Producing durable pellets from barley straw subjected to radio frequency-alkaline and steam explosion pretreatments

Kingsley L. Iroba*, Lope G. Tabil, Shahab Sokhansanj, Venkatesh Meda

(*Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon SK S7N 5A9, Canada*)

Abstract: Pelletization, a form of densification, increases bulk density and improves the convenience and accessibility of biomass feedstock due to the uniform shape and size. Pretreatment of biomass enhances the breakdown and accessibility of the cross-linking lignin, which acts as a binding agent. In this study, pelletization of radio frequency-alkaline and steam explosion pretreated barley straw was performed. Three levels of temperature (70°C, 80°C, and 90°C), five levels of the mass ratio of biomass to NaOH solution (1:4, 1:5, 1:6, 1:7, and 1:8), one hour equilibration time, biomass screen size of 1.6 mm, 1% NaOH concentration, and 20 min residence time in the radio frequency chamber were used for the radio frequency-alkaline pretreatment. Three levels of steam temperature (140°C, 160°C, and 180°C), three levels of moisture content of 8%, 30%, and 50% (mass fraction of total mass), and 5 min and 10 min exposure to steam were tested for the steam explosion pretreatment. The effects of both pretreatment methods were evaluated by pelletizing the pretreated and non-pretreated barley straw samples in a single pelleting unit. The pellet density, tensile strength, durability, dimensional stability, and color of the pellets were determined. Radio frequency-alkaline pretreatment with the use of 1% NaOH solution and a ratio of biomass: NaOH solution of 1:8 has significant effect ($P<0.05$) on the breakdown of the lignified matrix, resulting in pellets with superior physical characteristics. The steam exploded samples pretreated at higher temperatures (180°C) and retention time of 10 min resulted into pellets with good physical qualities.

Keywords: radio frequency, steam explosion, densification, biomass pellets, and alkaline pretreatment
DOI: 10.3965/j.ijabe.20140703.009

Citation: Kingsley L. Iroba, Lope G. Tabil, Shahab Sokhansanj, Venkatesh Meda. Producing durable pellets from barley straw subjected to radio frequency-alkaline and steam explosion pretreatments. Int J Agric & Biol Eng, 2014; 7(3): 68－82.

1 Introduction

The reliance on fossil fuel (coal and petroleum) of the energy infrastructure in most parts of the world causes serious environmental problems. In recent times, there has been a high level of consciousness and awareness to reduce the dependence on fossil fuels. There is tremendous interest and emphasis towards sustainable and environmentally friendly sources of alternative fuels[1]. As part of the strategies to lessen the severity of the above mentioned effect; reduce the carbon footprint and also enhance sustainability of energy supply, lignocellulosic biomass is one of the alternatives that is readily available, renewable, and carbon sink source of energy[2], with annual production of approximately 200 billion tonnes worldwide[3]. Lignocellulosic biomass straws are a major part of crop residues which are considered as important feedstocks for biofuel applications, because they have low nutritional value when used as feed for animals[4].

Lignocellulosic biomass is a complex formation of

Received date: 2014-02-15 **Accepted date:** 2014-04-11

Biographies: Lope G. Tabil, PhD, P.Eng, research interests: bioprocessing engineering, value-added engineering, post-harvest handling of crops, pre-processing and densification of biomass for biorefinery and conversion of lignocellulosic waste into bioproducts. Email: lope.tabil@usask.ca. **Shahab Sokhansanj**, PhD, P.Eng, research interests: feedstock engineering, focusing on harvesting, drying, fractionating, and densification of cellulosic biomass. Email: shahabs@chbe.ubc.ca. **Venkatesh Meda,** PhD, P.Eng. research interests: post-harvest engineering- storage, drying, extraction and processing of agricultural, food, feed and biological materials. Email: vem281@campus.usask.ca.

*** Corresponding author: Kingsley L. Iroba,** PhD candidate, Department of Chemical and Biological Engineering, University of Saskatchewan. Tel: +1-306-966-5318; Fax: +1-306-966-5334; Email: kli931@mail.usask.ca.

cellulose, hemicellulose, and lignin. The lignin (which is normally deposited at maturity) acts as an external cross-linked aromatic polymer based on phenylpropanoid units binding hemicellulose and cellulose with cellulose positioned at the inner core of the structure[5]. Modification of the structural arrangement of cellulose-hemicellulose-lignin matrix during the pretreatment process can enhance the binding characteristics of lignocellulosic straw biomass, without necessarily using any expensive artificial binder during pelletization[6]. Radio frequency (RF) heating has been used as a treatment method on lignocellulosic biomass[7], to inhibit the growth of fungus in wood samples in an industrial 40 kW dielectric oven at temperatures between 60℃ and 70℃ for 2 min[8]. RF has been successfully applied to leather drying[9], thermal therapy[10], and in other research fields such as food processing (blanching, tempering, pasteurisation, sterilisation) and medicine[11]. Recently, Izadifar et al.[12] demonstrated that RF can be used for the extraction of podophyllotoxin from rhizomes of *Podophyllum peltatum*. The use of steam explosion as a pretreatment method on the lignocellulosic biomass have been extensively studied by Toussaint[13]; Mosier et al.[14]; Tanahashi et al.[15]; Chornet[16]; Heitz et al.[17]; Chundawat[18]; Chum et al.[19]; Kaar et al.[20].

Biomass can either be used directly for combustion and co-firing for home heating, providing process heat for industrial facilities, generation of electricity, or application as liquid and gas fuels in the form of bioethanol or biogas, as well as a source of variety of bioproducts[2]. Production of energy from biomass will to a large extent complement energy from fossil fuel even if it cannot completely replace it in this century. Loose plant-based biomass has low bulk density depending on the plant species, particle density and particle size[21]. In their natural form, biomass crops are bulky and dispersed, hence they are difficult to handle and utilize as a fuel[22]. The bulk density of loose dry biomass cereal straw (wheat, barley) can be as low as 40 kg/m^3, 40-80 kg/m^3 for corn stover, and 250 kg/m^3 for some wood residues[23-24]. Biomass has energy content in the range of 16-20 MJ/kg for dry plant matter[23] Biomass as an energy source and as a feedstock for biorefineries does not present easy, economical and efficient transportation, handling and storage characteristics due to large volume requirements[22-23,25-26]. To reduce the production, transportation, and storage costs of biofuel, it is important to densify the biomass, while increasing its heating value per unit volume[23,27]. Densification, particularly pelletization, is an important strategy for the biomass market, because it improves the convenience and accessibility of biomass due to the uniform shape and size, clean, stable fuel. A pelletized biomass can be easily adopted into the direct-combustion or co-firing with coal, gasification, pyrolysis, and biomass-based conversion reactors[28-29]. Pelletization increases flowability of biomass products, decreases the porosity, spillage and wind loss, and improves its utilization performance[30-33]. Despite the difficulties of handling, the direct combustion of loose biomass in conventional combustion chambers is associated with very low thermal efficiency. Conversion efficiencies may be as low as 40% with widespread air pollution in the form of very fine particulates matters with increased risk of fire and explosions[23,34]. In order to develop a large-scale biomass unit, it is necessary to convert biomass into high-density and high-value solid format like pellets. Manufacturing good quality pellets, briquettes and cubes is largely thought as an art rather than a science by many operators[23,30]. Cost is a challenge in biomass densification because of the high energy consumption. Low production costs, high quality pellets and briquettes together with safe handling of biomass will make biomass competitive with fossil fuels.

The objective of this study was to investigate the effects of radio frequency-alkaline and steam explosion pretreatments on the physical characteristics (density, tensile strength, durability, and dimensional stability) of densified barley straw, which could be used as feedstock for the production of bio-energy via thermochemical process.

2 Materials and methods

2.1 Sample collection and preparation

Barley straw of the ‘Xena’ variety was obtained in October, 2009 from RAW Ag Ventures Limited, (Maymont, SK) and was grown at 52.667297°N and 107.794311°W. The straw was ground using a hammer mill (Glen Mills Inc., Maywood, NJ) with screen size of 1.6 mm to increase the surface area of the biomass. A dust collector (House of Tools, Model no. DC-202B, Saskatoon, SK) was connected to the outlet of the hammer mill to provide flow of the biomass in and out of the hammer mill, to control dust and collect the ground biomass during operation. The initial moisture content of the straw was 8.09% (mass fraction of total mass). The moisture content was measured based on ASABE standard method, ASAE S358.2 DEC1988 (2008). This test was performed in replicates of three. For details of the measurement, calculations, and results of the physical characteristics of the barley straw grind, see Iroba et al.[7].

