



Effect of Glycerol on Densification of Agricultural Biomass

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ABSTRACT Experiments were conducted to verify whether glycerol can be used as binder for pelleting of selected agricultural residues, namely, wheat, barley, oat and canola straw. Single pelleting tests were employed to study the effect of biomass type, mill screen size and crude glycerol, co-product of biodiesel industry, on pellet quality and gross heat of combustion. The four types of biomass were milled at three different hammer mill screen sizes (6.4, 3.2 and 1.6 mm). Each biomass was mixed with three levels of glycerol (2.5, 5.0 and 7.5%). Pellets were made using single-pelleter at a pre-set load of 4400 N corresponding to a pressure of 138.9 MPa. Quality of pellets were determined by measuring pellet density, relaxed density, durability and the 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 (988-1133 kg/m³) and relaxed density (992-1142 kg/m³) were obtained from biomass ground using a hammer mill screen size of 6.4 mm. Decreasing mill screen size reduced durability. The highest durability of biomass obtained from hammer mill screen size of 6.4 mm ranged from 97 to 100%. Glycerol decreased ash content in majority of pellets. The most appropriate level of glycerol addition was 7.5% which made durable biomass pellets.

Keywords: Biomass, Biofuels, Glycerol, Pelleting, Caloric value, Heating value.

INTRODUCTION

Agricultural crop residues are potential feedstocks for bioenergy and biofuels production. The total surplus of wheat, barley, oat and flax straw residue available for biofuel production in Canadian prairies has been estimated at over 15 Mt (Sokhansanj et al., 2006). 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 (Demirbas, 2001; Tripathi et al., 1998). Therefore, handling and transportation of straw is more difficult than wood residue. Densification of biomass straw into pellets increases the bulk density of biomass and eventually, the net gross heat content per unit volume is improved (Bhattacharya et al., 1989) and the storage, transport and handling of the material is easier and cheaper (Kaliyan and Morey, 2006). Since the chemical structure of agricultural straw is a lignocellulosic matrix, the ground biomass could be bonded using physico-chemical and biological pre-treatment such, as application of different chemicals and additives, microwave treatment, steam explosion and other treatments (Kashaninejad and Tabil, 2011).

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 seriously being considered. A good renewable fuel alternative is biodiesel which has many environmental benefits when compared with conventional petroleum-based fuels. For instance, biodiesel decreases the net emission of greenhouse gas (CO_2), polyaromatic hydrocarbons and other noxious emissions leading to a decreased environmental impact and health risk (Sharma et al. 2008). 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 (Figure 1). This reaction is performed in the presence of catalysts such as metal hydroxides and metal alkoxides. The reaction is shown in the following equation (Srivastava and Prasad, 2000; Gok, 2011):

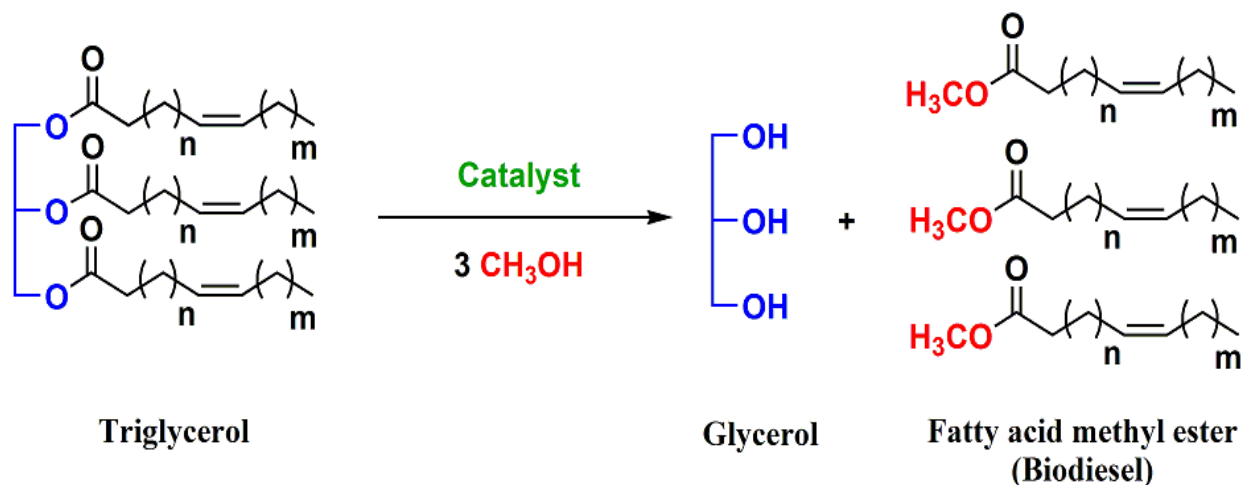


Figure 1. Equation for main reaction during biodiesel production showing glycerol as byproduct.

For every 10 kg of biodiesel produced, there will be 1 kg of crude glycerol co-produced through transesterification of triglyceride feedstock (Diversified Energy, 2012). Crude glycerol contains an energy potential (16 MJ/kg) and can be utilized as alternative form of energy and as an additive for agricultural biomass feedstock.

