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Determination of the Exergy of Four Wheat Straws

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ABSTRACT

Exergy is a measurement of how far a certain material deviates from a state of equilibrium with the environment. It is a useful tool for improving the efficiency of energy-resource use. The exergy values of four wheat straws (Absolvant, Max, Monopol and Vuka) were determined in this study. The effects of physical and chemical properties (moisture content, ash content, LHV and S, C, O, H and N contents) were evaluated. The moisture related exergy varied from 281.834 kJ kg^{-1} (Monopol) to 366.766 kJ kg^{-1} (Absolvant), accounting for 1.311-1.734% of the total exergy of wheat straws. A negative linear relationship between the exergy value and moisture content was observed. The ash related exergy varied from 53.468 kJ kg^{-1} (Absolvant) to 117.675 kJ kg^{-1} (Vuka), accounting for 0.253-0.556% of the total exergy of wheat straws. A negative linear relationship between the exergy value and ash content was observed. The S related exergy ranged from 6.817 kJ kg^{-1} (Max) to 11.077 kJ kg^{-1} (Vuka), accounting for 0.032-0.052% of the total exergy of wheat straws. A positive linear relationship between the exergy value and S content was observed. The O/C, H/C and N/C atomic ratios and the correlation factors varied in ranges of 0.7133-0.7537, 1.3475-1.5457, 0.0063-0.0225 and 1.133-1.138, respectively. The exergy values of the four wheat straws were between 21.156 MJ kg^{-1} (Absolvant) and 21.503 MJ kg^{-1} (Monopol). They were mainly determined by the correlation factors and the LHVs. A positive linear relationship between the exergy value and LHV was observed. The combined contribution of ash, moisture and S related exergy to the total exergy was very small (1.694-2.212%) and can be neglected.

Keywords: Exergy, LHV, Wheat Straw, Moisture, Ash, S, C, O, H, N, Correlation Factor

1. INTRODUCTION

Wheat is a staple food for 2.45 billion people (35 percent of the world's population) and about 30 million people are engaged in wheat cultivation (Lumpkin, 2011). The global wheat production increased from 589.3 million tonnes in 2001 to 694.5 million tonnes in 2011, about 17.84% increase (FAO, 2011; Zhang *et al*., 2012). The cultivation and processing of wheat resulted in about 534.23 million tonnes of wheat straw in 2011 (Zhang *et al*., 2012).

Wheat straw is currently used as feedstuff (Shrivastava *et al*., 2012), a soil conditioner (Xie *et al*., 2011), in pulp and paper industry (Hedjazi *et al*., 2009), production of nano-materials (Chen *et al*., 2010) and production of bioethanol (Talebnia *et al*., 2010). Wheat straw can also be used as a renewable energy source in thermochemical conversion processes such as pyrolysis (Wild *et al*., 2012), combustion (Wang *et al*., 2009) and gasification (Ren *et al*., 2010).

Although the physical, chemical and thermochemical properties of wheat straws (moisture content, bulk density, particle size, porosity, heating values, proximate analysis, ultimate analysis, ash composition, ash characteristics and degradation kinetics) are well studied (Ghaly and Al-Taweel, 1990; Natarajan *et al*., 1998; Guo *et al*., 2012; Igathinathane *et al*., 2010; Zhang *et al*.,

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2012), no detailed analysis of the exergy of wheat straw has been reported. The main objectives of this study were: (a) to determine the exergy values of four different wheat straws and (b) to determine the effects of some physical and chemical properties (moisture content, ash content, S, C, O, H and N contents) on the exergy values of wheat straws.

2. EXERGY ANALYSIS OF BIOMASS FUELS

Exergy is the amount of work obtainable when a matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings such as environmental condition by means of reversible processes, involving interaction only with the components of natural surroundings (Szargut, 1980). It is a measurement of how far a certain system deviates from a state of equilibrium with its environment (Wall, 1986). Unlike energy, exergy is not subject to conservation law (except for ideal or reversible processes). It is consumed or destroyed due to unavoidable irreversibilities in any real process.

