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CONFERENCE PAPER

Fast pyrolysis of biomass mixtures in a fixed bed reactor: Characterization of bio-oil product

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ABSTRACT

In this work, pyrolysis was carried out at 650 °C for 1 hour under an inert nitrogen atmosphere in a fixed bed reactor to determine the bio-energy potential of the chicken manure. The thermal decomposition of chicken manure was investigated by a thermogravimetric analysis technique. Ultimate analysis, FT-TIR and ED-XRF techniques were used to characterize the raw materials. Techniques such as FT-IR and GC-FID have been used to characterize the liquid bio-oil product produced by pyrolysis of chicken manure.

Keywords: Chicken manure, pyrolysis, fixed bed reactor, TGA, GC-FID

1. INTRODUCTION

The energy crisis is one of the most important problems today due to the increasing population [1]. In recent years, many scientists have searched for alternative energy sources [2]. Clean and stable energy supply has been demanded and desired in this context. Fossil energy sources such as coal, oil and natural gas have been gradually depleted over the past few decades, contributing to the development of clean energy sources such as solar, geothermal and biomass [3]. In the last 30 years, most researchers have focused on biomass energy (56%), which is a renewable energy source. Other energy sources include solar energy (26%), wind energy (11%), geothermal energy (5%) and hydroelectric (2%) energy [4]. Biomass is the world's fourth-largest energy source [5].

Biomass, because of its abundant supply and low life-cycle carbon emissions, is an important energy source [6]. Biomass resources such as dedicated energy crops, agricultural residues, forestry residues, aquatic plants, animal wastes, municipal solid wastes and poultry litter, are being investigated as potential resources for fuels and chemicals [7]. Chicken manure wastes, which are among the biomass resources, are a type of biomass with significant potential for use in the energy industry [8]. Turkey is the world's fourth largest poultry exporter. It is reported that the number of chickens is 266 million in 2013. Poultry in Turkey produce approximately 70 kg of waste per year per animal [9, 11]. Therefore, as a result of breeding poultry a large amount of poultry waste expose in Turkey and evaluation or disposal of these wastes creates a significant problem. Poultry farm waste entering the animal waste category is an ideal candidate for energy production due to the high yield of biomass production [9,10]. Biomass is one form of renewable energy source used for both heat and power generation through thermochemical and bio-chemical conversion processes like combustion, gasification, pyrolysis [11]. One of the transformation processes applied to biomass species is the pyrolysis process in which the materials are degraded thermally in an oxygen-free environment. Particularly biomass pyrolysis technology produces bio-oil, carbon-rich solid (bio-char) and hydrocarbons rich gas (bio-gas) products [12, 21]. Pyrolysis process is divided into three groups as slow, fast and flash pyrolysis depending on working conditions (retention time, heating rate, temperature etc.). In the fast pyrolysis method, biomass is converted to fuel at a very high heating rate (10-1000 °C s^{-1}) and in a short time (0.5-2 s) [21].

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In this study, the fast pyrolysis of chicken manure was carried out in a fixed bed reactor at a temperature of 650 °C, a heating rate of 20 °C min^{-1} for a 1 hour reaction time. Operating conditions (1 hour, 20 °C min^{-1}, 650 °C) were determined according to the fast pyrolysis conditions. Characterization of the raw chicken manure (CM) was performed by ultimate analysis (C, H, N, S and O analysis), FT-IR analysis, Thermogravimetric analysis, ED-XRF analysis (Energy Separated X-Ray Fluorescence Spectrometer). Characterization of the liquid product obtained after pyrolysis was performed using FT-IR analysis and GC-FID analysis.

2. MATERIALS & METHOD

2.1. Material and characterization

The chicken manure (CM) sample was collected from Samsun city of Turkey. The sample was dried in a 70 °C oven overnight, crushed, and sieved to a particle size of 60–120 µm. Ultimate analysis (%C, H, N, and S) was performed with a CHNS-932 LECO brand analyzer. For XRF (X-ray-fluorescence) analysis, CM sample were dried in an incubator and then grounded in spex mill. The obtained powder was sieved using a 140 mesh sieve and then stirred for 25 min. Then, sample was pressed into 40 mm diameter pellets. The measurement parameters were set up by using the Epsilon 5 EDXRF system's inbuilt software. Sample was irradiated by X-rays from Gd tube under a vacuum equipped with a liquid nitrogen cooled PAN-32 Ge X-ray detector having been window thickness of 8 µm.

