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Experimental Studies on Enhancement of Bio-Oil Production Using Agro Waste Materials Pre-Treated with Alkaline Solutions

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Abstract: This paper reports experimental results of the effect of pre treatment on the yield of bio-oils obtained from the pyrolisis of pre-treated agro waste materials. Five different agro waste materials of plants/crop residues like *Glycine max* (soya husk), *Oryza sativa L* (rice husk), *Gossypium arboretum* (cotton stalk), *Saccharum officinarum* (bagasse) and *Dalbergia sissoo* (wood sawdust-sesame) were pre-treated with NaOH solutions. Different pre-treatment solutions were prepared with Sodium Hydroxide dissolved in distilled water with concentrations of 50 g/L, 100 g/L and 150 g/L. The selected biomass materials after treatment with these solutions were kept for 24 hours for stabilization. The pre-treated agro waste materials were placed in an electrically heated tubular batch pyrolysis reactor at a temperature of 600ºC. Nitrogen gas was injected into the reactor with a flow rate of 20 mL/min. Results showed that about 35.7% to 269 % higher yield was obtained with NaOH treated samples in comparison with the untreated biomass samples. The samples pre-treated with 50 g/L of NaOH solution yielded the highest bio-oil production amongst all biomass samples.

Key words: Pyrolysis · Pre treatment · Biomass materials · Alkali metals · Bio-oil

INTRODUCTION

Biomass is one of the most attractive renewable energy sources in view of the fast depleting finite reserves of fossil fuels and their environmental impacts. Major sources of biomass are crop residues in addition to wood and forest waste. Organic municipal solid waste is also available on a large scale. Pyrolysis of biomass residues has an attractive option for liquid fuel production [1, 2]. The growing demand in industrial sector, for electricity production from gas turbines fed with liquid biofuels has created renewed interest in this technology [3, 4].

Pre-treatment process is used for removing lignin and hemi-cellulose, to reduce the crystallinity of cellulose and to increase the porosity of the lingo-cellulosic materials [5]. The chemical pre-treatment methods reported are more effective and fast compared to biological and physical pre-treatment methods. Mosier *et al*., [6] has reported the effect of different type of pre-treatment methods on the chemical composition and c hemical/physical structural changes of biomass materials. Investigators have showed that the alkaline pre-treatment of lingo-cellulosic biomass materials with Lime provided more of the accessible surface area, minor removal of hemi-cellulose and removal /change of lignin structure. Alkaline pre-treatments were found to be effective for agricultural residues with low lignin content and used in enzymatic digestion [7]. The effect of alkaline pre-treatment on crop residues was utilized to study the effect on bio-oil production using pyrolysis process.

Crop residues like Soya husk, rice husk, cotton stalk, bagasse and wood sawdust (Sesame) were selected for this study, as they are available in most of the countries. Biomass materials used in the reactor were in powdered form (particle size 212 µm) as large particle size created problems in heat transfer and affected bio-oil yield. Small particle size offers higher potential of bio-oil production, while larger particles may decrease the bio-oil yield and increase the charcoal as well as gas yield. When the temperature was increased, the charcoal yield decreased.

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The charcoal yield increased as the particle size increased. High temperature and smaller particle size increased the heating rate, resulting in lower charcoal yield [8]. Cellulose, hemi-cellulose and lignin could degrade at different temperature ranges [9].

Many researchers have used pre-treatment methods for biomass degradation but limited articles were found adopting pre-treatment of biomass for bio-oil production. Efforts were made to pre-treat the five selected biomass materials with NaOH for maximization of bio-oil production. The effect of chemical pre-treatment using NaOH, H_2O_2 and $Ca(OH)_2$ on Empty Palm Fruit Bunches (EPFB) to degrade EPFB lignin before pyrolysis has been reported [10]. In the available literature, the effect of chemical pre-treatment on bio-oil production has not been studied well on these selected biomass materials.

MATERIAL AND METHODS

Physico-Chemical Analysis of Biomass: The selected biomass materials were procured from the near by villages of Indore city, Madhya Pradesh, India. The selected biomass materials are listed with their botanical names and common Indian names in Table 1.

The American Society for Testing and Materials (ASTM) standards for coal and coke was utilized for proximate analysis of biomass materials and charcoal. This method covers moisture content (ASTM method D3173), ash (ASTM method D3174) and volatile matter (ASTM D3175). Fixed carbon analysis was carried out by weight difference method [11]. Ultimate analysis of biomass was carried out by using CHNS (O) analyzer (Flash EA 1112 series model, Thermo Fennigan, (Italy make) for elemental analysis. The analyzer works on the principle of the Dumas method, which involves complete and instantaneous oxidation of the sample by flash combustion. Calorific value of biomass was analyzed using automatic bomb calorimeter (Toshniwal make) which follows ASTM E870-82 (2006) (E711) test method. Na and K content in biomass material was analyzed using Spectrum flame photometer (Model no. 335, Systronics make).

