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Spectroscopic and Thermal Degradation Study of Cow-Dung during Combustion and Pyrolysis

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Abstract: *This study reports the analysis of gases evolved during controlled pyrolysis and combustion of cow-dung. The combined thermogravimetric (TG)/ Fourtier transform infrared (FTIR)/ mass spectrometry (MS) were employed to analyze the evolved gaseous products. The results revealed that the thermal decomposition of cow-dung occurs in three steps assigned to drying of the sample, fast thermal decomposition and further cracking. The complete combustion of cow-dung occurs at 500°C, while during pyrolysis the total weight loss of 58.91 wt.% was found at 950°C. The release of gaseous product during pyrolysis was CO_2, CO, methanol, formaldehyde, formic acid, acetic acid, whereas the products during combustion were CO_2, CO. Among them, CO_2 was the dominant gaseous product in the whole combustion process.*

Keywords: *Cow-dung; Thermal degradation; Hazardous materials; TG-FTIR-MS.*

1. INTRODUCTION

More than half of the global population lacking clean cooking facilities lives in India, China and Bangladesh," says the UN report. According to WHO countries like India, Nepal, Pakistan and Sri Lanka used biomass as fuel for daily household cooking. Nearly 3 billion people depend on solid fuels (biomass and coal) for cooking and heating and this number is expected to grow until at least 2030 [1, 2]. Incomplete combustion of biomass is the main source of indoor air pollution worldwide [3] and in most developing countries; it is burned in open that produces a lot of smoke. The biomass produced from the undigested residue of plant matter, which has passed through the animal's gut of bovine animal species such as buffalo, cows, camels, is referred as "Animal Dung" and when this is produced from cow it is named as "Cow-dung", a faecal matter rich in minerals, comprised of organic matter including fibrous material. Exact chemical composition of cow-dung is mostly carbon, hydrogen, oxygen, nitrogen, phosphorus and urea, mucus as well as cellulose, lignin and hemicellulose. Color ranges from greenish to blackish, often darkening in color soon after exposure to air. Cow-dung generally combined with soiled bedding and urine is often used as manure (agricultural fertilizer). In many parts of the developing world, people use caked and dried cow dung as a fuel for their major source of domestic energy [4, 5]. The burning of this material in open fires and stoves for domestic cooking results in high concentrations of particulate matter, carbon monoxide, nitrogen dioxide, as well as volatile and semi-volatile organic species in the indoor environment and is important causes of indoor air pollution [6-8]. This is linked to a number of respiratory problems, [9, 10] and considered an important factor for the development of tuberculosis in the rural women of the developing world [11-16].

The combustion of cow-dung produces higher concentration of the carcinogenic polycyclic aromatic hydrocarbon (PAHs) in the breathing zone at the cooking site than that with liquid petroleum gas (LPG) and firewood [17]. It was reported that the continued use of bio-energy in cooking exposes the rural women to greater levels of DNA damage [18]. On the other hand, it is negligent to allow the animal manure to decompose naturally; as such, decomposition emits two highly potent greenhouse gases (GHGs) – nitrous oxide and methane [19, 20]. However, no detailed studies on the real time analysis of gases released during the pyrolysis (under inert) or combustion (under oxidative conditions) of animal dung, more specifically cow-dung is reported.

In the present study, the gases evolved during pyrolysis and combustion of cow-dung are investigated using TG–FTIR–MS. This is a powerful method for the characterization of the gaseous products, analysis of the decomposition kinetics, investigation of the combustion conditions and the parameters during the combustion of a variety of fuels [21]. Helium is used as the carrier gas during pyrolysis and the weight loss with temperature is recorded automatically. The combustion characteristics at oxygen atmosphere are also studied, because incineration is the most important technology for organic waste disposal. This study is essential for developing comprehensive pyrolysis and combustion models for cow dung and can provide valuable input for their protected disposal and use as a fuel in the rural area of the developing world.

