Properties of Densified Solid Biofuels in Relation to Chemical Composition, Moisture Content, and Bulk Density of the Biomass

Jamileh Shojaeiarani,[a,]* Dilpreet S. Bajwa,[a] and Sreekala G. Bajwa [b]

Global energy consumption is expected to grow by 56% between 2010 and 2040. Renewable energy is one of the fastest-growing energy resources, and biomass is a major feedstock for providing renewable energy. It constitutes up to 35% of the main energy consumption in developing countries. Densified solid biofuel with high density gets a lot of attention due to its uniform shape and low heating cost. When considering densified solid biofuels as a viable solution for energy production, its quality needs to be improved. Solid biofuel quality is a function of the chemical composition and physical properties of the raw materials. It is widely reported that the raw material chemical composition has a major effect on the final solid biofuel quality, as it influences the heating value, ash content, and mechanical durability. The moisture content influences the net heating value, combustion efficiency, and mechanical durability of solid biofuels. The bulk density influences the mechanical durability, thermal characteristics, as well as handling and storage costs of solid biofuels. This work reviewed the latest developments on the effects of the chemical composition, moisture content, and bulk density of raw materials on the thermal efficiency, emission, and mechanical durability of densified solid biofuels.

Keywords: Renewable energy; Biofuel; Chemical composition; Physical properties; Thermal properties

*Contact information: a: Department of Mechanical Engineering, North Dakota State University, Fargo, ND 58102 USA; b: Montana Agricultural Experiment Station, Montana State University, Bozeman, MT 59717 USA; United States; *Corresponding author: jamileh.shojaeiarani@ndsu.edu*

INTRODUCTION

Threat and Status of Fossil Fuels

For the last several decades, the global energy demand has been growing at an alarming rate, and the indiscriminate use of fossil fuels has led to serious problems, including ozone layer depletion, global warming, and climate change (Rintoul *et al*. 2018). Environmental pollution is one of the major disadvantages of using fossil fuels. Fossil fuel is a net carbon-emitting energy source, and extensive use of it produces carbon dioxide (CO_2), carbon monoxide (CO), and other gases that are primarily responsible for global warming and ocean acidification (Rahman and Miah 2017). The rise in the temperature of the earth as a result of global warming causes melting of polar ice caps, flooding of low-lying areas, and a rise in sea levels (Wright *et al*. 2018). If such conditions last, Earth might face severe consequences in the near future.

Global energy consumption is expected to grow by 56% between 2010 and 2040, from 553 quintillion joules (J) to 866 quintillion J (Conti *et al*. 2016). However, the global consumption and production of energy do not supplement each other, and the available traditional energy resources may not meet the future demand.

To strike a balance between the energy demand and limited conventional energy sources, such as coal, oil, and natural gas, increased attention has focused on alternate natural renewable energy sources (Bergstrom and Randall 2016). Many countries, including the U.S., are attempting to decrease greenhouse gas emissions by increasing the application of renewable energy sources (Nejat *et al*. 2015).

Renewable energy is the fastest-growing energy source in the world, and it has been projected to generate one-third of global power by 2040 (Sieminski 2014). Among all different types of renewable energy resources, biomass is the only carbon-based energy source and is derived from plants and plant-derived materials, such as wood, agricultural waste, and forestry and industrial by-products (Long *et al*. 2017). Biomass energy can be turned into convenient forms, such as solid, liquid, and gaseous forms, *via* different conversion processes (Bergstrom and Randall 2016). Solid biofuels such as pellets, briquettes and cubes are a densified form of biomass and have received great attention in recent decades. Their growth has resulted in it becoming the second most commonly used renewable energy source (Van Loo and Koppejan 2012).

Emerging energy trends, high demand for energy security, and global climate change intensify the importance of secure transition from fossil fuel to a source of energy which is low-emission, sustainable, efficient, and environmentally friendly. This paper reviews the most current findings in the field of densified biomass. The focus of this paper is to explore the influence of the chemical composition, bulk density, and moisture content on solid biofuel properties.

