



## Research article



# Characterization of bovine ruminal content focusing on energetic potential use and valorization opportunities

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## ABSTRACT

This work characterized the bovine ruminal content excluding stomach tissue obtained from a slaughterhouse plant located in Cordoba, Colombia. The goal is to establish possible energetic uses and valorization potential instead of risky local current contaminant practices. Samples of ruminal content (RC) were collected under two conditions as-fresh and dry. Microbiological and bromatological quality, density, proximate and elemental analysis, and calorific power values were measured. There were complemented with optical microscopy, SEM, XEDS, FTIR, TGA, and TGA-MS analysis for both conditions. Ashes of combustion products from mixtures of natural gas and RC were studied, using XRD and XRF techniques. Results showed that fresh-state RC has an important microbiological quality without some human risk pathogens, such as *Salmonella* sp, *E. coli*, and vegetable risk pathogens, such as nematodes. Dry and sieved state RC is lignin-cellulosic heterogeneous biomass, with a real density of 164 kg/m<sup>3</sup>, a calorific power between 12 and 15 kJ/kg, and ashes rich in alkaline-earth elements. These results indicate that RC might have a good potential in co-combustion, gasification, and other energy processes. However, important considerations should be done about management of RC, because its direct application as fertilizer could carry out a negative effect, which was demonstrated in the growth of a model plant.

## 1. Introduction

The meat production is considered the most polluting industry in the food sector at the worldwide. By-products and waste generated by meat processing could lead to a high degree of contamination due to specific environmental problems by inappropriate management of these [1,2]. An organic waste that is obtained from bovine slaughterhouse is the ruminal content (RC). This material is mainly constituted from vegetable material, as forage, solids and doughy mass. The RC is founded in the first stomachs (reticulum or bonnet, rumen), especially in the rumen, which during the sacrificial tasks did not manage to be digested [3].

The ruminal content is one of the agroindustrial wastes with the greatest potential for environmental impact. The quantity of

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ruminal content varies widely with the age, size, transport, and rest time to which the animal has been subjected. Each slaughtered cow generates between 50 and 60 kg of wet ruminal content. Much of the ruminal content is deposited directly on crops, especially pastures, in landfills, and in wastewater, promoting contamination. These wrong practices have been observed in some countries of Latin America, therefore it is necessary to explore the potential uses of RC [4].

Colombia exported 35 kt of meat for a value of US\$145 million in 2021, which confirms that this country is an important both livestock and meat producer of Latin America. Cordoba is a north coast department of Colombia, which contribute around 8% of the total livestock of this country [5]. According to the information summarized in Fig. 1, Cordoba obtained around 165 kt of wet ruminal content per year from benefit plants. Inadequate RC handling and disposal could cause a negative impact on the environment because of ammonia nitrogen oxide emissions. The abovementioned compounds are formed as a secondary product of the denitrification process and also methane is formed during the decomposition of ruminal content in anaerobic conditions [6]. There are basically three strategies for the use of ruminal content: biological, (including anaerobic digestion and chemical recovery), production of biofuel, and thermal recovery processes [7].

Bovine rumen and ruminal content have been studied widely from viewpoints of digestibility, animal nutrition, and decomposition. Analysis of these results could be the best approach to establish the level of degradation of cellulose, hemicellulose, and lignin ingested in animal feeding. Mathematical modeling was established to understand the reduction of cellulose content in rumen digestion [8,9]. Lignin content was determined as an overriding factor in the degradation of complex hemicellulose-lignin during digestion [10]. In the rumen has been identified a great biodiversity of microorganisms covering phylum Protista and fungi, like, the domain of bacteria and archaea, its metabolic activity allowing vegetal biomass degradation [11,12]. There was established a clear correlation between high lignin content and low degradability of biomass content by rumen and methanogens microorganisms [13,14]. Climate and geolocation were important factors in the lignin content and complex chemical composition of pastures ingesting bovine, influencing ruminal fermentation and methane production [15]. On the other hand, several investigations have shown the effectivity of rumen microorganisms on degraded lignin-cellulose biomass aiming to obtain biogas via fermentation [16,17]. Nevertheless, there is not overall framing that covers physical-chemical and energetic aspects of ruminal content that allow estimating potential uses of this material, which is the goal of this paper.

A common practice of some slaughterhouses in Colombia is packing the rumen content in bags and stockpiling. After the material is non-restricted transported in trucks is disposed of at the final destination. Generally, this material is negligently used as fertilizer for the pasture, using it directly without any prior treatment. In the worst case, this material is directly disposed of in water sources. In this work, a complete characterization of the ruminal content was carried out, in order to establish opportunities for its use, focusing on energy potential and valorization, especially, with the least added value.

## 2. Materials and methods

### 2.1. Ruminal content sampling

No animals were used for experimentation in this study. The work was based on one of the main residues generated in a slaughterhouse. Two samples as ruminal content (dried and sieved sample) and a fresh sample (without sieved) were used for the characterization analyses, which were obtained from a slaughterhouse in the city of Montería, Colombia. In the slaughterhouse, the rumen is obtained from the first stomach of the cow, which is opened and the ruminal content is dragged by water, passing through a series of gutters until it is taken to the collection site (See Fig. 2a to c), were is compressed to remove excess water and then it is placed in the greenhouse for final drying. The rumen sampling was carried out with an adaptation of the ASTM D-2234 [18] standard and the NTC 5424 [19] standards, to ensure a representative sample of the material for the determination of quality and reliability of the characterization analyses. For this, the pile-type sampling was adapted, selecting different bags from the final place where the rumen content was disposed. After, were collected samples corresponds to old samples (between 30 and 45 days) and fresh (between 1 and 20 days) see Fig. 3a to c. Its continued with the homogenization of material using a shovel, to then carry out the quartering and final packaging of the samples in sterile ziploc bags.

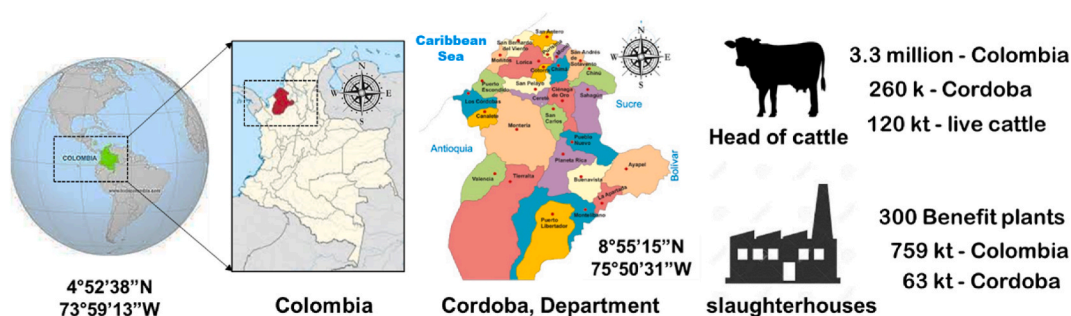


Fig. 1. General information of meat industry production in Cordoba, Colombia 2021.



