

On-farm storage of baled and pelletized canola (*Brassica napus* L.) straw: variations in the combustion related properties.

Leticia Chico-Santamarta*, Richard John Godwin, Keith Chaney, David Richard White, Andrea Claire Humphries.

Harper Adams University College, Edgmond, Newport, TF10 8NB, UK.

Abstract

Brassica napus L. (canola/oilseed rape) straw presents a suitable alternative combustion fuel due to its availability, relatively high calorific value and low moisture content. Pelletization enabled the bulk density of canola straw to be improved, enhancing its potential as an alternative combustion fuel. The aim of the paper was to determine the effect of on-farm storage on the gross calorific value, ash content, volatile content and elemental composition of canola straw bales (stored for up to 20 months) and pellets (stored for up to 12 months). Statistically significant changes occurred to the elemental composition of straw bales and pellets during on-farm storage, but these changes were not of practical significance in terms of the materials suitability as a combustion fuel.

Keywords

Canola straw; pellet; storage; chemical composition; combustion properties.

1. Introduction

The global harvested area of canola (*Brassica napus* L.) increased from 258 thousand km² to 316 thousand km² between 2000 and 2010. This is as a consequence of a global increased demand for canola oil, which significantly increased from approximately 13 million tonnes in 2000 to over 22 million tonnes in 2010. In the United Kingdom, the total harvested area increased from 4,020 km² to 6,420 km² during this time[1]. There

* Corresponding author: Telephone: +44 (0) 7799387383 Fax: +44 (0) 1952 825107 E-mail address: lchicosantamarta@iagre.biz

is not a significant market for canola straw with the majority of it being chopped and incorporated into the soil through ploughing. Canola yields a considerable volume of straw, but because it breaks down into small pieces when it is harvested, it is associated with a relatively low yield of 2.5 tonnes per hectare [2]. More pessimistic authors suggest a lower yield of 1.5 tonnes per hectare [3, 4]. Based on these figures, and taking 2010 as a reference year, the amount of recoverable canola straw produced in the UK was between 963 thousand tonnes and 1.6 million tonnes. The gross calorific value (GCV) of canola straw is on average 17.4 MJ kg^{-1} [5], suggesting between 4.6 TWh and 7.7 TWh of energy was contained in the canola straw produced in the UK in 2010. Furthermore, previous research has suggested that the use of agri-residues based pellets as a source of energy has the potential of reducing greenhouse gases (GHG) emissions by 50%, 250% and 350% compared to wood pellets, natural gas and coal, respectively [6]. As a consequence, it has been suggested canola straw presents a potential source of biomass for energy generation [7]. The main disadvantage with straw for combustion purposes is its relatively low density when baled. Straw typically has a bulk density ranging from 50 kg m^{-3} for forage harvested straw to 240 kg m^{-3} for high density baled straw [8]. The relative low density of straw makes it more expensive to transport compared to wood chips (150 kg m^{-3} to 300 kg m^{-3}), house coal (850 kg m^{-3}) and anthracite ($1,100 \text{ kg m}^{-3}$). This also means a larger storage area/volume is required for baled straw compared to other compressed material (e.g. straw pellets with a bulk density of 600 kg m^{-3} or briquettes with a bulk density of 320 kg m^{-3}). Densification increases the bulk density of biomass [9, 10] and as a result, the net calorific content per unit volume is increased [11] and the storage, transport and handling of the material is easier and cheaper [11, 12, 13].

The use of canola straw as a fuel could involve the storage of the biomass for variable periods of time, for example if year-round fuel supply is required. One of the main advantages of using canola straw is that it is associated with a low moisture content (typically below than 16 %) that means the material does not need to be dried before it can be used as a combustion fuel or for the production of pellets [14]. Drying of biomass is considered a long process and it is associated with large storage areas of material and high transport and storage costs [15].

However, research has shown that the storage of biomass can alter the properties of the material. Variations in the carbon and hydrogen content were found during the storage of logging residues [16] as well as a decrease in the calorific value as a consequence of a carbon increase during the storage of pine woodchips [17]. Furthermore, the properties of the unprocessed raw material (i.e. canola straw bales) can be significantly different from those of pelletised biomass, which can consequently result in differences in the physical, chemical and biological characteristics of the biofuel [18]. Pellets have been shown to have higher ash content and lower heating value than the raw materials used to produce the pellets [18]. Thus, it is important to understand the effects of storage on the properties of canola straw if it is to be used for combustion.

