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ORIGINAL ARTICLE

Thermo-Gravimetric Analysis and Kinetic Characterization of Co-Pyrolysis of Municipal Sewage Sludge with Sugarcane Bagasse

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ABSTRACT

To study the kinetic characteristics of municipal sewage sludge with bagasse, pyrolysis experiments and thermo-gravimetric analysis were performed. The characterization of sludge and bagasse shows that sludge contains a low amount of carbon and volatile matter for bagasse. The kinetic parameters are calculated by using the Coats and Redfern based on TG and DTG. The results show by adding bagasse in the sewage sludge during pyrolysis, the pyrolysis range decreases as volatile matter releases fast. As bagasse contains a higher amount of volatile matter, it helps in burning the sludge at comparatively lower temperatures. The average activation energy for the 50-50 % mixture of sludge and bagasse is lower than sludge itself so a low amount of energy is required to carry out pyrolysis.

Keywords — *Arrhenius equation; Activation energy; Co-pyrolysis; TGA–DTG; Municipal sewage sludge; Biomass*

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Introduction

Sludge is a waste by-product obtained from a municipal wastewater treatment plant (MWTP). The increasing amount of sewage sludge produced from MWTP creates a problem because sludge has the potential to affect human health and pollute the environment [1]. Because sludge contains microorganisms and harmful substances, such as poorly biodegradable materials, heavy metals, bacteria, pharmaceuticals, viruses, and hormones [2-3], the disposal of sludge economically and efficiently is necessary. Sewage sludge disposed of by various methods such as agriculture use, landfill, and incineration create air or soil pollution [4]. Pyrolysis is one type of thermal process in which raw material is heated at high temperatures in the absence of oxygen (inert atmosphere). Pyrolysis products are gas, bio char, and bio-oil [5]. Pyrolysis of sludge often produces poor-quality bio-oil. So that, modified pyrolysis process is required to enhance the quality [6]. Biomass is used in addition to sludge in co-pyrolysis [7]. By the synergetic effects of biomass and sludge mixture, the quality of pyrolysis products improved. Bagasse (biomass) is a residue obtained after the extraction of juice from sugarcane. [8-12].

Material and Methods

Materials

Sewage sludge (named S) was procured from Vadodara municipal corporation and bagasse (named B) were collected from local market from Ahmedabad, India. Table 1 shows the typical characterization of S and B material. The result showed that carbon content of bagasse is much higher than the carbon content of sludge. The oxygen content of sludge is 50.67% which is very high in nature. The ash content of sludge and bagasse is 45.7% and 6.4% respectively. Due to the higher amount of ash present, pyrolysis of sludge gives lower yields of pyrolysis oil.

Table 1 Typical Characterization of Sludge (S) and Bagasse (B)

Composition	S (%)	B (%)
Carbon	21.440	41.80
Hydrogen	03.302	04.80
Nitrogen	02.640	00.71
Oxygen	70.618	52.69
Moisture	00.300	00.40
Volatile matter	44.700	88.20
Fixed carbon	04.000	08.00
Ash	51.000	03.40

Methods

The percentage loss of mass degradation with increasing of temperature upto 800ºC was measured by TGA analyser with the heating rate of 10ºC/min. Argon was used to maintain the inert atmosphere to conduct the procedure. Coats and Redfern method was used to calculate kinetic parameters from TGA studies [13]. The fundamental kinetic equation of pyrolysis is expressed by Arrhenius equation:

$$\frac{dX}{dt} = Ae^{(-\frac{E}{RT})}(1-X)^n \text{ ---- (1)}$$

Where, A is the pre-exponential factor (min^{-1}), t is time, X is thermal conversion of material at time t, E is the activation energy and R is the universal gas constant.

Thermal conversion of sample $X = \frac{m_0 - m_t}{m_0 - m_f}$ ---- (2)

Where, m_0 is the initial sample weight, m_t is the sample weight at time t, and m_f is the final sample weight [13-15].

Heating rate β (K/min) denoted by equations (3)

$$\beta = \frac{dT}{dt} \text{ ----- (3)}$$

Thus, $\ln\left[\frac{-\ln(1-X)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT}$ ----(4)

A conversion straight line was plotted with the help of $\ln[-\ln(1-X)]/T^2$ vs $1/T$ data due to first order reaction [14].