Biomass

Biomass includes all organic, natural, and plant-based materials. Taken together, this biomass has a production that is eight times greater than the total annual global consumption of all other source of energy; it ranks fourth largest source of energy after coal, oil, and natural gas, and the demand for biomass will reach 10 million tons to 18 million tons by 2030 (Proskurina *et al*. 2017). Biomass as a widely utilized form of energy constitutes up to 35% of the primary energy consumption in developing countries. Biomass is considered to be a domestic energy resource and its accessibility makes it independent of price variations and supply uncertainties that apply to imported petroleum-based fuels, such as oil and natural gas (Lamers *et al*. 2015). Biomass-based energy is unique in that it effectively stores solar energy when the plant is growing, and then during combustion it releases heat and CO_2. In other words, the combustion of biomass is the reversal of the photosynthesis process (Moskovits 2015).

Biomass materials with an intrinsic chemical energy content include agricultural by-products, forest biomass, industrial waste, and energy crops (Bilandzija *et al*. 2018). The use of biomass-based energy from forest and agricultural residues is projected to reach 140 EJ/year to 170 EJ/year by 2100 (Daioglou *et al*. 2016). There are different conversion processes in which biomass materials can be used to provide heat and energy. Biomass can be utilized for direct heating as a part of industrial or household applications, in the production of steam for power generation, and for the generation of gaseous and liquid fuels.

Although biomass materials are low-cost, environmentally friendly, and abundantly available, utilization of these materials for energy applications has some important challenges arising from its inherent properties. In contrast with fossil fuels, which has a high energy density, biomass exhibits low thermal efficiency. The low energy content in the original form of biomass is generally caused by the low bulk density (typically 80 to

100 kg/m^3 for agricultural straws and grasses and 150 to 200 kg/m^3 for woody biomass (Mani *et al.* 2006a), high moisture content, and high oxygen content of raw feedstocks that limits direct burning (Bajwa *et al*. 2018).

High transportation and storage cost of biomass is another issue limiting its application as a source of energy in original form (Hosseini *et al.* 2015). Therefore, the conversion of bulky biomass into a densified form needs to be considered as an essential step to facilitate the possible contribution of biomass to the future global energy supply. Densification is a solution for improving the capability of biomass as a reliable source of energy, as the energy content of the biomass per unit weight can be increased *via* densification (Iroba *et al*. 2017). Also, solid biofuels can be qualified for burning in standard boilers with reduced emissions and an increased heat release and thermal efficiency to ensure optimum combustion (Khalsa *et al*. 2016). Emissions generated from biomass can be declined substantially due to the increase in the density of solid. In addition, the low transport and handling costs for densified biomass is another advantages of solid biofuels over bulky biomass (Sahoo *et al.* 2019).

Solid Biofuels

Densification of biomass into solid biofuel increases the efficiency of its transport and improving its competitiveness with fossil energy due to its enhanced thermal efficiency and mechanical strength. Densification process compresses biomass to remove inter- and intra-particle voids and increase the bulk density of the material from ~40 to the range 600 to 800 kg/m^3 (Kaliyan *et al.* 2009).

Pellets, briquettes, and cubes are popular densified biomass products, as they have consistent shape, which make it easier to handle, store, and feed into combustion chamber.

Wood residues from primary and secondary wood processing industries are the main raw materials used in solid biofuel production. The narrow resources of wood in contrast with the abundant resource of high-yielding energy crops and large volume of agricultural residues has increased attention on how biomass and agricultural by-products can be used in energy applications. Recently, residues from energy crops, such as straw, and by-products from food industries are becoming an important source of sustainable and renewable energy (Smith *et al*. 2017). Although there is an emerging trend in many countries for the utilization of biofuels from biomass, approximately 52% of agricultural residues are annually disposed (Kamel *et al*. 2018). Using agricultural by-products for producing energy does not conflict with food production because this type of biomass is not considered as food. In addition to environmental advantages, providing agricultural residue does not require any land use changes (Pongratz *et al*. 2018).

The raw material, chemical composition, and physical characteristics (moisture content and bulk density) have a notable effect on the thermal utilization of solid biofuel (fuel supply, fuel conversion, and solid and gaseous emissions) (He *et al*. 2018). To evaluate the full potential of solid densified biofuels, it is necessary to consider several aspects such as the chemical composition, moisture content, and bulk density (Miranda *et al*. 2018). In particular, the effect of the chemical composition, moisture content and bulk density on the solid biofuel quality has been studied in several works (García *et al*. 2018; Oveisi *et al*. 2018). A search of journal papers regarding biofuels showed that more than 5000 papers were published on this subject in the last seven years (Fig. 1).