To date no research has been conducted that investigates (i) the effect of on-farm storage of canola straw bales and pellets on the properties of the material that are relevant to its use as a combustion fuel or (ii) the effect of storage of canola straw bales prior to pelletisation on the properties of the pelletised straw.

The aim of this paper was to determine the effect of on-farm storage on the physical and chemical properties of canola straw bales (stored for up to 20 months) and pellets

(stored for up to 12 months). The effect of storage time on the fuel's gross calorific value (GCV), ash content, volatile content and chemical analysis was studied. The moisture content, ambient temperature and the internal temperature of the bales were monitored and presented in previous work [14] and related to the properties presented in the current paper. Possible relationships between the variations in the baled straw properties and those of the resultant pellets were also examined.

2. Materials and methods

2.1. Canola straw, pellets and storage conditions

Canola straw bales and pellets were supplied and/or produced as described previously [14]. Bales of canola straw, harvested in 2008 and 2009, were stored under cover in a shed (with roof and three open sides) at Harper Adams University College (HAUC) Farm at ambient temperature and for varying lengths of time, as shown in Table 1a. At each storage period, samples were taken from three bales in triplicate. Samples were taken from the centre and two outer points within the bale [14], and analysed for GCV, ash content, volatile content and elemental composition. Canola straw pellets were stored as 10.0 kg \pm 0.5 kg lots in plastic airtight zip bags (305 mm x 405 mm) (Harrison Packaging, Lancashire, UK) in an enclosed shed at HAUC for varying lengths of time, as shown in Table 1b. Samples were taken from three bags of canola straw pellets and analysed in triplicate for GCV, ash content, volatile content, and elemental composition. Calcium lignosulfonate (Borregard-Lignotech, Sarpsborg, Norway) was added to milled straw prior to pelletisation at a concentration of 5 % (w/w) as a lubricant/binder. The composition of the binder was analysed by TES Bretby Laboratory (Burton-upon-Trent, UK) and is shown in Table 2.

2.2. Elemental composition

Samples from canola straw bales and pellets were milled to 1 mm and analysed to determine the content of carbon (C), sulphur (S), nitrogen (N), hydrogen (H), oxygen (O), sodium (Na), magnesium (Mg), aluminium (Al), phosphorus (P), chlorine (Cl), potassium (K), calcium (Ca) and iron (Fe).

The content of C and S (% weight d.b.) were determined using a LECO automatic analyzer (LECO SC-144 DR, LECO Corp., St. Joseph, USA); Hydrogen content (% weight d.b.) was determined by TES Bretby Laboratory (Burton-upon-Trent, UK) using an Exeter Analytical CE 440 Analyzer. Samples of H were analyzed once (and not in triplicate). The oxygen content was calculated by subtracting from 100 % the sum of (C, H, N, S and ash) contents in percentage. Hydrogen and oxygen concentrations were used as indicative values to ease the discussion.

The total N (% weight d.b.) of straw and pellets was determined using a LECO automatic analyzer (LECO FP-528, LECO Corp., St. Joseph, USA). The concentrations of the remaining elements (i.e. Na, Mg, Al, P, Cl, K, Ca and Fe) were determined using a DigiPREP digestion system (Qmx Laboratories, Thaxted, Essex, UK). 0.25 g \pm 0.02 g of dried and milled sample was weighed with a Precisa XT220A balance (Precisa Instruments Ltd, Dietikon, Switzerland) in a DigiTUBE (Qmx Laboratories, Thaxted, Essex, UK) and 7.5 mL of HNO₃ (69 %; BDH Laboratory Supplies, Dorset, UK) was added to each tube. The tubes were placed in the DigiPREP and heated in three steps:

- From ambient temperature to 40 °C (Ramp over 40 minutes and hold for 30 minutes).
- From 40 °C to 65 °C (Ramp over 35 minutes and hold for 5 minutes).

- From 65 °C to 95 °C (Ramp over 15 minutes and hold for 60 minutes).

The samples were diluted to 50 mL with purified water in the calibrated DigiPREP tube. Calibration graphs were produced for the elements Na, Mg, Al, P, Cl, K, Ca and Fe (Romil Ltd, Cambridge, UK) by analyzing 'calibration elements' diluted to four concentrations. All standards and samples include 10 µg kg⁻¹ of Ga, Rh and Ir as internal standards. Samples were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Thermo Fisher Scientific Inc, Hemel Hempstead, UK) to determine the level of Na, Mg, Al, P, Cl, K, Ca and Fe in the straw and pellets.

