

Thermochemical characterisation of straws and high yielding perennial grasses

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ABSTRACT

The research is concerned with thermochemical characterisation of straws and high yielding perennial grasses. Crops selected for this study include wheat straw (*Triticum aestivum*), rape straw (*Brassica napus*), reed canary grass (*Phalaris arundinacea*) and switch grass (*Panicum virgatum*). Thermogravimetric analysis (TGA) was used to examine the distribution of char and volatiles during pyrolysis up to 900 °C. Utilising multi-heating rate thermogravimetric data, the Friedman iso-conversional kinetic method was used to determine pyrolysis kinetic parameters. Light and medium volatile decomposition products were investigated using pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) up to 520 °C. The 22 highest yielding identifiable cellulose, hemicellulose and lignin biomass markers were semi-quantified taking into consideration peak areas from GC chromatograms. Notable differences can be seen in butanedioic acid, dimethyl ester (hemicelluloses decomposition products), 2-methoxy-4-vinylphenol (lignin marker) and levoglucosan (intermediate pyrolytic decomposition product of cellulose) content when comparing perennial grasses with straw. From results presented in this study, perennial grasses such as switch grass, have the most attractive properties for fast pyrolysis processing. This is because of the observed high volatile yield content of 82.23%, heating value of 19.64 MJ/kg and the relatively low inorganic content.

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1. Introduction

The projected decline in fossil fuel availability, concerns over the environment and security of supply have attracted increased interest in renewable energy; in particular energy derived from biomass. Bio-oil is a biomass derived liquid product obtained from the fast pyrolysis process together with char and gas by-products. Compared to orthodox liquid fuels, bio-oil has a number of distinct environmental advantages. Firstly, biomass derived liquids are usually considered to be carbon neutral, in terms of their global warming potential as they replace fossil fuels, and secondly they have insignificant levels of sulphur (therefore no sulphur oxide emissions are generated) (Mohan et al., 2006).

The European Commission in 2009 projected that biomass is expected to contribute to approximately two thirds of the renewable energy requirements by 2020. To reach this goal all available resources, of biomass must be considered. Existing agricultural residues such as straws will need to be utilised alongside dedicated energy crops. The perennial energy grasses, switch grass (*Panicum virgatum*) and reed canary grass (*Phalaris arundinacea*), have been identified as suitable energy crops for the northern hemisphere (Christian et al., 1999). These crops are sown from seed and can

produce high yields with low establishment costs and little inputs. Wheat (*Triticum aestivum*) straw is highly abundant in Europe, together with rape (*Brassica napus*) straw and barley (*Hordeum vulgare*) straw (Copeland and Turley, 2008). There is no commercial market for the straw from rape and it is therefore another candidate for the bioenergy sector. Wheat straw does however have a low grade commercial market in the animal husbandry sector, and is also used for power generation in dedicated straw combustion plants. Scarlat et al. (2010) estimated that the total amount of crop residues produced for all 27 European Union states was on average 258 Mt (on dry basis) per year, with wheat straw (42% of 258 Mt) being the highest contributor, and rape straw (7% of 258 Mt) in the fourth place. The study showed that on average, based on a lower heating value of 17.5 MJ/kg dry matter, the amount of crop residue available for the bioenergy sector within all European Union member countries was 1530 PJ/year.

The main components of biomass are cellulose, hemicellulose, lignin, organic extractives and inorganic minerals (Mohan et al., 2006). Cellulose is an unbranched polymer (linear homopolysaccharide) of β-D-glucopyranose moieties joined by (1–4)-glycosidic bonds (Alen et al., 1996; Berg et al., 2002; Wu et al., 2009). Hemicellulose is an inhomogenous glycan (heteropolysaccharide) composed of two or more monomer units, namely hexoses (D-glucose, D-mannose and D-galactose) and pentoses (D-xylose and L-arabinose) (Alen et al., 1996; Berg et al., 2002; Wu et al., 2009). Lignin is a highly crosslinked three-dimensional structure

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Table 1
Compositional content, yield and estimated production cost for perennial grasses and residues.

	Straws		Grasses	
	Rape	Wheat	Switch	Reed Canary
Composition content^a				
Cellulose	37.6	33.2	36.0	24.0
Hemicellulose	31.4	24.0	31.6	36.0
Acid detergent lignin	21.3	15.1	6.1	2.0
Yield and costs				
Harvest yields (t/ha/y on dry basis)	1.6 ^b	3.1 ^b	5.4–9.6	~5.5
Cost/t (£) to produce	18–30 ^c	~20 ^c	30–57	43–73
References	DEFRA (2010), Dziurka et al. (2005)	DEFRA (2010), Karp and Shield (2008)	Karp and Shield (2008), Riche (2006)	Lee et al. (2007), Riche (2006)

^a wt% on dry basis.

^b Straw (on average – wheat straw ~45% and rape straw is ~40% of whole crop (Scarlat et al., 2010)).

^c Main cost of production allocated to the production of the grain, hence its low cost (bailing, carting and fertiliser).

consisting of a non-regular arrangement of phenyl propane units (monolignols). The common monolignols are: *para*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Alen et al., 1996; Grabber, 2005; Wu et al., 2009). The compositional content, yield per hectare and the reported production costs for the perennial grasses and straws are shown in Table 1. In comparison with the perennial grasses, the straws are reported to have the highest lignin content. Switch grass, although difficult to establish in comparison to reed canary grass, has a lower production cost and requires less fertilizer and pesticide inputs (Riche, 2006). The yield and estimated production cost is lower for the straws. This is because approximately half of the crop yield is removed in the form of grain or seed, and that costs are only associated with bailing, carting and additional fertiliser requirements.