Exergy analysis is a methodology that uses the conservation of energy principle (embodied in the first law of thermodynamics) together with non-conservation of entropy principle (embodied in the second law) for the analysis, design and improvement of energy systems (Rosen and Bulucea, 2009; Dincer, 2002). The exergy method is useful for improving the efficiency of energy-resource use. It quantifies the locations, types and magnitudes of wastes and losses. In general, more meaningful efficiencies can be evaluated with exergy analysis rather than energy analysis, since exergy efficiencies are always a measure of the approach to the ideal condition (Rosen and Bulucea, 2009).

The exergy of a material can be calculated from its chemical potential and concentrations in its actual state and reference state (Wall, 1986). For irregular materials such as biomass fuels with unknown chemical potential, the exergy values can be obtained as follows (Szargut *et al.*, 1988):

$$ex = \beta(\mathrm{LHV} + \eta_w h_w) + 9683\eta_s + ex_{ash}\eta_{ash} + ex_w\eta_w \qquad (1)$$

where:

- ex = The exergy of the fuels (kJ kg^{-1})
- β = The correlation factor
- h_w = The evaporation enthalpy of moisture (kJ kg^{-1})
- η_w = The moisture content (%)
- η_s = The weight percentage of sulfur (%)
- η_{ash} = The weight percentage of ash (%)
- ex_{ash} = The exergy of ash (kJ kg^{-1})
- ex_w = The exergy of water (kJ kmol^{-1})
- LHV = The lower heating value of biomass fuels (kJ kg^{-1})

The value of 2442 kJ kg^{-1} was reported for the evaporation enthalpy of moisture by Szargut *et al.* (1988) and the value of 900 kJ kmol^{-1} was reported for the exergy of water by Moran *et al.* (2011). The correlation factors of biomass materials can be obtained through the following equations based on the biomass type and elemental composition (Szargut *et al.*, 1988):

(a) For solid hydrocarbons

$$\beta = 1.0435 + 0.0159\frac{H}{C} \qquad (2)$$

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

$$\beta = 1.0438 + 0.0158\frac{H}{C} + 0.0813\frac{O}{C} \qquad (O/C \leq 0.5) \quad (3)$$

$$\beta = \frac{1.0414 + 0.0177\frac{H}{C} - 0.3328\frac{O}{C}(1 + 0.0537\frac{H}{C})}{1 - 0.4021\frac{O}{C}} \qquad (O/C \leq 2) \quad (4)$$

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

$$\beta = 1.0437 + 0.0140\frac{H}{C} + 0.0968\frac{O}{C} + 0.0467\frac{N}{C} \qquad (O/C \leq 0.5) \quad (5)$$

$$\beta = \frac{1.044 + 0.0160\frac{H}{C} - 0.3493\frac{O}{C}(1 + 0.0531\frac{H}{C}) + 0.0493\frac{N}{C}}{1 - 0.4124\frac{O}{C}} \qquad (O/C \leq 2) \quad (6)$$

(d) For wood:

$$\beta = \frac{1.0412 + 0.2160\frac{\eta_H}{\eta_C} - 0.2499\frac{\eta_O}{\eta_C}(1 + 0.7884\frac{\eta_H}{\eta_C}) + 0.0450\frac{\eta_N}{\eta_C}}{1 - 0.3035\frac{\eta_O}{\eta_C}} \qquad (7)$$

where:

- C = The number of carbon in the molecular formula of fuel
- H = The number of hydrogen in the molecular formula of fuel
- O = The number of oxygen in the molecular formula of fuel
- N = The number of nitrogen in the molecular formula of fuel
- η_C = The weight percentage of carbon (%)
- η_H = The weight percentage of hydrogen (%)
- η_O = The weight percentage of oxygen (%)
- η_N = The weight percentage of nitrogen (%)

3. MATERIALS AND METHODS

3.1. Straw Collection and Preparation

The four wheat straws used in this study are Absolvant, Max, Monopol and Vuka. The straw samples were obtained from harvested field at a farm located 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 each were brought to the laboratory.

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 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 ground straw samples were dried at 105 °C for 24 hours in a force-air drying oven. The dried samples were then stored in airtight plastic containers.

3.2. Moisture Content

Moisture content was determined for the naturally dried 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). The dish was first weighed and 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.