2. Experiments

2.1. Materials and Methods

Cow-dung samples were collected from the rural area of South East Asia and were crushed and pulverized into a size of lower than 0.2 mm for further analysis. The TG–FTIR–MS experiments were performed using thermogravimetric (STD 600 TA) Instrument coupled with FTIR (Bruker Tensor 27) and mass spectrometer (Thermo). Helium was used as carrier gas with a flow rate of 100 ml/min during pyrolysis on the other hand oxygen was used as oxidant during combustion at the same flow rate. The coupling system TG–FTIR–MS was heated at 200°C to prevent condensation of evolved gases, while the heating rates of the furnace was 10, 20, 30 and 50°C/min. It was found that the intensity of the thermal decomposition and the emission of gaseous products were slowed down at lower heating rates. Therefore a heating rate of 30°C/min was adopted for thermal decomposition of cow dung. During TGA/FTIR experiments, spectral data are repeatedly collected in the form of interferograms and then processed to build up a Grame Schmidt reconstruction, each point of which corresponds to the total IR absorbance of the evolved components in the range of 4000 to 500 cm^{-1}.The mass spectrometer was operated at 70 eV electron energy. The m/z was carried out from 1 to 100 amu to determine which m/z has to be followed during the thermal degradation of cow dung. The ion curves close to the noise level were omitted. Finally, only the intensities of 13 selected ions (m/z = 12, 15, 17, 18, 26, 27, 28, 29, 30, 34, 43, 44, and 45) were monitored with the thermogravimetric parameters.

3. Results and Discussion

Coupling a TG instrument with evolved gas analyzers, such as FTIR and a mass spectrometer, produces a very powerful analytical tool that gives important information regarding the nature and mechanism of thermal decomposition. The TG–FTIR–MS system has suitable interfaces to carry the gaseous decomposition products from the TG furnace to the detection system of FTIR and MS spectrometers, i.e. the method consists of carrying the evolving volatile products out of the furnace directly into the FTIR gas cell and MS where the gases are analyzed.

The TG and derivative thermogravimetric analysis (DTG) data were collected for the thermal degradation of the cow dung during pyrolysis, combustion of 950°C pyrolyzed residue, TG and DTG curves at a heating rate of 30°C/min are shown in Figure 1. The pyrolysis process (Figure 1A) can be divided into three zones: drying zone (<170°C), main pyrolysis zone (200–500°C) and cracking zone (>500°C). The first mass loss (3.28%) occurs between 50 and 200°C corresponds to the vaporization of moisture and desorption of water. The most significant mass loss (about 45.26% of the total weight of the sample) appears between 200 and 500°C and the maximum weight loss rate (15.11%/min) occurred at 348.17°C. The last zone is the further cracking process of the residues in a wider temperature range, from 500°C to 950°C and the total weight loss of 58.19 wt.% was discovered at 950°C during pyrolysis with 41.09 wt.% of non-degraded sample. When it is subjected to complete combustion and about 32.51 wt.% lost occurred between 300°C and 550°C and no further degradation was observed throughout the experiment temperature rang (Figure 1B).

Comparatively as seen from combustion thermogram (Figure 1C), slightly higher weight loss (8.33%) occurs in the first zone, 51.22 wt.% weight lost observed between 200°C and 340°C and 9.71 wt.% weight loss between 340°C and 500°C. Therefore the total weight loss of 60.93 wt.% was seen in the second zone. In this zone, DTG curve (Figure 1C), shows the maximum weight loss rate (134.3%/min) occurred at 312.88°C. The combustion of the cow-dung finishes after the weight loss peak between 200°C and 500°C. The total weight loss of 72.36 wt.% was discovered at 950°C in cow-dung combustion. There are no other solid products except ash content for cow-dung combustion at high temperature in oxidizing atmosphere. The comprehensive analysis for combustion and pyrolysis shows that almost all the solid products generated from cow dung pyrolysis can be burnt at high temperature, and 500°C is enough for complete combustion of this material.