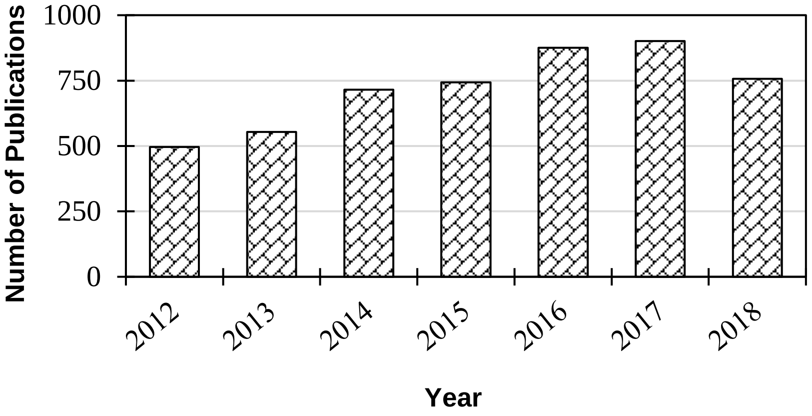

Fig. 1. Annual number of publications on solid biofuels quality as a function of different inputs from 2012 to 2017 (compiled October 2018); searches were conducted with Science Direct using the topics solid biofuels and densified biomass

CHEMICAL COMPOSITION

The chemical composition of biomass is an inherent characteristic of the raw material and heavily influences the properties and potential applications of biofuels (Ozgen *et al*. 2017). Understanding the interaction between the raw material chemical composition and subsequent biofuel quality provides insights into how raw material diversity can influence the solid biofuel combustion process. Because of the wide range of biomass materials, the physical characteristics of biomass are highly variable. However, analyses have shown narrow ranges for common compounds in the chemical composition of woody biomass (Sommersacher *et al*. 2016). Cellulose, hemicellulose, lignin, and extractives are the most common organic compounds found in nearly all types of woody biomass. Table 1 shows the chemical composition of some biomass materials.

Table 1. Proportions of the Main Chemical Compound Groups within Various Types of Biomass

Feedstock	Chemical Compound (wt.%)		
	Cellulose	Hemicellulose	Lignin
Softwood	45.0	25.0	30.0
Hardwood	50.2	26.2	15.3
Straw stalks	40.0	45.1	15.2
Sunflower	42.7	24.0	23.2
Rice straw	39.2	23.5	36.1
Bagasse	33.1	28.0	18.4
Barley straw	37.5	25.3	26.1
Bamboo	73.0	12.0	10.0
Sugarcane	48.6	31.1	19.1
Olive husk	24.0	23.6	48.4
Eucalyptus	45.0–51.0	11.0–18.0	29.0
Switch grass	31.0-45.0	20.0-31.0	12.0-18.0

(Magid *et al.* 2004; Karthikeyan & Visvanathan 2013; Räisänen and Athanassiadis 2013; Cai *et al.* 2017; Jawaid *et al*. 2017)

The concentrations of each compound depend on the origin and type of biomass. Elemental analyses of biomass have shown that biomass elements are divided into three separate groups, which are major (> 1.0%), minor (0.1% to 1.0%), and trace elements (< 0.1%). The elemental concentrations are calculated on a dry basis. The major elements normally include carbon (C), oxygen (O), and hydrogen (H). The minor elements are nitrogen (N), silicon (Si), sulfur (S), magnesium (Mg), calcium (Ca), aluminum (Al), sulfur (S), chlorine (Cl), iron (Fe), phosphorus (P), copper (Cu), zinc (Zn), boron (B), and sodium (Na). Manganese (Mn) and titanium (Ti) are the most common trace elements in biomass (Yaman 2004). The effect of the raw material chemical components on the solid biofuel quality will be discussed in the following section. A comparison of the elemental composition of some selected types of biomass is shown in Table 2.

Table 2. Comparison of the Chemical Compositions of the Selected Types of Biomass

Feedstock	Average Composition (wt.%)				
	Carbon	Hydrogen	Oxygen	Sulfur	Nitrogen
Wood	51.0	6.3	41.5	0.03	0.3
Switchgrass	44.7	5.8	49.1	0.18	0.3
Wheat straw	48.0	5.5	39.0	0.04	0.3
Tall fescue	42.2	5.6	50.6	-	1.5
Rice straw	48.2	6.5	45.1	0.1	0.01
Barley straw	45.7	6.1	38.3	0.04	0.4
Miscanthus	47.9	5.8	43.0	0.1	0.5
Sorghum	45.8	5.3	42.3	0.2	1.0
Bagasse	47.3	6.2	46.2	0.02	0.2
Reed canary grass	44.9	5.8	31.9	-	0.9
Oak	42.5	7.2	49.7	0.02	0.1
Cotton gin	42.8	5.4	35.0	-	1.4

