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Research Article

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Influences of Physical and Thermochemical Properties on the Exergy of Cereal Straws

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Abstract

Exergy is a measurement of how far a material deviates from a state of equilibrium with the environment. The energy values of the barley, oat, rye and wheat straws were determined and the influences of LHV, moisture content, ash content, S, C, O, H and N on the exergy of cereal straws were evaluated. The moisture content of the four cereal straws varied from 10% (oat straw) to 17% (rye straw). The moisture related exergy value of the four cereal straws varied from 283.954 kJ/kg (oat straw) to 479.747 kJ/kg (rye straw), accounting for 1.376-2.275% of the total exergy of cereal straws. A positive linear relationship between the exergy value and moisture content of cereal straws was observed. The ash content of the four straws varied from 1.635% (rye straw) to 4.554% (oat straw). The ash related exergy value varied from 25.912 kJ/kg (rye straw) to 111.061 kJ/kg (oat straw), accounting for 0.123-0.538% of the total exergy of cereal straws. A negative linear relationship between the exergy value and ash content of cereal straws was observed. The S content of the four straws varied from 0.058% (rye straw) to 0.144% (oat straw). The S related exergy value varied from 5.626 kJ/kg (rye straw) to 13.944 kJ/kg (oat straw), accounting for 0.027-0.068% of the total exergy of cereal straws. A negative linear relationship between the exergy value and S content of cereal straws was observed. The results showed that the combined contribution of the exergy values of moisture, ash and S contents to the total exergy of cereal straws (1.982-2.424%) is very small and can be neglected. The O/C, H/C and N/C atomic ratios varied from 0.7184 to 0.7780 (8.30%), from 1.4214 to 1.5457 (8.74%) and from 0.0026 to 0.0254 (876.92%), respectively. The correlation factors varied from 1.133 to 1.142 (0.8%). The exergy values of the four cereal straws varied from 20.631 MJ/kg (oat straw) to 21.156 MJ/kg (wheat straw). They were mainly determined by the correlation factors and the LHVs. A positive linear relationship between the exergy value and LHV of cereal straws was observed.

Keywords: Exergy; Cereal straws; Barley; Oat; Rye; Wheat; LHV; Moisture; Ash; S; C; O; H; N; Correlation factor; O/C; H/C; N/C

Introduction

Wheat, barley, oat and rye are the most popular cereal crops for over 2.45 billion people in the world (35 percent of the world's population). These cereal crops are cultivated in over 100 countries [1]. The world production of wheat, barley, oat and rye in 2013 was estimated to be 701.10, 137.88, 22.49 and 15.26 million metric tons, respectively. This amounts to a total world production of 876.73 million metric tons [2]. Wheat production alone surpassed the milled rice production in 2013 which was estimated to be 479.3 million metric tons.

Straws from these cereal crops are abundantly available on a yearly basis. The straw produced from the four cereal crops was estimated to be 674.41 million metric tons in 2013. Cereal straws are currently used as feedstuff, as fertilizer, in the pulp and paper industry, for production of nano-materials and for production of biofuels [3-7]. They are also important energy sources and can be used in thermochemical conversion processes such as pyrolysis, combustion and gasification [8-11]. The energy contents are in the ranges of 19.36-19.96, 18.18-19.38, 18.96-19.50 and 19.25-19.36 MJ/kg for the wheat, barley, oat and rye straws, respectively [12].

The physical, chemical and thermochemical properties of barley, oat, rye and wheat straws are well studied by several researches [12-16]. These properties include moisture content, bulk density, particle size, porosity, heating values, proximate analysis, ultimate analysis, ash composition, ash characteristics and degradation kinetics. However, no detailed exergy studies of barley, oat, rye and wheat straws have been reported in the literature. Furthermore, the effects of these physical and chemical properties of cereal straws on the exergy are not well documented.

The main objectives of this study were: (a) to determine the exergy of barley, oat, rye and wheat straws and (b) to determine the contributions of physical and chemical properties (LHV, moisture content, ash content, S, C, O, H and N contents) to the exergy values of these cereal straws.

Materials and Methods

Straw collection and preparation

The four cereal straws used in this study are Leger barley straw, Tibor oat straw, Kustro rye straw and Absolvant wheat straw. The straw samples were obtained from harvested fields at different farm locations in the Annapolis Valley, Nova Scotia, Canada. Small rectangular bales of 850 mm ×500 mm ×350 mm as well as loose straw samples of 15 kg of each type of straw were brought to the Bioenergy Laboratory at Dalhousie University.

The naturally dried straw samples were coarse ground through a 20-mesh sieve (0.85 mm) on a medium size Wiley Mill (Model X876249, Brook Crompton Parkinson Limited, Toronto, Ontario). The coarse

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ground samples were then reground through a 40-mesh sieve (0.425 mm) on the Wiley Mill in order to narrow the range of particle size and thus obtain homogeneous samples. The particle size distributions of the four cereal straws are shown in Table 1.

Determination of moisture content

Moisture content was determined for the naturally dried ground straw samples using the oven-drying method E871–82 (ASTM 2006). A large aluminum dish was weighed using a digital balance (Model PM 4600, Mettler Instrument AG, Greifensee, Zurich). A straw sample weighing approximately 1.0 kg was placed in the dish. The dish and straw sample were then placed in an air-forced drying oven (Heratherm, Thermo Fisher Scientific Inc., Waltham, USA) and kept at 105°C until a constant weight was achieved. The dish containing the dried sample was cooled to the room temperature in a desiccator and then weighed. The moisture content was calculated on wet basis. The same procedure was carried out with the four straws using three replicates for each straw. The dried samples were then stored in airtight plastic containers.

