Catalytic mixed pyrolysis of bagasse and polystyrene using chemically treated fly ash catalyst

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Abstract **- Bioenergy has been widely accepted with the potential to deliver a significant portion in projected renewable energy provisions of the future. Pyrolysis of plastics mixed with biomass found to reduce the adverse effects of plastic recycling on the environment. The present work was carried out to produce high-grade pyrolytic oil from a mixture of biomass, plastic and modified fly ash. The resultant oil obtained from non-catalytic mixed pyrolysis of sugarcane bagasse (SB) and polystyrene (PS) were chemically comparedusing FTIR spectrum with the oil of catalytic co-pyrolysis. The oil yield was also improved from 58 to 63.2 % with catalytic co-pyrolysis when compared with non-catalytic co-pyrolysis.**

Keywords **- bagasse, biomass, polystyrene, fly ash, pyrolysis, co-pyrolysis**

INTRODUCTION

The rapid development of technology and advancements led to intensive use of fossil fuels in transportation and industrial sector. Energy security of the countries and irregularities fossil fuel supply accelerated research and development of alternative fuels.The world's fuel requirement has been expected to rise to 56% by 2040[1]. But some studies have reported that the crude oil reserves will exhaust by 2042 and coal reserves will reduce by 2112[2]. Thus exploration of sustainable energy sources such as solar, wind, biomass, geothermal, tidal, fusion, etc. has been intensified. Biomass is most abundant and renewable resource. The pyrolysis technique has been widely employed for the conversion of biomass to bio-oil[3], [4]. The pyrolysis liquids obtained from various solid wastes have been generally employed as fuel for combustion in boilers, turbines, engines, etc.[5]. But, the bio-oil from biomass obtained via pyrolysis process is inferior when compared to fossil fuels with attributes of high acid content, water content, and oxygen content. These attributes cause oil less stable and require upgradation of oil[6].

Many methods have been widely employed to upgrade bio-oil. The methods include catalytic cracking, hydrodeoxygenation (HDO), esterification, emulsification, steam reforming, upgrading with supercritical fluids, etc. [7]. Although catalytic cracking is an inexpensive method, it produces an undesirable amount of coke up to 25 % of total weight with inferior fuel quality. The up-gradation of oil using HDO significantly increased hydrocarbons in low-grade pyrolytic oil conversion. But, the process has disadvantages like costly equipment, high-pressure operation, complex operation procedures, catalytic requirements, etc. The other methods of upgradation have inherent limitations such as use of chemicals, high costs, large-scale operation complexities, etc.

However, the complicated equipment, need for catalysts, and high pressure required for the reaction has made the method very complex and costly. Similarly, steam reforming, emulsification, supercritical fluids, and esterification have also some advantages and limitations. Somehow, these processes are too expensive, not cost-effective and not suitable for large-scale production. Therefore, a new approach is sought after to reduce this cost. The co-pyrolysis technique overcomes these limitations. Since co-pyrolysis of biomass and plastics offered promising results enhancing the properties of bio-oil. Many studies showed co-pyrolysis improve oil quality and yield. This was based on the fact that the hydrogen fraction present in plastics is higher than that of biomass.Thus, the pyrolysis liquid produced by plastics is free of water. The yields and quality of the oils obtained by co-pyrolysiscan befurther enhanced by numerous approaches to meet their end applications. One such approach is the use ofinexpensive catalysts in pyrolysis reaction.

The co-utilization of biomass and waste plastics for generating alternative fuels found to be cost-effective in addressing solid wastes in landfills, surplus biomass combustion in agricultural fields, etc. Extensive research has been done on co-pyrolysis of various lignocellulosic materials along with waste plastics like HDPE, LDPE, polystyrene, etc. [3], [8], [9]. India is a leading producer of sugarcane in the world with annual production of approximately 0.35 billion tonnes[10]. While bagasse is the waste product in sugar production process which is generally used for direct combustion. On the other hand, polystyrene or Styrofoam is extensively used plastic with limitations of disposal in landfill due to its low density.Fly ash is a by-product from steel or thermal power plants. Also fly ash is composed of aluminum and silica elements. Fly ash is found to have attributes of catalystlike uniform pore size, large surface area, etc. Thus fly ash was employed as catalyst in co-pyrolysis of sugarcane bagasse and polystyrene in the present work.