(Yaman 2004; Fahmi *et al.* 2008; Queensway 2010; Vassilev *et al.* 2010; Carpenter *et al.* 2014; Miranda *et al.* 2015; Platace *et al.* 2015)

PHYSICAL PROPERTIES

Moisture Content

The biomass moisture content is an essential property that can negatively govern the quality of solid biofuels if the optimum moisture content of approximately 8 to 10% is exceeded (Matúš *et al.* 2015). When dealing with biomass, intrinsic and extrinsic moisture are two different forms of moisture that can affect the behavior of materials in different ways. Intrinsic moisture is the moisture content that materials naturally contain, regardless of the environmental conditions. In contrast, extrinsic moisture incorporates the effect of ambient conditions on the overall moisture content of the biomass. Typically, the extrinsic moisture content is of more interest and practical value, as the intrinsic moisture content is only achieved under specific laboratory conditions (Van Loo and Koppejan 2012). Moisture is stored in spaces within the dead cells and cell walls of biomass. Water is an essential part of all types of biomass for converting biological raw materials into densified solid biofuels. The moisture content of biomass in the form of extractable water and serves as a binding agent and lubricant to make dense pellets and decreases the friction during pellet production. The inherent moisture in the raw material improves the van der Waals forces between the particles by increasing the contact area (Klemm *et al*. 2018). Furthermore, it can influence the mechanical durability, as well as the heat value of solid biofuels. To improve the mechanical durability and heat value, several researchers have recommended an optimum moisture content (8% to 10%) for solid biofuels (Rupar-Gadd and Forss 2018). The optimum moisture content presents the right amount of required moisture in the raw materials for achieving optimal self-bonding responses in lignocellulosic constituents as a result of high temperatures and pressure during the pelletizing process (Kurchania 2012). The moisture content of the raw materials should be in the proper range to soften the biomass for compaction. In general, the moisture content in solid biofuels is greater than the equilibrium value; otherwise, swelling might occur in the solid biofuels during storage and transportation. Also, disintegration is another consequence of an improper moisture content in solid biofuels and occurs under humid atmospheric conditions.

Bulk Density

Bulk density, as an important quality parameter for biomass, is used to estimate the space requirements for handling, transport, and storage, as well as transportation and storage costs. The bulk density is defined as the ratio of the mass of all of the particles that occupy a unit volume, and it depends on the material, moisture content, particle size, and shape (Samuelsson *et al*. 2012; Liu *et al*. 2016). Bulk density has a huge influence on the durability and transportability of solid biofuels, and any change in the bulk density can create additional logistical issues. In particular, there is a reverse relationship between the bulk density of densified biomass and moisture content of the raw material. Therefore, the bulk density of solid biofuels should be identified using the moisture content (Huang *et al*. 2017). The bulk density of raw material for solid biofuels is determined following the standard ASABE S269.4 (2002), which is applicable for cubes, pellets, and crumbles as long as the unprocessed agricultural by-products are fluffy and loose. The general fuel quality and specifications for solid biofuels of raw and processed materials are also evaluated through ISO 17225-2 standard (Alakangas 2014).

Table 3. Comparison of Bulk Density, Heating Value, and Ash Content of the Selected Types of Biomass

Feedstock	Average value			
	Bulk density (kg/m^3)	Heating value (MJ.kg^{-1})	Ash content (%)	Mechanical durability
Wood	420 to 670	30.2	0.5 to 1.2	98.8
Switchgrass	68 to 323	17.4	4.3 to 5.5	-
Wheat straw	24 to 121	17.4	4.0 to 8.3	46.5
Rice straw	50 to 120	15.2	7.3 to 15.0	-
Barley straw	82	15.4	6.0 to 10.7	95.5
Miscanthus	130 to 150	18. 7 to 19.1	2.7 to 3.5	89.8
Sorghum	240	19.3	6.6 to 9.5	85.7
Corn stover	111	16.4 to 17.4	5.9 to 7.3	75.2
Sunflower stalk	111.78 to 116.05	13.6 to 20.8	7.0 to 11.8	-
Bagasse	635	9.5	1.7-5.5	95.3

