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Agglomeration of Pet Coke and Rice Straw as Mixed Fuel for Power Generation

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Abstract

The study examined the agglomeration properties of pet coke and rice straw mixed fuel for power generation. Pet coke and rice straw were collected from two plants. The samples were agglomerated in three different ratios. Proximate analyses and calorific values were obtained based on ASTM. X-ray diffractometer (XRD) was used to determine the various phases present in ashes of the samples. The microstructure was observed using a scanning electron microscope (SEM). The thermal stability of the samples was studied. Fluidization tests and the carbon utilization efficiencies (CUE) were evaluated. The results showed that the addition of both fuels improved the volatile matter for pet coke and the fixed carbon for rice straw. The calorific value of the agglomerates (3500 to 5000 kcal/g) were lower compared to the pet coke (8500 kcal/g). Quartz was the predominant phase in the ashes of both samples with more peaks and intensities in pet coke ash. The pet coke contained compact carbon with high graphitization within its microstructure. The CUE (93.42 - 98.31%) were higher than that of pet coke. The presence of pet coke improved the thermal stability of the agglomerates. The 70:30 and 80:20% of rice straw to pet coke samples were the best combinations as fuel based. The results of the analyses depicted that a mixture of rice straw and pet coke is needed to mitigate the disadvantages of each.

Keywords: Rice straw; Pet coke; Thermogravimetric analysis; Agglomeration; Carbon utilization efficiency.

1. Introduction

Renewable energy and non-renewable energy are the two energy resources classifications ^[1]. Renewable energy sources are thought to be sustainable while non-renewable energy resources cannot be replenished as it would be exhausted ^[1-2]. The demand for electricity generation increases on daily basis, which demands an increase in daily usage of fossil fuels leading to the production of greenhouse gases. The excessive usage of fossil fuels drastically changes our environment through the introduction of harmful emissions after combustion. These harmful emissions lead to various harmful effects as a result of increased atmospheric pollution. The reduction of these effects on the environment can be achieved through the utilization of biomass fuel as an alternative energy source, which will serve the same purpose with continuous development. The usage of biomass as fuels is amongst other means of reducing non-renewable resources utilization ^[3]. Biomass, as a renewable energy source, can be obtained from agricultural residues (such as rice husk/hull, rice straw, corn cobs, and so on as well as forest-related activities such as saw dusts, wood chips and bark), municipal solid wastes and industrial wastes ^[4-9]. It has gained more attention as a renewable energy source due to its contribution to greenhouse gas emission reduction as well as its sustainability ^[5, 10].

There are huge numbers of agricultural residues in loose form of fuel which are being burnt thereby increasing environmental air pollution.

Rice straw is an agricultural residue, which is obtained from rice plantation. It produces low content of CO, SO_x and NO_x gases ^[11]. Due to high rice plantation in India, rice straw is found in abundance. More so, Punjab on the average produces about 11% of India's rice and 2% of the world's rice production. These rice straws can be converted into biomass fuel for electricity generation by combusting them so as to produce steam that will run the turbine, which invariably produce the electricity. Moreover, rice straw can be used to produce energy in fluidized bed combustors. Petroleum coke is usually referred to as pet coke, which is a refinery's by-product from the heavy oil fractions upgrade in order to produce lighter hydrocarbons ^[12]. It has found good utilization in firing fixed bed combustor boilers with or without blends of coals to produce energy ^[13]. Its specific ash content as well as high sulfur content makes it an effective source of energy that increases the plant economy. Pet coke is a carbonaceous solid which can be derived from the coker unit of an oil refinery. It has become a competitive fuel hence, very popular in process or power boilers.

Fluidized bed combustors are used for production of energy in power plants ^[14]. It is one of the most suited combustion technologies for pet coke combustion due to its ability to handle low volatile and high sulphur content fuels ^[15]. The fluidized bed combustion systems mechanism has been explained by Anthony ^[12]; Sharma et al. ^[14] and many more researchers. As reported by Chen and Lu ^[16] the operating experiences of circulating fluidized bed boilers have proved its feasibility for petroleum coke combustion, although, the amount of loss of unburnt flv ash is relatively high. Sharma et al. ^[14] investigated and compared the usage of pet coke and its combination with rice husk in a fluidized bed combustion chamber. 100% pet coke and combined pet coke (80%) and rice husk (20%) were used separately to generate heat energy in a mini power plant. Jaygopal et al. ^[15] studied pet coke and Indian sub-bituminuous coal combustion characteristics in a fluidized bed combustion facility. The combustion characteristics of the two fuels used were compared. It was reported that pet coke exhibited stable combustion due to the temperature profile analysis done. High sulphur content and low ash content were detected in the pet coke in which limestone was added in situ to capture sulphur and to maintain bed inventory. Rice straw was made into pellets and used as biomass fuel in a fluidized bed combustor in a study conducted by Okasha ^[17]. Char combination and elutriation bed particle ejection, volatile release and segregation, and some post combustion above the bed were the main factors considered during the experimentation.