Determination of lower heating value

A bomb calorimeter (Parr Model 1241, Automatic Adiabatic Calorimeter, Parr Instrument Company, Moline, Illinois, USA) was used to determine the higher heating values (HHVs) of the straw samples. The higher heating value was determined following the American Society for Testing and Materials Standard Test Method D5865–10a (ASTM 2010). To avoid the sudden release of volatiles and expelling the straw particles from the combustion crucibles, which can result in incomplete combustion, the ground straw samples were made into 0.5-1.0 g pellets in a moulding die by a hydraulic press of 50 MPa (Parr Instrument Company, Moline, Illinois, USA). The same procedure was used for all four straw types with three replicates each. The lower heating values (LHVs) of the straws were then calculated as follows: [17]

$$HHV = LHV + 21.978\,\eta_H \tag{1}$$

Where:

$\eta_{H:}$ is the weight percentage of hydrogen (%)

Determination of ash content

The American Society for Testing and Materials Standard Test Method for determination of ash in biomass (E1755–01) were followed to determine the ash percentage in the straw samples (ASTM 2007). The ash samples were obtained by ashing the coarse ground straws in porcelain crucibles using a muffle furnace (Model F47900, Thermo Fisher Scientific Inc., Asheville, USA) at 600°C for one hour at first. The ash samples were cooled in a desiccator and then weighed. The ashing was again performed for one hour and the samples were cooled again in a desiccator and then weighed. This process was repeated until a constant weight was achieved. The same procedure was followed with all four straw types with three replicates each. The ash was stored in airtight plastic containers till send for ash composition analyses.

Size range (mm)	Weight percentage (%)[a]			
	Barley straw	Oat straw	Rye straw	Wheat straw
0~0.212	3.86	3.66	6.61	3.30
0.212~0.300	5.17	4.49	7.13	4.76
0.300~0.355	6.32	5.23	7.84	5.42
0.355~0.425	7.22	6.46	8.78	7.60
0.425~0.500	8.36	7.74	9.33	8.25
0.500~0.710	12.79	14.22	13.37	16.02
0.710~0.850	13.15	19.15	14.11	16.25
>0.850	43.13	39.05	32.83	38.40

[a]Average of three replicates

Table 1: Particle size distribution of cereal straws.

Determination of ash composition

The ash composition analysis was performed at the Mineral Engineering Laboratory of Dalhousie University. During the ash composition analysis, the weight fractions of SiO_2, K_2O, CaO, P_2O_5, MgO, Al_2O_3, Fe_2O_3, Na_2O, SO_3 and ZnO were determined. An LECO induction furnace method and atomic absorption were used. The analyses were performed on all four straws and three replicates were carried out for each type.

C, O, H, N and S contents

The weight fractions of C, H, N and S of the ground and oven-dried straw samples were determined and the weight fraction of O was calculated by the difference. The weight fractions of C, H and N were determined at the Mineral Engineering Laboratory of Dalhousie University using a Perkin-Elmer Model 240 CHN Elemental Analyzer (Perkin Elmer Inc., California, USA). The S weight fraction was determined using the American Society for Testing and Materials ICP induction coupled plasma-atomic method D6349–09 (ASTM 2009). The analyses were performed on all four straws and three replicates were carried out for each type.

Exergy value

The exergy values of biomass fuels were obtained using the following correlation provided by Szargut et al. [18]:

$$ex = \beta(LHV + \eta_w h_w) + 9683\,\eta_s + ex_{ash}\,\eta_{ash} + ex_w\,\eta_w \tag{2}$$

Where:

ex is the exergy of the fuels (kJ/kg)

β is the correlation factor

h_w is the evaporation enthalpy of moisture (2442 kJ/kg)

η_w is the moisture content (%)

η_s is the weight percentage of sulfur (%)

η_{ash} is the weight percentage of ash (%)

ex_{ash} is the exergy of ash (kJ/kg)

ex_w is the exergy of water (900 kJ/kmol)

LHV is the lower heating value of biomass fuels (kJ/kg)

The following equations can be used to calculate the correlation factor (β) for biomass fuels [18]:

(a) For solid hydrocarbons

$$\beta = 1.0435 + 0.0159\frac{H}{C} \tag{3}$$

(b) For solid fuels containing C, H and O

$$\beta = 1.0438 + 0.0158\frac{H}{C} + 0.0813\frac{O}{C} \quad (O/C \le 0.5) \tag{4}$$

$$\beta = \frac{1.0414 + 0.0177\frac{H}{C} - 0.3328\frac{O}{C}(1 + 0.0537\frac{H}{C})}{1 - 0.4021\frac{O}{C}} \quad (O/C \le 2) \tag{5}$$

(c) For solid fuels containing C, H, O and N

$$\beta = 1.0437 + 0.0140\frac{H}{C} + 0.0968\frac{O}{C} + 0.0467\frac{N}{C} \quad (O/C \le 0.5) \quad (6)$$

$$\beta = \frac{1.044 + 0.0160\frac{H}{C} - 0.3493\frac{O}{C}(1 + 0.0531\frac{H}{C}) + 0.0493\frac{N}{C}}{1 - 0.4124\frac{O}{C}} \quad (O/C \le 2) \quad (7)$$

