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Enhancement of Coal Quality by using Bioextracts of *Carissa carandas* Fruits

ULAVAPALLI GANGADHARA REDDY[1,2], KOYILAPU RAMBABU[1*], GOPI REDDY VENKATA SUBBA REDDY[3] and DUVVURI SREEDHAR REDDY[2]

[1]Department of Chemistry, Koneru Lakshmaih Education Foundation, Green fields, Vaddeswaram, 522502, Andhra Pradesh, India.
[2]Rayalaseema Thermal Power Project, Kadapa 516380, Andhra Pradesh, India.
[3]Department of Engineering Chemistry, JNTU College of Engineering, Anantapur constituent Unit of J .N. T. University Anantapur, Ananthapuramu 515 002, Andhra Pradesh, India.
*Corresponding author E-mail: drkrambabu@kluniversity.in, rambabukoyilapu@gmail.com

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ABSTRACT

The major problem faced by coal fired power stations in India is high ash content. Commercially it is big loss to transport high ash content coal as leads to higher specific coal consumption in addition to environmental issues like suspended particulate matter. This research study aims to develop a chemical method using weak organic acids from plant extracts to reduce ash content in the coal. In this context *Carissa carandas* fruit extract is used to treat with coal samples at optimum conditions and found this bio extract effectively leaches ash from coals. This treatment process is applied to different coals used for combustion at Rayalaseema thermal power project, Kadapa, India and found 6 to 7% reduction in ash content and increased gross calorific value of coal by more than 600 units. These findings are proved in proximate and ultimate coal analysis and supported by IR and XRD spectral studies. By using the optimized conditions of the laboratory scale, a prototype simulator is designed. This coal beneficiation method resulting in accomplishment of technical, environmental most importantly commercial benefits as cost of generation has reduced from Rs 2.66 to Rs 2.32 per unit of energy. This results in the total savings of approximately more than 178 crore per year in 600 MW unit alone, in an eco friendly manner.

Keywords: Plant extract, *Carissa carandas*, Coal quality enhancement, Power generation, Ash, Gross calorific value.

INTRODUCTION

Due to shifting of economy from primary sector (Agricultural sector) to industry and service sectors in the developing nations, the demand for electricity has been increased. As per the global power scenario, coal and oil are the major fuels empowering our economies[1]. As on May, 2023 current power generation capacity in India is 4,17,668MW[2] in which nearly 50% of installed capacity is based on coal only and hence it is playing significant role in fulfilling the energy needs of our society. Although contribution from renewable energy sources increasing year by year, still power sector largely depends on coal for power generation due to its reliability to generate maximum power whereas solar and wind power generation largely based on climatic conditions. As per the data mentioned in the reference US-DOE[3], "coal projected to retain the largest market share of electricity generation". Decayed vegetable organic matter under earth crust subjected to chemical, physical and biological changes at high pressure and temperature, over millions of years leads to formation of coal. Depending upon the maturity, various quality coals may be listed as Peat, Lignite, Bituminous and Anthracite coals. Generally, Indian boilers are designed for sub bituminous coals that is life of boilers metallurgy is well suited for these coals. Coal mainly has four components viz., moisture, ash, volatile matter and fixed carbon content. During the formation of coal, sedimentary rocks present under earth crust are entrapped into the coal matrix, this mineral matter is the ash content of the coal that is un burnt rocky material which is left behind after the combustion of coal is treated as ash. Higher hydrocarbons constitute volatile matter. Fixed carbon present in the coal is the principle source of energy during combustion process where as moisture present in the coal results in loss of net available energy during combustion of coal.

Thermal stations situated in Andhra Pradesh, India receive Bituminous and Sub Bituminous coals from mines situated in other states ; Telangana and Orissa of India .These mines include Manuguru, Sattupally, Yellandu, Rudrampur, Tadikelapudi, Manchiryal and Sri Ramakrishnapur, Anantha, Jagannadha, Bhuvaneswari, etc., Depending upon the coal mine, mineral content that is ash% of these domestic coals is ranging from 38 to 62%. Ash content of more than 45% leading to the increase in the specific coal consumption that is coal consumed per unit power generation increases due to this high ash content ,further problems arises due to ash evacuation and pollution issues.

In the field of coal beneficiation, different physical methods are implemented for coal quality enhancement[4-7]. In order to understand the effectiveness of process of beneficiation, it is necessary to aware of various technologies of beneficiation. In general, coal contains organic and inorganic matter. Organic matter mainly composed of fixed carbon and volatile matter where as inorganic matter is the mineral matter composed of Silica, Alumina etc., In the process of beneficiation, efforts are generally oriented to reduce the mineral components from untreated (raw) coals and thereby, enhancing the quality of coal used for combustion. In the physical methods of beneficiation, separation task first and foremost based on exploiting the differences between biotic components in coal and non-biotic components in ash which are present in the raw coal[8]. Physical methods of beneficiation include sort by size and gravity-based separation, froth flotation and flit jig washing. Consideration in the difference of density between ash components and carbon components of the coal is the main factor in washeries used for coal beneficiation. In Jig washing[9-11] dense particles are set apart in water flit jig portion by pulsing pneumatical or hydrodynamical ways. Separation of the coal, based on mass/volume of the particles is achieved by the process of the jigging proposition and thus, the removal gauged materials from the coal is possible. Froth flotation[12-16] technology of beneficiation consists of bubbling of air through the coal immersed in water to separate the coal particles as they are hydrophobic in nature. Ash reduction methodologies that is beneficiation of coal based on the usage of pure chemicals depends upon ability of chemical to dissolve the mineral matter in the coal and several advanced chemical leaching techniques are available[17]. For this purpose, various acids, bases, their combinations and oxidising agents are used. The acids used are: H_2SO_4, HCl, HF, HNO_3 and acetic acid[18-24] and bases: KOH and NaOH[25-26]. Leaching of coals with acidic environment and followed by basic culture or vise versa are also examined as like as different combinations (HF-HNO_3; NaOH-HCl etc) have been used[27-28]. In recent studies catalytic oxidation methods[29] are also used. These pure chemical methods of beneficiation have more limitations for practical use due to hazardous nature and corrosive characteristics. Hence green methods using phyto extracts of various plants which contains weak organic acids and poly phenyl compounds for the reduction of ash content from the untreated coal is gaining the significance and one such successful effort is published recently[30]. These bio extracts contain complexing agents that forms coordinating chelating compounds with metals present in the untreated coal at the optimum methodological requirements. The objective of the present research study is to enhance the quality of coal by reducing ash content in the coal. To achieve this objective, high ash coals are treated with bio extracts derived from fruits of *Carissa carandas* plant.