The combustion characteristics of rice husk and their fluidization behaviour were studied by Rozainee *et al.* ^[18]. It was reported that rice husk fluidization behaviour was better when compared to char. The bubbling velocity of rice husk was nearly same as that of char and their mixture. Although, poor movement of fluidization of mixed husk, ash and char was reported at lower air velocity. According to Unchaisri and Fukuda ^[19], Chaivatamaset *et al.* ^[20] and Teixeira *et al.* ^[21], the physical and chemical properties of rice straw make it to be considered a difficult biomass for energy production due to the high alkali contents they contain. Hence, during combustion, severe problems could be developed. Therefore, in this study rice straw, pet coke and their combinations have been utilized on different power plants to produce electrical energy.

2. Materials and method

The materials used for this study were pet coke and rice straw (Figure 1) obtained from Shri Ganesh Paper Mill and Punjab Biomass Power Limited Patiala, respectively. Shri Ganesh Paper Mill used pet coke while Punjab Biomass Power limited used rice straw as fuel for generating energy. Study related to fluidization was done and samples collected from both places. A schematic showing the details of the fluidized bed combustion process is presented in Figure 2. Agglomerations of rice straw and pet coke were formed at different mixing ratios, as shown in Table 1. The Punjab Biomass Power limited boiler was used for the study of the agglomerates.



Figure 1. Samples of (a) Rice straw (b) Pet coke



Figure 2. Line diagram of FBC process

Table 1. Different mixing ratios of pet coke and rice straw

| Sample | Rice straw (wt.%) | Pet coke (wt.%) |
|------------|----------------------|--------------------|
| Rice straw | 100 | - |
| Pet coke | - | 100 |
| R90P10 | 90 | 10 |
| R80P20 | 80 | 20 |
| R70P30 | 70 | 30 |

2.1. Proximate analysis

The raw and agglomerates were characterized using proximate analysis which consist of moisture, ash, volatile matter, and fixed carbon contents determination. The analyses were carried out using standard on the screened particle size (-72 BS mesh).

2.1.1. Determination of moisture content

Air dried sample (1 g) was placed in a glass disc and heated at 105±5°C for one hour in an oven according to ASTM E871-82 standard ^[22]. The discs were then taken out of the oven and the materials were weighed. The percentage moisture content was calculated using Equation 1. MC (%) = $\frac{M_f}{M_i} \times 100$ (1)

where ${\tt M}_{\rm f}$ is the mass of sample after drying and ${\tt M}_{\rm i}$ is the mass of sample before oven-drying.

2.1.2. Determination of ash content

Air dried sample (1 g) was measured into a shallow silica disc and kept in a muffle furnace which was maintained at 775±55°C till complete burning was achieved in accordance with ASTM E1755-01 standard ^[22]. The weight of the residue was taken using an electronic balance. The percentage weight of the ash contained in the sample was calculate using Equation 2.

Ash (%) = $\frac{\text{Wt. of residue obtained}}{\text{Initial wt.ofsample}} \times 100\%$

(2)

2.1.3. Determination of volatile matter

Air dried sample (1 g) was measured and placed in a cylindrical silica crucible which was covered with a silica lid. The crucible was placed in a muffle furnace set 925±5°C and kept there for 7 minutes according to BS EN 15148 standard ^[24], after which it was removed and air cooled. The devolatilized samples were weighed using a digital balance and the percentage loss in weight of each of the sample was calculated. The percentage volatile matter in the sample was determined using Equation 3.

Volatile matter (VM%) = % loss in weight – % moisture (3)

2.1.4. Determination of fixed carbon

The fixed carbon in the simple was determined using Equation 4. FC (%) = 100 - (% MC + % VM + % Ash) (4) where FC is fixed carbon; MC is moisture content and VM is volatile matter.

2.2. Thermo-gravimetric analysis

The evaluation of the gasification reactivity was carried out with the aid of Perkin Elmer thermal analyzer using the isothermal method. The procedure involved heating powdered samples of 8.2 mg in a nitrogen gas atmosphere with a flow rate was 100 mL/min. The samples were heated from ambient temperature until there was no increase in the thermogravimetric rates ^[25].