3.3. Lower Heating Value

A bomb calorimeter (Parr Model 1241 Automatic Adiabatic Calorimeter) was used to determine the higher heating values (HHVs) of the straw samples. The higher heating values were 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 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 lower heating values (LHVs) of the straws were then calculated (Bilgen *et al*., 2004).

3.4. Ash Content and Compositions

The standard test method for ash in biomass (E1755–01) was followed to determine the ash percentage in the straw sample (ASTM 2007). The ash samples were obtained by ashing the coarse ground straw in porcelain crucibles using 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 ash was stored in airtight plastic containers till send for ash composition analysis. 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. LECO induction furnace method and atomic absorption were used.

3.5. 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). S was determined using the ICP induction coupled plasma-atomic method D6349–09 (ASTM 2009).

4. RESULTS AND DISCUSSION

4.1. Characteristics of Straws

4.1.1. Moisture Content

The moisture contents of the four wheat straws are shown in **Table 1**. The moisture contents of the four wheat straws varied between 10% and 13% (30% variation).

Table 1. Moisture contents, LHVs and ash contents of wheat straws.

Wheat straw	Moisture content (%)	LHV (MJ kg^{-1})	Ash content (%)[a]
Absolvant	13	18.31	2.69
Max	12	18.38	3.19
Monopol	10	18.71	3.23
Vuka	12	18.29	4.23

[a] On as received basis.

The Absolvant wheat straw had the highest moisture content whereas the Monopol wheat straw had the lowest moisture content. These differences may be due to variations in climatic conditions, soil types, cultivation methods and fertilizer types (Zhang *et al*., 2012).

Liang *et al*. (2003) and Pommier *et al*. (2008) stated that high moisture content can increase the biodegradation rate of organic material during storage, resulting in the loss of calorific value of the fuel. High moisture content of wheat straw can also substantially affect its quality as a fuel source (Zhang *et al*., 2012). Ghaly and Al-Taweel (1990) and Chen *et al*. (2009) reported that an increase in moisture contents of the fuels caused deterioration and decreased their heating values. A dry material is thus preferred for storage, gasification and combustion (Zhang *et al*., 2012).

4.1.2. Lower Heating Value

Tesfa *et al*. (2013) stated that LHV is one of the most important physicochemical properties of biofuels. The LHVs of the four wheat straws are shown in **Table 1**. The LHVs of the four wheat straws varied between 18.29 MJ kg^{-1} (Vuka) and 18.71 MJ kg^{-1} (Monopol), a variation of 2.30%. These values (18.29-18.71 MJ kg^{-1}) are higher than the value of 15.78 MJ kg^{-1} reported by Lin *et al*. (2003) and the value of 13.882-14.275 MJ kg^{-1} reported by Wang *et al*. (2009) for wheat straws. Vargas-Moreno *et al*. (2012) stated that the LHV of a biomass fuel can be affected by elemental composition, structure and physical properties of biomass.

4.1.3. Ash Content

Ash content is an important thermochemical property of an energy resource. The ash contents of the four wheat straws are shown in **Table 1**. The ash contents of the four wheat straws varied from 2.69% (Absolvant) to 4.23% (Vuka), a variation of 57.25%. These values (2.69-4.23%) are lower than the 8.73-10.1% reported by Çöpür *et al*. (2012) for Turkish wheat straws but within the range of 2.06-5.16% reported by Petrik *et al*. (2013) for Danish wheat straws.

The ash content affects the property of a fuel as an energy resource. Vargas-Moreno *et al*. (2012) and Zhao *et al*. (2012) stated that the ash content of a fuel can reduce its heating value and cause agglomeration. Ghaly and Al-Taweel (1990) stated that the ash content indicates the potential for the formation of undesirable bonded deposits on combustor surfaces. Ergüdenler and Ghaly (1993) reported on the agglomeration of wheat straw in a fluidized bed gasification system. Lower ash content fuels are, therefore, preferred.

4.1.4. Ash Compositions

The detailed ash compositions of the four wheat straws are shown in **Table 2**. All the straw varieties had high contents of SiO_2 (0.141-0.214 mol kg^{-1} fuel) and K_2O (0.073-0.229 mol kg^{-1} fuel) and low content of ZnO (0.000-0.001 mol kg^{-1} fuel). The differences in mineral oxide concentrations could be the result of the variations in climatic conditions, soil types, cultivation methods and fertilizer types (Zhang *et al*., 2012).