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. (2010) 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 investigate the use of crude glycerol from biodiesel production as an additive in making pellets from different agricultural biomass. The application of crude glycerol could enhance the bulk density and flowability of pellets, improves the activation of natural binders during pellet formation, and eventually increases the energy density of the pellets.

MATERIAL AND METHODS

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 the 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 rpm. The chopper was fabricated 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; 230 Brookdale, St. Maywood, NJ) using three different mill screen sizes of 6.4, 3.2 and 1.6 mm.

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 heated crude glycerol was mixed with moisture-adjusted straw grinds at 0% as blank, 2.5, 5.0, and 7.5%. Each mixture was blended for about 15 min to provide a uniform distribution of glycerol in the straw grinds. The mixtures were then stored in air-tight bag at 4°C and mixed every 12 h for at least 72 h.

The ground straw-glycerol samples were pelleted in a single-pelleting unit as shown by (Kashaninejad and Tabil, 2011) and used in previous studies (Tabil and Sokhansanj, 1996, 1997; Adapa et al., 2002; Mani et al., 2006; Shaw et al., 2009). The device is composed of a steel cylindrical die with internal diameter of 6.35 mm and 125 mm long. The die was wrapped with a heating element maintaining the temperature at 95±1°C to simulate frictional heating in commercial pelleting (Adapa et al., 2006; Mani et al., 2006; Kashaninejad and Tabil, 2011). A plunger was mounted to the upper moving crosshead of Instron testing machine (3360 Dual Column Tabletop Testing Systems, Instron Corp. Norwood, MA). The cylindrical die sat 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 the sliding gate was opened. Moisture-adjusted grind-glycerol mix (0.5-0.6 g) was loaded into the die when the temperature was stable (95±1°C). The compressive force applied using the Instron machine fitted with a 5000 N load cell and a pre-set load of 4400 N corresponding to a pressure of 138.9 MPa was used to densify the samples. The crosshead speed of plunger was set at 50 mm/min. When the compression load achieved the pre-set load, the plunger stopped and was retained in place for 60 s to start the relaxation phase (Kashaninejad and Tabil, 2011) and also to avoid spring-back of biomass sample (Mani et al., 2006). The plunger was then moved up to release the compression force, the sliding gate was opened, and the plunger moved down after 30 s to eject pellet through the bottom of die and base. 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.

Particle Size Analysis, Bulk Density, Ash and Moisture Content The geometric mean diameter of ground straw samples was determined using ASAE Standard S319 (ASABE, 2011). 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 round stainless steel bar across the container in two perpendicular directions. The container was then weighed. The mass per unit volume gave the bulk density of the biomass grind 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 (AOAC, 1995) in duplicate. The moisture content of ground straws was determined in duplicate using AACC standard 44-15A (AACC, 2005), where 2-3 g of material was oven-dried at 130°C for 90 min. 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.

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.

Pellet Durability Durability of pellets was measured in ten replicates using the drop test method (Al-Widyan and Al-Jalil, 2001; Khankari et al., 1989; Sah et al., 1980; Shrivastava et al., 1989), 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.

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). The gross energy has the latent heat of vaporization recovered during the condensation of the water vapor in the bomb calorimeter, unlike net energy (Riggins et al., 1981). The calorimeter was standardized using 1.00 g Parr standard benzoic acid, formed to a pellet, with calorific value of 26456000 J/kg. A single length of fuse wire having a length of 10 cm and 963 J/m heat of combustion was used to combust the sample in the bomb calorimeter. About 1 g sample was measured in a metal combustion capsule and placed in the sample holder in the bomb head (Figure 2A). The fuse wire was connected to the electrodes of the bomb head. The bomb head was fitted to the bomb cylinder. The bomb was sealed by turning the screw cap down firmly. The bomb was filled with oxygen at 172369 Pa gage pressure and emptied three times using a valve on the bomb to purge the air inside the bomb (Figure 2B). Then, the bomb with 172369 Pa oxygen was submerged in an oval bucket containing 2000 g deionized water. The external connections of electrodes were connected and the calorimeter was covered by its lid (Figure 2C). The stirrer was started for 5 min to attain thermal equilibrium between the bomb and the water in the bucket. A thermocouple was passed through the hole in the lid to measure the water temperature (Figure 2D). The thermocouple was connected to a Campbell data logger (Model CR10X, Campbell Scientific, Inc. Logan, UT) to record temperature to the nearest 0.001°C in 1.0 s intervals. The data logger was turned on followed by pressing the button on the ignition unit to combust samples in the bomb. Data was recorded for about 5 min to measure temperature rise; the data was then transferred from the data logger to a laptop computer. The bomb was lifted from the bucket and the remaining oxygen was released. The bomb was opened and the length of unburned fuse wire was measured and subtracted from 10 cm initial length. The following equations were used to calculate the heat of combustion in three replicates (Parr Instrument Company, 1970):

$$W = \frac{H.m_a + e}{t} \quad (1)$$

$$H_g = \frac{t.W - e}{m} \quad (2)$$

where W = energy equivalent of calorimeter (J/°C); H = gross heat of combustion of standard benzoic acid (J/kg); m_a = mass of benzoic acid (kg); t = corrected temperature rise (°C); e = correction for heat of firing fuse wire (J); m = mass of sample in combustion capsule (kg); and H_g = heat of combustion of sample (J/kg). The unit of H_g value was converted to MJ/t and reported as gross heat of combustion.



