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Monitoring of Waste Gasification Products: Solid, Liquid and Syngas

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ABSTRACT

In this study, biomass and waste gasification efficiencies were investigated in a lab-scale fixed bed reactor by the use of cyclone separator. Solid, liquid and gas products were monitored both during and after the completion of the process. Solid residue and liquid product obtained from waste gasification were studied through the use of Thermo-Gravimetric Analysis (TGA); and chemical properties were identified by elemental analysis and X-Ray Fluorescence (XRF) analyzer. Walnuts and pine cones were gasified as biomass. Syngas production being a function of temperature was monitored by analyzing H_2, CH_4, CO gases with a continuous gas analyzer. Mass reduction of 64%, 80% and 77% were achieved during the gasification of biological wastewater treatment sludge, walnut and pine cone, respectively. Syngas with almost 1500 kcal m-3 calorific value was produced. As for biomass syngas calorific value, it increased up to 2800 kcal m-3 for walnuts and 2500 kcal m-3 for pine cones.

Key Words:
Waste Management; Thermochemical Process; Gasification; Waste to Energy.

INTRODUCTION

Waste management hierarchy is one of the leading alternatives which are not desired to be disposed via storage. Some of its disadvantages can be counted as the need for wide area due to the high amount and volume of wastes and the high costs to minimize contamination risks. The management of waste sludge based on waste water treatment facilities focuses on reducing sludge weight and volume to reduce disposal costs, and on reducing potential health risks of disposal options. Thermochemical processes such as pyrolysis and gasification are among safe methods that are applied to this end. In this way, volume and weight of waste can be reduced and the amount of waste transferred to storage fields can be minimized and microbial stabilization of wastes can be achieved at high temperatures. Another important approach is to obtain products having an economic value through these processes. Within the scope of "waste to energy", energy recycling can be achieved from waste materials and valuable products that can be used in solid, liquid and/or gas form can be obtained. These processes called zero emission technologies lead to more environment-friendly waste management mechanisms [1-3]. There are many environmental benefits that can be derived from the use of waste reduction, waste reuse and recycling methods. The most significant environmental benefit caused by gasification will occur in air emissions. The overall reduction of total sulphur gases using gasification technology will also reduce odor [5]. Gasification allows a reduction of the amount of residues to be disposed in landfills and achieves co-gasification of different kind of wastes, including bottom ashes from conventional combustion units [6]. Gasification of wastes and/or biomasses may improve techno-economic situation of gasification process.

Gasification has been widely studied and numerous literature can be found about biomass gasification [7-10]. Gasification is a process that converts a combustible fuel into a partially oxidized gas called "syngas" with economically valuable heating value. Syngas is basically a mixture of CO, H_2, CO_2, CH_4 and H_2O. Fuel as a feedstock is converted into useful energy carriers and can be any hydrocarbon regarding to parameters such as feedstock composition, moisture, ash content, particle size, density, reactivity, etc. [7, 11]. Ramey et.al.

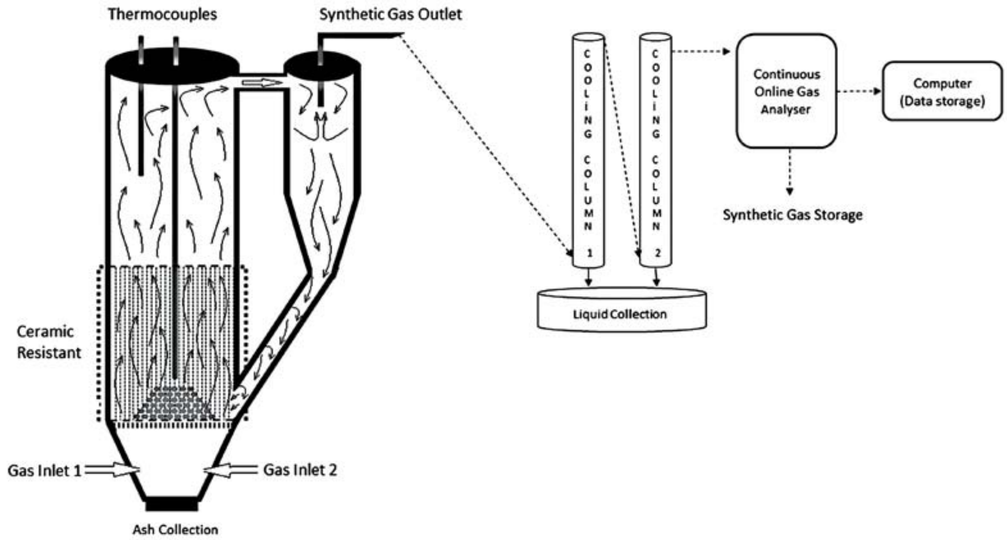

Figure 1. Schematic diagram of reactor.