**Fig. 2.** Detail of the rumen content processing. (a) Sieve and compression, (b) arranged in bags accumulate over time, and (c) ruminal content aspect after over time.



**Fig. 3.** Detail of the rumen samples, where differences in color and texture can be seen dependent on the storage time. (a) 5-day sample; (b) 30-day sample, (c) 45-day sample.

## 2.2. Elemental and calorific power measurements

Elemental and proximate analysis were carried out in sieved dry-condition samples of ruminal content. Carbon, Hydrogen, and Nitrogen contents were determined through standard ASTM D 5373–21 [20], while Sulphur and Oxygen contents were determined using ASTM D 4239 [21] and ASTM D 3176 [22], respectively. Calorific power, residual humidity, ashes, and volatile material were determined using the standard ASTM D 3172–13 [23].

## 2.3. Bromatological analysis

A bromatological analysis was developed using fresh-condition of ruminal content. The moisture, humidity, dry matter, and volatilization content, Ether extract, Raw fiber, Acid detergent fiber, Neutral detergent fiber, Organic nitrogen, Raw protein, Nitrogen free extract, Lignin, Cellulose, and Hemicellulose were determined according to Ref. [24].

## 2.4. Physical and chemical analysis

A physical and chemical analysis was developed using fresh-condition of ruminal content. Physical characteristics were determined using gravimetric, potentiometric and conductometric technique under the standard NTC-5167 [25]. The characterization of the mineral fraction was determined using the standards NTC-234 [26], NTC-370 [27], NTC-1154 [28], and NTC-1860 [29].

## 2.5. TGA and TGA-MS analysis

The TGA is defined as the technique in which the mass variation of a sample is measured against time or temperature, while it is subjected to a controlled temperature program in a specific atmosphere, when coupled to a mass analyzer, it allows analysis of the decomposition products of the sample. For this study, the TGA analysis was performed from 20 °C to 800 °C with a speed of heating at 10 °C.min<sup>-1</sup> under a nitrogen atmosphere, and upon reaching 800 °C, it was changed to air atmosphere using a Shimadzu®Discovery TGA 550. Thermogravimetry technique coupled with mass spectroscopy (TGA-MS) analysis is a technique that allows analyzing the

decomposition products of a sample. In this investigation was used a Thermal Advantage Q600 SDT, with Nitrogen flux of 60 ml min<sup>-1</sup>, a heat rate of 10 °C.min<sup>-1</sup>, and data range between 40 °C and 1000 °C. Data were analyzed using TA universal analysis 2000 software.

## 2.6. FTIR analysis

The FTIR analysis of ruminal content in sieved dry-state was carried out in a Shimadzu IRTracer –100. Measurements were developed using diamond crystal and ATR technique. The spectra were collected in the range from 4000 to 400 cm<sup>-1</sup>. There was used a spectral resolution of 10 cm<sup>-1</sup>, and 3 scans were taken per sample. Each sample was tested three times.

## 2.7. Morphology and microchemical analysis

Scanning Electron Microscopy was utilized to visualize the morphology and chemical composition of the delivered materials, it was used a JEOL JSM-7100F microscope (FE-SEM). For this, the two samples were deposited in a copper cylinder and plated with a thin layer of gold. Also, the samples were visualized by means of a stereomicroscope (LEICA EZ410). On the other hand, to know the chemical composition of the samples, they were analyzed by means of X-ray energy dispersive spectrometry (EDS).

## 2.8. Microbiological analysis

The biological quality analysis is carried out on biomass or organic fertilizers [30] and included: Test of maturity and stability, pH, Test of effect on plants, Test of biological safety to establish the presence and number more probable (MPN) of (Total coliforms, fecal, *Salmonella*, pathogenic nematodes or helminth eggs, *Escherichia coli*). The analysis was carried out at the National Soil Laboratory of the Agustín Codazzi, Geographical Institute, Colombia. 1 kg of fresh ruminal material it was required.

## 2.9. Ash chemical analysis

The X-ray fluorescence (FRX) analysis was performed on the samples ashes generated in a combustion process of ruminal material mixed with natural gas (50/50 natural gas/rumen mixture). The samples were taken from the combustion chamber and the chimney, and analyzed in a Panalytical Epsilon 1 equipment, which has a 100 KV X-ray lamp and Germanium detector. The equipment was calibrated for each of the reported elements. Using this calibration and the intensities obtained by subjecting the samples to fluorescence, the concentrations of the elements were determined, which are reported in percentage.

## 3. Results and discussion

### 3.1. Elemental and calorific value analysis

Results of combustion properties experimentally measured on a dry and as-fresh basis of the RM are shown in Table 1. The measured calorific value of RM is directly related to its lignin, hemicellulose, and cellulose content (see Table 2). RM owns a low calorific value (CV) of 15.5 MJ/kg, meanwhile, that is similar to other biomass, such as flax straw (18.2 MJ/kg), wheat straw (17.9 MJ/kg), oat straw (17.5 MJ/kg), barley straw (17.9 MJ/kg), rice husk (15.5 MJ/kg), elephant grass variety (16–18 MJ/kg), and sugarcane bagasse (16 MJ/kg) [38,39]. CHONS measured values in RM are similar to the abovementioned biomasses within a range lower than 5%. However, volatile matter content (60.3%) is less than straw biomass (70%–80%) [39], still, the ruminal material is feasible for biofuel production. The stoichiometric air mass requirement for RM is remarkably lower compared to, for example, coal [40]. This can be explained by the high content of oxygen (O<sub>2</sub>: 29.27%) in the RM chemical composition. The percentages of N and S on a dry matter of RM exceed 2%, which allows us to infer that it is extremely feasible to clean or filter the combustion gases so as not to generate pollutants. Despite this, another possibility of use, currently even the most applied, is methane generation. The methanation power of the rumen is between 40% and 75%, obtaining a calorific value of 21–39.8 MJ/m<sup>3</sup> [41,42].

**Table 1**

Results of calorific value, proximate and ultimate analysis of ruminal cow content on a dry and as-fresh basis.

