Effect of glycerol on densification of agricultural biomass

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Abstract: Experiments were conducted to verify the effect of adding glycerol for pelleting of selected agricultural crop residues, namely, wheat, barley, oat and canola straw. Single pelleting tests were conducted to study the effect of biomass type, hammer mill screen size, and crude glycerol content (co-product of biodiesel industry) on pellet quality (density and durability), ash content and gross heat of combustion. Four types of biomass were ground at three different hammer mill screen sizes of 6.4, 3.2 and 1.6 mm. Each biomass was mixed with three levels of glycerol of 2.5%, 5.0% and 7.5% by weight. Pellets were made at a pre-set load of 4 400 N (138.9 MPa) using single-pelleting unit attached to an Instron testing machine. Quality of pellets was determined by measuring pellet density, relaxed density, durability (measured by pellet drop test) and specific energy required to make a pellet. The gross heat of combustion and ash content of pellets were also determined and compared. The highest pellet density (988-1 133 kg/m^3) and relaxed density (992-1 142 kg/m^3) were obtained from biomass ground using a hammer mill screen size of 6.4 mm. A decrease in hammer mill screen size resulted in reduced durability. The highest durability of biomass obtained from hammer mill screen size of 6.4 mm ranged from 97%-100%. Addition of glycerol resulted in lower ash content in majority of pellets. The highest gross heat of combustion was observed in pellets made from wheat straw with 7.5% glycerol content (38.3 MJ/kg). Addition of glycerol resulted in lower pellet densities, lower ash content, no change in durability and higher gross heating values.

Keywords: biomass, biofuels, glycerol, pelleting, caloric value, heating value
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1 Introduction

Agricultural crop residues are potential feedstock for bioenergy and biofuels production. The total annual surplus of wheat, barley, oat and flax straw residues available for biofuel production in Canadian prairies has been estimated over 15 Mt[1]. Cereal straw has relatively low density in its original (40 kg/m^3) or baled (100 kg/m^3) form. Whereas, unprocessed wood residue has bulk density of approximately 250 kg/m^3[2-3]. Therefore, handling and transportation of straw is more difficult than wood residue. Biomass can be densified using mechanical densification. In the mechanical densification, pressure is applied on the biomass to compress it which increases its density. Mechanical densification is used in different forms to make bale, pellet, cube, or briquettes depending on the biomass type, transportation distance, and its final application[4]. Pellets have relatively higher density and durability during shipping and handling with a lower waste.

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Densification of biomass straw into pellets increases the bulk density of biomass and eventually, the net gross heat content per unit volume is improved[5] and the storage, transport and handling of the material are easier and cheaper[6].

With increasing world population, resources for production of conventional non-renewable fossil fuels are rapidly diminishing, and attempts to promote and utilize alternative renewable fuels are underway. A good renewable fuel alternative is biodiesel, which has many environmental benefits when compared with conventional petroleum based fuels[7]. Canada has been the largest canola producer in the world. The potential growth of the biodiesel industry in the upcoming years will produce co-products such as crude glycerol and increase the pressure to utilize them. Biodiesel is produced by transesterification of triglycerides and/or esterification of fatty acids with low molecular weight alcohols to generate long chain fatty acid alkyl ester called biodiesel. This reaction is performed in the presence of catalysts such as metal hydroxides and metal alkoxides[8,9].

It is estimated that 1 kg of crude glycerol will be co-produced during production of every 10 kg of biodiesel through transesterification of triglyceride feedstock[10]. Traditionally prior to 2004, crude glycerol has been used in manufacturing of high-value products such as food products, personal care products, oral care products, and in tobacco and pharmaceuticals[11]. However, with the emergence of biodiesel industry in 2004, it was projected that the world biodiesel market would reach 37 billion gallons by 2016, which implied that approximately 4 billion gallons of crude glycerol would be produced[12,13]. Surplus supply of glycerol from biodiesel production resulted in lower prices, e.g. in 2007 the refined glycerol's price was approximately $0.30 per pound (compared to $0.70 before the expansion of biodiesel production) in the United States. Accordingly, the price of crude glycerol decreased from about $0.25 per pound to $0.05 per pound[14]. Consequently, an urgent need to find new applications was desired, especially new uses for unrefined crude glycerol, including ingredient in animal feed (cattle and poultry feed), possible building blocks for many chemical compounds (epichlorohydrin, 1, 3 propanediol, hydrogen, methanol, etc.), and as an energy source since the calorific value of glycerol can vary from 19-25 MJ/kg depending on purity[11]. According to literature [15], the energy content of glycerol (16 MJ/kg) is significantly lower than methanol (22 MJ/kg) and ethanol (30 MJ/kg); however, the volumetric energy density of glycerol (20 MJ/L) is higher than methanol (18 MJ/L) and comparable to ethanol (22 MJ/L). Therefore, in this study we have explored the option of using crude glycerol as an additive for agricultural biomass feedstock to enhance its volumetric energy content to be utilized as an alternative form of energy source.