Lin *et al*. (2003) stated that agglomeration and defluidization in a fluidized bed was affected by the ash composition. Liu *et al*. (2009) stated that the alkali metals such as K and Na which exist in the outer layer of straw particles will melt and coat on the surfaces of ash particles, making ash particles sticky and adhere to the surfaces of bed particles.

Table 2. Mineral oxide compositions of wheat straws.

Wheat straw	Mineral oxide composition ($\times 10^{-3}$ 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
Absolvant	141	73	72	18	35	1	1	7	8	0
Max	214	81	64	13	43	3	1	4	6	0
Monopol	147	124	62	15	34	2	2	5	10	1
Vuka	188	229	64	16	32	3	2	7	11	1

Table 3. C, H, O, N, and S contents (wt.%) of wheat straws.

Wheat straw	C	H	O	N	S
Absolvant	39.985	5.150	38.959	0.296	0.104
Max	40.515	5.069	38.535	0.730	0.070
Monopol	41.373	5.202	39.735	0.495	0.108
Vuka	38.949	4.374	39.142	1.021	0.114

On as received basis.

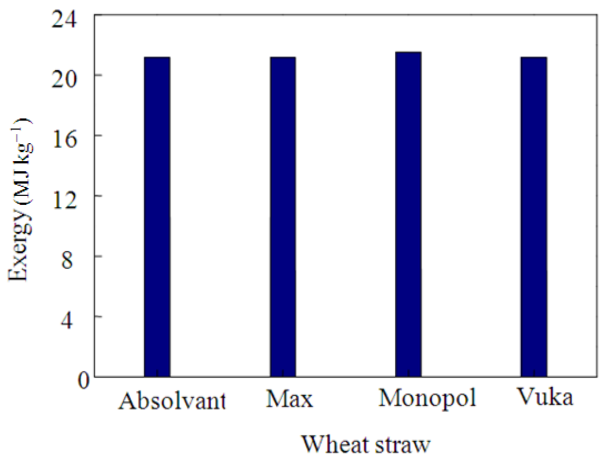

Fig. 1. Exergy values of wheat straws

The large-sized ash particles may act as the necks in the formation of agglomerates. The small-sized ash particles, however, contribute to the formation of coating layers which is the direct reason for bed defluidization.

4.1.5. C, O, H, N and S Contents

Table 3 shows the C, H, O, N and S contents of the four wheat straws. Although different straws had different C, H, O, N and S contents, all the straws had high contents of C (38.949-41.373 wt.%) and O (38.535-39.735 wt.%) followed by H (4.374-5.202 wt.%), N (0.296-1.021 wt.%) and S (0.070-0.114 wt.%). Lin *et al*. (2003) reported the percentages of 48.84%, 7.08%, 41.56%, 1.28% and 0.23% for the C, H, O, N and S contents of a wheat straw, respectively. Wen *et al*. (2013) reported that the C, H, O, N and S contents for coal were 53.6-73.7%, 3.2-5.4%, 3.2-16.7%, 0.8-1.0% and 0.6-1.4%, respectively. The coals have much higher LHVs than wheat straws because of their higher carbon contents.

4.2. Exergy Values of Wheat Straws

4.2.1. Exergy Values

The exergy values (**Fig. 1**) were 21.156, 21.171, 21.503 and 21.172 MJ kg^{-1} for the Absolvant, Max, Monopol and Vuka wheat straws, respectively. These exergy values are within the range of 16.723-21.964 MJ kg^{-1} reported by Zhang *et al*. (2011) for biomass fuels.

4.2.2. Effect of LHV

The exergy values of straws were determined from their LHVs. The results showed that the higher the LHV the higher the exergy value. The Monopol wheat straw had the highest LHV (18.71 MJ kg^{-1}), and, thus, had the highest exergy (21.503 MJ kg^{-1}).

