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Original Paper

Competence of Cow Manure as a Sustainable Feedstock for Bioenergy and Biofertilizer Production

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***Abstract*—Livestock development sector remained conspicuous in many developed and developing countries. Nevertheless, animal manure management became an increasing concern relative to environmental and economic constraints. The daily cow manure varies between 60-85 kg per 1000 kg of body biomass. Thus, 33 to 70 % of biomass could be recovered in the form of cow dung for value added products such as bioenergy and biofertilizer. Halhale dairy farm of Eritrea has a potential to produce approximately 25 tonnes of fresh cow manure per day. Proximate analysis of Halhale dairy manure (HDM) revealed that it contains a mean value of 14.35% of total solids, which inherently composed of 64.8% of Volatile solids and 23.3% of ash content. Detailed elemental analysis using X-ray fluorescent showed that it has 43.1% of C, 0.31% of S, 0.21% of P and 1.18% of K. Hydrogen and nitrogen contents of 4.57% and 1.58% were evaluated for HDM. Thermophysical parameters such as P^H, SG and lower heating value(LHV) estimated as 7.025, 1.68 and 19.97 MJ kg^{-1} respectively. Significant LHV values indicate the aptness of HDM for fuel substitute. In addition, estimated C/N values of 25.68-27.3, ensure their best suitability for the biogas generation. Rich organic matter and high moisture content in HDM support large number of earthworms in vermicomposting. HDM have showed excellent N:P_2O_5 of 3.84 to favor the growth of any crop. Higher Si content of 4.32% along with desired micronutrients of 0.043% of Zn, <0.02% of Cu and 241 ppm of Mn, were measured for HDM samples. The effect of sodicity on soil measured in terms of sodium absorption rate (SAR), and a mean value of 0.84 was estimated for HDM.**

Keywords*— *Cow Manure Management, Characterization, Dairy waste, Renewable resource, Bioenergy and biofertilizer

I. Introduction

Livestock development and management has become one of the prominent sector in many developing nations of the world and in Africa as well. Livestock is an integral part of agricultural system of emerging countries for dairy and meat production, draft animals adopted to plow the fields and transport heavy objects, Cattle skin used for the production of leather, and dung for fuel and agricultural fertilizer [1]. In other words, development of dairy farms stabilize the market for dairy products and meat, create job opportunities, and supports agricultural sector. India had the largest cattle inventory, reported at 305.5 million head in 2021, followed by Brazil and China. Thus, India, Brazil and China together accounted for roughly 65% of the world's inventory of 996 million in 2021[2]. In Africa, 370 million cattle head reported in 2020 and Ethiopia had the largest number of cattle [3]. The livestock and meat market projected to register a CAGR of 4.5% during the forecast period of 2022-2027[4].

The management of livestock manure has become an increasing concern for the livestock industry. Manure management is a critical activity for the economic and environmental sustainability of dairy farms [5]. The amount of manure produced depend on type of livestock, diet, age, productivity, season, environmental conditions and other factors [6,7]. The manure production in intensive production systems ranges from 60 to 85 kg (wet basis) per 1000 kg livestock mass per day [7]. In other words, a dry weight of 2 kg dung per cow per day was assessed in the earlier studies, equivalent to an annual yield of approximately 700 kg per cow [6,8]. Another study reported that dairy animals produce about 1.61 ft^3 (12.0 gal) of fresh manure (feces and urine) per 1,000lb average live weight per day [9]. The manure sources of livestock varies considerably between countries and depends on capacity of dairy farms, number of cows per individual households etc.

Manure management, including production, collection, storage, treatment, transfer, and utilization is a key factor for the sustainable livestock production [10]. It is a complex process involving the considerations of environmental regulations, economic constraints, agronomic conditions, social and health issues [11]. Due to the annual increase in cattle number, the raw cow dung is becoming a more and more available source of biomass. Further, it can be accessed at free of cost or at low cost in many places of the world.

Globally, the importance of cow manure increasing in fuel applications as it contains substantial calorific values. In India, animal manure for thermal utilization is performed on a large scale, and it is considered as the main fuel in electricity production in a biogas plant [12]. In Turkey, pyrolytic potential of cow manure tested by Zuhal and confirmed that kinetic and thermodynamic parameters have shown that cattle manure blended with recycled polyester is a remarkable feedstock for bioenergy [13]. Gudina and Sanderine have briefed that cow manure is a potential biomass feedstock for energy briquettes as solid fuel and for biogas production in Ethiopia and other sub Saharan African countries [6]. Recently, a study in Poland revealed that cow dung pellets can be used as potential source of renewable energy [12]. Rigorous studies on anaerobic digestion of cow manure for biogas production [14, 15, 16] and its upgradation to biomethane for electricity generation [17] conducted in various countries [41].

Animal waste contributes high concentrations of nitrogen (N) and phosphorous (P) and has been used as organic rich manure for thousands of years. In addition, livestock manure is a good source of potassium (K), sulfur (S), and micronutrients such as copper (Cu), zinc (Zn), manganese (Mn) and many other trace elements that are needed for crop growth [18,19]. In contrast, elemental analysis aid in detection of the presence of undesired chemicals such as cadmium (Cd), nickel (Ni), lead (Pb) and mercury (Hg) which does not have any biological functions in the plant growth despite they reduce yield. Manures with added bedding are also an excellent source of organic matter which improves soil quality when applied to land. The water, nutrient and organic matter contents of manures, however, vary greatly making them more difficult to manage than synthetic fertilizers [19].

Livestock manure traditionally managed by direct application to agricultural land and open composting, causing environmental problems such as greenhouse gas emissions, soil/groundwater contamination and eutrophication [20]. In the context of that, in many countries, the cow manure is used as a fertilizer, fuel, thermal insulator, and building material [14,15] but its independent fuel and fertilizer application has not been tested widely yet. Therefore, the objective of this research is to understand the aptness of cow manure for bioenergy and biofertilizer production. Recently, Eritrea focused on improving dairy production, in view of that Halhale Dairy farm project initiated in the late 2017 with the importation of 660 cattle, of which the nine were bulls and currently it has 3000 cows (shabait.com) and produces significant cow manure daily. Proximate and ultimate analysis of Halhale Dairy Manure (HDM) performed to assess thermophysical and chemical attributes of the samples. X-ray fluorescence analysis of HDM organized to estimate detailed elemental concentrations. Furthermore, essential nutrients and micronutrients evaluated to understand their appropriateness for the substitution of synthetic fertilizers.