Making pellet from ground agricultural straw biomass is difficult because of its low bulk density, poor flowability and its inherent inability to bind during densification. Ground straw may clog or may not produce any pellets in the pellet mill. Adapa et al.[16] reported that oil must be added (up to 10% by weight) to increase bulk density and improve the flowability of biomass through the pilot-scale pellet mill. Therefore, the objective of this study was to use crude glycerol from biodiesel production as an additive in making pellets from wheat, barley, oat and canola straw and determine its effect on bulk density, flowability and energy density of the pellets.

2 Materials and method

2.1 Biomass samples

Barley, canola, oat and wheat straws were obtained in small square bales from a farmer in the Central Butte area of Saskatchewan, Canada in summer of 2008. All samples were chopped using a chopper equipped with six blades which were mounted at a shearing angle of 14° and rotated at 460 r/min. The chopper was made in the Bioprocessing Lab, Department of Chemical and Biological Engineering, University of Saskatchewan, Canada. The chopped samples were then ground using a hammer mill (Serial no. 6M13688; Brookdale Company, St. Maywood, NJ) using three different mill screen sizes of 6.4, 3.2 and 1.6 mm. Proximate analysis of straw material was performed to determine its protein, fat, starch, lignin, hemicellulose and ash content and already

reported by Adapa et al.[16,17].

2.2 Sample preparation and densification

Crude glycerol, obtained from Milligan Bio-Tech Inc. (Foam Lake, SK), was heated to 100°C in water bath to reduce the viscosity. The melted crude glycerol was mixed with moisture-adjusted straws at 0% as blank, 2.5, 5.0, and 7.5% by weight (wet basis). Each mixture was blended for about 15 min to provide a uniform distribution of glycerol in straws. The mixtures were then stored in air-tight bag at 4°C and mixed every 12 h for at least 72 h.

Ground straw samples were pelleted in a single-pelleting unit as shown in literature [18] and used in previous studies[19-23]. The device consisted of a steel cylindrical die having internal diameter and length of 6.35 and 125 mm, respectively. The die was wrapped with a heating element to maintain its temperature at 95±1°C in order to simulate frictional heating in commercial pelleting[18, 22, 24]. A plunger was mounted to the upper moving crosshead of Instron testing machine (3360 Dual Column Tabletop Testing Systems, Instron Corp. Norwood, MA) to apply compressive force on biomass. The cylindrical die was placed on a raised base equipped with sliding gate at the bottom. On the base, there was a hole allowing the densified sample to be discharged from the die when sliding gate was opened. Moisture-adjusted grind (0.5-0.6 g) was loaded into the die when the temperature was stable (95±1°C). A pre-set compressive load of 4 400 N (138.9 MPa) was applied using the Instron machine fitted with a 5 000 N load cell to densify the materials. The crosshead speed of plunger was set at 50 mm/min. Upon reaching the pre-set compressive load, the plunger was stopped and retained in place for 60 s[18] and also to avoid spring-back of biomass[22]. Subsequently, the plunger was retracted to release compressive pressure. Afterwards, the sliding gate at the base of the die was opened and the plunger was lowered down after 30 s to eject pellet through the bottom of die. The force-deformation and force-time data during compression and relaxation were logged in the computer. Compression energy was calculated by integration of the area under the force-displacement curve using the Bluehill software (Version 2.12, Illinois Tool Works, Inc., 2010) and converted to specific energy values in MJ/t by dividing it by the pellet mass. The specific energy calculations did not include the energy consumed for milling and for operating the Instron testing machine. The specific energy was determined in ten replicates.

2.3 Particle size analysis, bulk density, ash and moisture content

The geometric mean diameter of ground straw samples was determined according to ASABE Standard S319[25]. A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used for particle size analysis. The sieve series selected were based on the range of particles in the samples. For grinds obtained from mill screen size of 6.4 mm hammer mill, U.S. sieve numbers of 10, 16, 20, 30, 50 and 70 (sieve opening sizes: 2.000, 1.190, 0.841, 0.595, 0.297 and 0.210 mm, respectively) were used. For grinds obtained from mill screen size of 3.2 and 1.6 mm hammer mill, U.S. sieve numbers 16, 20, 30, 50, 70 and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210 and 0.149 mm, respectively) were used. The sieves were placed on a Ro-Tap sieve shaker for 10 min sieve shaking time. The geometric mean diameter (d_{gw}) and geometric standard deviation (S_{gw}) were calculated in three replicates for each ground straw sample.

