Thermal Science and Engineering 2024, 7(2), 5943.
https://doi.org/10.24294/tse.v7i2.5943

Article

The effect of co-combustion of cattle manure and sawdust on energy recovered

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CITATION

Inna S, Abazeh B, Richard K. The effect of co-combustion of cattle manure and sawdust on energy recovered. Thermal Science and Engineering. 2024; 7(2): 5943.
https://doi.org/10.24294/tse.v7i2.5943

ARTICLE INFO

Received: 22 February 2024
Accepted: 2 April 2024
Available online: 10 April 2024

Abstract: The co-hydrothermal carbonization of biomasses has shown many advantages on charcoal yield, carbonization degree, thermal-stability of hydrocar and energy recovered. The goal of this study is to investigate the effect of co-combustion of cattle manure and sawdust on energy recovered. The results show that ash content ranged between 10.38%–20.00%, indicating that the proportion of each variable influences energy recovered. The optimum is obtained at 51% cattle manure and 49% sawdust revealing 37% thermal efficiency and 3.9 kW fire power. These values are higher compared to cattle manure individually which gives values of 30% and 2.3 kW respectively for thermal efficiency and fire power. Thus, the mixture of biomasses enhances energy recovered both in combustion and hydrothermal carbonization. Volatile matter is lower in mixture predicting that the flue gas releases is lower during combustion. Fixed carbon is higher in mixture predicting that energy recovered increases during the combustion of mixture than cattle manure individually. Higher Carbon content was noticed in mixture than cattle manure indicating that the incorporation of sawdust enhances heating value. The incorporation of sawdust in cattle manure can also enhance energy recovered and is more suitable for domestic and industrial application.

Keywords: biomasses; mixture; co-combustion; energy enhancing

1. Introduction

One of the main challenges faced by most developing countries like Cameroon is the lack of clean and affordable fuels for domestic cooking and other industrial activities [1,2]. In these countries, the populations use gas, electricity, wind and solar energies for their various energy activities [3,4]. Furthermore, in the most remote areas of these countries, citizens do not have the means to access these fuels due to their high cost [5]. Thus, they use wood for their energy needs which contributes to fast deforestation [6,7]. Indeed, the use of some of these energies causes environmental problems, mainly the emission of greenhouse gases which is the origin of global warming of the planet [8–11]. These limits lead to find other alternatives energy sources [12,13]. The valorization of biomass is considered as promising route due to its availability and diversity [14–16]. The choice of biomass as energy sources in a given area depends on its availability [17–19]. Thus, in the Adamawa region of Cameroon, cattle breeding predominates peasant life with a herd of around 3.5 million head and produces approximately 1,900,000 dry bons tons of cattle manure per year [20]. The conversion of cattle manure into energy would permit to recycle this waste and clean up the environment as his higher heating value is ranged between 14 MJ/kg and 18 MJ/kg in function of manure origin animal diet and housing system [20–23].

However, the direct use of biomass as energy sources is limited by some unappropriated properties such as high moisture content, low heating value, high heterogeneity, high alkali content, poor grindability, low bulk density and storage problems [24,25]. Hence, for an efficient use as energy, biomass needs to be converted [20]. Thus, literature reveals many efficient processes of converting biomass to energy biofuels namely physical, thermochemical and biochemical [25]. In physical method of conversion, biomass is densified into solid briquettes while thermochemical process of conversion includes combustion, pyrolysis, gasification and biochemical route consists to convert biomass to ethanol and methane by fermentation and anaerobic digestion [22,25].

Among the methods of converting biomass into energy, the production of fuel briquettes seems to be appropriated for underprivileged populations [25,26]. However, briquettes made from cattle manure often causes problem during combustion due to the high ash content ranging between 22% to 30% in function of housing system. In fact, Kenney et al. [27], Samomssa et al. [20] have shown that biomasses with high ash content more than 10% pose the problem of sintering, agglomeration, deposition, erosion and corrosion caused by the low melting point of ashes. Furthermore, Li et al. [28] indicated that the mixture of biomasses with varied biochemical compositions (cellulose, hemicellulose and protein) enhanced energy recovered during thermochemical conversion. These studies have been investigated on hydrocarbonization process and satisfactory result were obtained on charcoal yield, carbonization degree, thermal-stability of hydrocar and energy recovered. More so, Wang et al. [29], Bardhan et al. [30], Leng et al. [31] justified this result by the fact that the interaction between cellulose, hemicellulose and proteins improves the energy properties during carbonization which occurs in anaerobic conditions and some time at subcritical water conditions under self-generated pressures [32]. The question we ask is the mixture of biomass can also improve energy recovered during combustion which occurs in aerobic conditions? Thus, the sawdust which is abundant in Adamawa region of Cameroon is estimated at 69,000 dry bones tons per year [33] can be combined with cattle manure to probably increase its energy efficiency during combustion. The objective of this study is the valorization of cattle manure and sawdust for the production of energy briquettes. More precisely, it will be: find the best formulation which gives better combustion; carry out a physico-chemical and energetic characterization; produce briquettes and evaluate their properties.

