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Assessment of Cow Dung Pellets as a Renewable Solid Fuel in Direct Combustion Technologies

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Abstract: Recently, biomass application as a renewable energy source is increasing worldwide. However, its availability differs in dependence on the location and climate, therefore, agricultural residues as cow dung (CD) are being considered to supply heat and/or power installation. This paper aims at a wide evaluation of CD fuel properties and its prospect to apply in the form of pellets to direct combustion installations. Therefore, the proximate, ultimate composition and calorific value were analyzed, then pelletization and combustion tests were performed, and the ash characteristics were tested. It was found that CD is a promising source of bioenergy in terms of LHV (16.34 MJ·kg^{-1}), carbon (44.24%), and fixed carbon (18.33%) content. During pelletization, CD showed high compaction properties and at a moisture content of 18%,and the received pellets' bulk density reached ca. 470 kg·m^{-3} with kinetic durability of 98.7%. While combustion, in a fixed grate 25 kW boiler, high emissions of CO, SO_2, NO, and HCl were observed. The future energy sector might be based on biomass and this work shows a novel approach of CD pellets as a potential source of renewable energy available wherever cattle production is located.

Keywords: cow dung; biofuel; renewable energy; pelletization; combustion; ash

1. Introduction

The current energy policy of the European Union (EU) aims at replacing fossil fuels with renewable sources, including biomass [1,2]. Biomass is the most widespread and used renewable energy source and characterized by a high energy potential [3]. It has the largest technical potential as a biofuel, which in Poland is estimated at 684.6 PJ per year, which includes 407.5 PJ in solid biofuels, where its sources are agriculture (195 PJ), fruit industry (57.6 PJ), forestry (101 PJ), and wood waste (53.9 PJ) [4,5] (Figure 1). In fact, biomass advantages are contributed to its high availability, thus lower transportation costs, what's more, through its compaction, using compression and extrusion systems the bulk density can increase by 4–5 times reducing the storage area by 4–5 times. Therefore, there is a necessity of investigation for alternative and commonly available fuels characterized by a low, competitive price, and a high energy value. Some of the sources, especially agricultural residues require a specific pre-treatment before their utilization in heat and/or power generation systems [6,7].

In recent years, the agricultural sector has been producing huge amounts of animal residues (as liquid manure and slurry) in many parts of the world [8–10]. In the United States, the main source of fertilizers is the waste of cows, beef cattle, poultry, and pigs. Approximately, 250 million tons of cow dung (CD) is produced in the United States annually, which corresponds to the energy balance of 21 billion gallons of gasoline [11]. However, animal manure that contains great amounts of available carbon is also responsible for greenhouse gases (GHG) emissions when left underlying topsoil [12,13]. In many countries, the CD is used as a fertilizer, fuel, thermal insulator, and building material [14,15] but its independent fuel application has not been tested widely yet. Due to the annual increase in cattle population, the raw CD is becoming a more and more available source of biomass.

Furthermore, it isa non-cost substrate that may improve the economical profits of biofuels production [16].
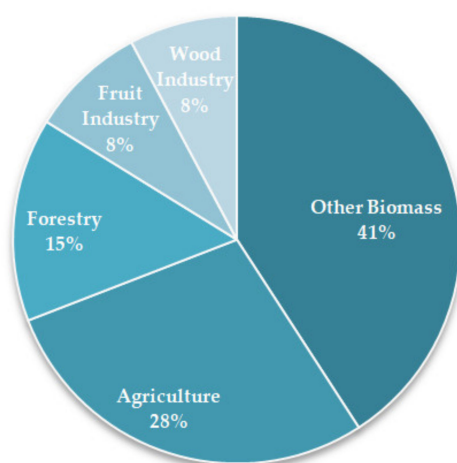
Figure 1. Share of biomass sources for energy purposes in Poland [5].