(d) For wood:

$$\beta = \frac{1.0412 + 0.2160\frac{\eta_H}{\eta_C} - 0.2499\frac{\eta_O}{\eta_C}(1 + 0.7884\frac{\eta_H}{\eta_C}) + 0.0450\frac{\eta_N}{\eta_C}}{1 - 0.3035\frac{\eta_O}{\eta_C}} \quad (8)$$

Where:

C is the number of carbon in the molecular formula of fuel

H is the number of hydrogen in the molecular formula of fuel

O is the number of oxygen in the molecular formula of fuel

N is the number of nitrogen in the molecular formula of fuel

η_C is the weight percentage of carbon (%)

η_H is the weight percentage of hydrogen (%)

η_O is the weight percentage of oxygen (%)

η_N is the weight percentage of nitrogen (%)

Results and Discussion

Characteristics of cereal straws

Moisture content: The moisture contents of the four cereal straws used in this study are shown in Table 2. The moisture content of the cereal straws varied from 10% (oat straw) to 17% (rye straw), 70% variation. The variation in moisture content could be due to crop type, soil type, fertilizer type or variations in climatic conditions and cultivation methods [13].

Varying values of moisture content for cereal straws were reported by other researchers. Moisture content values in the ranges of 4.6-13.5, 6.90-12.00 and 11-15% were reported for barley straws by Adapa et al. [19], Mani et al. [20] and Ghaly and Al-taweel, [12] respectively. Hansen et al. [21] reported a moisture content of 12.1% for a barley straw. Moisture content values in the ranges of 4.1-13.1, 10-12 and 11.9-12.7% were reported for oat straws by Adapa et al. [19], Ghaly and Al-taweel [12] and Kraiem et al. [22], respectively. Moisture content values of 5.6 and 6.8% were reported for oat straws by Dererie et al. [23] and Sapci [10], respectively. Moisture content values of 5.4, 5.9, 7.4 and 10% were reported for rye straws by Franceschin et al. [24], García-Cubero et al. [25], Varnaitė and Raudonienė [26] and Perez-Cantu et al. [27], respectively. Ghaly and Al-taweel [12] reported moisture content in the range of 17-18% for rye straws. Moisture content values in the ranges of 4.0-15.6, 5.02-7.79, 6.16-12.10 and 10-13% were reported for wheat straws by Adapa et al. [19], Zhang et al. [13], Mani et al. [20] and Ghaly and Al-taweel [12], respectively. Moisture content values of 9.0 and 10.0% were reported for wheat straws by García-Cubero et al. [25] and Hansen et al. [21], respectively.

Straw	Moisture content (%)	LHV (MJ/kg)	Ash content (%)[a]
Barley	15	18.20	3.587
Oat	10	17.80	4.554
Rye	17	18.15	1.635
Wheat	13	18.31	2.688

[a]On as received basis

Table 2: Moisture contents, LHVs and ash contents of cereal straws.

Liang et al. [28] and Pommier et al. [29] stated that high moisture content can increase the biodegradation rate of organic material during storage, resulting in the loss of solid fuel. Zhang et al. [13] stated that high moisture content of straw can also substantially affect its quality as a fuel source. Ghaly and Al-Taweel [12] and Chen et al. [30] stated that high moisture content of biofuels can cause deterioration and decrease their heating values. A dry material is thus preferred for storage, gasification and combustion [13].

Lower heating value: The LHVs of the four cereal straws are shown in Table 2. The LHV value of the cereal straws varied from 17.80 MJ/kg (oat straw) to 18.31 MJ/kg (wheat straw), a variation of 2.87%. These differences may be due to variations in the straw varieties. Vargas-Moreno et al. [31] stated that the LHV of a biomass fuel can be affected by its elemental composition, structure and physical properties, all of which are related to the type of straw.

Other researchers reported similar values for different cereal straws. Mani et al. [20] reported the LHV values of 16.12 and 16.81 MJ/kg for barley and wheat straws, respectively. Hansen et al. [21] reported the LHV values of 17.99 and 17.85 MJ/kg for barley and wheat straws, respectively. Sapci [10] reported the LHV values of 18.8 and 18.3 MJ/kg for barley and oat straws and the LHV range of 19.0-19.2 MJ/kg for wheat straws. Ghaly and Al-taweel [12] reported LHV values in the ranges of 17.07-18.20, 17.66-18.21, 17.95-18.15 and 18.29-18.71 MJ/kg for barley, oat, rye and wheat straws, respectively.