2.3. Gross calorific value

The GCV at constant volume on a dry basis was determined according to CEN 14918 [19]. A 0.50 g ± 0.02 g sample of dried milled straw and pellet sample was weighed with a Precisa XT220A balance and burnt in the presence of high-pressure oxygen in a Parr bomb calorimeter (Parr Instrument Company, Moline, Illinois, U.S.A.). There were three replications for each sample.

2.4. Ash content

The ash content of samples was determined according to CEN 14775 [20]. 1.0 g ± 0.1 g of oven-dried sample was heated in a furnace (Gallenkamp muffle furnace, size 3, GAFSE 620, Gallenkamp, Loughborough, UK) to 550 °C ± 10 °C for 60 minutes. There were three replications for each sample.

2.5. Volatile content

The volatile content of biomass was measured according to the standard CEN 15148 [21]. 1.0 g ± 0.1 g of milled straw or pellet sample were burnt in a Gallenkamp muffle furnace (size 3, GAFSE 620, Gallenkamp, Loughborough, UK). The furnace

temperature was maintained at $900\text{ }^{\circ}\text{C} \pm 10\text{ }^{\circ}\text{C}$ for 7 minutes. Samples were analysed in triplicate.

2.6. Statistical analysis

Statistical analysis was completed using GenStat Release 13.1 [22]. Three different statistical analyses were carried out for the canola straw:

- (i) For the straw harvested in 2008, a 2 x 5 analysis of variance (ANOVA) was completed with a level of probability of 5 % ($P < 0.05$) to identify the possible effect of canola straw bale storage time and bale sample point (i.e. inner and outer points) on the GCV, ash content, volatile content and elemental composition of the straw. Thus, the two factors used in the factorial experiment were: (a) storage of the straw which is defined by the experimental treatments 1, 3, 4, 7, 10 and 20 months and (b) the point within the bale with inside and outside as experimental treatments.
- (ii) For the straw harvested in 2009, a 2 x 3 ANOVA was used for the same purpose as described in (i) above. However, the factor storage of the straw was defined for the experimental treatments 1, 3 and 7 months.
- (iii) A simple linear regression with groups where the response variables were GCV, ash content, volatile content and elemental composition. Two explanatory variables were described, the variate which was the storage period and the factor, which was the year. Thus, the difference between years 2008 and 2009 was estimated to determine if the relationship between the response variables and the storage period was different in the two years. The results were analyzed based on the P values.

In the case of canola straw pellets, two different ANOVA analyses were completed:

- (i) The effect of canola straw pellet storage time and bale storage time prior to pelletization on GCV, ash content, volatile content and elemental composition was conducted with a 3 x 5 ANOVA analysis. The 'pellet storage' factor had five experimental treatments: 2, 4, 12, 24 and 48 weeks. The factor 'bale storage time prior pelletization' had three experimental treatments: 3, 7 and 10 months.
- (ii) The effect that the year of harvest of the canola straw could produce in the pellets was analyzed with a 2 x 4 factorial analysis. The factor year is defined by the experimental treatments year 2008 and year 2009, while the factor pellet storage was defined by the experimental treatments 2, 4, 12 and 24 weeks.

3. Results and discussion

3.1. Elemental composition

The variation in the elemental composition (i.e. carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine, sodium, magnesium, aluminium, phosphorous, potassium, calcium and iron) of canola straw bales with the storage is shown in Table 3. The elemental composition of canola straw pellets stored for different periods and produced from straw harvested in different years and stored for different periods is shown in Tables 4 and 5. Table 6 shows the statistical significance of (i) bale storage time, the sample position and the year of harvest on the elemental composition of canola straw and (ii) the pellet storage time, bale storage time and year of harvest on the elemental composition of canola straw pellet.

The elemental composition of baled canola straw harvested in 2008 and 2009 did not vary significantly with the point from which samples were taken suggesting the

elemental composition of canola straw was uniform throughout the bale, with the exception of S (%) in 2009. Whilst there was a statistically significant variation in the S content of straw sampled from the inner and outer points of straw bales, this variance was not considered of practical significance. In all instances the S content of straw bales was above concentrations that are expected to result in operational issues during combustion. Concentrations of S higher than 0.1 % are believed to cause corrosion and those higher than 0.2 % can cause problems of SO_x emissions [23]. However, no problems were found in the combustion of canola straw pellets regarding SO₂ emissions [24] or ash deposition [25].