Figure 2. Bomb calorimeter set-up: (A) bomb calorimeter and related parts, (B) filling bomb calorimeter with oxygen, (C) bomb calorimeter and bucket, (D) bomb calorimeter, stirrer and thermocouple.

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), the hammer 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 the 0.05 level) were performed using the Statistical Analysis System (Version 9.2, SAS Institute Inc., Cary, NC) by the GLM procedure to evaluate the effect of each variable and their interactions.

RESULTS AND DISCUSSION

Particle Size and Bulk 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 3 to 6. All samples ground by hammer mill screen of 6.4 mm contained more than 40% particles having 1.19 mm diameter. Table 1 shows the geometric mean diameter of samples ranging from 0.99 mm for hammer mill screen of 6.4 mm to 0.36 mm for hammer mill screen of 1.6 mm. There were some variations in geometric mean diameter of samples ground with the same screen. That was related to the variation in moisture content of samples and also difference in mechanical properties of samples (Mani et al., 2006). As the particle size decreased, the bulk density increased (Table 1), which was in agreement with the results of Mani and co-workers (2006). Canola straw grinds had the highest and barley and wheat straw grinds had the lowest bulk density in the corresponding screen sizes.

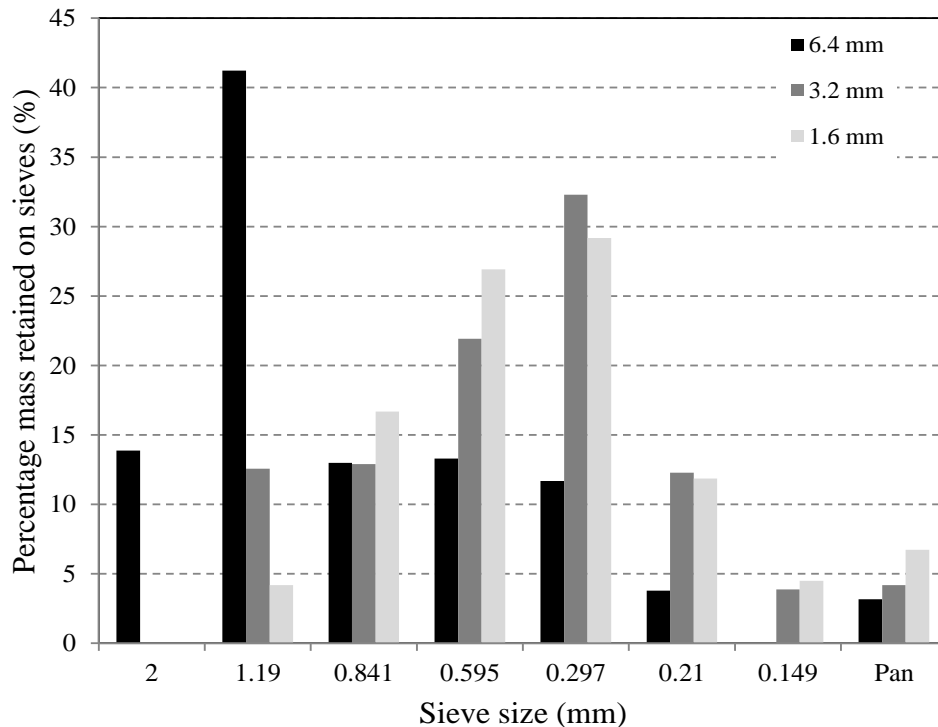


Figure 3. Mass retained over sieves representing particle size distribution of ground barley straw.