2.2. Thermogravimetric Analysis

Thermogravimetric analysis of CM was performed by a thermogravimetric analyzer (TG-DMAQ800) at heating rates of 20 °C min^{-1} under a N_2 atmosphere with a flow rate of 100 mL min^{-1} with sample of approximately 5 mg.

2.3. GC-FID Analysis

Analysis of the examined bio-oil product was performed on a gas chromatography–mass spectrometry (Shimadzu, GC-2010Plus) using FID detector. The GC separation of pyrolysis vapors was performed with a 30 m×0.25 mm×0.25 µm RTX-5 column from Agilent with helium carrier gas flow of 1 mL min^{-1}. The GC inlet was at 270 °C, and a split ratio of 20:1 was used. The oven was programmed to start at 50 °C. It was held at 50 °C for 4 min and then heated at 5 °C min^{-1} to a final temperature of 270 °C and kept for 7 min.

2.4. FTIR Spectroscopy

The FTIR spectrum of the raw CM and bio-oil was recorded on a FTIR spectrometer (Perkin Elmer, Spectrum Two, ABD) in the range of 4000-600 cm^{-1}. ATR was used for all measurements.

2.5. Pyrolysis Experiment

The pyrolysis of CM (10 g) was carried out in the fixed bed reactor. The pyrolysis experiment was conducted by nitrogen gas a flow rate of 100 mL min^{-1} at 650 °C and 20 °C min^{-1}. The reactor temperature was checked with a thermocouple placed inside the reactor. The pyrolysis experiment took about 60 minutes. The liquid product obtained at the end of the pyrolysis experiment was collected in the dichloromethane solvent. The solvent was then separated from the bio-oil using a rotary evaporator.

3. RESULTS & DISCUSSION

3.1. Characterization of CM

The chicken manure was characterized by using ultimate analyses, and calorific analyses the experimental results are submitted in Table 1. As shown in this table, the carbon values of mixtures are 23.17%. Chicken manure has high nitrogen content due to the presence of proteins and amino acids in the sample, as it is in mixture with feed, wood and other biomass species. In general, the nitrogen value of chicken manure varies between 2.50 and 4.25% in the literature [13].

The nitrogen content of the CM is higher than the literature results. The sulfur value of CM (0.48%) is lower than the literature results [14]. When the elemental analysis results are compared with the literature, blends of chicken manure can be evaluated for the wastes during pyrolysis process.

Table 1. Ultimate Analysis of raw CM

Ultimate analysis (wt.%)	CM
C	23.17
H	5.81
N	4.58
S	0.48
Oa	65.96
Calorific value (MJ kg^{-1}) [8]	12.74

The composition of raw chicken manure is shown in Table 2. Table 2 shows that the content of Ca element is 22.85%. P, K and Ca raw chicken manure are also the main compounds. Studies in the literature have shown that poultry wastes contain high levels of Ca and K [13].

Table 2. Compositions of CM (%wt)

Sample	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	Others
CM	6.10	4.30	13.04	22.10	6.51	20.96	22.85	2.19	1.95

The FTIR spectrum of raw Chicken manure is present in Fig 1. The large peak at 3317 cm_{-1} is attributed to the stretching of primarily O-H groups. The symmetric and asymmetric stretching vibration associated with the peak at 2972 cm_{-1} of C single bond H are alkyl and aliphatic chains. The stretch of C=O in FTIR spectrum of raw CM is 1651 cm_{-1}. Moreover, the C=O group is mainly from the acids, aldehydes and ketones [15].