(2015) reported that gasification is a promising technology to treat wastewater solids, and potentially enabling energy recovery. The authors also claimed that gasification is suitable for wastewater solids for several reasons. Volatile matter is converted to syngas, solid and liquid residuals are stabilized and running at autothermal conditions lower than 900 ^{o}C results reduced complexity of reactor operation. Mainly two types of reactors were used for gasification of municipal solid waste (MSW) or biomass [12]. Fluidized bed requires more investment while fixed bed requires less investment and it is more suitable for smaller capacity MSW treatment. Fixed bed reactors for gasification process are commonly used for real systems which have a relatively smaller MSW yield [13].

In the study, monitoring of gasification products and identification of syngas composition were studied. Two different biomass and a real industrial wastewater treatment sludge were used as feedstock. Waste minimization efficiency regarding to mass and volume loss after thermal treatment was reported. Syngas calorific value for each feedstock was calculated according to the CO, H_2 and CH_4 content of syngas produced.

Table 1. Chemical properties of biomass and waste.

Properties, wt.%	*Walnuts*	*Pine cones*	*Bio. Chem.*
C	*50,85*	*44,54*	*24,3*
H	*6,62*	*5,48*	*5,18*
N	*2,05*	*0,71*	*4,57*
S	-	-	-
O	*40,48*	*49,27*	-
Ash	*2,8*		*35*
Moisture	*4,5*	*3,8*	*11*
Volatile Matter	*60,1*	*64,5*	*65*
HLV, MJ kg^{-1}	*20,8*	*18,85*	*6,70-7,12*

EXPERIMENTAL

Sample characterization

Biologically treated wastewater treatment sludge derived from a leather industry and two biomasses (walnuts and pine cones) were used as fuels during experiments. Product monitoring was investigated and conversion of physical forms was recorded. Table 1 shows the chemical properties of biomass and treatment sludge.

As can be expected, the carbon content of organic substances was found higher than the one of sludge collected from biologic waste water treatment facility. In all samples, carbon is remarkable as the dominant element. Comparing calorific values a similar result was observed. Oxygen within biomasses was calculated by subtracting it from the total mass. Change in the chemical properties of fuels directly affected the efficiency of gasification process.

Experimental approach

Thermochemical experiments were carried out in a fixed bed steel reactor by the use of a cyclone separator at 40 cm height and 7 cm diameter. The reactor was equipped with two gas inlet lines allowing gasification gases (dried air and/or pure oxygen) to enter and one exhaust line allowing generated syngas to pass through the continuous gas analyzer.

Dried air was used as partial oxidizer for gasification and flow rate varied was adjusted by a HOSCO-brand flow meter to 0.05 Lmin^{-1}. In the experiments, 20 g of

Table 2. Higher heating values of some common fuels.

HHV	Density	MJ m-3	kcal m-3
H_2	0.0899	12.77	3050
CO	1.25	12.64	3020
CH_4	0.717	39.82	9520

waste sludge and 50g of biomass were used. Gasification experiments were carried out at 750°C and gas composition variance depending on process temperature was recorded. The condensable part of the syngas was collected by cooling columns with water jacket. Then, syngas was directed to the continuous gas analyzer. CO, CO_2, H_2, CH_4 and O_2 content of syngas was monitored. Process temperature was followed up with two thermocouples extended into middle and upper internal zone of reactor. During gasification studies, composition of syngas produced with continuous gas analyzer was analyzed and recorded every minute.

Calculations

Syngas composition was determined by ABB-brand, The Advance Optima process gas analyzers equipped with thermo-magnetic and infrared photometers. Calorific value of syngas generated during gasification experiments was calculated. For calculations, values presented in Table 2 were used [14].

RESULTS AND DISCUSSION

TGA Analysis

Thermogravimetric Analysis results conducted in order to detect thermal behaviors of samples are presented in Figure 2.

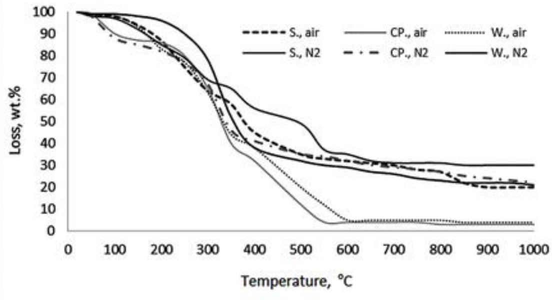

Figure 2. Thermogravimetric comparison of feedstock.