Bulk density of ground straw samples was determined using a 0.5-L cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB) filled using a funnel, with its discharge opening located 55 mm above the top edge of the container. The funnel was removed from top of the container; the container was tapped on a wooden table for approximately 10 times to allow the material to settle down. The container was leveled by rolling a cylindrical stainless steel bar across the container in two perpendicular directions. Subsequently, the container was weighed. The mass per unit volume gave the bulk density of the biomass in kg/m^3. The bulk density was determined in three replicates for each sample.

The total ash content was determined using AOAC standard method 942.05[26], where 2 g of sample was heated at 600°C in a preheated furnace in duplicate. The moisture content of ground straws was determined in duplicate using AACC standard 44-15A[27], where 2-3 g of material was oven-dried at 130°C for 90 min in

duplicates. The required amount of water was calculated by mass balance between the original ground sample and the sample with 10% moisture content. The sample was re-moistened by adding required water and mixed in an air-tight bag. Samples were stored in a cold room at 4°C and mixed every 12 h for at least 72 h to ensure moisture equilibration.

2.4 Pellet density and relaxed density

Length, diameter and mass of newly formed pellets were measured using a digital caliper to calculate the initial pellet density. Each pellet was stored in air-tight bag individually at room temperature. The diameter, length and mass of pellets were determined again two weeks after compression to calculate the relaxed density (kg/m^3) and determine the stability of the pellets. Pellet density and relaxed density were determined in ten replicates.

2.5 Pellet durability

Durability of pellets was measured in ten replicates using the drop test method[28-31], where a single pellet was dropped from a 1.85 m height on a metal plate. The ratio of the weight of the larger portion of the pellet retained intact to the initial weight of pellet was expressed as the percentage durability of the pellet.

2.6 Heat of combustion

Gross heat of combustion of samples was determined using an oxygen bomb calorimeter (Series 1300 Plain Calorimeter, Parr Instrument Company, Inc., Moline, IL) using the ASTM standard test[32]. The gross energy has the latent heat of vaporization recovered due to condensation of the water vapor in the bomb calorimeter[33]. The colorimeter was standardized using 1.0 g Parr standard benzoic acid, formed to a pellet, with calorific value of 26.5 MJ/kg.

2.7 Statistical analysis

The effect of biomass type, particle size and glycerol level on the compaction characteristics were determined using a completely randomized experimental design with factorial treatment structure. There were three variable factors, the biomass type (barley, canola, oat and wheat straws), the mill screen size (1.6, 3.2 and 6.4 mm) and the glycerol level (0.0, 2.5%, 5.0% and 7.5%). Analysis of variance (ANOVA) and comparison of means (Duncan's multiple range test at $P = 0.05$) were performed using the Statistical Analysis System (Version 9.2, SAS Institute Inc., Cary, NC) using the GLM procedure to evaluate the effect of each variable and their interactions.

3 Results and discussion

3.1 Particle size, bulk density and particle density

The particle size distribution of grinds of barley, canola, oat and wheat straw, which were ground by 1.6, 3.2 and 6.4 mm hammer mill screens, is shown in Figures 1-4. All samples ground by hammer mill screen of 6.4 mm contained more than 40% particles having 1.19 mm diameter. Table 1 shows geometric mean diameter of samples ranging from 0.99 mm (for mill screen of 6.4 mm) to 0.36 mm (for mill screen of 1.6 mm). There were some variations in geometric mean diameter of samples ground with the same mill screen. That was related to the variation in moisture content of samples and also difference in mechanical properties of samples[22].

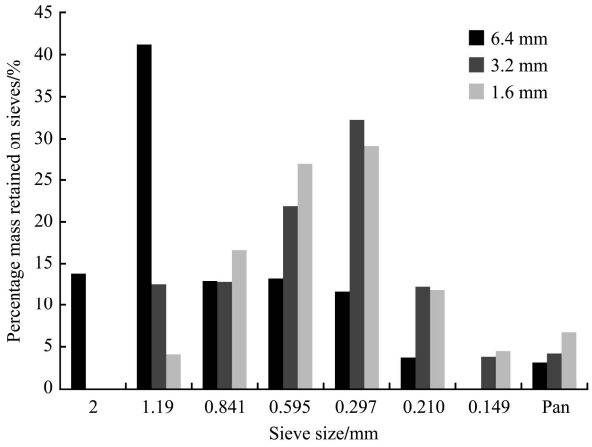

Figure 1 Mass retained over sieves representing particle size distribution of ground barley straw