2.2 Radio frequency pretreatment

The pretreatment was performed using radio frequency (RF) machine (1.5 kW and 27.12 MHz laboratory dryer, Strayfield, Theale, Reading, U.K.). To understand the interactions between the process and material variables, the study was based on a factorial experiment in a completely randomized design. The variables shown in Table 1 and a blown glass reactor (4.25 L volume) with the dimensions shown in Figure 1 were employed.

The ground barley straw samples and the 1% w/v NaOH solution were mixed thoroughly in the reactor based on the ratio indicated in Table 1. Selective heating (due to presence of aqueous solution which results in excitation to different levels at various locations within the reactor) can also be minimised by adequate mixing. For details of the radio frequency-assisted alkaline pretreatment see Iroba et al.[7].

Table 1 Material and operating variables during radio frequency alkaline pretreatment of ground barley straw using a blown glass reactor

Variables	Levels
Hammer screen size	1.6 mm
NaOH solution concentration	1% w/v
Biomass: NaOH solution ratio	1:4 - 110 g biomass and 440 g NaOH solution
	1:5 - 110 g biomass and 550 g NaOH solution
	1:6 - 100 g biomass and 600 g NaOH solution
	1:7 - 100 g biomass and 700 g NaOH solution
	1:8 - 90 g biomass and 720 g NaOH solution
Equilibration time	1 h
Temperature	70, 80, and 90 °C
Residence time	20 min

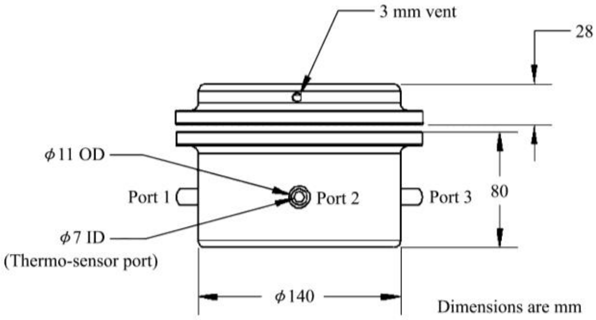

Figure 1 Schematic diagram of blown glass reactor used for radio frequency pretreatment of samples: ID – internal diameter, OD – outer diameter. The vent is use for pressure release, to avoid pressure build up within the reactor

2.2.1 Washing of the RF alkaline pretreated samples

Four treatment combinations were randomly selected for washing to remove the NaOH solution in the RF alkaline pretreated samples. After heating the mixture of biomass-NaOH solution in the RF machine, it was placed in a vacuum filter consisting of a perforated porcelain funnel 200 mL with Whatman filter paper (size 40). Tap water (approximately 1 L) was repeatedly used for the washing until the pH reached around 7.0. The RF alkaline pretreated washed samples were dried to 10% moisture content (mass fraction of total mass) using a forced-air convection dryer[35] set at 40°C.

2.3 Steam explosion pretreatment

Ground barley straw samples were re-conditioned to the desired moisture content by spraying a calculated amount of water on the samples, mixed thoroughly and kept in a conditioned environment (~6°C) for 48 h before the pretreatment process. Three process parameters were studied for the steam explosion (SE) treatment. These variables (temperature, moisture content, and retention time) were investigated to determine the optimum condition for steam explosion pretreatment of ground barley straw, to enhance formation of pellet with good quality characteristics. The experimental design was based on completely randomized approach, which resulted in eighteen treatment combinations. Table 2 shows the levels of these independent variables:

A temperature range of 140-180°C was selected to pretreat the biomass within the softening temperature range for lignin. It was reported that the softening temperature of lignin is in the range of 130-190°C, and the thermal stability of probable linkages between lignin and polysaccharides is compromised at temperatures above 200^{o}C[36]. Thermal degradation of lignin starts at 270-280^{o}C[36].

Table 2 Independent variables with corresponding levels used for the steam explosion pretreatment of ground barley straw

Variables	Levels
Temperature /^{o}C	140, 160, 180
Moisture content /% mass fraction of total mass	8, 30, 50
Retention time /min	5, 10

2.3.1 Steam explosion process description and operation procedures

The steam explosion pretreatment set up used for this investigation is located at the Clean Energy Research Center, University of British of Columbia. Figure 2 shows the process flow sheet of the closed system steam explosion batch unit.

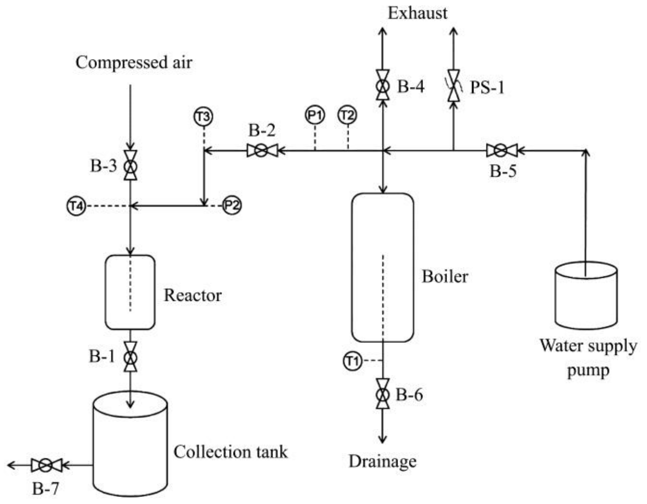

Figure 2 Process flow diagram of the closed system steam explosion unit (B: Ball valve, PS: Pressure relief valve, P: Digital pressure transducer, T: Thermocouple) [24]

Biomass of about 28-30 g was loaded through the small opening (about 10 mm) at the top of the reactor. The unit consisted of a 2 L steam generator, which generates saturated steam, and a 1 L reactor for steaming lignocellulosic biomass feedstock. A 3 zone tubular furnace (Lindberg/Blue M, STF55666C, Thermo Fisher Scientific Inc., Waltham, MA) was used for the generation of the steam heat. The 1 L reactor was equipped with a 12.7 mm diameter ball valve, controlled by an electrical actuator for sudden discharge of the treated biomass into the collection vessel at ambient pressure. The service and maintenance heat of the reactor and the steamline were supplied by a temperature controller. The details and functions of valves in the experimental setup unit are summarized elsewhere[37]. Temperatures and pressures were measured by 1.6 mm diameter K-type thermocouples (Omega, Stamford, CT) and digital pressure transducers (Omega, Stamford, CT), respectively. Data were collected by LabView 8.2 software (National Instruments, Austin, TX). The collected steam exploded solid biomass product was weighed to determine the mass loss or gain and kept in sealed Ziploc^{TM} containers at 6^{o}C for further analysis. Each test was replicated twice. For details of the steam explosion pretreatment see Iroba et al[38].

2.4 Densification of RF-assisted alkaline and steam exploded pretreated and non-treated samples

To evaluate the efficiency of the RF-assisted alkaline and steam explosion pretreatment processes, densification of the pretreated and non-treated samples was performed. The samples were densified using a single pelleting unit mounted in an Instron tester (Model No. 3366, Instron Corp., Norwood, MA). This unit included a steel cylindrical die with a plunger/piston connected to the upper moving crosshead which provides the load necessary to compress the biomass samples. The die is surrounded with a heating element to provide the required heat for the process. About 500-700 mg of the biomass feedstock was loaded into the die cylinder. The pre-set load (4 kN) and the required temperature (95±0.3)^{o}C were adjusted to compress the charge material. Once the pre-set load was achieved, the plunger was stopped and held in position for 60 s retention time to avoid spring-back effect of biomass[25], thereafter, the pellet was ejected. The Instron was typically set to lower the plunger (and compress the biomass) at a rate of 50 mm/min. The single pelleting unit was connected to a computer which recorded the time and force-displacement data. Eighteen replicates were produced for each sample. The pellets were stored at room condition (to simulate the real condition during storage or transportation) for further analysis.

2.4.1 Durability test

The durability of the pellets was measured after two weeks of storage, by dropping the pellets from a height of

1.85 m[39]. This represents the agitation, rotating, shear, impact, and tumbling during transportation, storage and handling. The percentage durability was calculated by dividing the remaining piece by the original mass and multiplied by 100. Ten replicates were made for each sample.