MATERIALS AND METHODS

Raw materials and chemicals

The sugarcane bagasse (SB) was procured from Sakthi sugars Ltd., Cuttak, Odisha, India. The waste polystyrene (PS) was collected from the waste yards of National Institute of Technology Rourkela, Odisha, India. Fly ash was obtained from Rourkela steel plant, Odisha, India. All the chemicals were procured from Merck India and Himedia India.

Preparation of raw materials and catalyst

Sugarcane bagasse (SB) obtained was dried at 40°C for 24 h and grounded using a domestic mixer. The powdered biomass was sieved with BSS mesh to obtain size range of 0.7-0.89mm. The waste polystyrene (PS) was kept in oven for one hour at 80°C to make it hard and brittle. The low volume polystyrene was grounded to powder and screened similarly as bagasse. Also, the fly ash was screened through a BSS 80 mesh to eliminate large particles. The fly ash particles were calcined at 600°C for 2 h to eliminate volatile materials. Subsequently, after calcination the material was treated with HCl to reduce the concentrations of iron and alkali oxides. Then, sodium hydroxide was fused with pretreated fly ash in a steel tray by keeping at 550°C for 1 h. Equal proportion (1:1 by weight) of NaOH and fly ash were taken. The mixture was then cooled to room temperature, grounded, and mixed with deionized water (10 g of fly ash in 100 ml water). The slurry was mixed thoroughly and kept undisturbed at 90°C for 6 h. The precipitate obtained was washed repeatedly with deionized water to remove excess NaOH. The resultant substance was filtered and dried. The fly ash was characterized using XRD, SEM, EDX and BET and comparison was made between treated and untreated fly ash.

Fly ash was calcined at 600 °C for 2 hours to remove unburnt carbon and other volatile materials. After calcination, fly ash samples were treated with HCl to reduce the concentration of iron and alkali oxides. The scanning electron microscopic (SEM) analysis was carried out to find the surface morphology of the chemically treated fly ash sample at 20kV, 1000X, and 2000X. Also, Brunauer–Emmett–Teller (BET) analysis was also carried out for untreated and pre-treated fly ash which revealed the surface area of 16.718 and 27.68 $m^2 g^{-1}$. The x-ray diffraction analysis showed the increase in crystallinity in modified fly ash. The energy-dispersive X-ray spectroscopy(EDX) study confirmed theremovalof Fe traces from the fly ash samples. Thus, chemically modified fly ash was found to be suitable for the use as a catalyst.

Characterization of fly ash

The physical analysis of fly ash before and after treatment was carried out using XRD, BET, SEM, and EDX

XRD analysis

The crystallinity of fly ash samples was determined using X-ray diffractometer model PW 3040/00 (X-Pert, Panalytical, Netherlands) The radiation employed was Cu K-alpha radiation with k value of 0.15418 nm. The operating current and voltage were 20 mA and 30 kV, respectively. The 2θ range was given from 10° to 80° at a scan rate of 2° min^{-1} for recording XRD patterns.

EDX analysis

The composition of fly ash can be determined by elemental analysis using Energy Dispersive X-ray spectroscopy (EDX). The fly ash samples were kept on a carbon tape coated and subsequently coated with zinc. Oxygen was sent and a pressure of 2 bar was kept. EDX was performed to analyze the elemental composition.

SEM Analysis

The scanning electron microscopy analysis was carried out using different magnifications of 1000X and 2000X at 20 kV using JSM-6480LV (Jeol). SEM images show the magnified structures of pores and morphology. This allows us to identify the effect of treatment.

BET analysis

The surface area of fly ash samples was analyzed using low-temperature N2 adsorption method with a Quantachrome Instruments BET analyzer. Liquid nitrogen at -196 °C was used at a relative pressure (P/P_o) varying between 0.01 and 0.995. Here, P is equilibrium pressure at low temperature adsorption and P_o is saturation pressure. The surface areas were obtained using quantachrome software.

Experimental set-up

The reactants (SB, PS, fly ash) were kept in a stainless steel cylindrical reactor (17.5 cm length with 4.7 cm outer diameter) for performing pyrolysis. To maintain inert conditions inside reactor, nitrogen was purged inside the reactor at a flow rate of 30 ml min^{-1} for 5 minutes. The pyrolysis reactor contains a furnace with a highly sensitive PID controller for maintaining temperature. The temperature was measured by Cr-Al K-type thermocouple. The experiments were carried out initially with SB and PS at different pyrolysis temperatures viz. 500, 525 and 550°C. Then, the high yield temperature was chosen for further experiments. Different proportions of SB and PS were chosen such viz. 1:1, 3:1 and 1:3 for co-pyrolysis. Additionally, 3g of treated fly ash was added to these blending ratios and pyrolysis was carried out to determine the effect of catalyst.The experimental setup is shown in Fig.1.