2.3. Calorific values analysis and carbon utilization efficiency

Calorific values of the samples were obtained with a Parr 6200 Oxygen Bomb Calorimeter (Model No: A1290DDEE). The carbon utilization efficiencies (CUE) of the fuels (pet coke and rice straw) coupled with the agglomerates (mixed fuel) were calculated using Equation 5 from the data (Table 2) obtained from the two plants (Figure 3).

 $CUE = \frac{(F_0 - (F_4 + F_5))}{F_0} \times 100$

(5)



Figure 3. (a) FBC Boiler (Courtesy: Punjab Biomass power limited) (b) Hopper (Courtesy: Punjab Biomass power limited)

| Table 2 Darameters used | for the colculation | of the CLIE obtained | from the plante |
|--------------------------|---------------------|-------------------------|-----------------|
| Table 2. Parameters used | | I UI LITE CUL UDLAITIEL | |

| Parameters | Pet coke | Biomass | R90P10 | R80P20 | R70P30 |
|--------------------------------------|----------|---------|--------|--------|--------|
| Feed rate of carbon in g/s (F0) | 735.00 | 116.24 | 116.24 | 116.24 | 116.24 |
| Carbon rate from fly ash in g/s (F4) | 0 | 5.3 | 4.4 | 2.1 | 1.12 |
| Unburnt pet coke/biomass in g/s (F5) | 77.38 | 0 | 3.24 | 1.69 | 0.84 |

3. Results and discussion

3.1. XRD analysis

XRD analysis is veritable to evaluate the different phase of mineral matter in coke and biomass ash in readiness for a larger industrial application such as was employed in this study. The XRD diffractogram for rice straw (Punjab furnace) ash and pet coke (Shri Ganesh furnace) ash are shown in Figure 4.





The pattern in the XRD depicted that residue of the pet coke at Shri Ganesh paper mill consist of large quantity of inorganic substances, which further reduced the utilization efficiency of carbon in plant coke ^[25-27]. The dominant mineral in coke ash was quartz, which spread across various 2Theta. Although it was present in the paddy straw ash, however; it was fewer. The other minerals were anhydrite, hematite, magnetite, and some traces content of kaolinite, illite, calcite, pyrite, plagioclase, feldspar and gypsum, and occasionally dolomite, ankerite, siderite, iron-oxyhydroxides and sulphates, which could the unpronounced peaks ^[28]. What may be responsible for abrasion of the furnaces is excessive presence of quartz especially

in coke ash ^[29]. The use of pet coke as fuel therefore could pose serious problems like periodic plant shut down and inefficient combustion. Thus, the need for combine use of the coke fuel and paddy straw for efficient combustion.

3.2. SEM analysis

Figure 5 shows the image of the samples collected from Shri Ganesh paper mill (Pet coke) and Punjab Biomass power limited (rice straw) while Figure 6 shows the microstructural analysis of both samples. A close examination of Figure 5 shows that it is easier to break the rice straw agglomerate by hand than to break that of pet coke. The SEM analysis in Figure 6 revealed that bonding between the particles of pet coke is very high as particles are merged into each other. Meanwhile, the presence of globular pores in the microstructure of rice straw indicates low particle bonding and accounts for ease of breakability of the rice straw agglomerate [14]. The strong inter-particle bonding in pet coke agglomerate can be attributed to the compact carbon structure and high degree of graphitization which inhibits gasification. However, rice straw contains some alkali elements which are catalysts for gasification [30]. Therefore, the addition of pet coke to rice straw will increase the strength of the rice straw biomass while retaining the ease of gasification.



Figure 5. The agglomerates of (a) pet coke at Shri Ganesh paper mill (b) Rice straw at Punjab Biomass power limited



Figure 6. SEM images of the (a) pet coke at Shri Ganesh paper mill (b) Rice straw at Punjab Biomass power limited

3.3. Proximate analysis

The results of the proximate analyses are shown in Table 3. The results show that pet coke had the least volatile matter content (52%), while rice straw sample recorded the highest (61.68%). With the addition of pet coke to rice straw biomass, the volatile matter content reduced from 60.12% in R90P10 to 58.30% in R70P30. Similarly, pet coke sample had the highest fixed carbon content (40.10%) while the lowest was recorded for rice straw biomass (14.02%). The addition of pet coke to rice straw led to an increase in the fixed carbon content of the biomass from 21.73% in R90P10 to 28.90% in R70P30, thereby increasing the energy value of the fuel. Pet coke had the lowest ash content of 1.60% while rice straw biomass recorded the highest ash content of 20.49%. The high ash content of rice straw may be attributed to the presence of high concentration of alkali elements in the area of harvest [31]. This implied that the use of pure rice straw as fuel will produce great deposit of ash which will become a major challenge in the combustion chamber of the thermal power plant. Li et al. ^[32] recommended that washing grassy biomass with water, leaching and the use of additives are measures that reduce the ash content of biomass. The addition of pet coke to rice straw agglomerate led to a reduction of the ash content in the agglomerates. As the percentage of pet coke in the agglomerate increased from 10 - 30%, the ash content reduced from 10.05 to 8.90%. Conversely, the moisture content of rice straw (4.30%) is lower than that of pet coke (6.00%). Ignition is dampened by moisture content as more heat is required to dry the fuel before ignition can take place. More energy is therefore required to keep the fuel burning, which will affect the consumption rate of fuel during combustion. Moisture provides a dampening effect on fuel by reducing the height of the flame and temperature thereby leading to smoldering, which has negative health and environmental implications ^[33]. It was on this note that Yuntenwi & Ertel ^[34] warned against the use of extremely wet or dry fuels.