(Mani *et al.* 2004; Erlich *et al.* 2005; Kaliyan and Morey 2009; Kargbo *et al.* 2010; Serrano *et al.* 2011; Brosse *et al.* 2012; Cardoso *et al.* 2013; Ivanova *et al.* 2014; Bhagwanrao and Singaravelu 2014; Lizotte *et al.* 2015)

The bulk density also governs the energy density in solid biofuels, as the bulk density and lower heating value determine the energy density of biomass (Costa *et al*. 2017), and a high bulk density in any form of solid biofuel (*i.e.*, pellet or briquettes) denotes a higher energy density. Table 3 summarizes bulk density, heating value, ash content, and mechanical durability of selected biomass types.

Particle size of the raw materials is another parameter that influences the bulk density. A smaller particle size results in the formation of solid biofuels with a higher bulk density (Kang *et al*. 2018).

IMPACT OF THE CHEMICAL COMPOSITION, MOISTURE CONTENT, AND BULK DENSITY ON THE COMBUSTION QUALITY

Heating Value

The calorific value is a characteristic of a fuel and is the amount of heat released during the combustion of a specified amount of fuel. Heating value is usually measured using a bomb calorimeter. The higher heating value (HHV) of any type of fuel is an indication of the total energy released per unit mass or unit volume of the fuel during complete combustion. For any unit that provides heat, information on the heating value and all the parameters that influence it is essential. The lower heating value (LHV) also known as net heating value is determined by subtracting the latent heat of evaporation of the water vapor formed by the combustion.

The heating value of biofuels is mostly governed by the chemical composition of the raw materials. Among the different elements in biomass, the most important components in solid biofuels for the heating value are C, O, S, and H. Carbon and H have an impact on the gross heat value of the fuel, as they become oxidized during combustion by exothermic reactions.

The effective heating value of wood positively correlates with the lignin content (Carrillo *et al*. 2014). Filbakk *et al*. (2011) examined the influence of the bark content of scots pine on the quality parameters of densified pellets and found a higher heating value of bark as a response to higher extractives and lignin contents. Chen *et al*. (2018) also reported a higher heating value for lignin than for cellulose. Demirbas *et al*. (2018) explained that the heating value of lignocellulosic fuel samples is a function of the lignin content of the raw materials, and the higher heating value of the renewable densified biofuels can be calculated by considering the lignin content, which can be measured using elemental analysis (Acar *et al*. 2016).

Numerous mathematical models have been identified to exhibit a relationship between the heating value and chemical composition of biofuels. The mathematical equations that define the combustion efficiency of biofuels while considering the elemental components are summarized in Table 3. The energy content of biomass contributes significantly to C and H content and as the N content of biomass is negligible, the contribution of this elements is relatively low. In biomass combustion, the released heat originates from broken adjacent carbon, hydrogen and oxygen molecules bonds. Due to higher energy content in carbon–carbon bonds than carbon–oxygen and carbon–hydrogen bonds, there is a negative relationship between oxygen content and HHV (McKendry 2002). Woody biomass, including bark, possesses a higher C content compared with herbaceous biomass fuels; therefore, they generate a higher heating value under the same ignition conditions (Garcia-Maraver and Carpio 2015).

Table 3. Mathematical Equations Exhibiting the Relationships between the Chemical Compositions of the Biofuel Raw Materials and Higher Heating Value

HHV (MJ/kg)	Reference
$HHV = -3.393 + 0.507X_{\mathrm{C}} + 0.341X_{\mathrm{H}} + 0.067X_{\mathrm{N}}$	Callejón-Ferre *et al*. (2011)
$HHV = 7.464 + 0.1545X_{\mathrm{C}} + 0.00159X_{\mathrm{C}}^2$	García *et al*. (2014)
$HHV = 0.303X_{\mathrm{C}} + 1.423X_{\mathrm{H}}$	Anastasakis and Ross (2015)
$HHV = 0.3491X_{\mathrm{C}} + 1.1783X_{\mathrm{H}} + 0.1005X_{\mathrm{s}} - 0.0151X_{\mathrm{N}} - 0.10340X_{\mathrm{O}} - 0.0211X_{\mathrm{ash}}$	Parikh *et al*. (2007)
$HHV = 0.350X_{\mathrm{C}} + 1.01X_{\mathrm{H}} - 0.0826X_{\mathrm{O}}$	Shi *et al*. (2016)