2.4.2 Tensile strength

Diametral compression test was used to evaluate the tensile strength of the pellets[8] using the Instron tester. Pellets were cut diametrically using a scalpel into specimens with thickness of about 2.50 mm. The specimen was placed on its edge on the lower padded plate and compressed with 1 000 N load cell by the upper plunger (also padded) at a crosshead speed of 1 mm/min until failure occurred. Fractures that caused the specimens to break or crack in two halves along the loading axis were accepted and other fracture types were discarded[40,41]. Upon failure, the fracture force was recorded and the tensile strength of tablets was calculated using Equation (1) below. Ten replicates were made for each sample.

$$\delta_x = \frac{2F}{\pi d l} \tag{1}$$

where, δ_x is tensile (horizontal) stress (Pa); F the load at fracture (N); d the specimen diameter (6.67 mm), and l the specimen thickness (mm).

2.4.3 Pellet density and dimensional stability

The mass, length, and diameter of the pellets were measured immediately after pelleting and after 14 d of storage. These parameters were used to calculate the density. The change in density after two weeks of storage was used to evaluate the dimensional stability of the pellets.

2.5 Color measurement

The color difference between the pretreated and non-treated was measured and compared using the HunterLab Color Analyzer (Hunter Associates Laboratory Inc, Reston, VA). The color was characterized using a three-dimensional color parameters (CIE L^*, a^* and b^*). The scale L^* ranges from 0 for black to +100 for white. The a^* and b^* have no specific numerical limits; Positive a* is red; Negative a^* is green; Positive b^* is yellow; Negative b^* is blue. The total color difference, ΔE^*, was also computed using Equation (2)[42]. This single value takes into account the differences between the L^*, a^*, and b^* of the pretreated and the control (non-treated) material. Three replicates were performed for each sample.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

$\Delta L^* = L^*_{\text{Treated}} - L^*_{\text{NT}}$; $\Delta a^* = a^*_{\text{Treated}} - a^*_{\text{NT}}$; $\Delta b^* = b^*_{\text{Treated}} - \text{b}^*_{\text{NT}}$. These parameters ΔL^*, Δa^*, and Δb^* indicate how much the non-treated (NT) and the pretreated differ from one another in L^*, a^*, and b^*.

2.6 Statistical analysis

2.6.1 Analysis of variance (ANOVA)

Linear regression was performed on the collected data to investigate the main effects of the independent variables on the dependent variables at 95% confidence level using IBM SPSS Statistics (Superior Performing Statistical Software, version 20 for Windows, 2012; IBM, Armonk, New York, NY). Further analysis was also performed to evaluate the effects of the interaction among the independent variables on the response variables.

2.6.2 Tukey's statistical comparison of means on pellet properties

ANOVA shows if the independent variables have significant effect or not on the dependent variables. However, the ANOVA does not indicate where the differences lie. For this reason, there is a need to carry out one more statistical analysis to elucidate the mean differences. Statistical comparison of means using the Tukey's test method was performed on density, durability, tensile strength, and fracture load to evaluate the mean differences among the variables.

3 Results and discussion

3.1 Force-time densification profile

Figure 3 depicts the densification profile (force-time graph) of a ground barley straw sample. A-E represents the different stages of the densification process. The starting stage of the process is represented by A which is prior to application of pressure on the biomass grind. The three main stages involved during the densification process upon the application of pressure as summarized by Tabil[8] are represented by B-D. The particle rearrangement and elastic and plastic deformation are represented by B-C. Particle rearrangement involves the rearrangement of the particles and breaking down the initial unstable packing arrangements, which is often called ‘arches’ or ‘bridges’; this stage happens at low pressures resulting to a closer packing. The initial physical qualities of the original particles are maintained. Energy is expended as a result of particle-wall friction. The elastic and plastic deformation happens at higher pressures and involves two stages that correspond to elastic and plastic deformation. Due to the higher pressures, the particles are force to flow into the existing void spaces, resulting in porosity decrease which increases the contact area between the particles. At this point, if the pressure is released, the particles can recover their former state (elastic deformation). Continuous application of the pressure leads to particle fracture into fragments, followed by rearrangement of the fragments (plastic deformation). This stage progresses until the compact density is close to the solid density of the material. The third stage where the predefined retention time is applied involves the mechanical interlocking of particles and local melting of some constituents, which may result from the two earlier stages above. This stage is represented by C-D. Local melting of the materials occurs if the melting points of the constituents (such as lignin) are reached, causing binding. If this stage is not reached, it can lead to disintegration of the pellets/briquettes[22]. DE represents the instantaneous time when the ejection of the produced pellet was initiated. The drop from D to E is gradual when the produced pellet is expelled from the die.

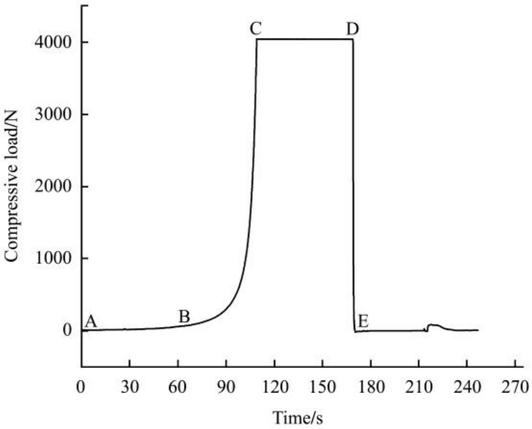

Figure 3 Typical force-time densification profile of ground barley straw sample

3.2 Durability rating, tensile strength, and fracture load - RF-assisted alkaline pretreated samples

3.2.1 Durability rating

The disruption and deconstruction resulting from the interaction between NaOH solution and the biomass matrix in the presence of RF heating assisted in improving the binding characteristics. It also seems that the disruption and deconstruction of the lignified matrix is associated with the dipole interaction, flip flop rotation, and friction generated between the electromagnetic charges from the RF radiation and the ions and molecules from the NaOH solution and the biomass[7]. During the alkaline pretreatment process, the ester bonds between lignin and the complex carbohydrates (cellulose and hemicellulose) are disrupted, some portion of lignin is broken down, degraded, and perhaps solubilised[7]. It also enhanced compressing the pretreated ground barley straw sample upon application of pressure and heat at a predefined residence time. Table 3 shows the durability, tensile strength, and the fracture load values of the produced pellets. RF-assisted alkaline pretreatment with 1% w/v NaOH concentration produced pellets with higher durability, tensile strength, and fracture load as compared to the non-treated ground barley straw. This was a result of the swelling pores created on the biomass matrix during the RF alkaline pretreatment process, and subsequently made the binder (lignin) easily accessible during the densification process. Statistical analysis shows that the use of NaOH solution significantly affected ($P<0.05$) the quality of the produced pellets. Nlewem and Thrash[43] reported that the swelling initiated by NaOH created pores on the biomass matrix which helps in enhancing the accessibility of the soluble lignin. The observed data shows that temperature and the ratio of biomass to NaOH solution influences the durability of the produced pellet. Almost in all cases, higher temperature and lower ratio of biomass:NaOH solution resulted in higher durability of the produced pellets. Higher temperature helps in the local melting of some constituents[22], which subsequently enhanced the production of pellets with good physical characteristics. Decreasing the ratio of biomass:NaOH solution (e.g. 1:8) correspondingly enhanced more reactivity and activity within the biomass matrix leading to the subsequent release of the natural binder (soluble lignin). During compression and compaction of biomass, the smaller (fine) particles rearrange and fill in the void space of larger (coarse) particles therefore producing denser and more durable compacts[22]. Analysis of variance shows that the interaction between temperature and ratio of biomass:NaOH solution have significant effects ($P<0.05$) on the durability of the produced pellets. Based on the available collected data from this investigation, RF alkaline pretreatment with ratio 1:8 at the three investigated temperatures represented the optimum condition for producing pellets with better durable features. RF assisted alkaline pretreatment increased the durability of produced pellets by up to 57% over that of pellets from non-pretreated biomass.