Based on the TG curves as a function of temperature, the mass loss range cannot be divided into zones since every single slope indicates independent behaviors against rising temperature. It can be said that all samples showed similar behavior in TG analysis conducted in N_2 environment. A slight mass loss, around 5-20%, was observed due to the removal of water within the materials between the ranges of 150-200 °C. With temperature rising, a high mass loss was observed (more than 50%) up to 350-400 °C. This zone was detected as where organic substance was pyrolytically decomposed. In this zone, there was the decomposition of hemicellulose, cellulose, and lignin-like contents especially within biomasses [4-6]. In the zone up to 1000 °C, on the other hand, mass loss continued degressively and mass loss was fixed at 80% for walnut and pine cone. It was fixed at 65% for sludge sample. At the end of the TG analysis conducted with air, there was an increase in mass losses due to the oxidation of organic content with oxygen. High mass loss was detected within similar 200-600 °C range for biomass samples as expected. At the end of the test, similar behavior was observed for both biomasses with a loss of 95%. On the other hand, sludge sample had approximately 75% mass loss based on the low organic substance content.

Thermochemical Processes

The gasification test was conducted with 0.05 L min^{-1} dry air volume at 750 °C. Data related to the mass and volume changes obtained from the tests are presented in Table 3.

Analyzing the sludge sample in terms of waste management and minimization, 64% mass and 62% volume decrease was recorded at the end of the process. Especially considering the problems derived from the coverage areas of wastes to be disposed from the storage areas, 62% volume decrease can be considered as a satisfactory minimization for wastes having organic and inorganic contents. In addition, the economic value of products in both liquid and gas form is considered as another advantage of the process. On the

Table 3. Conversion ratios - mass and volume.

Loss, mass	Inlet, g	LP., g	SR., g	Loss, g	Loss, wt.%	Syngas, g.
Bio. Sludge	20	2,2	7,2	12,8	64	10,6
Walnut	50	14,8	10,2	39,8	79,6	25
Pine cone	50	13,5	11,3	38,7	77,4	25,2
Loss, volume	Inlet, ml	LP., ml	SR:, ml	Loss, ml	Loss, vol.%	Syngas, m^3 kg^{-1} fuel
Bio. Sludge	40	-	15,2	24,8	62	0,45
Walnut	70	-	11,7	58,3	83	1,85
Pine cone	72	-	13,5	58,5	81	1,94

BS.: Biologically treated sludge WS.: Walnut shell PC.: Pine cone LP.: Liquid product SR.: Solid residue

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other hand, solid waste is considered as an addition agent that can be used in mixtures such as adsorbent or concrete, asphalt etc. based on its content. In this case, a process in line with the zero-waste approach can be conducted as each form that might be obtained from the waste sludge being used as fuel can be useful. In the literature, it is reported that 2.5 m^3 syngas can be obtained from 1 kg wood[15]. The syngas volumes; 1.94 and 1.85 m^3 kg^{-1} obtained from pine cone and walnut shell, respectively, in a fixed bed reactor show that the process was conducted satisfactorily.

Table 4. Composition of syngas

vol.%	Walnut	Pine Cone	B. Sludge
H_2	11-13	10-12	7-9
CO	28-31	21-23	17-19
CH_4	13-16	14-16	6-8
CO_2	15-20	15-20	10-14
O_2	1-2	1-3	1-3

Table 5. Average calorific values of syngas

HHV.	Walnut	Pine Cone	B. Sludge
kcal m^{-3}	2420-2855	2270-2585	1300-1610
MJ m^{-3}	10,5-12,1	10,1-10,8	5,1-6,7

Table 6. XRF results of raw and thermal treated samples.

wt.%	Raw sample	Treated sample
Na_2O	1,484	8,005
Al_2O_3	1,859	11,333
SiO_2	1,113	5,478
SO_3	2,167	1,854
CaO	5,078	17,455
Cr_2O_3	4,654	13,91
NiO	ND.	ND.
Fe_2O_3	0,282	1,395
ZnO	0,024	0,080
MgO	0,504	1,212
CuO	ND.	ND.
MnO	ND.	ND.
As_2O_3	ND.	ND.
PbO	ND.	ND.

ND.: not detected

Table 7. Results of Elemental Analysis.

	Elemental Analysis, wt.%			
	C	H	N	S
Biologic (Raw)	24,30	5,18	4,57	-
Biologic (Treated)	13,36	1,09	2,99	-
Walnuts (Raw)	50,85	6,62	2,05	-
Walnuts (Treated)	28,50	1,25	0,75	-
Pine cones (Raw)	44,54	5,48	0,71	-
Pine cones (Treated)	26,80	1,26	0,22	-

Syngas composition and calorific value

Maximum gas percentages obtained during tests are presented in Table 4. Here, values represent the highest value ranges detected based on the temperature. The syngas compositions produced from each fuel type are presented in volume type as %.