METHODS AND MATERIALS

Rayalaseema Thermal power project (RTPP)

This thermal power generating station is located on the bank of river Penna at Muddanur near Kadapa, Andhra Pradesh, India. RTPP has 5 number of 210MW capacity and one unit of 600MW. 600MW unit is functioning since 2016 and boiler of this unit designed for 4400 Kcal/Kg gross calorific value. Beneficiation of coals used for this unit are discussed in this paper. RTPP consumes the coal received from Sattupally, Rudrampur, Tadikelapudi, Manugur and Srirampur mines pertaining to coal company Singareni Calories and Company Limited (SCCL, in the state of Telangana, India) and from Jagannatha, Anantha, Bharatpur, Balaram mines of Talcher (In the state of Orissa, India). The quality of coal from one mine significantly differs from other mine, ash content of these coals are in the range of 38 to 62%. But the boiler of 600MWs Unit is designed for Ash 34%; gross calorific value 4400K Cal/Kg; Inherent Moisture 5%; Volatile matter 28.3%. At present the raw coals received to thermal station from various mines having high ash content are subjected to combustion process in the boiler without any effort for improving the quality of coal. This led to generation of more ash and consequently more specific coal consumption coupled with ash disposal problems, air pollution, hence attaining of designed gross calorific value of the boiler by regulating ash content in the coal is of great importance to maximize generation and to minimize losses apart from protecting the environment. Coals of Sattupally, Rudrampur and Jagannath sources are used in this experiment.

Coal samples collection

Representative coal samples pertaining to the sources of Sattupally, Rudrampur and Jagannath mines were collected by standard rake sampling procedure explained in the Indian Standard 436: 2020. As per this standard procedure 15 coal wagons were randomly selected among 59 wagons in a coal rake and from each wagon approximately 25 Kg of coal sample is collected, this procedure resulted in total of 375 kg of coal sample with 70 increments. By proper mixing of entire 375 kg of coal sample and by following method of coning and quartering this is finally reduced to 1 kg of coal sample. Same procedure is applied for all the three sources of coal that is Sattupally, Rudrampur and Jagannath coals. Then these true representative samples were crushed to fine powder (212-micron sizes) by using pulverisers. The whole ideology is to collect a representative coal sample in the pulverized form such that its reaction with weak organic acids and poly phenols of bioextract is effective.

Biomaterials

Carissa carandas is a Apocynaceae family which native to India and grown in various places in the world and plant extracts of *Carissa carandas* have been used as medicine for traditional disease treatments as well as found as antioxidative property. *Carissa carandas* fruits extract juice is used as complexing agent in this experiment. Its pH is approximately 2.8 hence its juice is sour to taste. This bio extract consisting of polyphenols and weak organic acids having ability to complex with Iron and Aluminum compounds of coal and acidic nature of the juice, have enlightened our thoughts to use this biomaterial for beneficiation of coal. Fruits of *Carissa carandas* plant were collected and properly cleansed with distilled water and these fruits are crushed to semisolid paste. 100 g of this paste was properly mixed with 500 mL of distilled water, then this mixture was taken in a beaker and subjected to heating for one hour at the temperature 60^{0}C with continuous stirring. Then mixture was brought to room temperature by cooling and then filtered. The filtrate so obtained is the bio extract and it used in the treatment process with pulverized coal samples. No separate organic solvent is used for extraction.

Treatment of raw (untreated) coal with the bio extract and method of isolating ash from coal

10 g raw coal sample of Sattupally source collected as per the procedure explained in section 2.2, was taken in a 250 mL round bottom flask and 25 mL of bio extract is mixed. Round bottom flask fitted with condenser for circulation of water. Then the mixture in the flask was heated for a span of 2 h at a temperature of 60^{0}C. Then heating was stopped, temperature of reaction medium was reduced to 28^{0}C and washed with distilled water several times for ensuring neutrality and then filtered. This filtration was carried out to isolate some of the

ash components in the form of filtrate. Then filtrate is separated and precipitate part is the enriched (beneficiated) coal. This filtrate was found to contains ash components like Al_2O_3, FeO, CaO, MgO etc., as bio extract is successful in leaching out these components of ash present in the coal which results in reduction in the ash content in the coal. Then drying of enriched coal was carried by using Oven operating at 108^{0}C for 1 hour. This dried enriched coal was subjected to proximate,ultimate analysis, XRD and IR studies.

The above methodology was applied Rudrampur and Jagannath coals also that is total of three types of subbituminous coals are used in this research investigation. Further series of same experiments were carried with varying volumes of bio extract 50, 75 and 100 mL for all the three sources of coal and precipitates of beneficiated coals were taken to chemical laboratory for characterization and proved reduction in the ash content and increase in gross calorific value of coals. Further it is observed that with increase in the concentration of bio extract, PH values of filtrate were increased due to effective leaching of alkali and alkaline metal oxides present in the coal by the bio extract.

The various stage of this coal beneficiation process was presented in Figure1.

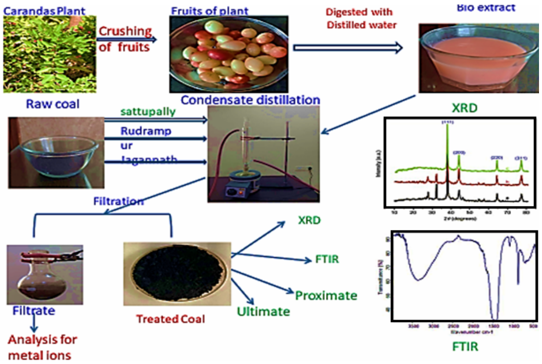

Fig. 1. various stages of coal beneficiation process and characterization

Characterization

Proximate and ultimate analysis were carried to all coal samples that is both for raw(untreated) and treated coals pertaining to Sattupally, Rudrampur and Jagannath mines. Proximate analysis gives the results of ash, volatile matter, inherent moisture and fixed carbon. Ultimate analysis gives the elemental composition that is the percentage of Carbon, Hydrogen, Nitrogen and Sulphur. Further these coal samples were also characterized with the help of XRD and FTIR spectral investigations. Ash analysis is also carried out to confirm the reduction of mineral oxides in treated coals.