CD is used as a source of energy especially in India, South Africa, and Nepal [17], mainly to heat the household stoves [18]. In India, animal manure thermal utilization is performed on a large scale, and it is considered as the main fuel in electricity production in a biogas plant [19–21]. Notwithstanding, it contains large amounts of energy for use as a solid, sustainable, and renewable energy source, which contributes to so-called organic waste [22]. The low heating value of CD ranged from 10 to 17 $MJ \cdot kg^{-1}$ depending on its moisture content, and the amount of heat released during combustion of 10 $kg \cdot h^{-1}$ was reported ca. 38.3 kW [23,24]. However, conducted investigations of CD used as a solid biofuel mainly detail its combustion in household stoves [25,26], co-combustion with coal [27], biochar production [28], its use as a binder in pellet [29,30], or briquette production [31].

The objective of the present study was to investigate CD fuel properties such as proximate and ultimate composition, high heating value (HHV), low heating value (LHV), and the exhaust composition after combusting it in the form of pellets in a prosumer boiler installation. The abovementioned parameters are commonly used to evaluate the quality of biomass for heat and/or electricity generation, however, so far, no literature reports were found detailing the quality of pellets containing only CD and its emission characteristics. The majority of analytical tests were carried out following the technological procedures of the Institute for Chemical Processing of Coal in Zabrze, Poland. Basing on the obtained results, the dependence of analytical moisture on the LHV was determined. The received data of CD biomass was compared with the results given in the literature for dried feces of domestic animals (cattle) in India in the summer season of 2009, CD obtained in the Czech Republic [32] and China [33]. Afterward, the CD was pelletized and then combusted in the form of pellets in a 25kW fixed grate boiler with an automatic fuel feeding system, where the concentrations of CO_2, CO, NO, SO_2, HCl, and O_2 in the exhaust were investigated. The conducted study brings a wide overview of the tested agro-residue in terms of its possible future use as a renewable solid fuel in direct combustion technologies.

2. Materials and Methods

2.1. Feedstock

The CD solid biomass was obtained from a private farm located in the village of Dziękonie, in the Podlasie Voivodeship, Poland. The farm had an inventory of 40 cows, which, to indicate intensive fattening, were kept in the barn all year round. The combined total sample of cow dung manure was collected from 10 primary samples from the cowshed.

2.2. Methodology

In the present study, the analyzes were performed according to the plan given at Figure 2.

Figure 2. Systematic scheme of the research.

2.2.1. Proximate and Ultimate Analysis

The proximate and ultimate analysis of CD samples was carried out after drying the raw material in a laboratory dryer at 40 °C for 10 h. A shorter drying time (8h), which is suggested by Biomass Analytical Laboratories procedures was insufficient due to the too-high total moisture content of the sample. After drying, the samples were equilibrated with ambient moisture content and ground to analytical grain fraction below 0.42 mm. The HHV, total moisture and analytical moisture content, volatile matter, fixed carbon, ash, total carbon, and sulfur content were determined according to the procedures given in Table 1.

Table 1. Analytical methods provided in the research.

Determined Parameter	Method/Device	Reference
Total moisture content	Weight loss method/Laboratory type drier TC 100 SalvisLab	[34]
Analytical moisture content Ash content	Thermogravimetric method/ TGA LECO 701	[35]
Volatile matter	Thermogravimetric method/Netzsch TG 209 Libra F1	[36]
Fixed carbon	Calculated	–
Total carbon content Total sulfur content	High-temperature combustion method with IR detection/ LECO SC-144DR analyzer	[37] [38]
Hydrogen content	Calculated	[39]
High heating value	Calorimetric method/ LECO AC500 calorimeter	[39]
Low heating value	Calculated	

The total moisture content was determined by measuring the sample's weight loss while drying at 40 °C until it reached a constant mass [34]. The evaluation of the analytical moisture content was performed by the thermogravimetric method [35]. For a sample mass of 1.0 g, the moisture content was evaluated in the ambient atmosphere of nitrogen (99.5% purity) at 105 °C, ash content in an oxygen atmosphere (99.5% purity) at 600 °C. The

volatile matter was determined using a thermogravimetric method [36], where the sample was heated up to 800 °C and held for 7 min in nitrogen (99.999% purity). In accordance with the obtained results, the hydrogen content (H) was calculated [39] as

$$H = \frac{100 - MC - AC}{16} (\%),\tag{1}$$

where MC—moisture content (%) and AC—ash content (%).

