175. Biofuels Production Through Agrowaste Pyrolysis

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Abstract

Alternative energy resources are needed to fill the gap caused by the increased energy demand and depletion of fossil fuel. In agricultural countries agronomical waste is one of the most reliable, sustainable and renewable resources for energy generation. Different technologies can be used for the conversion of biomass into fuel. Wheat straw and rice straw is a seasonal agricultural waste so converting them to RDF is the best option. The current study was conducted to determine the influence of different parameters such as particle size, biomass type and binders, characteristics on product yields of agro waste pyrolysis. For this rice straw and wheat straw of three particle sizes (5-10mm, 2-5mm and <2mm) were used along with two binders grass clippings and banana peelings. Proximate analysis, energy content and heavy metal analysis were computed according to ASTM standards. Maximum moisture content was found in banana peels i.e. 90%. Higher volatile combustible matter resulted in wheat straw of particle size (5-10mm) that is 82%. A sample of rice straw of particle size <2mm combined with banana peels has the highest ash content of 24%. The highest fixed carbon is16%, found in two samples one is grass clippings and other is of rice straw of particle size (2-5mm), combined with banana peels. The highest energy content of 43.5 MJ/Kg revealed in a sample of wheat straw of size (2-5mm) combined with grass clippings. The top five samples of highest calorific value were pyrolyzed at 550 ^oC on lab-scale pyrolysis unit to determine the percent yields of oil, char and gas. Further the pyrolytic oil was analyzed through FTIR to determine the composition of liquid product. FTIR shows that in pyrolytic oil nitro compounds, alkanes, alkyl, halides, alcohols, carboxylic acids, ethers, esters, aldehydes, ketones and alkynes was found.

Keywords: *Agrowaste; Biofuel; Pyrolysis, Energy, RDF*

1. Introduction

With the industrialization, there is a population boom because of which there is also a great demand for energyin developing countries [1-2]. Pyrolysis is a thermochemical process and has given consideration for recovering energy from biomass and solid waste. It is very attractive and suitable approach for the countries having large agriculture sector to convert easily available biomass into fuel. Three main products of this process at different temperatures are biogas, a liquid product (tars and oil); and biochar[3].Pakistan contains vigorous capacity for biofuels by which country's mostly oil needs can be fulfilled, 80% from which are now being fulfilled through imports [4].By pyrolysis, this energy can be recovered into usableforms such as bio-oil and gasses [5].Physical parameters of pyrolysis of biomass like temperature, heating rate and residence time greatly affect the product yields and composition of products. Bio-oil has many applications it can be used as gas turbine fuel, diesel engine, and boiler and for numerous types of chemical production as use of bio-oil mainly relies on its quality. Bio-oil contains more chlorine and nitrogen but less sulfur as compared to petroleum [6]. Bio oil yield of fast pyrolysis become the promising option to substitute petroleum fuels to be used for power generation and heat [7].

The aims of the study is to determine the quality of RDF by performing proximate analysis, heavy metal analysis and finding calorific value; study the influence of different biomass, binders and particle size on calorific value of RDF and run the samples of highest energy content on pyrolysis unit to estimate their yields and explore the composition of pyrolysis oil by FTIR; estimate the potential of combustible hydrogen gas for subsequent fuel use. Three-way ANNOVA was applied to demonstrate the relationship among biomass, binders, particle size and calorific value by using IBM SPSS 22.0.

2. Materials and methods

Wheat straw and rice straw was supplied from the fields of Punjab University at the harvest time. Banana peels were collected from different cafes of Punjab University and grass clippings was taken by CEES department. Sample preparation (drying and shredding) was carried out in the laboratory. Wheat straw and rice straw were grounded in three different sized samples by passing through different sized sieves. The samples (wheat straw and rice straw) and binders (banana peelings and grass clippings) were oven dried until their moisture content becomes less than 10%. Samples of wheat straw and rice straw were sieved through a set of sieves arranged as 4mm, 2mm, and 1mm.After this 12 samples of wheat straw and rice straw were prepared by mixing half Kg of each particle size of wheat straw with½of both binders separately.

2.1 Analysis

To check the quality of RDF proximate analysis, calorific value and heavy metal analysis were carried out according to relative ASTM standards. Then the samples of wheat straw and rice straw of different particle sizes portrayed highest energy content were run in lab-scale pyrolysis unit at a temperature of 550^{o}C to determine the end products and composition of the pyrolytic oil.