II. Materials And Methods

A. Raw Material Samples

Six fresh cow manure samples of approximately 2 kg of each collected randomly from the Halhale Dairy farm in the month of March 2022. All the samples were packed in airtight LDPE bags, labelled systematically, and first brought to the CRE (Chemical Reaction Engineering) lab, MCoET for the proximate analysis, later samples dispatched to Bisha Assay Lab for the ultimate and detailed elemental analysis.

B. Chemicals and Reagents

Analytical grade chemicals and reagents supplied by Sigma-Aldrich and ACE (Associated Chemical Enterprise Company) to Bisha Assya Lab used for detailed elemental analysis with permission. 65% nitric acid (HNO_3), 30% hydrogen peroxide (H_2O_2), 98% sulphuric acid (H_2SO_4) and 32% Hydrochloric acid (HCl) used for acid digestion purposes in a partial digestion. For complete digestion system (peroxide fusion), Sodium peroxide (Na_2O_2) and Sodium Hydroxide (NaOH) were used. Ultrapure-deionized water utilized throughout the analysis. Both vials and glassware soaked in 3M HNO_3 prior to analysis for the whole night and rinsed with deionized water to minimize the chances of interferences. All the chemical analyses were conducted under extractor hood and a digital IR Vortex Mixer (S/N296058 made in Italy) was used for mixing the solutions.

C. Proximate Analysis

All the dung samples of analysed for moisture (M) and dry dung (Total Solids) content of fresh cow manure using hot air oven drying method at 40℃ for 10 hr. Dry weight of the sample confirmed when it showed constant weight. Dried samples pulverized finely to a size of 53% of sample passes through ⩽2 mm screen. Analytical moisture (AM) content of the dried samples measured at 105±5℃ in the oven [12]. Volatile Matter (VM) determined by loss of ignition (LOI) test from 2g of dried and powdered samples allowing to burn for 4 hr at 550℃ in a muffle furnace. The retained solid residue measured for ash content (AC). Thus, the fixed carbon (FC) of the samples calculated as [9],

$$FC=100-(VM+AC+AM)$$

Using proximate results, Hydrogen content calculated as follows [12],

$$H=(100-AM-AC)/16\%$$

D. pH Determination by Proxy Test

Measurement of P^H of cow manure samples using a P^H meter (HANNA instruments, UK) carried out by a proxy test. 10 g of manure from thoroughly mixed samples added to 300ml water of known P^H and blended well using a magnetic stirrer. Pre-calibrated P^H meter inserted in to the samples and waited to get a stable reading on P^H meter [12].

E. Specific Gravity (SG) Determination

Specific gravity measured by using volumetric flask method. The weight of the dried and empty 100 ml volumetric flask (W_1) measured initially and later it is determined by filling upto the meniscus mark with water (W_2). A 5-20gram sample is then transferred to the empty volumetric flask and weighed (W_3), which is then wetted with water and carefully filled with water to the same meniscus mark and measured again its weight(W_4). The specific gravity is obtained from the following calculation,

$$SG=\frac{(W_3-W_1)}{(W_2-W_1)(W_4-W_3)}$$

F. Determination of Carbon and Sulphur by LECO method

The CS230, Carbon/Sulphur determinate is a microprocessor based software and the instrument consist an induction furnace for combustion. Total Carbon and Sulphur were determined through combusting 1 g of sample and then analyzing the exhaust using IR detection. In the pure oxygen environment (99.9% purity), combustion of samples was carried out and the resultant gases were cleaned from the dust and moisture. The contents of SO_2 and CO_2 measured by IR detection from which S and C contents were calculated by the software [12].

G. Detailed Elemental Analysis

Acid digestion of samples in HNO_3, HCl and H_2SO_4 solutions followed by instrumental analysis using wavelength dispersive X-Ray Fluorescence (XRF) spectroscope carried out to determine Ag, Bi, Hg, Se, Te, Ti and Na elemental contents. XRF analysis of samples after peroxide fusion using sodium peroxide (Na_2O_2) conducted to measure alkali metals (Na, K, Li), alkaline-earth metals (Be, Mg, Ca, Sr, Ba) and other minerals[12].

H. Assessment of Heating Value for Cow Manure

Total Heating value, known as HHV of cow manure calculated using Dulong's formulae based on the weight fractions of carbon, hydrogen and sulfur as follows [21],

$$HHV = 14495C + 61000H + 5770S \text{ Btu/lb}$$

LHV of the feedstock calculated in terms of using [12],

$$LHV = HHV - 24.42(AM + 8.94H)10^{-3} \text{ MJ/kg}$$

III. RESULTS AND DISCUSSIONS

A. Proximate and Ultimate Characteristics of HDM

Dairy manure composition has a great spectrum of variance in terms of many different types of analysis reported so far. Proximate and ultimate analysis reveals primary cow manure composition such as moisture, total solids, fixed carbon, volatile matter and ash contents. As shown in table 1, fresh cow manure samples from Halhale dairy farm consist 85.65 % (weight) of total moisture on average and the remained dried dung amount of 14.35% accounted for total solid (TS) content. In addition, the amount of TS comprised of volatile solids (VS) of 10.88% and 3.47 % of inert content (Ash). Measured values of moisture, TS, VS and Ash contents are accord to the range reported by the previous studies [12, 15, 22] for the fresh dairy manure. In other words, Volatile solids (VS) of Halhale dairy samples estimated about 75.8 % (weight) of TS along with 24.2% of TS evaluated for Ash.

TABLE I. COMPARISON OF PROXIMATE ANALYSIS OF COW MANURE ON WET BASIS

Content (weight %)	Halhale Dairy Manure	Szymajda et al 2021 [12]	Ayhan& Aysenur 2017 [15]	S. Chen et al 2003 [22]
Moisture	85.65	86.0	86.6	86.61
Total Solids	14.35	14.0	13.4	13.39
Volatile Solids	10.88	11.536	11.01	11.21
Inerts (Ash)	3.47	2.464	2.39	2.18

It has been proposed that the C and H elemental composition determines the energy potential of an organic substance whereas N and S composition provides the intensity of harmful gases on combustion. Proximate and ultimate characterization of dry cow dung is essential in assessing solid fuel and nutrient applications. Dried samples left with little moisture content in addition to volatile matter (VM), fixed carbon and residue contents as displayed in the table 2. VM evaluated in this study is in agreement with earlier studies conducted [12, 23].