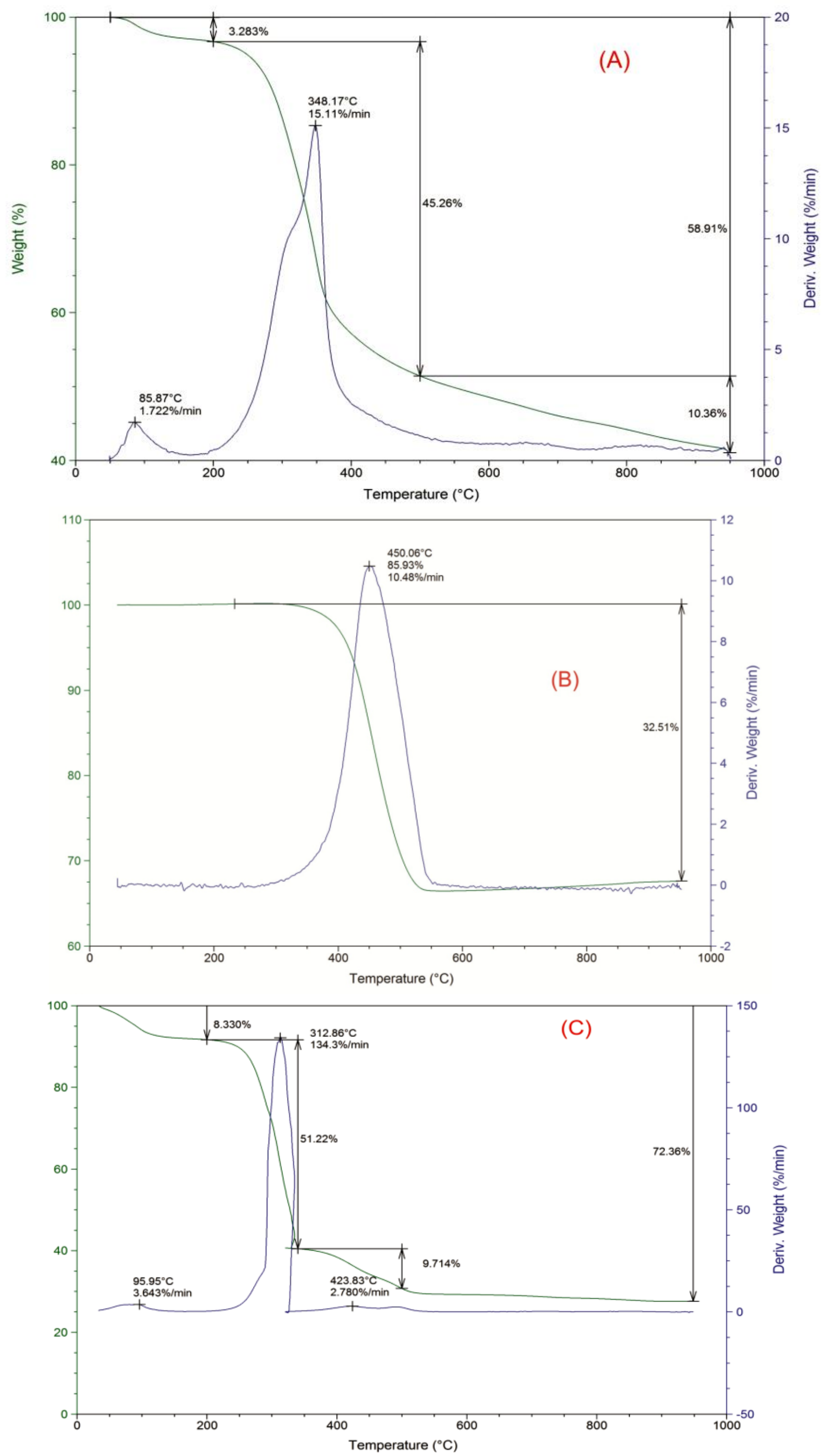


Figure1. *TG/DTG Profiles During Thermal Degradation of Cow Dung; (A) Pyrolysis, (B) Combustion Of 950°C Pyrolyzed Residue, (C) Combustion.*