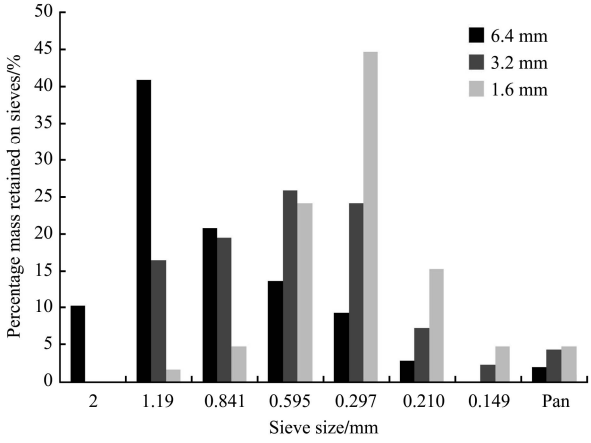

Figure 2 Mass retained over sieves representing particle size distribution of ground canola straw

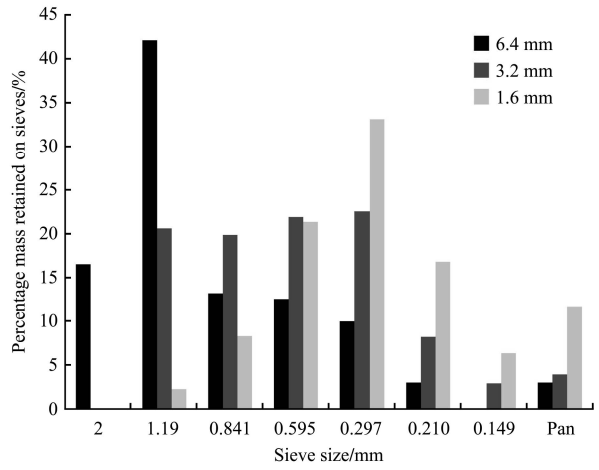

Figure 3 Mass retained over sieves representing particle size distribution of ground oat straw

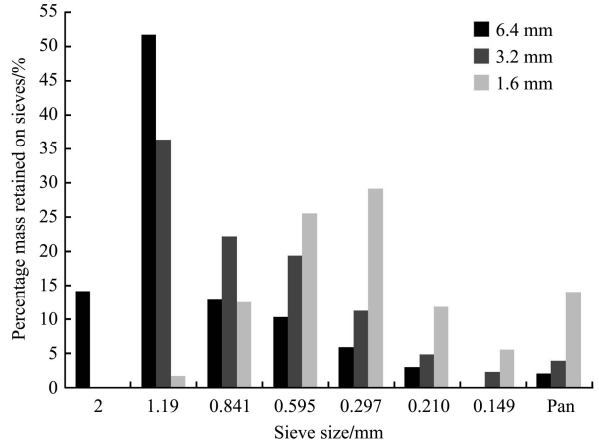

Figure 4 Mass retained over sieves representing particle size distribution of ground wheat straw

Table 1 Moisture content, geometric mean diameter (d_{gw})[a] and bulk density[b] of ground straw samples (n=3)

Straw sample	Hammer mill screen size /mm	Moisture content /% (wb)	d_{gw} /mm	Bulk density /kg·m^{-3}	Particle density /kg·m^{-3}
Barley	6.4	8.2	0.883±0.025	96±2	1016±137
	3.2	8.7	0.463±0.016	149±3	1089±32
	1.6	7.9	0.456±0.004	155±1	1149±02
Canola	6.4	7.5	0.885±0.020	144±2	1019±19
	3.2	7.7	0.521±0.061	190±9	1192±11
	1.6	8.1	0.367±0.001	203±11	1309±02
Oat	6.4	8.9	0.935±0.013	111±8	873±18
	3.2	8.3	0.566±0.015	156±4	1093±38
	1.6	8.5	0.404±0.014	196±4	1240±18
Wheat	6.4	8.5	0.997±0.038	107±2	1078±14
	3.2	8.7	0.719±0.015	141±2	1225±11
	1.6	9.2	0.452±0.016	154±2	1269±23

Note: [a] n = 3, Geometric mean diameter ±geometric standard deviation; [b] n = 3, Mean ± standard deviation; wb: wet basis.

As the particle size decreased, both bulk and particle density increased (Table 1), which was in agreement with the results of Mani and co-workers[22]. Canola straw grinds had the highest, and barley and wheat straw grinds had the lowest bulk and particle densities at 1.6 mm screen size.

3.2 Pellet density and relaxed density

The effect of biomass type, hammer mill screen size, glycerol level and the effect of interaction of biomass type and hammer mill screen size as well as the interaction of biomass type and glycerol level were significant (P<0.01) on pellet density and relaxed density, except for the effect of glycerol on relaxed density (Table 2).