The carbon content (C) (%) of a fuel is important because it positively affects the heating value of the material [9]. Whilst there was a statistical variation in the C (%) with the year of harvest (i.e. 2008 and 2009) and length of storage, this is not considered important from a practical point of view because the variations were minimal and the GCV did not vary greatly with the carbon content. For example, there was a significant increase in the C (%) content from 42.07 % ± 0.05 % after 4 months storage to 44.54 % ± 0.14 % after 20 months storage. This result is in agreement with Nurmi [16] who found a significant increase in the C (%) during 10 months storage of hammermilled logging residue. An equation was developed to calculate the GCV based on the C, H, S, O, N and ash content of biomass [26]. The equation assumes the GCV of a fuel is directly related to the carbon content. In the current study, the GCV decreased slightly with a slight increase in carbon content. There was no clear evidence that the variations in the C (%) affected the GCV (MJ kg⁻¹) of the canola straw.

In contrast to the current study, a decrease in the C (%) was found by other researchers when woodchips were stored for up to 12 months [17]. They attributed these changes to

an increase in the O content, indicating the biomass underwent oxidation or degradation during storage. However, in the present work the O content of canola straw bales did not vary greatly, and no trend was observed in the O content during storage.

Furthermore, the current study found no relationships occurred during the storage of canola straw bales between the C (%), H (%), O (%) or GCV (MJ kg^{-1}).

The C (%) of the canola straw pellets was affected by the straw used to produce them. The general tendency was the C (%) in the pellets was approximately 1 % lower than in the straw used to produce them. Although there is no clear evidence to explain why the C (%) was slightly lower in the pellets compared with the straw used to produce them, the results do demonstrate that the addition of calcium lignosulfonate as a binder did not increase the C content (%) of the pellets. The C (%) in canola straw pellets was also affected by the length of storage and the year of harvest of the straw. However, the variations in the C (%) of the pellets with storage were minimal (See Table 4) and the variations between years were due to the C (%) of the canola straw used to produce the pellets (Table 3).

The hydrogen content (H) (%) did not seem to follow any particular trend for straw bales harvested in 2008 and showed a decrease during storage in 2009. Previous research showed that the hydrogen content of logging residues decreased during storage and was likely to be caused by a loss of volatile matter [16]. No relationship between the variations of volatile content and hydrogen were found in the present work.

The nitrogen content (N) (%) of canola straw bales (%) was slightly higher in straw harvested in 2008 compared to 2009. Although, the farm practice was the same in both years, a seasonal variation in the uptake of nitrogen by the crop can be expected. The N (%) of canola straw bales harvested in 2008 and 2009 varied significantly during

storage. The N (%) of canola straw was lowest when it was taken directly from the swath (i.e. $0.49 \% \pm 0.02 \%$). There was no evidence to explain why the N (%) was higher once the straw was baled. Similar result was found previously in the spruce needles of logging residue [16]. A nitrogen content of 9.8 mg g^{-1} was measured in the live trees, whilst a nitrogen content of 11.65 mg g^{-1} was measured after 9 months storage of the residue. No clear explanation of this fact was given [16].

The N (%) of canola straw pellets was significantly affected by the straw used to produce the pellets, the year that the straw was harvested and the storage period which is similar to the trend observed for the C (%). The N (%) of the pellets was lower than that of the straw used to produce the pellets suggesting the addition of calcium lignosulfonate (i.e. 0.2 %) did not increase the N (%) of the pellets.

The N (%) of canola straw pellets was significantly different in the pellets produced with the straw harvested in 2008 and 2009. This was due to differences in the N (%) of the straw harvested in 2008 and 2009 that was used to produce the pellets. The variations in N (%) during storage were minimal for the pellets produced with canola straw harvested in 2008 and stored for 3 and 7 months prior to pelletisation and with canola straw harvested in 2009 and stored for 3 months prior to pelletisation. However, the N (%) in the pellets increased during storage for the pellets produced with straw harvested in 2008 and stored for 10 months prior to pelletisation. The N content (N) (%) of a combustion fuel is important because of NO_x emissions. It is recommended that values of N should be less than 0.6 wt % (d.b.) to reduce these emissions [27].

Whilst the N (%) was lower in pellets of canola straw than in bales, the content remained higher than 0.6 %, suggesting NO_x emissions during combustion may be

problematic. However, no problems were found in the combustion of canola straw pellets regarding NO or NO₂ emissions [24].

The content of S (%) in canola straw bales harvested in 2008 increased significantly during storage. However, these variations did not follow a continuous incremental trend over the period of storage.