2. Materials and methods

2.1. Sampling

The cattle manure was provided by School of Veterinary Medicine and Sciences of the University of Ngaoundere while, the sawdust was collected from the furniture factory in Ngaoundere city. These samples were taken in bags to the Analytical Chemistry laboratory of ENSAI. The compositional characteristics were reported by Samomssa et al. [20] and Tchouanti et al. [34] and is presented in **Table 1**.

Table 1. Compositional characteristics of cattle manure on dry basis (%) [20,34].

Structural analysis		
Cattle manure [20]		**Ayous sawdust [34]**
Cellulose	32.21 ± 0.02	46.5 ± 3.54
Hemicellulose	15.67 ± 0.06	16.2 ± 1.56
Lignin	18.50 ± 2.12	16.2 ± 1.56
Proximate analysis		
Volatile matter	64.67 ± 2.08	98.10 ± 0.06
Ash	22.31 ± 2.52	1.90 ± 0.06
Fixed carbon	13.02 ± 4.06	10.90 ± 0.38
Ultimate analysis		
Carbon	37.72 ± 1.84	-
Hydrogen	4.69 ± 0.12	-
Oxygen	34.74 ± 0.63	-
Nitrogen	0.80 ± 0.04	-

2.2. Formulation of best mixture

The best mixture from cattle manure and sawdust was found by the mean of simplex centroid mixture design. Variables were the proportions of cattle manure (X_1) and sawdust (X_2) while the response is ash content. The model is expressed using Schefe model and is presented by Equation (1). This equation does not have a constant and can justify the fact that the sum of the proportion of each experiment has to be equal to 1. The experiment with proportions (1/2, 1/2) and (5/2, 6/2) were added to allow better statistical analysis of the results and the construction of more precise iso-response surfaces. This matrix gives the total of seven (7) experiments.

$$Y = b_1X_1 + b_2X_2 + b_1b_2X_1X_2 \quad (1)$$

2.3. Characterization of the best mixture

The characterization of the best mixture from cattle manure and sawdust included Fourier transformation infrared (FTIR), scanning electron microscope (SEM), thermogravimetry (TGA), proximate, ultimate and structural analyses.

FTIR:

FTIR analysis was performed on a Perkin Elmer FTIR spectrometer. The samples were placed on an ATR crystal, pressed down and irradiated with a narrow band of IR light (middle part of the spectrum). The signal of the reflected IR light is detected.

Thermogravimetry:

Thermogravimetry analysis was performed on a Q500 thermogravimeter. The raw and pre-treated biomasses were heated at 650 °C, 10 °C/min heating rate in nitrogen atmosphere as described by Samomssa et al. [25]. A thermocouple measured the temperature difference between the sample and the control. In the absence of transformation, the temperature difference between the control and the sample was low and the thermogram was flat. When a transformation takes place in the sample, a peak is recorded whose orientation indicates whether it is an endothermic or exothermic reaction. Approximately 5 mg of sample was used each time. The heating rate was 10 °C/min and the nitrogen flow rate was 500 mL min^{-1}.

Scanning electron microscope (SEM):

The morphological, micrograph and microstructure were conducted using Scanning Electron Microscope (SEM) Hitachi S4800 based on interaction between electron and sample. The preparation of the samples consists in dispersing a small quantity on a double-sided carbon adhesive glued to an aluminum sample holder.