Table 3 Durability, tensile strength, and fracture load of pellets made from RF-alkaline pretreated ground barley straw

Temperature /^{o}C	NaOH conc. /%	Biomass: NaOH solution ratio	Durability /%	Tensile Strength /MPa	Fracture load /N
24^{NT}	-	-	$63.37(3.40)^{a}$	$0.27(0.04)^{A}$	$7.11(1.01)^{f}$
	1	1:6	$65.63(2.68)^{a}$	$0.82(0.12)^{B}$	$21.57(3.08)^{g}$
	1	1:7	$72.64(5.61)^{c}$	$0.86(0.12)^{B}$	$22.76(3.26)^{g}$
70	1	1:4	$65.80(3.55)^{a}$	$0.67(0.14)^{A}$	$17.54(3.77)^{f}$
	1	1:5	$65.92(4.39)^{a}$	$0.87(0.13)^{AC}$	$22.92(3.31)^{g}$
	1	1:6	$66.22(2.27)^{a}$	$0.64(0.10)^{A}$	$16.89(2.68)^{f}$
	1	1:7	$70.34(3.60)^{b}$	$0.99(0.12)^{BC}$	$26.09(3.28)^{g}$
	1	1:8	$91.37(4.59)^{c}$	$1.30(0.15)^{D}$	$34.19(4.01)^{h}$
80	1	1:4	$66.44(4.17)^{ab}$	$0.68(0.12)^{AB}$	$17.92(3.19)^{f}$
	1	1:5	$68.67(5.87)^{ad}$	$0.95(0.10)^{AC}$	$25.01(2.66)^{gik}$
	1	$1:5^{W}$	$64.10(2.96)^{bf}$	$0.45(0.0)^{BE}$	$11.76(1.84)^{h}$
	1	1:6	$68.59(2.40)^{ad}$	$0.91(0.08)^{C}$	$24.04(2.17)^{gk}$
	1	1:7	$71.09(2.20)^{d}$	$1.06(0.11)^{C}$	$27.98(2.87)^{i}$
	1	$1:7^{W}$	$71.99(2.92)^{d}$	$0.80(0.11)^{C}$	$20.92(2.85)^{j}$
	0	$1:7^{DW}$	$60.36(1.60)^{e}$	$0.83(0.10)^{C}$	$21.82(2.55)^{jk}$
	0	$1:7^{TW}$	$62.79(1.87)^{f}$	$0.39(0.07)^{E}$	$10.20(1.91)^{h}$
	1	1:8	$85.99(5.56)^{g}$	$1.39(0.13)^{F}$	$36.68(3.31)^{l}$
90	1	1:4	$57.19(4.23)^{a}$	$0.62(0.13)^{A}$	$16.23(3.34)^{fh}$
	1	1:5	$71.31(3.87)^{b}$	$0.91(0.10)^{BC}$	$23.94(2.55)^{g}$
	1	$1:5^{W}$	$64.69(3.18)^{c}$	$0.52(0.05)^{A}$	$13.58(1.42)^{f}$
	1	1:6	$71.67(3.19)^{b}$	$0.75(0.11)^{BD}$	$19.65(2.90)^{h}$
	1	1:7	$82.97(3.18)^{d}$	$1.03(0.13)^{C}$	$27.09(3.43)^{i}$
	1	$1:7^{W}$	$78.61(1.98)^{e}$	$0.63(0.09)^{AD}$	$16.51(2.44)^{fh}$
	1	1:8	$99.17(0.40)^{f}$	$1.67(0.19)^{E}$	$43.82(4.92)^{j}$

Note: Value in parenthesis is standard error; n = 10; Conc. = concentration; W = washed; DW = distilled water; TW = tap water; NT = non-treated biomass; Means with the same superscript letter within the same set (same temperature) in the same column are not significantly different with respect to ratio of biomass:NaOH solution using Tukey's Mean Comparison Test. The mean difference is significant at the 5% significance level.

3.2.2 Tensile strength and fracture load

The already released or broken down lignin components assisted in the particle binding mechanisms and behavior resulting in higher tensile strength and fracture load. The softening of the RF alkaline pretreated sample enhanced the creation of the mechanical interlocking of the biomass particles and supported the strength of the bonds between the adhering partners upon application of pressure and temperature. Kashaninejad and Tabil[44] reported that pellets made from barley straw pretreated with microwave technique with 1% w/v NaOH have higher tensile strength and fracture load compared to the non-treated samples. The authors reported that the pellets have 2.36 MPa and 53.63 N as tensile strength and fracture load, respectively. These researchers used biomass: NaOH solution ratio of 1:9 as against the lowest ratio of 1:8 used in this present investigation, this may account for the difference in the tensile strength and fracture load values. The samples pretreated with water (distilled or tap) have lower tensile strength and fracture load. This is due to the hydrophobic nature of the lignin matrix, which implies that just water and heat are not enough to breakdown the lignocellulosic matrix. The ratio of biomass:NaOH solution affects the tensile strength and fracture load of the pellets. The lower the ratio, the better the tensile strength and fracture load. RF alkaline pretreatment increased the tensile strength and fracture load of produced pellets by up to 518% and 516%, respectively, over that of pellets from non-pretreated biomass. Temperature also plays a vital role on the tensile strength and fracture load, which depends on the interaction with the ratio of biomass:NaOH solution. Analysis of variance performed on the data shows that temperature, ratio of biomass to NaOH solution, and the interaction between the two variables have significant effects ($P<0.05$) on the tensile strength and fracture load of the produced pellets. Ratio 1:8 at the three investigated temperatures represents the optimum yield of pellet with better compressive strength and fracture load.

Iroba et al.[7] reported that the use of 1% w/v NaOH solution increased the ash content of the RF pretreated biomass by about 60% to 140% depending on the ratio of biomass to NaOH solution. The ash content increased with the decreasing ratio of biomass to NaOH solution. This is primarily due to the high concentration of mineral content of sodium in the NaOH solution at lower ratio. This problem of increased ash content can be addressed by washing the pretreated samples. Washing the pretreated samples reduced the ash content by about 25%-55% depending on the ratio of biomass to the NaOH solution. However, washing of the RF pretreated samples reduced the durability, tensile strength, and fracture load of the produced pellets, which may be a result of loss of the soluble lignin (biomass binding agent) during the washing process. It reduced the durability and strength of the pellets by about 5.26%-9.28% and 25%-53%, respectively, depending on the treatment combinations.

3.3 Durability, tensile strength, and fracture load – steam explosion pretreated samples

Table 4 shows the durability, tensile strength, and the fracture load values of the pellets produced from the steam exploded and non-treated biomass. The observed data shows that temperature and retention time are important process conditions for the physical characteristics of the pellets. The higher the temperature and retention time, the higher the durability, tensile strength, and fracture load of the pellets. High temperature and long retention time helped in the local melting of some constituents (such as lignin), which subsequently enhanced the production of pellets with good physical characteristics. The analysis of variance shows that temperature significantly affected ($P<0.05$) the durability of the pellets. Temperature, retention time, and the interaction between temperature and retention time have significant effect ($P<0.05$) on the tensile strength and fracture load of the produced pellets. At lower temperature (140-160°C), increase in the moisture content tended to decrease the quality of the pellets because it takes longer time and higher energy to evaporate the moisture before the local melting of some constituents. However, at higher temperature (180°C) increase in the moisture content contribute positively to the durability, tensile strength, and fracture load of the produced pellets. This may be due to higher temperature enhances higher removal rate of moisture from the pretreated biomass, as such the optimum moisture (8%-10% mass fraction of total mass) of the pretreated biomass was achieved, which is needed for a good interlocking/ binding of the charged particles to take place, as well as avoiding spring back effect. While at lower temperature, the moisture content of the pretreated biomass was higher than the optimal, therefore, resulting in a lower physical property of the produced pellets.

Based on the available data collected from this investigation, steam explosion pretreatment increases the durability, tensile strength, and fracture load of the produced pellets by up to 22%, 488%, and 481%, respectively, over that of pellets from non-pretreated biomass.