Pre-Treatment of Biomass: The solution was prepared by dissolving 50 g, 100 g and 150 g of NaOH (Merck grade) in 1.0 Liter distilled water respectively. The prepared alkaline solutions were sprinkled on 1 kg of individual biomass material and kept at room temperature for a duration of 24 hours. Distilled water was used for washing the treated samples 2 to 3 times to ensure the removal of NaOH. The samples were then dried in an oven and mixed well. The same procedure of pre-treatment was adopted for all the selected biomass materials. 100 g samples of each pre-treated and untreated materials were used in the reactor.

Pyrolysis Reactor: The pyrolysis system mainly comprises of an insulated reactor or bare reactor, condenser or condenser train, inert gas flow system or vacuum pump and an electrical heater or heat source. Demirbas *et al*.,[12] used a horizontal tube reactor with a height of 127 mm and diameter 17 mm. Peters *et al*., [13] used a furnace chamber (height 10 cm × diameter 5 cm). The height of the reactor was kept longer as compared to the width to facilitate rapid and easy heat transfer among the particles of biomass samples.

The experimental setup developed for our experiment consists of a tubular fixed bed pyrolysis reactor, mesh and condenser arrangement for the supply and control of sweep gas as well as the Pyro-gas condensing train. The schematic diagram of a tubular fixed bed reactor is shown in Fig. 1.

The cylindrical reactor was fabricated using stainless steel sheet (SS-304) having a thickness of 2 mm. Stainless steel was preferred due to its sustainability at higher temperatures and as it possesses anti corrosion properties. The outer dimensions of the tubular fixed bed pyrolysis reactor were taken to be 78 cm × 8 cm and the inner dimensions were chosen to be 74 cm × 6 cm (length x diameter) with a holding capacity of 300 g providing uniform heat transfer throughout the biomass sample. The mesh (sample holder) fitted inside the reactor was made using 1 mm thick stainless steel sheet, welded in the form of a cylindrical pipe. The mesh height was maintained at 74 cm. The inner and outer

Table 1: List of biomass materials with their botanical names and common Indian names

S.No	Common Indian names of collected Biomass materials	Botanical names of Plants/Crop	Family
1	Soya husk (Crushed stem residue)	Glycine max	Fabales: Fabaceae
2	Rice husk (Seed cover residue)	Oryza sativa L	Gramineae
3	Cotton stalk (Crushed stem residue)	Gossypium arboreum	Malvaceae, the marsh mallow family
4	Bagasse (Sugarcane residue after juice extracted)	Saccharum officinarum	Gramineae
5	Wood saw dust (Powdered residue material of Dalbergia sissoo wood from Saw mills)	Dalbergia sissoo	Fabaceae

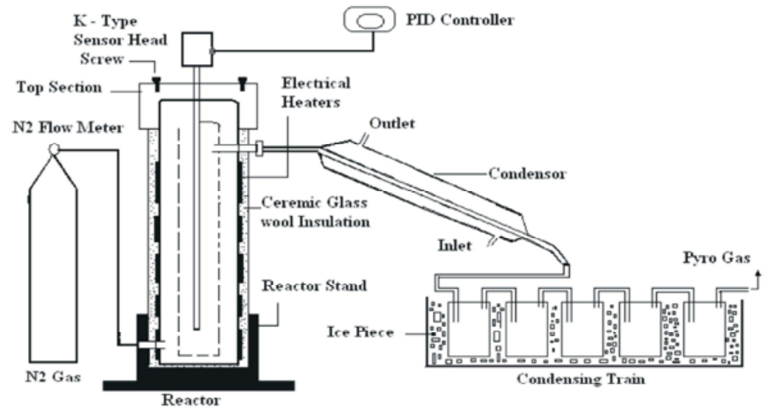

Fig. 1: Schematic diagram of a tubular fixed bed reactor

Fig. 2: Pyrolysis set up for bio-oil production

diameters of the pipe were 5 cm and 6 cm respectively. Biomass was filled in it before starting the reactor and residual charcoal was recovered from it after the pyrolysis.

Five electrical heaters of 400 W each were wrapped uniformly all along the length around the outer surface of cylindrical reactor. The reactor was then covered with a ceramic blanket insulation of 50 mm thickness to reduce thermal losses. A K-type thermocouple was fixed at the center of the reactor and connected to a PID controller. The PID controller measured and controlled the temperature of the reactor. The PID controller and thermocouple were calibrated before use. Photograph of the complete experimental setup is shown in Fig. 2.