Elemental dispersive Xray analysis (EDX):

The EDX analyses were studied to obtain elemental composition by the mean of Hitachi S4500. The measuring device is the Hitachi S4500 microscope operating under vacuum and at an acceleration voltage varying from 0.5 to 30 kV and coupled to an EDX thermofisher detector allowing chemical analysis on the samples from the boron element. It is equipped with a field emission cannon which allows very good spatial resolution. This microscope has been used in environmental mode to limit the charge effects due to the accumulation of electrons on poorly conductive surfaces

Structural analysis:

The cellulose content experiment consisted to treat 1 g of mixture with 5 mL of concentrated nitric and boil the whole in a bain-marie thermostated at 95 °C for 1 h. After decantation and subsequent filtration, a new treatment was carried out under the same conditions. The operation was repeated three times on the same sample. At the end of the third boiling, the white paste obtained was washed with ethanol (20 mL) and then dried in an oven at 105 °C. The residue obtained represents the cellulose content.

The lignin content is determined by taking 50 mL of sulfuric acid (72%) and introducing in the beaker which previously contain 1 g (mL) of sample. The mixture was heated for 3 h, and subsequently filtered. The filtrate was dried for 24 h at 105 °C then incinerated at 550 °C for 4 h. The masses after drying and incineration were weighed and noted m_S and m_I respectively. The lignin content was calculated by the Equation (2).

$$\%\ \text{Lignine} = \frac{m_S - m_I}{m_1} \times 100 \tag{2}$$

The alkaline extraction method was used to assess hemicellulose content. 1 g (m_1) of sample was mixed with 25 mL of 0.5 M NaOH. And the was boiled for 4 h, filtered and washed with distilled water until total elimination of residual NaOH. The residues obtained were dried at 105 °C to constant mass (m_2, representing hemicellulose).

Proximate analysis:

Moisture content (MC), volatile mater (VM), ash content (AC) were estimated according to ASTM E871-82 (2006) [35], ASTM E872-82 (2006) [36], and ASTMD 1102-84 (2007) [37] respectively.

Moisture content consisted to weight 1 g of sample (*M*1) then dry at 105 °C for 24 h in oven ad weight again (*M*2). The moisture content was given by Equation (3):

$$MC = \left(\frac{M1 - M2}{M1}\right) \times 100 \tag{3}$$

The volatile matter (VM) was carried out by drying 1 g of powder in an oven at 105 °C until constant mass (*M*1). The dried powder was then calcined in a muffle furnace at 550 °C for 30 min in an anaerobic crucible ad weight (*M*2). The volatile matter content was given by Equation (4):

$$VM = ((M1 - M2)/M1) \times 100 \quad (4)$$

The determination of ash content (AC) follows the same process as the volatile matter, with the difference that the dried sample is calcined at 550 °C in the muffle furnace for 4 h in an aerobic crucible and the mass obtained was noted $M3$. The expression for AC is given by Equation (5).

$$AC = (M3/M1) \times 100 \quad (5)$$

Fixed carbon (FC) expressed as a percentage is calculated using Equation (6):

$$FC = 100 - (VM + AC) \quad (6)$$

where: FC (%) the fixed carbon, VM (%) the volatile matter, AC (%) the ash content.

Ultimate analysis and higher heating value modeling:

The carbon (C), hydrogen (H), total nitrogen (N), sulfur (S), oxygen (O) and higher heating value were calculated according to the models illustrated by Equations (7)–(13). These models have been developed in order to solve the accessibility of the CHNOS analyser and bomb calorimeter. These models were reviewed by Samomssa et al. [20].

$$C = 0.637FC + 0.455MV \quad (7)$$

Mass concentration of hydrogen (H)

$$H = 0.052FC + 0.062MV \quad (8)$$

Mass concentration of total nitrogen (N):

$$N = 2.10 - 0.020MV \quad (9)$$

Oxygen mass concentration:

$$O = 0.304FC + 0.476MV \quad (10)$$

Sulfur mass concentration (S):

$$S = 100 - (H + C + O + N) \quad (11)$$

$$HHV = 3.393 + 0.507[C] - 0.341[H] + 0.067[N] \quad (12)$$

$$HHV = 27.239 - 0.306 \times [AC] - 0.089 \times [VM] \quad (13)$$

2.4. Fuel briquette production and characterization

Fuel briquettes were produced using Hydraulic mechanic press. Preliminary tests and literature review guided to fix some parameters such as briquetting mass, briquetting pressure and raw material moisture content at 10 g, 10 MPa, 12% respectively. Mechanical and combustion properties were assessed to the obtained fuel briquettes by the method described by Samomssa et al. [25].