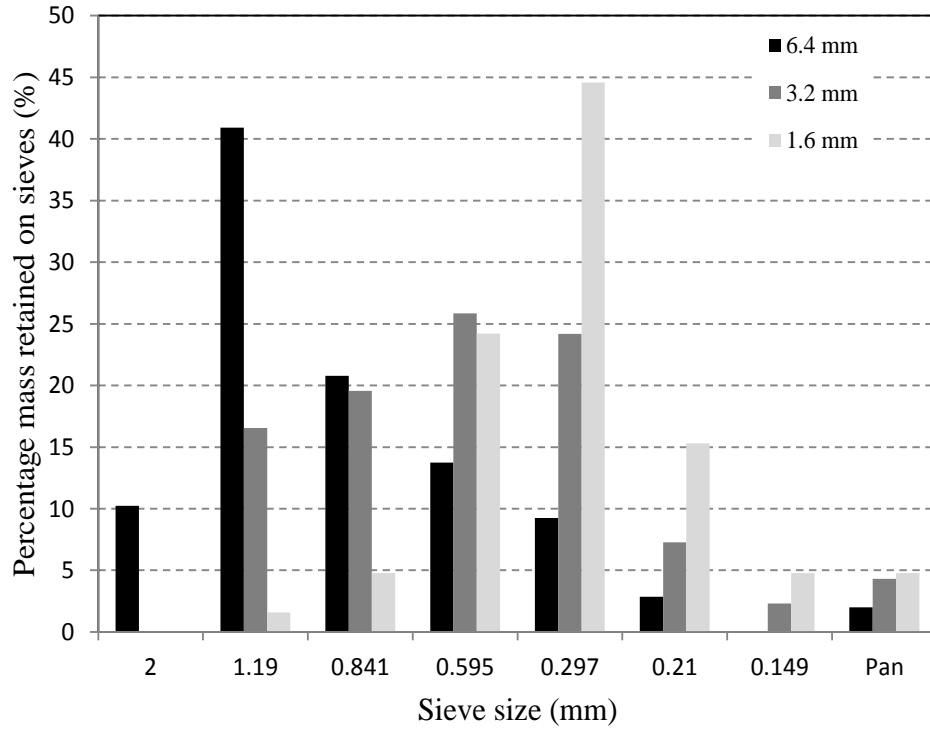


Figure 4. Mass retained over sieves representing particle size distribution of ground canola straw.

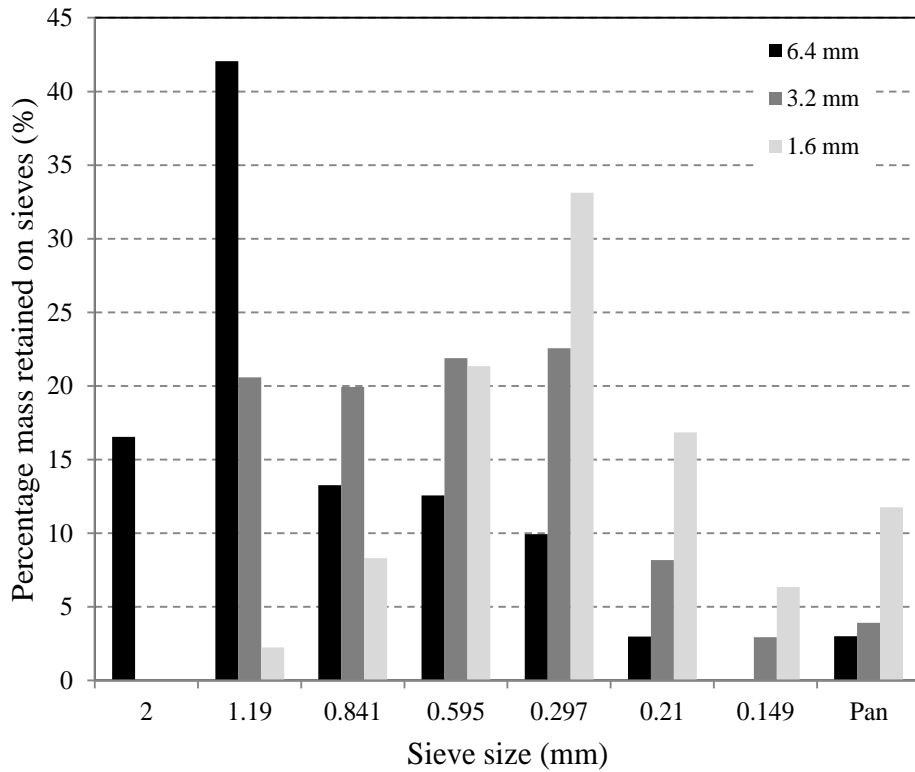


Figure 5. Mass retained over sieves representing particle size distribution of ground oat straw.

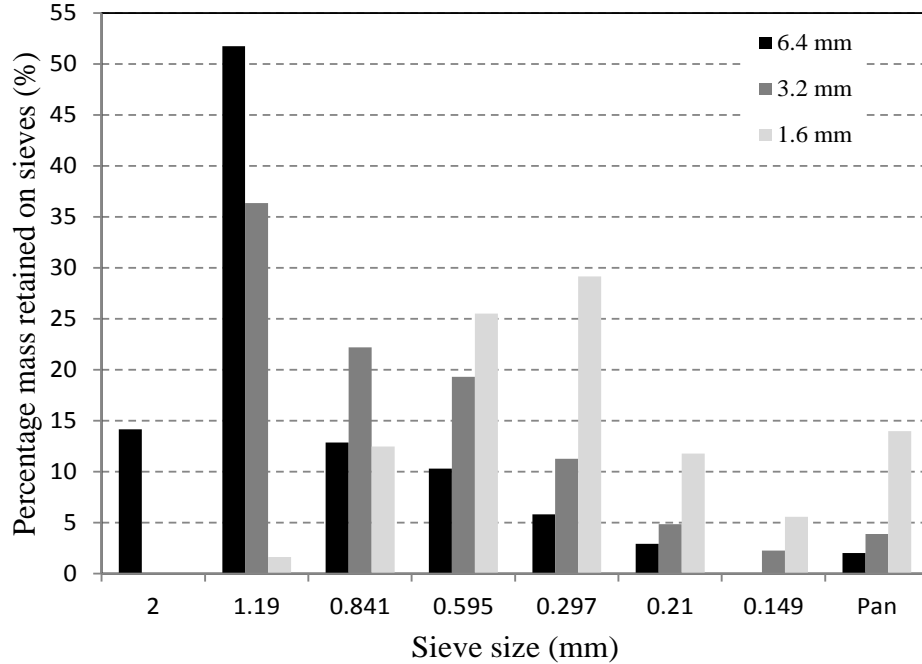


Figure 6. Mass retained over sieves representing particle size distribution of ground wheat straw.