TABLE II. COMPARISON OF PROXIMATE AND ULTIMATE ANALYSIS OF COW MANURE ON DRY BASIS

Parameter	Proximate Analysis (weight %)				
	This Work	***Szymajda et al 2021 [12]***	***Venkat et al 2010 [23]***	***Venkat et al 2010 [23]***	***Wang et al 2020 [24]***
Analytical Moisture (AM)	3.65	5.80	4.36	4.62	0
Volatile Matter(VM)	64.8	64.07	52.8	67.32	48.01
Fixed Carbon (FC)	8.25	18.33	11.68	7.99	14.14
Ash Content (AC)	23.3	11.80	31.16	20.07	37.85
Element	**Ultimate Analysis (weight %)**				
C	43.1	44.24	32.52	41.14	25.65
H	4.57	4.97	3.85	4.97	4.18
N	-	-	1.84	0.90	2.64
S	0.31	0.25	0.18	0.19	0.80

The degree of dryness changes the composition of VM and FC. Biomass compounds mainly comprised of the basic elements such as C, H, N, O and S. Presence of C and S determined from XRF study and H estimated using proximate parameters of dry dung. The content of C and H elements in the dry dung represents the quantity of organic matter in the manure that can be recovered and reused for several applications. Nonetheless, ultimate composition of cow manure primarily a function of cattle feed composition, the rate of feeding, and intake of water. Mean value of S for the samples tested are accord to the values reported by the earlier studies as presented in the table 2. Organic Nitrogen was not analyzed experimentally in the study, but estimated from other reports as given in the Table 2 and Table 5. The presence of elemental nitrogen along with phosphates and potassium represents nutrient potential of the manure for the plant growth.

B. Thermophysical Parameters of Cow manure

The physical characteristics of manure depend on multiple factors and practices before and after excretion. The physical state of the manure explained by the P^H values, inherently it determines the presence of nutrients and microbial activities. P^H value of the samples examined has a spectrum of 6.84 to 7.39 whereas Katheem et al has reported a range of 6.5 to 7.5, which varies according to the physical conditions, feed composition and water intake to feed rate ratio. However, the mean value of

7.025 represents the neutrality of manure as it neither alkaline nor acidic and it is comparable with reported range as shown in table 3. P^H values serve as indicators of favorable conditions for microbial growth in biochemical conversion processes such as vermicomposting, anaerobic digestion etc.

TABLE III. COMPARISON OF PROXIMATE ANALYSIS OF COW MANURE ON WET BASIS

Parameter	This Work	Earlier Reports
P^H	7.025	7.19±0.06 [25]
SG	1.63-1.74	1.37-2.323 [26]
HHV (MJ/kg)	21.06	17.59 [12]
LHV (MJ/kg)	19.97	16.29 [12]

Specific gravity (SG) is a measure of heavier solids presence in the manure, and it was measured in between 1.63 to 1.74, without a significant variation when compared with a study from Indonesia as provided in the table 3. Type of bedding such as sand or grass arranged for the cattle determines their presence and causes for higher SG values of manure collected. As TS includes all solids, heavier and lighter, SG and density of cow manure can be explained as a function of TS (weight %). There was a sharp rise to 1740 kg/m^3 and deep fall to 1630 kg/m^3 of bulk density in between 15 to 15.67 % of TS. Void fraction and manure collection practices cause for these kind of abrupt changes in density, otherwise bulk density increases gradually with TS content [26]. A polynomial model developed to describe the variance of density of raw cow manure (ρ_{CM} in kg/m^3) in the range of 12 -18 % of TS from the data regression analysis shown in figure1 as,

$$\rho_{CM} = -230.31TS^5 + 17778TS^4 - 547298TS^3 + 8\times10^6TS^2 - 6\times10^7\,TS + 2\times10^8$$

Many different relations developed in the reported works to relate density for different ranges of TS values. Landry et al described bulk density in kg/m^3 as a polynomial function of TS at higher TS concentrations for dairy manure of 10-50 % TS as

$$\rho_{dairy} = 0.0367TS^3 - 2.38TS^2 + 14.6\,TS + 1000$$

The findings concluded that the density increase gradually with TS. Hui et al has confirmed that the bulk density of pre-digested cow manure increase from 990 to 1065 kg m^{-3} as the TS level increase from 1.5% to 13 % [26].

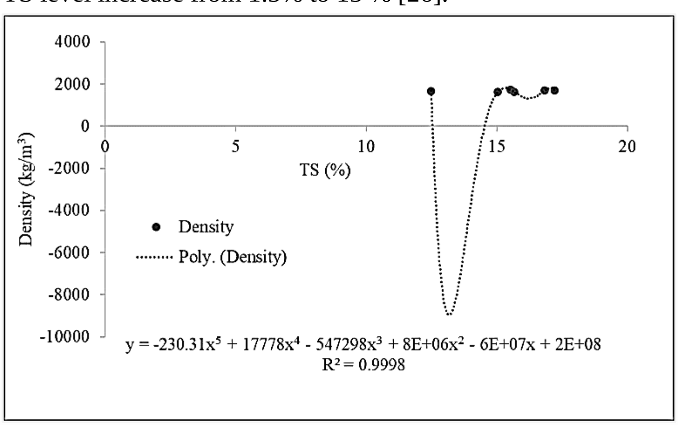

Fig 1. Density of Raw Cow manure (ρ_{CM} in kg/m^3) versus Total Solid (%)

Cow manure used as a source of energy in many countries like India, South Africa including Eritrea, mainly to heat the household stoves. Cow manure is rich in carbon content which can compete with other biomass resources for energy production. High heating value (HHV) and low heating value (LHV) represent the energy potential of any fuel substance. HHV and LHV of dry cow manure determined as 21.06 MJ/kg and 19.97 MJ/kg respectively at mean elemental composition of C (43.1%), H (4.57%) and S (0.31%) using Dulong's relation as mentioned in methods. Carbon content determines the heating value of organic fuel substances and fitness for the use of alternative source for energy in power plants [12]. An increase in carbon content by 1% provides an increase in the calorific value by 390 kJkg^{-1}. Nonetheless, huge differences occur among various types of biomass, and measured different carbon contents for the samples of cow manure as shown in Table 2. Estimated values are slightly higher than the reported values as shown in Table 3. In other words, 1% of increment in the ash content result in reduction of calorific value by 200 kJkg^{-1} [27]. Doulong's method has been applied for solid fuels substances, mostly for coal, it has estimated to be slightly higher than experimental values reported from the literature. However, cow manure has been claimed as promising source of bioenergy in terms of LHV and HHV.