Results and Discussion

TG/DTG analysis

Fig 1 shows the pyrolysis profiles (TG-DTA) of the sewage sludge, bagasse, and their 50-50% blend at a heating rate of 10°C/min. In Fig. 1a, the initial and final temperatures of volatile matter released in sewage sludge is 250°C and 800°C respectively, and for bagasse is 200°C and 650°C. The 50-50 % blend of sludge with bagasse shows a pyrolysis range of 200°C to 500°C. Weight loss of municipal sewage sludge up to 800ºC is 46.4%, which was due to the very high amount of ash content of sludge. Major weight loss of sludge is in the temperature range of 250-500ºC, which is known as the pyrolysis zone. Weight loss at temperature higher than 500ºC is very low. Weight loss of bagasse up to 800ºC is 96.91% and pyrolysis range is between 200 to 450ºC. Weight loss of 50:50 mixtures of sludge and bagasse is 70.18% and pyrolysis range is between 200 to 500ºC. Fig 1b shows the DTG of municipal sewage sludge. The maximum peak, which shows the maximum pyrolysis rate in the curve, is at 250°C for sludge and 300°C for bagasse and their blend.

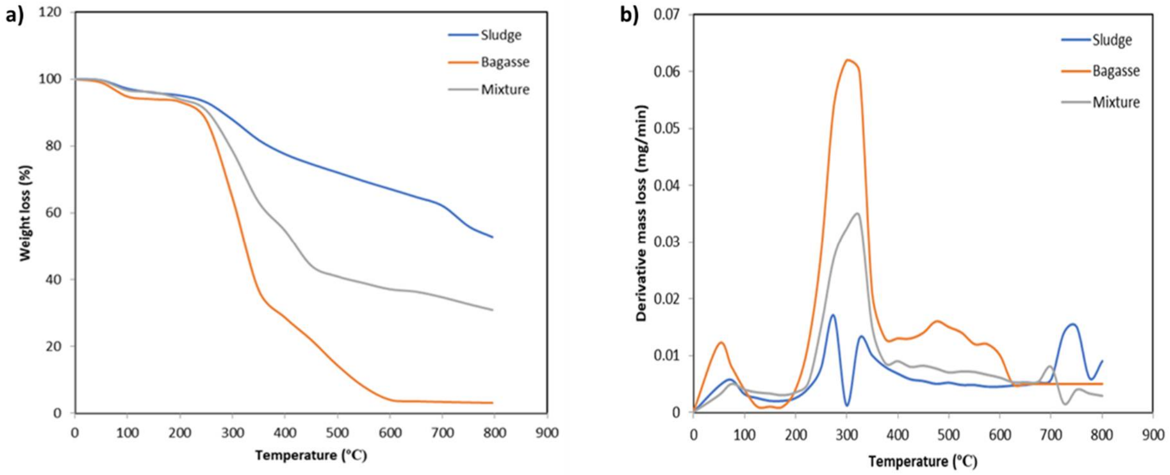
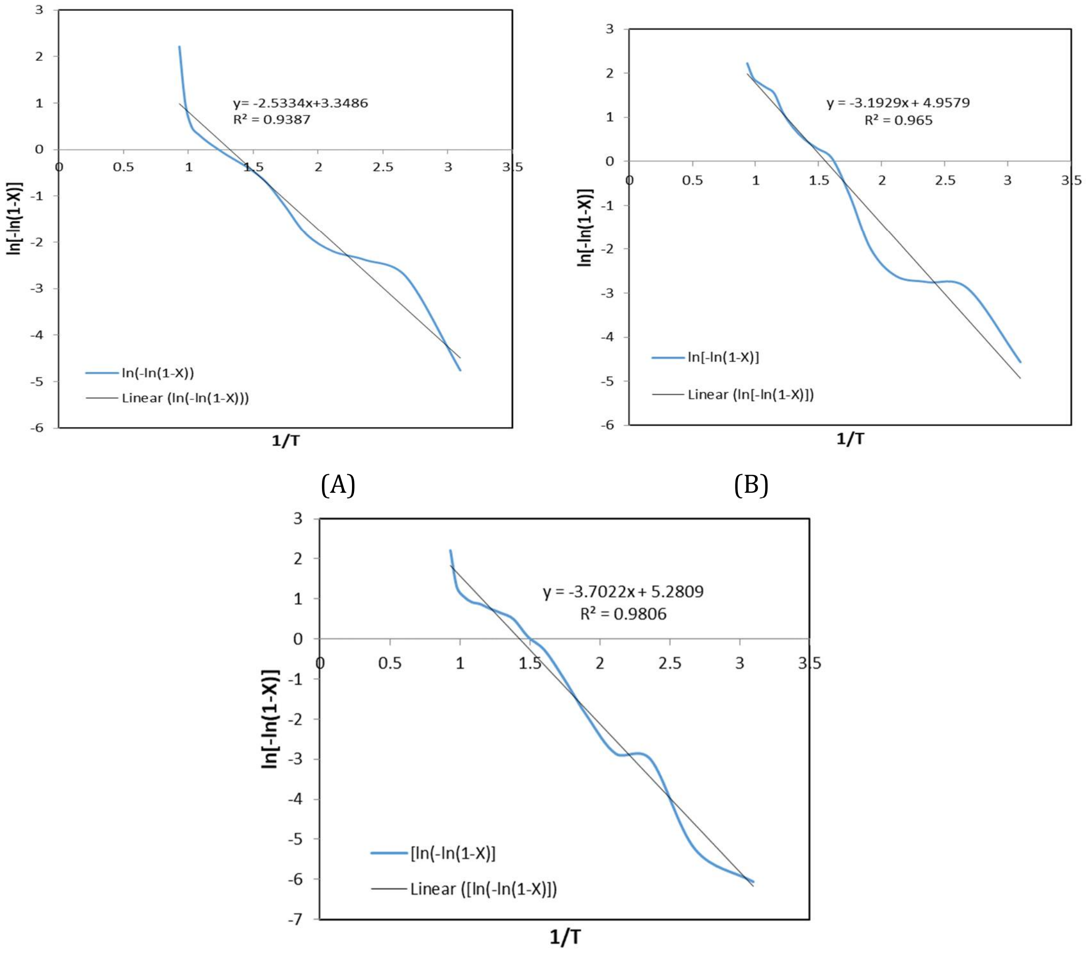