Table 4 Durability, tensile strength, and fracture load of pellets made from steam explosion pretreated ground barley straw

Temperature /°C	Moisture content /%*	Retention time /min	Durability /%	Tensile strength /MPa	Fracture load /N
24^{NT}	8	-	60.01(3.07)	0.34(0.06)	9.06(1.45)
140	8	5	60.64(1.42)^{a}	0.34(0.05)^{A}	9.00(1.24)^{f}
	30	5	58.99(3.31)^{a}	0.29(0.04)^{A}	7.57(0.96)^{f}
	50	5	55.46(4.43)^{a}	0.28(0.03)^{A}	7.40(0.82)^{f}
	8	10	61.99(3.97)^{a}	0.45(0.07)^{A}	11.87(1.90)^{f}
	30	10	63.01(3.29)^{a}	0.31(0.02)^{A}	8.50(0.39)^{f}
	50	10	58.17(4.06)^{a}	0.42(0.07)^{A}	11.07(1.72)^{f}
160	8	5	62.08(4.28)^{ad}	0.39(0.03)^{A}	9.70(0.87)^{f}
	30	5	59.97(2.20)^{a}	0.32(0.07)^{A}	9.03(1.85)^{f}
	50	5	59.96(4.65)^{a}	0.33(0.08)^{A}	9.39(2.00)^{f}
	8	10	72.64(4.04)^{b}	0.67(0.14)^{B}	17.62(3.57)^{g}
	30	10	66.13(3.30)^{cd}	0.46(0.08)^{C}	11.99(2.08)^{f}
180	8	5	66.23(4.82)^{a}	0.61(0.11)^{AC}	16.16(2.89)^{f}
	30	5	68.13(5.61)^{a}	0.95(0.11)^{BD}	24.90(2.95)^{gh}
	50	5	70.77(3.41)^{ac}	0.78(0.10)^{CD}	20.53(2.73)^{fg}
	8	10	73.03(4.27)^{bc}	1.00(0.13)^{D}	26.39(3.42)^{h}
	30	10	69.28(5.12)^{ac}	1.57(0.17)^{E}	41.29(4.49)^{i}
	50	10	72.39(3.08)^{c}	2.00(0.25)^{F}	52.61(6.59)^{k}

Note: Value in parenthesis is standard error; $n = 10$; * = % mass fraction of total mass; NT = non-treated biomass; Means with the same superscript letter within the same set (same temperature) in the same column are not significantly different with respect to moisture content and retention time using Tukey's Mean Comparison Test. The mean difference is significant at the 5% significance level.

3.4 Pellet density and dimensional stability – RF assisted alkaline pretreated samples

Table 5 shows the density, % density change, and dimensional stability values of the pellets produced from the RF assisted alkaline pretreated and non-treated samples. Samples pretreated with 1% w/v NaOH concentration have higher density than the non-pretreated sample. This is due to the released of the binding agent (lignin) which increased the adhesion between the particles, favored the generation of the intermolecular bonds within the contact area of the biomass particles, and subsequently enhances the mechanical interlocking of the particles. A similar result was reported by Kashaninejad and Tabil[44]. The authors reported that the pellets have 1371 kg/m^3 and 995 kg/m^3 as the initial density of the microwave alkaline pretreated and non-treated barley straw grind, respectively. These researchers used 1% NaOH with ratio 1:9 of biomass to NaOH solution. When biomass is subjected to heat, lignin tends to become soft, melts and exhibits thermosetting binder resin properties to produce pellets with higher density and dimensional stability[22]. The pretreatment temperature and ratio of biomass:NaOH solution played a predominant role in producing pellets with high density. The three investigated temperatures (70-90^{o}C) and low biomass:NaOH solution ratio (1:8) resulted to higher pellet density. Analysis of variance shows that temperature, ratio of biomass:NaOH solution and the interaction between the two variables have significant effects (P<0.05) on the density and dimensional stability of the produced pellets. Washing of the pretreated samples also seems to decreased the pellet density. This might be also due to the reason that the available released soluble lignin was washed away during the washing process. The positive and negative % density change in Table 5 corresponds to diametric or longitudinal expansion and contraction, respectively, of the pellets after two weeks of storage. Pellets with diametric or longitudinal expansion resulted in density decrease, while pellets with diametric or longitudinal contraction led to density increase. The pellets density was obtained from mass per unit volume, and volume was calculated from the diameter and height of the pellets ($\pi r^2 h$). Therefore, any change in diameter and the height will have a corresponding effect on the density, which also translated into the dimensional stability of the produced pellets. The lesser the % density change, the better the dimensional stability of the produced pellets. The percentage of density change and dimensional stability showed that RF alkaline pretreatment was effective at all the temperatures and ratios studied. The density increase was about 9% to 35% over that of pellets from non-pretreated biomass, with percentage density change of -2.93% to 2.26%, and 97.74% to 102.93% dimensional stability. This implies that all the pellets produced from the RF alkaline pretreated samples will present easy, economical, and efficient transportation, handling, storage characteristics (less volume requirements), and utilization as a fuel. They can also withstand the shear, impact, rotation, and tumbling during the transportation stage, without causing wide spread of air pollution in the form of very fine particulate matters as described by Tabil[22,25-26,34]. This also implies that RF alkaline pretreatment can enhance the biomass volumetric calorific/heating value per unit volume, which can be easily adopted into the direct-combustion or co-firing with coal, gasification, pyrolysis, and biomass-based conversion reactors[28-29]. RF assisted alkaline pretreatment increases the pellet density by up to 35% over that of pellets from non-pretreated biomass. This will further increase the thermal and conversion efficiency by a similar percentage factor. In this current investigation, ratio 1:8 at the three levels of investigated temperatures represented the optimum yield of the pellets density. Treatment combinations of ratio 1:6 and 1:7 at room temperature resulted in producing pellets with good physical quality characteristics. This shows that biomass can be pretreated even at room temperature if the required optimum ratio of biomass:NaOH solution is used with the required pretreatment retention time. From the statistical analysis performed on the collected data, the ratio of biomass:NaOH solution presented to be more significant than temperature on the density, durability, and tensile strength.

3.5 Pellet density and dimensional stability - Steam explosion pretreated samples

Similar changes were observed in the density and dimensional stability of pellets produced from the SE pretreated samples. However, the pellets density produced from the steam exploded samples are not as high as the pellets density produced from the RF-assisted alkaline pretreated samples. The pretreatment temperature and retention time play a pre-dominant role in producing pellets with good physical properties. The higher the temperature and retention time, the higher were the pellet density and dimensional stability values. At higher temperature, there is a characteristic softening and exhibition of thermosetting binder resin properties in biomass that enhances the production of pellets with good physical qualities[22]. Statistical analysis shows that temperature, retention time, and the interaction of both variables significantly affected ($P<0.05$) the density and dimensional stability of the produced pellets. Increasing the moisture content at lower temperature (140-160°C) decreases the density and dimensional stability of the produced pellets. High moisture at lower temperature tends to create a buffer effects, damp the biomass and prevent lignin from getting to it melting point. However, increasing the moisture content at higher temperature (180°C) led to higher density and dimensional stability. This implies that optimum window of moisture content of biomass is required for the manufacture of dimensionally stable and high density pellet. At a required temperature, water acts as a binding agent by strengthening the bonding in the material. Water helps to develop van der Waals forces by increasing the area of contact between particles[34]. Analysis of variance shows that moisture content and the interaction of moisture content, temperature, and retention time significantly affected ($P<0.05$) the density and dimensional stability of the produced pellets. The density increase from the non-pretreated biomass sample to the steam explosion pretreated was about 25%.

Table 5 Pellet density, density change, and dimensional stability during two weeks of storage of RF alkaline pretreated and non-treated ground barley straw

Temperature/°C	NaOH conc./%	Biomass:NaOH solution ratio	Density1/kg m^{-3}	Density2/kg m^{-3}	Density change/%	Dimensional stability/%
24^{NT}	-	-	1004.49(1.61)^{a}	995.19(2.21)^{A}	0.93	99.07
	1	1:6	1230.29(0.94)^{b}	1220.82(1.69)^{B}	0.77	99.23
	1	1:7	1252.25(1.05)^{b}	1244.33(1.39)^{B}	0.63	99.37
70	1	1:4	1129.82(2.18)^{a}	1113.24(2.06)^{A}	1.47	98.53
	1	1:5	1165.09(1.70)^{a}	1154.87(1.75)^{A}	0.88	99.12
	1	1:6	1175.70(1.49)^{a}	1167.52(1.94)^{B}	0.70	99.30
	1	1:7	1180.15(12.05)^{a}	1214.68(7.62)^{C}	-2.93	102.93
	1	1:8	1324.71(2.14)^{b}	1309.10(2.31)^{D}	1.18	98.82
80	1	1:4	1154.88(1.37)^{a}	1142.20(2.26)^{A}	1.10	98.90
	1	1:5	1222.76(3.65)^{b}	1212.84(2.77)^{BC}	0.81	99.19
	1	1:5^{W}	1136.82(1.54)^{a}	1127.16(2.18)^{A}	0.85	99.15
	1	1:6	1239.29(1.39)^{b}	1225.19(1.39)^{B}	1.14	98.86
	1	1:7	1215.34(3.30)^{bc}	1213.83(2.25)^{BC}	0.12	99.88
	1	1:7^{W}	1171.33(5.31)^{ac}	1174.08(3.78)^{AC}	-0.23	100.23
	0	1:7^{DW}	1007.50(2.13)^{d}	1000.45(1.78)^{D}	0.70	99.30
	0	1:7^{TW}	989.95(3.33)^{d}	974.79(2.96)^{D}	1.53	98.47
	1	1:8	1342.82(1.24)^{e}	1326.98(1.69)^{E}	1.18	98.82
90	1	1:4	1108.69(3.46)^{a}	1083.59(2.11)^{A}	2.26	97.74
	1	1:5	1201.40(3.79)^{b}	1213.48(1.70)^{B}	-1.01	101.01
	1	1:5^{W}	1205.89(2.58)^{b}	1178.69(2.84)^{B}	2.26	97.74
	1	1:6	1180.15(3.39)^{b}	1167.54(3.08)^{B}	1.07	98.93
	1	1:7	1270.22(2.53)^{c}	1263.88(2.01)^{C}	0.50	99.50
	1	1:7^{W}	1205.81(1.45)^{b}	1200.35(1.59)^{B}	0.45	99.55
	1	1:8	1358.39(1.34)^{d}	1342.91(2.02)^{D}	1.14	98.86