C. Elemental Composition of Cow manure

Inorganic content of cow manure in the form of ash has a significant effect on combustion when it applied as a fuel. Non-volatile ash compounds can melt and remain on the surfaces as permanent layers depending on the process temperature, particle's chemical structure and surrounding gases [28]. As shown in the Table 2, mean content of ash measured as 23.3% and varied greatly among reported studies. Biomass inert solids mainly composed of mineral salts, which were determined using X-ray fluorescence and their mean values displayed in the Table 4. Ash content varied randomly between 11-38% for different cow manure samples tested as shown in the Table 4. Increase in ash content reduce the ability for fuel substitute as stated earlier. Inert content classified in to alkali and alkaline earth metals, non-metals and half metals and other metal compounds for potential comparison with reported values.

TABLE IV. COMPARISON OF INORGANIC COMPOSITION OF HALHALE DAIRY MANURE

Alkali and Alkaline Earth Metals		
Element	***This Study***	***Szymajda et al 2021 [12]***
Na	0.86	0.17
Ca	0.626	10.0
Mg	0.59	0.50
Sr	0.07	0.05
Other Metals		
Al	0.54	0.04
Fe	0.78	0.51
Cu	<0.02	0.10
Zn	0.043	0.34
Mn	0.24	0.40
Non-metals and half metals		
Si	4.32	0.51
P	0.21	1.24
K	1.18	2.02

The quality of the feed decides the intake composition of minor substances, which were not broken down by the digestive system of cattle, excreted as manure. In other words, cattle bedding system and cow manure collecting practices also determines the presence of minerals from the clay or sand beddings. Thus from the Table 4, it was clearly observed that the significant presence of silica (Si). Aluminum and iron metal compositions were comparatively higher in the samples analyzed whereas copper (Cu), zinc (Zn) and manganese (Mn) presented at lower concentrations. Sodium (Na) and potassium (K) levels found higher than reported for the Halhale dairy samples

D. Biomass Recovery through Cow Manure

Generalized assessment of biomass feed to cattle and the cow manure production rates led to understand the recovery rate of biomass in the form of cow manure. The total dry matter requirement of cattle is around 2-3 % of their body weight though high yielding animals may eat at a rate more than 3%. However, feeding rate of animals depend on their age, seasonal conditions, processing of feeds, palatability etc. [29]. Water intake by the cattle is a function of dry matter intake and ambient temperature in between 40 to 90°F varies seasonally for many different geographical conditions. However, a lactating cattle needs two gallons of water per 100 pounds of body weight whereas a non-lactating cow or bull consumes one gallon at 90 °F [30]. In addition to main products such as milk, meat and other industrial products, cattle excrete 6 to 8.5 kg of cow manure as a byproduct generate per every 100 kg of body mass. Findings from several reports on characteristics of cow manure reveal that 11 to 21 % of total solids present in the fresh dung [9, 26]. Thus, a cow manages to recover 33 to 70 % of biomass in the form of byproduct for several commercial applications including biogas production for energy recovery and to enrich the soil as a biofertilizer.

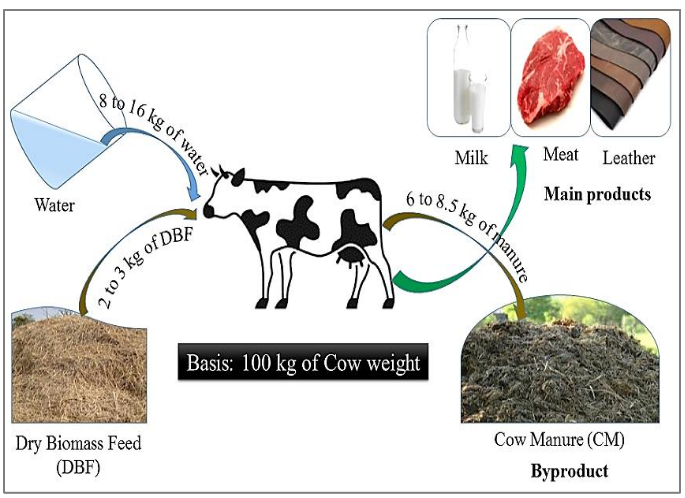

Fig. 2. Schematic diagram showing biomass balance on Cow

In other words, Budiyono *et al* [25] estimated dry solids content of 20.23 ± 1.94 % on average whereas authors of this study determined a mean value of TS as 14.35% of fresh cow manure collected from Halhale Dairy Farm, Eritrea. The causes of variation in TS quite complex to describe as it depends on many factors such as age, feed rate, fodder composition, animal bedding construction, seasonal variations etc. Noteworthy to remind that a daily dry dung production of 2kg per cow assessed by many earlier reports [6,31] and as cattle are mostly range-fed, 60% of totally produced dung accounted for accessible bioresource. Halhale dairy farm currently produce a daily dry dung of 3.6 tonnes and may gradually increase as the farm trying to expand in future. Thus, cow manure could be a sustainable source for bioenergy in several energy conversion technologies.

E. Assessment of cow manure as a feedstock for bioenergy and biofertilizer

Rising of global warming issue due to excess deposition of methane (CH_4) coupled with CO_2 in the atmosphere, creates alarming situation to find immediate substitute to fossil fuels. In other words, depletion of fossil deposits jeopardizing the world to search for renewable fuel feedstocks. In context to the fact, improper management of animal manure causes to contribute significantly to the environmental issues by releasing methane gases into atmosphere. Recently, agricultural sector of developed and developing countries has accounted for huge amounts of manure at the aforementioned production rates per cow. Therefore, the prudent utilization of cow manure has opened door for bioenergy and biofertilizer applications.