RESULTS AND DISCUSSION

Soya husk, rice husk, cotton stalk, bagasse and wood sawdust have been characterized and the results are shown in Table 2. Cellulose, hemi-cellulose and lignin played a wider role during the pyrolysis process. It varied from 30-44%, 12-32% and 16-23.3% respectively for cellulose, hemi-celluloses and lignin in the selected biomass materials. Densities of all the selected biomass materials were found to be in the range of 2.43 - 2.83 g/cc. A close look at Table 2 indicates that the percentage of Na and K were higher in bagasse as compared to other biomass materials; however in wood saw dust, Na and K percentage was lower in comparison to other tested biomass materials. The calorific values of all the tested biomass materials were in the range of 3142 – 4578 Kcal/kg. Wood saw dust had the highest calorific value followed by cotton stalk when compared to other tested biomass materials. This might have been due to the high percentage of C and H.

The highest carbon percentage was found in wood saw dust (54.96 %) and in rice husk (48.91 %) in comparison with the other three biomass materials like soya husk (42.05 %), cotton stalk (41.21 %) and bagasse (42.39 %). The highest percentage of oil was found in wood sawdust (22.41%) and rice husk (23.52%), which indicated that a higher percentage of carbon would help to induce higher percentage of oil because the quantity of hydrogen was nearly the same in most of the biomass materials. These results were compared with the values

Table 2: Characteristics of selected biomass materials

Components of Biomass materials	Units	Soya husk	Rice husk	Cotton stalk	Bagasse	Wood saw dust (Sesame stalk)
Cellulose	%	41	36	38	44	34.4
Hemi-cellulose	%	27	26	32	30	28
Lignin	%	16	23	20.88	19	23.3
Extractive matter	%	16	15	9.12	7.0	14.3
Volatile Matter	%	77.3	66.7	67.0	75.7	80.2
Ash Content	%	7.2	22.0	16.8	3.1	2.0
Sodium Na	mg/L	18.4	12.7	17.8	30.0	13.7
Potassium K	mg/L	27.3	41.3	21.8	38.0	11.7
C	%	42.05	48.91	41.21	42.39	54.96
H	%	6.37	5.85	4.92	6.15	6.16
N	%	3.56	0.58	1.98	0.0	0.0
O (calculated by difference)	%	48.02	44.66	51.89	51.46	38.89
Calorific value	Kcal/kg	3570	3142	4386	3186	4578
Density	gm/cc	2.71	2.83	2.83	2.43	2.53

Table 3: Effect of Pre-treatment on volatile matter and ash content with Bio-oil production from untreated and NaOH treated biomass materials

S. No	Type of Biomass Units	VM %	Ash %	Bio oil Yield gm of bio oil produced/gm of biomass material used	Bio-oil %
1	Soya husk (untreated)	77.3	7.2	0.195	19.5
	Soya husk (5 % NaOH)	85.71	5.3	0.504	50.4
	Soya husk (10 % NaOH)	82.10	4.06	0.393	39.3
	Soya husk (15% NaOH)	80.10	3.84	0.323	32.3
2	Rice husk (untreated)	66.7	22	0.235	23.5
	Rice husk (5 % NaOH)	80.58	18.08	0.424	42.4
	Rice husk(10% NaOH)	77.14	17.04	0.319	31.9
	Rice husk (15 % NaOH)	75.57	16.75	0.275	27.5
3	Cotton stalks (untreated)	67	16.8	0.171	17.1
	Cotton stalk (5 % NaOH)	78.62	14.24	0.365	36.5
	Cotton stalk (10 % NaOH)	73.81	12.26	0.331	33.1
	Cotton stalk (15 % NaOH)	69.81	11.32	0.290	29.0
4	Bagasse (untreated)	75.7	3.1	0.122	12.2
	Bagasse (5 % NaOH)	82.81	2.49	0.450	45.0
	Bagasse (10 % NaOH)	81.08	2.12	0.448	44.8
	Bagasse (15 % NaOH)	82.81	1.72	0.411	41.1
5	Wood saw dust (Untreated)	72.99	2.0	0.224	22.41
	Wood saw dust (5 % NaOH)	80.2	1.75	0.537	53.7
	Wood saw dust (10% NaOH)	86.78	1.5	0.407	40.7
	Wood saw dust (15 % NaOH)	87.98	1.29	0.388	38.8

reported in the literature and were found to be well within the stipulated range [14]. Bio-oil production depends on the presence of volatile matter and ash content in the biomass. Higher volatile matter enhanced the bio-oil production, however higher ash content decreased the production of bio-oil in the same conditions of pyrolysis.