Ash content: The ash contents of the four cereal straws are shown in Table 2. The ash content of the cereal straws varied from 1.635% (rye straw) to 4.554% (oat straw), a variation of 187.53%. Varying values of ash content for cereal straws were reported by other researchers. Ash content values of 2.18, 2.4, 3.47, 4.1, 4.3, 9.8 and 10.72% were reported for barley straws by Adapa et al. [32], Hansen et al. [21], Pronyk and Mazza [16], Sapci [10], Sevilla et al. [33], Thevannan et al. [34] and Mani et al. [20], respectively. Viola et al. [35] reported an ash content in the range of 6.1-7.5% for barley straw. Ash content values of 2.19, 3.92 and 7.5% were reported for oat straws by Adapa et al. [32] Pronyk and Mazza [16] and Dererie et al. [23] respectively. Ash content values in the ranges of 6.4-8.1 and 6.5-7.2% were reported for oat straws by Viola et al. [35] and Kraiem et al. [22]. Ash content values of 2.1, 3.0, 3.1, 3.4, 3.9 and 6.15% were reported for rye straws by Gullón et al. [36], Sun et al. [37], García-Cubero et al. [38], Franceschin et al. [24], Perez-Cantu et al. [27] and Sun and Cheng [39], respectively. Ash content values of 2.36, 5.7, 7.0 and 8.32% were reported for wheat straws by Adapa et al. [32], García-Cubero et al. [38] Sapci [10] and Mani et al. [20] respectively. Ash content values in the ranges of 2.06-5.16 and 7.3-8.9% were reported for wheat straws by Petrik et al. [40] and Viola et al. [35] respectively.

Zhang et al. [13] stated that the ash content affects the property of biomass fuels. Vargas-Moreno et al. [31] and Zhao et al. [41] stated that the ash content of a fuel can reduce its heating value and cause agglomeration. Ghaly and Al-taweel [12] stated that the ash content indicates the potential for the formation of undesirable bonded deposits on combustor surfaces. Ergudenler and Ghaly [42] reported an agglomeration phenomenon of wheat straw ash in a fluidized bed gasification system. Lower ash content fuels are therefore preferred.

Ash composition: The ash compositions of the four cereal straws are shown in Table 3. The barley straw had the highest contents of SiO_2

(0.320 mol/kg), Al_2O_3 (0.020 mol/kg), Fe_2O_3 (0.006 mol/kg) and ZnO (0.00004 mol/kg), the oat straw had the highest contents of K_2O (0.198 mol/kg), CaO (0.072 mol/kg), P_2O_5 (0.028 mol/kg), MgO (0.060 mol/kg) and SO_3 (0.012 mol/kg), the wheat straw had a CaO content (0.072 mol/kg) similar to oat straw and the highest content of Na_2O (0.007 mol/kg). The differences in the concentrations of mineral oxide could be due to straw variety, soil type, fertilizer type or the variations in climatic conditions and cultivation methods [13].

Other researchers reported varying values for the ash composition of cereal straws. Hansen et al. [21] reported the SiO_2, K_2O, CaO, MgO, P_2O_5, Al_2O_3, SO_3, Na_2O and Fe_2O_3 weight fractions of 22, 41, 18, 2.1, 4.9, 0.64, 4.3, 1.9 and 0.67% for barley straws and 62, 14, 8.1, 1.8, 2.4, 1.7, 2.6, 0.36 and 2% for wheat straws, respectively. Ghaly and Al-taweel [12] reported weight fractions for the SiO_2, K_2O, CaO, MgO, P_2O_5, Al_2O_3, SO_3, Na_2O, Fe_2O_3 and ZnO in the ranges of 25.59-53.59, 8.00-40.59, 5.91-11.78, 2.39-4.30, 6.10-7.25, 1.16-5.60, 1.62-2.00, 0.79-0.85, 0.62-2.81 and 0.05-0.12% for barley straws, 14.75-65.54, 10.76-40.98, 3.76-8.92, 2.13-6.63, 3.00-8.65, 0.28-5.30, 0.70-2.12, 0.74-1.95, 0.24-2.49 and 0.02-0.05% for oat straws, 40.31-47.05, 13.92-18.37, 8.11-15.81, 4.05-5.46, 6.37-9.00, 1.44-5.89, 1.07-1.15, 0.95-1.55, 1.43-2.52 and 0.07-0.07% for rye straws and 26.71-40.33, 23.87-51.03, 8.43-15.05, 3.07-5.37, 5.50-9.65, 0.54-1.08, 2.10-2.52, 0.70-1.66, 0.59-0.86 and 0.06-0.20% for wheat straws, respectively.

Lin et al. [43] stated that agglomeration and de fluidization in a fluidized bed was affected by the ash composition. Liu et al. [44] stated that alkali metals such as K and Na which exist in the outer layer of straw particles will melt and coat the surfaces of ash particles, making ash particles sticky and adhere to the surfaces of bed particles. The large-sized ash particles may act as the seed for the formation of agglomerates. The small-sized ash particles, however, may contribute to the formation of coating layers which is the direct reason for bed de fluidization.

C, H, O, N and S contents: Table 4 shows the C, H, O, N and S contents of the four cereal straws. Although different straws had different C, H, O, N, and S contents, all the straws had high contents of C (38.686-40.446%) and O (37.460-41.958%) followed by H (4.633-5.150%), *N* (0.116-1.197%) and *S* (0.058-0.144%). The differences observed among the cereal straws were very small.