In summary of several studies that detail fuel applications of cow dung. The LHV of cow manure of 10 to 17 MJ/kg, depending on moisture content, used as a source for heat in combustion processes such as house hold stoves [32], co-combustion with coal, biochar production, co-pyrolysis of cow manure [13] and its use as a binder in pellet making [33], or briquette production. The HHV of cow manure indicates theoretical energy content whereas LHV serve as available energy for utilization. Cow manure of Halhale dairy measured with 19.97 MJ/kg of dry dung, which is substantially consist higher energy content. A kilogram of oven-dried biomass theoretically contains a calorific value of about 17–22 MJ, but it decreases with increasing moisture contents. The lower heating values of different crop residues vary from 13–19 MJ/kg [34].

Production of biogas via anaerobic digestion (AD) is considered a cleaner and renewable source of energy, which is the most impending ‘biorefinery’ solution for the global energy hassles and simultaneously helps in tumbling the carbon credits [20,35]. In Europe, more than 18000 AD plants, and more than 2100 AD plants in USA including 254 livestock manure digesters, most of which treat cattle manure, are in operation [20]. Biogas is a colorless, flammable gas that burns with clear blue flame similar to liquefied petroleum gas (LPG) [36]. Biogas production by anaerobic digestion includes a sequence of complex biochemical phases (hydrolysis, acidogenesis, acetogenesis and methanogenesis) reliant on various physicochemical and biological parameters such as feedstock composition in terms of volatile solids (VS), temperature, pH, hydraulic retention time (HRT), microbial diversity and C/N values [35].

Assessment of organic nitrogen was not determined experimentally in this work but extracted information from earlier studies [9, 12, 13, 23, 24, 37] utilized to develop an approximate model to interpret the relation between C and N as shown in figure 3. Nitrogen amount for all cow manure samples assessed approximately by the following polynomial model described as,

$$N(\%) = 0.0002C^3 - 0.0161C^2 + 0.3266C + 1.3966$$

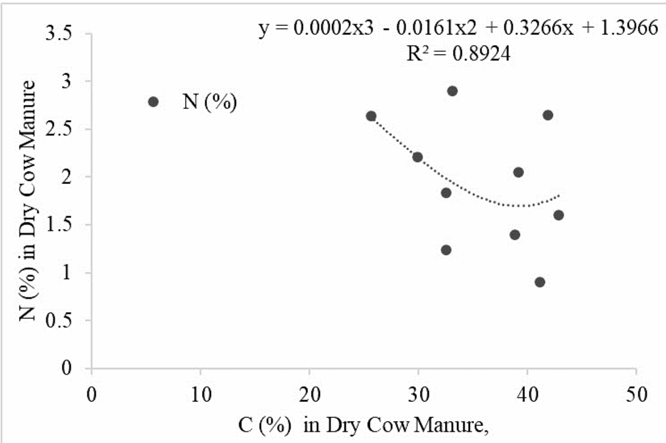

Fig. 3. Analysis of Elemental C (weight %) and N (weight %) of Cow Manure on Dry Basis

In addition, the trend curve describes that nitrogen content gradually decreases with increase in carbon composition of 39% and later it rises. Other words, the mean value of 1.58 % of nitrogen evaluated at an average carbon content of 43.1%. The organic nitrogen content also determines the levels of protein in the organic substances. Protein content of animal wastes usually estimated as 6.25 times of organic nitrogen content. Thus, the estimated protein and nitrogen are in agreement with the reported parameters as shown in the Table4.

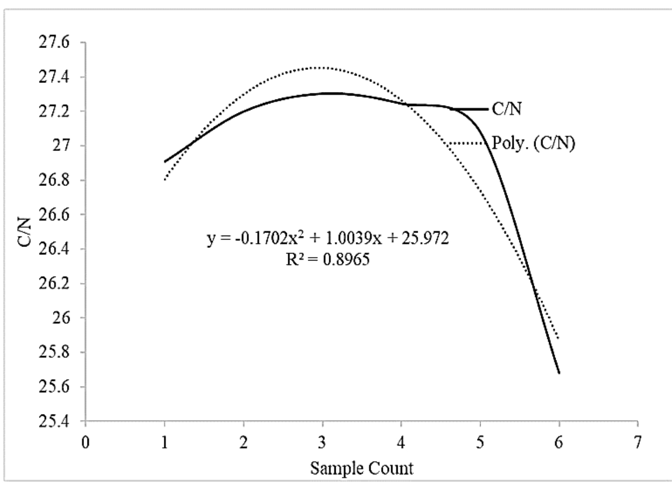

Fig. 4. Variation of C/N for Cow Manure Samples of Halhale Dairy

Nitrogen alone does not have much significance but C/N factor has greater role in microbial reaction that take place in vermicomposting and anaerobic digestion processes for biogas production. The feasibility of biogas production from Halhale dairy manure in terms of C/N ratio detailed through figure 4. Table 2 reveal that C and N elemental composition varies randomly among different cow manure samples and thus C/N greatly fluctuated in the range of 25.68 to 27.3. At 41.3 % of carbon content, the highest C/N recorded as 27.3 and then drastically down to a least value of 25.68 at the carbon content of 45.6% ash shown in figure4. However, it has been proposed that C/N of 25 to 30 as an optimum ratio for efficient anaerobic digestion (AD) systems [14]. Animal manures with large amounts of C-rich bedding materials often have relatively high C:N ratios. Thus, Halhale dairy manure have shown favourable C/N values for biogas production. The C:N ratios for the beef manures were higher and the range was broader due to the addition of varying amounts of bedding for the cattle as well as the amounts of bedding in the samples sent for analyses [19].

Protein is one of the major organic component of cow manure, which has significant contribution in microbial activities. Rich organic substrates support large number of earthworms in vermicomposting process [12]. Analyzed samples of cow manure has a mean protein value of 9.87 % (weight) as shown in Table 5 and they are accord to the reported quantities as it was measured by the conversion factor method. Other organic components such as cellulose, hemicellulose and lignin quantities not covered by the present work but they have been reported by the earlier studies. Budiyono et al have estimated average values of cellulose and hemicellulose and lignin of cow manure as 35.57 ± 8.76, 14.94 ± 4.80 and 25.97 ± 11.13 respectively. Organic components are complex chemical structures derived from plant cells. In other words, the animal feed composition decides the organic composition in manure [25].