Table 2 Effect of biomass type (S), hammer mill screen size (Z) and glycerol level (G) on pellet density, pellet relaxed density, durability and specific energy required for densification of biomass

Source of variation	DF	Pellet density	Relaxed density	Durability	Specific energy
		P-value	P-value	P-value	P-value
S	3	<0.01	<0.01	<0.01	<0.01
Z	2	<0.01	<0.01	<0.01	<0.01
G	3	<0.01	<0.01	0.14	<0.01
S × Z	6	<0.01	<0.01	<0.01	<0.01
S × G	9	<0.01	<0.01	<0.01	0.31
Z × G	6	0.73	<0.01	0.26	0.19
S × Z × G	18	0.32	<0.01	<0.01	<0.01
Residuals	432	---	---	---	---
Total	479	---	---	---	---

Note: DF: degrees of freedom, P: probability.

The pellet density in canola and oat straws was higher than that in barley and wheat straws (Table 3), which is directly related to ground straw bulk densities. The highest pellet density was obtained in hammer mill screen size of 6.4 mm followed by screen sizes of 3.2 and 1.6 mm. This could be attributed to interlocking of longer fibers and distribution of grind sizes, which has a balance between coarse and finer grinds (Figures 1-4). In the majority of biomass samples, the pellet density decreased with an increase in glycerol levels having the highest density for blank sample, containing 0.0% glycerol, and the lowest density was obtained from pellets containing 7.5% glycerol. This could be due to presence of glycerol, which acted as a barrier to the binding process. Similar results were observed for relaxed density of pellets; canola and oat straws had higher relaxed density than barley and wheat straws.

Table 3 Pellet density (ρ_p), relaxed density (ρ_r), durability, specific energy required for densification (SE), ash content and gross heat of combustion (GH) of pellet samples made at different mill screen sizes (MSS) and glycerol levels (mean ± standard deviation)