Analyzing gas compositions, it can be observed that CO gas is dominant. At the same time, CH4 gas was detected over 10% in tests conducted especially with biomasses. It was observed that the produced synthesis gas was the complete synthesis of H_2, CO and CH_4 gases. It can be said that CO_2 reduction was achieved at high temperatures based on high CO values (R.1). Char is gasified producing mainly methane according to the exothermic hydro-gasification reaction (R.2) [3]:

$$C + CO_2 \dashrightarrow 2CO \quad \Delta H°r = +172\ kJ/mol \quad (R.1)$$

$$C + 2H_2 \dashrightarrow CH_4 \quad \Delta H°r = -74.6\ kJ/mol \quad (R.2)$$

Syngas calorific values which were obtained at the end of the calculations made on the basis of values as can be seen in Table 4 are presented in Table 5.

Medium calorific syngas was achieved from biomasses according to the gas compositions given in Table 4. Calorific value of syngas from sludge sample was lower and it can be classified as “low calorific syngas”.

XRF and elemental analysis results of biologic treatment sludge

Both initial and post-process XRF analysis was conducted on sludge sample in order to observe thermal behavior of complex composition including organic and inorganic substances. The results are presented in Table6.

At the end of the analysis, some changes were detected in chemical contents of samples. An increase was detected especially in amounts of Na, Al, Si, Ca and Cr compounds detected within samples. This case can be explained by the condensation in non-volatile parts due to the loss of organic contents in samples. Keeping metal compounds within sludge at the end of heat treatment will make the remaining sludge to have environmental risk. In this case, the use of solid waste in alternative areas will be restricted and even more, it will be a must to manage it via waste management mechanisms. Furthermore, it is believed that keeping metallic forms within sludge can make it easy to control these types that can lead to air pollution. However, more tailed studies should be conducted to detect the relationship with air pollution.

Pre-process and post-process elemental analysis was conducted in order to observe elemental changes of sample and the obtained findings are presented in Table 7.

It was observed that carbon content of samples decreased but did not completely ended up at the end of the gasification tests conducted at 750 °C. This case can be affiliated with the limited performance of fixed bed reactor. Due to the lack of homogenous contact between the heat and sample, carbon which cannot take part in reactions and thus it is collected as solid residual at the end of the test. In this case, it is assumed that different reactor types such as fluid bed etc. should be tried for efficiency. The increase of gasification will lead to increase in the volume of produced syngas and thus amount of gas which is rich in calorific value will increase as well.

CONCLUSIONS

In this study, products in solid, liquid and gas forms obtained at the end of the gasification of treatment sludge which was collected from biologic treatment unit of two different biomass facilities and an industrial waste water treatment facility were monitored and their mass transformations were determined. In addition, composition of the produced synthesis gas composition was determined and calorific value calculations were made. The results obtained based on the data are as follows:

- Gasification is a very effective system to reduce the volume and mass of solid wastes just as in combustion. The advantage of this process compared to combustion is less emission. At the end of the gasification tests, it was found that waste sludge volumetrically decreased at 60-62% and biomasses decreased at 83-85%.
- Metallic forms in sludge intensified following the process and stayed within the sludge. This case puts the sludge into a more risky classification within the terms of waste management. Analysis on accessibility of metals to receiving environments from the sludge by means of toxicity characteristic leaching procedure (TCLP) will be one of the fundamental topics for further studies.
- Mass reduction was achieved as follows; 64% for Bio. Sludge, 79.6% for walnut and 77.4 for pine cone. TGA analysis reported more reduction that it was observed after thermal processes. The reason for that is believed to be the effect of reactor type and size. Related to the insufficient heat transfer through the feedstock material, thermal degradation was not as sufficient as it was in TGA.
- CO was the dominant compound of the produced syngas for each sample. It was found 28-31% for walnut; 21-23% for pine cone and 17-19% for sludge sample.
- 11-13%, 10-12% and 7-9% hydrogen was detected at the end of the gasification of walnut, pine cone and sludge, respectively.
- Methane is one of the syngas components. 13-16%, 14-16% and 6-8% methane production could be achieved for walnut sample, pine cone and sludge sample, respectively.

- Syngas having calorific value between the range of 2420-2855 kcal m^{-3} with walnuts; 2270-2585 kcal m^{-3} with pine cone and 1300-1610 kcal m^{-3} with biologic treatment sludge was produced.
- Some restrictions derived from the reactor type were observed during the use of carbon content of the fuel. It was detected that approximately half of the carbon content of fuels are left within the post-process solid residual.

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