Bilgen and Kaygusuz (2008) used HHVs to calculate the exergy of coals. Hosseini *et al*. (2012) and Hepbasli (2008) used LHVs to calculate the exergy of biomass fuels. Zhang *et al*. (2011) reported the LHVs and exergy of three biomass fuels and found the exergy to be affected by the LHVs of the fuels. In this study, a positive linear relationship between the exergy value and LHV was observed as shown in **Fig. 2**. The relationship can be described by the following linear equation ($R^2 = 0.945$):

$$Ex=5.683+0.845\ LHV \qquad (18.29\leq LHV\leq 18.71) \qquad (8)$$

The results showed that increasing the LHV from 18.29 MJ kg^{-1} to 18.71 MJ kg^{-1} (2.30%) increased the exergy of wheat straw from 21.156 MJ kg^{-1} to 21.503 MJ kg^{-1} (1.64%). Similar results were reported by Bilgen *et al*. (2004) that the exergy value of coal varies proportionally with the heating value.

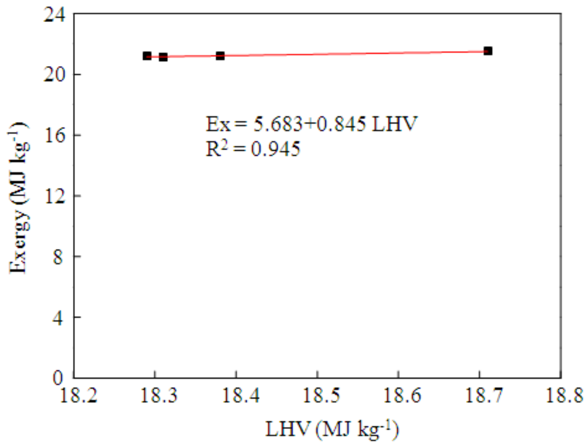

Fig. 2. Relationship between exergy value and LHV

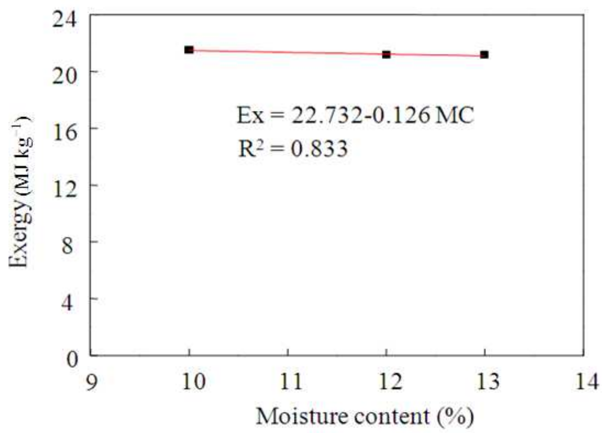

Fig. 3. Relationship between exergy value and moisture

Table 4. Exergy values of mineral oxides (Szargut *et al*., 1988).

Mineral oxide	Exergy value (kJ mol^{-1})
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

4.2.3. Effect of Moisture Content

The moisture related exergy values were 366.766, 338.038, 281.834 and 339.600 kJ kg^{-1} for the Absolvant, Max, Monopol and Vuka wheat straws, respectively.

Table 5. Values and fractions of exergy of mineral oxide compositions.

Mineral oxide	Values and fractions							
	Absolvant		Max		Monopol		Vuka	
	Value (kJ kg^{-1})	Fraction (%)	Value (kJ kg^{-1})	Fraction (%)	Value (kJ kg^{-1})	Fraction (%)	Value (kJ kg^{-1})	Fraction (%)
SiO_2	1.112	2.080	1.694	3.148	1.158	1.607	1.486	1.263
K_2O	29.979	56.070	33.437	62.127	51.220	71.075	94.720	80.493
CaO	7.950	14.869	7.106	13.203	6.851	9.507	7.012	5.959
P_2O_5	7.542	14.106	5.526	10.268	6.106	8.473	6.768	5.751
MgO	2.325	4.348	2.843	5.282	2.243	3.112	2.153	1.830
Al_2O_3	0.285	0.533	0.678	1.260	0.464	0.644	0.524	0.445
Fe_2O_3	0.024	0.045	0.021	0.039	0.025	0.035	0.026	0.022
Na_2O	2.133	3.989	1.069	1.986	1.498	2.079	2.205	1.874
SO_3	2.108	3.943	1.441	2.677	2.483	3.446	2.766	2.351
ZnO	0.009	0.017	0.005	0.009	0.018	0.025	0.014	0.012
Total	53.468	100.000	53.819	99.999	72.065	100.003	117.675	100.000

The exergy value for water is 900 kJ $kmol^{-1}$ (Moran *et al*., 2011). Therefore, the moisture related exergy values were proportional to the moisture contents of wheat straws. The Absolvant wheat straw had the highest moisture content (13%) and highest moisture related exergy (366.766 kJ kg^{-1}) whereas the Monopol wheat straw had the lowest moisture content (10%) and the lowest moisture related exergy (281.834 kJ kg^{-1}).