2.1.1Proximate analysis

Proximate analysis of 12 samples was carried out by following related standard methods. Moisture content was carried out by ASTM D 3173-11 [8]. Volatile matter was carried out by ASTM D 3175-11 [9]. Ash content was carried out by ASTM D 3174-12 [10].

2.1.2 Energy content

According to the ASTM E711-87 [11] calorific value of each sample was carried out. By using an automatic bomb calorimeter LECO AC 500 this test was done.

2.1.3 Heavy metal analysis

Five metals (As, Cr, Mn, Zn, Cu) were estimated in four samples i.e. wheat straw, rice straw, banana peels and grass clippings. For heavy metal detection acid digestion of the samples was done [12]. Heavy metal concentration was detected by using atomic absorption spectrophotometer.

2.1.4 Pyrolysis –FTIR

Lab-scale pyrolysis unit (Batch type fixed bed reactor) was used. It consists of a closed chamber furnace. With the supply of electricity it starts up and to maintain temperature it contains a digital LED meter. Gasses formed in the condenser chamber cooled down with the continuous flow of water. This complete experiment is being performed under inert conditions. Two times nitrogen gas is supplied to flush the gasses into the valve. Firstly, before starting the experiment to avoid other reactions and secondly when the yield was collected from the reactor. In whole process 10 Psi pressure was maintained. Product yields were obtained in the form of gas, oil and char. Out of 12 samples pyrolysis (in the absence of oxygen decomposition of combustible components) was carried out for only 5 samples of highest energy content. One by one each sample was put into the reactor chamber of the pyrolysis unit and pyrolyzed at the temperature of 550℃. In the condensing chamber resulting vapours were condensed and the liquid comprising hydrocarbons was collected in the air tight bottles for the FTIR analysis.

3. Results and discussion

3.1 Proximate analysis

Proximate analysis of the individual components of biomass and their combinations with binders was done in laboratory after complete drying, shredding, and sieving. As banana peels contain more water content within it, their percentage of moisture content found higher than others and it is 90%. Moisture content of wheat straw (a, b, c) and rice straw (a, b, c) found almost close to each other i.e. (8%, 7%, 7%) and (10%, 8%, 8%) respectively. The volatile matter was found high for wheat straw (a) i.e. 82% and least for banana peels i.e. 6.4%. Second highest value lies within wheat straw (b and c) and that is 80%. Volatile matter of rice straw a, b and c are nearly equal that is 76%, 75%, and 74% respectively.

Highest ash content was showed in rice straw c i.e. 12% and lowest was found in banana peels that are 1.28%. The second highest value lies within rice straw a and b that is 10%. Ash content of wheat straw of all 3 sizes is 4%, 6%, and 8% respectively. 15% is the highest fixed carbon found in rice straw and 0.32% is the lowest fixed carbon found in the banana peel. Fixed carbon of wheat straw a, b, rice straw a, and c is 14%. In a research it was revealed that rice straw and grass clippings contain VCM 65.47% and 76.69% respectively [13].

According to Tock[14], for wheat straw values of volatile matter, ash content, and fixed carbon is 71.78%, 9.27% and 18.95% respectively. And for rice straw values of VCM, ash content, and fixed carbon are 77.30%, 3.40% and 18.30% respectively.

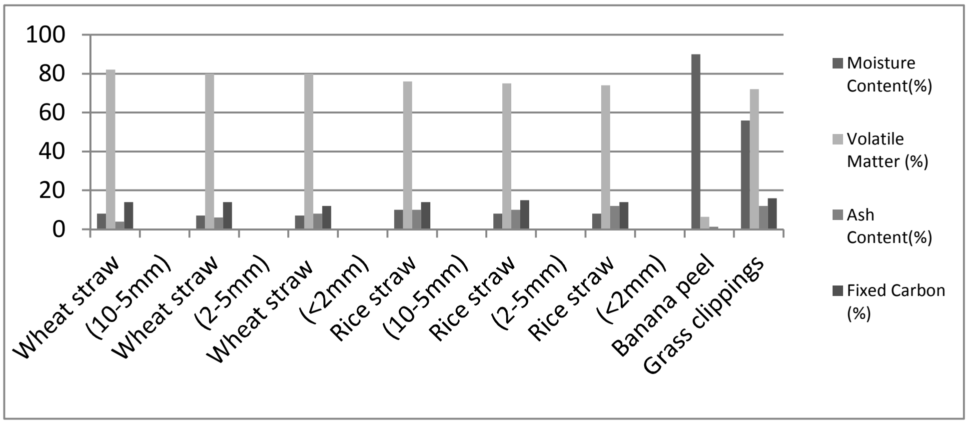

Fig. 1. Moisture content and adjusted values of VCM, Ash content, and fixed carbon