Note: Value in parenthesis = standard error; *n* = 18, NT = non-treated; Conc. = concentration; Density1 = density of pellets immediately after the pelleting, & Density2 = density of pellets after two weeks of storage at room condition; Means with the same superscript letter within the same set (same temperature) in the same column are not significantly different with respect to ratio of biomass:NaOH solution using Tukey's Mean Comparison Test. The mean difference is significant at the 5% significance level.

Table 6 Pellet density, density change, and dimensional stability during two weeks of storage of steam exploded pretreated and non-treated ground barley straw

Temperature/^{o}C	Moisture content/%*	Retention time/min	Density1/kg m^{-3}	Density2/kg m^{-3}	Density change/%	Dimensional stability/%
24^{NT}	8	-	942.57 (9.68)	907.46 (9.34)	3.72	96.28
140	8	5	944.32 (3.88)^{a}	928.83 (4.46)^{A}	1.64	98.36
	30	5	906.70 (8.57)^{a}	862.68 (7.60)^{B}	4.86	95.14
	50	5	936.80 (9.66)^{a}	843.99 (6.14)^{B}	9.91	90.09
	8	10	958.93 (3.70)^{a}	929.35 (5.87)^{A}	3.08	96.92
	30	10	906.59 (5.86)^{a}	828.31 (8.76)^{B}	8.63	91.37
	50	10	932.10 (5.57)^{a}	851.29 (11.01)^{B}	8.67	91.33
160	8	5	898.57 (10.52)^{a}	856.73 (13.30)^{A}	4.66	95.34
	30	5	954.63 (3.44)^{a}	937.69 (3.56)^{B}	1.77	98.23
	50	5	958.02 (3.74)^{a}	887.15 (5.15)^{AB}	7.40	92.60
	8	10	1035.05 (6.08)^{b}	1020.26 (6.84)^{C}	1.43	98.57
	30	10	938.57 (7.20)^{a}	862.07 (8.15)^{A}	8.15	91.85
180	8	5	1040.80 (9.56)^{a}	1005.86 (7.20)^{A}	3.36	96.64
	30	5	1086.45 (4.74)$_{a}$	1038.58 (5.02)^{A}	4.41	95.59
	50	5	1060.89 (3.55)^{a}	1011.87 (7.91)^{A}	4.62	95.38
	8	10	1177.38 (3.65)^{b}	1147.04 (4.46)^{B}	2.58	97.42
	30	10	1174.35 (3.49)^{b}	1150.87 (3.75)^{B}	2.00	98.00
	50	10	1152.08 (5.47)^{b}	1146.55 (5.88)^{B}	0.48	99.52

Note: Values in parentheses is standard error; n = 10; * = % mass fraction of total mass; NT = non-treated biomass; Means with the same superscript letter within the same set (same temperature) in the same column are not significantly different with respect to moisture content and retention time using Tukey's Mean Comparison Test. The mean difference is significant at the 5% significance level.

3.6 Color analysis

3.6.1 Radio frequency-alkaline pretreated samples

Table 7 shows the mean values of the color parameters of L^*, a^*, and b^* of the RF-alkaline pretreated and non-treated ground barley straw. Color characteristics of the pretreated samples are through reflection of the degree of the pretreatment conditions. The alkaline solution and ratio of biomass:NaOH solution are the key variables responsible for the color changes. The degree of lightness (L^*) and yellowness (b^*) decreased as the ratio of biomass:NaOH solution decreases from 1:4 to 1:8, indicating that the samples become more brownish. Increasing temperature increased the darkness and blueness of the samples; however, this was not the case for all the treatment combinations.

Washing the RF alkaline pretreated samples increases the lightness and yellowness of the samples. The redness (a^*) of the RF alkaline pretreated samples increased with decreasing ratio of biomass:NaOH solution and increasing temperature. Washing decreases the redness of the samples and makes it to become greener. The lightness (L^*) of the non-treated samples are higher but lower for the scale parameter a^* and b^* compared to the RF alkaline pretreated samples. The total color difference (ΔE^*) between the RF alkaline pretreated and non-treated samples increases with decreasing ratio of biomass:NaOH solution; however, this was also not the case for all the treatment combinations. The effect of temperature on color difference is not as much as that of ratio. Washing reduces the total color difference.

3.6.2 Steam explosion pretreated samples

Table 8 shows the mean values of the color parameters of L^*, a^*, and b^* of the steam exploded and non-treated samples. The collected data indicates that color characteristics of the pretreated samples are associated with the severity of the pretreatment conditions. The lightness (L^*) of steam exploded ground barley straw decreased with increasing temperature and retention time. This implies that, the higher the severity of the pretreatment conditions, the darker the pretreated samples. In most cases, the yellowness of the steam exploded samples decreased with increasing temperature and retention time, except for samples pretreated at 160°C, moisture content of 8%-30% (mass fraction of water) and at 5-10 min retention time.

Table 7 Color characteristics of radio frequency alkaline and non-treated ground barley straw

Temperature /°C	NaOH conc. /%	Biomass: NaOH solution ratio	*L**	*a**	*b**	Δ*E**
24^{NT}	-	-	63.22(0.25)	7.32(0.01)	21.90(0.12)	-
	1	1:6	54.17(0.01)	7.64(0.01)	34.44(0.01)	15.47(0.25)
	1	1:7	53.62(0.02)	7.90(0.00)	34.31(0.02)	15.70(0.25)
70	1	1:4	54.45(0.01)	7.71(0.00)	35.14(0.00)	15.89(0.24)
	1	1:5	51.98(0.01)	7.75(0.00)	33.79(0.01)	16.37(0.26)
	1	1:6	51.88(0.00)	8.07(0.00)	33.61(0.01)	16.32(0.26)
	1	1:7	50.38(0.01)	8.45(0.00)	33.60(0.01)	17.41(0.27)
	1	1:8	50.99(0.01)	8.52(0.01)	33.72(0.01)	17.05(0.26)
80	1	1:4	54.60(0.01)	7.81(0.01)	33.96(0.01)	14.83(0.24)
	1	1:5	52.97(0.01)	7.81(0.00)	34.68(0.01)	16.39(0.25)
	1	$1:5^{W}$	61.55(0.00)	6.61(0.00)	30.10(0.01)	8.40(0.18)
	1	1:6	50.79(0.01)	8.60(0.00)	33.94(0.01)	17.35(0.27)
	1	1:7	51.11(0.00)	8.46(0.01)	33.61(0.01)	16.88(0.26)
	1	$1:7^{W}$	60.71(0.01)	6.19(0.00)	30.46(0.03)	9.00(0.21)
	0	$1:7^{DW}$	58.45(0.33)	7.43(0.00)	26.40(0.02)	3.05(0.26)
	0	$1:7^{TW}$	60.24(0.01)	7.65(0.01)	22.45(0.01)	6.57(0.44)
	1	1:8	50.12(0.01)	8.73(0.01)	33.68(0.03)	17.67(0.27)
90	1	1:4	53.04(0.01)	8.00(0.10)	33.89(0.41)	15.75(0.06)
	1	1:5	51.32(0.01)	8.21(0.00)	34.14(0.02)	17.10(0.26)
	1	$1:5^{W}$	60.32(0.01)	6.37(0.01)	31.14(0.02)	9.73(0.20)
	1	1:6	51.51(0.01)	8.26(0.00)	33.52(0.00)	16.52(0.26)
	1	1:7	50.39(0.01)	8.83(0.00)	32.66(0.00)	16.81(0.27)
	1	$1:7^{W}$	60.79(0.00)	6.36(0.01)	29.45(0.03)	7.99(0.22)
	1	1:8	49.60(0.02)	8.61(0.01)	32.95(0.01)	17.58(0.26)

Note: Value in parentheses = standard error; number of replicates, *n* = 3; conc. = concentration; The scale *L** represents from 0 for black to +100 for white; The *a** and *b** have no specific numerical limits; Positive *a** is red; Negative *a** is green; Positive *b** is yellow; Negative *b** is blue; and Δ*E** = total color difference.