The total content of carbon [37] and sulfur [38] was determined through combusting the sample and then analyzing the exhaust with IR detection (Table 1). The combustion was carried out in oxygen with a purity of 99.95% at 1350 °C (sample masses for carbon and sulfur were 0.15 and 0.35 g, respectively). The resulting gases were cleaned of dust and moisture, and contents of SO_2 and CO_2 were determined by IR detection from which C and S contents were calculated by the software. HHV was analyzed using the calorimetric method where a 0.2 g pellets sample was combusted in an oxygen atmosphere (99.5% purity) and cooled to 25 °C, under a pressure of 2.7 MPa (at a constant volume). To check the correctness of results, all determinations were made in triplicate. LHV of the feedstock was calculated using the equation [39]

$$\text{LHV} = \text{HHV} - 24.42 \cdot (\text{MC} + 8.94 \cdot \text{H}) \left(\text{MJ} \cdot \text{kg}^{-3} \right).\tag{2}$$

The content of alkali and alkaline earth metals and contents of Al, Si, P, Cl, K, Fe, Cu, Zn, and Mn in CD were analyzed by Wavelength Dispersive X-Ray Fluorescence (WDXRF)—AxiosmAX—4.0 kW PAN alytical fluorescence dispersion spectroscope. In the spectrometer, the samples were excited with a Rh SST-mAX 4 kW X-ray tube with a rhodium anode. Measurement data were compiled using the Omnian application. The presented results represent an average of 3 samples taken monthly from January to March.

2.2.2. Pelletization Process and Pellets' Quality Determination

The pelletization process of cow dung biomass was performed on a laboratory setup where the main element was a P-300 pelletizer fabricated by Protechnika [40]. The pelletizer's working system contained a flat rotary die with 6 mm holes in diameter and 28 mm in length and two stationary compacting rolls. The setup was in detail described in the previously published manuscript [41]. The tests were carried out at a constant die rotational speed of 270 rpm and material mass flow rate of 40 kg·h^{-1}. Prior pelletization, the feedstock was communized to particles below 5 mm and its moisture content was increased up to 18% by adding a calculated amount of water ca. 24h before the experiment. A day after the pelletization experiments, the quality of pellets was verified by evaluating their particle density, bulk density, and kinetic durability. In order to investigate the pellets' particle density, 10 randomly selected specimens were ground to obtain a roll shape as accurately as possible, then they were measured by an electronic caliper (accuracy of 0.01 mm) and weighted on a laboratory balance (accuracy of 0.0001 g). The particle density (ρ_f) was calculated as follows:

$$\rho_f = \frac{4m_g}{\pi d_g^2 h_g} \left(kg \cdot m^{-3} \right),\tag{3}$$

where m_g—pellet's mass (kg), d_g—pellet's diameter (m), and h_g—pellet's high (m).

Furthermore, the bulk density was tested in accordance with [42] and the kinetic durability test was performed using the Holmen method [43].

2.2.3. Combustion and Exhaust Analysis

Combustions tests were carried out at the laboratory stand of Low Emission Technologies, which was previously described in [44,45]. The main elements of the laboratory setup were a UnicaVentoEko boiler produced by Moderator (Hajnówka, Poland) and a Dr.

Födisch MCA10 flue gas analyzer. During the experiment, ca. 10 kg of cow dung pellets were fed into the combustion chamber with a mass flow of 3.2 kg·h^{-1}. Due to a highly inaccurate air flow indication on the boiler's controller, an exact value of air was not given here. However, instead, the excess air factor λ was calculated according to the formula

$$\lambda = \frac{21.5}{21.5 - O_2''} \, (-), \tag{4}$$

where O_2''—the obtained oxygen content in the flue gas (%)

The hot exhaust was collected at ca. 1.5 m above the grate, and concentrations of CO_2, CO, NO, SO_2, HCl, and O_2 were analyzed in real-time. The results were obtained in terms of normal conditions (1013.25 hPa, 0 °C) and then, for comparison to European standards—EcodesignDirective [46], normalized to 10% of O_2 concentration as follows

$$ZS_2 = \frac{21 - O_2'}{21 - O_2''} \cdot ZS_1 \left(\%, \, mg \cdot Nm^{-3} \right), \tag{5}$$

where Z_{s1}—the component content in the flue gas (%,mg·Nm^{-3}), Z_{s2}—the component content in the flue gas for a given oxygen content (%,mg·Nm^{-3}),and O_2'—the set oxygen content in the flue gas (%).