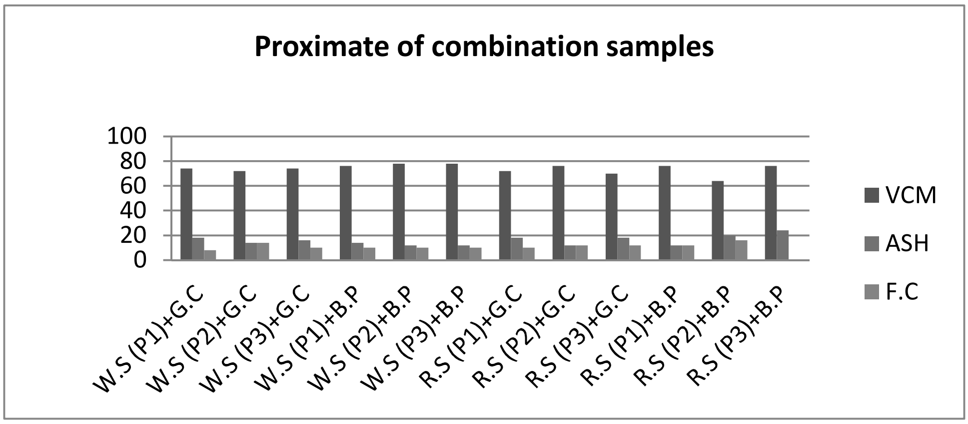

Fig. 2. Values of VCM, Ash content and Fixed carbon of samples of different combinations

Fig 2 shows that Highest Volatilematter was found high in two samples i.e. W.S (P_2) +B.P and W.S (P_3)+B.P that are 78%. Lowest volatile matter was of the sample R.S (P_2) +B.P that is 64%. 24% is the highest ash content found in the sample of R.S (P_3)+B.P and 12% is the lowest value of ash content found in samples W.S (P_2)+B.P, W.S (P_3)+B.P, R.S (P_2)+G.C and R.S (P_1)+B.P.Highest fixed carbon is 16% which was found in sample R.S (P_2) +B.P and lowest fixed carbon value is 0% which was found in sample R.S (P_3) +B.P.

3.2 Energy content

The calorific value of individual components and combination of these samples of different particle sizes with binders was conducted with the help of bomb calorimeter. Lowest calorific value is 14.01 MJ/Kg which is portrayed by three samples i.e. banana peels, rice straw of particle size (5-10mm) and rice straw of particle size (2-5mm) combined with grass clippings. Among all samples highest energy content is portrayed by a sample of wheat straw of particle size (2-5mm) combined with grass clippings that 43.20MJ/Kg. Second highest is showed by wheat straw of (5-10mm) with banana peels and that is 37.50MJ/Kg. Third highest value is 36.30 MJ/Kg which is portrayed by rice straw of (2-5mm) particle size combined with banana peels. 4th highest value of wheat straw of particle size (5-10mm) combined with grass clippings that are 34MJ/Kg.