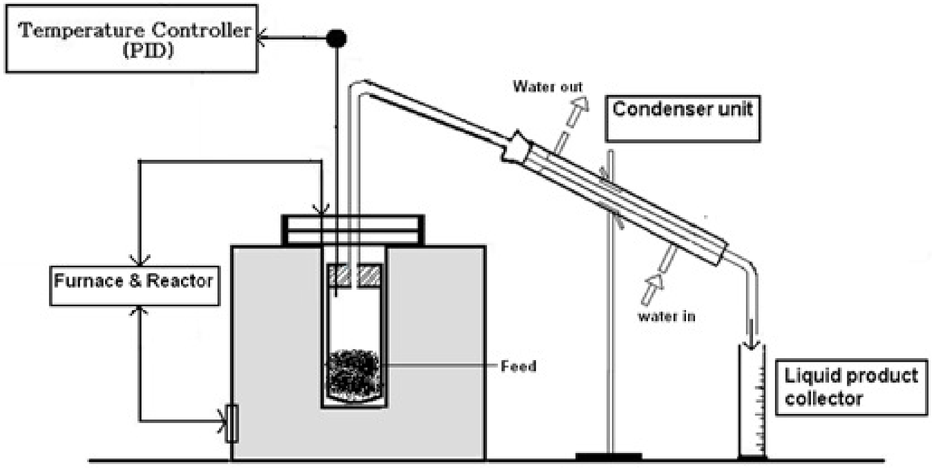


Fig.1. Experimental setup for pyrolysis

FTIR analysis

The chemical nature of pyrolytic oil produced was characterized using Fourier transform infrared spectroscopy (FTIR) using Spectrum Two, Perkin Elmer FTIR. The oils obtained by co-pyrolysis and catalytic pyrolysis were compared using FTIR peaks. The analysis was carried out in the range of 400 – 4000 cm^{-1}. The sample was prepared by dropping 10µl of oil on 13 mmKBr pellet. The pellet was prepared by using 200 mg potassium bromide powder and pressed using a hydraulic press. The functional groups were obtained from spectrum of FTIR spectroscopy.