Figure 1 a) TGA b) DTA curve of Sludge, Bagasse and Mixture

Kinetic analysis

Arrhenius method

Arrhenius method is used to calculate activation energy of given sample. Figure 2 (a–c) are graphs for ln[-ln(1-X)] versus 1/T for sludge, bagasse and their mixture. Activation energy is calculated from the value of slope. Slope is multiplied by universal constant R for evaluating value of activation energy. Equation for graph is Y = mX + C. Where m = value of slope and C = constant.



(A) (B)

(C)

Figure 2 ln[-ln(1-X)] versus 1/T for a) sludge, b) bagasse, c) mixture

Table 2 gives information about activation energy which is calculated by Arrhenius method. Activation energy for sludge is high in temperature range of 500-800ºC because major complex compounds present in sludge are decomposing in this temperature range. Average activation energy of bagasse is higher than sludge. Because bagasse has high amount of degradable organic volatile matter [15]. Organic matter of sludge decomposes in temperature range of 200-500ºC. Average activation energy is 21.062 KJ/mol for sludge, 26.545 KJ/mol for bagasse and 30.780 KJ/mol for their mixture.

Table 2 Activation energy calculated by Arrhenius equation

Temperature range (ºC)	Activation energy (KJ/mol)		
	Sludge	**Bagasse**	**Mixture**
0-200 (1st zone)	21.495	16.085	30.115
200-500 (2st zone)	23.226	35.88	35.041
500-800 (3st zone)	54.673	28.652	34.992
Total Range	21.062	26.545	30.780

Table 3 represents the fitting results of pyrolysis kinetic equation for Arrhenius equation. The linear correlation coefficients are near to one. This means that the correlation is good.

Table 3 The fitting results of pyrolysis kinetic equation by Arrhenius equation

Sample	Fitting equation	Correlation coefficient
Sludge	Y = -2.5334X + 3.3486	0.9387
Bagasse	Y = -3.1929X + 4.9579	0.9650
Mixture	Y = -3.7022X + 5.2809	0.9806

Table 4 shows comparison of activation energy calculated by Arrhenius method with values of activation energy obtained from literature.