Varying values of C, H, O, N and S contents were reported by other researchers. Ghaly and Al-taweel [12] reported C, H, O, N and S contents in the ranges of 44.54-46.01, 5.12-5.61, 41.59-44.57, 0.20-0.82 and 0.10-0.19% for barley straw, 44.94-46.30, 5.51-6.02, 43.47-46.62, 0.13-1.33 and 0.05-0.16% for oat straw, 45.67-46.61, 5.62-6.04, 45.14-45.85, 0.14-0.33 and 0.07-0.09% for rye straw and 44.26-46.04, 4.97-5.92, 43.79-44.78, 0.34-1.16 and 0.08-0.13% for wheat straw, respectively. Sapci [10] reported C, H, O and N contents of 47.7, 5.6, 41.5 and 0.4% for barley straw, 41.6, 5.4, 39.4 and 0.4% for oat straw and 47.9 - 48.4, 5.7-5.8, 41.6 and 0.5-0.6% for wheat straw, respectively. Hansen et al. [21] reported C, H, O, N, and S contents of 41.5, 5.4, 49.87, 0.7 and 0.13% for barley straw and 42.5, 5.2, 45.75, 0.6 and 0.15% for wheat straw, respectively. Thevannan et al. [34] reported C, H, O and N contents of 45.2, 6.3, 47.9 and 0.4% for barley straw, respectively. Sevilla et al. [33] reported C, H, O and N contents of 46.8, 5.65, 41.4 and 1.85% for barley straw, respectively. Wörmeyer et al. [45] reported C, H, O and N contents in the ranges of 57.96-68.07, 5.42-7.58, 23.40-33.31 and 0.17-2.12% for rye straw lignin, respectively. Lin et al. [43] reported C, H, O, N and S contents of 48.84, 7.08, 41.56, 1.28 and 0.23% for wheat straw, respectively.

Exergy values of cereal straws

Total Exergy: Table 5 shows the exergy values of the four cereal straws. The exergy values were 21.049, 20.631, 21.088 and 21.156 MJ/kg for the barley, oat, rye and wheat straws, respectively. The wheat straw had the highest exergy value (21.156 MJ/kg) whereas the oat straw had the lowest exergy value (20.631 MJ/kg). The variation (0.525 MJ/kg or 2.54%) in the exergy values of the four cereal straws was very small.

The exergy values of cereal straws were mainly determined from their LHVs. The wheat straw had the highest LHV (18.31 MJ/kg) and the highest exergy value (21.156 MJ/kg) whereas the oat straw had the lowest LHV (17.80 MJ/kg) and the lowest exergy value (20.631 MJ/kg). These values (20.631-21.156 MJ/kg) are within the range of 16.723-21.964 MJ/kg reported by Zhang et al. [46] for biomass fuels. However, they are higher than the exergy value of 16.100 MJ/kg reported by Hepbasli [47] for a moist straw and lower than the exergy value of 38.88 MJ/kg reported by Bilgen et al. [17] for coal.

Influence of LHV: Bilgen and Kaygusuz [48] used the HHV value to calculate the exergy of coals. Hosseini et al. [49] and Hepbasli [47] used the LHV value to calculate the exergy of biomass fuels. Zhang et al. [46] found the exergy to be affected by the LHV of the fuel [46]. Bilgen et al. [17] stated that the exergy value of coal varies proportionally with its lower heating value. In this study, a positive linear relationship between the exergy value and the LHV was observed for biomass fuels (Figure 1). The relationship can be described by the following linear equation (R^2=0.940):

Straw	Mineral oxide composition (mol per kg of straw)									
	SiO_2	K_2O	CaO	P_2O_5	MgO	Al_2O_3	Fe_2O_3	Na_2O	SO_3	ZnO
Barley	0.320	0.035	0.064	0.018	0.038	0.020	0.006	0.005	0.007	0.00004
Oat	0.112	0.198	0.072	0.028	0.060	0.001	0.001	0.005	0.012	0.00002
Rye	0.110	0.032	0.046	0.007	0.022	0.002	0.001	0.004	0.002	0.00001
Wheat	0.141	0.073	0.072	0.018	0.035	0.001	0.001	0.007	0.008	0.00003

Table 3: Mineral oxide compositions of cereal straws.

Straw	C	H	O	N	S
Barley	39.109	4.633	37.460	0.332	0.085
Oat	40.446	4.959	41.958	1.197	0.144
Rye	38.686	4.665	38.056	0.116	0.058
Wheat	39.985	5.150	38.959	0.296	0.104

On as received basis

Table 4: C, H, O, N, and S contents (wt.%,) of cereal straws.

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Straw	Exergy values (MJ/kg fuel)
Barley	21.049
Oat	20.631
Rye	21.088
Wheat	21.156

Table 5: Exergy values of cereal straws.

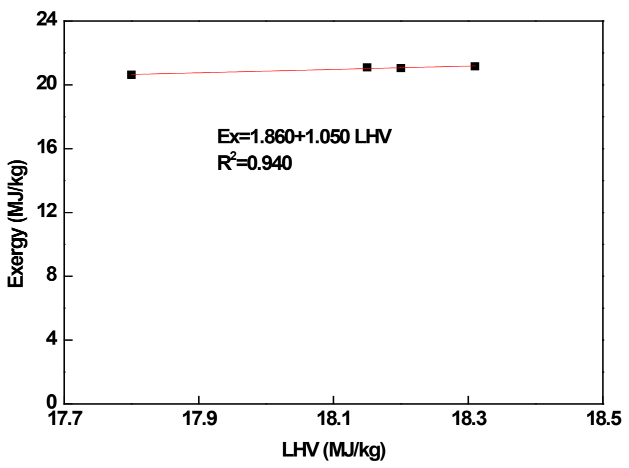

Figure 1: Relationship between exergy value and LHV.

Ex=1.860 + 1.050 LHV (17.80 ≤ LHV ≤ 18.31)

The results obtained from this study showed that increasing the LHV from 17.80 MJ/kg to 18.31 MJ/kg (2.87%) increased the exergy of cereal straws from 20.631 MJ/kg to 21.156 MJ/kg (2.54%).