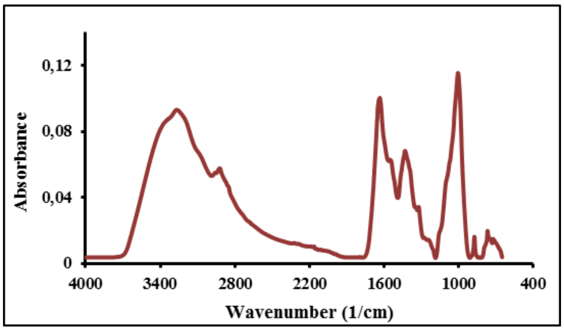

Fig 1. FTIR Spectrum of CM

3.2. *Thermogravimetric Analysis*

The results of thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG) of chicken manure at a heating rate of 20 °C min^{-1} are given in Fig 2.

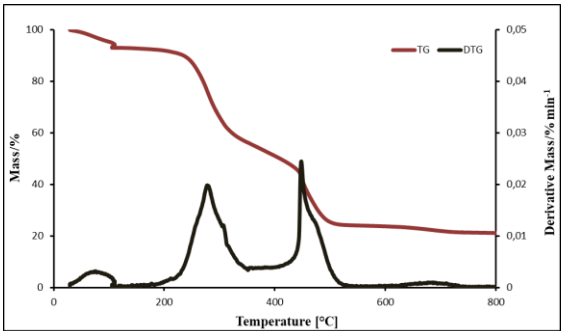

Fig 2. TG-DTG curves of CM

Therogravimetry (TG) and differential thermogravimetric analysis (DTG) curves were used to determine the mass loss steps of the chicken manure in the pyrolysis process. In pyrolysis or combustion reaction studies made with a TGA device, differential thermogravimetric analysis (DTG) curves give more precise results when determining the points at which the reaction reaches the start, end and maximum velocity. When we examine the DTG curve, a weight loss was observed at about 100-200 °C in chicken manure. At this stage, the moisture from the sample and the low molecular weight substances on the surface has disappeared. The main decomposition range of chicken manure was determined to be 200-560 °C from DTG curves.

3.3. *FT-IR spectrum of bio-oil*

The FTIR spectrum of the liquid product (bio-oil) obtained from the chicken manure pyrolysis are shown in Fig 3.

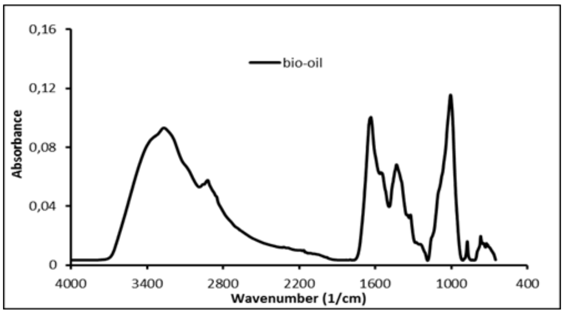

Fig 3. FTIR Spectrum of pyrolysis liquid product

When the FTIR spectrum of the pyrolysis liquid product is examined, the peak observed at 3000 cm^{-1} are the C-H stress vibrations of aliphatic hydrocarbons and wide vibration seen at 3281 cm^{-1} is the O-H stretching vibration. In the spectrum, the strong peak of the C=O asymmetric stretching vibration appears at 1650 cm^{-1}. This peak indicates that the compounds are acid, aldehyde and ketone groups. The peak observed at 1448 cm^{-1} shows the C-H bending vibration of the aliphatic hydrocarbons. It can be said that the peaks observed at about 1000-1500 cm^{-1} belong to the C-O, C-N and C-C stretching vibrations, and that these peak consist of compounds such as ether, alcohol and acid [16, 17].

Table 3. FTIR Analysis Results of CM

Functional group	Wavenumber (cm^{-1})	Species
	Raw CM	
O-H stretching	3317	H2O
C-H stretching	2972	Aliphatic hydrocarbons
C=O stretching	1651	Aldehydes, ketones, acids
C-H bending	1444	Aliphatic hydrocarbons
C-C,C-O,C-O-C stretching	1000-1500	Alcohols, phenols, ethers
	Bio-oil	
O-H stretching	3266	H2O
C-H stretching	2921	Aliphatic hydrocarbons
C=O stretching	1634	Aldehydes, ketones, acids
C-H bending	1431	Aliphatic hydrocarbons
C-C,C-O,C-O-C stretching	1000-1500	Alcohols, phenols, ethers

3.4. GC-FID Analysis

Pyrolysis of chicken manure was carried out in a fixed bed reactor at 650 °C. Gas Chromatograph-Flame Ionization Detector (FID) was used for the characterization of the resulting liquid product. The data in the literature have been used for the identification of the substances corresponding to the peaks observed in the chromatogram. The chromatogram showing the peaks corresponding to the different retention times of the pyrolysis product bio-oil is shown in Fig 4.