In this study, a negative linear relationship between the exergy of wheat straw and moisture content was observed (**Fig. 3**). The relationship can be described by the following linear equation (R^2=0.833):

$$Ex=22.732-0.126\,MC \qquad (10\leq MC\leq 13) \qquad (9)$$

where:

MC = The moisture content (%)

The results showed that increasing the moisture content from 10% to 13% (30%) decreased the exergy of wheat straw from 21.503 MJ kg^{-1} to 21.156 MJ kg^{-1} (1.61%). The change in exergy due to changes in moisture content is quite small and the contribution of moisture content to the total exergy of wheat straw is very small and can be neglected. Similar results were reported by Bilgen and Kaygusuz (2008) for coal and Song *et al*. (2012) for biomass.

4.2.4. Effect of Ash

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) are presented in **Table 4**. The values and fractions of mineral oxides obtained for different wheat straws are shown in **Table 5**. For all wheat straws, K_2O contributed the most (56.070-80.493%) to the exergy values of ash, followed by CaO (5.959-14.869%), P_2O_5 (5.751-14.106%), MgO (1.830-5.282%), Na_2O (1.874-3.989%), SO_3 (0.445-1.260%), Fe_2O_3 (0.022-0.045%) and ZnO (0.009-0.025%).

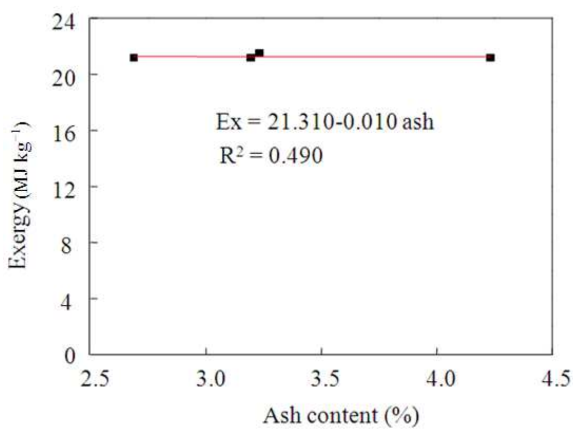

Fig. 4. Relationship between exergy value and ash content

Although SiO_2 had the highest weight fractions (up to 40.33%), it ranked the seventh in terms of its contribution to the total exergy values of ash. This is due to the fact that the exergy value of SiO_2 (7.9 kJ mol^{-1}) is the lowest among the exergy values of the ash components (7.9-413.10 kJ mol^{-1}).

The total ash related exergy values were 53.468, 53.819, 72.065 and 117.675 kJ kg^{-1} for the Absolvant, Max, Monopol and Vuka wheat straws, respectively. The Vuka wheat straw had the highest total ash related exergy (117.675 kJ kg^{-1}) whereas the Absolvant wheat straw had the lowest total ash related exergy (53.468 kJ kg^{-1}). This is mainly due to the ash content as the Vuka wheat straw had the highest ash content (4.23%) whereas the Absolvant wheat straw had the lowest ash content (2.69%).

Song *et al*. (2012) estimated the exergy of solid and liquid fuels and reported decreases in exergy when the ash content increased.