The S (%) of the canola straw pellets was affected by the straw used to produce the pellets, the storage period and the year of harvest. However, no trends were found in the S (%) during storage. In 2008, the canola straw had a lower S (%) than in 2009, resulting in a lower S (%) content in the pellets produced from this straw. The S (%) of canola straw pellets was significantly higher ($P < 0.001$) than the S (%) of the canola straw used to produce the pellets. The highly significant increase in S (%) in the pellets can be attributed partly to the addition of lignosulfonate at a concentration by weight of 5 %, which mathematically would give a 0.15 % increment in the S (%). However, the increment of S (%) was higher than this mathematical value in all cases, except for the pellets that were stored for 2 weeks and produced from canola straw bales harvested in 2008 and stored for 10 months prior to pelletisation. This may be due to an uneven distribution of binder within the pellets, or due to the inaccurate application of binder to the milled straw prior to pelletisation. These levels of sulphur could be a potential problem, as together with Cl, high S concentrations in the canola straw could result in corrosion and SO_x emissions.

The content of Cl (%), in the canola straw fluctuated significantly during storage, but it did not follow any particular trend. It is noted the Cl (%) was lower in the swath than once it was baled and the Cl (%) continued to decrease during storage.

The straw, the length of storage and the year of harvest affected the Cl (%) in the pellets. The variations during the storage of the pellets did not follow any clear trends, so they might be attributed to natural variations. The Cl (%) in the canola straw pellets is of importance because it could cause corrosion and HCl emission problems during combustion because the concentration of Cl in the fuel is above 0.1 wt % (d.b.) [27]. However, no problems were found in the combustion of canola straw pellets regarding HCl emissions [24] or ash deposition [25].

The storage of canola straw bales had a significant effect on the rest of the elemental composition, [Na (mg kg⁻¹), Mg (mg kg⁻¹), Al (mg kg⁻¹), P (mg kg⁻¹), K (%), Ca (%) and Fe (mg kg⁻¹)] in 2008 and 2009, except for the Mg in 2009 and the P in 2008. There was no clear tendency in the variation of any of these elements with storage (i.e. an increase or a decrease in the concentrations with storage), except for the concentration of Na in the straw harvested in 2009, which decreased from 1740.91 mg kg⁻¹ ± 246.69 mg kg⁻¹ to 1076.13 mg kg⁻¹ ± 106.75 mg kg⁻¹. There was no evidence that any contamination from the farm environment affected the bales, as no differences were found between the inside and outside points of the bales, suggesting the changes during storage were caused by natural variation. It has been demonstrated previously that although elemental variations during the storage of spruce needles were statistically significant, they were considered only unimportant minor changes in the concentration [16].

The content of Na, Mg and Al were significantly lower in the swath and the values increased after baling for straw harvested in 2009.

It was noticeable that for some of the elements, such as Mg, Al, Ca or Fe, the concentration was higher in the pellets than in the baled straw, which can be explained by the addition of the binder.

The fluctuations of the elemental composition in the canola straw pellets did not follow any particular trend, as was the case with the canola straw bales, and the small changes are believed to be caused by natural variations. Also, the variability of the elements in the canola straw bales were much higher (as shown in the standard error) than for the pellets, suggesting that the pellets are more uniform than the straw.

3.2. Gross calorific value

The variations in the Gross Calorific Value (GCV) of canola straw bales and pellets during storage are shown in Figure 1. The point within the bale from which straw samples were taken (i.e. inner or outer points) did not significantly affect the GCV of straw harvested in 2008 and 2009 ($P = 0.822$ and $P = 0.234$, for 2008 and 2009 respectively). Linear regression suggested the GCV (MJ kg^{-1}) of canola straw bales did not change significantly with the year of harvest ($P = 0.162$) suggesting that the GCV was uniform within the bale and harvest season.