The application of thermogravimetric analysis (TGA) to investigate thermal properties is extremely useful to determine how thermal properties of potential bioenergy crops vary with temperature. The understanding of biomass thermal behaviour is of great importance because the process parameters have a direct impact on the final chemical composition (quality and quantity) of products. A quick, simple and reliable analytical method to investigate thermal decomposition is by TGA. This has been employed by a large number of researchers to investigate general and specific thermal characteristics of a range of organic materials (Antal and Varhegyi, 1995; Coats and Redfern, 1964; Deng et al., 2008; Gronli et al., 1999; Kumar et al., 2008; Nowakowski et al., 2008; Park et al., 2009). The kinetics of heterogeneous condensed phase reactions can be divided into model fitting and non-model fitting. The model fitting kinetic approach (summative approach) for biomass is still in early development. This is because it requires highly detailed investigations into the chemical and thermal reactions and further advanced modelling into biomass thermal decomposition pathways (Biagini et al., 2008). Iso-conversional non-model fitting kinetics have been under scrutiny from numerous researchers (Biagini et al., 2008; Budrugaec and Segal, 2001; Várhegyi, 2007; Vyazovkin and Dollimore, 1996), yet the advancement to the underlying theory has remained almost unchanged for many years. Non-model fitting kinetics are based on the Arrhenius equation given in Eq. (1) and the reaction rate of thermal decomposition in Eq. (2). Eqs. (1) and (2) can be combined to form Eq. (3) for non-isothermal data:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

$$\beta \left(\frac{d\alpha}{dt}\right) = Af(\alpha) \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

In the above equations k is the reaction rate, A the pre-exponential factor, E_a the activation energy, R the gas constant, T the temperature, α the conversion, t the time, $f(\alpha)$ the differential function of conversion (reaction model) and β the heating rate. E , A and $f(\alpha)$ are known as the kinetic triplet. A number of mathematical methods have been developed to derive the kinetic triplet, and are classified into either integral or differential methods.

The differential method uses multiple heating rates. The apparent activation energy is dependent on the degree of conversion and is independent of the function of conversion. It should be noted that the function of dependence of E_a on the degree of conversion is indicative of the reaction model or function of conversion (Vyazovkin and Dollimore, 1996). In addition, systematic errors are also removed because no approximation of the temperature integral is required. An assumption of this method is that for a constant extent of conversion, the rate of conversion is dependent on temperature only, and the kinetic parameters are independent of heating (Budrugaec and Segal, 2001; Cai and Bi, 2009).

Thermal analysis using multiple heating rates can be beneficial to the understanding of the thermal decomposition process especially when used in conjunction with other analytical techniques. This is because the thermal decomposition is associated with bond cleavage, bond redistribution and with the formation of new products. Potentially, TGA kinetic data offers a mechanistic insight into the thermal break down, and can be extrapolated to be representative of high heating rate situations faced in industry (Saddawi et al., 2010). A recent review by White et al. (2011) shows how TGA can be used to investigate the impacts of heating rates, particles size, residence times, processing temperature and atmosphere. The pyrolysis thermal decomposition products can be studied using Py–GC–MS. This is a very useful technique that can be used as a rapid screening technology to investigate potential bioenergy crops. The heating rates and process temperature can be tailored to be representative of potential industrial processing conditions. The advantage is that this will help to initially investigate the potential pyrolysis products and their relative abundance within the bioenergy crop.

The main aim of the work is to compare straw and perennial grasses as potential sources of bioenergy. Thermal analysis has been investigated using single- and multi-heating rate thermogravimetric analysis. The chemical content and pyrolysis thermal decomposition products have been investigated using a range of analytical equipment. This work helps to provide a better

understanding of the possible industrial implications of fast pyrolysis as a conversion technology for energy and chemical products.

2. Experimental

2.1. Materials

The energy crops were grown at Woburn experimental farm in Bedfordshire, UK (52°01'N, 00°36'W, ca. 90 m AOD) on sandy soils that are known to be low yielding and therefore less desirable for food production. Switch grass (*P. virgatum*, cv *Cave-in-rock*) and reed canary grass (*P. arundinacea*, cv *Palaton*) were both sown in 2001 using standard farming machinery and both crops were harvested annually. In the 2003 growing season, reed canary grass received 60 kg N/ha of "Nitram" (ammonium nitrate) fertiliser in late spring while switch grass remained unfertilised. In late winter of 2004 samples were taken from both the harvested crops after the crops had fully senesced. The crop material was immediately removed from the field and placed in a re-circulating oven at 80 °C for 36 h. The dried material was then hammered milled to pass through a 1 mm sieve, and stored at room temperature in an air tight container awaiting future analysis. The agricultural straws, rape straw (*B. napus*) and wheat straw (*T. aestivum*) were collected from commercially produced crops at Rothamsted experimental farm in the southeast of England in 2008. The crops were harvested in July and August respectively, and the straws were collected and baled. Straw samples were again immediately dried at 80 °C for 36 h in a re-circulating oven and hammered milled to pass through a 1 mm sieve. Characterisation and analysis of all samples were carried out in 2008 using particle size fractions of 150–250 μm for all analytical analyses.

2.2. Elemental analysis and calorific values

Elemental analysis for carbon, hydrogen and nitrogen was carried out using a Carlo-Erba EA1108 elemental analyser. Carbon, hydrogen and nitrogen content (wt.%) were analysed in duplicate, and average values were taken. Metals and other inorganic components were determined by digestion, and carried out using a PerkinElmer Optima 7300DV Induced Coupled Plasma (ICP) Emission Spectrometer. The digestion procedure involved a number of steps. The biomass material was dried at 80 °C for 4 h and then cooling in a desiccator. This was then added (0.25 g) to a digestion tube with 5 ml of nitric or perchloric acid and mixed at room temperature for 2 h. The sample was then heated overnight, and 5 ml of 25% HCl was added the following day and further heated at 80 °C. After cooling, the sample was analysed by ICP. Analysis was conducted in triplicate.

The higher heating value (HHV) was calculated using an empirical equation (4) (Channiwala and Parikh, 2002):

$$\text{HHV} = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot O^* - 0.0151 \cdot N - 0.0211 \cdot \text{ash} \quad (4)$$

where * is the wt.% oxygen by difference.