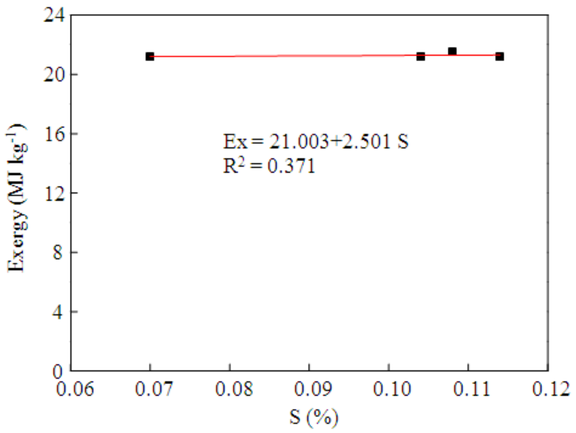

Fig. 5. Relationship between exergy value and S

In this study, a negative linear relationship between the exergy value and ash content was observed (**Fig. 4**). The relationship can be described by the following linear equation ($R^2 = 0.490$):

$$Ex=21.310-0.010\ Ash \qquad (2.688 \leq Ash \leq 4.233) \qquad (10)$$

where:

Ash = The ash content (%)

The results showed that increasing the ash content from 2.69% to 4.23% (57.25%) decreased the exergy of wheat straw from 21.503 MJ kg^{-1} to 21.156 MJ kg^{-1} (1.61%). The results indicated that the effect of ash content on the exergy value of wheat straw is very small and can be neglected. Hepbasli (2008) and Szargut *et al.* (1988) 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.

4.2.5. Effect of S

The S related exergy values of straws were directly determined by the weight fractions of S. The S related exergy values were 10.109, 6.817, 10.458 and 11.077 kJ kg^{-1} for the Absolvant, Max, Monopol and Vuka wheat straws, respectively. The Vuka wheat straw had the highest S content (0.114%) and the highest S related exergy value (11.077 kJ kg^{-1}) whereas the Max wheat straw had the lowest S content (0.070%) and the lowest S related exergy value (6.817 kJ kg^{-1}).

Bilgen *et al.* (2004) calculated the exergy of coals and reported increases in exergy when the S content increased. On the other hand, Govin *et al.* (2000) estimated the exergy of liquid substances and reported decreases in exergy when S content increased.

Table 6. Percentages of moisture, ash and S related exergy.

Wheat straw	Percentage (%) Moisture	Ash	S	Total
Absolvant	1.734	0.253	0.048	2.034
Max	1.597	0.254	0.032	1.883
Monopol	1.311	0.335	0.049	1.694
Vuka	1.604	0.556	0.052	2.212

Table 7. Molecular structure and atomic ratios of wheat straws.

Wheat straw	Molecular structure	Atomic ratios O/C	H/C	N/C	β
Absolvant	$C_{158}H_{244}O_{115}N$	0.7307	1.5457	0.0063	1.135
Max	$C_{65}H_{97}O_{46}N$	0.7133	1.5013	0.0155	1.133
Monopol	$C_{98}H_{147}O_{70}N$	0.7203	1.5088	0.0103	1.134
Vuka	$C_{45}H_{60}O_{34}N$	0.7537	1.3475	0.0225	1.138

In this study, a positive linear relationship between exergy value and S content was observed as shown in **Fig. 5**. The relationship can be described by the following linear equation ($R^2 = 0.371$):

$$Ex=21.003+2.501\ S \qquad (0.070 \leq S \leq 0.114) \qquad (11)$$

where:

S = The S content (%)

The results showed that when the S content increased from 0.070% to 0.114% (62.857%), the exergy of wheat straws increased from 21.156 MJ kg^{-1} to 21.503 MJ kg^{-1} (1.64%). The results indicated that the effect of S on the exergy value seems to be very small and can be neglected.

4.2.6. Exergy Distribution

The percentages of moisture related exergy, ash related exergy and S related exergy are shown in **Table 6**. The percentages of moisture related exergy varied between 1.311% and 1.734% (1.734%, 1.597%, 1.311% and 1.604% for the Absolvant, Max, Monopol and Vuka wheat straws, respectively), indicating that the contribution of moisture content to the exergy of biomass fuels is, therefore, negligible.

The percentages of ash related exergy varied from 0.253% to 0.556% (0.253%, 0.254%, 0.335% and 0.556% for the Absolvant, Max, Monopol and Vuka wheat straws, respectively), indicating that the ash related exergy values were very small and can be neglected.