Ítem	Standard	As-fresh	Dry
Total humidity (% weight)	ASTM D 3302 [31]	14.43	–
Ashes (% weight)	ASTM D 7582 [32]	16.82	19.66
Carbon (% weight)	ASTM D 5373 [33]	37.29	43.58
Hydrogen (% weight)	ASTM D 5373 [33]	4.56	5.36
Nitrogen (% weight)	ASTM D 5373 [33]	1.46	1.71
Sulphur (% weight)	ASTM D 4239 [34]	0.36	0.43
Oxygen (% weight)	ASTM D 3176 [35]	25.04	29.27
Calorific value	ASTM D5865/D5865 M – 19 [36]	–	15.5 MJ/kg
Volatile matter	ISO 562–10 [37]	–	60.3 %-mass



**Table 2**  
Bromatological analysis of fresh sample of ruminal cow content.

Variable	Percentage	Used Technique
Ether extract	0.9%	Ether/Gravimetric [24]
Raw fiber	41.1%	Acid mixture/Gravimetric [24]
Acid detergent fiber	50.6%	Acid detergent/Gravimetric/ICA 1985
Neutral detergent fiber	71.1%	Neutral detergent/Gravimetric/ICA 1985
Organic nitrogen	1.3%	Kjeldahl mixture/Volumetric [24]
Crude protein	8.3%	Kjeldahl mixture/Volumetric [24]
Nitrogen free extract	42.0%	Calculation
Lignin	11.6%	Sulfuric acid solution/Gravimetric/ICA 1985
Cellulose	31.4%	Calculation
Hemicellulose	20.5%	Calculation

### 3.2. Bromatological analysis

The importance of knowing the bromatological quality of the RM is due to indicate the degree of nutrition and degradability of the food consumed by cattle and is related to the quality of their food, grass species principally, can influence their energetic capacity. Further, the abovementioned information is useful is to predict possible toxic gases generated in its combustion, such as NO<sub>x</sub> and SO<sub>2</sub>.

Bromatological analysis results of fresh state RC are shown in Table 2. Raw fiber value (41.1%) indicates a high percentage of organic compounds that have not been degraded yet, which is consistent with the digestion process of cows [43]. The high percentage of fibers requires pretreatment such as milling to be able to be used in combustion and pyrolysis processes, as occurs with other biomass [44]. Nitrogen-free extract (42%) indicates the nutrients that are grouped by digestible carbohydrates, as well as vitamins and other organic compounds such as starches, sugars, organic acids, pectins and mucilages. The aforementioned result is probably attributed to a higher percentage of carbohydrates present in ruminants' diet, which are mainly represented in starches and sugars of grasses and legumes [45]. The cellulose content in RC has the highest percentage value, followed by hemicellulose and lignin. Probably the action of microorganisms is responsible for these values, which makes RC a useful material for anaerobic digestion and fermentation processes [16–46].

### 3.3. Physical and chemical properties analysis

Results of physical and chemical properties analysis of the as-fresh state of RC are shown in Table 3. The pH value of RC is near the neutrality value, 6.64, which allows this to be a possible acidic soil conditioner. Nevertheless, other parameters such as electrical conductivity, cation exchange capacity, humidity retention, and C/N ratio, make it a possible very polluting material. To mitigate this, RC requires a process that prior reduces the C/N ratio [47].

**Table 3**  
Physical and chemical properties analysis of fresh sample of ruminal cow material.

Variables	Unit	Used Technique
pH	6.64	Saturation paste/Potentiometric/NTC 5167 [25]
Electric conductivity	1.39 dS/m	Saturation paste/Conductometric/NTC 5167 [25]
Humidity retention	3.39	Saturation paste/Gravimetric/NTC 5167 [25]
Cation exchange capacity	34.3% meq/100g	Ammonium acetate/Volumetric/NTC 5167 [25]
Real density (dry basis)	0.164 g/cm <sup>3</sup>	Direct/Gravimetric/NTC 5167 [25]
Total oxidizable organic carbon	22.5%	Sol. Potassium Dichromate/Colorimetric/NTC 5167 [25]
Carbon/Nitrogen relation	31.00	Mathematical relation
Humidity	40.2%	70 °C/Gravimetric/Bernal [24]
Dry material	59.8%	Calculation
Ashes	7.6%	700 °C/Gravimetric/Bernal [24]
Volatilization losses	7.6%	Calculation
Total Nitrogen	0.730%	Sum of Nitrogen species
Organic Nitrogen	0.730%	Micro-Kjedahl/Volumetric/NTC 370 [27]
Total Phosphorus	0.375%	MVH Nitric acid: Perchloric acid/Colorimetric/NTC 234 [26]
Total Potassium	0.103%	MVH Nitric acid: Perchloric acid/EAA/PlantAnalysis Procedures [54]
Total Calcium	0.294%	MVH Nitric acid: Perchloric acid/EAA/PlantAnalysis Procedures [54]
Total Magnesium	0.101%	MVH Nitric acid: Perchloric acid/EAA/PlantAnalysis Procedures [54]
Total Sulphur	0.087%	MVH Nitric acid: Perchloric acid/Colorimetric/NTC 1154 [28]
Total Iron	184 mg/g	MVH Nitric acid: Perchloric acid/Colorimetric/NTC 234 [26]
Total Manganese	30.7 mg/g	MVH Nitric acid: Perchloric acid/Colorimetric/NTC 234 [26]
Total Copper	7.43 mg/g	MVH Nitric acid: Perchloric acid/Colorimetric/NTC 234 [26]
Total Zinc	35.6 mg/g	MVH Nitric acid: Perchloric acid/Colorimetric/NTC 1860 [29]
Total Boron	8.83 mg/g	MVH Nitric acid: Perchloric acid/Colorimetric/NTC1860 [29]
Total Sodium	0.141%	MVH Nitric acid: Perchloric acid/EAA/PlantAnalysis Procedures
Silicite (Soluble in HF)	2.460%	MVH HF/EAA/NTC 5167 [26]
Acid insoluble residue	2.470%	MVH Nitric acid: Perchloric acid/Colorimetric/NTC 5167 [26]

RM chemical composition is an important factor to consider in emissions in both combustion and pyrolysis systems, since the high content of N, P, K and Cl in this type of biomass could adversely affect the particulate material emissions [48,49]. In addition, the presence of forage material or grasses in RC generally increases the Silica content, affecting the melting temperature of the ashes and the release of alkali-earth metals [50]. On the other hand, the results of RC chemical composition show high contents of total Fe, Mn, Zn, B, Cu, and Si, which are directly related to the herbaceous feeding of cattle. These elements can be found in the particulate material generated in the combustion and pyrolysis of several biomasses, such as wheat straw, corn stalk, oak, and rice husk, among others [51, 52]. The aforementioned implies considering to use of adequate filtration systems to reduce the effects of air pollution, however, it is important to consider that this also could enrich the ashes for possible use as fertilizer. In the other hand, in biodigestion process of RC, the presence of these metals would not imply a higher particle material emission, due its the low temperature of processing. Nevertheless, it is recommended to clean the biogas to eliminate NO<sub>x</sub>, CO<sub>2</sub>, and H<sub>2</sub>S mainly [53].

### 3.4. Microbiological analysis

Biological quality analysis is important to explore other possible uses of the ruminal content (RC), such as organic fertilizer or composting. Additionally, it is useful to establish the presence of possible pathogenic organisms that may hinder its use both in crops, and its direct manipulation without protection (gloves, masks, etc.).