2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a PerkinElmer Pyris 1 analyser following the E1131-03 ASTM standard (ASTM, 2003). A sample of 3.0 ± 0.1 mg was pyrolysed to a maximum temperature of 900 °C at a heating rate of 25 °C/min, with a nitrogen purge at a flow rate of 30 ml/min and hold time of 15 min. For the kinetic evaluation three heating rates were employed (β : 5, 8, 10 °C/min). The combustion study employed the same method as the pyrolysis TGA method but at a heating rate of only 25 °C/min in

an air atmosphere. Ash content analysis in an air atmosphere was investigated at the maximum temperature of 575 °C, with a hold time of 15 min at a heating rate of 5 °C/min.

2.4. Kinetic method

The Friedman method, the differential non-isothermal approach, was used to determine the kinetic triplet parameters and is shown in Eq. (5) (Friedman, 1963):

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln A + n \ln(1 - \alpha) - \frac{E_a}{RT} \quad (5)$$

The method is based on the inter-comparison $\ln(d\alpha/dt)$, for a given fraction of conversion versus the reciprocal of temperature at linear heating rates. The activation energy and pre-exponential factor can be calculated at each given fraction of conversion (α). Fraction of conversion is defined as $\alpha = (m_s - m_t)/(m_s - m_f)$, where m_s is the initial dry sample weight, m_t the sample weight during the reaction and m_f the final sample at the maximum pyrolysis temperature. These have been selected over a range of the mass loss between 5% and 95% (on graphs marked as 0.05–0.95) fraction of conversion at 5% increments. The apparent activation energy is determined from the slope ($-E_a/R$) and the pre-exponential factor is determined from the intercept ($\ln(A(1 - \alpha)^n)$) at zero, first and second order, only first order is reported.

2.5. Analytical pyrolysis (Py-GC-MS)

Analytical pyrolysis was investigated using a heating rate of 20 °C/ms. A single sample of approximately 3 mg was used for the pyrolysis experiment with a final pyrolysis temperature of 520 °C. Py-GC-MS tests were performed on each sample using a CDS 5200 pyrolyser coupled to a Varian 450-GC chromatograph and 220-MS mass spectrometer. The column used was a Varian factor FOUR® (30 m, 0.25 mm id., 0.25 μm df). The gas chromatograph oven was held at 45 °C for 2.5 min and then ramped at 5 °C/min to 250 °C, with a dwell time of 7.5 min. The devolatilised components were transferred via a heated transfer line maintained at 310 °C onto the GC column via an injector port (PTV1070 type) held at 275 °C. Mass spectra were obtained for the molecular mass range $m/z = 45$ –300. Proposed assignments of the main peaks were made from mass spectra detection using (NIST05 MS library) and from literature assignments (Faix et al., 1990, 1991). Selected cellulose, hemicellulose and lignin key markers were identified for the most abundant thermal degradation compounds for all biomass samples, and these are listed in Appendix A, together with the main MS fragmentation patterns and their relative abundances to the base peak (100%) using the NIST05 MS library.

3. Results and discussion

3.1. Elemental analysis and calorific values

Ultimate, proximate, metal and calorific values for the perennial grasses and straws are shown in Table 2. The complexity and relative ratios of the major constituents varies with the plant species, and it is well known that biomass is constructed from oxygen rich polymeric organic material. Ultimate analysis and calorific values are of typical findings, and are representative of current literature values (Bridgeman et al., 2008; Lemus et al., 2002; Mani et al., 2010; Nowakowski et al., 2007). Potassium content within straw is higher in contrast to the perennial grasses. Wheat straw was found to have a potassium content approximately six times higher than of switch grass and four times higher than reed canary grass. The rape straw potassium content was found to be ten times higher than in switch grass and six times higher than it was in reed canary grass. Wheat

Table 2
Proximate analysis, ultimate analysis, inorganic content analysis and higher heating values for biomass samples.

	Wheat straw	Switch grass	Rape straw	Reed canary grass
Ultimate analysis (wt.%)^(d,b)				
C	47.24	49.02	48.35	48.05
H	6.00	6.15	5.80	6.08
N	0.66	0.42	1.15	0.26
O ^a	46.09	44.40	44.70	45.61
Proximate analysis (wt.%)				
Moisture	4.56	4.61	4.64	4.96
Volatile matter ^(d,b)	79.92	83.23	76.9	77.45
Fixed carbon ^(d,b)	15.18	11.04	11.88	12.99
Ash ^(d,b)	4.89	5.73	6.58	4.60
Higher heating value (MJ/kg)^(d,b)				
	18.69	19.64	18.94	19.12
Inorganic content analysis (wt.%)^(d,b)				
Al	0.01	0.02	0.03	0.01
Ca	0.51	0.50	1.65	0.28
Fe	0.02	0.01	0.03	0.01
K	0.57	0.09	0.90	0.14
Mg	0.07	0.06	0.09	0.06
Mn	0.01	–	0.01	–
Na	0.01	0.02	0.02	0.01
Ni	–	–	–	–
P	0.04	0.05	0.20	0.08
S	0.09	0.06	0.32	0.06

(d,b), dry bases; –, not detected.

^a Oxygen by difference.

straw and the perennial grasses are harvested after the crop naturally senesces, therefore reducing the concentration of nutrients in the straw. Oilseed rape on the other hand rarely senesces and is either chemically pre-treated or swathed prior to harvest, thus retaining even higher concentrations of plant nutrients within the harvested straw. The perennial grasses are harvested in late winter several months after the crop has fully senesced, and studies have shown that this delay in harvest time dramatically reduces the inorganic content, including potassium, in the standing crop (Yates and Riche, 2007). This could be due to the natural weathering and leaching, of more mobile elements such as potassium, from the standing crop through the winter period. The level of inorganics in biomass used for fast pyrolysis processing has an impact on the thermal decomposition pathways, pyrolysis product yields and bio-oil quality and stability. DiBlasi (2008) found that by increasing phosphorus content pyrolysis liquid yields were decreased and char yields increased. The percentage content of volatile matter from the proximate analysis was found to be lowest for rape straw, this may be partly related to the phosphorus content.