Influence of moisture content: Table 6 displays the values and percentages of moisture related exergy for the four cereal straws. The moisture related exergy values were 422.462, 283.954, 479.747 and 366.766 kJ/kg for the barley, oat, rye and wheat straws, respectively. Since the exergy of water is 900 kJ/kmol, the moisture related exergy values were, therefore, proportional to the moisture contents of cereal straws [50]. The rye straw had the highest moisture content (17%) and the highest moisture related exergy value (479.747 kJ/kg) whereas the oat straw had the lowest moisture content (10%) and the lowest moisture related exergy value (283.954 kJ/kg).

In this study, a positive linear relationship between the exergy of cereal straw and moisture content was observed Figure 2. The relationship can be described by the following linear equation (R^2=0.364):

Ex= 20.151 + 0.060 MC (10 ≤ MC ≤ 17) (10)

where:

MC stands for Moisture content

The results showed that increasing the moisture content from 10% to 17% (70%) increased the exergy of cereal straws from 20.631 MJ/kg to 21.156 MJ/kg (2.54%). The effect of moisture content on the exergy of cereal straws is, therefore, very small. The percentage of moisture related exergy was 2.007% for the barley straw, 1.376% for the oat straw, 2.275% for the rye straw and 1.734% for the wheat straw. These values (1.376-2.275%) are very small, indicating that the contribution of moisture content to the total exergy of cereal straw can be neglected. Similar results were reported by Bilgen and Kaygusuz [48] for coal and Song et al. [51] for biomass.

Influence of ash: Table 7 shows the exergy values of mineral oxides (SiO_2, K_2O, CaO, P_2O_5, MgO, Al_2O_3, Fe_2O_3, Na_2O, SO_3 and ZnO). Table 8 shows the values and fractions of exergy of mineral oxide compositions. The exergy fractions of SiO_2, K_2O, CaO, P_2O_5, MgO, Al_2O_3, Fe_2O_3, Na_2O, SO_3 and ZnO were 6.117, 34.876, 17.029, 18.300, 6.187, 9.557, 0.252, 3.277, 4.376 and 0.027% for the barley straw, 0.795, 73.687, 7.187, 10.311, 3.621, 0.226, 0.010, 1.451, 2.705 and 0.005% for the oat straw, 3.346, 50.834, 19.605, 11.686, 5.708, 1.787, 0.093, 4.674, 2.258 and 0.012% for the rye straw and 2.080, 56.070, 14.869, 14.106, 4.348, 0.533, 0.045, 3.989, 3.943 and 0.017% for the wheat straw, respectively. Although SiO_2 had the highest weight fractions (up to 53.59%), it contributed small amounts (0.795-6.117%) to the exergy values of ash for the straws. This is due to the fact that the exergy value of SiO_2 (7.9 kJ/mol) is the lowest among the exergy values of the ash components (7.9-413.10 kJ/mol).

Table 9 shows the values and percentages of ash related exergy for the four cereal straws. The ash related exergy values were 41.312, 111.061, 25.912 and 53.468 kJ/kg for the barley, oat, rye and wheat

Straw	Moisture related exergy	
	Value (kJ/kg fuel)	Percentage (%)
Barley	422.462	2.007
Oat	283.954	1.376
Rye	479.747	2.275
Wheat	366.766	1.734

Table 6: Values and percentages of moisture related exergy.

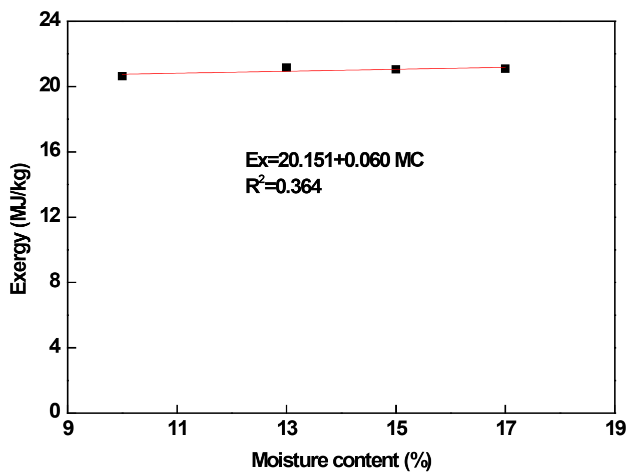

Figure 2: Relationship between exergy value and moisture content.

Mineral oxide	Exergy value (kJ/mol)
SiO_2	7.90
K_2O	413.10
CaO	110.20
P_2O_5	412.65
MgO	66.80
Al_2O_3	200.40
Fe_2O_3	16.50
Na_2O	296.20
SO_3	249.10
ZnO	22.90

Table 7: Exergy values of mineral oxides. [18].