The GCV of canola straw bales varied significantly during storage from straw harvested in 2008 ($P < 0.001$), but did not change significantly in 2009 ($P = 0.85$), suggesting that the GCV of canola straw was uniform during storage in 2009. Although the GCV varied significantly during storage in 2008, it is not considered important from a practical point of view because the variation was relatively small; the GCV ranged between $16.91 \text{ MJ kg}^{-1} \pm 0.06 \text{ MJ kg}^{-1}$ and $17.89 \text{ MJ kg}^{-1} \pm 0.06 \text{ MJ kg}^{-1}$ after 7 months storage. The variations did not follow any particular trend. A slight decrease in the GCV of willow chips during storage was found in previous research, but these were

considered marginal [28]. Similarly, other authors [17] found a decrease in the lower heating value. However, the variations were attributed to the changes in C during storage. In the results presented here, the changes in the GCV did not follow any trend with the chemical composition as discussed in section 3.1. Thus, the changes in the GCV of the canola straw were attributed to natural variations within the straw bales. The GCV of canola straw pellets was significantly affected by the straw used to produce the pellets ($P = 0.01$) and the length of storage ($P < 0.001$). The year of harvest of the canola straw had a significant effect on the GCV of the canola straw pellets ($P < 0.001$) (Fig. 1c). The GCV of the canola straw pellets was slightly higher than that of the straw, contrary to the results found by Lehtikangas [18]. Lehtikangas suggested the reduction in the CV in the pellets was due to the loss of volatile extractive compounds during drying [18]. However, no drying was required in the canola straw. This fact, together with the addition of the binder may be the reason for a higher GCV in the pellets.

3.3. Ash content

The point within the bale from which straw samples were taken (i.e. inner or outer points) did not significantly affect the ash content of straw harvested in 2008 ($P = 0.995$) or 2009 ($P = 0.55$). Simple linear regression analysis suggested the ash content (%) did not change significantly with year of harvest ($P = 0.864$), demonstrating the uniformity of the canola straw bales because there were no significant variations in the ash content within the bale and harvest season.

The ash content of canola straw bales harvested in 2008 and 2009 varied significantly with the length of storage ($P < 0.001$ and $P = 0.003$ for 2008 and 2009, respectively).

The variations in the ash content did not seem to follow any particular trend and no

relationship between the volatile and ash content was found. The ash variations during storage were attributed to natural variations [29]. Previous research has shown the ash content of willow chips stored in piles marginally increased with storage but the changes were considered not to be significant [28]. Significant changes in the ash composition with the storage were found by [17], and it was postulated these changes were due to the exposure of the woodchip pile to the weather conditions (e.g. rain). Rain water may have dissolved soluble compounds (e.g. soluble salts) [30, 31]. The ash content of switchgrass bales increased during 26 weeks outside, unprotected storage [32]. However, it was found that it could be a systematic error in the determination of the ash content [32]. In the current study canola straw bales were stored under cover (i.e. protected from rain water). Variations in the ash content during storage of the canola straw bales are considered to be due to natural variations.

The ash content of canola straw pellets was significantly affected by the straw used to produce the pellets ($P < 0.001$) and the length of storage ($P < 0.001$) (Figure 2b). The year of harvest of the canola straw had a significant effect on the ash content of the canola straw pellets ($P < 0.001$) (Figure 2c). The ash content of the pellets was significantly higher than the ash content of the straw, which was also found by other researcher [18] who attributed this increment to the thermal treatment in the process that could have caused a reduction in the extractives, leading indirectly to an increase in ash content of the material. Also, in the present work, the increase in the ash content could be due to the addition of binder.

The ash content of canola straw pellets ranged from 6.74 ± 0.08 % to 9.75 ± 0.03 % overall. The ash content of a fuel is important because high ash content could affect the carbon monoxide (CO) emissions and efficiency requirements when the pellets are

burnt. Previous research, has shown that the combustion of pelletised herbaceous (i.e. Brassica) pellets resulted in CO emissions and efficiency requirements that were within the European requirements. However, the CO emissions and efficiency of Brassica pellets were worse than for poplar pellets, which was attributed to the higher ash content of the Brassica (10.7 %) compared to poplar [33]). Further work could be completed to investigate how the ash content of canola straw pellets could be reduced. Previous research has shown the ash content of grape pomace was as significantly reduced when it was mixed with Pyrenean oak pellets [34].

3.4. Volatile content

The point within the bale from which straw samples were taken (i.e. inner or outer points) did not significantly affect the volatile content of straw harvested in 2008 ($P = 0.535$) or in 2009 ($P = 0.462$) and did not change significantly with the year ($P = 0.729$) according to the simple linear regression analysis. This suggests the canola straw bales were uniform, as mentioned for previous properties (Figure 3).

The volatile content of canola straw bales varied significantly with the length of storage for straw harvested 2008 and 2009 ($P < 0.001$ for both cases) (Figure 3b). Although, the changes in volatile content were statistically significant the volatile content appears to be stable over the storage period.