Degradation rate of briquette (DRB) was determined by the ratio of the burned distance as a function of time. Thermal efficiency and fire power were also determined by the Equations (14) and (15) respectively.

$$\text{Thermal efficiency} = \frac{Vi \times Cp \times \Delta T}{m \times HV} \times 100 \quad (14)$$

where, Vi = Initial volume of distilled water (kg), Cp: Specific heat of water (kcal/kg), ΔT: Rise in temperature of water (°C), m: Mass of fuel used to boil water (kg), HV: Heating value, kcal/kg.

$$\text{Fire power} = \frac{m \times HV}{60 \times \Delta T} \quad (15)$$

Index resistance impact (IRI) was evaluated by dropping the fuel briquette several times without initial Vitesse until it breaks. Ten drops were set as a standard for all experiments. IRI is expressed by Equation (16).

$$\mathrm{IRI} = \frac{100 \times \text{Nomber of drops}}{\text{Nomber of broken pieces}} \quad (16)$$

3. Results and discussion

3.1. Best mixture

Table 2 presents the experimental design and showing that ash content ranged between 10.38%–20.00%, indicating that the proportion of each variable influences the response. Taking individually, ash content of cattle manure is 20%, then this value decreases until 10.38% when sawdust is incorporated. According to this result, it can be concluded that, the mixture of biomasses with different biochemical composition improves energy recovered both in combustion and in hydrothermal carbonization. The result in hydrothermal carbonization has been demonstrated by Li et al. [28] and Wang et al. [29]. The viability of result obtained in combustion is better explained by the validation condition of the model presented in **Table 3**.

Table 2. Response matrix.

Experiments	Cattle manure proportion (g)	Sawdust proportion (g)	Ash content (%)
1	2.00	0.00	20.00
2	1.50	0.50	12.02
3	1.00	1.00	10.38
4	0.50	1.50	11.03
5	1.75	0.25	15.81
6	1.25	0.75	12.97
7	2.00	0.00	20.00

Table 3. Validation of model using validation index.

Validation index	Values	Validation condition
R^2	0.98	$R^2 \geq 0.90$
AAD	0.07	AADM = 0
Bf	0.99	0.75 Bf 1.25
Af_1	0.99	0.75 Af_1 1.25
Af_2	1.02	0.75 Af_2 1.25

The conditions used to validate the model are reviewed by Samomssa et al. [25] that adjusted R^2 closer to 100%, absolute average deviation (AAD) closer to zero, bias and exactitude factors ranged between 0.75 to 1.25. It is evident from **Table 3** that the validation index is in the intervals set, thus the model of ash content in function of proportion of cattle manure and sawdust is valid and it is illustrated by Equation (13) where X_1 and X_2 represent the proportions of cattle manure and sawdust respectively.

This equation reveals that the proportion of cattle manure (X_1) and sawdust (X_2) positively influence ash content. This influence is two time more observed for cattle manure than sawdust. From Equation (17), the interaction of cattle manure (X_1) and sawdust (X_2) decreases ash content. This result can justify the fact that, the mixture of biomasses enhances energy recovered during combustion probably due to interaction between cellulose, hemicellulose and protein of each biomass as indicated by Li et al. [28] and Wang et al. [29] in the case of hydrothermal carbonization. In fact, Torgrip and Fernandeze [38] reported that heating value increases when ash content decreases. The influence of each proportion is better described by iso curve response presented in **Figure 1**.

$$\text{Ash content} = 18.786X_1 + 10.918X_2 \times 8.125X_1X_2 \quad (17)$$

This figure reveals two plots notably red and blue. The red plot indicates that the proportion of sawdust decreases ash content while the blue plot illustrates that the proportion of cattle manure increases it. The intersection of the two plots shows the lower value of ash content and justified the fact that the mixture of biomasses enhances energy recovered during combustion. The probability is 0.03 which is less than 0.05 attesting to the viability of the model. The optimum is indicated by the intersection of the two plots revealing 51% of cattle manure and 49% of sawdust.