Straw sample	MSS /mm	Glycerol level/%	Peak load /N	ρ_p /kg·m^{-3}	ρ_r /kg·m^{-3}	Durability /%	SE /MJ·t^{-1}	Ash /%	GH /MJ·kg^{-1}
Barley	6.4	0	4497±3	1032±33^{ijklmnop}	1064±33^{efghij}	97±5^{abcd}	39.4±2.5^{ghijkl}	9.55±0.64^{b}	24.9±2.2^{efghijkl}
		2.5	4504±7	1040±46^{ghijklmno}	1055±43^{fghijkl}	98±2^{abc}	38.4±1.9^{ghijkl}	4.68±0.01^{l}	24.5±0.3^{fghijkl}
		5.0	4507±9	996±59^{opqrstv}	1014±63^{ijklmnop}	98±3^{abc}	37.8±2.7^{hijkl}	8.17±0.05^{d}	25.2±1.1^{efghijkl}
		7.5	4562±15	977±60^{rstv}	992±66^{nop}	99±1^{abc}	38.8±4.3^{ghijkl}	5.90±0.08^{jhi}	24.7±1.4^{fghijkl}
	3.2	0	4487±4	1020±22^{jklmnopqr}	1122±25^{abc}	89±10^{abcdef}	40.2±4.9^{efghijkl}	8.01±0.45^{d}	25.5±1.3^{defghijkl}
		2.5	4493±8	994±27^{opqrstv}	1000±33^{mnop}	88±8^{bcdef}	40.0±3.9^{fghijkl}	5.55±0.01^{ijk}	25.9±1.4^{defghijkl}
		5.0	4507±19	977±23^{rstv}	989±25^{op}	94±7^{abcde}	39.7±6.2^{ghijkl}	10.40±0.05^{a}	25.1±0.9^{efghijkl}
		7.5	4522±17	968±45^{stv}	872±19^{r}	92±7^{abcde}	37.2±8.0^{ijkl}	5.63±0.03^{ijk}	26.6±1.3^{cdefghijk}
	1.6	0	4481±4	1015±23^{klmnopqrs}	1073±54^{cdefghi}	76±12^{ghij}	42.0±9.7^{defghij}	5.71±0.04^{ijk}	31.0±2.2^{b}
		2.5	4491±6	991±21^{pqrstv}	1036±32^{hijklmno}	88±8^{cdef}	41.6±4.2^{defghijk}	5.72±0.04^{ijk}	29.2±2.6^{bcde}
		5.0	4504±7	1005±25^{mnopqrst}	1107±40^{abcde}	87±15^{def}	43.3±7.3^{cdefghi}	5.93±0.03^{hij}	30.6±2.1^{bc}
		7.5	4508±10	977±30^{rstv}	1069±28^{defghi}	88±11^{def}	41.2±5.1^{efghijk}	6.76±0.06^{ef}	27.3±3.2^{bcdefghij}
Canola	6.4	0	4490±4	1095±15^{abcdef}	1122±20^{abc}	99±1^{abc}	47.6±4.6^{bcd}	1.47±.05^{pq}	22.1±0.4^{klm}
		2.5	4485±2	1124±18^{abcd}	1116±18^{abcd}	100±0^{a}	50.9±4.2^{b}	1.34±0.10^{q}	23.1±1.3^{jklm}
		5.0	4494±4	1124±22^{abcd}	1116±18^{abcd}	100±0^{a}	50.7±5.6^{b}	1.51±.04^{pq}	23.3±0.6^{jkl}
		7.5	4493±27	1127±26^{abc}	1127±20^{ab}	99±1^{a}	58.8±2.1^{a}	1.49±0.31^{pq}	25.1±2.2^{efghijkl}
	3.2	0	4479±2	1074±15^{efghi}	1088±16^{bcdefg}	80±18^{fghi}	39.0±6.5^{ghijkl}	1.98±0.39^{op}	23.3±2.1^{ijkl}
		2.5	4478±4	1084±22^{cdefg}	1031±14^{ijklmno}	80±18^{fghi}	47.7±6.4^{bcd}	2.22±0.20^{no}	24.5±0.3^{fghijkl}
		5.0	4482±4	1082±23^{cdefg}	1043±31^{ghijklmn}	88±19^{def}	46.4±4.5^{bcde}	2.39±0.16^{mno}	24.8±1.7^{efghijkl}
		7.5	4491±4	1085±27^{bcdefg}	1083±62^{bcdefgh}	74±16^{ij}	36.5±2.0^{jkl}	2.76±0.21^{m}	24.6±0.6^{fghijkl}
	1.6	0	4480±2	1041±13^{ghijklmno}	1062±21^{efghijk}	52±11^{l}	35.6±8.6^{jkl}	1.44±0.28^{q}	24.8±3.1^{fghijkl}
		2.5	4478±2	1050±48^{fghijklm}	1029±18^{ijklmno}	49±9^{l}	39.4±8.3^{ghijkl}	1.36±0.10^{q}	28.7±5.3^{bcdefg}
		5.0	4483±4	1080±178^{defgh}	1039±16^{ghijklmno}	51±9^{l}	41.3±6.2^{efghijk}	2.69±0.80^{mn}	23.5±0.0^{ijkl}
		7.5	4492±5	1022±33^{jklmnopqr}	1042±20^{ghijklmn}	62±10^{k}	39.1±7.7^{ghijkl}	2.48±0.11^{mno}	27.7±3.1^{bcdefghi}
Oat	6.4	0	4500±4	1110±29^{abcde}	1115±20^{abcd}	100±1^{a}	36.7±1.7^{ijkl}	6.82±0.16^{ef}	22.4±0.3^{klm}
		2.5	4504±8	1132±32^{a}	1112±30^{abcde}	100±0^{a}	39.3±2.3^{ghijkl}	6.72±0.05^{ef}	22.9±2.2^{jklm}
		5.0	4514±7	1131±37^{ab}	1105±30^{abcde}	100±0^{a}	38.7±2.0^{ghijkl}	6.97±0.03^{e}	22.6±1.8^{klm}
		7.5	4508±4	1133±37^{a}	1142±31^{a}	98±6^{abcd}	39.2±2.8^{ghijkl}	6.91±0.17^{e}	23.4±0.7^{ijkl}
	3.2	0	4485±4	1057±22^{fghijk}	1070±27^{defghi}	89±9^{abcdef}	35.2±3.5^{kl}	5.61±0.5^{ijk}	22.7±1.0^{klm}
		2.5	4498±4	1094±28^{abcdef}	1102±33^{abcdef}	89±13^{abcdef}	39.7±6.3^{ghijkl}	5.91±0.01^{hij}	24.5±3.0^{ghijkl}
		5.0	4502±7	1095±24^{abcdef}	1107±16^{abcde}	97±5^{abcd}	38.4±2.9^{ghijkl}	5.97±0.01^{ghi}	22.9±1.3^{jklm}
		7.5	4517±11	1067±44^{efghij}	1030±39^{ijklmno}	94±10^{abcde}	37.4±3.1^{ijkl}	6.57±0.54^{ef}	24.8±2.2^{efghijkl}
	1.6	0	4485±5	1009±21^{lmnopqrst}	1032±22^{ijklmno}	70±11^{jk}	35.5±6.0^{jkl}	5.44±0.09^{ijk}	25.5±1.2^{defghijkl}
		2.5	4493±4	1045±113^{ghijklmn}	1030±23^{ijklmno}	68±17^{jk}	35.8±5.2^{jkl}	5.38±0.23^{jk}	25.9±1.5^{defghijk}
		5.0	4500±5	1058±21^{fghijk}	1032±46^{ijklmno}	67±12^{jk}	35.0±4.5^{kl}	5.62±0.11^{ijk}	23.7±1.4^{hijkl}
		7.5	4520±7	1026±25^{ijklmnopq}	1007±36^{lmno}	72±16^{ijk}	33.5±6.5^{l}	5.51±0.15^{ijk}	24.2±2.8^{hijkl}
Wheat	6.4	0	4488±3	1053±23^{fghijkl}	1063±24^{efghijk}	99±2^{abc}	49.1±6.3^{bc}	8.71±0.54^{c}	25.9±2.0^{defghijkl}
		2.5	4495±8	1032±37^{ijklmnop}	1045±28^{ghijklm}	99±1^{ab}	49.3±6.2^{bc}	5.70±0.05^{ijk}	23.5±0.3^{ijkl}
		5.0	4495±6	1035±36^{hijklmnop}	1024±26^{ijklmno}	99±2^{abc}	59.2±4.5^{a}	5.59±0.05^{ijk}	23.3±1.8^{ijkl}
		7.5	4514±13	988±72^{pqrstv}	997±76^{lmnop}	99±2^{abc}	44.1±6.4^{cdefgh}	5.55±0.05^{ijk}	21.4±0.8^{lm}
	3.2	0	4485±5	1035±19^{hijklmnop}	1038±16^{ghijklmno}	86±8^{efg}	41.9±4.2^{defghij}	6.36±0.07^{fgh}	19.0±1.6^{m}
		2.5	4488±8	990±40^{pqrstv}	1011±20^{lmnop}	86±11^{efg}	44.5±3.7^{cdef}	10.16±0.02^{a}	26.5±2.6^{cdefghijk}
		5.0	4498±17	978±37^{rstv}	945±59^{q}	69±6^{jk}	35.7±3.5^{jkl}	5.18±0.02^{k}	23.5±1.0^{ijkl}
		7.5	4505±13	984±28^{qrstv}	1012±46^{klmnop}	90±9^{abcde}	46.3±5.3^{bcdef}	5.46±0.08^{ijk}	28.8±1.6^{bcdef}
	1.6	0	4487±4	1035±36^{hijklmnop}	1147±11^{a}	86±16^{efg}	34.1±6.9^{l}	6.67±0.07^{ef}	28.0±5.7^{bcdefgh}
		2.5	4492±4	999±13^{nopqrstv}	1027±26^{ijklmno}	73±10^{ij}	39.1±3.1^{ghijkl}	10.46±0.05^{a}	28.9±0.2^{bcdef}
		5.0	4510±6	954±18^{v}	997±28^{mnop}	75±10^{hij}	38.4±3.2^{ghijkl}	5.32±0.03^{k}	29.6±2.4^{bcd}
		7.5	4533±6	964±26^{tv}	973±27^{pq}	84±16^{efgh}	37.6±4.0^{hijkl}	6.45±0.04^{efg}	38.3±5.6^{a}