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Mineral oxide	Values and fractions							
	Barley straw		Oat straw		Rye straw		Wheat straw	
	Value (kJ/kg)	Fraction (%)	Value (kJ/kg)	Fraction (%)	Value (kJ/kg)	Fraction (%)	Value (kJ/kg)	Fraction (%)
SiO_2	2.527	6.117	0.883	0.795	0.867	3.346	1.112	2.080
K_2O	14.408	34.876	81.838	73.687	13.172	50.834	29.979	56.070
CaO	7.035	17.029	7.982	7.187	5.080	19.605	7.950	14.869
P_2O_5	7.560	18.300	11.452	10.311	3.028	11.686	7.542	14.106
MgO	2.556	6.187	4.022	3.621	1.479	5.708	2.325	4.348
Al_2O_3	3.948	9.557	0.251	0.226	0.463	1.787	0.285	0.533
Fe_2O_3	0.104	0.252	0.011	0.010	0.024	0.093	0.024	0.045
Na_2O	1.354	3.277	1.611	1.451	1.211	4.674	2.133	3.989
SO_3	1.808	4.376	3.004	2.705	0.585	2.258	2.108	3.943
ZnO	0.011	0.027	0.006	0.005	0.003	0.012	0.009	0.017
Total	41.312	99.998	111.061	100.000	25.912	100.003	53.468	100.000

Table 8: Values and fractions of exergy of mineral oxide compositions.

Straw	Ash related exergy	
	Value (kJ/kg fuel)	Percentage (%)
Barley	41.312	0.196
Oat	111.061	0.538
Rye	25.912	0.123
Wheat	53.468	0.253

Table 9: Values and percentages of ash related exergy.

straws, respectively. The oat straw had the highest ash related exergy (111.061 kJ/kg) whereas the rye straw had the lowest ash related exergy (25.912 kJ/kg). This is due to the ash content as the oat straw had the highest ash content (4.554%) whereas the rye straw had the lowest ash content (1.635%).

In this study, a negative linear relationship between the exergy value and ash content was observed Figure 3. The relationship can be described by the following linear equation (R^2=0.446):

$$Ex=21.451 - 0.151\ Ash\ (1.635 \leq S \leq 4.554) \quad (11)$$

where:

Ash is the ash content (%)

The results showed that increasing the ash content from 1.635% to 4.554% (178.53%) decreased the exergy of cereal straws from 21.156 MJ/kg to 20.631 MJ/kg (2.48%), the effect of ash content on the exergy of cereal straws is, therefore, very small. The percentage of ash related exergy was 0.196% for the barley straw, 0.538% for the oat straw, 0.123% for the rye straw and 0.253% for the wheat straw. These values are very small, indicating that the contribution of ash content to the total exergy of cereal straws can be neglected.

Song et al. [51] estimated the exergy of solid and liquid fuels and reported decreases in exergy when the ash content increased. However, Hepbasli [47] and Szargut et al. [18] stated that the exergy of ash can usually be neglected because the change in total exergy of fuel due to the change in ash content is very small.

Influence of S: The S related exergy values of the four cereal straws are shown in Table 10. The S related exergy values were 8.231, 13.944, 5.626 and 10.109 kJ/kg for the barley, oat, rye and wheat straws, respectively. These values were directly determined by the weight fractions of S. The oat straw had the highest S content (0.144%) and the highest S related exergy value (13.944 kJ/kg) whereas the rye straw had the lowest S content (0.058%) and the lowest S related exergy value (5.626 kJ/kg).

In this study, a negative linear relationship between the exergy value and S content was observed Figure 4. The relationship can be described

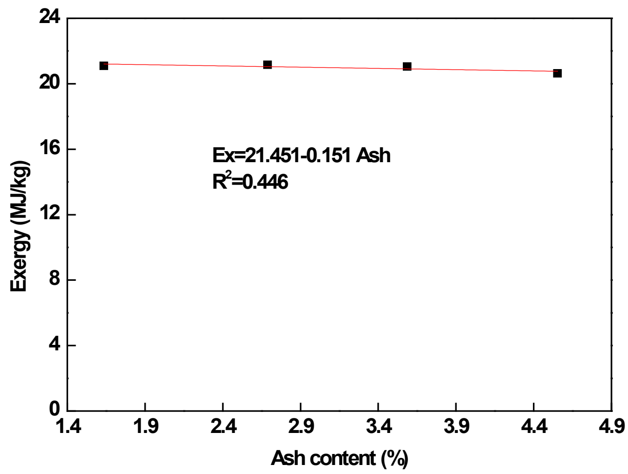

Figure 3: Relationship between exergy value and ash content.

Straw	Ash related exergy	
	Value (kJ/kg fuel)	Percentage (%)
Barley	8.231	0.039
Oat	13.944	0.068
Rye	5.626	0.027
Wheat	10.109	0.048

Table 10: Values and percentages of ash related exergy.

by the following linear equation (R^2=0.424):

$$Ex= 21.480 - 5.155\ S\ (0.058 \leq S \leq 0.144) \quad (12)$$

where:.

S is the S content (%)

The percentages of S related exergy of the four cereal straws are shown in Table 10. The percentage of S related exergy was 0.039% for the barley straw, 0.068% for the oat straw, 0.027% for the rye straw and 0.048% for the wheat straw. These values are very small, indicating that the S related exergy is a very small part of the total exergy of cereal straws.

Bilgen et al. [17] calculated the exergy of coals and reported increases in exergy when the S content increased. On the other hand, Govin et al. [52] estimated the exergy of liquid substances and reported decreases in exergy when S content increased. However, the results obtained from this study showed that increasing the S content from 0.058% to 0.144% (148.28%) decreased the exergy of cereal straws from 21.156 MJ/kg to 20.631 MJ/kg (2.48%), indicating the effect of *S* content on the exergy of cereal straws is very small and can be neglected.