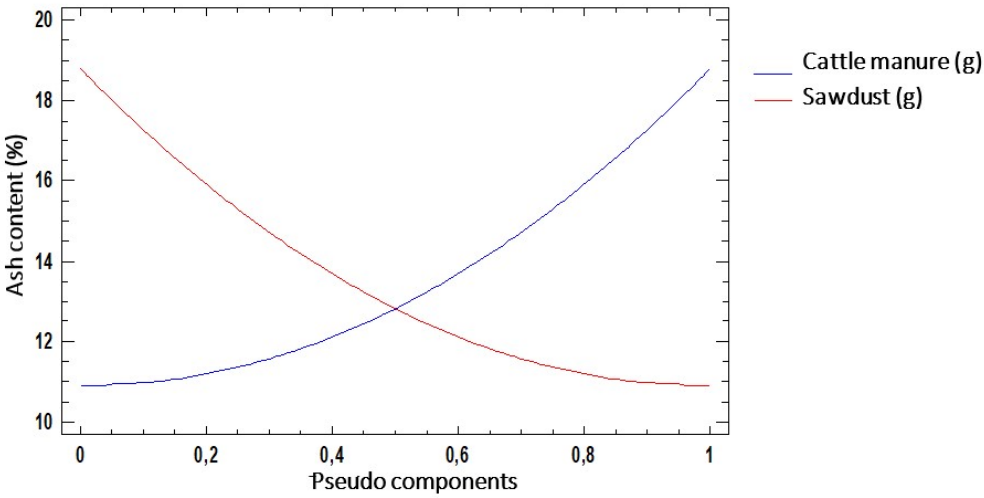

Figure 1. Iso curve response.

3.2. Characterization of the best mixture

Functional groups:

Figure 2 shows infrared spectra illustrating four main adsorption bands, namely between 3100–3500 cm^{-1}; 2000 cm^{-1}; 1500 cm^{-1} and 1000–500 cm^{-1}. The wide absorption band between 3100 cm^{-1} and 3500 cm^{-1} is attributed to the elongation vibration of OH bonded alcohol. This would be due to the presence of cellulose hemicellulose and lignin. The thin absorption band at 2000 cm^{-1} reveals the presence of the C–H elongation bond. The adsorption band at 1500 cm^{-1} is characteristic of elongation of the C–O bond and corresponds to the C–C bond. The absorption band between 1000 cm^{-1} and 500 cm^{-1} are attributed to KCl, $CaCl_2$, phosphate (PO_4^{3-}) and carbonate (CO_3^{2-}) due to the inorganic halogen compounds and mineral components.

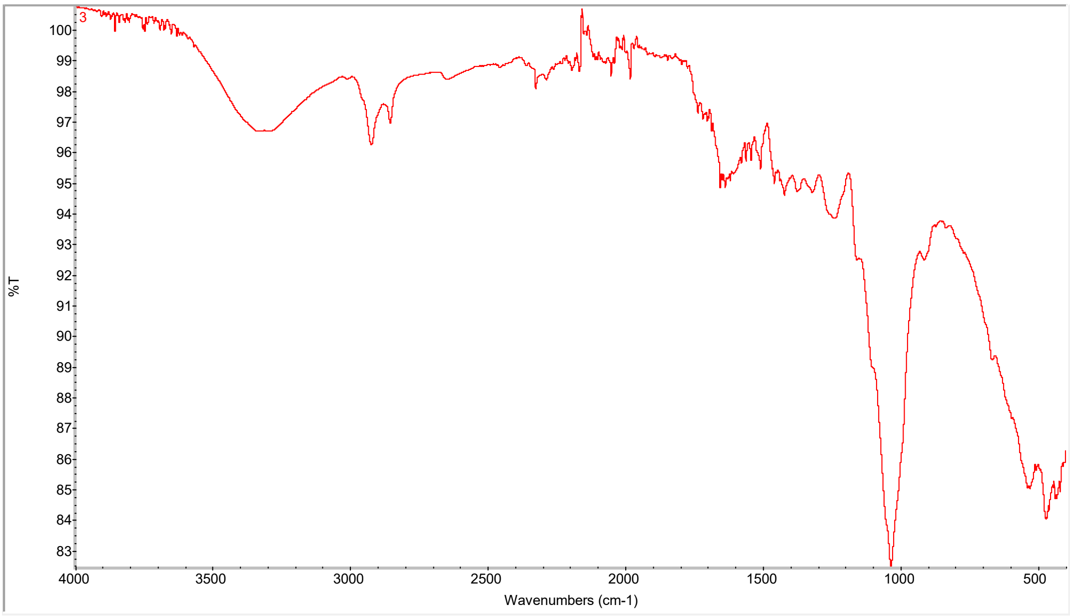

Figure 2. FTIR spectra.