Table 4 Comparison of activation energy data with literature value

Type of sample	Zone	Activation energy (KJ/mol)
		Experimental value in this study - Arrhenius equation
Sludge	1	21.495
	2	23.226
	3	54.673
	Average	21.062
Bagasse	1	16.085
	2	35.880
	3	28.652
	Average	26.545
Mixture	1	30.115
	2	35.041
	3	34.992
	Average	30.780

Activation energy for sludge is varies between 21-54 KJ/mol for zone-1. Activation energy for sludge in zone-2 23.226 KJ/mol which is quite comparable with literature value [16]. Activation energy for sludge in zone-3 is quite high because heavy inorganic compound present in sludge decomposed at high temperature range. Overall activation energy for sludge is 21.062 KJ/mol respectively. Shuang-quan found average activation of sludge is 19.66 KJ/mol, which is near to experimental value [17]. For bagasse, values of activation energy vary between 16-35 KJ/mol. In literature, values of activation energy are in the range of 3-37 KJ/mol, which is quite near to the values of activation energy in this experiment. Activation energy for 50:50 by weight mixture of sludge with bagasse is varies between 30-35 KJ/mol. Overall activation energy of mixture is 30.780 KJ/mol. Overall activation energy for mixture is higher than that of sludge, because bagasse requires high energy to decompose organic compounds [18]. This could be understood by comparing activation energy data for zone-2. Activation energy for mixture in zone-2 is high. Overall activation energy required for sludge is less than overall activation energy of bagasse because bagasse has significant number of degradable components. As concentration of bagasse is increased in sludge the activation energy required is also increased.

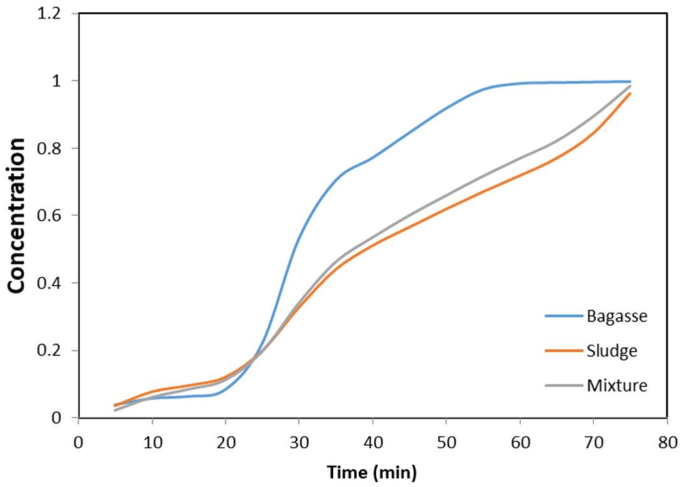


Figure 3 Conversion vs Time graph for Bagasse, sludge and their 50-50% Blend

For bagasse, conversion rate increases in temperature range of 250-400ºC because major organic degradable volatile matter decomposing in this temperature range. Bagasse has a high number of volatile matters. For sludge, conversion rate increases slowly due to sludge has low number of organic matters.

CONCLUSION

Proximate and ultimate analysis reveals that sludge has a lower amount of carbon, hydrogen and volatile matter as compared to that of bagasse. Also, sludge contained significant amount of ash and bagasse contained very low amount of ash. Biomass has a significant amount of energy. Biomass can be used as a raw material along with sewage sludge in pyrolysis. The present study concludes that sugarcane bagasse is a good source of renewable energy, which can be used in co-pyrolysis along with municipal sewage sludge. Pyrolysis characteristics of materials were studied by thermo-gravimetric analysis. Activation energy was calculated by using TGA data. During pyrolysis, major de-volatilization step occurs between 250-500ºC, 240-450ºC and 250-450ºC for sludge, bagasse and their mixture respectively. In this study, Arrhenius equation method is used to calculate activation energy. Activation energy for sludge varies between 21-54 KJ/mol. For bagasse, values of activation energy vary between 16-35 KJ/mol. Activation energy for blend of sludge and bagasse (50:50) varies between 30-35 KJ/mol.

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