3.2. Thermal decomposition studies (TGA)

Fig. 1 shows the pyrolysis differential thermogravimetric (DTG) profiles for all samples. For the DTG profiles, the derivative weight is reported and is representative of the percentage weight loss per minute. The shape of the decomposition profile is functionally related to the composition of the biomass investigated, which is well documented (Deng et al., 2008; Park et al., 2009). A clear distinction between samples can be seen by comparing the degree of maximum weight loss and the temperature of its occurrence. The maximum rate of weight loss is found to fall between 365 and 395 °C for all samples investigated. The thermal decomposition of cellulose is primarily thought to occur between these temperatures. A shoulder-like feature can be seen for switch and reed canary grasses at a temperature of 339 and 338 °C, respectively. This second peak is considered to be partly related to the hemicellulose content within the sample. The thermal decomposition temperature of hemicellulose has been found to take place at lower

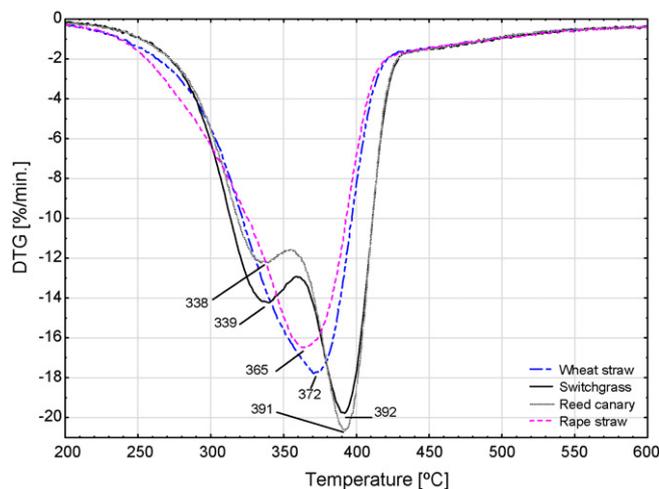


Fig. 1. Differential thermogravimetric pyrolysis profiles.

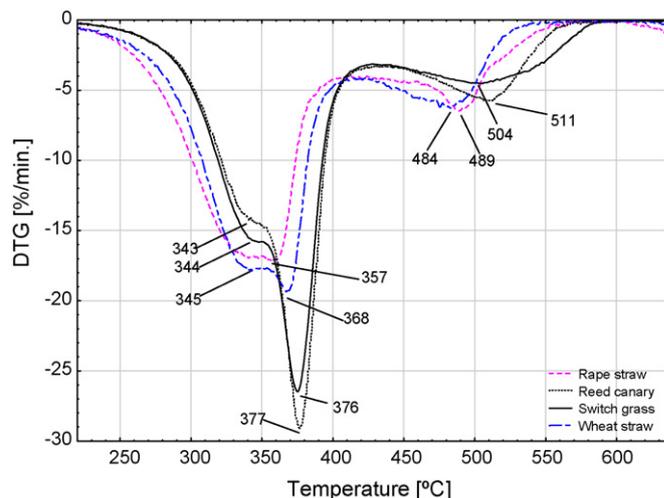


Fig. 2. Differential thermogravimetric combustion profiles.

temperatures in comparison to cellulose, as observed by Varhegyi et al. (1989). It should be noted that the extent of the maximum thermal decomposition rate is reflective of the cellulose, hemicellulose, lignin and inorganic content. Yang et al. (2007) found that the lignin thermal decomposition occurs over a broad temperature range and partially contributes to the hemicellulose and cellulose decomposition regions. Inorganic content, in particular alkali metals such as potassium and sodium, are known to influence the thermal decomposition profile due to their catalytic activity. This may be partly responsible for the reduction in the shoulder-like feature seen in the straws because of their high potassium content. A comparison of the ratio of hemicellulose to cellulose in Table 1 indicates that perennial grasses have higher hemicellulose levels. Fuentes et al. (2008) found that potassium and phosphorus content strongly catalyses the thermal degradation process. This subsequently reduces the main degradation temperature and the main temperature region.

The thermal degradation in an air atmosphere is shown in Fig. 2 at a heating rate of 25 °C/min. The DTG profile shows two distinct decomposition regions that are thought to exist due to the initial volatile combustion and char burnout. Rape straw appears to have the largest second step at 489 °C with a maximum rate of decomposition of 6.5%/min. It is considered that the extent of the second step on the DTG profile reflects the lignin content. From the reference table (Table 1) it was found that the straws contain the

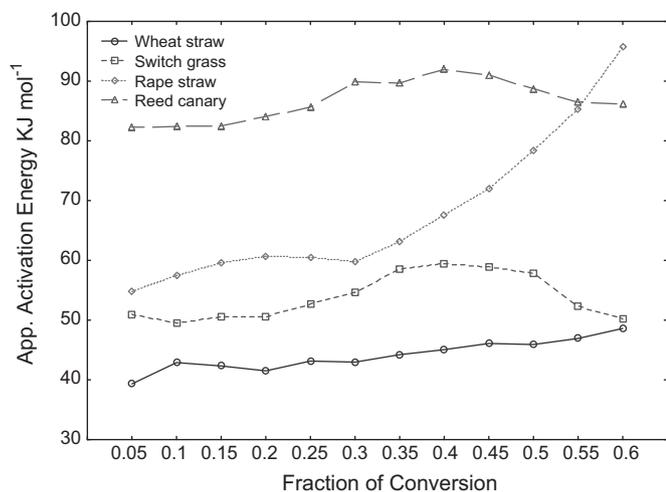


Fig. 3. Apparent activation energy with fraction of conversion using the Friedman method.

Table 3

Pre-exponential factor A , apparent activation energy E_a , and accuracy using the Friedman method.