Note: * Mean values with the same letter are not significantly different at the $P = 0.05$.

The lowest relaxed density was observed in pellets with 7.5% glycerol. Generally, all blank samples, containing 0% glycerol, contracted in diameter and length and as a result, their density increased after two weeks which was in agreement with Kashaninejad and co-workers[18] work. Majority of treatments in barley and wheat straws showed similar results (Table 3); the relaxed density was higher than the initial pellet density. This phenomenon was related to the effect of heat on lignin compound during densification. Lignin may have melted by heat during densification and created thermosetting conditions to cause irreversible hardness. The change between initial pellet density and relaxed density in canola and oat pellets was not consistent.

3.3 Durability

The biomass type, mill screen size and their interaction were significant ($P < 0.01$) on pellet durability (Table 2). The durability decreased with a reduction in hammer mill screen size, which is in agreement with the pellet density trend (Table 3). No significant effect was observed at different glycerol levels. High durability values (97%-100%) were obtained for biomass pellets made from hammer mill screen size of 6.4 mm. Pellets made from biomass at hammer mill screen size of 3.2 mm showed durability from 74% to 97% and those made from hammer mill screen size of 1.6 mm had durability from 49% to 88%. The trend of changes in durability versus hammer mill screen size was in agreement with Adapa co-workers[16] where it was reported that the highest and lowest durability were from grinds of hammer mill screen size of 6.4 and 1.6 mm, respectively. Since all biomass pellets with mill screen size of 6.4 mm showed high durability values, this screen size is recommended in the production of fuel pellet. The bigger hammer mill screen opening is preferred because less energy would be required for milling straw, which is advantageous in pellet manufacturing. In addition, high durability values were obtained at all glycerol levels. As a result, adding glycerol to biomass does not reduce pellet durability, and therefore crude glycerol, co-product of biodiesel industry, could be used as an additive in fuel pellet manufacturing. Pellets with higher durability produce less dust and fine materials and therefore, are more suitable for transportation and storage. As a result of this research, adding glycerol up to 7.5% to biomass would be appropriate to make durable pellets.