HHV – higher heat value; X_{C} – dry mass fraction of carbon; X_{O} – dry mass fraction of oxygen; X_{H} – dry mass fraction of hydrogen; X_{S} – dry mass fraction of sulfur; X_{N} – dry mass fraction of nitrogen; and X_{ash} – dry mass fraction of ash

Biomass generally has a lower heating value compared with coal and its thermal characteristics, such as the specific heat value, thermal conductivity, and emissivity, are greatly affected by the moisture content. Moisture content is another factor that can govern the heating value of biomass. The moisture content above the optimum level (8 to 10%) greatly affects the combustion process and can result in a poor ignition with a low combustion temperature. A high moisture content in densified biofuels can reduce the thermal efficiency (Danso-Boateng *et al.* 2013). In general, burning solid biofuels that contain extra moisture results in the formation of a higher amount of liquid product. In turn, a portion of the generated heat is used to evaporate the extra moisture and consequently lowers the heating efficiency of the solid biofuels (Zhao *et al*. 2014).

Arranz *et al*. (2015) conducted a study on the effect of the bulk density on the combustion attributes of biomass. A higher energy density in the densified biofuels was reported with a higher bulk density. At a constant moisture content, the thermal conductivity of biomass increases linearly as the bulk density of solid biofuels increases (Dahlquist 2013). Ahn *et al*. (2009) determined the thermal conductivity, thermal diffusivity, and volumetric heat capacity of 12 compost bulk materials. Different bulk densities, particle sizes, and water contents were used to explore the thermal properties of the densified biomass. Their results showed that oat straw, wheat straw, cornstalk, soybean straw, alfalfa hay, and wood shavings produced the lower thermal conductivity and volumetric heat capacity values than their densified form. Also, their results showed that there was a linear relationship between the thermal conductivity, volumetric heat capacity, and bulk density, while the thermal diffusivity exhibited a nonlinear response to the bulk density variation (Ahn *et al*. 2009). Opoku *et al*. (2006) illustrated that there are little or no linear relationships between the thermal diffusivity and bulk density of timothy hay, which has a low bulk density. Ray *et al*. (2017) found that a low bulk density limits the energy density of biomass. Additionally, the bulk density impacts the energy efficiency of biofuels (Williams *et al*. 2016).

Emissions

Although the replacement of fossil fuels by biomass can decrease the net emissions of greenhouse gases, the incomplete or inadequate biomass combustion under poor operating conditions releases a range of emissions of uncombusted pollutants into the atmosphere. Different components of biomass emissions influence the local, regional, and global environments. Particularly, the particulate emissions caused by incomplete combustion influence the local environment. Gaegauf *et al*. (2001) characterized particle pollution generated from a variety of small-scale biomass combustion systems. They reported that particle emissions include 95% fine particles with a particle size range of 30 nm to 300 nm. The regional environment is affected by acid precipitation mainly produced by the emission of sulfur (SO_x) and nitrogen oxides (NO_x). Acid rain and ozone depletion are the main consequences of acid precipitation. The global environment is affected by emissions of indirect greenhouse gases and ozone depletion (Van Loo and Koppejan 2012). Additionally, volatile and gaseous carbonaceous compounds, such as CO and methane, account for large amounts of burning emissions from biomass and all other combustion processes (Schauer *et al*. 2001). In general, the raw material origin, growth conditions, and fuel preparation methods strongly influence the type and amount of greenhouse gas emissions.

The greenhouse gas emissions from biomass are a challenge that needs to be considered, as they are projected to cause noticeable changes to the global warming. The acceptable level of global greenhouse gas emissions should be 50 to 55% below 1990 levels in 2050 to reach the 400 ppm target (Adger 2006). One of the parameters that affects gas emissions is particle size; the combustion of small particles will result in the lower level of gas emissions (Meng *et al.* 2018).

Emissions from complete combustion

Carbon dioxide is the most important combustion product of biomass-based fuels. It is indicative of the C content in the biomass and is the main source of global warming. The quantity of C released in the form of CO_2 is referred to as the combustion efficiency (Demirbas 2004).

Hydrogen chloride (HCl), also called hydrochloric acid, is a part of the Cl content in biomass that is released during combustion. Higher amounts of Cl in biomass fuels can result in a remarkable amount of HCl (Lummukka 2014).