Conventional parameters

Proximate analysis

A) Ash

Ash in treated and untreated coals is determined by using the procedure mentioned in Indian Standard 1350 Part 1. Muffle furnace is the instrument used for the determination of ash percentage in the coal. Procedure consists of placing the 1 g of air dried fine powdered (212 microns) coal sample in crucible made up of Silica and this crucible is kept for heating in Muffle furnace at temperature 815^{o}C for one hour. Then heating is stopped, later the crucible was cooled to temperature of approximately 28^{o}C and the unburnt rock material left in the crucible was expressed as percentage of mineral content that is ash. Ash content of raw and treated coals pertaining to the mines Sattupally, Rudrampur and Jagannath were found by using Muffle furnace and the results were tabulated (Table1). The exact mineral composition of ash present in the coals of Sattupally, Rudrampur and Jagannath coals for both raw and treated coals were analyzed for their compositions and were shown in the Table 2.

B) Gross Caloric Value (GCV)

The energy content produced from coal that is gross calorific value (GCV) was measured as per clauses mentioned in the Indian standard 1350: Part II, Reaffirmed 2020. GCV is the amount of heat produced in Kcal upon complete combustion of unit quantity that is one Kg of coal, GCV generally expressed as Kcal/Kg. Bomb calorimeter is the instrument used for determination of GCV. One gram of pulverized coal sample with particle size 212 microns is air dried and pressed into the pellet form and kept in the bomb, Oxygen was used for combustion of sample and the value of GCV was recorded in Leco Bomb Calorimeter. It is observed that GCV calculated from ash and inherent moisture values is also in good agreement with GCV analyzed in

Bomb calorimeter. GCV values of coals before and after treatment are tabulated in Table 1.

C) Inherent Moisture

The moisture that is present in the pores of the coal in the coal mine itself is referred as inherent moisture that is it is the moisture left in the coal after removal of free surface moisture. It is determined by the procedure mentioned in the Part 1 of Indian standard 1350: 2020. Hot Air Oven is used for determination of Inherent Moisture. 1 g of pulverized coal sample of size 212 microns was spread in a crucible of silica and kept in Oven operating at 108°C for one hour. This results in the removal of inherent moisture present in the coal hence reduction in the mass of coal sample, expressed as percentage was taken as inherent moisture. Inherent moistures of untreated and enriched coals were determined and tabulated in Table 1.

D) Volatile Matter (VM)

Hydrocarbon content present in the coal is the main contributory factor for volatile matter. It was estimated as per detailed methodology mentioned in Indian Standard 1350: Reaffirmed 2019. One gram of pulverised coal sample containing particles of size 212 microns was kept in a crucible made up of silica and introduced in a Muffle furnace operating at 900°C for 7 min, with proper precautions to avoid entry of external air. Then sample temperature was brought to laboratory conditions and the mass of coal sample was noted. After subtracting inherent moisture, the percentage of volatile matter was calculated. Volatile matter of un treated and enriched coals were estimated and shown Table 1.

E) Fixed Carbon

By using formula Fixed carbon=100-(Ash+Inherant Moisture+Volatile Matter), fixed carbon content value of raw coals pertaining to Sattupally, Rudrampur and Jagannath and treated coals were calculated and these results were shown in Table1.

Ultimate Analysis

By using CHNS analyser the elemental proportion of Carbon, Nitrogen, Hydrogen and Sulphur were analysed in the samples coal, before and after treatment, as per the Indian standard 1350: Part 3 Reaffirmed 2020. The results were shown in Table 3.

XRD spectral analysis

XRD spectral studies were carried to both raw and treated coal samples by using PAN-X-ray diffract meter inbuilt with Cu K source at 1.54A°. The spectral pertaining to these investigations is presented in Figure 2(A); (B) and (C).

FTIR Analysis

The infrared spectral studies carried for both raw and treated coal samples with BRUKER ALFA FTIR spectrophotometer by using KBr pellet method in the wave number range 4000–400 cm^{-1}. This spectral data was presented in Figures 3.

RESULTS AND DISCUSSION

Coal quality assessment

Proximate Analysis

The raw coal of Sattupally, Rudrampur and Jagannath coals and treated coals were subjected to proximate analysis. The proximate analysis results are shown in Table 1. From Table 1, it is inferred that with increase in the concentration of bio extract from 25 mL to 100 mL, the content of ash was reduced from 51.90% to 45.62% in the case of Sattupally coal; 44.26% to 38.21% in the case of Rudrampur coal and 39.81% to 33.40% with Jagannath coal. As the reduction in ash content is noticed in various sources of coal, the objective of this research study is achieved. The reduction in the ash content in the coal is due to the fact that bio extract which is used in this treatment contains poly phenols and weak organic acids having ability to complex with Alumina, Iron pyrets, alkali and alkaline metal oxides present in the coal (Some of the ash components) and hence percentage of ash in various coals is decreased. This fact is further supported by analysis of ash in untreated and beneficiated coals presented in Table 2A and 2B.