TABLE V. COMPARISON OF INORGANIC COMPOSITION OF HALHALE DAIRY MANURE

Parameter (weight %)	**Present Study**	**Sandhya and Krishna 1990 [39]**	**S. Katheem *et al* 2015 [12]**	**Budiyono et al 2011 [25]**
Organic Nitrogen	1.58	1.55	1.4 ± 0.15	-
Protein	9.87	9.68	8.9 ± 0.09	8.28 ± 1.54

F. *Nitrogen (N), Phosphorous (P), Potassium (K) and Sulfur (S) Nutrients for the Crops*

Nitrogen is an essential building block of protein and nucleic acids, and huge amounts required for crops but often found deficient amounts in the soil, which limit the yield of the crops [40]. Halhale dairy farm manure measured nitrogen in the range of 1.58-1.77%. Although good amounts of nitrogen present in the cow manure, entire nitrogen cannot be available for the plant absorption. In the same way, all forms of life supported by inorganic P in the form of phosphates (PO_4). Manure discovered as an excellent source of P for all the crops and tested cow manure samples consist P in the range of 0.11 to 0.28 % with a mean value of 0.21 % as shown in Table 4.

The estimated $N:P_2O_5$ provide indication of supply ratio of N for every unit of P_2O_5 by the manure. Halhale Dairy samples measured 2.6-6.3 of $N:P_2O_5$ with a mean value of 3.84 as shown in the Figure 5, which could be considered potentially higher ratios as actual available nitrogen was not measured in the study. Most of the crops require three to four units of available N per unit of P_2O_5 [19].

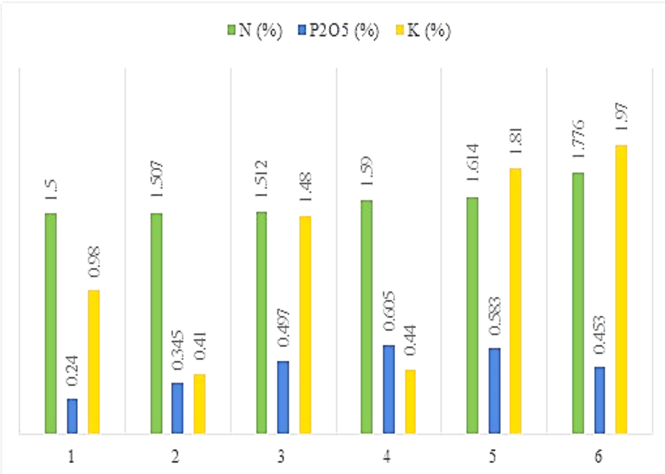

Fig. 5. N, P_2O_5 and K values of Halhale dairy manure samples

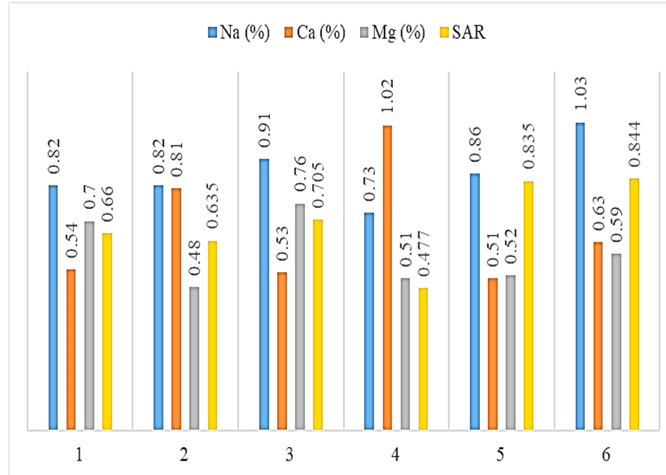

Fig. 6. Salts Composition in Halhale Dairy Manure Samples

Potassium (K) is another essential element of plant nutrition and necessary for the function of all living cells. Manure is an abundant source of K, many times found as more than required by the crops. Potassium amount in the manure measured varied greatly in the range of 0.41 to 1.97%. In addition, the entire content of K in the inorganic form readily dissolve in the water and hence consumed by the plants easily. All plants also need Sulfur (S), unfortunately manure contain S in reduced forms that cannot be used directly by the crops [19].

G. Micronutrients & Trace Components in Cow Manure & their effect on Plant or Animal Life

The presence of element in minute amounts, particularly identified as trace elements. Micronutrients such as copper (Cu), manganese (Mn), zinc (Zn), cobalt (Co), molybdenum (Mo) and boron (B) are minute components required by the crops or animals in little amounts. These elements measured for cow manure samples has very small amounts as shown in Table 6. Zn and Cu elements identified with significant presence in Halhale dairy samples. However, excess intake result is toxic and deficient yields. In contrast, trace elements such as cadmium (Cd), lead (Pb) and mercury (Hg) have no biological functions in plants and animals [19]. Fitzgerald and Racz (2001) found that concentrations of some undesirable metals such as Cd, Ni and Pb were closely correlated with elements added as nutritional supplements or for disease suppression, suggesting the Cd, Ni and Pb were most likely contaminants in the mineral supplements [19]. Composition of Pb observed in higher amounts for cow manure tested in comparison with other contaminants. The presence of many of these unwanted elements in the manure altered by changing the source of mineral supplements.

TABLE VI. COMPARISON OF INORGANIC COMPOSITION OF HALHALE DAIRY MANURE

Element	Amount	Element	Amount
Cu	<0.02 %	B	<50 ppm
Mn	241 ppm	Cd	<10 ppm
Zn	0.043 %	Pb	<0.02 %
Co	<10 ppm	Hg	<1 ppm
Mo	<20 ppm	Ni	<10 ppm

H. Salt Composition of Cow Manure & Its effect on Soil Fertility

Halhale Cow manure noted significant amounts of sodium (Na), calcium (Ca) and magnesium (Mg) salts as shown in figure 6. Sodium in manure mostly present as NaCl, and measured in the range of 0.73-1.03 % (weight). The excess salts (salinity) and soil quality adversely impacted by the excessive sodium, causes to sodicity, detrimentally affect plants. Subsequently, sodicity result in soil crusting. Ca and Mg in the manure present in the form of sulphate or bicarbonate, which are water-soluble and they estimated in the spectrum of 0.51-1.02% and 0.48-0.765 respectively for the Halhale dairy samples.