Nitrogen oxide emissions from fuel combustion mainly result from complete N oxidation. Thermal NO_x, prompt NO_x, and fuel NO_x are three forms of NO_x. Thermal NO_x is produced by a combustion process at high temperatures from the N content in the air. A fast-chemical reaction between N, O, and hydrocarbons can result in the formation of prompt NO_x at high temperatures. The NO_x is created by the direct oxidation of the N content in the biomass. Additionally, NO is the predominant form of NO_x produced in industrial combustion processes (Garcia-Maraver and Carpio 2015). When the amount of N in the fuels is higher, more NO_x is formed. The temperature of exhaust gas is another factor that influences NOx emissions. A higher temperature generally would result in the formation of more NO_2. In general, emission-related issues for solid biofuels can be expected when the N content in the fuel is above 0.6 wt.% (dry basis). This problem happens in particular during the combustion of straws, cereals, grasses, grains, and fruit residues (Obernberger *et al*. 2006).

Sulfur oxide is a result of complete S oxidation. Sulfur oxide is mainly SO_2. However, some SO_3 may be formed at lower temperatures as more O is bonded into S

(Garcia-Maraver and Carpio 2015). The S concentration is usually low in woody biomass and the noticeable amounts of SO_x may be produced during combustion if lignosulphonate is used as a binding agent in pellets (Lora 2008).

Emissions from incomplete combustion

Carbon monoxide is the product of incomplete combustion of carbonaceous fuel into CO_2. Therefore, CO emissions can be regarded as a good indicator of incomplete combustion of biomass and carbon monoxide emission levels are minimal at an optimum air ratio (air ratio is 5.7 for a typical biomass with an HHV of 18.6 GJ/ton) (Overend 2004). The high amount of combustion air also cools the combustion chamber down and increases CO emissions. The major contributors of CO to the atmosphere are biofuel combustion and industrial fuels. They contribute approximately 50% of the estimated global CO emissions (Yevich and Logan 2003).

Methane is an essential transitional product formed in the conversion of C to CO_2 and H to H_2O during biomass combustion. Methane is usually mentioned separately from other hydrocarbons because it is a direct greenhouse gas (Pérez-Lombard *et al*. 2008).

The combustion quality of biomass is affected by the moisture content in the fuels. Biofuels with a high moisture content generate a higher amount of pollutants compared with dried biofuels. Increasing the moisture content from 25% to 45% would double the amount of hazardous particle materials (Foppa Pedretti *et al*. 2010).

Solid biofuels with particle sizes too small (particulate matter 2.5) or too large (particulate matter 10) have a negative influence on handling, combustion characteristics, and emissions. Unburned emissions, including CO, total hydrocarbons, NO_x, and particles in the flue gas, are the consequence of solid biofuel combustion with particles that are too small. However, in the biofuels with larger particles, the high surface area would increase the chance of complete combustion and decrease the formation of CO and NO_X. (Paulrud and Nilsson 2004).

Ash Content

The mass of inorganic residue that remains after complete burning under specific conditions as a fraction of the original mass is known as the ash content. The major ash-forming elements in biomass include Si, Na, Ca, K, Mg, P, Al, Fe, Mn, and various heavy metals (Biedermann and Obernberger 2005; Magdziarz *et al*. 2016). The formation of biomass ash can cause several operational problems during biomass processing, combustion, and emission.

The formation of non-volatile ash compounds in boilers would cause operational problems, such as slag build-up when ash possesses a low melting temperature and begins to melt during combustion. This, in turn, can lead to the deposition of slag or ash vitrification in the bottom of the combustion chamber. The presence of different elements such as Na and K in biomass can lower the melting point of ash, and this, in turn, can result in an increase in ash deposition and fouling of boiler tube. However, the presence of some other materials such as bauxite, kaolinite, limestone, and magnesium oxide in biomass can increase the ash melting point (Melissari 2014).

Agglomeration and ash deposit formation on the surface of the combustion chamber is another operational problem that manifests itself during biomass combustion, results in corrosion problems, and affects the burning rate during combustion. It was reported that the combustion of different type of biomass with a high content of Na, K, P, and Cl would accelerate the corrosion and erosion in boilers and lower heat transfer efficiency due to a high tendency in forming ash agglomeration (Jiang *et al.* 2016).

There should be enough information on the volume and chemical components of the ash content from different types of solid biofuels to design appropriate ash removal systems. Ash formed as a result of biomass combustion is divided into the categories of bottom and fly ash. Fly ash components typically consist of fine particles in flue gases. In contrast, larger particles that fall to the bottom of the burner during combustion are primarily collected as bottom ash.