The results obtained for the maturity and stability tests, and effect test on plants, are shown in Table 4. The tests are based on the capacity of the sample, to inhibit the germination of a model plant. The plant used in the analysis was cabbage, *Brassica oleraceae*, and the effects analyzed on the plant are: biomass of emerged seedlings (at 5 days), -average stem length (at 5 days), -average length of root (after 5 days), -stem/root ratio.

According to the results reported in Table 4, it is evident that the RC is not a suitable substrate to be applied directly to the crop. Germination percentage of the model plant, cabbage, was lower than the control (peat), obtaining values of 35.4% for RC in a mixture ratio of 1:3 RC/peat, and 96.9% for peat. Additionally, it is highlighted that when the 1:0 and 1:1 RC/peat ratios were tested, there was no germination, demonstrating that RC should be not used as organic fertilizer. For RC to be able to be used as fertilizer, it must be subjected to transformation processes of organic matter, such as composting. Otherwise, it can become a soil contaminant or a germination inhibitor in a crop [55].

For the other morphometric parameters evaluated in the cabbage plant such as: biomass of emerged seedlings, -average stem length, -average root length, and -stem/root ratio, the differences are significant between the 1:3 RC/peat substrate and the peat, being that the values obtained for the control are significantly higher. Also, biomass, which is one of the main parameters that indicates the quality of a biofertilizer on the yield of a crop, shows an average of 0.092 g for the RC in contrast to an average of 0.53 g for the peat. The same occurs for the other measures of physiological variables of a plant, which indicate the quality growth, such as: stem length,

**Table 4**

Results of the ruminal cow material maturity and stability tests, and effect test on model plant (*Brassica oleraceae*).

<b>Germination % (5 days)</b>				
Treatments (sample ratio: control substrate)				
Reply	1:0	1:1	1:3	0:1 Control
1	–	–	6.67	93.75
2	–	–	37.50	100
3	–	–	33.33	93.75
<b>Biomass of emerged seedling (g) (5 days)</b>				
Treatments (sample ratio: control substrate)				
Reply	1:0	1:1	1:3	0:1 Control
1	–	–	0.003	0.405
2	–	–	0.097	0.690
3	–	–	0.087	0.500
<b>Average stem length (mm) (5 days)</b>				
Treatments (sample ratio: control substrate)				
Reply	1:0	1:1	1:3	0:1 Control
1	–	–	4.000	19.067
2	–	–	5.500	35.563
3	–	–	6.800	25.867
<b>Average root length (mm) (5 days)</b>				
Treatments (sample ratio: control substrate)				
Reply	1:0	1:1	1:3	0:1 Control
1	–	–	10.000	10.800
2	–	–	3.667	30.188
3	–	–	3.000	18.400
<b>Stem/root ratio</b>				
Treatments (sample ratio: control substrate)				
Reply	1:0	1:1	1:3	0:1 Control
1	–	–	0.025	1.921
2	–	–	0.693	1.299
3	–	–	0.927	1.317

Control substrate: peat. Number of treatments: 4. Number of replicates: 3. Seed: *Brassica oleraceae* (cabbage).

which proved to be superior in the peat with an average value of 26.8 mm versus a value 5.4 mm for RC; finally, the length of the root with an average value of 19.8 mm for the peat and 3.3 mm for the RC. Biological safety and microbiological quality (BSMQ) test results are shown in Table 5.

The BSQM analysis measured the presence/absence of pathogens such as *Salmonella*, and nematodes as one of the main phytopathogens in soils and biofertilizers. Further, the most probable number (MPN) of fecal coliforms and *E. coli*, measuring the viability of cells of these microorganisms capable of forming colonies in a substrate [56,57]. The results showed that these microorganisms are not present in the RC sample, which indicates that is suitable for handling by operators for use as valorization energy or other treatments, providing the use of personal protective equipment.

### 3.5. TGA analysis

Fig. 4 shows the TGA analysis for the fresh ruminal cow sample (Fig. 4a) and the dry and sieved sample (Fig. 4b). The two samples show three thermal stages, the first stage occurs between 20 °C and 120 °C and could be related to the presence of water in the samples. The second thermal stage occurs between 200 °C and 600 °C. The third stage occurred due to the change to air atmosphere [58]. This change of atmosphere favors the degradation of the carbonaceous material present in the samples. The amount of this degraded material for the fresh and dry sample was 9.4% and 13.6%, respectively. The dry sample had an ash percentage of 20.4%, which may be mainly composed of Si and Ca as evidenced by the FRX analysis, showed in Table 7. The fresh sample, as expected, has a higher percentage of moisture compared to the dry sample. In general, hemicellulose is reported to decompose between 250 °C and 300 °C, cellulose between 300 °C and 350 °C, and lignin degrades at temperatures above of 400 °C, in addition, it is noteworthy that biomasses without delignification pretreatments broaden the range of degradation and cause an increase in temperatures, to 900 °C, for complete biomass decomposition to occur [59,60]. The behavior of the RC degradation trend is similar to that reported for several biomasses, such as corn stalk [61], banana peel [62], flax straw [63], and waste *Miscanthus* grass [64].

### 3.6. TGA-MS analysis

Mass spectrometry coupled thermogravimetric analysis (TGA-MS) provides information about the species involved, both organic and inorganic, and the products of decomposition reactions that occur in a thermochemical conversion process. One of the limitations of this technique is that some polar products and/or non-volatile gas phase products may be lost in the process [65]. Even though in general cellulose, hemicellulose, and lignin are the main components of biomass, there are other organic and inorganic chemical compounds. However, it is difficult to define organic compounds precisely, mainly due to the technological limitations of the equipment. For example, the mass spectrometry does not have a wide enough scanning range, or the gas chromatographic identity cannot match the exact moment of gas release [66]. The results of the main compounds identified in the ruminal cow material are shown in Table 6.

In the TGA-MS analysis the following **species that can be identified with their own signal**: H<sub>2</sub> (Hydrogen), O<sub>2</sub> (Oxygen), CO<sub>2</sub> (Carbon dioxide), C<sub>2</sub>H<sub>4</sub>O (Acetaldehyde), C<sub>3</sub>H<sub>8</sub> (Propane), CH<sub>2</sub>O<sub>2</sub> (Methanoic Acid). The following **species that have mixed signals**: C<sub>2</sub>H<sub>2</sub> (Ethyne), CO (Carbon monoxide), C<sub>2</sub>H<sub>4</sub> (Ethene), C<sub>2</sub>H<sub>6</sub> (Ethane). The following **species not found in the database**: C (Carbon), CH<sub>2</sub> (Methylene), CH<sub>2</sub>O (Formaldehyde), C<sub>2</sub>H<sub>6</sub>O (Ethanol).