The Sodium Absorption Rate (SAR) is the ratio of Na to Ca and Mg, which is used as measure of salt concentrations, causes soil sodicity. Evaluated SAR have shown much variation and lie in the range of 0.477-0.844 for Halhale dairy manure samples as displayed in Fig 6.

IV. CONCLUSIONS

Physicochemical and thermal properties of Halhale dairy manure were evaluated primarily to assess the potential applications for the production of bioenergy and biofertilizer. Proximate analysis of fresh cow manure has revealed a mean TS content of 14.35 % with a volatile matter of 64.8% and ash content of 23.3%. Average carbon and sulfur contents measured using X-ray fluorescence as 43.1% and 0.31%. Hydrogen and nitrogen compositions were evaluated as 4.57 % and 1.58 % respectively. Thermophysical parameters such as P^H, SG and LHV determined as 7.025, 1.68 and 19.97 $MJkg^{-1}$ for the manure samples examined. Higher calorific values of Halhale dairy manure evident that it could be a sustainable fuel substitute for the energy production. The optimum C/N values of cow manure evaluated in the range of 25.68-27.3, ensure their best aptness for the biogas generation. Halhale dairy manure determined as an organic rich substance with an average protein content of 9.87% on dry basis and accompanied a moisture content of 85.65% on wet basis ensure their appropriateness to support large number of earthworms in vermicomposting process. Manure characterized with a mean proportion of N:P_2O_5 as 3.84 along with rich concentrations of potassium in the spectrum of 0.41-1.97%, which corroborates that it can support the growth of all kinds of crops. In addition, Halhale dairy manure found as rich in providing desired micronutrients such as Zn, Cu and Mn for the plant growth despite of significant Pb levels, which does not have any biological functions in the plant cell. Sodium salts in the manure samples measured as high as 1% with SAR of 0.84, which help to control the soil sodicity. However, this study has evaluated many parameters that are helpful to select cow manure as a feedstock for bioenergy or biofertilizer production, it has certain constrains in the evaluation of nitrogen and LHV as they depend on applied model precision and its validation.

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REFERENCES

[1] M. Shahbandeh, *Cattle population worldwide 2012-2022*, retrieved from www.Statista.com, accessed on 13, June 2022.

[2] Rob Cook. *Ranking of Countries with The Most Cattle*, www.Beef2Live.com, retrieved from https://beef2live.com/story-world-cattle-inventory-ranking-countries-0-106905, accessed on 13, June 2022.

[3] Julia Faria. *Countries with the largest cattle population in Africa 2020*, retrieved from www.Statista.com, accessed on 13, June 2022.

[4] Mordor Intelligence. *Livestock and Meat Market - Growth, Trends, Covid-19 Impact, and Forecasts (2022-2027).* Retrieved from https://www.mordorintelligence.com, accessed on 13, June 2022.

[5] Hui Wang, Horacio A. Aguirre-Villegas, Rebecca A. Larson and Asli Alkan-Ozkaynak. *Physical Properties of Dairy Manure Pre- and Post-Anaerobic Digestion*, Appl. Sci. 9, 2019, 2703; doi:10.3390/app9132703

[6] Gudina TT and Sanderine N (2015), *Bio-Wastes as an Alternative Household Cooking Energy Source in Ethiopia,* Energies, 8, 2015, pp. 9565-9583; doi:10.3390/en8099565

[7] Yao Yao, Gordon Huang, Chunjiang An, Xiujuan Chen, Peng Zhang, Xiaying Xin, Jian Shen, Joy Agnew. *Anaerobic digestion of livestock manure in cold regions: Technological advancements and global impacts,* Renewable and Sustainable Energy Reviews, 2019 https://doi.org/10.1016/j.rser.2019.109494

[8] Batzias, F.A.; Sidiras, D.K.; Spyrou, E.K. *Evaluating livestock manures for biogas production: A GIS based method.* Renew. Energy, 30, 2005, pp. 1161–1176.

[9] S. Katheem Kiyasudeen, Mahamad Hakimi bin, Ibrahim and Sultan Ahmed Ismail. *Characterization of Fresh Cattle Wastes Using Proximate, Microbial and Spectroscopic Principles,* American-Eurasian J. Agric. & Environ. Sci., 15 (8), 2015, pp. 1700-1709, DOI: 10.5829/idosi.aejaes.2015.15.8.235

[10] Engler CR, Jordan ER, McFarland MJ, Lacewell RD. *Economics and environmental impact of biogas production as a manure management strategy.* In: Texas animal manure management conference: 1999 proceedings. College Station, TX, USA: Texas A & M University

[11] Karmakar S, Lague C, Agnew J, Landry H. *Management practices for swine manure in the Canadian Prairies region.* In: Proc. Of CSBE/SCGAB 2006 annual conference; Edmonton Alberta.

[12] Szymajda, A.; Łaska, G.; Joka, M. *Assessment of Cow Dung Pellets as a Renewable Solid Fuel in Direct Combustion Technologies.* Energies, 14, 2021, 1192. https://doi.org/10.3390/en14041192

[13] Zuhal Akyurek. Sustainable Valorization of Animal Manure and Recycled Polyester: Co-pyrolysis Synergy, Sustainability, 11, 2019, 2280; doi:10.3390/su11082280

[14] Song, Y.J, Oh, K.S, Lee, B., Pak, D.-W.; Cha, J.-H. Park, J.-G. *Characteristics of Biogas Production from Organic Wastes Mixed at Optimal Ratios in an Anaerobic Co-Digestion Reactor.* Energies 2021, 14, 6812. https://doi.org/10.3390/en14206812

[15] Ayhan Varol, Aysenur Ugurlu. *Comparative evaluation of biogas production from dairy manure and co-digestion with maize silage by CSTR and new anaerobic hybrid reactor,* Engineering in Life Sciences, 17, 2017, pp.402-412.

[16] Bodius Salam, Sumana Biswas, Md Sanaul Rabbi. *Biogas from Mesophilic Anaerobic Digestion of Cow Dung Using Silica Gel as Catalyst*, Procedia Engineering, 105, 2015, pp. 652 – 657.

[17] Giulio Bortoluzzi, Manuele Gattia, Alberto Sognia, Stefano Consonnia. *Biomethane production from agricultural resources in the Italian scenario: techno-economic analysis of water wash,* Chemical Engineering Transactions, 37, 2014.