Table 1. Calorific value of individual samples as well as of combinations

Biomass	Binders	Particle size	Calorific value MJ/Kg
No biomass	No binder	No Particle Size	.[a]
		(10-5mm)	.[a]
		(2-5mm)	.[a]
		(<2mm)	.[a]
	Grass clippings	No Particle Size	16.020
		(10-5mm)	.[a]
		(2-5mm)	.[a]
		(<2mm)	.[a]
	Banana peels	No Particle Size	14.010
		(10-5mm)	.[a]
		(2-5mm)	.[a]
		(<2mm)	.[a]
Wheat straw	No binder	No Particle Size	.[a]
		(10-5mm)	15.100
		(2-5mm)	14.990
		(<2mm)	20.000
	Grass clippings	No Particle Size	.[a]
		(10-5mm)	34.000
		(2-5mm)	43.200
		(<2mm)	33.900
	Banana peels	No Particle Size	.[a]
		(10-5mm)	37.500
		(2-5mm)	15.760
		(<2mm)	14.340
Rice straw	No binder	No Particle Size	.[a]
		(10-5mm)	14.010
		(2-5mm)	14.300
		(<2mm)	26.020
	Grass clippings	No Particle Size	.[a]
		(10-5mm)	15.890
		(2-5mm)	14.010
		(<2mm)	24.500
	Banana peels	No Particle Size	.[a]
		(10-5mm)	25.560
		(2-5mm)	36.300
		(<2mm)	24.000

3.3 Heavy metal analysis

Fig. 3 shows the concentration of heavy metals in different samples.The standard value of As for RDF is 10 mg/g. Arsenic concentration in samples of wheat straw and rice straw is beyond the limit that was 215 and 100mg/g respectively. On the other hand concentration of arsenic in grass clipping and in banana peelings is BDL. The standard value of Cr for RDF is 200mg/g. And its concentration in every sample was below the standard which was 148.75, 4.5, BDL and 3.1 for wheat straw, rice straw, banana peelings and grass clippings respectively.

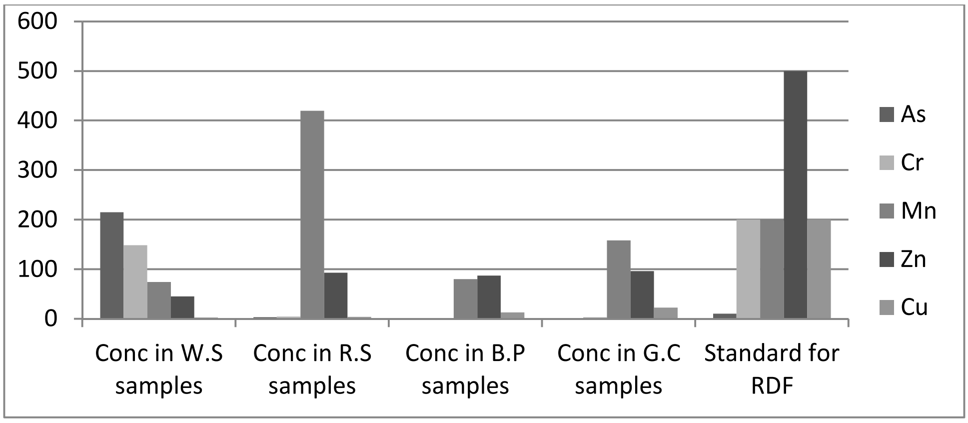

Fig. 3. Comparison of heavy metals concentration in samples with standard for RDF

The standard value of Mn for RDF is 200mg/g. In the sample of rice straw, Mn concentration was found above the limit which is 419.4mg/g. And in samples of wheat straw, banana peelings and grass clippings Mn concentration were 74.25, 79.8 and 158mg/g respectively. Standard of Zn concentration for RDF is 500mg/g. And in all samples, Zn concentration was found within the limit. The 45, 92.8, 87 and 96mg/g was concentration values found in samples wheat straw, rice straw, banana peels and grass clippings respectively. The standard value of Cu for RDF is 200mg/g. In samples of wheat straw, rice straw, banana peels, and grass clippings Cu concentration was 2.75, 3.8, 12.6 and 22.4 respectively.

3.4 Influence of combustible characteristics on calorific value of feedstock

Pearson’s correlation was applied to find the relation of VCM, ash content and fixed carbon with calorific value. It is portrayed by fig. 4 and fig. 6 that there is a strong negative correlation among calorific value and VCM and b/w fixed carbon and calorific value. It demonstrated that if one variable is increasing other will be decreased. Fig. 5 shows that there is a strong positive correlation between ash content and fixed carbon. It means if one parameter is increasing there will be an increase in other too.