Gram-Schmidt reconstructs based on vector analysis of the acquired interferograms allows plots of the total evolved gases detected by the spectrometer to be generated shown in Figure 2. The detector signal has been plotted as a function of sample temperature and qualitatively approximated DTA curves recorded during the TG experiments under different controlled conditions. It should be noted that the peaks in the Gram-Schmidt plot are shifted to higher temperatures than the corresponding DTG curve and this is due to the delay time between the gas generation and its detection in the FTIR equipment. The first peak of small intensity observed in the Gram-Schimid plot during pyrolysis (Figure 2A), suggest that the amount of evolved gas in this stage is low and with low infrared extinction coefficients. Whereas only one peak of high intensity was observed in the Gram Schimid plot during combustion of 960°C pyrolyzed residue of cow-dung (Figure 2B), suggested that the amount of the evolved gases in this region is larger and with high infrared extinction coefficients. During the combustion of cow- dung (Figure 2C), three evolved gas regions can be identified and they are related to the mass losses recorded in the DTG curve. First peak is bigger compare to other two peaks of identical intensities, confirms that the amount of the evolved gases in this region is larger with high infrared extinction coefficients. In contrast, the other two peaks are composing of small amount of evolved gases with low infrared extinction coefficients. Figure 3 shows 3D FTIR spectra for the evolved products produced from thermal degradation, whereas the spectrograms at different temperature during pyrolysis and combustion of cow dung are shown in the supplementary material Figures SF1– SF5.