The S related exergy value varied from 6.817 kJ kg^{-1} to 11.077 kJ kg^{-1} (0.048%, 0.032%, 0.049% and 0.052% for the Absolvant, Max, Monopol and Vuka wheat straws, respectively), indicating that the S related exergy values were very small and can be neglected.

The total contribution of moisture related exergy, ash related exergy and S related exergy accounted for only1.694-2.212% of the total exergy and can be neglected. Similar results were reported by Hepbasli (2008), Szargut *et al*. (1988), Song *et al*. (2012) and Bilgen and Kaygusuz (2008).

4.2.7. The Correlation Factor (β)

The effects of C, O, H and N can be demonstrated by studying the correlation factors. Based on the C, O, H and N contents, the C, H, O and N atomic structure was determined for each straw as shown in **Table 7**. The numbers of C, H and O atoms varied among the various wheat straws. For every atom of N, the wheat straws contained 45-158 atoms of C, 60-244 atoms of H and 34-115 atoms of O. The Absolvant wheat straw had the highest atoms of C (158), H (244) and O (115) whereas the Vuka wheat straw had the lowest atoms of C (45), H (60) and O (34). This did not agree with the LHVs of wheat straws shown in **Table 1** where the Monopol wheat straw had the highest LHV (18.71 MJ kg^{-1}) whereas the Vuka wheat straw had the lowest LHV (18.29 MJ kg^{-1}). This also did not agree with the exergy values of wheat straws shown in **Fig. 1** where the Monopol wheat straw had the highest exergy value (21.503 MJ kg^{-1}) whereas the Absolvant wheat straw had the lowest exergy value (21.156 MJ kg^{-1}). This is resulted from the fact that the LHV and exergy of a biomass fuel can be affected not only by the data from its elemental analysis but also from its proximal analysis, structural analysis and physical properties (Vargas-Moreno *et al*., 2012).

The O/C, H/C and N/C atomic ratios were also calculated as shown in **Table 7**. The O/C, H/C and N/C atomic ratios varied in the ranges of 0.7133-0.7537, 1.3475-1.5457 and 0.0063-0.0225 for the Absolvant, Max, Monopol and Vuka wheat straws, respectively. The O/C atomic ratios (0.7133-0.7537) were higher than 0.5. Equation 6 was selected for the determination of the correlation factors (**Table 7**). The correlation factors were 1.135, 1.133, 1.134 and 1.138 for the Absolvant, Max, Monopol and Vuka wheat straws, respectively. Similar results were also reported by various researches. Bilgen *et al*. (2004) reported correlation factors between the exergy values and HHVs for coals in the range of 1.0587-1.1260. Zhang *et al*. (2011) reported correlation factors between the exergy values and LHVs for biomass fuels in the range of 1.05-1.19. Nilsson (1997) reported a correlation factor of 1.16 between the exergy value andLHV for a moist straw.

5. CONCLUSIONS

The exergy values of the four wheat straws were determined and the effects of moisture content, ash content, S, C, O, H and N were calculated. The moisture related exergy varied from 281.834 kJ kg^{-1} (Monopol) to 366.766 kJ kg^{-1} (Absolvant), accounting for 1.311-1.734% of the total exergy of wheat straws. A negative linear relationship between the exergy value and moisture content was observed. The ash related exergy varied from 53.468 kJ kg^{-1} (Absolvant) to 117.675 kJ kg^{-1} (Vuka), accounting for 0.253-0.556% of the total exergy of wheat straws. A negative linear relationship between the exergy value and ash content was observed. The S related exergy varied from 6.817 kJ kg^{-1} (Max) to 11.077 kJ kg^{-1} (Vuka), accounting for 0.032-0.052% of the total exergy of wheat straws. A positive linear relationship between the exergy value and S content was observed. The O/C, H/C and N/C atomic ratios and the correlation factors varied in ranges of 0.7133-0.7537, 1.3475-1.5457, 0.0063-0.0225 and 1.133-1.138, respectively. The exergy values of the four wheat straws were between 21.156 MJ kg^{-1} (Absolvant) and 21.503 MJ kg^{-1} (Monopol). They were mainly determined by the correlation factors and the LHVs. A positive linear relationship between the exergy value and LHV was observed. The combined contribution of ash, moisture and S related exergy to the total exergy was very small (1.694-2.212%) and can be neglected.

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