Table 1. Geometric mean diameter (d_{gw})^a and bulk density^b of ground straw samples (n=3)

Straw sample	Hammer mill screen size (mm)	d_{gw} (mm)	Bulk density (kg/m ³)
Barley	6.4	0.883±0.025	96±2
	3.2	0.463±0.016	149±3
	1.6	0.456±0.004	155±1
Canola	6.4	0.885±0.020	144±2
	3.2	0.521±0.061	190±9
	1.6	0.367±0.001	203±11
Oat	6.4	0.935±0.013	111±8
	3.2	0.566±0.015	156±4
	1.6	0.404±0.014	196±4
Wheat	6.4	0.997±0.038	107±2
	3.2	0.719±0.015	141±2
	1.6	0.452±0.016	154±2

^a n = 3, Geometric mean diameter ± geometric standard deviation

^b n = 3, Mean ± standard deviation

Pellet Density and Relaxed Density The effect of biomass type, mill screen size, glycerol level and the interaction effects of biomass type and mill screen size as well as that of biomass type and glycerol level were significant ($P < 0.01$) on pellet density and relaxed density (Table 2). The pellet density in canola and oat straws was higher than that in barley and wheat straws (Table 3). The highest pellet density was obtained using hammer mill screen size of 6.4 mm followed by screen sizes of 3.2 and 1.6 mm. In the majority of biomass samples, the pellet density decreased as glycerol level increased as the highest density was observed in blank sample, containing 0.0% glycerol, and the lowest density was obtained from pellets containing 7.5% glycerol. Similar results were observed for relaxed density of pellets; canola and oat straws had higher relaxed density than barley and wheat straws. The lowest relaxed density was observed in pellets with 7.5% glycerol. Generally, all blank samples, containing 0.0% glycerol, contracted in diameter and length and as a result, their density increased after two weeks which was in agreement with Kashaninejad and Tabil (2011) 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 is melted by heat during densification and shows thermosetting properties having irreversible hardness. The change between initial pellet density and relaxed density in canola and oat pellets was not consistent.

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	
		SS	P-value	SS	P-value	SS	P-value	SS	P-value
S	3	757340.20	<0.01	261182.77	<0.01	11736.67	<0.01	4036.98	<0.01
Z	2	235651.78	<0.01	150321.29	<0.01	59316.65	<0.01	3640.95	<0.01
G	3	36682.74	<0.01	190158.29	<0.01	542.35	0.14	484.19	<0.01
S × Z	6	72167.84	<0.01	298118.91	<0.01	15290.36	<0.01	4138.89	<0.01
S × G	9	103804.05	<0.01	185806.48	<0.01	2425.53	<0.01	382.87	0.31
Z × G	6	6968.00	0.73	41517.35	<0.01	757.80	0.26	315.66	0.19
S × Z × G	18	39607.64	0.32	286783.63	<0.01	4125.50	<0.01	2864.99	<0.01
Residuals	432	838446.09	---	939850.34	---	42110.82	---	---	---
Total	479	2090668.34	---	2354743.79	---	136305.68	---	---	---

DF: degrees of freedom, SS: Sum of squares, P: probability

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 \pm standard deviation)