Table1: Proximate analysis of various coal samples before and after treatment

Source	Before digestion	Digestion with 25 mL Plant Extract	Digestion with 50 mL	Digestion with 75 mL	Digestion with 100 mL
			*(A) Ash Content, %		
Satupally	51.90	50.02	48.91	46.98	45.62
Rudrampur	44.26	43.12	42.02	40.16	38.21
Jagannath	39.81	38.42	36.75	35.21	33.40
			*(B) Gross Calorific Value, KCal/Kg		
Satupally	3004	3210	3344	3569	3681
Rudrampur	3620	3765	3875	4110	4321
Jagannath	3920	4082	4269	4443	4642
			*(C) Inherent Moisture, %		
Satupally	4.1	3.9	3.7	3.4	3.3
Rudrampur	4.6	4.4	4.3	4.1	3.7
Jagannath	5.4	5.2	5.0	4.8	4.6
			*(D) Volatile Matter, %		
Satupally	22.4	22.3	21.8	21.7	21.5
Rudrampur	23.2	23.1	23.1	22.9	22.9
Jagannath	27.5	27.4	27.4	27.2	27.1
			*(E) Fixed Carbon, %		
Satupally	21.60	23.78	25.59	27.92	29.58
Rudrampur	27.94	29.38	30.58	32.84	35.19
Jagannath	27.29	28.98	30.85	32.79	34.90

*The values are the average of 5 estimations: S.D:=/-0.01

Ash Analysis

Composition of ash for coal samples pertaining to the sources of Rudrampur, Sattupally and Jagannath were assessed for both raw and treated coals and results are shown in Table 2. The various sedimentary rocks like lime stone, sand stone, bauxite, dolomite are present under earth crust and entrapped in the coal matrix during the formation of coal. During the combustion of coal these sedimentary rocks remain as unburnt and constitutes ash. This is mixture of various elemental metal oxides. The metal ions may also arise from entrapped inorganic mineral content during lifetime of the plant material that was later decayed and converted as coal.

Table 2(A): The composition of Ash obtained from various sources of untreated coal

	Analysis of Ashes (in %)							
Sources	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	Na_2O	K_2O
Satupally	62.5	25.9	2.2	1.02	1.12	3.88	0.21	0.12
Rudrampur	62.1	24.7	2.2	1.03	1.11	3.08	0.31	0.11
Jagannath-MCL	62.1	23.8	2.1	1.60	3.1	2.9	0.32	0.11

Table 2B: Analysis of Ashes obtained from treated coals

	(i): Analysis of Ashes (in %)* after treatment							
Sources	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	Na_2O	K_2O
Satupally	70.6	20.5	1.39	0.74	0.42	3.82	0.11	0.06
Rudrampur	71.2	18.7	1.30	0.61	0.5	3.12	0.16	0.05
Jagannath-MCL	72.3	16.9	1.10	0.98	1.0	2.88	0.15	0.04

From Table 2 (A) it is evident that *Silica* value of raw coals is varying between 62.5 to 62.1%, Alumina 25.9 to 23.8: CaO 2.2 to 2.1%: MgO 1.60 to 1.02: Fe_2O_3 3.10 to 1.11:TiO_2 3.88 to 2.90: Na_2O 0.32 to 0.21and K_2O from 0.12 to 0.10. Comparative study of ash analysis results of untreated and treated coals presented in Tables 2(A) and 2(B) clearly indicates that the percentages of Alumina (Al_2O_3) is decreased upto 21-28%: Iron oxide: 62-68%: CaO:39: MgO:30%: Na_2O:50% K_2O:50%. Hence it is inferred that that plant extract is useful in removing the some of the metal oxides (ash components) from the coal. The reduction in the contents of Alumina, Iron, Calcium, Magnesium Sodium and Potassium oxides in the ash may be due to reaction of metal ions of the coal with the poly phenyl compounds and other week organic acids present in the plant bio extract. By carrying analysis of filtrate metal ions Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} are identified. These experimental results supporting the fact that the plant extract derived from Carandas plant is effective for enhancement of coal quality by reducing the ash content in the coals, and the same conceptual observations were noticed for all three different sources of coal.

Gross Calorific value (GCV)

Energy content that is GCV of coals of Suturally, Rudrampur and Jagannath mines before and after treatment were recorded by using bomb calorimeter and shown in the Table 1(B). GCV value represents the amount of heat produced from coal upon complete combustion of one kilogram of coal and this is very essential parameter in assessing the energy content of coal. The designed value of GCV for 600 MW unit of Rayalaseema Thermal Power Project is 4400 kcal/Kg and for remaining 5 units the value is 3686 Kcal/Kg. From the data presented in above table it is inferred that with increase in the volume of plant extract, GCV value were also increased:For Sattupally coal GCV increase from 3004 to 3681:Rudrampur 3620 to 4321 and Jagannath 3920 to 4642 in the units of Kcal/Kg. Gross calorific value of the coal is inversely proportional to inherent moisture and ash content of the coal. As bio extract is successful in leaching out the some of the ash components from the coal, this resulted in the increase in gross calorific value of the coal and hence objective of the present research investigation is achieved. These experimental observations suggest that it is possible to enrich the quality of raw coals to the required designed level of GCV by increasing the concentration of plant extract derived from Carandas plant and there by maximum power generation can be achieved with ideal combustion. Further as design parameters of the boiler are met with regards to volatile matter and fixed carbon, efficient combustion is possible in the thermal station hence specific coal consumption can be reduced and heat rate can be maintained properly with the optimum utilization of beneficiated coals and hence, the life of generating unit can be enhanced. This is one of the merits of this investigation.

Inherent moisture (IM)

The inherent moisture values of various raw coals and treated coals pertaining to Sattupally, Rudrampur and Jagannath mines were analyzed and shown in the Table 1(C), it is inferred from the analysis results that as the volume of plant extract is increased the IM is reduced slightly. Inherent Moisture leads to wastage of energy in the combustion process of coal in the form of latent heat.

Net Calorific Value of coal = Gross calorific value --latent heat

As inherent moisture decreases, net calorific value of coal increases. In thermal power generation any effort to reduce inherent moisture is very significant. The decrease in inherent moisture may be due to the fact that the said plant extract contains certain completing agents having ability in removing some of the moisture content present in the pores of coal which is contributing to Inherent Moisture. Further water of hydration ($Fe_2O_3.xH_2O$: $Al_2O_3.XH_2O$) which is associated with rocks (ash content) in the coal is also removed as bio extract is reducing the ash content. As inherent moisture is decreased the latent heat losses are reduced hence as fired (net) caloric values of the coal are increased. Reduction in ash content and associated inherent moisture also making contribution to enhanced gross calorific value of coal and hence objective of this research is successfully achieved.