[18] Jongkwan Park, Kyung Hwa Cho, Mayzonee Ligaray and Mi-Jin Choi. *Organic Matter Composition of Manure and Its Potential Impact on Plant Growth,* Sustainability, 11, 2019, 2346; doi:10.3390/su11082346

[19] MAFRD (Manitoba Agriculture, Food and Rural Development). *Properties of Manure*, 2015, retrieved from https://www. manitoba.ca/agriculture on 14/03/2022.

[20] Gahyun Baek, Danbee Kim, Jinsu Kim, Hanwoong Kim and Changsoo Lee. *Treatment of Cattle Manure by Anaerobic Co-Digestion with Food Waste and Pig Manure: Methane Yield and Synergistic Effect,* Int. J. Environ. Res. Public Health, 17, 2020, 4737; doi:10.3390/ijerph17134737

[21] O.A. Hougen, KM. Watson, RA Ragatz, *Chemical Process Principles,* A combined volume of Pat I, Part II and Part III, John Wiley & sons, Incorporation, 1943. Chapman and Hall Limited, New York, USA.

[22] S. Chen , J.H. Harrison, W. Liao, D. C. Elliott, C. Liu, M. D. Brown, Z. Wen, A. E. Solana, R. L. Kincaid, D. J. Stevens. *Value added Chemicals from Animal Manure,* U.S. Department of Energy Reports, 2003.PNNL-14495.

[23] Vankát, A.; Krepl, V.; Kára, J. *Animal dung as a source of energy in remote areas of Indian Himalayas.* Agric. Trop. Subtrop. 43, 2010, pp. 140–142.

[24] Wang, J.; Ma, M.; Bai, Y.; Su, W.; Song, X.; Yu, G. *Effect of CaO additive onco-pyrolysis behavior of bituminous coal and cow dung*. Fuel 2020, 265, 116911.

[25] Budiyono, I N. Widiasa, S. Johari and Sunarso. *Study on Slaughterhouse Wastes Potency and Characteristic for Biogas Production.* Internat. J. of Waste Resources, Vol. 1(2), 2011 pp. 4-7.

[26] Hui Wang, Horacio A. Aguirre-Villegas, Rebecca A. Larson and Asli Alkan-Ozkaynak. *Physical Properties of Dairy Manure Pre- and Post-Anaerobic Digestion,* Appl. Sci. 9 (2703) 2019. doi:10.3390/app9132703

[27] Reumerman, P.; van den Berg, D. Reduction of Fouling, Slagging and Corrosion Characteristics of Miscanthus (The BIOMIS Project) Report. Retrieved from http://cordis.europa.eu/project/rcn/48287_en.html on 6 January 2021.

[28] Nunes, L.J.R.; Matias, J.C.O.; Catalao, J.P.S. *Wood pellets as a sustainable energy alternative in Portugal*. Renew. Energy, 85, 2016, pp. 1011–1016.

[29] TNAU Agritech Portal, *Feed management, Animal Husbandry*, Retrieved from https://agritech.tnau.ac.in/animal_husbandry/animhus_cattle_%20feed%20management.html#:~:text=The%20total%20dry%20matter%20requirement,influence%20the%20dry%20matter%20consumption. on 14 June 2022.

[30] Rick J. Rosby, Troy M. Walz (2011). *Water requirement for beef cattle, Institute of Agriculture and Natural resources*, University of Nebraska-Lincoln Extension. Retrieved from https://beef.unl.edu/water-requirements-for-beef-cattle, on 14 June 2022.

[31] Batzias, F.A.; Sidiras, D.K.; Spyrou, E.K. *Evaluating livestock manures for biogas production: A GIS based method*. Renew. Energy, 30, 2005, pp. 1161–1176.

[32] Birzer, C.; Medwell, P.; MacFarlane, G.; Read, M.; Wilkey, J.; Higgins, M.; West, T. A *Biochar-producing, dung-burning cook stove for humanitarian purposes*. Procedia Eng, 78, 2014, pp. 243–249.

[33] Iftikhar, M.; Asghar, A.; Ramzan, N.; Sajjadi, B.; Chen, W. Biomass densification: Effect of cow dung on the physicochemical properties of wheat straw and rice husk based biomass pellets. Biomass Bioenerg, 122, 2019, pp. 1–16.

[34] Rosillo-Calle, F. The Biomass Assessment Handbook: Bioenergy for a Sustainable Environment; Earthscan: London, UK, 2007.

[35] Apurva Mishra, Manish Kumar, Nanthi S. Bolan, Atya Kapley, Rakesh Kumar, Lal Singh. *Multidimensional approaches of biogas production and up-gradation: Opportunities and challenges,* Bioresource Technology, 338, 2021, pp. 125514.

https://doi.org/10.1016/j.biortech.2021.125514

[36] Alemayehu Gashaw, Abile Teshita. *Co-Digestion of Ethiopian Food Waste with Cow Dung for Biogas Production*, Int Journal of Research, 1, Issue-7, 2014, pp. 475-500.

[37] Mmabyalwa Sebola, Habtom Tesfagiorgis, Edison Muzenda. *Effect of particle size on anaerobic digestion of different feedstocks*, South African Journal of Chemical Engineering, 20 (3), 2015, pp. 11- 26.

[38] Sandhya Xavier and Krishna Nand. *A preliminary study on Biogas production from Cowdung using Fixed-Bed Digesters.* Biological wastes, 34, 1990, pp. 161-165.

[39] Y. Han, C.T. Chang, S.L. Zhu, A. Inoue, D.V. Louzguine-Luzgin, E. Shalaan, F. Al-Marzouki, *Fe-based soft magnetic amorphous alloys with high saturation magnetization above 1.5 T and high corrosion resistance*, Intermetallics, 54, 2014, pp. 169-175.

[40] Hidayat E, Afriliana A, Gusmini G, Taizo M, Harada H. Evaluate of Coffee Husk Compost. International Journal on Food, Agriculture and Natural Resources. 2020;1(1):37-43

[41] Wang Y, Zhang Y, Li J, Lin J, Zhang N, Cao W. Biogas energy generated from livestock manure in China: Current situation and future trends. Journal of Environmental Management. 2021;297:113324.