A.T. Ahmed, C.R. Johnston, D.W. Rooney, Physicochemical characterization of miscanthus and its application in heavy metals removal from wastewaters, *Environmental Progress & Sustainable Energy* 37(3) (2018) 1058-1067.
- [19] I. Bicu, F. Mustata, Cellulose extraction from orange peel using sulfite digestion reagents, *Bioresource Technology* 102(21) (2011) 10013-10019.
- [20] J. Kaknics, F. Defoort, J. Poirier, Inorganic Phase Transformation in Miscanthus Ash, *Energy & Fuels* 29(10) (2015) 6433-6442.
- [21] D.P. Mishra, S.K. Das, A study of physico-chemical and mineralogical properties of Talcher coal fly ash for stowing in underground coal mines, *Materials Characterization* 61(11) (2010) 1252-1259.
- [22] C.M. Santos, J. Dweck, R.S. Viotto, A.H. Rosa, L.C. de Moraes, Application of orange peel waste in the production of solid biofuels and biosorbents, *Bioresource Technology* 196(Supplement C) (2015) 469-479.
- [23] B. Zapata, J. Balmaseda, E. Fregoso-Israel, E. Torres-García, Thermo-kinetics study of orange peel in air, *Journal of Thermal Analysis and Calorimetry* 98(1) (2009) 309.
- [24] A.I. Osman, J.K. Abu-Dahrieh, F. Laffir, T. Curtin, J.M. Thompson, D.W. Rooney, A bimetallic catalyst on a dual component support for low temperature total methane oxidation, *Applied Catalysis B: Environmental* 187 (2016) 408-418.

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➤ **Highlights:**

- NO_x gases were generated during the combustion process under air atmosphere.
- Pt/TiO₂/ZSM-5 did reduce the NO_x emissions to a manageable level.
- Coupling the DeNO_x catalyst with urea during the combustion effectively reduced NO_x emissions.
- NO_x emissions were converted into nitrogen and water over Pt/TiO₂/ZSM-5 coupled with urea during the combustion.