Sample	MSS (mm)	Glycerol level (%)	Peak load (N)	ρ_p (kg/m ³)	ρ_r (kg/m ³)	Durability (%)	SE (MJ/t)	Ash (%)	GH (MJ/kg)
Barley	6.4	0.0	4497 \pm 3	1032 \pm 33 ^{ijklmnop}	1064 \pm 33 ^{efghij}	97 \pm 5 ^{abcd}	39.4 \pm 2.5 ^{ghijkl}	9.55 \pm 0.64 ^d	13.3 \pm 0.2 ^{mnpa}
		2.5	4504 \pm 7	1040 \pm 46 ^{ghijklmno}	1055 \pm 43 ^{efghijkl}	98 \pm 2 ^{abc}	38.4 \pm 1.9 ^{ghijkl}	4.68 \pm 0.01 ^l	13.1 \pm 0.2 ^{opq}
		5.0	4507 \pm 9	996 \pm 59 ^{opqrstv}	1014 \pm 63 ^{ijklmnop}	98 \pm 3 ^{abc}	37.8 \pm 2.7 ^{ghijkl}	8.17 \pm 0.05 ^d	13.4 \pm 0.6 ^{lmnopq}
		7.5	4562 \pm 15	977 \pm 60 ^{rstv}	992 \pm 66 ^{nop}	99 \pm 1 ^{abc}	38.8 \pm 4.3 ^{ghijkl}	5.90 \pm 0.08 ^{hi}	13.2 \pm 0.8 ^{nopq}
	3.2	0.0	4487 \pm 4	1020 \pm 22 ^{ijklmnopqr}	1122 \pm 25 ^{abc}	89 \pm 10 ^{abcdef}	40.2 \pm 4.9 ^{efghijkl}	8.01 \pm 0.45 ^d	13.6 \pm 0.7 ^{klmnop}
		2.5	4493 \pm 8	994 \pm 27 ^{opqrstv}	1000 \pm 33 ^{mnpop}	88 \pm 8 ^{bcdef}	40.0 \pm 3.9 ^{efghijkl}	5.55 \pm 0.01 ^{ijk}	13.8 \pm 0.7 ^{klmnop}
		5.0	4507 \pm 19	977 \pm 23 ^{rstv}	989 \pm 25 ^{op}	94 \pm 7 ^{abcde}	39.7 \pm 6.2 ^{ghijkl}	10.40 \pm 0.05 ^a	13.4 \pm 0.5 ^{lmnopq}
		7.5	4522 \pm 17	968 \pm 45 ^{stv}	872 \pm 19 ^f	92 \pm 7 ^{abcde}	37.2 \pm 8.0 ^{ijkl}	5.63 \pm 0.03 ^{jk}	14.2 \pm 0.7 ^{ijklmnop}
	1.6	0.0	4481 \pm 4	1015 \pm 23 ^{klmnopqrs}	1073 \pm 54 ^{cdefghi}	76 \pm 12 ^{ghij}	42.0 \pm 9.7 ^{defghij}	5.71 \pm 0.04 ^{ijk}	16.6 \pm 0.2 ^{cdefghij}
		2.5	4491 \pm 6	991 \pm 21 ^{pqrstv}	1036 \pm 32 ^{hijklmno}	88 \pm 8 ^{cdet}	41.6 \pm 4.2 ^{defghijk}	5.72 \pm 0.04 ^{ijk}	15.6 \pm 1.4 ^{tghijklmn}
		5.0	4504 \pm 7	1005 \pm 25 ^{mnpopqrst}	1107 \pm 40 ^{abcde}	87 \pm 15 ^{def}	43.3 \pm 7.3 ^{cdefghi}	5.93 \pm 0.03 ^{hij}	16.3 \pm 1.1 ^{defghij}
		7.5	4508 \pm 10	977 \pm 30 ^{rstv}	1069 \pm 28 ^{defghi}	88 \pm 11 ^{def}	41.2 \pm 5.1 ^{efghijk}	6.76 \pm 0.06 ^{ef}	14.6 \pm 0.7 ^{ijklmnop}
Canola	6.4	0.0	4490 \pm 4	1095 \pm 15 ^{abcdef}	1122 \pm 20 ^{abc}	99 \pm 1 ^{abc}	47.6 \pm 4.6 ^{bcd}	1.47 \pm 0.05 ^{pq}	16.7 \pm 0.3 ^{cdefghi}
		2.5	4485 \pm 2	1124 \pm 18 ^{abcd}	1116 \pm 18 ^{abcd}	100 \pm 0 ^a	50.9 \pm 4.2 ^b	1.34 \pm 0.10 ^q	17.5 \pm 0.1 ^{cdefgh}
		5.0	4494 \pm 4	1124 \pm 22 ^{abcd}	1116 \pm 18 ^{abcd}	100 \pm 0 ^a	50.7 \pm 5.6 ^b	1.51 \pm 0.04 ^{pq}	17.6 \pm 0.5 ^{cdefgh}
		7.5	4493 \pm 27	1127 \pm 26 ^{abc}	1127 \pm 20 ^{ab}	99 \pm 1 ^a	58.8 \pm 2.1 ^a	1.49 \pm 0.31 ^{pq}	19.0 \pm 1.7 ^{bc}
	3.2	0.0	4479 \pm 2	1074 \pm 15 ^{efghi}	1088 \pm 16 ^{bcdefg}	80 \pm 18 ^{fghi}	39.0 \pm 6.5 ^{ghijkl}	1.98 \pm 0.39 ^{op}	17.6 \pm 1.6 ^{cdefgh}
		2.5	4478 \pm 4	1084 \pm 22 ^{cdefg}	1031 \pm 14 ^{ijklmno}	80 \pm 18 ^{fghi}	47.7 \pm 6.4 ^{bcd}	2.22 \pm 0.20 ^{no}	18.5 \pm 0.2 ^{cde}
		5.0	4482 \pm 4	1082 \pm 23 ^{cdefg}	1043 \pm 31 ^{ghijklmn}	88 \pm 19 ^{def}	46.4 \pm 4.5 ^{bcde}	2.39 \pm 0.16 ^{mno}	18.8 \pm 1.3 ^{bcd}
		7.5	4491 \pm 4	1085 \pm 27 ^{bcdefg}	1083 \pm 62 ^{bcdefgh}	74 \pm 16 ^{ij}	36.5 \pm 2.0 ^{kl}	2.76 \pm 0.21 ^m	18.6 \pm 0.5 ^{cde}
	1.6	0.0	4480 \pm 2	1041 \pm 13 ^{ghijklmno}	1062 \pm 21 ^{efghijk}	52 \pm 11 ^l	35.6 \pm 8.6 ^{ijkl}	1.44 \pm 0.28 ^q	18.7 \pm 0.3 ^{bcd}
		2.5	4478 \pm 2	1050 \pm 48 ^{efghijklm}	1029 \pm 18 ^{ijklmno}	49 \pm 9 ^l	39.4 \pm 8.3 ^{ghijkl}	1.36 \pm 0.10 ^q	21.7 \pm 0.4 ^a
		5.0	4483 \pm 4	1080 \pm 178 ^{defgh}	1039 \pm 16 ^{ghijklmno}	51 \pm 9 ^l	41.3 \pm 6.2 ^{efghijk}	2.69 \pm 0.80 ^{mn}	17.8 \pm 0.0 ^{cdefg}
		7.5	4492 \pm 5	1022 \pm 33 ^{ijklmnopqr}	1042 \pm 20 ^{ghijklmn}	62 \pm 10 ^k	39.1 \pm 7.7 ^{ghijkl}	2.48 \pm 0.11 ^{mno}	21.0 \pm 2.3 ^{ab}