Volatile Matter

The main contributory factors for volatile matter in the coal is Hydrocarbons and it represents the tendency of coal to catch the fire to initiate combustion process. If Volatile matter is less than the designed value then coal may not undergo efficient combustion which results in unburnt carbon after combustion on the other hand if volatile matter is more, coal may catch fire with high rate of oxidation and may undergo spontaneous combustion in the stockyard itself and/or at the mills of thermal power station, which may result in blasting of mills hence leads to wastage of huge quantity of coal. Designed value of volatile matter for efficient combustion is approximately 28% for 600MW unit of Rayalaseema project, India. The results of volatile mater obtained for raw and treated coals of Sattupally, Rudrampur and Jagannath mines were shown in the Table 1(D). It may be concluded that there is no significant change in volatile matter in this beneficiation process.

Fixed Carbon It is the main source for release of energy from coal.

$C+O_2 \rightarrow CO_2+93$ Kcal

Above equation indicates 12 g of carbon on firing with 32 g of oxygen can release 93 Kcal of heat energy. Fixed carbon values were calculated for Sattupally, Rudrampur and Jagannath Raw coals for treated coals based on Ash, Inherent Moisture and Volatile Matter values of respective coals and results are tabulated in Table 1(E). It is evident that with increase in the addition of volume of plant extract derived from carandas plant, the percentage of fixed carbon is increasing and hence energy content of the coal as represented by Gross Calorific Value of coal is also increased. In case of Sattupally coal FC increased from 21.6 to 29.58, Rudrampur from 27.94 to 35.19 and Jagannath from 27.29 to 34.9: This finding proves the successful beneficiation of coal by using bio extract of plant Carissa carandas fruits.

Elemental Analysis

Analysis for composition of various elements like Carbon, Hydrogen, Nitrogen and Sulphur present in raw and treated coals of Sattupally, Rudrampur and Jagannath coals was carried by using Elemental Analyzer (CHNS analyser) as per the Indian standard 1350. Part 3: Reaffirmed 2020. The values were shown in Table 3. As per the data presented in Table 3 it is evident that with increasing in the concentration of plant-extract derived from the fruits of Carandas plant, carbon percentage was increased hence the energy content in the coal as represented by gross calorific value also increased as discussed in the proximate analysis. Hydrogen and Oxygen percentages slightly decreased due to this treatment process as inherent moisture in coal was reduced as explained in the proximate analysis part. Another added advantage in this treatment is significant reduction in the percentage of Sulphur was observed for all beneficiated coals. Iron pyretes is the ore of Sulphur which is entrapped in the structure of coal, is the main source of sulphur oxide emissions during combustion of coal. As the coordinating ability of naturally occurring weak organic acidic compounds present in plant extract is capable of forming water soluble complexes with Fe^{3+} present in the coal, hence reduction in the content of Iron Sulphide (FeS) is observed and hence sulphur is reduced in treated coals. This fact is further proved in Infrared and XRD spectral studies. Coal with nil Sulphur or at least minimum content, is always suggestable to use in power generating stations due to the fact that during combustion of coal, Sulphur is converted to Sulphur oxides viz. SO_2 & SO_3 which are acidic in nature and they are responsible for acidic rains. As this treatment is reducing Sulphur content in the coal this methodology of coal beneficiation not only enhancing quality of coal but also protecting environment from acid rains.

Table 3: Elemental Analysis of various coal samples: before and after treatment:

Source	Before digestion	Digestion with 25 mL Plant Extract	Digestion with 50 mL	Digestion with 75 mL	Digestion with 100 mL
			*(A) Carbon in %		
Sattupally	30.12	34.21	36.98	39.20	42.3
Rudrampur	36.12	39.13	41.62	44.21	47.4
Jagannath	41.03	43.81	46.38	47.82	50.62
			*(B) Hydrogen in %		
Sattupally	3.16	3.15	3.13	3.12	3.11
Rudrampur	3.38	3.32	3.30	3.26	3.25
Jagannath	3.46	3.44	3.39	3.32	3.30
			*(C) Nitrogen in %		
Sattupally	0.81	0.80	0.82	0.83	0.83
Rudrampur	0.83	0.82	0.85	0.84	0.87
Jagannath	0.86	0.85	0.85	0.90	0.85
			*(D) Sulphur in %		
Sattupally	0.43	0.40	0.38	0.36	0.35
Rudrampur	0.44	0.42	0.41	0.38	0.33
Jagannath	0.48	0.46	0.43	0.41	0.39
			*(E) Oxygen in %		
Sattupally	10.28	10.24	10.03	9.98	9.71
Rudrampur	11.34	11.21	10.28	10.12	9.97
Jagannath	12.05	11.98	11.18	10.92	10.84

*The values are the average of 5 estimations: S.D: +/-0.10

Characterization

Powdered diffraction Analysis

XRD spectra of Sattupally untreated and treated coal were presented in Fig. 2(A), (B) & (C). The XRD peaks pertaining to Sattupally raw coal noticed at 2 values are: sharp peaks at 12.450 and 20.450 pertaining to Kaolinite; very strong sharp peak at 26.670 corresponds to quartz; small peaks at 42.50 and 54.970 corresponds to Iron Pyrites: and small peaks at 60.020 and 62.380 corresponds to Alumina.

- As the concentration of Bio-extract is increased, peaks pertaining to Alumina at 60.02 and 62.38 are decreased in intensities
- Peaks corresponding to Iron Pyrites at 42.5 is very low intensified in treated coal with 100 mL Bio-extract.
- There are no noticeable changes on the position and intensities of Quartz and Kaolinite.

The below observations supporting the fact that bio-extract is successful in leaching Iron and Aluminum to some extent. In general Silica, Alumina, Iron compounds and alkali and alkaline metal oxides are the components of ash.