The volatile content of canola straw pellets was significantly affected by the straw used to produce the pellets ($P < 0.001$) and the length of storage ($P < 0.001$). There was a statistical interaction between the raw material used to produce the pellets and the length of storage post-pelletisation ($P < 0.001$). The year of harvest of the canola straw had a significant effect on the volatile content of the canola straw pellets ($P < 0.001$) (Figure 3c).

3.5. Conclusion

- No variations between inside and outside points within the canola straw bale were found and hence they can be considered uniform throughout the bale. Thus, it can be concluded that the canola straw bales did not suffer any contamination from the farm environment.
- Generally, the storage of canola straw bales and pellets significantly affected the elemental composition, gross calorific value, ash and volatile content of the straw and pellets ($p < 0.05$). However, the variations are considered minimal and are believed to be caused by natural variations, as no correlations between properties were found
- The concentrations of nitrogen, sulphur and chlorine of the canola straw taken from the swath were significantly lower than the composition of the straw after baling.
- The content of sulphur, magnesium, aluminium, calcium, and iron increased when the straw was pelletised. In contrast the carbon, sulphur and chlorine content were lower in the pellets.
- The concentration of sulphur, magnesium, aluminium, calcium, and iron increased when the straw was pelletised, potentially attributable to the addition of the binder. In contrast the carbon, sulphur and chlorine content were lower in the pellets compared to the baled straw which may be due to volatilisation during the pelletisation process.

- The variations in the GCV of canola straw bales and pellets with storage were minimal, and no correlations between the GCV and the chemical composition were found.
- The ash and volatile content of canola straw bales and pellets were stable during storage. However, the ash content was higher in the pellets, hence consideration should be given to a reduction in the amount of binder used to keep the ash content to a minimum.

4. Acknowledgments

The authors would like to thank the staff at the Princess Margaret Laboratory, the Farm and the Crop and Environment Research Centre (CERC) at Harper Adams University College. We also would like to thank the Douglass Bomford Trust and Claas Stiftung for supporting this project.

5. References

- [1] FAO (Food and Agriculture Organization of the United Nations). 2010. FAO Statistics [Internet]. FAO. [Cited 2012 July 23]. Available from:
<http://www.fao.org/corp/statistics/en/>
- [2] Garrad Hassan and Partners Ltd. Scotland's Renewable Resource 2001 – Volume II. Scottish Executive Report 2850/GR/02; 2001 [Internet]. Available from:
<http://www.scotland.gov.uk/Resource/Doc/47176/0014634.pdf>
- [3] Newman, R. 2003. A trial burn of rape straw and whole crops harvested for energy use to assess efficiency implications. B/U1/00768/00/00 URN 03/1569. Department of Trade and Industry.

- [4] Biomass Energy Centre.org [Internet]. Straw quantities of straw – grown in the UK; 2006. [Cited 14th July 2011]. Available from: <http://www.biomassenergycentre.org.uk/>.
- [5] Chico-Santamarta L, Humphries AC, White D, Chaney K., Godwin RJ. Effect of pre- and post-pelletisation storage of canola (oilseed rape) straw on the quality and properties of pellets. ASABE Annual International Meeting. Paper number 096105; 2009 June 21-24; Reno, Nevada.
- [6] Sultana, A., Kumar, A. 2011. Development of energy and emission parameters for densified form of lignocellulosic biomass. *Energy*, 36, 2716-2732.
- [7] Booth J, Cook P, Ferguson B, Walker K. Economic evaluation of biodiesel production from oilseed rape grown in north and east Scotland. [Internet]. Scottish Agricultural College, Edinburgh; 2005 [Cited 2011 Jul 14]. Available from: <http://www.hie.co.uk/HIE-economic-reports-2005/sacbiodiesel-full-report-2005.pdf> .
- [8] Butterworth B. *The straw manual: a practical guide to cost effective straw utilization and disposal*. London: Spon; 1985.
- [9] Obernberger I, Thek G. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. *Biomass Bioenergy*. 2004; 27:653-69.
- [10] McMullen J, Fasina OO, Wood AW, Feng Y. Storage and handling characteristics of pellets from poultry litter. *Appl Eng Agric*. 2005; 21:645-51.
- [11] Bhattacharya S, Sett S, Shrestha RM. State of the art for biomass densification. *Energy Sources* 1989;11:161–82.
- [12] Samson P, Duxbury P, Drisdelle M, Lapointe C. Assessment of pelletized biofuels [Internet]. 2000 [cited 2011 May 12]. Available from:

http://www.reapcanada.com/online_library/Reports%20and%20Newsletters/Bioenergy/15%20Assessment%20of.PDF.