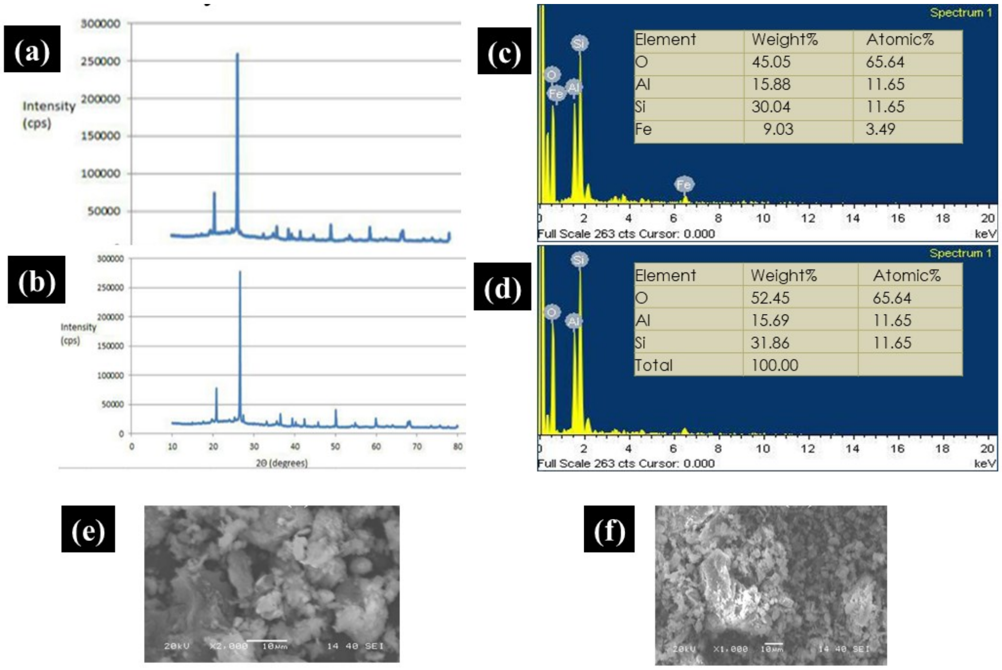
RESULTS AND DISCUSSION

Characteristics of fly ash

The fly ash was treated with various chemicals to improve catalytic characteristics. The variations in crystalline structure, elemental composition, and morphology before and after treatment are shown in Fig.2. Many researchers characterized fly ash, and it was known to contain crystalline minerals such as quartz (SiO2), hematite, calcium oxide, etc. Thus, changes in peak intensities were visualized using XRD spectrums before and after pretreatment. The Fig.2b clearly shows the increase in intensity of the peak at a 2θ of 27° corresponding to increase in crystalline nature of pretreated fly ash compared to untreated fly ash in Fig.2a. EDX analysis of the fly ash revealed the elements in fly ash such as oxygen, aluminum, silicon and iron as shown in Fig.2c and 2d. The chemically pretreated fly ash is free from iron as shown in Fig.2d. It suggests that iron compounds were leached during pretreatment.

The scanning electron microscopic images obtained at 1000x and 2000x magnification of untreated and pretreated fly ash is shown in Fig.2e and 2f. The images depict morphological changes after pretreatment in 2f. The pores on the surface were also increased along with the number of small spherical structures. It confirmed that the chemical treatment of fly ash increased porous nature that is suitable catalysis. The BET analysis of the fly ash was performed to determine the surface area of the samples. The pretreated samples surface area was found to be 27.68 $m^2\ g^{-1}$ increased from untreated fly ash which was 16.718 $m^2\ g^{-1}$.

The pyrolysis of individual raw materials viz. sugarcane bagasse and polystyrene were conducted at 500, 525, and 550°C. Maximum oil yields of 72.6% and 86.58% were obtained at 525°C for SB and PS respectively. Thus 525°C was found to be optimum for the high yield of oil. After that, from 525 to 550°C, the yield was decreased. The decrease in yield is due to the cracking of higher hydrocarbons to lighter carbons and release of more non-condensable vapours. Thus, a reduction in liquid yield was observed with increase in vapour yield. Table 1a and 1b show the effect of temperature on yields of various pyrolysis products of SB and PS such as pyrolysis liquid, char, and vapor. Thus, 525°C was chosen for further experiments. Different blends of SB and PS such as 1:1, 3:1, 1:3 were chosen for co-pyrolysis. Table 1c shows maximum oil yield of 58% achieved with co-pyrolysis of 1:3 blend. This is due to the presence of more polystyrene which was obvious reason that PS produces more oil compared to SB from individual study of pyrolysis. But the least oil yield was obtained with 1:1 blend.Further, 3 g of pretreated fly ash was added as a catalyst in all the blends and pyrolysis was performed. A maximum of 63.2% was obtained with 1:3 blend as shown in Table 1d. This suggests the improvement of oil yields with the addition of catalyst. The gross calorific value, density, kinematic viscosity (at 40 ºC) and pH of the co-pyrolysis oil were 43.2 MJ kg^{-1}, 0.858 g ml^{-1}, 2.18 Cst, and 5.8, respectively.



Element	Weight%	Atomic%
O	45.05	65.64
Al	15.88	11.65
Si	30.04	11.65
Fe	9.03	3.49

Element	Weight%	Atomic%
O	52.45	65.64
Al	15.69	11.65
Si	31.86	11.65
Total	100.00	

Fig.2. X-Ray Diffraction pattern of (a) untreated raw fly ash (b) treated fly ash. EDX pattern with the elemental composition of (c) untreated raw fly ash (d) treated fly ash. Scanning electron microscopic images of (e) untreated raw fly ash (f) treated fly ash.

Table 1 Pyrolysis experiments carried out with raw materials and catalysts at various temperatures and the product yields

Temperature (°C)	Blending ratio	Pyrolysis liquid (%)	Char (%)	Vapour (%)
		(a) Pyrolysis yields of sugarcane bagasse products		
500	NA	62.4	35	2.6
525	NA	72.6	20	7.4
550	NA	67	24	9
		(b) Pyrolysis yields of polystyrene products		
500	NA	79.56	4.7	15.74
525	NA	86.58	3.2	10.22
550	NA	84.24	3.8	11.96
		(c) Co-pyrolysis yields of different blends of sugarcane bagasse and polystyrene products		
525	1:1	53	24	23
525	1:3	58	25	17
525	3:1	56	22	22
		(d) Co-pyrolysis yields of different blends of sugarcane bagasse and polystyrene products supplemented with 3 g of fly ash (catalyst)		
525	1:1	58	13.3	28.7
525	1:3	63.2	11.33	25.47
525	3:1	60.8	12.46	26.74