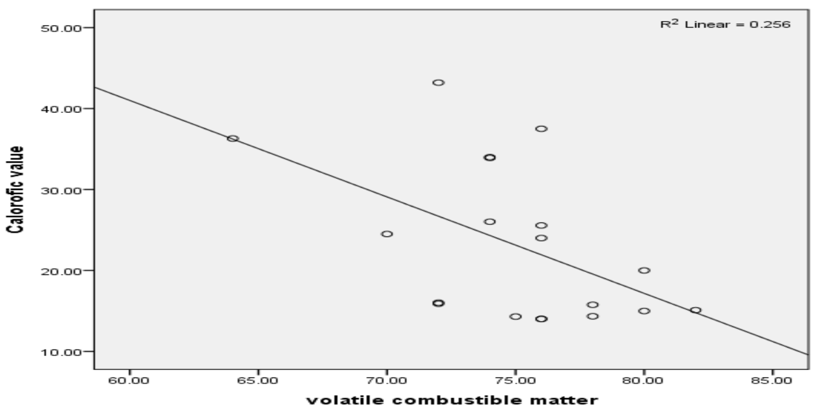

Fig. 4. Relationship between volatile combustible matter and calorific value

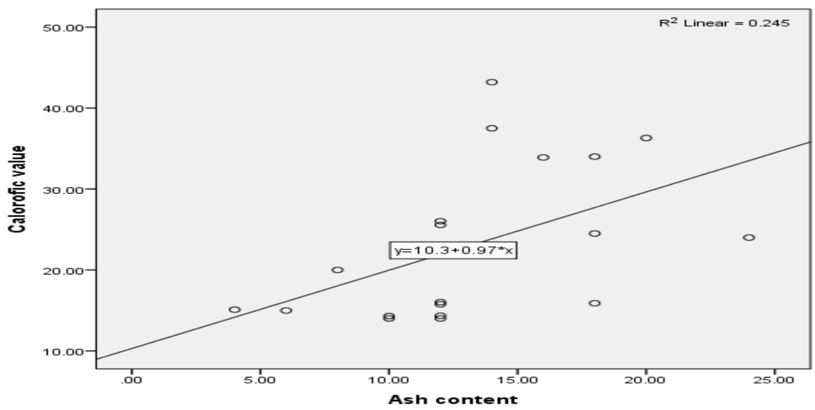

Fig.5. Relationship between ash content and calorific value

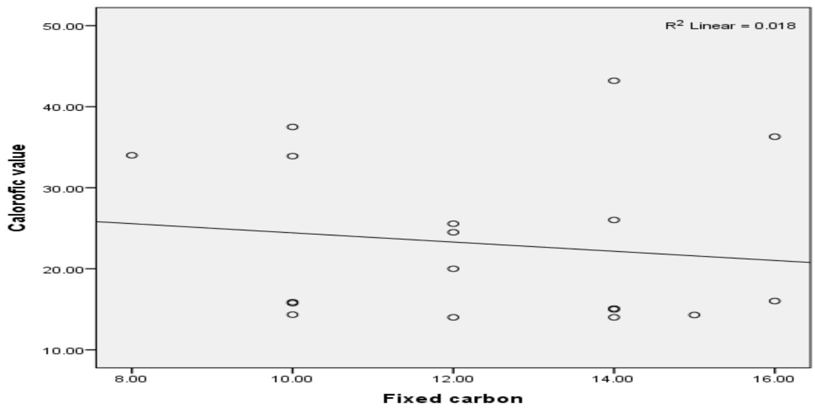

Fig.6. Relationship between fixed carbon and calorific value

3.5 Effect of biomass, binders and particle size on Calorific value of feedstock

To determine how calorific value is changing with different binders, in different combinations of the biomass of different particle size with binders, 3-way ANNOVA is applied on the data set.

It is showed by this test that significance level of biomass* binders*P.S is .000 which is less than .05. It satisfies the ($p < .05$) that means biomass, binders, and particle size strongly influence the calorific value of feedstock. With the changing of particle size, same biomass can show different energy content. With the different combination of binders with biomass of different sizes, energy content will vary. Hence there is significant three-way biomass*binders*P.S interaction effect on the calorific value.