GC-FID analysis was performed to determine the organic compounds found in the structure of the liquid product obtained from the pyrolysis of CM. GC-FID chromotograms of the liquid product obtained as a result of the pyrolysis process at a temperature of 650 °C are shown in Figure 4 and the results are given in Table 4.

As shown in Fig 4, 15 peaks were determined on the chromotogram of the liquid product obtained as a result of pyrolysis of CM. Peaks with a total area of more than 1% were identified using the literature and the results in Table 4 were presented. The peak from the 3.36 retention time in the chromatogram has the largest (29.95%) largest area. The resulting liquid product (bio-oil) contains many different chemicals. Literature results suggest that this liquid product composition is composed of compounds containing furan, carboxylic acid and phenols in general [18, 19]. The bio-oil content obtained from pyrolysis from chicken manure in the literature consists of phenols, acids, N-containing compounds [20].

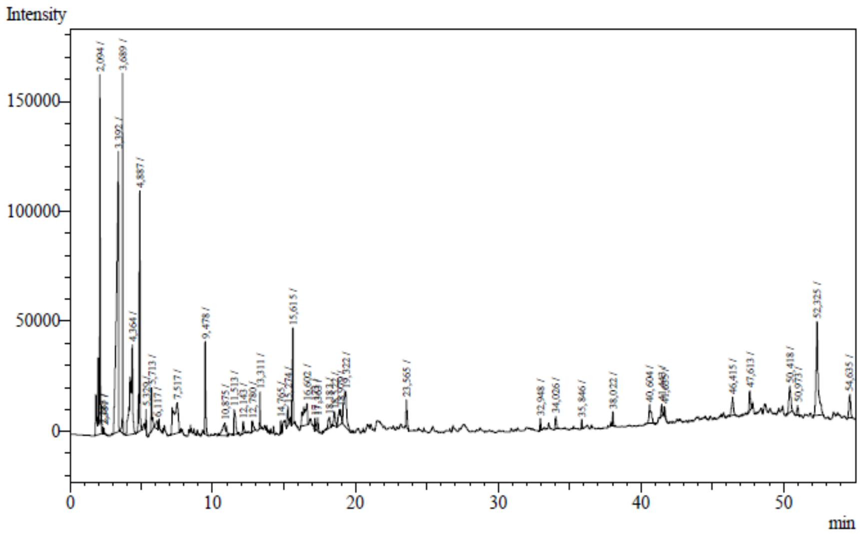

Fig 4. GC-FID chromatogram of bio-oil product obtained from pyrolysis of CM

Table 4. GC-FID Analysis Results of Bio-oil

Number	Retention time (min)	Area (%)
1	2.09	9.52
2	3.39	19.95
3	3.69	5.03
4	4.36	8.22
5	4.89	7.59
6	5.71	1.55
7	7.52	5.22
8	9.48	2.72
9	11.51	1.56
10	15.62	3.16
11	19.32	3.92
12	23.57	1.07
13	50.42	1.96
14	52.33	7.22
15	54.64	1.47

4. CONCLUSIONS

In this study, an important biomass source, chicken manure was pyrolysed in a fixed bed reactor at 650 °C for 1 hour during the reaction period. Characterization of the products obtained using ultimate analysis techniques for characterization of chicken manure was performed using FT-IR, GC-FID spectrum were taken. It can be regarded as fuel because it has both low pyrolysis temperature and pyrolysis product contains aliphatic and aromatic hydrocarbons compounds. As a result, in the case of waste in our country, high quality liquid product was obtained from chicken manure, which is one of the most important renewable energy sources in abundance.

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