2.2.4. Ash Characterization

The characteristic ash melting temperatures were determined using Katanax K2 Prime Electric Fluxer (in accordance to [47,48]), where ash pellets were heated in a specific oxidizing atmosphere, and the characteristic ash melting temperatures were observed:

- softening point (°C)—the temperature at which the first change in the shape or appearance of the shaped piece occurs,
- melting point (°C)—the temperature of the formation of semicircles equal to 2/3 of a cylindrical or cubic shape,
- pour point (°C)—the temperature at which the ash sample flows into a layer 1/3 of the hemisphere height.

To determine the content of alkali and alkaline earth metals and contents of Al, Si, P, S, Cl, K, Fe, Cu, Zn, and Mn, the CD ash samples were combusted at 600 °C in a muffle furnace. Afterward, the elemental ash composition was analyzed by WDXRF Wavelength Dispersive X-Ray Fluorescence—AxiosmAX—4.0 kW PAN analytical fluorescence dispersion spectroscope. In the spectrometer, the samples were excited with a Rh SST-mAX 4 kW X-ray tube with a rhodium anode. Measurement data were compiled using the Omnian application. The presented results represent an average of 3 samples taken monthly from January to March.

3. Results and Discussion

3.1. Proximate and Ultimate Analysis

Solid biofuels mainly containcarbon, hydrogen, and oxygen. Proximate and ultimate analysis of CD showed that the total contents of carbon (43.6–46.1%), sulfur (0.23–0.26%), and hydrogen (5.03–5.41%) were similar to the values obtained for CD in India, China, and the Czech Republic (Table 2) and comparable with the values obtained for other types of plant biomass, i.e., willow, sunflower hull, and wood chips [49,50]. The highest similarity has been found between Dziękonie CD and Vyskov CD. The other compared results present animal manure with significantly worse fuel properties. For instance, the most visible difference has been noted in the carbon content.The carbon content importance lays in its positive effect on the biomass calorific value, while for combustion, its oxidization to carbon dioxide (CO_2) through exothermic reactions. An increase in the carbon content by 1% gives an increase in the calorific value by 0.39 MJ·kg^{-1} [51]. However, big differences occur between the carbon content of various types of biomass. According to [52], wood-based

materials are mostly richer in carbon (51% and 49% for coniferous and deciduous wood, respectively), than herbaceous biomass (stems, leaves, straw, and husks), hence the second ones are characterized by lower calorific values [53,54]. Calorific value and carbon content are an important quality property for CD use as an alternative source of energy in power plants and combined heat and power plants.

Table 2. Fuel properties of cow dung (CD).

Property	Vyskov (India) [32]	Himalaya (India) [32]	Himalaya (India) [32]	Chomutov (Czech Republic) [32]	Prague (Czech Republic) [32]	Meihuajing, China [33]	Dziękonie (Poland)
Proximate analysis, wt.%							
Raw material moisture content (a.r.)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	86%
Analytical moisture (MC)	2.60	4.36	5.17	4.86	4.62	d.b.	5.80
Volatile matter (d.b.) (VM)	67.17	52.8	50.77	61.89	67.32	48.01	64.07
Fixed carbon (d.b.) (FC)	18.61	11.68	11.87	11.57	7.99	14.14	18.33
Ashes (d.b.) (AC)	11.62	31.16	32.19	21.68	20.07	37.85	11.80
Ultimate analysis (d.b.), wt.%							
C	42.87	32.52	29.89	39.79	41.14	25.65	44.24
H	5.69	3.85	3.43	5.48	4.97	4.18	4.97
N	1.60	1.84	2.21	1.13	0.90	2.64	-
S	0.18	0.18	0.20	0.13	0.19	0.80	0.25
O	35.44	26.09	26.91	26.93	28.11	28.88	-
Cl	0.14	0.20	0.27	0.10	0.14	n.d.	1.04
HHV (d.b.), MJ·kg^{-1}	17.59	13.41	11.95	15.72	16.31	n.d.	17.61
LHV (d.b.), MJ·kg^{-1}	16.29	12.47	11.08	14.41	15.12	n.d.	16.34