Increasing blueness also signifies that the samples get darker as the severity of pretreatment increased with respect to increasing temperature and retention time. The lightness (*L**) and yellowness (*b**) of the non-treated ground barley straw are higher as compared to the steam pretreated samples. The calculated differential color composite Δ*E** is a good indicator of color deviation between pretreated and non-treated samples. The total color difference between the steam exploded and non-treated samples increases with increasing temperature and retention time. The highest total color difference was observed at 180°C. Zhang and Cai[45] reported that the color changes observed in wood during steam treatment were as a result of series of chemical reactions. These are primarily due to the reactions between the chemical constituents of wood cell wall and extractives under high temperature and humidity conditions. Cellulose and hemicellulose are polysaccharides that can cause significant changes at a critical temperature of 120°C. Cellulose degrades to yellow when the temperature is above 140°C[45].

Table 8 Color characteristics of steam exploded and non-treated ground barley straw

Temperature /°C	Moisture content /%*	Retention time /min	*L**	*a**	*b**	Δ*E**
NT	8	-	60.83(0.01)	7.67(0.01)	20.36(0.02)	-
140	8	5	55.82(0.01)	8.31(0.01)	16.97(0.01)	6.08(0.01)
160	8	5	54.68(0.00)	9.13(0.01)	18.24(0.01)	6.67(0.02)
180	8	5	29.90(0.02)	7.23(0.03)	8.24(0.02)	33.22(0.02)
140	30	5	57.10(0.01)	8.74(0.00)	20.29(0.02)	3.88(0.01)
160	30	5	47.60(0.00)	9.03(0.01)	20.11(0.01)	13.30(0.01)
180	30	5	32.93(0.02)	9.08(0.00)	13.35(0.02)	28.80(0.00)
140	50	5	50.37(0.00)	9.01(0.00)	19.16(0.01)	10.61(0.01)
160	50	5	41.78(0.00)	8.28(0.01)	15.65(0.01)	19.63(0.01)
180	50	5	31.59(0.01)	6.75(0.01)	7.40(0.02)	32.00(0.02)
140	8	10	53.15(0.01)	9.20(0.00)	19.34(0.00)	7.89(0.01)
160	8	10	45.90(0.01)	10.18(0.01)	17.24(0.01)	15.46(0.01)
180	8	10	30.98(0.00)	9.18(0.01)	12.45(0.02)	30.91(0.01)
140	30	10	51.07(0.00)	9.23(0.01)	17.68(0.01)	10.24(0.01)
160	30	10	50.99(0.01)	9.58(0.00)	19.16(0.01)	10.09(0.01)
180	30	10	30.44(0.01)	8.01(0.01)	8.53(0.01)	32.62(0.01)
140	50	10	47.65(0.01)	9.25(0.00)	17.94(0.00)	13.49(0.01)
180	50	10	30.41(0.01)	6.58(0.01)	7.14(0.00)	33.18(0.01)

Note: Value in parentheses = standard error; number of replicates, *n* = 3; * = % mass fraction of total mass; The scale *L** represents from 0 for black to +100 for white; The *a** and b* have no specific numerical limits; Positive *a** is red; Negative *a** is green; Positive *b** is yellow; Negative *b** is blue; and Δ*E** = total color difference.

From the collected data in this current study, hemicellulose is more sensitive to temperature and easier to degrade than cellulose. During steam treatment furfural and some polysaccharides with low molecular weights are generated from the degradation of hemicellulose. Changes in lignin and extractives can also contribute to the color changes. Carboxylates and phenol may be produced within the lignin or extractive molecules at high temperatures and humidity[45]. All these put together might lead to color changes in the appearance of the ground barley straw during steam explosion pretreatment.

4 Conclusions

The present study shows several strategies to improve the durability of barley straw pellets. Radio frequency-alkaline pretreatment using 1% NaOH solution with the ratio of biomass: NaOH solution enhanced the deconstruction of the lignocellulosic matrix in barley straw. The lower was the biomass:NaOH solution ratio, the better was the quality of the produced pellets. Washing of the RF-alkaline pretreated samples resulted in pellets with low quality. A biomass:NaOH solution ratio of 1:8 at the three levels of temperature (70, 80, and 90^{o}C) studied are the RF optimum pretreatment conditions for the production of pellet with better pellet strength, pellet fracture load, density, durability rating, and dimensional stability.

The operating temperature and retention time represent two important variables in the steam explosion pretreatment that contributed significantly to the production of pellets with good physical properties. Higher temperature (180^{o}C), 10 min retention time at the three levels of moisture content are the optimum pretreatment condition that resulted in pellets with better physical quality compared to those from non-treated barley straw.

Therefore, this study confirmed that lignocellulosic biomass has a natural binder (lignin) which acts as an adhesive/glue that binds the biomass particles during densification process. Hence, there is a need to fully or partially break or disrupt the lignocellulosic matrix in the biomass via pretreatment before densification. In comparison with steam explosion, RF-assisted alkaline pretreatment of ground barley straw produced pellets with better physical characteristics. However, this combined approach (radio frequency in combination with alkaline pretreatment) involved longer pretreatment time compared to steam explosion pretreatment.

Acknowledgements

The authors appreciate the financial support of the Natural Sciences and Engineering Research Council of Canada and Agriculture and Agri-Food Canada through the Agricultural Bioproduct Innovation Program. The support from Dr. Zahra Tooyserkani and Mr. Bahman Ghiasi of the Department of Chemical and Biological Engineering, University of British Columbia and the technical support unit (Louis Roth, Bill Crerar, and R Lee Prokopishyn) of Chemical and Biological Engineering Department, University of Saskatchewan are highly appreciated.

[References]

[1] Fiona J W, Egginton P, Barrow E, Desjarlais C, Hengelveld H, Lemmen D S, et al. Background Information: Concepts, Overviews and Approaches. From Impacts to Adaptation: Canada in a Changing Climate, (Chapter 2). 2007; p. 33-34. Available: http://adaptation2007.nrcan.gc.ca. Accessed on [2013-09-01].

[2] Demirbas A, Fatih M, Balat M, Balat H. Potential contribution of biomass to the sustainable energy development. Energy Conversion and Manage, 2009; 50: 1746－1760.

[3] Zhang Y H P. Reviving the carbohydrate economy via multiproduct lignocellulose biorefineries. J. Ind. Microbiol. Biotechnol, 2008; 35: 367－375.

[4] Tavakoli H, Mohtasebi S S, Jafari A, Mahdavinejad D. Power requirements for particle size reduction of wheat straw as a function of straw threshing unit parameters. Aust J Crop Sci, 2009; 3(4): 231－236.

[5] Fan L T, Yong-Hyun L, Gharpuray M M. The Nature of Lignocellulosics and their Pretreatments for Enzymatic Hydrolysis. Adv Biochem Eng/Biotechnol, 2006; 23: 157－187.

[6] Iroba K L, Tabil L G. Lignocellulosic Biomass: Feedstock Characteristics, Pretreatment Methods and Pre-Processing for Biofuel and Bioproduct Applications, U.S. and Canadian Perspective. In: Zhang B, Wang Y, (Ed), editors. Biomass Processing, Conversion and Biorefinery, New York: Nova Science Publishers, Inc.; 2013; 61－98.

[7] Iroba K L, Tabil L G, Dumonceaux T, Baik O D. Effect of alkaline pretreatment on chemical composition of lignocellulosic biomass using radio frequency heating. Biosyst Eng, 2013; 116: 385－398.