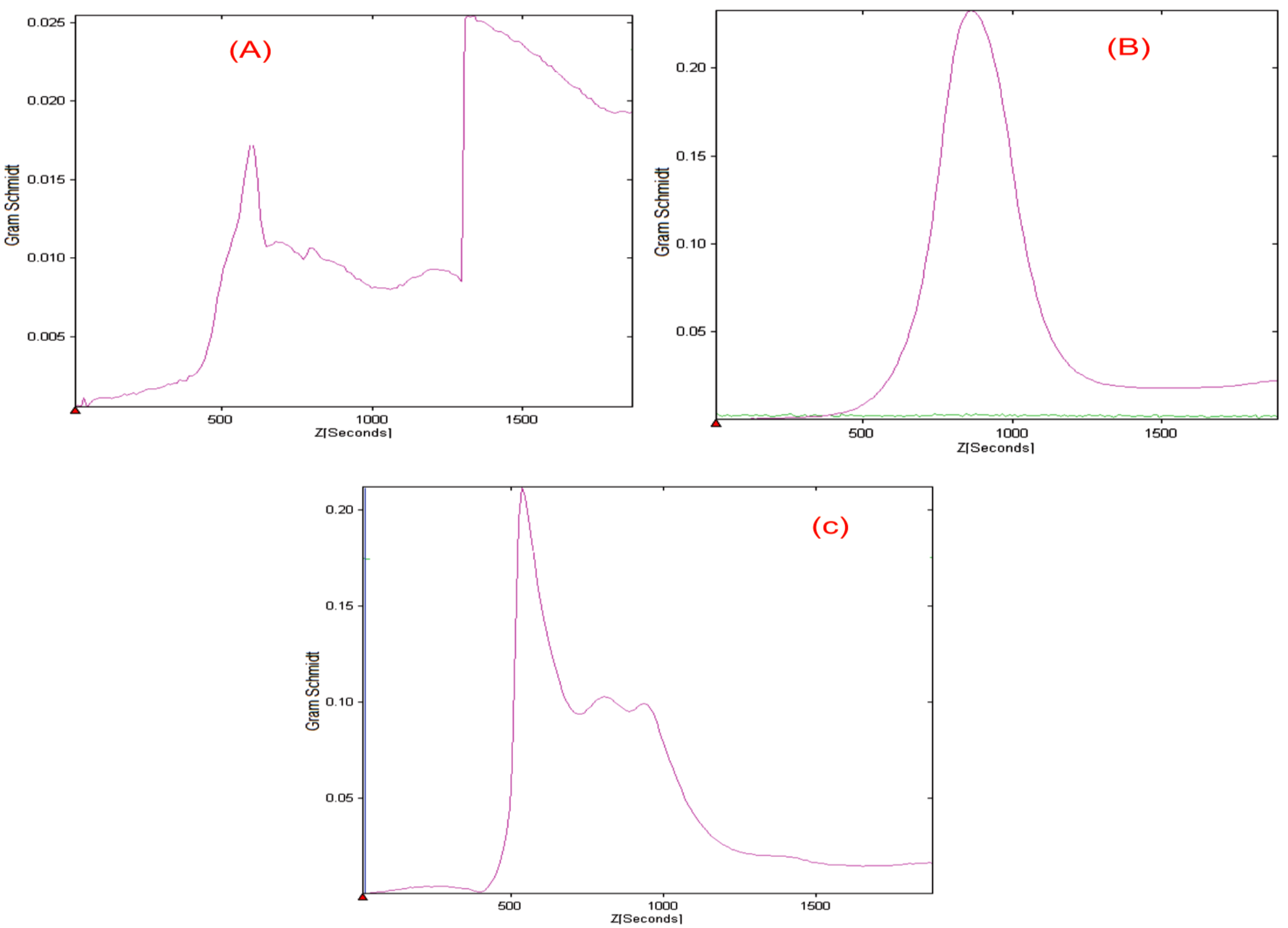


Figure2. *Gram-Schmidt Plot of Cow Dung During Thermal Degradation; (A) Pyrolysis, (B) Combustion of 950°C Pyrolyzed Residue, (C) Combustion.*