Main gases produced during the pyrolysis of RC were oxygen containing species derived from parent biopolymers and H<sub>2</sub>O, followed by CO and CO<sub>2</sub>, same as described for coffee grounds residues [67], and oil palm biomass and sawdust [68]. Among the organic compounds identified with their own signal, formic acid (methanoic acid) and acetaldehyde stand out. Organic acids and aldehydes are often found in pyrolysis, torrefaction, and thermochemical processes in other biomass, such as, wood, agricultural coproducts, herbaceous crops, sugarcane residues, among others [60,69,70]. A possible explanation for its presence in RC could be the cattle feeding with molasses, since this organic acid (formic acid) is found in honey, for example. Its acidity is relatively high since its pKa is 3.75, has a boiling point of 100.7 °C, is highly soluble in water, and is easily ionizable, reacts strongly with oxidants and bases generating fire and explosion hazards and attacking some plastics and metals [71]. Although these conditions are rarely found in combustion and pyrolysis systems, this compound should be considered during the RC energy process for structural components integrity.

On the other hand, acetaldehyde is widely used in the chemical industry and is one of the main intermediates for the manufacture of acetic acid, butanol, peracetic acid, pentaerythritol, and hexanol, among others. It is also used in the manufacture of flavorings, perfumes, dyes, pharmaceutical products, and pesticides [72]. This particular organic compound is likely associated with RC due to its

**Table 5**

Results of the biological safety test of the ruminal cow material.

Parameter/Method	Detection limit	Limit of quantification	Value obtained
<b>Fecal coliforms: Multitube fermentation, MPN (most probable number)</b>	1.80 NMP/g	594.3 NPM/g	>594.3 NMP/g
<b><i>Escherichia coli</i>: Multitube fermentation - enzymatic response, NMP (most probable number)</b>	1.80 NMP/g	196.1 NPM/g	59.4 NMP/g
<b>Total Coliforms: Multitube fermentation, MPN (most probable number)</b>	1.80 NMP/g	594.3 NPM/g	>594.3 NMP/g
<b><i>Salmonella</i>: Surface seed plate culture. Presence/absence</b>	N.A.	N.A.	N.D.
<b>Sampled nematodes: sieving and quantification</b>	N.A.	N.A.	N.D.

N.A.: not apply. N.D.: not detected.

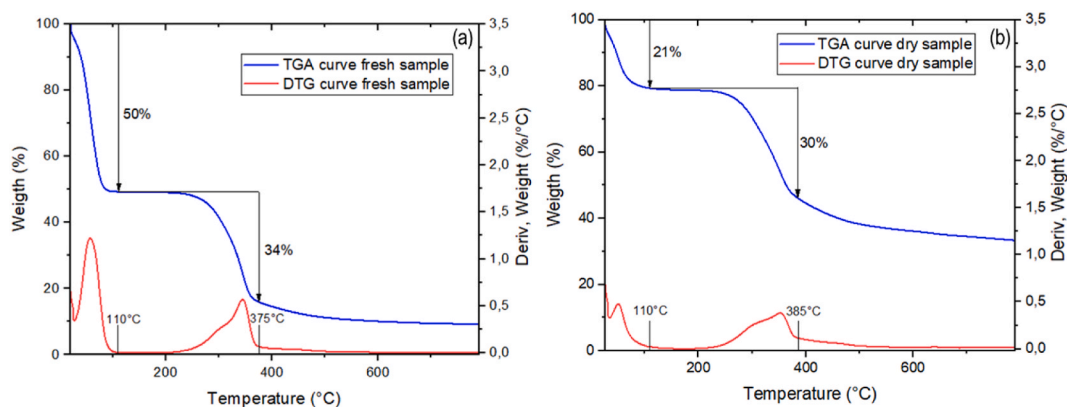


Fig. 4. TGA analysis of Ruminal cow content, (a) fresh sample, (b) dry and sieved sample.

Table 6

TGA-MS analysis of ruminal cow material. masses present for the species found.

Hydrogen	H <sub>2</sub> : <u>2</u> .	-> [H <sub>2</sub> :2]
Oxygen	O <sub>2</sub> : <u>32</u> , 16, 34, 33.	-> [O <sub>2</sub> :32]
Ethyne	C <sub>2</sub> H <sub>2</sub> : 26, 25, 13, <b>24</b> , 27, 12, 14, 28.	-> [C <sub>2</sub> H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>4</sub> O:24]
Carbon monoxide	CO: 28, 12, 29, <b>16</b> , 14, 30.	-> [CO/O <sub>2</sub> /CO <sub>2</sub> /CH <sub>2</sub> O <sub>2</sub> :16]
Ethene	C <sub>2</sub> H <sub>4</sub> : 28, 27, 26, 25, 14, <b>24</b> , 13, 29, 12	-> [C <sub>2</sub> H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>4</sub> O:24]
Ethane	C <sub>2</sub> H <sub>6</sub> : 28, 27, 30, 26, 29, <b>15</b> , 25, 14, 31.	-> [C <sub>2</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub> :15]
Carbon dioxide	CO <sub>2</sub> : 44, 28, 16, 12, 45, <u>22</u> , 46, 13, 29.	-> [CO <sub>2</sub> :22]
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O: 29, 44, 43, <b>42</b> , 26, 25, 27, 41, 28, 24.	-> [C <sub>2</sub> H <sub>4</sub> O:42]
Propane	C <sub>3</sub> H <sub>8</sub> : 29, 26, 28, 15, 27, 44, 14, 43, <u>39</u> , 41.	-> [C <sub>3</sub> H <sub>8</sub> :39]
Methanoic Acid	CH <sub>2</sub> O <sub>2</sub> : 29, 46, 45, 28, <u>17</u> , 44, 16, 12, 13, 30.	-> [CH <sub>2</sub> O <sub>2</sub> :17]

\*Unique masses per species are underline. In bold, the least repeated mass is presented, in case of not having a single mass.

Table 7

FRX results and elemental analysis of the oxides obtained for the analyzed samples.

Oxide species of the chemical element	Concentration %	
	RM/NG 50/50 Chamber	RM/NG 50/50 Chimney
MgO	6142	6071
Al <sub>2</sub> O <sub>3</sub>	2326	2409
SiO <sub>2</sub>	<b>50,440</b>	<b>55,703</b>
P <sub>2</sub> O <sub>3</sub>	4302	4040
SO <sub>3</sub>	2218	1203
Cl	0,384	0582
K <sub>2</sub> O	0,607	0697
CaO	14,540	13,004
TiO <sub>2</sub>	0,164	0175
MnO	0,120	0145
Fe <sub>2</sub> O <sub>3</sub>	1658	3237
NiO	0,005	0015
CuO	0,018	0009
ZnO	0,064	0400
SrO	0,026	0020
PbO	0,006	0006

(\*) The reported values are based on the most stable or basic oxide for each element.

use in pesticides since it could be the most direct relationship found in grass species and cattle feeding. Moreover, this is a compound that results from the thermal degradation of lignin. A possible problem with the presence of this compound in the TGA-MS analysis is that it is highly volatile, flammable, and genotoxic [73,74].

