Municipal sewage sludge/Biomass co-pyrolysis in a batch reactor: Physico-Chemical analysis of the products

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Abstract*: Municipal sewage sludge (MSS) was co-pyrolysed with sugarcane bagasse (SCB) (50 wt %) at 500 ℃ in a batch reactor in the presence of nitrogen under atmospheric pressure to produce modified biooil. In comparison with only MSS pyrolysis, the yield of the biooil and gas improved by 100% and 14%, respectively. Furthermore, yield of char (residue) decreased by 42%. GC/MS analysis showed that the co-pyrolysis afforded a reduction of sulfur and nitrogen compound significantly. Physical characteristics demonstrated that MSS derived biooil exhibited alkaline nature, whereas, SCB shows acidic nature. Thus, pH of co-pyrolysis derived biooil increases. Moreover, water content is slightly increases. In contrast to this, density and viscosity marginally reduced. Such a property of biooil favors its use as a transport fuel. Thus, co-pyrolysis technique has a potential to modify the properties of biooil significantly.

***Keywords*: Municipal sewage sludge, bagasse, biomass, pyrolysis, copyrolysis, biooil.**

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I. Introduction

Due to high rate of increasing population, urbanization and industrialization in India, sewage generation expected to increase at a faster rate. Thus, massive quantity of municipal sewage sludge (MSS) produced from the sewage treatment plant (STP). The Ministry of Environment, Forest and Climate change of India estimated generation of sewage water close to 61948 million liter per day (MLD). Accordingly, generation of MSS from the urban areas of India calculated nearly 4 million tons [1]. Due to high risk of health and environmental issues associated with various disposal methods, such as landfills [2], fertilizer [3] and incineration [4], they are not an attractive solution. Hence, MSS calls for the development of environmentally benign and energy efficient techniques for its disposal in an eco-friendly manner. In this circumstance, thermal processes for energy recovery, such as pyrolysis or gasification, are become the attractive option. Hence, pyrolysis of solid waste referred by number of researchers for large scale feasible disposal of sewage sludge resulting to biofuels or oxygen containing chemicals [5, 6, 7].

Among the three products (liquid oil, gas and char) from MSS pyrolysis, one of the potential products, i.e. liquid oil known as biooil is a dark brown liquid. Yield of MSS derived biooil observed 50-60 wt%, is a complex mixture of water, oxygenates, hydrocarbons, nitrogen and sulfur containing compound. Thus, biooil exhibited heterogeneity in nature, and resulting to instability. Since nitrogen and sulfur containing compounds in a biooil creates an issue of NOx and SO_2 emission in an exhaust gases and limit its application as a fuel [8]. Thus, biooil need to be upgraded by lowering oxygenates and also needs to reduce nitrogen and sulfur containing compounds. The search for new upgraded alternative fuels and simultaneously reduces the negative environmental impact of MSS has led to the idea of studying co-pyrolysis of MSS with one of the solid residue (biomass) from sugar mill, namely sugarcane bagasse (SCB).

Co-pyrolysis of sewage sludge and lignocellulosic biomass (in 50% wt.) studied in a conical spouted bed reactor, showed significant synergistic effect in terms of reduced oxygenates and nitrogen-containing products. Moreover, it was seen free of sulfur containing compounds [9]. Significant reduction in pyrolytic temperature and apparent activation energy investigated for catalytic co-pyrolysis of paper sludge and municipal solid waste with metal oxide, such as MgO, Al_2O_3 and ZnO [10]. Co-pyrolysis of sewage sludge too was reported with oil shale showed improvement in gas generation, in particular methane [11]. Comprehensive study on the co-pyrolysis behavior of MSS and SCB mixture in terms of yield of products and its characterization is little reported.

In view of the vast availability of these two types of waste materials: (i) MSS (ii) SCB in India, the aim was to show the effect of co-pyrolysis upon addition of SCB with MSS on biooil produced by performing experiments in a batch reactor at a slow heating rate.

II. Experimental

A. Materials

First, MSS used in this work was collected from sewage treatment plant located at Vadodara, India. SCB used in this study was kindly provided by Shree Khedut Sahakari Khand Udyog Mandli Ltd., Bardoli, India. Both the material were cleared of physical impurities, ground and sieved. Homogeneity of MSS and SCB (50% wt.) was achieved by mixing in a ball mill for 10 minutes.