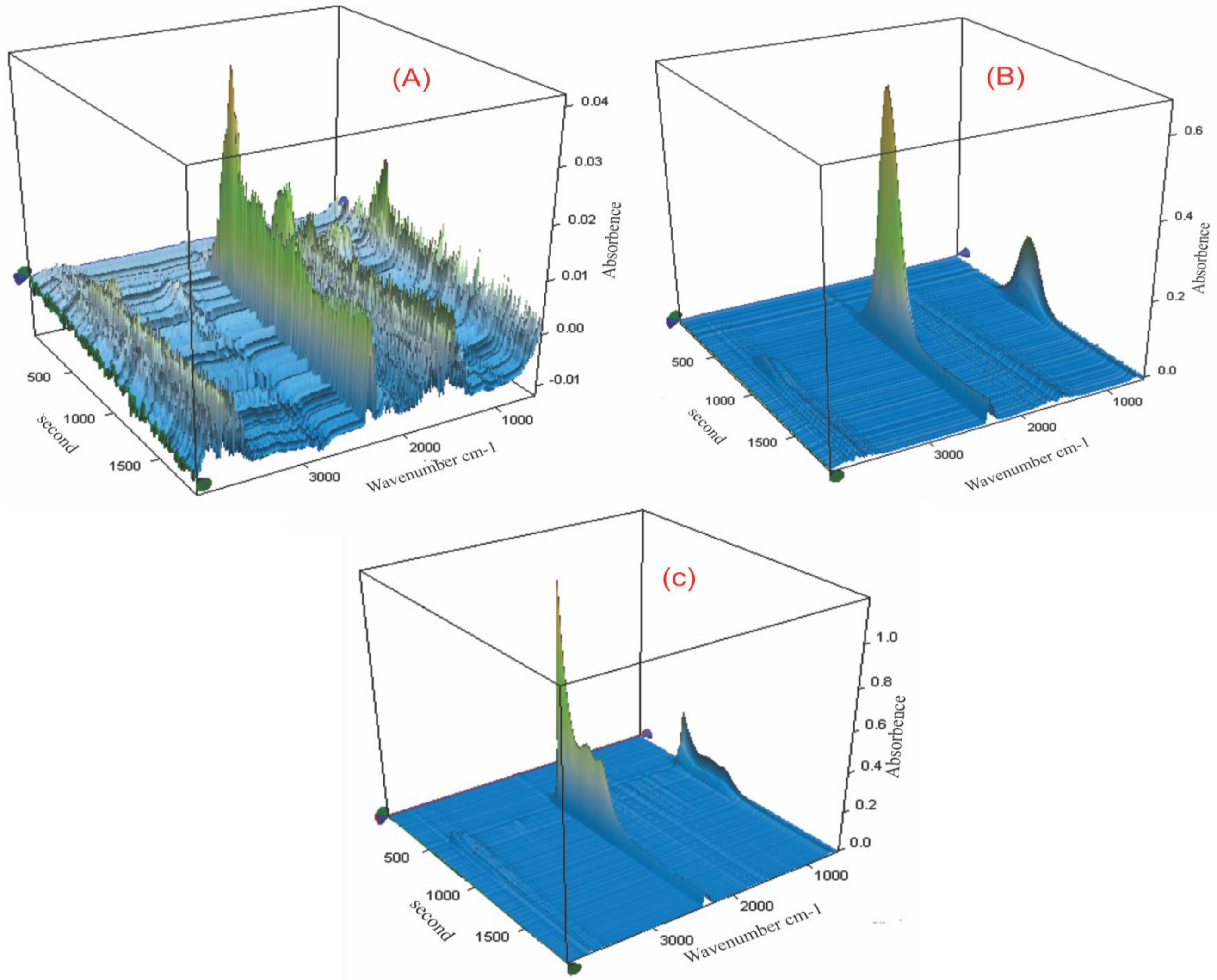


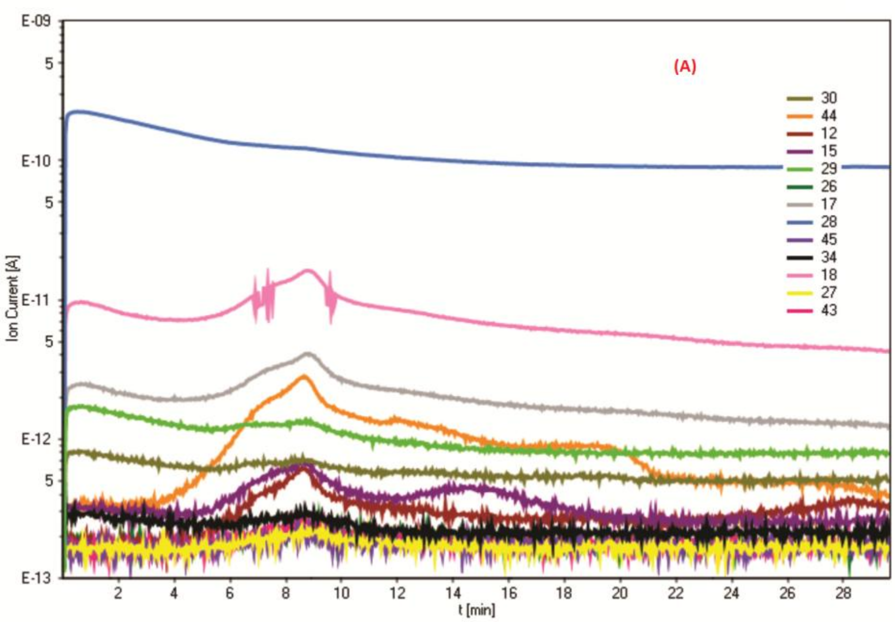
Figure3. *3D FTIR Spectra of Evolved Products During Thermal Degradation of Cow Dung; (A) Pyrolysis, (B) Combustion of 950°C Pyrolyzed Residue, (C) Combustion.*

Based on the maximum point of the DTA curve, two representative temperatures 348°C and 500°C are chosen for two different pyrolysis stages, whereas temperatures of 312°C and 500°C are chosen for combustion stages, and 450°C is chosen as the representatives of the combustion of 950°C pyrolyzed cow-dung residue. The largest quantity and variety of gases are released out during the main devolatilization. The spectrum of evolved products at 348°C in the main devolatilization stage during pyrolysis is shown in supplementary File 1. The characteristic bands of CO_2 at 670 cm^{-1}, 2316–2356 cm^{-1}, and CO at 2180 cm^{-1} indicate their formation in this stage. The absorption bands at 2935 cm^{-1} show the presence of hydrocarbons, of which methane is the most abundant [22]. The bands between 1114 cm^{-1} and 1751cm^{-1} indicate the release of some organics, including alcohols, aldehydes, acids, methanol, formaldehyde, acetic acid, and formic acid are generated in this stage. The nitrogen takes little proportion in ultimate analysis, so the absorbance bands of nitrogen containing product are very weak. The peaks appear in the range 3589–3860 cm^{-1} suffers interferences from water absorption, therefore it is concluded that the main gas products are CO_2, CO, methane, and some organics such as methanol, formaldehyde, acetic acid and formic acid.