Sample	MSS (mm)	Glycerol level (%)	Peak load (N)	ρ_p (kg/m ³)	ρ_r (kg/m ³)	Durability (%)	SE (MJ/t)	Ash (%)	GH (MJ/kg)	
Oat	6.4	0.0	4500±4	1110±29 ^{abcde}	1115±20 ^{abcd}	100±1 ^a	36.7±1.7 ^{kl}	6.82±0.16 ^{ef}	15.7±0.2 ^{ghijklm}	
		2.5	4504±8	1132±32 ^a	1112±30 ^{abcde}	100±0 ^a	39.3±2.3 ^{ghijkl}	6.72±0.05 ^{ef}	16.0±1.5 ^{efghijk}	
		5.0	4514±7	1131±37 ^{ab}	1105±30 ^{abcde}	100±0 ^a	38.7±2.0 ^{ghijkl}	6.97±0.03 ^e	15.9±1.3 ^{efghijkl}	
		7.5	4508±4	1133±37 ^a	1142±31 ^a	98±6 ^{abcd}	39.2±2.8 ^{ghijkl}	6.91±0.17 ^e	16.4±0.5 ^{defghij}	
	3.2	0.0	4485±4	1057±22 ^{efghijk}	1070±27 ^{defghi}	89±9 ^{abcdef}	35.2±3.5 ^{kl}	5.61±0.5 ^{ijk}	15.9±0.7 ^{efghijkl}	
		2.5	4498±4	1094±28 ^{abcdef}	1102±33 ^{abcdef}	89±13 ^{abcdef}	39.7±6.3 ^{ghijkl}	5.91±0.01 ^{hij}	17.1±1.1 ^{cdefgh}	
		5.0	4502±7	1095±24 ^{abcdef}	1107±16 ^{abcde}	97±5 ^{abcd}	38.4±2.9 ^{ghijkl}	5.97±0.01 ^{ghi}	16.0±0.9 ^{efghijk}	
		7.5	4517±11	1067±44 ^{efghij}	1030±39 ^{ijklmno}	94±10 ^{abcde}	37.4±3.1 ^{ijkl}	6.57±0.54 ^{ef}	17.4±1.5 ^{cdefgh}	
	1.6	0.0	4485±5	1009±21 ^{lmnopqrst}	1032±22 ^{ijklmno}	70±11 ^{jk}	35.5±6.0 ^{kl}	5.44±0.09 ^{ijk}	17.9±0.1 ^{cdefg}	
		2.5	4493±4	1045±113 ^{ghijklmn}	1030±23 ^{ijklmno}	68±17 ^{jk}	35.8±5.2 ^{kl}	5.38±0.23 ^{jk}	18.2±1.1 ^{cdef}	
		5.0	4500±5	1058±21 ^{efghijk}	1032±46 ^{ijklmno}	67±12 ^{jk}	35.0±4.5 ^{kl}	5.62±0.11 ^{ijk}	16.6±0.9 ^{cdefghij}	
		7.5	4520±7	1026±25 ^{ijklmnopq}	1007±36 ^{lmno}	72±16 ^{ijk}	33.5±6.5 ^l	5.51±0.15 ^{ijk}	17.0±0.9 ^{cdefghi}	
	Wheat	6.4	0.0	4488±3	1053±23 ^{efghijkl}	1063±24 ^{efghijk}	99±2 ^{abc}	49.1±6.3 ^{bc}	8.71±0.54 ^c	15.1±1.2 ^{hijklmno}
			2.5	4495±8	1032±37 ^{ijklmnop}	1045±28 ^{ghijklm}	99±1 ^{ab}	49.3±6.2 ^{bc}	5.70±0.05 ^{ijk}	13.7±0.2 ^{klmnop}
			5.0	4495±6	1035±36 ^{ijklmnop}	1024±26 ^{ijklmno}	99±2 ^{abc}	59.2±4.5 ^a	5.59±0.05 ^{ijk}	13.6±1.0 ^{klmnop}
			7.5	4514±13	988±72 ^{pqrstv}	997±76 ^{lmnop}	99±2 ^{abc}	44.1±6.4 ^{cdefgh}	5.55±0.05 ^{ijk}	12.5±0.4 ^{pq}
3.2		0.0	4485±5	1035±19 ^{hijklmnop}	1038±16 ^{ghijklmno}	86±8 ^{etg}	41.9±4.2 ^{defghij}	6.36±0.07 ^{fgh}	11.1±0.9 ^q	
		2.5	4488±8	990±40 ^{pqrstv}	1011±20 ^{lmnop}	86±11 ^{efg}	44.5±3.7 ^{cdef}	10.16±0.02 ^a	15.5±0.5 ^{ghijklmno}	
		5.0	4498±17	978±37 ^{rstv}	945±59 ^q	69±6 ^{jk}	35.7±3.5 ^{ijkl}	5.18±0.02 ^k	13.7±0.6 ^{klmnop}	
		7.5	4505±13	984±28 ^{qrstv}	1012±46 ^{klmnop}	90±9 ^{abcde}	46.3±5.3 ^{bcdef}	5.46±0.08 ^{ijk}	16.8±0.9 ^{cdefghi}	
1.6		0.0	4487±4	1035±36 ^{hijklmnop}	1147±11 ^a	86±16 ^{efg}	34.1±6.9 ^l	6.67±0.07 ^{ef}	16.4±0.3 ^{defghij}	
		2.5	4492±4	999±13 ^{nopqrstv}	1027±26 ^{ijklmno}	73±10 ^{ij}	39.1±3.1 ^{ghijkl}	10.46±0.05 ^a	16.9±0.1 ^{cdefghi}	
		5.0	4510±6	954±18 ^v	997±28 ^{mno}	75±10 ^{hij}	38.4±3.2 ^{ghijkl}	5.32±0.03 ^k	17.3±1.4 ^{cdefgh}	
		7.5	4533±6	964±26 ^{tv}	973±27 ^{pq}	84±16 ^{efgh}	37.6±4.0 ^{hijkl}	6.45±0.04 ^{efg}	22.4±3.3 ^a	