### 3.7. FTIR analysis

Fig. 5a and b shows the FTIR analysis of RC, dry and sieved sample, and as-fresh sample, respectively. In general, the spectra do not present significant differences and the functional groups of both samples are quite similar. In general, the vibration around 3295 cm<sup>-1</sup>

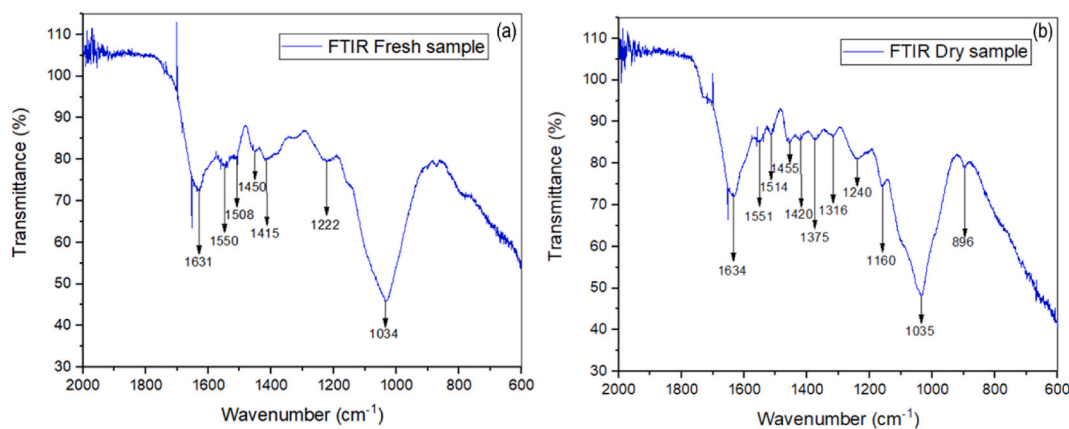


Fig. 5. FTIR analysis of Ruminal cow content (a) dry and sieved sample and (b) fresh sample.

corresponds to the vibration of the group functional O–H. The vibrations at  $2920\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  are due to the vibration of the C–H functional group from aromatic, aliphatic and alkali structures, in addition to possible methylene [75]. In RC the band around  $1640\text{ cm}^{-1}$  is attributed to the vibration of the functional group C=O in carboxylates, esters and ketones, as reported at [63] for flax straw. The vibration at  $1515\text{ cm}^{-1}$  corresponds to the vibration of the functional group C=C of the aromatic ring of lignin and hemicellulose, like the kraft biomass, among others [13,76]. The vibration at  $1245\text{ cm}^{-1}$  is associated with the vibration of the C–O functional group of carboxylic acids and for the hemicelluloses and cellulose [77,78], being that this result agrees with the analysis of TGA-MS, this band and the band around  $1640\text{ cm}^{-1}$  they can be attributed to formic acid. The vibration at  $1040\text{ cm}^{-1}$  is due to the vibration of the C–O functional group of polysaccharides [78]. Finally, vibrations between  $1530\text{ cm}^{-1}$  to  $1250\text{ cm}^{-1}$  can also be associated with the functional group C–N, as reported at [79] for poplar biomass.

### 3.8. SEM/EDS analysis

In stereomicroscopic images can be observed the bundles of cellulose fibers and different morphologies that could be analyze in detail on the SEM images. In general, RC is a very heterogeneous material, mainly of fibers and other agglutinated solids, as shown in Fig. 6a to c.

SEM analysis shows that in RC dry and sieved, and as-fresh samples, remaining vegetable material that has not been digested in the intestinal tract of the animal, porous structures in both samples, and a conglomerate of fibers in different degrees of degradation, similar to those described and shown at [80]. A measurement of the size of the cellulose fibers was carried out and it was found that, for the dry and sieved sample, the approximate thickness was  $143\text{ }\mu\text{m}$ , while for the fresh sample it was approximately  $71.5\text{ }\mu\text{m}$ . The biggest size in the dry sample can be related to the union of different fibers during the process of drying, as is shown in Fig. 7a to f, and Fig. 8a to f. Are also observed microbial cellular structures, corresponding to bacillary and cocci forms, and others that could be spores of fungi, similar to those reported at [11,81].

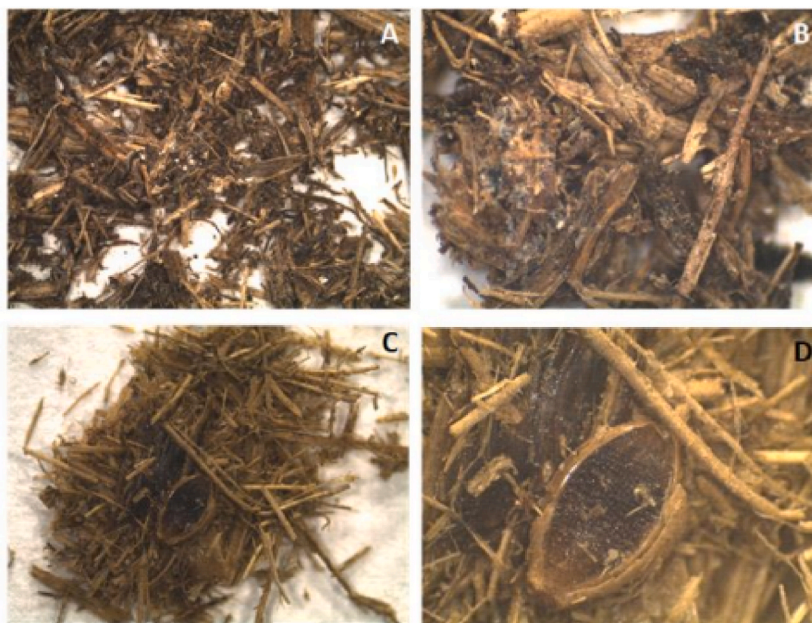
Fig. 9a to e shows EDS maps of a region with a conglomerate of fibers. Semiquantitative analysis displays high content of C, which is usually in biomass. The ruminal material is also composed of N, Si, Cu, Ca, Na, Mg, Fe and S, elements that are in less quantity, see Table 3. On the other hand, Fig. 10a to c shows a chemical microanalysis of a region containing mixed fibrous and non-fibrous material. The semiquantitative analysis shows the high presence of C, since this is the structural element of lignin, cellulose and hemicellulose, in addition to other elements such as Si and Ca which are observed concentrated in small specific regions. Si enters the solid natural biomass, through the absorption of monosilicic or orthosilicic acid from the soil, mainly from the minerals present in the soil, from the decomposition of vegetables, silicate fertilizers (which increases resistance to diseases and drought in plants), and the irrigation water [82]. Therefore, finding Si in RC, possibly coming both from decomposing plant material, as well as from soil and silicate salts present in fertilizers and in livestock feed supplements.