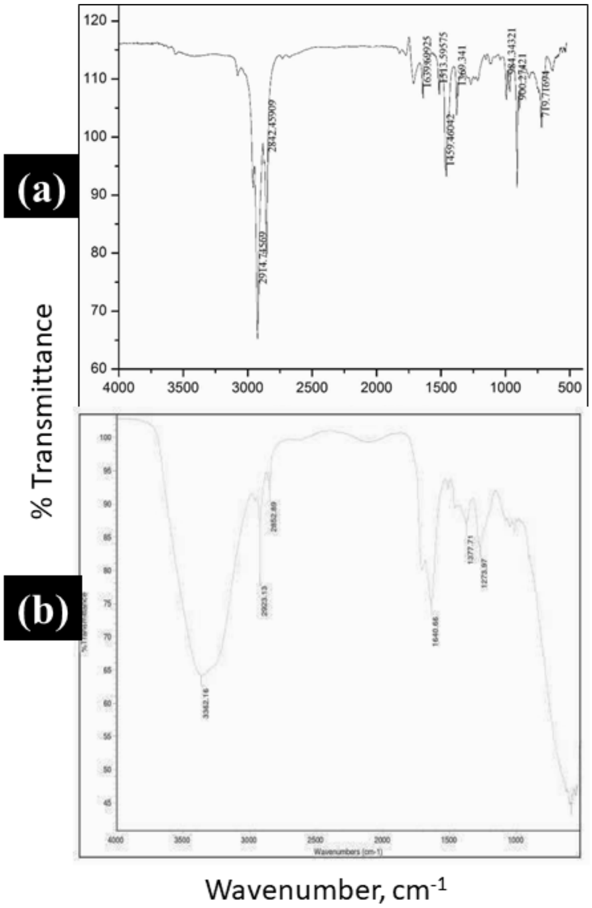


Fig.3. FTIR spectrum of co-pyrolysis liquid obtained from a mixture of sugarcane bagasse and polystyrene in the ratio of 1:3 (a) without any catalyst and (b) with the presence of catalyst

The pyrolysis liquid obtained with and without the addition of catalyst was chemical characterized using FTIR spectroscopy. The Fig. 3a and 3b show respective spectrum of co-pyrolysis liquid obtained without and with the presence of fly ash.The oil obtained from non-catalyzed co-pyrolysis contains alkanes, alkenes, amines, alcohols, and phenols. The peak at 2914 cm^{-1} and 2842 cm^{-1} corresponds to CH_3, CH_2, and CH suggests the presence of alkanes. Moreover, peak observed at 1459 cm^{-1} also relates to CH_3 and CH_2 suggests the present of alkanes. The peak at 1369 cm^{-1} corresponds to hydroxyl groups suggests the presence of alcohols or phenols. The peak at 1513 corresponds to NH suggests the presence of secondary amines. Finally, the peak at 1639 corresponds to NH^2 and =CH, and $=CH_2$ suggests the presence of amines and alkenes. On the other hand, catalytic pyrolysis oil contains carboxylic acids and derivatives. The peak at 2852 cm^{-1} and 2923.13 cm^{-1} corresponds to CH_3, CH_2, and CH suggests the presence of alkanes. The peak at 1377 cm^{-1} and 2362.16 cm^{-1} corresponds to hydroxyl groups suggests the presence of alcohols or phenols. The peak at 1273 cm^{-1} corresponds to CO suggests the presence of carboxylic acids or their derivatives.Thus variations were evident with the presence of chemically treated catalyst used in co-pyrolysis.

CONCLUSION

The co-pyrolysis of sugarcane bagasse and polystyrene was studied with and without the presence of chemically treated fly ash catalyst. Characterization of treated fly ash by XRD, SEM, EDX, and BET revealed the crystal nature, elemental composition, morphology, increased number of pores and surface area Pyrolysis was carried out in a batch reactor in the temperature range of 500 to 550 °C with a heating rate of 20 °C min^{-1} using different biomass to plastic ratios of 1:1, 1:3 and 3:1. The maximum liquid yield of non-catalytic mixed pyrolysis of sugarcane bagasse and PS alone was 58% at 525 °C. Whereas, the catalytic increased the yield up to 63.2% with 1:3 blend of SB and PS.

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