The chemical composition of the materials has a remarkable effect on the ash content. Qin and Thunman (2015) studied the effect of a variety of chemical components on the combustion reactivity of various biofuels. It was observed that woody pellets have a lower ash content (< 0.5%) compared with bark (approximately 2% to 3%). Furthermore, it was determined that straw exhibited the highest ash content (approximately 7%) compared with wood and bark char (Qin and Thunman 2015).

Mechanical Durability

Mechanical durability refers to the friability or abrasive resistance of densified solid biofuels. It is a quality parameter that is important during the loading and unloading process. It indicates how dense the solid biofuel is and how well it can withstand handling and transportation. The mechanical durability of densified biomass is mainly evaluated by using a mechanical durability tester following the procedures described in the standard ASABE S269.4 (2002). In this standard method, the mass fraction of the densified biomass before and after tumbling is measured, and the mechanical durability is calculated using following equation.

$$Mechanical\ Durability\% = \frac{Mass\ of\ samples\ after\ trumbling}{Mass\ of\ samples\ before\ trumbling} \times 100$$

The chemical components of raw materials significantly influence the mechanical durability of solid biofuels (Niedziółka *et al*. 2015). A number of studies have shown that the lignin content has a positive effect on the mechanical durability of pellets (Arshadi *et al*. 2008; Castellano *et al*. 2015). The presence of lignin in raw materials improves the mechanical durability of solid biofuels, as lignin in the cell wall of wood acts as a natural binder and can greatly increase the mechanical strength of densified biomass during preheating of the material (Castellano *et al*. 2015). The lignin content varies to some degree according to the biomass types and it has its highest amount at woody biomass (Lerma-Arce *et al*. 2017). When biomass is heated in the densification process, lignin melts, becomes soft, and exhibits thermosetting properties in solid biofuels (van Dam *et al*. 2004).

The moisture content remarkably affects the mechanical durability of densified solid biofuels. Mani *et al*. (2006a) suggested that the mechanical durability and strength of briquettes are a function of the moisture content. The highest mechanical durability values (90% and higher) were observed in corn stover briquettes at moisture contents of 5% and 10%, and the briquette mechanical durability declined when the moisture content increased to 15% (Mani *et al*. 2006b). Several studies have shown that the mechanical strength and durability of densified biofuels improved as the moisture content was increased to an optimum level (8 to 10%), and it decreased as the moisture content exceeded the optimum level (Kaliyan and Morey 2009a; Kaliyan and Morey 2009b; Serrano *et al*. 2011). In fact, the moisture content and mechanical durability have a strong negative linear relationship above the optimum moisture content because additional water reduces inter-granular friction and cohesive forces (Koppejan *et al*. 2013).

Storage and Handling

The irregular shape and size and low bulk density of biomass pose a challenge to handling, transportation, storage, and utilization in its original form. The bulk density is considered to be an important physical characteristic that affects storage and transportation, and has a great influence on the feedstock delivery cost. The design of feeding systems strongly depends on the biomass bulk density (Motta *et al*. 2018). Even in the biorefinery sector, the bulk density of materials has a notable effect on material handling and storage (Igathinathane and Sanderson 2018).

CONCLUSIONS

The present work reviewed the impact of the chemical components and physical properties of raw materials, including moisture content and bulk density, on the quality of densified solid biofuels such as mechanical durability, ash content, emission, and heating value. The chemical composition of solid biofuels has an important impact on the heating value, ash formation and emission. The main components of biomass, C, H, and O are of special importance because they considerably influence the thermal efficiency of solid biofuels. The presence of different elements in solid biofuel also impacts the emission types and amounts. The combustion of biofuels with higher contents of elements such as N, S, K, P, and Cl can lead to the higher emissions of NO_X, SO_X and increased ash, corrosion problems, and deposits as heavy metals have a strong influence on ash disposal. The lignin content of various biomasses largely controls the viscoelastic properties of biomass and influences the mechanical durability of densified solid biofuels as a natural binder. The biomass moisture content above the optimum value is one of the most detrimental parameters in the pellet industry, lowering the mechanical durability of solid biofuels as well as its combustion efficiency. Poor ignition and a reduction in the combustion temperature are tied to the high moisture content in the raw materials. The bulk density affects the pellet industry in two ways, as it influences the thermal characteristics of solid biofuels and impacts handling and storage costs.

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