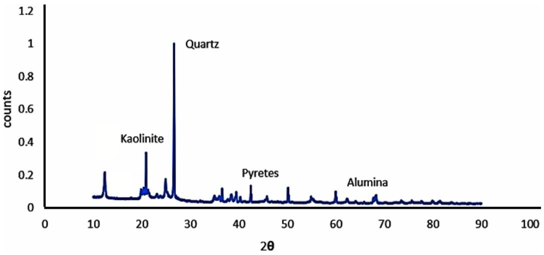

Fig. 2(A). XRD of raw coal from Sattupally

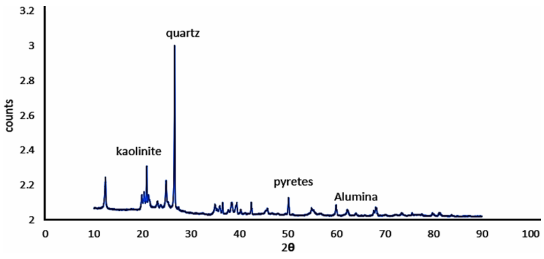

Fig. 2(B). XRD of treated Sattupally coal with 50 mL of bio extract

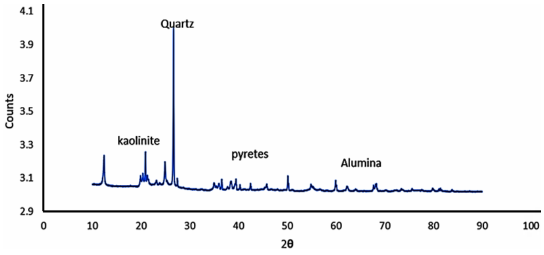

Fig. 2(C). XRD of treated Sattupally coal 100 mL of Bio-extract

Among all these components Silica, Alumina and Iron components are major components. Demineralization observed in this research study supported by decrease in the intensities of peaks in diffraction patterns from raw coal to conditioned coals. The presence of weak organic acids and poly phenyl compounds in bio extract of carandas fruits reacted with metal ions present in the coal which were formed water solubilized metal complexes. With increasing the concentration of bio extract, the diffraction patterns of pyretes and Alumina were low intensified which is supporting the fact that this bio extract is efficient for beneficiation of coals.

Spectroscopic confirmation (FTIR)

Conditioned coals and unconditioned coals were analyzed by FTIR. Spectral data analyzed for the confirmation of composition present in the unconditioned coal (sattupally) which was shown in Fig. 3. Free-OH stretching frequency observed in sattupally raw coal at: 3694.94 and 3621.66 cm^{-1}; alkyl '-CH_2– 'symmetric stretching at 2981.41 cm^{-1} of; alkenyl C=C=C or C=C= stretching at 2341 and 2358 cm^{-1}; carbonyl 'C=O–' sharp and high intense stretching at 1757.79 cm^{-1}; aromatic 'C=C' stretching at 1584.24 and 1371.14 cm^{-1}; silica'–Si-O-Si-(inner core bonds) 'or'-Si=O (silicate bond)' stretching observed at 1031.73 and 1005 cm^{-1} and alumina showed 'Al-O' stretching at 912.16 cm^{-1}; for the iron pyrites'–Fe=O'/Fe-O stretching showed at 795.56 cm^{-1}, and 777.2 cm^{-1}; Chalco pyrites shoed at 750.13 cm^{-1}. Bending vibrations of Fe_2O_3 at 479.28 cm^{-1}, 467.66 cm^{-1} and 458.97 cm^{-1}; -Mg-O/ CaO/TiO stretching at 439.69, 431.0, 421.37 and 409.79 cm^{-1}.

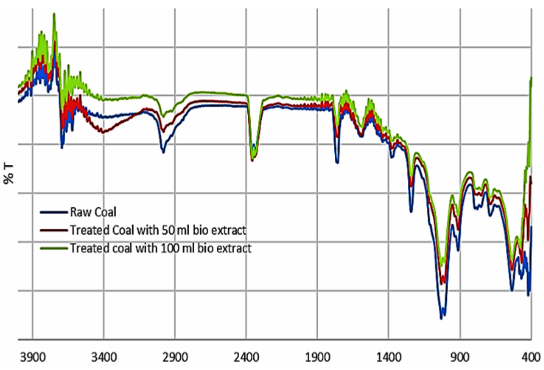

Fig. 3(A). FTIR spectrum of raw and treated of Sattupally coal

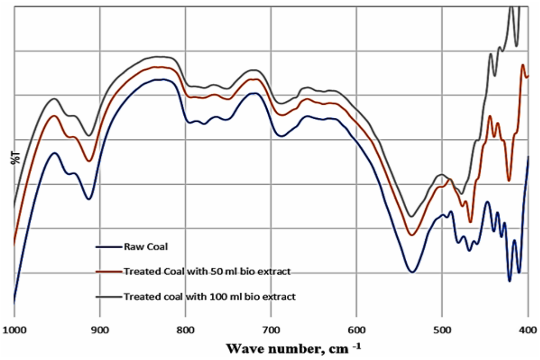

Fig. 3(B). FTIR spectrum of raw and treated of Sattupally coal

The significant differences observed in FTIR studies between the raw and treated (conditioned) coals are as follows:

Decrements in intensity of various functional group stretching frequencies in conditioned coal confirmed that removal of unwanted matters in the raw coal. Reduced intensity of '-C=O' and '-C-O' stretching frequency at 1757.79 cm^{-1} and 1242.89 cm^{-1} indicates decrease in volatile matter. There is no considerable changes in silica due to its inert in nature during the beneficiation process as no change is observed for the peaks noticed at 1031.73 and 1005 cm^{-1} (sharp, strong but overlapping) of '– Si-O-Si-' or '-Si=O' stretching. Due to the ability of complex formation with aluminum and weak acids, Alumina peak shifted to 912 cm^{-1} to 938 cm^{-1} with decrease in intensity in treated coals. Fe=O/Fe-S stretching peaks at 793.56, and 776.2 cm^{-1} peaks were decreased in intensity in conditioned coals due to reduction in Sulphur content. In the treated coal 'O-Fe-O' stretching frequency shifted from 687.5 cm^{-1} and 643.14 cm^{-1} to 688.42 and 640.21 cm^{-1} respectively with falling of in intensity. Attributional changes observed in the bending vibrations of Fe_2O_3 (479.28 cm^{-1}, 465.66 cm^{-1} and 457.97 cm^{-1} bending vibrations shifted to 482.11 cm^{-1}, 468.62 cm^{-1} and 459.93 cm^{-1} respectively). In this beneficiation process -MgO/CaO/TiO stretching are completely disappeared.

Simulator Design

The experiments performed in the laboratory scale were carried in a prototype simulator by using the same optimum conditions established on laboratory. The description of simulator is presented hereunder and various components of simulator shown in Figure 4.