*Mean values with the same letter were not significantly different at the 0.05 level.

Durability The effect of biomass type, mill screen size and their interaction was significant ($P < 0.01$) on pellet durability (Table 2). The durability decreased with decreasing hammer mill screen size (Table 3). No significant effect was observed at different glycerol levels. High durability values (97-100%) were obtained for biomass pellets made from 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 mill screen size was in agreement with Adapa co-workers (2010) 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, a co-product of biodiesel industry, could be used as a binder in fuel pellet manufacturing. Pellets with higher durability produces 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.

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 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 (2010) 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 (2009). It was related to lignocellulosic structure of these to biomass. 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 Tabil (2011) for compression of non-treated straw biomass.

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 make them all relatively unsuitable fuel. Therefore, care should be taken to avoid increasing ash content during processing of biomass into 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 (Table 3). In barley and wheat straws, the highest ash content was obtained in blank samples (0.0% glycerol) and the lowest in samples contacting 7.5% glycerol. Overall, the highest ash content was observed in wheat and barley straw pellets followed by oat and canola straw pellets.

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	SS	P-value	DF	SS	P-value
S	3	398.58	<0.01	3	375.13	<0.01
Z	2	3.31	<0.01	2	182.93	<0.01
G	3	3.44	<0.01	3	32.49	<0.01
S × Z	6	18.54	<0.01	6	43.11	<0.01
S × G	9	74.81	<0.01	9	40.12	<0.01
Z × G	6	23.00	<0.01	6	21.18	<0.05
S × Z × G	18	40.94	<0.01	18	101.05	<0.01
Residuals	48	2.62	---	96	156.61	---
Total	95	566.24	---	143	952.63	---

DF: degrees of freedom, SS: Sum of squares, P: probability

Gross Heat of Combustion The heating value of pellets was reported as gross heat of combustion. The effect of biomass type, mill screen size, glycerol level and their interactions on gross heat of combustion was significant ($P < 0.01$, Table 4). The average gross heat of combustion in different mill screen size was in the order: 1.6 > 3.2 > 6.4 mm. The highest gross heat of combustion was obtained in samples containing 7.5% glycerol (12.5-22.4 MJ/kg) (Table 3). The gross heat of combustion of blank samples was similar to those listed by Adapa and co-workers (2010) 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. It was related to having similar potential energy value in biomass and glycerol (approximately 16 MJ/kg).

CONCLUSION 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 pellets with 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. As a result, crude glycerol, a co-product of biodiesel industry, could be used as ingredient and binder in biofuel industry. 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. As preliminary tests confirmed, adding higher glycerol level (>7.5%) to the biomass grind resulted in the separation of glycerol from the pellets as the latter was extruding from the die, instead of staying in the pellet as binder.

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