B. Pyrolysis in Batch Reactor

Materials (100 g) was taken in a stainless steel cylindrical (50 mm ID X 190 mm length) reactor (Fig.1). It was placed in a muffle furnace maintaining 500 °C at 10 °C/min. Air left in the rector was purged with flowing nitrogen. Solid residue left behind in each run was measured by weighing the reactor before and after each experimental run. Volume of gas produced was measured through displacement of water and cross verified by subtracting the weight of liquid and residue from the sample feed, and the error was within ±5%. The liquid product was collected in a glass impinger bottle placed in an ice bath.

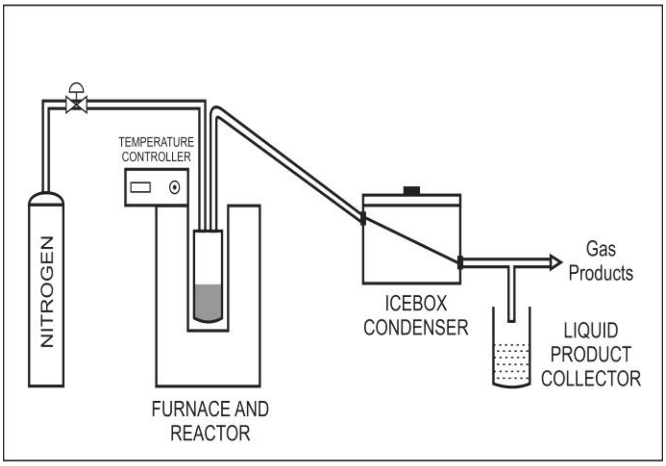

Fig. 1. Schematic diagram of experimental setup

C. Biooil characterization

Pyrolysis oil obtained from each run was determined by Perkin Elmer Autosystem XL GC with Turbomass using Pe-5 MS (30 m, 0.025 mm) capillary column with 0.25 µm thick stationary phase (100% methyl polysiloxane). Elemental analysis for carbon, hydrogen, nitrogen and sulfur of biooil were analyzed by elementar analyzer model vario Macro cube Elementar. Physical characteristics of biooil, e.g. water content, viscosity, acid value and calorific value of each biooil were determined with the use of standard protocol.

III. Results and discussion

A. Product yield

Table 1 shows a typical product distribution observed for the pyrolysis of MSS, SCB and its mixture (1:1 wt %) at 500°C. As shown in table, in contrast to merely MSS pyrolysis, upon addition of SCB in MSS, yield of biooil and gas increased by 100% and 14%, respectively, whereas yield of char (residue) decreased by 42%. Higher ash content of MSS was resulting to more char formation in MSS pyrolysis, i.e. 57%. MSS-SCB co-pyrolysis produces less quantity of residue, Early stage of degradation of SCB, produced biooils interact with MSS leading to increased production of volatiles and carbonization (to residue formation) of the bio-products is suppressed. Similar reasoning had been advanced to explain lower residue formation in co-pyrolysis kinetic study of sewage sludge and bagasse using multiple normal distributed activation energy model [12].

TABLE I. Product yield by co-pyrolysis of MSS with SCB (1:1 wt %)

Feed	Yield of Products, wt%				
	Two phase of biooil, wt%		*Biooil*	*Char*	*Gas*
	Organic	*Aqueous*			
MSS	7.4	13.6	21.0	57.0	22.0
SCB	15.3	22.7	38.0	35.1	26.9
MSS:SCB (1:1)	15.8	25.6	41.4	32.8	25.8

Moreover, to investigate whether interactions existed between MSS and SCB, the difference of yield was defined. It signifies the difference of yield of the products obtained as a result of co-pyrolysis mass and the calculated yield of the products obtained as a result of individual pyrolysis of MSS and SCB. The extent of synergistic effect was observed The calculated yield (CY) of co-pyrolysis mass were derived from (1).

$$CY = 0.5(M+S) \quad (1)$$

Where, M and S are the yield of product obtained by individual pyrolysis of MSS and SCB. Thus, difference of yield, Y described as (2).

$$Y = AY - CY \quad (2)$$

Where, AY is actual yield obtained by performing co-pyrolysis experiments

As shown in Fig. 2 extent of synergistic effect, described as "Y' during the co-pyrolysis indicate an increase of about 40% and 5% in biooil and gas yield and decrease of 28% in char yield.