Table 2. Effect of biomass, binders and particle size on calorific value of RDF

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Corrected Model	5196.446[a]	19	273.497	436.172	.000
Intercept	22949.536	1	22949.536	36599.796	.000
Biomass	194.940	1	194.940	310.889	.000
Binders	1049.223	2	524.612	836.648	.000
P.S	5.063	2	2.532	4.037	.025
Biomass * Binders	1588.208	2	794.104	1266.432	.000
Biomass * P.S	353.247	2	176.623	281.678	.000
Binders * P.S	801.741	4	200.435	319.653	.000
Biomass * Binders * P.S	809.701	4	202.425	322.827	.000
Error	25.082	40	.627		
Total	36058.622	60			
Corrected Total	5221.528	59			

3.6 FTIR Analysis

The FTIR functional groups and the indicated compounds of the pyrolysis oil were determined by the absorption frequency spectra. The functional groups of the pyrolysis oil of the five samples of wheat and rice straw were determined by the absorption frequency spectra. The possible class of compounds is presented in Table 3.3. The alkane group is indicated by the absorbance peak of C-H vibrations (stretching) between 2870 and 2990 $cm^{-1,}$ C-H stretching between 2950 and 2850cm^{-1} and C-H bending between 2890 and 2850 cm^{-1}. The absorbance peaks between 1460 and 1450 cm^{-1}, 1440 and 1430 cm^{-1} represented the C-C stretching indicating the presence of aromatics. The frequency range of 1520 and 1490 cm^{-1} presents nitro compounds of N-O asymmetric stretching. The absorbance peak between 1390 and 1360 $cm^{-1,}$ 1370-1320cm^{-1}, 1565-1560cm^{-1} and between1565-1550cm^{-1} represented the C=O stretching, indicating the presence of carboxylic acids. The frequency range of 16600 and 1650 cm^{-1} presents amides and carboxylic acids of C=O stretching. The 1 alkyl halides group is indicated by the absorbance peak of C-H bending between 1280 and 1260 cm^{-1}.The frequency range of 1050 and 1000 cm^{-1} presents alcohols, carboxylic acids, esters and ethers of C-O stretching. The absorbance peak between 705 and 690 $cm^{-1}$and 760 and 735 cm^{-1}represented the C-H indicating the presence of aromatics. The frequency range of 1740 and 1710 cm^{-1} presents esters, aldehydes and ketones of C=O group. The frequency range of 2250 and 2210 cm^{-1} presents alkynes of C≡C group. The peak between 1660 and 1640 cm^{-1} are indication of the presence of carboxylic acids and amides due to C=O stretching.

Table 3. The FTIR functional groups and the indicated compounds of the wheat straw and rice straw pyrolysis oil

Observed wave no in (cm^{-1})	Frequency range (cm^{-1})	Group	Class of compound
2919	2990-2870	C-H Stretching	Alkanes
2851	2890-2850	C-H Stretching	Alkanes
1459	1460-1450	C-C stretching	Aromatics
1376	1390-1360	C=O	Carboxylic acids
1439	1440-1430	C-C stretching	Aromatics
1508	1520-1490	N-O asymmetric stretching	Nitro compounds
1655	1660-1650	C=O	Amide , carboxylic acids
1561	1565-1560	C=O	Carboxylic acids
1270	1280-1260	C-H	Alkyl halides
1034	1050-1000	C-O stretching	Alcohols, carboxylic acids, esters, ethers
695	705-690	C-H	Aromatics
746	760-735	C-H	Aromatics
2851	2890-2850	C-H stretching	Alkanes
2921	2950-2890	C-H stretching	Alkenes
1735	1740-1710	C=O	Esters, Aldehydes, Ketones
1655	1660-1640	C=O	Amide , carboxylic acids
1560	1565-1550	C=O	Carboxylic acids
1458	1480-1450	C-C stretching	Aromatics
1341	1370-1320	C=O	Carboxylic acid
2222	2250-2210	C ≡C	Alkynes

4. Conclusion

The current study concluded that rice straw of particle size (<2mm) portrays higher energy content of 26.02MJ/Kg. And after the addition of binders, calorific value is enhanced and maximum calorific value is 43.20MJ/Kg contained by the sample of wheat straw of particle size (2-5mm) combined with grass clippings. The binders used have easy access and their production is abundant in Pakistan which is why they can be utilized as potential binders. Grass clipping shows the good potential and the combination of grass clippings with wheat straw give the best results because from the top 5 highest calorific values 4 is portrayed by samples of a wheat straw combined with grass clippings. This type of fuel will require less cost on transportation and labor and can fulfil the demand of industries, however it requires energy for crushing and grinding process but appropriate RDF production can compensate it easily.

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