(d.b)—dry basis, wt.%—weight percent, (a.r.)—as received, n.d.—no data.

Previously conducted research has shown that CD properties differ during the winter-spring season, for instance, the highest amount of atomic carbon was observed in December, which is ca. 3% higher compared with March. Similar observations have been made in accordance with the analytical moisture content, which increased during the early spring months (March–April) [55]. Furthermore, as for woody biomass [56,57] and waste biomass [58], the value of LHV is affected by the fuel moisture content (Figure 3). An increase in the content of analytical moisture from 2.7% to 7.5% resulted in an 8% decrease inCD's LHV. Moreover, it has been reported in the literature [56,57,59] that drying biomass from the moisture of 60% to 10% results in a decrease in the LHV from 6 to 17 MJ·kg^{-1}. Gautam et al. [17] statesthat, inter alia, CD moisture content has a large effect on the stove performance and it is a critical property while combustion, due to the energy needed for water evaporation. Raw CD contains over 80% of water [55] and in terms of its use as a main fuel in direct combustion, it has to reach lower moisture contents. However, it has to be noted that drying is a highly energy-consuming process, which may result in a strong decrease in biomass economic efficiency. The solution to the problem might be its natural drying under atmospheric conditions (if a suitable area is available) or using a non-conventional energy source in the drying system, i.e., solar, microwave, far-infrared, or multistage drying [60]. In addition, in order to solve the total moisture content issue and increase the calorific value, the CD can be co-pelletized or co-briquetted with another biomass characterized by lower moisture content. As a result of processes, the homogeneity of biomass might improve and the bulk density might increase. Densified biomass such as briquettes and pellets have a bulk density in the range of 350–450and 700–750 kg·m^{-3},

respectively. Moreover, reduction in the material's moisture content improves its storage for longer times with minimum loss in quality [6,61,62].
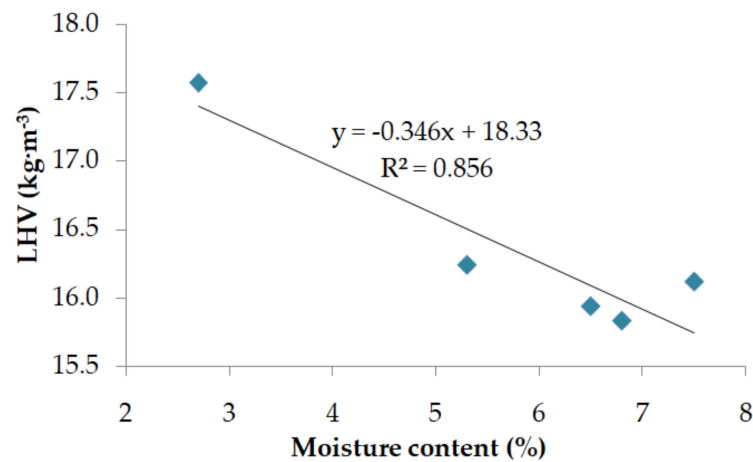
Figure 3. The influence of analytical moisture content on the low heating value (LHV).

Ash and its amount play a significant role in combustion processes [63]: the non-volatile ash compounds remaining in the combusting particles canmelt and remain on or in the particle surface, depending on the process temperature, particle's chemical structure, and surrounding gases [63]. Subsequently, formed ash particles of various origins can affect the operation of the boiler's elements, where they might be a course of, inter alia, deposition of slag and ash in the furnace and/or corrosion wear of metal boiler equipment [64,65]. Biomass ash ismainly mineral salts, which are chemically bound to the carbon structure (natural ash) and/or the mineral soil particles that have been taken up by the plant during its growth and vegetation or transferred to the biomass during harvest and transport as foreign ash [66].