Table 3 shows the bio-oil production from different untreated and treated biomass materials. Normally the high percentage of hemi-cellulose and volatile matter should produce maximum bio-oil but the results indicated that Na and K present in biomass materials seem to inhibit the reaction and affect the production of bio-oil.

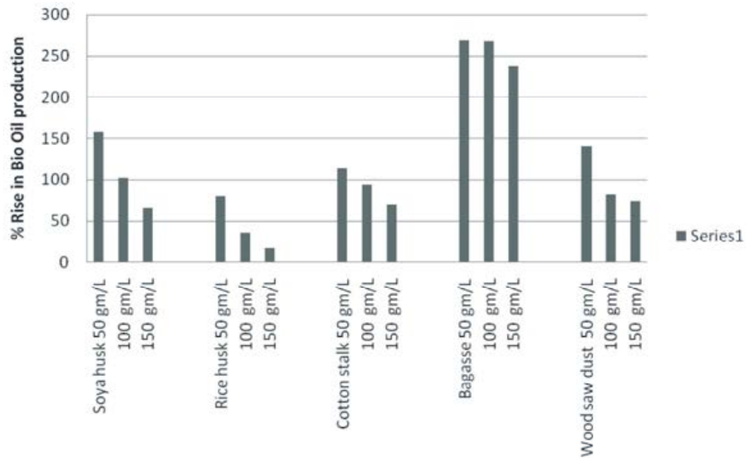

Fig. 3: Percentage rise in bio-oil production after pre-treatment of selected biomass materials with different strengths of NaOH solutions

The higher percentage of Na has reduced the bio-oil production from biomass material more dominantly in comparison to K present in the biomass materials. Wood sawdust (13.7 mg/L) and rice husk (12.7 mg/L) contain lower amounts of sodium as compared to the other three biomass materials. It has been found that lower amounts of Na induces higher amount of bio-oil in wood sawdust and rice husk biomass as shown in Table 2 and Table 3. It can also be seen from Table 3 that among the pre-treated biomass materials, the percentage of volatile matter was found to be the highest in wood saw dust (80.2%), followed by soya husk (77.3%). By using 5% NaOH pre-treatment the corresponding bio-oil production was found to be 53.76 % and 50.38% respectively. With an increasing percentage of NaOH, the quantity of volatile matter increased with wood sawdust only when compared to 50 g/L NaOH solution treatment and the ash content also reduced compared to untreated biomass. The highest bio-oil production was observed with the pre-treatment of 50 g/L NaOH solution; however, with further increase in the concentration of NaOH, bio-oil production started decreasing, but was always found to be higher than the untreated biomass materials. The bio-oil yield was calculated based on weight ratio and in terms of percentage as given below -

Bio-oil Yield = Weight of bio-oil produced /Weight of biomass material used in the reactor

% of Bio-oil = Bio-oil Yield × 100

Maximum bio-oil production was observed from all selected biomass materials, when treated with 50 g/L NaOH solution. The calculation of percentage rise in bio-oil production of pre-treated materials over the untreated materials have been plotted and shown in figure 3. It can be seen that alkaline pre-treatment appreciably increases the yield from 35.7% to 269% depending on the characteristics of the biomass materials. Maximum rise in bio-oil production after pre-treatment from Soya husk, rice husk, cotton stalk, bagasse and wood sawdust were nearly 158 %, 80 %, 112 %, 269 % and 139 % respectively in comparison with the bio-oil produced from same untreated biomass samples. The quantity of bio-oil obtained was minimum in bagasse samples but percentage increase of bio-oil production after pre-treatment was most effective in bagasse.

Studies conclude that bio-oil production increased after pre-treatment of biomass materials with NaOH. In general, treatment of biomass with NaOH of 50 g/L solution was found to be more effective when compared to 10 g/L and 15 g/L NaOH treatment. Pre-treatment with 50 g/L NaOH solution was found suitable for all selected biomass materials.

CONCLUSION

The analysis of biomass materials and bio-oil produced using biomass materials namely soya husk, rice husk, cotton stalk, bagasse and wood sawdust was carried out with identical stated conditions. The following conclusions are drawn from this experimental study-

- The pre-treatment of biomass with 50 g/L NaOH solution was found to be the best for maximum bio-oil production using pyrolysis process at 600°C.

- NaOH treated samples produced minimum 35.7% to maximum 269% more bio-oil in comparison with untreated biomass materials.

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