	Friedman method		
	β : 5, 8 & 10 °C/min		
	Avg. E_a (kJ/mol) (200–425 °C)	Avg. A (1st order; 200–425 °C)	Avg. accuracy r^2
Reed canary grass	86.70	2.91E+11	0.993
Rape straw	71.73	2.35E+14	0.993
Switch grass	53.41	9.80E+13	0.927
Wheat straw	44.50	5.85E+10	0.950

highest lignin and gives a noticeable peak in Fig. 2. Ghetti et al. (1996) found that thermal decomposition seen on the DTG (air atmosphere), takes place in two steps; firstly hemicellulose and cellulose, and secondly lignin. Ghetti et al. demonstrated this through a series of experiments with different lignin contents to determine a correlation between lignin content and extent of the second thermal decomposition region on the DTG profile. This is because of the different chemical structures; lignin being more aromatic than

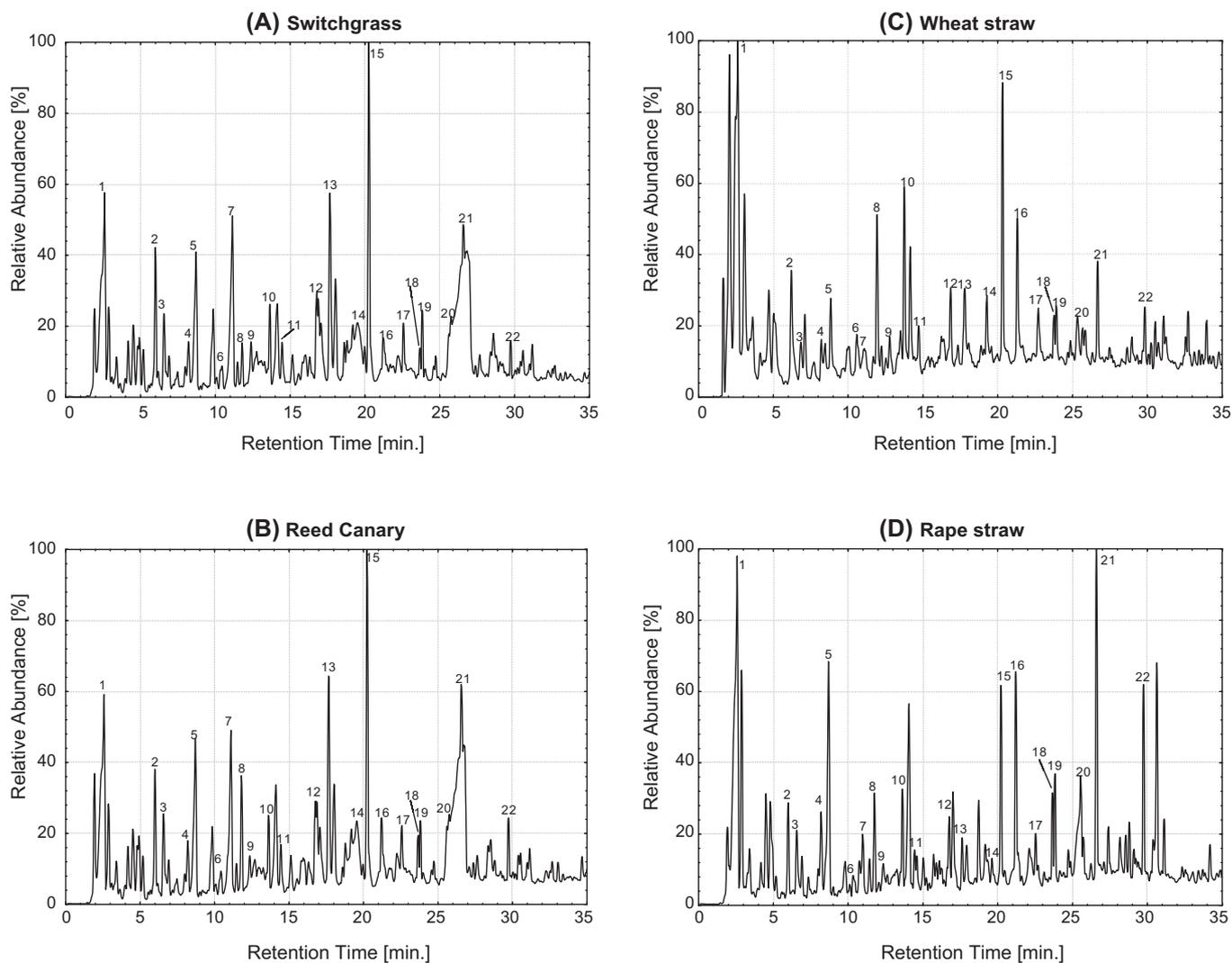


Fig. 4. Py-GC-MS chromatograms for (A) switch grass, (B) reed canary grass, (C) wheat straw and (D) rape straw. The main peaks assigned from mass spectral detection as follows: (1) acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 2(5H)-furanone; (5) 1,2-cyclopentanedione; (6) phenol; (7) butanedioic acid, dimethyl ester; (8) 3-methyl-1,2-cyclopentanedione; (9) 2-methylphenol; (10) 2-methoxyphenol; (11) 3-ethyl-2-hydroxy-2-cyclopentene-1-one; (12) 2-methoxy-4-methylphenol; (13) 3-methyl-benzaldehyde; (14) 4-ethyl-2-methyl-phenol; (15) 2-methoxy-4-vinylphenol; (16) 2,6-dimethoxy-phenol; (17) vanillin; (18) 1,2,4-trimethoxybenzene; (19) 2-methoxy-6-(2-propenyl)-phenol; (20) 1,6-anhydro- β -D-glucopyranose (levoglucosan); (21) 3'5'-dimethoxyacetophenone; (22) 2,6-dimethoxy-4-(2-propenyl)-phenol.