### 3.9. Ash chemical analysis

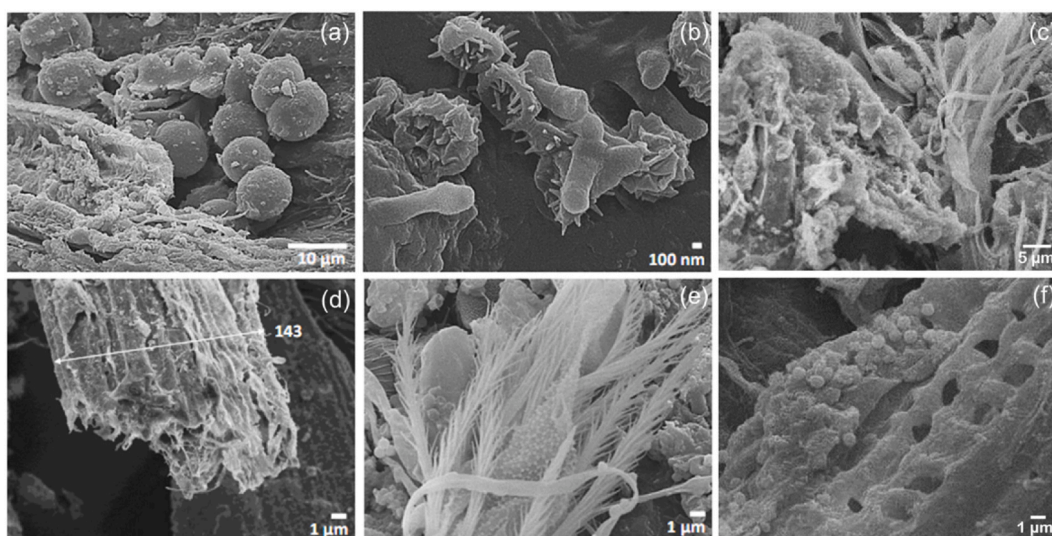
The oxides generated in the chamber and chimney samples, obtained from a combustion process of ruminal material mixed with natural gas (50/50 natural gas/rumen mixture) are shown in Table 7. In this analysis, the X-ray fluorescence equipment exclusively detects chemical elements, which are reported as the most stable oxide species of the element, which is why the total sum of oxidized species can exceed the value of 100%.

Table 7 showed that the highest percentage is for  $\text{SiO}_2$ , which represents the total silica present in the two types of ashes generated in the mixture RM/natural gas combustion process. According to Ref. [83], the total silica content ( $\%\text{SiO}_2$ ) in the ashes of biomass represents the largest proportion of the inert material that constitutes it and that could generate problems of corrosion by erosion and slag formation during process combustion inside the system. These authors determined an average  $\%$  of  $\text{SiO}_2$  of 57.66% in the ashes





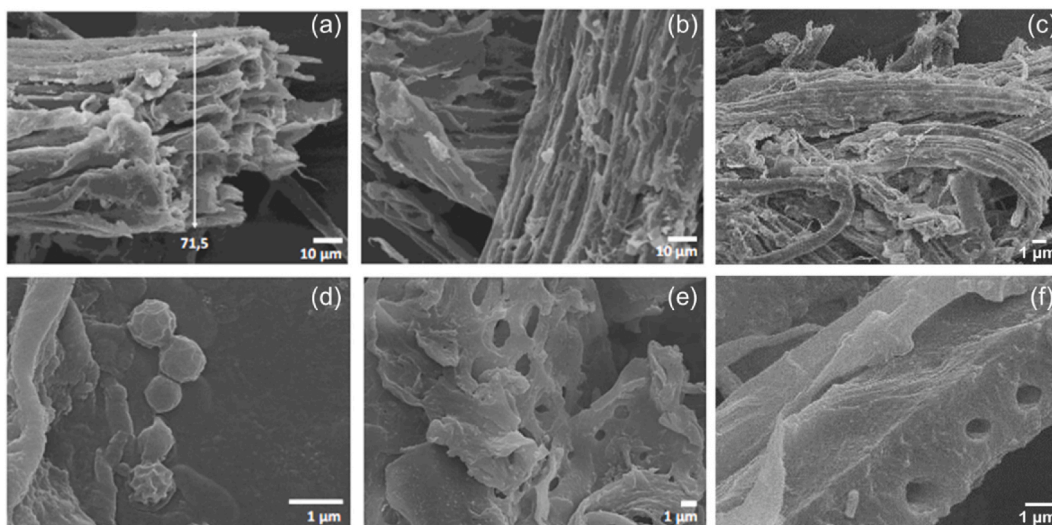
**Fig. 6.** Stereomicroscope images of the delivered samples. A) and B) Ruminal cow material (dry and sieved sample), C) and D) Fresh sample-ruminal cow material.



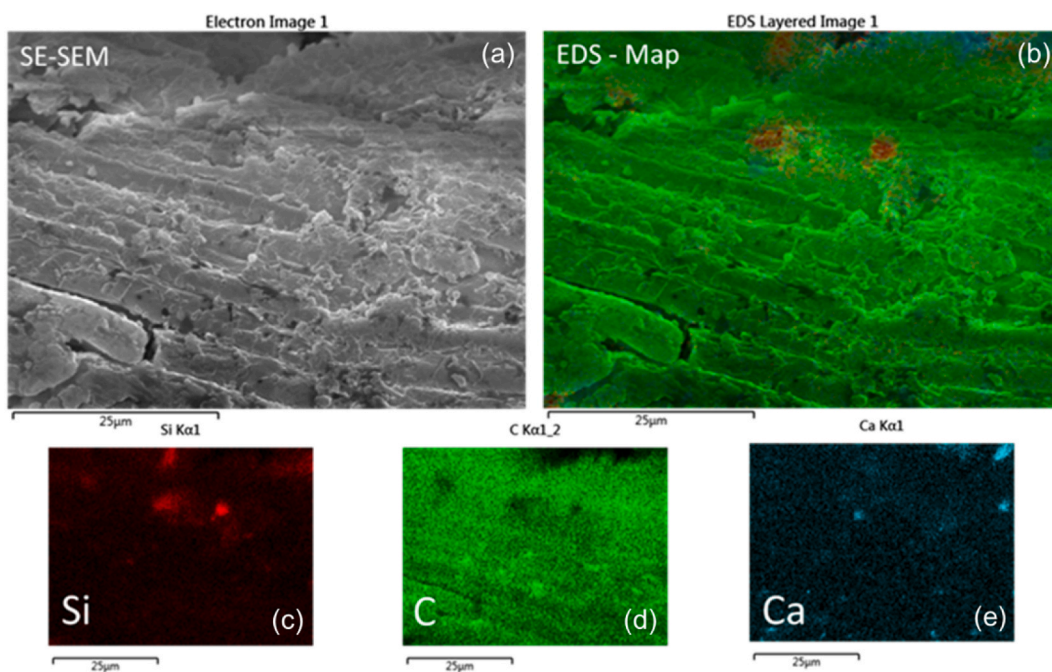
**Fig. 7.** SEM micrographs of the sample ruminal cow content (dry and sieved sample). (a) cocci forms, (b) bacillary forms, (c) conglomerate of fibers, (d) fibers with 143  $\mu\text{m}$  thickness, (e) undegraded fibers, (f) porous structure.