B. Gas Chromatography/Mass Spectrometry (GC/MS) of Biooil.

The chemical composition of biooil is essential to establish their potential utilization as fuel or other purposes. The area % of various compounds of biooil determined by GC/MS was classified as oxygenates, nitrogen, sulfur, hydrocarbon (HC)and steroids (cholestenes). Similar trend for such a compounds demonstrated for MSS pyrolysis pyrolysis [13, 14, 2]. As shown in table 2 significant reduction in sulfur containing compounds were seen upon co-pyrolysis. Moreover, nitrogen containing compounds, hydrocarbons and steroids were too reduced marginally. Various material combination, e.g. lignocellulosic materials, rice straw, oil shale, etc with sewage sludge reported that co-pyrolysis significantly reduces sulfur and nitrogen containing compounds in a different reactor configuration. [9, 15].

Gaseous phase secondary reaction of hydrocarbons with oxygenates believe to lowers the proportionate amount of hydrocarbon in a co-pyrolysed resulting biooil.

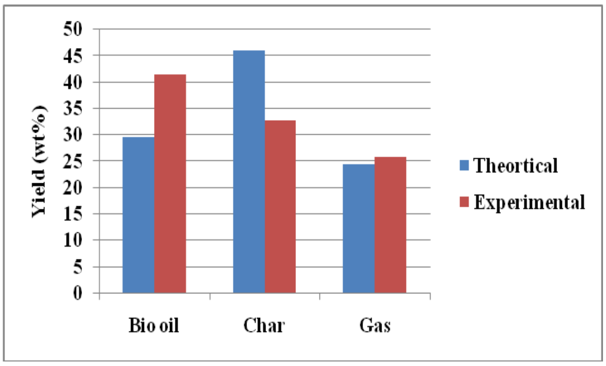

Fig. 2. Schematic diagram of experimental setup

TABLE II. COMPOSITION OF BIOOIL (AREA%)

Composition	MSS	SCB	MSS:SCB (1:1)
Oxygenates	32.52	37.82	36.63
Nitrogen compounds	17.21	3.77	12.24
Sulfur compounds	3.38	--	--
Hydrocarbons	4.54	--	1.56
Steroids(Cholestens)	4.89	--	--

C. *Physical Properties*

Table 3 summarizes the pH value, acid value, density, viscosity and water content for each of the three biooil. MSS derived biooil exhibited alkaline nature, whereas, SCB shows acidic nature. Thus, pH of co-pyrolysis derived biooil increases. Accordingly, acid value of biooil increases.

TABLE III. PHYSICAL PROPERTIES OF BIOOIL

	Density (kg/m^3)	Viscosity (cSt at 40°C)	pH	Acid value (mg KOH/g)	Water Content %
MSS	1217	20.2	7.4	60.5	45.3
SCB	1108	15.1	2.85	110.2	47.4
MSS:SCB (1:1)	1187	19.3	3.71	104.2	52.1

Moreover, water content is slightly increases. In contrast to this, density and viscosity marginally reduced. Such a property of biooil favor its use as a transport fuel. Thus, application of co-pyrolysis technique upgraded biooil properties.

IV. CONCLUSION

The synergistic effect observed in co-pyrolysis of MSS with SCB leading to enhanced biooil yield. in contrast to merely MSS pyrolysis, upon addition of SCB in MSS, yield of biooil and gas increased by 100% and 14%, respectively, whereas yield of char (residue) decreased by 42%. GC/MS analyses reveal that significant reduction in sulfur containing compounds was seen upon co-pyrolysis. Moreover, nitrogen containing compounds, hydrocarbons and steroids were too reduced marginally. A physical property such as pH, viscosity and density favors the use of biooil as a transport fuel. Statistical validation of data would be subsequently communicated.

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