Scanning electron microscope (SEM):

Figure 3 presents the microstructure of the mixture revealing heterogeneous particle size. Ormaechea et al. [39] justified the heterogeneous particle size by the variable proportion of cellulose, hemicellulose and lignin. **Figure 3** also reveals the macro porous structure. Samomssa et al. [25] and Tsai and Liu [40] reviewed that the porous structure is justified by the fact that the space between cellulose is filled by lignin which is distributed across the different layers of the cell wall and reduces the available surface area. Additionally, Tsai and Liu [40] reported that lignocellulosic constituents combined to C and O contain a few amount of mineral elements.

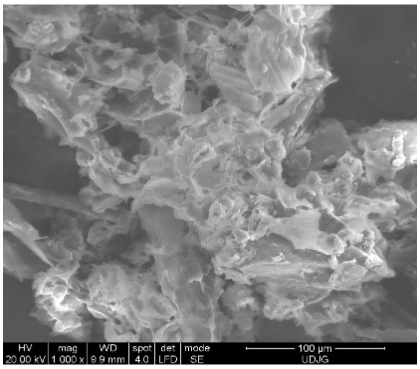

Figure 3. Micrograph of mixture.

It can be concluded that the mixture from cattle manure and sawdust gives macrostructural photography compared to cattle manure which indicated miso porous structure as reported by Ormaechea et al. [39]. Even more, during combustion, oxygen diffuses through the macro pores is more than micropore and can enhance combustion and energy recovered.

EDX:

Figure 4 shows EDX of mixture illustrating that carbon and oxygen are the highest elements followed by nitrogen. This result is in accordance with ultimate analysis obtained by models and can justified their viability to determine carbon and oxygen. Na, Mg, Al, Rb, Si, Sr, P, S, Cl, K, Ca, Ti, Cr, M, Fe and Ze are trace elements.

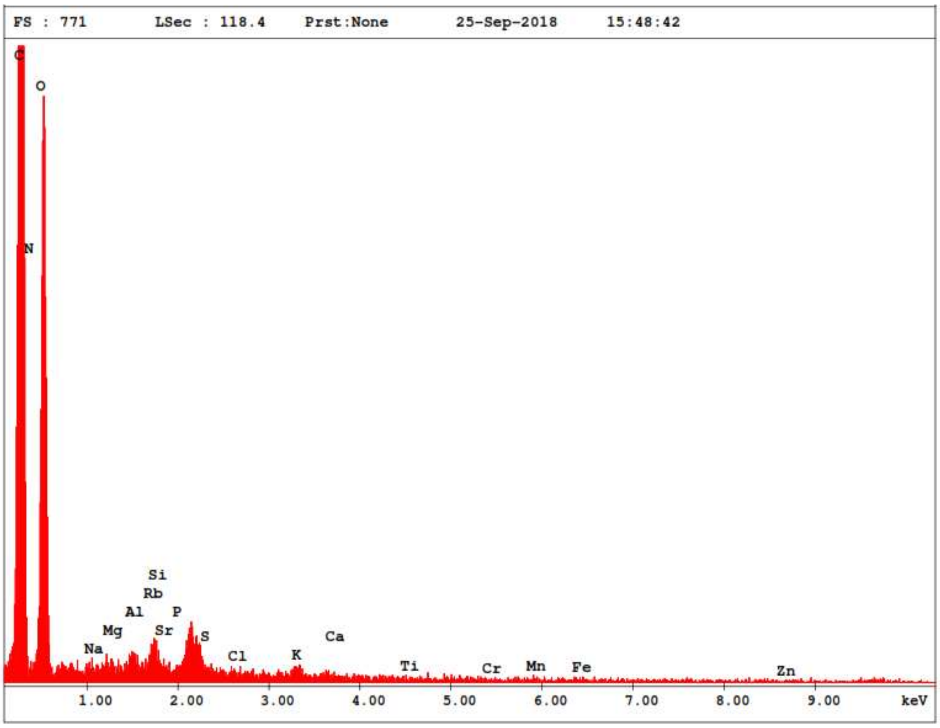

Figure 4. EDX of mixture.