Abovementioned mineral substances, which were not broken down in the cow's digestive system remain in CD (Table 3) and, thereafter, in CD ashes [67]. In the tested CD samples, ash content was on a similar level and ranged from 10.1 to 13.1 d.b.% (January–March). Reumerman and Bergen [68] reported that a 1% increase in the ash content in biomass results in a reduction in 0.2 MJ·kg^{-1} in its calorific value. Experimental results of CD obtained in India, China, and the Czech Republic, as well indicate that high contents of ash (from 20% to 38%) have a negative effect on its calorific value [32,54]. However, biomass ashes, due to the contribution of mineral substances after pre-treatment, may serve as fertilizers of natural origin [69].

3.2. Pellets Quality

To apply CD to controlled combustion, a solid shape had to be obtained. In the well-known pelletization process, as a result of internal and external forces, the material is compacted to a fixed shape, which enables its storage and further processing. Nonetheless, no previous research was focused on pelletization CD itself. The available data consider CD as a biomass binder in pelletization and briquetting processes [29,30,70]. However, in the current work, it was found that CD is characterized by good susceptibility to compaction at a fixed moisture content of 18%. Too-high moisture of biomass makes the pellets or briquettes expand, which results from higher residual stresses in these after ejection from the die.

Table 3. Content of metals and non-metals in CD.

Alkali and alkaline earth metals	(d.b.), wt.%
Na	0.17
Mg	0.50
Ca	10.0
Rb	0.51
Sr	0.05
Other metals	**(d.b.), wt.%**
Al	0.04
Fe	0.51
Cu	0.10
Zn	0.34
Mn	0.40
Non-metals and half-metals	**(d.b.), wt.%**
Si	0.51
P	1.24
K	2.02

The obtained granules indicated high kinetic durability of over 98% (Table 4), which is the required as standard for woody industrial pellets [71]. Therefore, as a result of strong chemical bonds and intermolecular interactions, CD pellets show high resistance to abrasion, which improves its transportation [72] and decreases the risk of explosion (dust generation) [73].

Table 4. CD pellets' quality properties.

Pellets	Properties		
	Kinetic durability, %	Bulk density, kg·m^{-3}	Particle density, kg·m^{-3}
CD	98.69 ± 0.46	471.41 ± 2.88	1250.98 ± 16.06
EN ISO 17225-2 A1	≥97.50	≥600	n.d.

Bulk density of CD received in this research is ca. 21% lower value than the required by [71]. The quality of the pellets depends on the process variables such as length to diameter (L/D) ratio, die diameter, and feedstock variables such as moisture content, particle size and shape.Taking into account the abovementioned high kinetic durability, the low bulk density might be an effect of the pellet length. Forasmuch, the greater the length of the particles, the less they fit each other and the larger spaces between them are observed. Therefore, an increase in the bulk density can be achieved by lowering the cutting knife below the pelletizer's die.

3.3. Combustion and Exhaust Composition

The results of CD pellets combustion presented in Table 5 were compared to woody pellets combusted in the same installation and Ecodesign requirements for boilers <50 kW with an automatic fuel feeding system [46].

Table 5. Exhaust composition while CD and woody pellets combustion.

Parameter	Cow Dung Pellets	Woody Pellets [7]	Ecodesign Limitations
CO_2, %	7.36	7.27	-
CO, $mg \cdot Nm^{-3}$	854.77	329.87	500
SO_2, $mg \cdot Nm^{-3}$	244.38	2.68	-
NO, $mg \cdot Nm^{-3}$	255.92	50.85	200
HCl, $mg \cdot Nm^{-3}$	80.79	0.00	-
O_2†, %	11.59	9.14	10
λ, -	2.17	1.74	-

† Actual oxygen content in the exhaust.