| | Proximate (%) | | | | |
|------------|---------------|-------|-------|------|--|
| Samples | VM | FC | Ash | MC | |
| Pet coke | 52.00 | 40.10 | 1.60 | 6.00 | |
| Rice straw | 61.68 | 14.02 | 20.49 | 4.30 | |
| R90P10 | 60.12 | 21.73 | 10.05 | 8.10 | |
| R80P20 | 59.80 | 26.06 | 9.80 | 8.40 | |
| R70P30 | 58.30 | 28.90 | 8.90 | 8.99 | |

Table 3. Proximate analyses of pet coke and rice straw

3.4. Gross calorific value and carbon utilization efficiency of the samples

Figure 7 displays a graph of the gross calorific values of the samples. It reveals that the pure pet coke recorded the highest calorific value of 8500 kcal/g, while the pure rice straw sample recorded the lowest calorific value (3000 kcal/g).

CUE (%)



Figure 7. Calorific values of raw samples and the F agglomerates s



Figure 8. Carbon utilization efficiencies for the samples

The addition of pet coke to rice straw biomass improved the calorific value of the biomass. As the percentage of pet coke in the agglomerate increased from 10% in R90P10 to 30% in R70P30, the calorific value increased from 3500 to 5000 kcal/g, respectively. The increment in the calorific value is attributed to the increment in the percentage fixed carbon of the mixtures and thus better performance. The carbon utilization efficiencies of the pet coke (89.47%) are lower compared to the 95.44% of the rice husk biomass in their respective plants, as shown in Figure 8. However, the value increased when both fuels were agglomerated. An increase in the rice husk within the agglomerates led to a higher CUE, which may be due to the nature of rice husk with higher volatile that maintained the combustion within the agglomerate [³⁻⁴].





Figure 9. Thermogravimetric curves for the samples

Figure 9 present, the thermogravimetric curves for the samples. The results showed that weight of pet coke decreased gradually up to 390°C due to very small amount of volatile matter and moisture before witnessing a sharp fall due to char combustion. Jaygopal *et al.* ^[15] reported that the ignition temperature of pet coke was 390°C. Meanwhile, temperature increment from ambient to about 100°C resulted in weight loss of 4 - 5% owing to water loss present in the samples and external water bounded

by surface tension. The initial decomposition of the rice straw started at the temperature of 235°C, whereas the final temperature of the first reaction zone was 340°C approximately.

However, the impact of adding pet coke to the rice straw biomass was evident, as the rate of weight loss was slightly reduced in increasing measure as the pet coke content of the mixture increased. The ignition temperature was also increased due to increase in moisture content, as shown in Table 3. The result of the study is line with the findings of Kamble *et al.* ^[35] and Cheng & Heidari ^[36] who described that gasification process is a three stage process which comprised of initial drying up of the carbonaceous material below 125°C, followed by an active pyrolysis stage between 125 and 500°C and finally, a passive pyrolysis stage at a temperature above 500°C. The loss in weight is due to the evaporation of the moisture content of the fuel as well as the vaporization of the volatile matter ^[3].

4. Conclusion

The agglomeration of pet coke and rice straw as mixed fuel for power generation has been experimented. Pet coke contained lower ash compared to the rice straw though dominated with quartz. The pet coke contained compact carbon structure with high graphitization that inhibited effective gasification when used alone. The addition of both fuels together improved the volatile matter for pet coke and the fixed carbon for rice straw. The calorific value of the agglomerates (3500 to 5000 kcal/g) were lower compared to the pet coke (8500 kcal/g) whereas the carbon utilization efficiencies (93.42 - 98.31%) were higher than the 89.47% of pet coke. The presence of pet coke improved the thermal stability of the agglomerates. The 70:30 and 80:20% of rice straw and pet coke samples were the best combination as fuel based on economic consideration and the efficiency. The agglomerates can be used in boiler operations and other thermal plants.

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