Proximate and ultimate analyses:

Table 4. Proximate and ultimate analyses.

Analyses	Cattle manure	Sawdust	Mixture
Proximate analysis			
Moisture content (MC) %	8.50 ± 0.70	5.75 ± 0.35	6.83 ± 0.62
Ash content (AC) %	21.79 ± 0.81	3.25 ± 0.35	10.38 ± 0.11
Volatile matter (VM) %	64.75 ± 1.40	73.94 ± 0.43	60.67 ± 2.02
Fixed Carbone (FC) %	13.50 ± 0.5	22.81 ± 0.08	28.95 ± 2.10
Ultimate analysis			
Carbon (C) %	31.67	48.16	41.35
Oxygen (O) %	32.12	42.12	38.91
Hydrogen (H) %	4.35	5.76	5.13
Nitrogen (N) %	0.93	0.62	0.73

Table 4 presents proximate and ultimate analyses of cattle manure, sawdust and their mixture. It is appeared from this table that moisture content of the three bio resources is less than 10% and according to Muhammad et al. [41] they can be directly used in combustion without pretreatment. Ash content of cattle manure is higher than mixture while it is lower in sawdust. This is explained by the fact that the incorporation of sawdust in cattle manure decreases ash content thus enhances energy recovered. **Table 4** also shows that volatile matter is lower in mixture predicted that the flue gas

releases is lower during combustion. From **Table 4** fixed carbon is higher in mixture and according to Jiang et al. [42], this result predicted that energy recovered increases during the combustion of mixture than sawdust and cattle manure individually.

In **Table 4**, it is observed that carbon is higher in mixture than cattle manure indicating the fact that the incorporation of sawdust enhances heating value. The same observation hydrogen tends to increase heating value while oxygen and nitrogen decrease heating value. Nitrogen and oxygen predict the quantity of gas emissions during combustion.

Obtained fuel briquettes and characterization:

The picture presented by **Figure 6** illustrated the view of produced fuel briquette and their properties is indicated in **Table 5**. This table presents that, the index resistance impact (IRI) of briquette is 1000 revealing that the obtained fuel briquettes would be handle and transport without breaking. The combustion properties show that the thermal efficiency is 37% and the fire power is 3.9 kW. As presenting in **Table 5**, physico-thermal properties of fuel briquette from cattle manure solely is less than the mixture which indicates that the mixture is better suitable for domestic and industrial application. The degradation rate of fuel mixture briquette is 0.7 cm/min reveals their potential to replace wood energy.

Figure 5. Image of fuel briquette from mixture of cattle manure and sawdust.

Table 5. Fuel briquette properties.

Experiments	Briquette from cattle manure	Briquette from mixture
IRI	1000	500
DRB (cm/min)	0.7	1.0
Thermal efficiency (%)	37.0	30
Fire power (kW)	3.9	2.3

4. Conclusion

The production of energy from biomass has become the points of interest. The main challenge is to put in place the efficient conversion technology and to maximize energy produced. This study presents the effect of cattle manure and sawdust mixture on energy recovered. The result show that ash content ranged between 10.38%–20.00%, indicating that the proportion of each variable influences energy recovered. The optimum is obtained at 51% cattle manure and 49% sawdust for 37% thermal efficiency and 3.9 kW fire power. These values are higher compared to cattle manure individually which gives values of 30% and 2.3 kW respectively for thermal efficiency and fire power. Volatile matter is lower in mixture predicted that the flue gas releases is lower during combustion. Fixed carbon is higher in mixture predicted that energy recovered increases during the combustion of mixture than cattle manure individually. Carbon is higher in mixture than cattle manure indicating the fact that the incorporation of sawdust enhances heating value.

Author contributions: Conceptualization, SI and KR; methodology, SI and BA; software, BA; validation, SI, KR and BA; formal analysis, SI; investigation, SI; resources, SI; data curation, BA; writing—original draft preparation, SI; writing—review and editing, SI; visualization, KR; supervision, KR; project administration, SI; funding acquisition, SI. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: The authors are thankful to the University of Ngaoundere through laboratory of Materials Sciences and inorganic chemistry for necessary put in our disposal.

Conflict of interest: The authors declare no conflict of interest.

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