when they used agroindustrial waste from sugarcane cultivation and subjected them to combustion to generate vapor gases. The value reported by the authors is similar to that obtained in the ashes from the combustion of ruminal material, whence it is necessary to take care in combustion systems.

Thermal degradation products during biomass combustion consist of volatile elements, steam (humidity), char, and ash. One of the main by-products of biomass combustion is ash since it can be used as an amendment for soil and fertilizers [84,85]. The content of humidity and ash in the fuel causes biomass ignition and combustion problems, which is why the analysis and knowledge of the chemical composition and physical properties of the ash make it possible to predict the tendency to form deposits in fuel components, combustion system, and its potential to cause corrosion, erosion, and abrasion [86]. Ash behavior in the system is highly fuel-dependent, particularly when it comes to agroindustrial waste or from crops. These fuels have a higher content of minerals, in particular Na, K, P, and Cl, high ash content with low melting points, and high corrosive potential [49]. On the other hand, the properties of ash such as high levels of porosity, functional groups, cation exchange capacity, pH buffering capacity, electron



**Fig. 8.** SEM micrographs of the fresh sample ruminal cow content. (a) fibers with 71,5  $\mu\text{m}$  thickness, (b) and (c) conglomerate of fibers, (d) possible fungal spores, (e) and (f) porous structures.

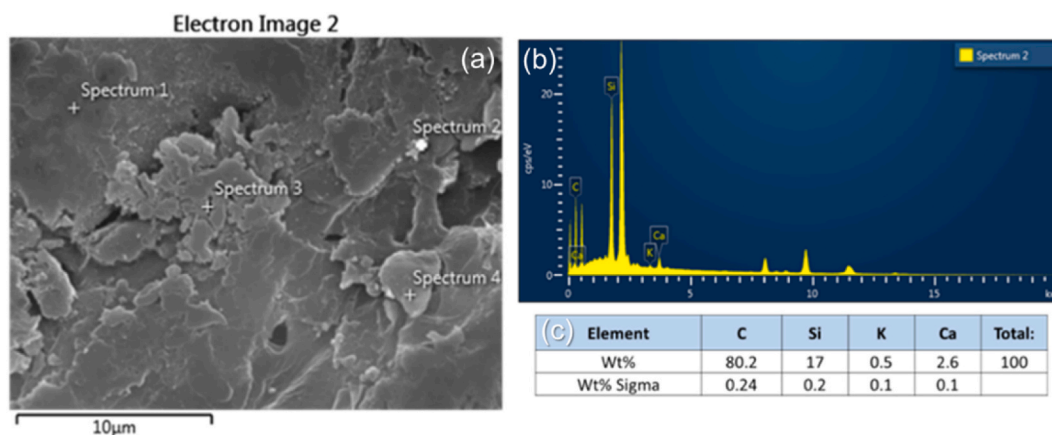


**Fig. 9.** EDS mapping of conglomerate fibrous region (a) in dry ruminal cow content. (b) EDS map, (c) Si, (d) C, (e) Ca.

conductivity, and macro-/micro-nutrients Na, K, Ca, Mg, P, S, Fe, among others, make it potential to be used in various applications such as anaerobic digestion, composting, microbial fermentation, hydrolysate detoxification, catalysis in biomass refinery and bio-diesel synthesis [87].

#### 4. Conclusions

In this work, the rumen content of cows without stomach tissue obtained from a slaughterhouse located in Córdoba, Colombia, was characterized in a fresh and dry state. Based on the results obtained, the following conclusions are disclosed.



**Fig. 10.** Mixed region of fibrous and non-fibrous material (a) EDS analysis in dry ruminal cow content. (b) diffractogram (c) semiquantitative chemical microanalysis.

- Ruminal content (RC) is a biomass with an appearance of fibrous highly heterogeneous, showing remains of undigested vegetable matter and elongated porous solid structures in both as-fresh and dry states.
- Chemical structure of RC is mainly composed of 11.6% of lignin, 31.4% of cellulose, 20.5% of hemicellulose, and other substances, such as organic compounds, organic acids, and minerals. RC is near pH neutral and it presents physical-chemical characteristics of high contaminant potential, especially the C/N ratio. However, this aforementioned aspect together with microbiological activity is key to establishing the suitability of RC for methane production.
- From the point of view of the maturity and stability and effect test on plants (model plant *Brassica oleraceae*), RC should be not used directly as organic fertilizer. It is necessary to apply treatments aiming to transform the organic matter and adequating for its use. Even though RC did not contain some dangerous pathogens for human risk, it is necessary to use personal protective equipment during its manipulation.
- RC exhibited a low calorific value (15.5 MJ/kg), a characteristic that places it as biomass with poor combustion power. This key aspect for the energetic valorization of RC versus not renewable fuels is complemented with a thermal degradation range between 110 °C and 350 °C where hemicellulose and cellulose are decomposed. Additionally, RM thermal degradation produces organic species such as formic and acetic acids, aldehydes, and acetaldehydes, which could affect equipment and structure integrity.
- The chemical and EDS analysis showed in RC (dry sieved and fresh samples) the presence of elements such as C, Si, K, Ca, Al, Na, Mg, Mn, S, Cl and Fe. These elements can cause corrosion and particulate material problems with combustion and pyrolysis systems, but they also enrich the ashes as fertilizers.
- Metallic and alkali-earth elements found in the chemical composition of RC are a remarkable aspect that should be considered in energetic valorization practices due to their incidence in particle emissions during combustion and the presence of CO<sub>2</sub>, NO<sub>x</sub> and H<sub>2</sub>S in biogas production.

#### Author contribution statement

Diana Marcela Ossa Henao: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Edwin Lenin Chica Arrieta: Conceived and designed the experiments; Analyzed and interpreted the data.

Andrés Colorado; Andrés Adolfo Amell Arrieta: Conceived and designed the experiments.

Jimmy Unfried-Silgado: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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#### Data availability statement

The data that has been used is confidential.



## Declaration of interest's statement

The authors declare no competing interests.

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