The spectrum of evolved products at 500°C in the main carbonization stage during pyrolysis is shown in (Figure SF2), confirms the same characteristic bands, while there are some differences in the transmittance of some peaks e.g., carbonyl group peak (1751 cm^{-1}) at 348°C (Figure SF1) almost disappeared in the spectrum of 500°C (Figure SF2). This is attributed to the complete removal of carbonyl group containing gases such as, formaldehyde, acetic acid and formic acid before entering in the main carbonization stage during pyrolysis, whereas the intensity of the peaks for water absorption almost double in the 500°C spectrum (Figure SF2) endorsed the fast removal of moisture. It can be noticed that the peak between 1114–1172 cm^{-1} at 348°C correspond to ether linkage (Fig. SF1) completely vanished in the 500°C spectrum (Figure SF2) attributed to the C–O bonds fracture. The main identified components at this stage are CO_2, CO, CH_4. The total infrared absorption becomes weaker with increasing temperature, indicating that the amount of volatiles evolving decreases.

The FTIR spectrum of evolved products during the combustion of 960°C pyrolyzed residue of cow-dung at 450°C is shown in (Figure SF3). As expected, spectrum shows only bend for CO_2 confirmed major evolved gas. This suggests that cow-dung can be used as a save fuel for domestic uses, if subjected to undergo controlled pyrolysis prior to its complete combustion. The FTIR spectra of evolved products during combustion at 312°C and 500°C at a maximum degradation rate are shown respectively in (Figure SF4) and (Figure SF5). The presence of CO, CO_2 were confirmed by the appearance of representative bands during the combustion at 312°C, while at 500°C the concentration of CO_2 is large and show strong band in the similar region with no evidence for CO. Taking account the above mention results it is possible to postulate that the main volatile products obtained are CO_2, CO, methanol, formaldehyde, formic acid, acetic acid (during pyrolysis) and CO_2, CO (during combustion).

The volatile products produced by the thermal degradation of cow dung were determined by thermogravimetry coupled to a mass spectrometer. The single ion current curves for the evolved products during pyrolysis, combustion of 960°C pyrolyzed residue are shown in Figure 4. The release of carbon dioxide during the degradation stage was confirmed by a fragment at m/z 44, 43 and 45 is also supported by FTIR data, where carbon dioxide has been observed. In all stages during thermal degradation of cow-dung, the fragment at m/z 28, 29, confirmed the release of CO during combustion and pyrolysis and the presence of H_2S in both type of thermal degradation is supported by the fragments at m/z 34. The releasing of water begins at 80°C and show fragments at m/z 18, 17 in the first and second degradation stage during pyrolysis and combustion of cow dung. The peaks at m/z 27 and 26, which appear with strong intensity in the second degradation step, can be assigned to HCN. The m/z 30, 12 (HCHO) is produced from the degradation of cow-dung in the second degradation step. In addition, It is found that there is no toxic product evolved during the combustion of 960°C pyrolyzed residue.