The correlation factor: The contributions of C, O, H and N can be demonstrated by studying the correlation factors. Based on the C, O, H and N contents, the molecular structure and atomic ratios of four cereal straws were determined as shown in Table 11. For every atom of N, the atoms of C, H and O were 138, 196 and 99 for the barley straw, 39, 58 and 31 for the oat straw, 388, 562 and 287 for the rye straw and 158, 244 and 115 for the wheat straw, respectively. Although the numbers of C (39-388), H (58-562) and O (31-287) atoms varied significantly among the various straws (894.87, 869.97 and 825.81% for the C, H and O atoms, respectively), the differences among the O/C (0.7184-0.7780) and H/C (1.4214-1.5457) atomic ratios were very small (8.30 and 8.74% for the O/C and H/C atomic ratios, respectively). However, the N/C atomic ratio variation (0.0026-0.0254) was much larger (876.92%). The O/C atomic ratios (0.7184-0.7780) were higher than 0.5 and Eq. 7 was, therefore, selected for determination of the correlation factors.

The correlation factors of the four cereal straws are shown in Table 11. The correlation factor was 1.133 for the barley straw, 1.142 for the oat straw, 1.135 for the rye straw and 1.135 for the wheat straw. Although the O/C, H/C and N/C atomic ratios varied from 0.7184 to 0.7780 (8.296%), from 1.4214 to 1.5457 (8.745%) and from 0.0026 to 0.0254 (876.923%), respectively, the correlation factor varied slightly from 1.133 to 1.142 (0.8%). Similar results were reported by various researches. Bilgen et al. [17] reported the correlation factors between exergy values and HHVs for coals were in the range of 1.0587-1.1260. Zhang et al. [46] reported the correlation factors between exergy values and LHVs for biomass fuels were in the range of 1.05-1.19. Nilsson [53] reported a correlation factor of 1.16 between the exergy value and LHV for a moist straw.

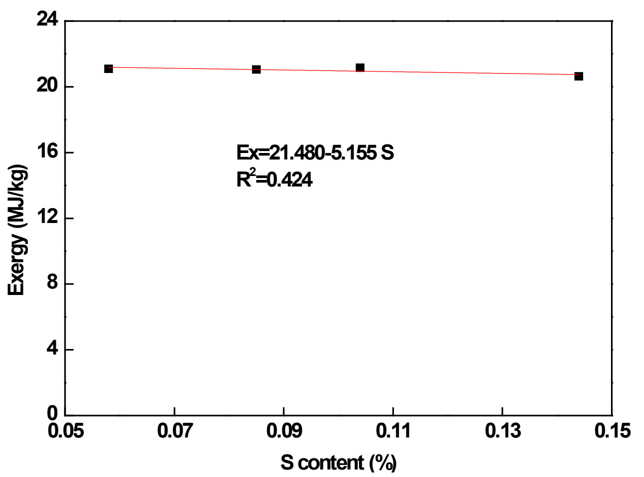

Figure 4: Relationship between exergy value and S content.

Straws	Molecular structure	Atomic ratios			β
		O/C	H/C	N/C	
Barley	$C_{138}H_{196}O_{99}N$	0.7184	1.4214	0.0073	1.133
Oat	$C_{39}H_{58}O_{31}N$	0.7780	1.4713	0.0254	1.142
Rye	$C_{388}H_{562}O_{287}N$	0.7378	1.4469	0.0026	1.135
Wheat	$C_{158}H_{244}O_{115}N$	0.7307	1.5457	0.0063	1.135

Table 11: Molecular structure and atomic ratios of cereal straws.

Conclusions

The exergy values of the barley, oat, rye and wheat straws were determined and the influences of LHV, moisture content, ash content, S, C, O, H and N on the exergy of cereal straws were evaluated. The moisture content of the four cereal straws varied from 10% (Oat straw) to 17% (Rye straw). The moisture related exergy value of the four cereal straws varied from 283.954 kJ/kg (Oat straw) to 479.747 kJ/kg (Rye straw), accounting for 1.376-2.275% of the total exergy of cereal straws. A positive linear relationship between the exergy value and moisture content of cereal straws was observed. The ash content of the four straws varied from 1.635% (Rye straw) to 4.554% (Oat straw). The ash related exergy value varied from 25.912 kJ/kg (Rye straw) to 111.061 kJ/kg (Oat straw), accounting for 0.123-0.538% of the total exergy of cereal straws. A negative linear relationship between the exergy value and ash content of cereal straws was observed. The S content of the four straws varied from 0.058% (Rye straw) to 0.144% (Oat straw). The S related exergy value varied from 5.626 kJ/kg (Rye straw) to 13.944 kJ/kg (Oat straw), accounting for 0.027-0.068% of the total exergy of cereal straws. A negative linear relationship between the exergy value and S content of cereal straws was observed. The results showed that the combined contribution of the exergy values of moisture, ash and S contents to the total exergy of cereal straws (1.982-2.424%) is very small and can be neglected. The O/C, H/C and N/C atomic ratios varied from 0.7184 to 0.7780 (8.30%), from 1.4214 to 1.5457 (8.74%) and from 0.0026 to 0.0254 (876.92%), respectively. The correlation factors varied from 1.133 to 1.142 (0.8%). The exergy values of the four cereal straws varied from 20.631 MJ/kg (oat straw) to 21.156 MJ/kg (wheat straw). They were mainly determined by the correlation factors and the LHVs. A positive linear relationship between the exergy value and LHV of cereal straws was observed.

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