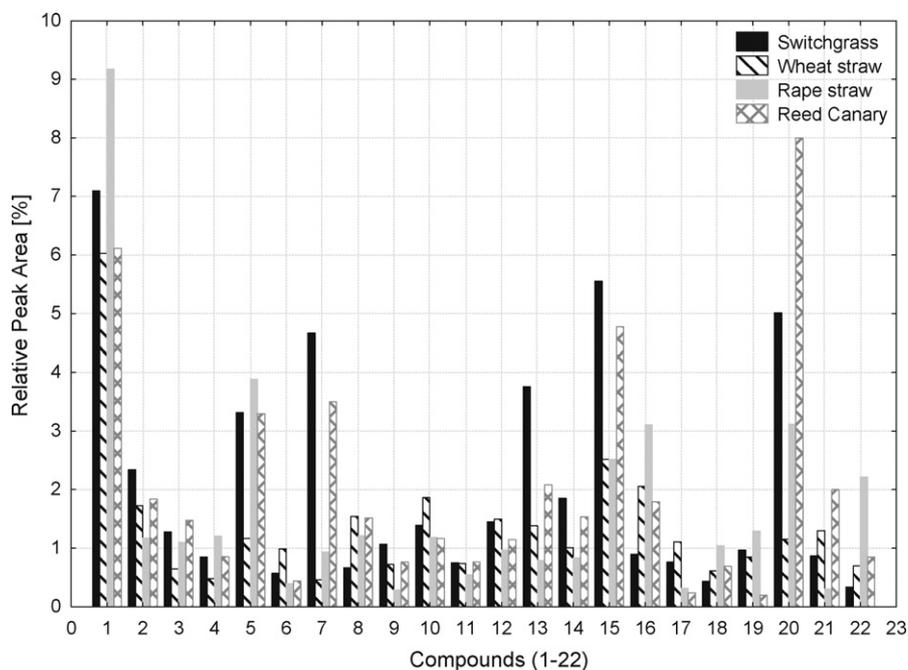


Fig. 5. Peak area comparison of key pyrolysis products. (1) acetic acid; (2) furfural; (3) 2-furanmethanol; (4) 2(5H)-furanone; (5) 1,2-cyclopentanediol; (6) phenol; (7) butanedioic acid, dimethyl ester; (8) 3-methyl-1,2-cyclopentanediol; (9) 2-methylphenol; (10) 2-methoxyphenol; (11) 3-ethyl-2-hydroxy-2-cyclopentene-1-one; (12) 2-methoxy-4-methyl-phenol; (13) 3-methyl-benzaldehyde; (14) 4-ethyl-2-methyl-phenol; (15) 2-methoxy-4-vinylphenol; (16) 2,6-dimethoxy-phenol; (17) vanillin; (18) 1,2,4-trimethoxybenzene; (19) 2-methoxy-6-(2-propenyl)-phenol; (20) 1,6-anhydro- β -D-glucopyranose (levoglucosan); (21) 3'5'-dimethoxyacetophenone; (22) 2,6-dimethoxy-4-(2-propenyl)-phenol.

cellulose and hemicellulose, thus requiring more energy to break bonds.

3.3. Pyrolysis kinetic evaluation (TGA)

The Friedman iso-conversional method has been used to determine the apparent activation energy and pre-exponential values. The average apparent activation energy and pre-exponential values obtained between 200 and 425 °C (for the initial and main active pyrolysis region) are shown in Table 3. These values are averaged and taken from between 5 and 60% conversion (0.05–0.60 fractional conversion). Below a conversion fraction of 60% apparent activation energy is relatively stable, when the conversion fraction exceeds 60% it is found that unrealistic values are obtained, and these are thought to be a result of increased calculation error. This is evident in the correlation coefficient of the fitting line used to determine the kinetic values. These fluctuations may be due to unstable char devolatilisation processes or degasification having passed from the active to the passive pyrolysis region. For this reason, values after conversion fraction of 60% have been disregarded from averages in Table 3. This ensures that the kinetic investigation concentrates on the initial and main active pyrolysis region and this helps to avoid additional problems mentioned by Biagini et al. (2008) within the passive pyrolysis region. In this study data points were selected at 5% weight loss increments to determine the kinetic parameters.

It can be seen in Fig. 3 that the apparent activation energy varies with fraction of conversion. In general, all biomass samples show an increment in apparent activation energy between 5 and 60% conversion. This is because the initial thermal decomposition is mainly associated with hemicellulose and cellulose, and not lignin which is more thermally stable. The thermal decomposition of lignin requires a higher energy input, due to its complex aromatic structure. The average apparent activation energy, ranking high to low, is as follows: reed canary > rape straw > switch grass > wheat straw. Due to the high lignin content found in straws, it is thought that their average apparent activation energy would

be higher when compared to the perennial grasses. However, this was not found to be the case, and it is suspected that the catalytic effects of potassium have contributed to a reduction in the average apparent activation energy. The apparent activation energy of rape straw is found to continually increase with conversion. This is thought to be related to the very high lignin content reported in the straws. The perennial grasses have a much lower lignin and potassium content. Reed canary grass was found to have the highest overall average apparent activation energy. This may be due to the lower volatile and calcium content, as compared to that of switch grass.

It is thought that the dependence of heating rate on the kinetic parameters is not well understood. In theory the frequency factor (pre-exponential factor) should be constant regardless of heating rate. Ferdous et al. (2002) found that the variation of heating rate had a minimal impact on the frequency factor. The lowest and highest pre-exponential factor values were found for wheat straw, ranging from $3.80E+10$ to $3.10E+11$, and rape straw from $1.53E+14$ to $1.25E+15$, for orders 0, 1 and 2, respectively. Understanding biomass pyrolysis kinetics is important when designing fast pyrolysis reactors, because thermal reactivity will influence the setup, i.e. fuel hold up, heat transfer and position of the feeding point. This is also important in order to better our understanding of the principles of the underlying biomass kinetics and their influence on product yields.