Description: This drum type simulator is made up of rotary wet mixing unit, fabricated with Stainless Steel drum (2Mt length,0.8Mt diameter and 8 mm thickness) with sliding door arrangement for unloading treated coal from bottom of the drum. This SS drum will be rotated with require RPM using Geared-Motor. A Carbon Steel pipe of Diameter 100 mm fitted with bearings at both ends will act as axil for rotation of drum. Spray nozzles are provided to spray the liquid bio-extract. The Sparay nozzles consists of orifices with very small diameter (2 mm). Coal particle size used in then treatment process is larger than the diameter of the orifices of spray nozzles. High pressure steam of 10atm pressure is passed through stainless steel coiled tube arranged along the axis of rotator and there by temperature of more than 60°C is maintained in the treatment zone of simulator. An Inlet hopper to feed raw coal is arranged on the upper surface of the rotator. Perforated stainless steel tray (sieve) of 2Mt x 1Mt was provided at rotator bottom with a watertight plate with movable option to permit the coal to fall on SS tray of size 2Mt X 1 Mt after treatment process. The tray is provided with two stairs in which stair located upper side is having pores with the size less than size of coal particles such that separation of enriched coal from liquor portion is possible. The lower portion of the tray is provided to collect the liquid portion which got filtered. This filtrate can be reused for treatment process based on the requirement by a motor arrangement.

Working: The raw coal of 8 Kg pertaining to the source of Sattupally, pulverised to the size of approximately 3 mm was taken in the simulator and 60 Lts of the plant extract (prepared from fruits of *Carissa carandas* plant) preheated to 60°C was arranged to pass through carbon steel pipe provided on the axis at a pressure 5 kg/m^2. Through nozzles of the tube, plant extract was poured out on the 3 mm sizes untreated coal. After this the mixing of plant extract was stopped. Then the rotation of simulator was started at rotational speed of 300 rpm. The effective reaction between the poor-quality raw coal and the plant-extract was ensured by using spilling, number of rotations, conditions of high temperature, pressure. These reactive conditions established in this simulator, removed the some of the ash mineral components present in the raw coal through coordinating nature of the poly phenyl compounds present in the plant extract. The rotation was stopped after 2 h, then the treated coal in the simulator was collected on the tray by moving horizontally the metallic plate of the rotator located at the bottom. Beneficiated coal was collected on the upper portion and the filtrate with inorganic mineral oxides is collected at the bottom portion of the tray. The treated coal further subjected to drying process to remove the external free moisture. The motor pump set with regulated discharge valve arrangement is used to recycle the plant bio-extract. The proximate analysis of treated coal by using this simulator were conforming to experimental laboratory results.

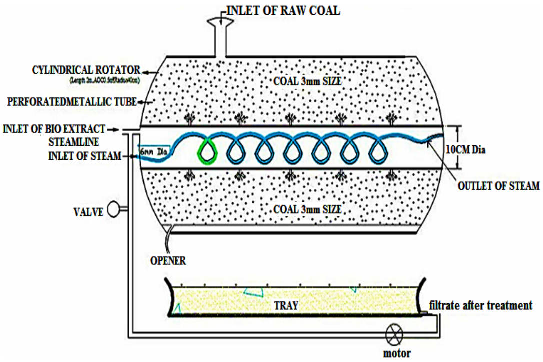

Fig. 4. Proto type simulator

Cost Analysis

Proximate analysis of treated coals of Rudrampur and Jagannath mines, clearly indicates the ash percentage can be reduced to the design of the boiler of 600 MW unit of Rayalaseema project, India and there by desired GCV of boiler 4400Kcal/Kg can be achieved. In Table 4, calculation pertaining to cost of production of one unit of power is presented with coal of Jagannath mines. For presentingthis calculation heat rate of 600 MW unit of Rayalaseema Thermal Power Plant, India 2390 Kcal/K watt Hr is taken, as heat rate of power generating unit is defines as amount of heat required to generate one K watt Hr that is one Unit of power.

For an increase of 722 units in GCV, correspondingly 722 MT of Coal is reduced in consumption of the fuel. From above table it is inferred that cost of production per unit of power reduces by 34 paise. As one 600MW unit produces 14.4 million units per day, the total savings will be crores of rupee annually.

Table 4: Cost Analysis

S. No	With raw coal(GCV3920 Kcal/Kg)	With treated coal(GCV 4642 Kcal/Kg)
Amount of coal needed to produce 14.4 million units (full generation from 600 MW generating station per day)	8780 MT	7414 MT
Coal cost per day Rs	3,83,33,480 @4366 Per MT	3,33,69,524 @4366 Per MT+12,00000 (inclusive of operational cost of additional crushers and total cost of plant extract)
Variable Cost per unit of power	Rs 2.66	Rs 2.32

• **Formula adopted for cost savings:** Heat Rate=Quality of Cal in GCVX quantity of Coal/Generation

CONCLUSION

In this investigation beneficiation of coal is achieved by using weak organic acids and poly phenyl compounds present in the bio extract derived from fruits of *Carissa carandas* plant. These chemicals present in the bio extract of fruits of *Carisaa carandas* plant are found to be effective in leaching out Alumina, Calcium Oxide, Iron oxide etc., (these are some of the components in the ash) and some portion of inherent moisture present in the coal, there by an increase in net calorific value of coal is observed. Usage of these treated coals results in maximum power generation at cheaper cost. The essential optimum requirements for treatment between bio extract and coal samples are established in this investigation. Further Iron Pyretes(FeS) from coal is also successfully removed in this treatment process consequently Sulphur present in the coal also found to be reduced in this investigation which is an important part of beneficiation of coal since Sulphur in coal contributes to acid rains. All these facts are proved in the quantitative analysis of coal that is proximate and elemental analysis further, XRD and FTIR studies also supporting these facts. To carry out the treatment process on macro level by using the fundamental conditions used in the laboratory scale, Proto type simulator is developed and treatment process carried out in the simulator also results in the enhancement of quality of Coal. Cost of generation is also calculated with raw coal and with treated coals by considering all factors involved in the treatment. As per this detailed calculations, usage of treated coals in power generation will results in reduction of 34 Paise in unit cost of power production and hence for entire thermal station considerable amount of money can be saved annually. Successful reduction of ash content in the coal by using bio extracts, opening the new avenues for continuation of research studies on the usage of various bio extracts from various plants, for enhancement of quality of coal as there is a serious and genuine need to reduce the ash content from domestic coals in India.