The obtained results indicate a high emission of CO, SO_2, NO, and HCl while combustion of CD pellets, and therefore, they are not suitable in accordance with the Ecodesign Directive as the main source of energy (Table 5). The excess air factor λ value of 2.17 indicates worse contact of the oxidizing agent and combustible particles than it has been obtained for woody pellets [7], which was a result of the higher ash content for CD. The phenomenon is proved by high emissions of CO, considered as a factor of incomplete combustion. The increased amount of CO, SO_2, and NOx wasalso reported by Shuma and Madyira [31] where CD and crushed cactus were used as a binder for briquette production in a 3:1 ratio with various agricultural residues. Apart from a particularly unfavorable effect of SO_2, NOx, and HCl in creating acid rain, they also contribute to the corrosive wear of boiler elements [73,74]. Problems related to SOx emissions are observed in biomass that contains over 0.2% wt. of sulfur [75]. The dominant source of nitrogen oxide emission is the nitrogen contained in the fuel, which during thermochemical reactions is oxidized and realized to the exhaust [76]. The chlorine content of the wood-derived biomass is usually very low (ca. 0.01%), and consequently, it was not found in the exhaust from industrial pellets combustion (Table 5). Much higher amounts are found in biofuels constituting agri-food waste, inter alia, wheat straw 0.4%, corn straw 0.25%, and barley grains 0.1% [53], which might be contained in the CD as digested feed and animal litter scraps. Therefore, it is suggested to utilize sulfur-, nitrogen-, and chlorine-rich biomass by co-firing with fuels containing its lower concentrations [77] or by the addition of bounding substances, inter alia, CaO [78]. It was found by Park et al. [79], in controlled combustion tests, that providing an increase in the heat flux from 25 to 50 $kW \cdot m^{-2}$ resulted in a reduction in the number of harmful compounds from CD thermal decomposition. Hence, the above-mentioned discussion outlines CD as fuel more suitable to be applied in high power units, perhaps as an agro-residue additive.

3.4. Ash Characteristics

The CD ash is characterized by high contents of calcium, potassium, and phosphorus, due to the structure of the biomass itself. However, the chemical composition of CD can change considerably, depending on the cow type, their age, quality of feed, animal condition, and the amount of litter used [80]. Sodium and potassium evaporate at high combustion temperatures, and at the boiler upper parts, they react with other exhaust components to form low melting compounds that deposit on heat-exchange surfaces. This process takes place differently in the fluid field, where the formation of sludge in the presence of sulfates, especially chlorine compounds, significantly accelerates high-temperature corrosion. Important parameters of fuel evaluation in combustion processes include also indicators characterizing ash behavior at high temperatures. This applies, e.g., to the characteristic ash melting temperatures, which depend on the ash chemical composition and the atmosphere surrounding the particles [81]. The chemical composition of CD ashes is presented in Table 6. In accordance with the nomenclature given by Zając et al. [64], CD ashes can be considered as calcium–potassium–phosphorus ashes (Ca–P–K). High contents of K and Ca are unfavorable in combustion processes since their reactivity with other compounds, inter alia, Si, and affinity for creating alkali characterized by low melting

points (ca. 700 °C). Moreover, K and Ca favor slagging and corrosion issues in the boiler's installation [64].

Table 6. Chemical composition of CD ashes.

Alkali and alkaline earth metals	(d.b.), wt.%
Na	2.21
Mg	7.95
Ca	34.11
Rb	0.03
Sr	0.06
Other metals	**(d.b.), wt.%**
Al	1.26
Fe	1.02
Cu	0.13
Zn	0.51
Mn	0.67
Non-metals and half-metals	**(d.b.), wt.%**
Si	15.52
P	18.31
S	3.47
Cl	2.11
K	8.23

The main source of high Si content in CD ashes results from the animal feed: tall grasses and straws due to their sturdiness or rigidity contain relatively large amounts of Si, however, Si, Al, Fe, Na, and Ti are possibly also introduced to biomass as sand, clay, etc. during its harvest, transportation, and processing [82]. Comparing the content of Rb in CD and CD ashes, a reduction in 95% has been observed, therefore, it is evidence of its transition into the gas phase. The Rb boiling temperature is reported to be 688 °C, hence it is lower than the temperature that occurred during preparation of the ash samples (600 °C), however, Rb might be bound in chemical structures with other contaminants that results in lower evaporation temperatures. This phenomenon is scarce in the available literature, therefore, it should be considered for further investigations.