3.4 Specific energy for making pellet

As shown in Table 2, the effect of biomass type, mill screen size, glycerol level and the interaction of biomass type and mill screen size as well as the interaction of all three variables were significant ($P<0.01$) on specific energy required to make a pellet. Overall, pellets from canola and wheat straws required more specific energy than pellets from barley and oat (Table 3). Similar trend was reported by Adapa and co-workers[16] for total specific energy required to manufacture pellets from agricultural biomass. However, the specific energy values obtained in the current study were about two times greater than values reported by Adapa and co-workers[34,35]. It was related to lignocellulosic structure of these biomass samples. At mill screen size of 1.6 mm, the specific energy obtained for barley was greater and for wheat was similar to the value reported by Kashaninejad and co-workers[18] for compression of non-treated straw biomass. In general, average specific energy decreased with an increase in glycerol levels; however, it was not significant. Also, specific energy decreased with a decrease in hammer mill screen size (Table 3).

3.5 Ash content

During biomass combustion, the organic compounds are gasified and the inorganic elements remain in the form of salt such as CaO, K_2CO_3 and MgO, which are called ash. Majority of agricultural biomass possess high ash content, low ash softening temperature, and high risk of corrosion and fouling, which all make them relatively unsuitable fuel. Therefore, care should be taken to avoid increasing ash content during any processing of biomass and making fuel pellets. The effect of biomass type, mill screen size, glycerol level and their interactions on ash content was significant ($P<0.01$, Table 4). The lowest average of ash content was obtained at 1.6 mm mill screen size, which could be attributed to better mixing of glycerol with fine grids (Table 3). In barley and wheat straws, the highest ash content was obtained in blank samples (0.0% glycerol)

and the lowest in samples containing 7.5% glycerol. Overall, the highest ash content was observed in wheat and barley straw pellets followed by oat and canola straw pellets. Except for canola straw, ash content of all straw samples decreased with an increase in glycerol levels. Therefore, higher glycerol levels results in pellets that are suitable for thermochemical operations resulting in lower down-time.

Table 4 Effect of biomass type (S), hammer mill screen size (Z) and glycerol level (G) on ash content and gross heat of combustion of pellets

Source of variation	Ash content		Gross heat of combustion	
	DF	*P*-value	*DF*	*P*-value
S	3	<0.01	3	<0.01
Z	2	<0.01	2	<0.01
G	3	<0.01	3	<0.01
S × Z	6	<0.01	6	<0.01
S × G	9	<0.01	9	<0.01
Z × G	6	<0.01	6	<0.01
S × Z × G	18	<0.01	18	<0.01
Residuals	48	---	93	---
Total	95	---	140	---

Note: *DF*: degrees of freedom, *P*: probability.

3.6 Gross heat of combustion

The heating value of pellets was reported as gross heat of combustion. The biomass type, hammer mill screen size, glycerol level, and their interactions on gross heat of combustion were significant (P<0.01, Table 4). The average gross heat of combustion increased with a decrease in hammer mill screen size (Table 3). The highest gross heat of combustion was obtained in samples containing 7.5% glycerol (21.4-38.3 MJ/kg). The gross heat of combustion of blank samples was slightly higher than those listed by Adapa and co-workers[16] who reported 16.4, 16.7, 16.4 and 17.0 MJ/kg for non-treated barley, canola, oat and wheat straws, respectively. Although, in most treatments, the highest gross heat of combustion was observed in samples with the highest glycerol level, there was no linear relationship or consistent trend between glycerol level and gross heat of combustion. This non-linear relationship could be due to non-uniform mixing of glycerol with agricultural straw grinds. The energy content of glycerol was not determined separately, however, as per literature it will in within the range of 16-25 MJ/kg, which may have resulted in a slightly higher value for pellets with higher levels of glycerol.

4 Conclusions

The application of glycerol in making biomass fuel pellets decreased the pellet density and relaxed density. The blank pellets, containing 0.0% glycerol, had higher pellet density and relaxed density than glycerol-added pellets. Pellets made from canola and oat straws had higher pellet density and relaxed density than those made from barley and wheat straws. However, the durability of samples containing glycerol was similar to blank samples. The most appropriate glycerol level was 7.5% as the majority of pellets at this glycerol concentration had high durability without marked changes in pellet density and relaxed density. In addition, higher glycerol levels resulted in lower ash content. As preliminary tests confirmed, adding higher glycerol level (>7.5%) to the mixture will result in extruding glycerol form die, instead of staying in the pellet. Adding glycerol to the biomass increased gross heat of combustion as treatments containing 7.5% glycerol showed average gross heat of combustion of 26.4 MJ/kg compared to the average of 24.6 MJ/kg in blank sample, containing 0.0% glycerol. As a result, although glycerol decreased pellet density, it increased gross heat of combustion, reduced ash content and no change in pellet durability. As a result, crude glycerol, a co-product of biodiesel industry, could be used as an ingredient to make fuel pellets.

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