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Conflict of interest

The author declare that we have no conflict of interest.

REFERENCES

1. Kober, T.; Schiffer, H. W.; Densing, M., Panos, E. *EnergyStartegy Reviews*., **2021**, *31* https://doi.org/10.1016/ j. esr. 2020.100523.
2. Power sector at a glance in all India, *Ministry of power*., **2022** https://powermin.gov.in/en/content/power-sector-glance-all-india.
3. Stephen, N. *International Energy Outlook. US energy information administration*., **2021**, https://www.eia.gov/outlooks/ieo/pdf/IEO2021_ReleasePresentation. pdf.
4. Yuemin Zhao.; Xuliang Yang.; Zhenfu Luo.; Chenlong Duan.; Shulei Song. *Int J Coal Science & Technology*., **2014**, *1*, 103–112 https://link.springer.com/article/10.1007/s40789-014-0014-5.
5. Zhenfu Luo.; Yuemin. Zhao.; Bo Lv.; Yonhong Fu.; Xuan Xu.; Changshuai Chen. *International Journal of Coal Preparation and Utilization*., **2022**, *42*, 986-1014. https://doi.org/10.1080/19392699. 2019. 1678469
6. Mohan Rao Andavarapu.; Vidyasagar,a.; Ranjit Prasad. *International Journal of Coal Preparationand Utilization*., **2022**, *42*, 3618-3636.
7. Liang Dong.; Ziming Wang. *International Journal of Coal Preparation and Utilization*., **2022**, *42*, 1105-1125 https://doi.org/10.1080/19392699.2019.1692339.
8. Groppo,j. An introduction to nature of Coal in Coal Combustion Products (CCP's). *Science Direct*, **2017**, 3-10 https://doi.org/10.1016/B978-0-08-100945-1.00001-0.
9. Gouri Charan, T.; Chattopadyay, U. S.; Singh, K. M. P. *Minerals & Metallurgical Processing*., **2011**, *28*, 21-23 https://link.springer.com/article/10.1007/BF03402320.
10. Shravan Kumar.; Venugopal, R. *International J of Coal preparation and Utilization*., **2017**, *40*, 107-115 http://dx.doi.org/10.1080/19392699.2017.1346631.
11. Boylu,E.; Tali,T.; Cetinel,M.S.; Celik. *International Journal of Mining and Processing*., **2014**, *129*, 27-35 https://doi.org/10.1016/j.minpro.2014.04.001.
12. Bharat, K. I.; Suresh, Nikkam.; Udayabhanu. *International J of Coal preparation and Utilization*., **2022**, *42*, 2685-2702 http://dx.doi.org/10.1080/19392699.2021.1876681.
13. Kopparthi, P.; R. Singh; D. Nag; A. K. Mukherjee. *International Journal of Coal Preparation and Utilization*., **2016**, *38*(1), 13–29.
14. Vasumathi, N.; Vijayakumar, T. *International Journal of Coal Science and Technology*. **2016**, *3*, 206–214 https://link.springer.com/article/10.1007/s40789-016-0129-y.
15. Chattopadyay, U. S.; Kalyani,V. K.; Gouri Chran,T. *International Journal of Coal Preparation and Utilization*., **2015**, *35*, 206-215.
16. Naveen kumar.; Shravan kumar. Performance analysis of beneficiation of coal tailings by froth flotation. Conference on Current trends in renewable and alternate energy., **2019.**
17. Heena Dhawan.; Durlab Kumar Sharma. *International Journal of Coal Science and Technology*., **2019**, *6*, 169-184.
18. Dash, P.S.; Kumar, S. S.; Banerjee, P. K.; Ganguly, S. *Miner Process Extract Metall Rev*., **2013**, *34*, 223–239.

19. Dash, P. S.; Sriramoju, S. K.; Kargupta, A.; Banerjee, P. K.; Ganguly, S. *International Journal of Coal preparation and Utilization.*, **2015**, *35*(5), 257-272.
20. Hacifazlioglu, H. *Energy Sour Part A Recov Util Environ Effects.*, **2016**, *38*(24), 3586–3592.
21. Honakar Rick.; Zhang Wencai.; Joshua Werner. *Energy & Fuels.*, **2019**, DOI: 10.1021/acs.energyfuels.9b00295.
22. Wang, F.; Zhang,Y. M. *International Journal of Mineral Processing.*, **2014**, *128*, 40-47 http://dx.doi.org/10.1016/j.minpro.2013.12.010.
23. Manoj, B. *Journal of Environmental Research and Development.*, **2012**, *6*, 653 https://www.researchgate.net/publication/258477400.
24. Sushanta, K.; Behera.; Sudipto Chakraborty.; Meikap, B. C. *Mineral Processing and Extractive Matallurgy Review.*, **2018**, *39*, 59-67.
25. Singh, J. P.; Mahapatra, S. K.; Singh, G.; Kumar, S.; Singh, S. K. *Iran.J.Chem.Chem. Eng.*, **2018**, *37*, 6. https://www.ijcce.ac.ir/article_31128_063e06e17d17472c25b239dc0f259880.pdf.
26. Duz, M. Z.; Saydut, A.; Erdogan, S.; Hamamci, S. *Energ. Explor. Exploit.*, **2017**, *27*(6), 391-400 https://www.jstor.org/stable/26160762.
27. Behera, S. K.; Chakraborty, S.; Meikap, B. C. *Fuel.*, **2017**, *196*, 102-109 https://doi.org/10.1016/j.fuel.2017.01.088.
28. Behera, S. K.; Kumari, U.; Meikap, B. C. *Journal of Mining and Metallurgy.*, **2018**, *54*, 1-24.
29. Waqas Ahmad.; Imtiaz Ahmad.; Ishraq Ahmad.; Amjad Ali Shah. *International Journal of Coal preparation and Utilization.*, **2023**, *43*, 1164-1184.
30. Gangadhara Reddy.; U.; Ravindhranath, K.; Subba Reddy, G.V.; Sridhar Reddy, D. *Bio mass conversion and Biorefinery.*, **2022**, https://link.springer.com/article/10.1007/s13399-022-03437-6.