3.4. Analytical pyrolysis (Py-GC-MS)

The pyrolysis–gas chromatography–mass spectrometry results for the straws and perennial grasses are shown in Fig. 4. Data obtained, but not shown in Fig. 4, was used to semi-quantify the 22 highest yielding identifiable cellulose, hemicellulose and lignin biomass markers. This takes into the consideration the GC peak areas, and this is shown in Fig. 5. Notable differences can be seen in butanedioic acid, dimethyl ester (hemicelluloses decomposition products), 2-methoxy-4-vinylphenol (lignin marker) and

levoglucosan (intermediate pyrolytic decomposition product of cellulose), when comparing the perennial grasses with straws. Switch grass had the highest content of butanedioic acid, dimethyl ester, and some lignin markers such 3-methyl-benzaldehyde and 2-methoxy-4-vinylphenol. Reed canary grass was found to have the highest content of levoglucosan while rape straw had the highest level of acetic acid and 1,2-cyclopentanedione (cellulose/hemicelluloses). Relative peak areas for levoglucosan were significantly higher in perennial grasses, and this may be due to the lower levels of potassium. Nowakowski et al. (2007) investigated the impact of catalysts on thermal breakdown, to find that inorganic content in biomass favoured production of hydroxyacetaldehyde (heterolytic mechanism of cellulose pyrolytic decomposition), whereas washed biomass (removal of the majority of the metals) favoured production of levoglucosan (homolytic mechanism of cellulose pyrolytic decomposition). Key lignin markers, such as phenol, 2-methoxyphenol and vanillin, were found to be highest in wheat straw.

The most important factor when considering the industrial implications of the results from the characterisation processes undertaken, appears to be related to the lignin and inorganic content. Lignin is the source of high molecular weight polyphenols, which interfere with refining techniques for extraction and purification of chemical specialities. The inorganics have a catalytic effect on the thermal degradation processes, through cracking vapours and reducing organic yields. This is most evident when comparing the perennial grasses relative compounds yields with the straws. The volatile decomposition products are thought to be representative of the bio-oil composition, since the heating rate and pyrolysis temperature can be tailored to simulate fast pyrolysis conditions. Based on results presented in this study, perennial grasses, in particular switch grass, have the most attractive properties for fast pyrolysis processing. This is because of the observed high volatile yield content of 82.23%, heating value of 19.64 MJ/kg and the relatively low inorganic content which would tend to maximise the yield of liquid bio-oil.

4. Conclusions

Biomass characterisation has been carried out to compare straws and perennial grasses commonly found in the UK. Straw

is well suited for renewable energy use because of its low cost and high abundance. There are a number of drawbacks associated with use of straws in comparison to perennial grasses. The main drawback appears to be associated with the high inorganic content, in particular potassium found in the straws. This is because, unlike perennial grasses, the harvest time cannot be varied because of the need to recover seeds or grain for the crop's primary use. The influence of potassium has been thought to have a major impact on thermal decomposition, kinetics and decomposition products. In addition, the high lignin content within the straws is thought to increase apparent activation energy making the material less thermally reactive.

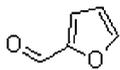
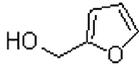
The average apparent activation energy ranking from high to low is as follows: reed canary > rape straw > switch grass > wheat straw. It should be stressed that the Friedman kinetic method for data analysis, as used in this paper, is only suited for determining a comparative biomass index as reported above. This is because iso-conversional kinetics only considers the thermal decomposition process as a single unit. Further research is required into the summative approach which incorporates all the main reactions involved, in order to obtain more accurate descriptions of the kinetic parameters.

This research gives a better insight into the thermochemical properties of straws and perennial grasses as a feedstock for fast pyrolysis. It suggests that the straws could be pre-treated to minimise inorganic content and thereby increase chemical yields. From results presented in this study, perennial grasses such as switch grass, have the most attractive properties for fast pyrolysis processing for liquids. This has implication for commercial development of fast pyrolysis for production of biofuels for heat and power.

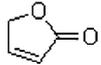
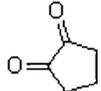
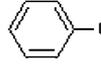
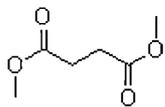
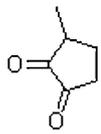
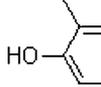
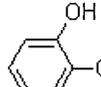
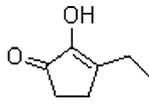
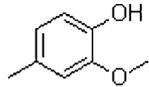
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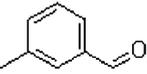
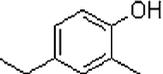
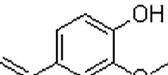
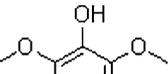
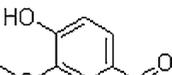
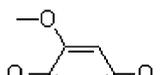
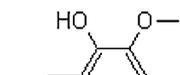
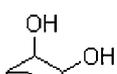
Appendix A. Key markers assignment for Py-GC-MS of biomass samples

Retention time	Compound	Structure	Formula	Type of key marker	Molecular weight	Base peak (100%)	Peak index mass (relative intensities)
2.36	Acetic acid		C ₂ H ₄ O ₂	C, H	60.05	43	45 (90.3), 60 (74.7), 15 (17.0), 42 (13.0), 29 (8.4), 14 (4.8), 28 (4.0), 41 (3.5), 18 (2.7)
6.04	Furfural		C ₅ H ₄ O ₂	C	96.08	96	95 (88.5), 39 (56.1), 29 (14.2), 38 (14.2), 37 (8.4), 97 (5.9), 40 (5.8), 67 (5.7), 42 (4.6)
6.63	2-Furanmethanol		C ₅ H ₆ O ₂	C	98.10	98	41 (68.0), 81 (57.0), 97 (52.4), 39 (51.0), 53 (46.9), 42 (39.3), 69 (32.6), 70 (30.1), 27 (23.2)

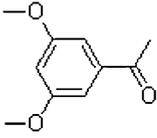
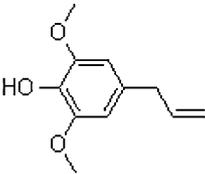
Appendix A. (Continued)