[8] Tubajika K M, Jonawiak J J, Mack R, Hoover K. Efficacy of radio frequency treatment and its potential for control of sapstain and wood decay fungi on red oak, poplar, and southern yellow pine wood species. J Wood Sci, 2007; 53: 258－263.

[9] Balakrishnan P A, Vedaraman N, Sunder V J, Muralidharan C, Saminathan G. Radio frequency heating-a prospective leather drying system for future, Drying Technol, 2004; 22: 1969－1982.

[10] Brausi M, Castagnetti G, Gavioli M, Peracchia G, de Luca G, Olmi R. Radio frequency (RF) ablation of renal tumours does not produce complete tumour destruction: results of a phase II study. Eur Urology Suppl, 2004; 3: 14－17.

[11] Piyasena P, Dussault C, Koutchma T, Ramaswamy H S, Awuah G B. Radio frequency heating of foods: principles, applications and related properties-A review. Critical Reviews in Food Sci Nutr, 2003; 43(6): 587－606.

[12] Izadifar M, Baik O D, Mittal G S. Radio frequency-assisted extraction of *podophyllotoxin*: Prototyping of packed bed extraction reactors and experimental observations. Chem Eng and Proc, 2009; 48, 1437－1444.

[13] Toussaint B, Excoffier G, Vignon M R. Effect of steam explosion treatment on the physico-chemical characteristics and enzymic hydrolysis of poplar cell wall components. Anim Feed Sci Technol, 1991; 32: 235－42.

[14] Mosier N, Wyman C, Dale B, Elander R, Lee Y Y, Holtzapple M, et al. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour Technol, 2005; 96: 673－86.

[15] Tanahashi M, Tamabuchi K, Goto T, Aoki T, Karina M, Higuchi T. Characterization of Steam-Exploded Wood II Chemical Changes of Wood Components by Steam Explosion. Wood Res, 1988; 75: 1－12.

[16] Chornet E, Overend R P. Phenomenological Kinetics and Reaction Engineering Aspects of Steam/Aqueous Treatments. Proceedings of the International Workshop on Steam Explosion Techniques. Fundam Ind Appl, 1988; 21－58.

[17] Heitz M, Capek-Menard E, Koeberle P G, Gagne J, Chornet E, Overend R P, et al. Fractionation of *Populus tremuloides* at the Pilot Plant Scale: Optimization of Steam Pretreatment Conditions using the STAKE II Technology. Bioresour Technol, 1991; 35: 23－32.

[18] Chundawat S P, Venkatesh B, Dale B E. Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility. Biotechnol Bioeng, 2006; 96(2): 219－31.

[19] Chum H L, Johnson D K, Black S K, Overend R P. Pretreatment-catalyst effects and the combined severity parameter. Appl Biochem Biotechnol 1990; 24/25: 1－14.

[20] Kaar W E, Gutierrez C V, Kinoshita C M. Steam explosion of sugarcane bagasse as a pretreatment for conversion to ethanol. Biomass Bioenergy 1998; 14(3): 277－87.

[21] Sokhansanj S Turhollow A F. Biomass densification-cubing operations and costs for corn stover. Appl Engn Agric, 2004; 20(4): 495－499.

[22] Tabil L G. Binding and pelleting characteristics of alfalfa. Ph.D. thesis. Saskatoon, Saskatchewan: Department of Agricultural and Bioresource Engineering, University of Saskatchewan, 1996.

[23] Tabil L G, Adapa P K, Kashaninejad M. Biomass Feedstock Pre-Processing – Part 1: Pre-Treatment, Biofuel's Engineering Process Technology, Dr. Marco Aurelio Dos Santos Bernardes editors. ISBN: 978-953-307-480-1, InTech 2011, p. 411-39. Available: http://www.intechopen.com/books/biofuel-s-engineering-processtechnology/biomass-feedstock-pre-processing-part-1-pre-treatment. Accessed on [2013-10-23].

[24] Sokhansanj S, Mani S, Bi X, Zaini P, Tabil L G. Binderless Pelletization of Biomass, presentation at the 2005 *ASAE* Annual International Meeting, Tampa Convention Centre, Tampa, Florida July 17-20, 2005. Paper Number: 056061.

[25] Mani S, Tabil L G, Sokhansanj S. Effects of Compressive Force, Particle Size and Moisture Content on Mechanical Properties of Biomass Pellets from Grasses. Biomass Bioenergy, 2006; 30: 648－654.

[26] Adapa P K, Tabil L G, Schoenau G J. Compression Characteristics of Selected Ground Agricultural Biomass. Agricultural Engineering International: the CIGR Ejournal. Manuscript, 2009; 1347, Vol XI

[27] Kaliyan N. Morey R V. Factors affecting strength and durability of densified products. ASABE Annual International Meeting, American Society of Agricultural and Biological Engineers, Portland, Oregon July 9-12, Paper Number 066077, 2950 Niles Road, St. Joseph, MI 49085-9659 USA 2006.

[28] Granada E, López-González L M, Míguez J L, Moran J. Fuel lignocellulosic briquettes, die design and products study. Renewable Energ, 2002; 27: 561－573.

[29] Kaliyan N, Morey R V. Factors affecting strength and durability of densified biomass products. Biomass and Bioenergy, 2009; 33: 337 - 359.

[30] Briggs J L, Maier D E, Watkins B A, Behnke K C. Effects of ingredients and processing parameters on pellet quality. Poultry Sci, 1999; 78: 1464－1471.

[31] Obernberger I, Thek G. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behavior. Biomass Bioenergy, 2004; 27: 653－669.

[32] Adapa P K, Tabil L G, Schoenau G J. Compaction characteristics of barley, canola, oat and wheat straw. Biosyst Eng, 2009; 104: 335－344.

[33] Adapa P K, Karunakaran C, Tabil L G, Schoenau G J. Potential Applications of Infrared and Raman Spectromicroscopy for Agricultural Biomass". Agricultural Engineering International: the CIGR Ejournal. Manuscript 2009;1081. Vol. XI.

[34] Grover P D, Mishra S K. Biomass briquetting: technology and practices. Regional wood energy development program

in Asia, GCP/RAS/154/NET, field document no. 46. Bangkok, Thailand: Food and Agriculture Organization of the United Nations, 1996. Available: http://www.fao.org/docrep/006/ad579e/ad579e00.pdf. Accessed on [2013-07-10].

[35] Shaw M, Meda V, Tabil L G, Opoku A. Drying and Color Characteristics of Coriander Foliage using Convective Thin Layer and Microwave Drying. J Microwave Power Electromagnetic Energ., 2007; 41(2): 59－68.

[36] Fengel D, Wegener G. Wood Chemistry, Ultrastructure, Reactions. New York: Walter de Gruyter & Co.: 1984, p. 337－338.

[37] Lam P S. Steam explosion of biomass to produce durable wood pellets. PhD thesis submitted to Department of Chemical and Biological Engineering, University of British Columbia, Canada 2011.

[38] Iroba KL, Tabil L G, Sokhansanj S, Dumonceaux T. Pretreatment and fractionation of barley straw using steam explosion at low severity factor. Biomass Bioenergy, 2013, In press.

[39] Al-Widyan M I, Al-Jalil H F. Stress-Density Relationship and Energy Requirement of Compressed Olive Cake. Appl Eng Agric. 2001; 17(6): 749－753.

[40] Fell J T, Newton J M. The tensile strength of lactose tablets. J Pharmacy Pharmacology, 1968; 20: 657－658.

[41] Fell J T, Newton J M. Determination of tablet strength by diametral compression test. J Pharmaceutical Sciences, 1970; 59(5): 688－691.

[42] Hunter Associates Laboratory, Inc. 2008. CIE L*a*b color scale. Applications Note 8(7). Available: http://www.hunterlab.com. Accessed on [2013-12-24].

[43] Nlewem K C, Thrash M E Jr. Comparison of different pretreatment methods based on residual lignin effect on the enzymatic hydrolysis of switchgrass. Bioresource Technol, 2010; 101: 5426－5430.

[44] Kashaninejad M, Tabil L G. Effect of microwave-chemical pre-treatment on compression characteristics of biomass grinds. Biosyst Eng, 2010; 108: 36－45.

[45] Zhang Y, Cai L. Effects of steam explosion on wood appearance and structure of sub-alpine fir. Wood Sci Technol, 2006; 40: 427－436.