[13] Kaliyan N, Morey RV. Factors affecting strength and durability of densified products. Proceedings of the ASABE Annual International Meeting; 2006 July 9–12; Portland, Oregon; St. Joseph (MI): ASABE; 2006. ASABE Paper No.: 066077

[14] Chico-Santamarta L, Humphries AC, Chaney K, White DR, Magan N, Godwin RJ. Microbial changes during the on-farm storage of canola (oilseed rape) straw bales and pellets. *Biomass Bioenergy*. 2011; 35:2939-49.

[15] Le Lostec, B., Galanis, N., Baribeault, J., Millete, J. 2008. Wood chip drying with an absorption heat pump. *Energy*, 33, 500-512.

[16] Nurmi J. The storage of logging residue for fuel. *Biomass Bioenergy* 1999;17:41-7.

[17] Casal MD, Gil MV, Pevida C, Rubiera F, Pis JJ. Influence of storage time on the quality and combustion behaviour of pine woodchips. *Energy*. 2010; 35:3066-71.

[18] Lehtikangas P. Quality properties of pelletised sawdust, logging residues and bark. *Biomass Bioenergy* 2001;20:351-60.

[19] CEN/TS 14918, 2005. Solid Biofuels – Method for the Determination of Calorific value.

[20] CEN/TS 14775:2004. Solid biofuels – Method for the determination of ash content. Brussels, Belgium: European Committee for Standardization.

[21] CEN/TS 15148: 2005. Solid biofuels – Method for the determination of content of volatile. Brussels, Belgium: European Committee for Standardization.

[22] GenStat DE. GenStat release 13.1. UK: VSN International Ltd; 2010.

- [23] Obernberger I, Brunner T, Bärnthaler G. Chemical properties of solid biofuels – significance and impact. *Biomass Bioenergy*. 2006;30:973-82.
- [24] Chico-Santamarta L, Khodier AHM, Humphries AC, Simms NJ, Oakey JE, Godwin RJ. The effect of on-farm storage of canola (oilseed rape) straw pellets on the combustion behaviour, Part 1: Gaseous emissions. Submitted to *Biosystems Engineering*. 2011.
- [25] Khodier AHM, Chico-Santamarta L, Simms NJ, Humphries AC, Oakey JE, Godwin RJ. The effect of on-farm storage of canola (oilseed rape) straw pellets on the combustion behaviour, Part 2: Deposition. Submitted to *Biosystems Engineering*. 2011.
- [26] Channiwala SA. On the biomass gasification process. PhD thesis, Indian Institute of Technology, Department of Mechanical Engineering, Bombay, India. 1992.
- [27] Obernberger I. Physical characteristics and chemical composition of solid biomass fuels. In: Eindhoven University of Technology, Department for Mechanical Engineering, Section Process Technology, editor. Script for the lecture “Thermochemical Biomass Conversion”. Eindhoven, the Netherlands; 2003 [Chapter 3].
- [28] Jirjis R. Effects of particle size and pile height on storage and fuel quality of comminuted *Salix viminalis*. *Biomass Bioenergy* 2005;28:193–201.
- [29] Lehtikangas P. Storage effects on pelletised sawdust, logging residues and bark. *Biomass Bioenergy* 2000;19:287-93.
- [30] Averlakis S, Gehrman H, Beckmann M, Koukios EG. Agglomeration problems during fluidized bed gasification of olive-oil residue: evaluation of fractionation and leaching as pre-treatments. *Fuel* 2003; 82,1261-70.

- [31] Doshi V, Vuthaluru HB, Korbee R, Kiel JHA. Development of a modelling approach to predict ash formation during co-firing of coal and biomass. *Fuel Processing Technology*. 2009; 90:1148-56.
- [32] Wiselogel AE, Agblevor FA, Johnson DK, Deutch S, Fennell JA, Sanderson MA. Compositional changes during storage of large round switchgrass bales, *Bioresource Technol*. 1996;56:103-9.
- [33] Diaz-Ramirez, M., Sebastian, F., Royo, J., Rezeu, A. 2012. Combustion requirements for conversion of ash-rich novel energy crops in a 250kWth multifuel grate fired system. *Energy*, 46, 636-643.
- [34] Miranda MT, Arranz JI, Román S, Rojas S, Montero I, López M, Cruz JA. Characterization of grape pomace and Pyrenean oak pellets. *Fuel Process Technol*. 2011;92:278-83.