Retention time	Compound	Structure	Formula	Type of key marker	Molecular weight	Base peak (100%)	Peak index mass (relative intensities)
~8.20	2(5H)-furanone		C ₄ H ₄ O ₂	C	84.07	55	84 (69.0), 27 (56.9), 26 (33.7), 54 (19.8), 39 (13.8), 28 (8.1), 38 (6.9), 37 (5.6)
~8.80	1,2-Cyclopentanedione		C ₅ H ₆ O ₂	C	98.10	98	55 (45.2), 42 (20.9), 41 (20.3), 69 (16.1), 43 (14.2), 27 (13.6), 39 (12.8), 70 (8.2), 99 (5.7)
10.57	Phenol		C ₆ H ₆ O	C, L	94.11	94	66 (38.7), 65 (26.6), 39 (24.3), 40 (11.4), 38 (9.2), 55 (7.9), 63 (7.1), 95 (6.8), 50 (6.3)
11.15	Butanedioic acid, dimethyl ester		C ₆ H ₁₀ O ₄	C, H	146.14	115	55 (43.7), 59 (35.1), 114 (23.3), 87 (12.6), 27 (5.4), 116 (5.0), 56 (4.9), 15 (4.8), 57 (4.3)
~11.90	3-Methyl-1,2-cyclopentanedione		C ₆ H ₈ O ₂	C	112.13	112	55 (49.0), 69 (47.2), 41 (36.2), 56 (27.3), 83 (25.7), 43 (25.7), 83 (25.7), 39 (20.6), 27 (16.9), 42 (12.8)
~12.80	2-Methylphenol		C ₇ H ₈ O	GL	108.14	108	107 (67.3), 79 (25.3), 77 (22.0), 90 (20.7), 39 (10.8), 80 (10.2), 51 (9.6), 89 (8.3), 109 (7.9)
13.71	2-Methoxyphenol		C ₇ H ₈ O ₂	GL	124.14	109	124 (87.0), 81 (60.7), 53 (13.4), 27 (10.1), 52 (9.2), 51 (8.3), 125 (6.8), 110 (6.8)
14.74	3-ethyl-2-hydroxy-2-cyclopentene-1-one		C ₇ H ₁₀ O ₂	C	126.15	126	55 (38.3), 83 (38.5), 69 (32.0), 43 (27.0), 84 (20.7), 41 (20.4), 27 (19.7), 39 (19.6), 97 (17.5)
16.78	2-Methoxy-4-methyl-phenol		C ₈ H ₁₀ O ₂	GL	138.16	138	123 (86.9), 95 (36.5), 67 (19.6), 55 (18.3), 77 (17.0), 39 (16.2), 41 (11.7), 51 (11.4), 139 (8.8)

Appendix A. (Continued)

Retention time	Compound	Structure	Formula	Type of key marker	Molecular weight	Base peak (100%)	Peak index mass (relative intensities)
17.80	3-Methyl-benzaldehyde		C ₈ H ₈ O	L	120.15	91	119 (93.2), 120 (86.3), 65 (25.3), 39 (15.2), 92 (11.4), 63 (11.3), 51 (8.5), 121 (7.8), 89 (7.6)
19.28	4-Ethyl-2-methyl-phenol		C ₉ H ₁₂ O	L	136.19	121	136 (26.5), 77 (15.2), 39 (13.5), 91 (12.9), 122 (12.5), 107 (12.2), 27 (12.0), 51 (9.7), 108 (7.0)
20.25	2-Methoxy-4-vinylphenol		C ₉ H ₁₀ O ₂	GL	150.17	135	150 (97.3), 107 (67.3), 77 (66.6), 51 (28.5), 79 (23.5), 15 (22.8), 39 (21.0), 53 (20.7), 78 (17.3)
21.23	2,6-Dimethoxy-phenol		C ₈ H ₁₀ O ₃	SL	154.16	154	139 (44.8), 111 (20.4), 93 (17.6), 96 (16.8), 65 (13.2), 39 (11.4), 155 (9.0), 51 (9.0), 68 (7.5)
22.74	Vanillin		C ₈ H ₈ O ₃	GL	152.15	152	151 (94.3), 81 (30.9), 109 (22.1), 123 (17.1), 51 (16.1), 52 (15.0), 53 (10.6), 65 (10.2), 39 (10.1)
23.70	1,2,4-Trimethoxybenzene		C ₉ H ₁₂ O ₃	GL	168.19	168	153 (86.9), 125 (48.9), 110 (16.2), 69 (14.5), 52 (12.0), 169 (10.5), 51 (10.2), 79 (10.1), 154 (8.4)
23.92	2-Methoxy-6-(2-propenyl)-phenol		C ₁₀ H ₁₂ O ₂	GL	164.20	164	131 (27.9), 103 (27.6), 77 (26.8), 121 (26.4), 149 (25.4), 91 (15.9), 39 (11.4), 104 (11.2), 65 (11.2)
25.43	1,6-Anhydro-β-D-glucopyranose (levoglucosan)		C ₆ H ₁₀ O ₅	C	162.14	60	57 (44.1), 73 (35.8), 29 (19.9), 56 (15.0), 70 (14.1), 43 (12.6), 42 (11.8), 31 (10.9), 55 (8.8)

Appendix A. (Continued)

Retention time	Compound	Structure	Formula	Type of key marker	Molecular weight	Base peak (100%)	Peak index mass (relative intensities)
~26.8	3',5'-Dimethoxyacetophenone		C ₁₀ H ₁₂ O ₃	L	180.20	165	180 (64.2), 137 (40.5), 122 (33.4), 43 (19.7), 77 (19.2), 107 (15.1), 63 (14.4), 79 (9.7), 166 (9.4)
29.77	2,6-Dimethoxy-4-(2-propenyl)-phenol		C ₁₁ H ₁₄ O ₃	SL	194.23	194	91 (36.8), 119 (24.4), 39 (21.6), 77 (18.4), 131 (16.9), 65 (14.2), 179 (13.6), 79 (13.7), 53 (13.6)

C, cellulose; H, hemicellulose; L, lignin; GL, guaiacyl lignin; SL, syringyl lignin.

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