Biomass ash-related difficulties are also the ash fusion characteristics (AFC), an important factor of the fuel propensity of creating slug on the boiler's heat exchange surfaces [83]. Compared with other experiments, the results of characteristic temperatures for CD ash behavior from this research (Table 7) were at ca. 100 °C higher levels. For instance, animal manure tested in India and the Czech Republic indicate ash softening temperature in the range of 1110–1170 °C, melting point in the range of 1130–1200 °C, and the pour point at 1140–1230 °C.

Table 7. Parameters of combustion of animal manure.

Temperature (°C)	Vyskov (India) [32]	Himalaya (India) [32]	Himalaya (India) [32]	Chomutov (Czech Republic) [32]	Prague (Czech Republic) [32]	Dziękonie (Poland)
Softening	1110	1120	1130	1170	1120	1280
Melting	1160	1130	1150	1200	1160	1295
Pour point	1210	1140	1160	1230	1170	1305

Biomass rich in Ca is usually reported to have a high melting temperature, however, observed in CD ashes, large concentrations of P and alkali metals should distinctly lower the melting point. The melting tendency of substances containing Ca and P is rather complex, thus it is affected also by Mg, K, and Fe [84]. Generally, lime calcium (Ca_2SiO_4)

and magnesium silicates ($Ca_3Si_3O_9$ and $CaMgSiO_4$) exhibit higher melting temperatures compared to potassium aluminum silicates ($KAlSi_2O_6$ and $KAlSiO_4$) [85], therefore, they may be a reason forthe better melting behavior of CD ashes.

Due to the high concentration of Ca in CD ashes, they could be developed as a fertilizer, neutralizing the soil pH value. Nevertheless, it has been reported by the Intergovernmental Panel on Climate Change (IPCC) that all carbon used in agriculture is after all released in the form of CO_2 to the atmosphere. Therefore, it was recommended to use fly ashes as an efficient substituent [83,86].

4. Conclusions

In recent years, various types of biomass have been tested to replace fossil fuels and obtain a satisfactory energy-emission balance. Consequently, increased interest ofanimal manure for energypurposes has been observed. In the frame of this research, CD fuel properties were investigated to give a significant step of its fuel advantages and challenges. The promising carbon content of above 44% and the LHV of ca. 16.5 $MJ \cdot kg^{-3}$ exhibit its fine application in heat and/or power generation systems. At the same time, however, high amount of CO, SO_2, NO, and HCl emissions require further investigations on itsenergetic prospect. It is important to mention that pellets produced from CD exhibit high-quality parameters as the kinetic durability above 98% and bulk density ca. 480 $kg \cdot m^{-3}$. This study outlined various research perspectives for future investigation on the sustainable application of CD as pellet fuel since the raw CD is widely available, is low cost and has higher fuel properties in comparison to other agricultural residue biomasses. Further research should be conducted on optimizing the combustion process of CD in various combustion technologies, which may provide a more eco-friendly perspective of its use as a fuel.

Nomenclature

Symbol	Description
CD	cow dung
MC	moisture content (%)
VM	volatile matter content (%)
AC	ash content (%)
FC	fixed carbon content (%)
LHV	lower heating value ($MJ \cdot kg^{-1}$)
HHV	higher heating value ($MJ \cdot kg^{-1}$)

Z_{s1}	the actual chemical content in the exhaust gas (%, mg·Nm^{-3})
Z_{s2}	content of the chemical compounds in the exhaust gas for a given oxygen content (%, mg·Nm^{-3})
O_2'	set value of the oxygen content in the exhaust (%)
O_2''	actual oxygen content in the exhaust gas (%)
λ	excess air factor (-)
wt.%	weight percent
a.r.	as received
d.b.	dry basis
n.d.	no data
m_g	pellet's mass (kg)
d_g	pellet's diameter (m)
h_g	pellet's high (m)

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