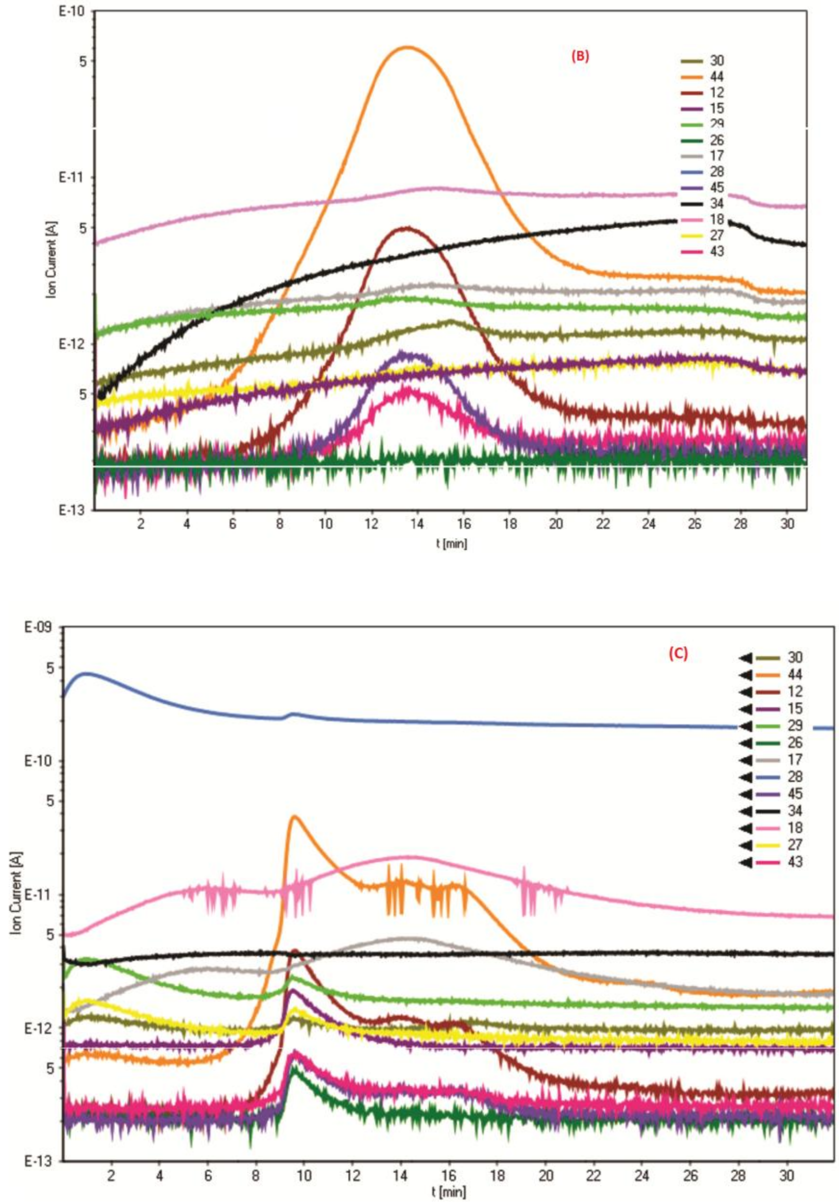


Figure4. *Single Ion Current Curves for Evolved Products During Thermal Degradation of Cow Dung; (A) Pyrolysis, (B) Combustion of 950°C Pyrolyzed Residue, (C) Combustion.*

The comparison between the results obtained with the TG–FTIR and the TG–MS shows some differences. For all profiles, fewer fluctuations appears on the curves of FTIR than on TG–MS ones. This is probably due to the optical cell of FTIR, which tends to average the signals because of its volume. In addition, a shift of curves appears between the two techniques. It can be explained by the different residence time induced by the experimental devices. In detail each gaseous compound H_2O and CO_2, the two profiles show same tendencies. Conversely, significant differences appear between the two analyses for CO and CH_4. With mass spectrometry, CO is followed with the fragment at m/z 28 as mentioned previously; the emission begins from 200°C during combustion. Some gasses also appear on this temperature range and their ion fragmentation produces a fragment at m/z 28. The same observation can be performed for CH_4. With FTIR, the release of CH_4 occurs only after last step degradation. With TG–MS, the fragment at m/z 16 shows an apparition of gases from 180°C due to the presence of water. Thus, the FTIR analysis and the mass spectrometry have advantages and disadvantages. However, using information provided by each of them, it is possible to have an identification of the gases emitted by degradation of cow dung during pyrolysis and combustion.

4. Conclusion

The aim of this work was to study the spectroscopic and thermal degradation study of cow-dung during pyrolysis and combustion. The result of TG-FTIR-MS revealed that the main volatile product obtained were CO_2, CO, methanol, formaldehyde, formic acid, acetic acid (during pyrolysis) and CO_2, CO (during combustion). Whereas the combustion of 960°C pyrolyzed residue of cow-dung at 500°C showed, only bend for CO_2, as major evolved gas. This study guides us in the assessment of environmental health-policy strategies linked with exposure to biomass burning in this sub-tropical region, taking into account the exposure distribution in the population. Moreover, the use of alternative fuels to biomass fuel and use of improved ventilated stove is highly desired to be promoted by concerned organizations.

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