Geosciences 2015, 5(4): 113-119
DOI: 10.5923/j.geo.20150504.01

Geochemical Characterization of Coals Using Proximate and Ultimate Analysis of Tadkeshwar Coals, Gujarat

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Abstract The present study aimed to characterize the coal in the area under study through chemical composition utilizing the parameters through proximate and ultimate analyses. The analytical evaluation of properties such as moisture, volatile matter, fixed carbon, and ash forms the proximate analysis. In the present study the moisture content in the coals samples ranges between 7.25 and 22.17 wt%. The fixed carbon content varies from 41.62 to 62.15 wt%, the ash content ranges between 7.74 and 29.10 wt%, volatile matter ranges between 37.85 and 57.69 wt%. The statistical analysis of the results show the average concentration of fixed carbon as 50.63 wt%, ash content as 17.10 wt%, moisture as 12.64 wt%, and volatile matter as 54.39 wt%. The increased volatile contents are characteristic of lower-rank coals, while the decreased values are indicative of higher-rank coals. The results of ultimate analyses of each element are discussed in detail wherein; the concentrations of carbon content ranges between 42.65 and 72.52 wt%, The oxygen content ranges between 20.02 and 42.16 wt%, the hydrogen ranges between 1.80 and 7.77 wt%, sulphur ranges between 0.84 and 6.31 wt% and nitrogen ranges between 0.08 and 0.90 wt%. The statistical analysis of the results show the average concentration of carbon as 58.55 wt%, hydrogen 5.11 wt%, nitrogen as 0.51, sulphur as 3.67, and oxygen as 28.81 wt%. The analytical results suggest the existing coal with varying thickness spread all over the region is of lignite rank. Moreover proximate and ultimate analyses when interpreted in detail may form an effective tool to characterize the coals of any area.

Keywords Tadkeshwar, Proximate, Ultimate, Coal, Geochemical Characterization

1. Introduction

The coal deposits have specific plant precursors and marked by the regional history followed by depositional and environmental conditions causing enrichment or depletion of different elements, phases or minerals giving rise to a unique fundamental code that characterizes the coal, whereas the mineral composition and association between mineral matter and organic matter mark the genetic code. The composition can be interpreted to infer type, properties, quality, and genesis of coal [1]. Each type of coal has a certain set of physical parameters which are mostly controlled by moisture, volatile content in terms of aliphatic or aromatic hydrocarbons and carbon and ash content evaluated as part of proximate analysis. Of these four components determined by proximate analysis, only the volatile matter and the fixed carbon actually burn and liberate thermal energy. The parameters for the present study proximate analysis are moisture, volatile matter, ash, and fixed carbon. Coal is characterized into four main types or *ranks*: lignite or brown coal, bituminous coal or black coal, anthracite and graphite. The coal is an organic rock mostly enriched with carbon (C), with minor concentration of hydrogen (H), oxygen (O), sulphur (S) and nitrogen (N), along with few inorganic constituents (minerals) and water. The ultimate analysis is the chemical approach to characterize the coals depending upon the amount of the presence of principal chemical elements as carbon and hydrogen to which on weight basis, carbon predominance the hydrogen constituting approximate 60% of 95% of the total. For the most coals of 90% or less carbon content the hydrogen content is generally in the range of 5% and it drops to nearly 2% for coals having 95% carbon. The nitrogen content of almost all coals is in the range of 1-2 %. The oxygen content is inversely related to carbon for instance, the coals of 65% carbon, may contain 30% oxygen, while coals of 95% carbon may contain only 2 -3 % oxygen. This appears significant as more oxygen a coal contains the easier it to burn to ignite. Sulphur content of coal is seen to be less variable. The present study aims to characterize the coal through proximate and ultimate analysis.

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Published online at http://journal.sapub.org/geo

2. Geological Setting of the Study Area

Geology of Gujarat mainly consists of Mesozoic and Cenozoic rocks [2], largely covered by alluvium, cultivated fields and prominently exposed by the Deccan Traps which are underlain by thick Mesozoic sediments. Stratigraphic sequence begins with Cretaceous to be followed upward by the Deccan volcanics, Tertiary and the Quaternary sediments. Structurally, the Cambay Basin a NNW-SSE trending intra-cratonic graben and a major Tertiary hydrocarbon belt of the country [3]. The basin flanked on the north-east by the Aravalli swell-Aravalli-Delhi Supergroups of rocks of Precambrian age, on the east by the Deccan craton, and on the south-east and west by the Saurashtra craton (Fig.1). An approximately complete Tertiary sequence is present below the thick alluvium of Quaternary age, overlying hte Deccan Trap of Late Cretaceous age that forms the Basement complex of the Cambay Basin and is overlain by the Olpad Formation of Palaeocene age. The Cambay Black Shale formation of Palaeocene-Early Eocene overlies the Olpad Formation. A coal-sand unit, the Kadi Formation of Early Eocene age is recognized within the Cambay Formation where, the Kalol Formation of Middle Eocene age conformably overlies the Cambay Black Shale. This formation is overlain conformably by the Tarapur Formation of Middle Eocene-Oligocene. The Early Miocene sequence of Kathna Formation overlies the Tarapur Formation with locally developed basal sandstone in various parts of the basin. The Babaguru and Kand Formations of Early-Middle Miocene overlie the Kathna Formation, which is in turn overlain by the Jhagadia Formation of Middle-Late Miocene. The Broach of Pliocene and Jambusar of Pleistocene Formations overlies the Miocene sequence. The Tertiaries in the area consists of sandstone, conglomerate clays, limestone, lignite, etc. ranging in age from Lower Eocene to Lower Miocene.

The subsurface lignite-bearing sequence encountered in southern Cambay at Rajpardi, Vastan, Tadkeshwar, etc. and is referred to as the Cambay Shale have been mentioned as Tadkeshwar Formation. The basement for the Tertiary in the studied area is composed of the basal sediments of Vagadkhol Formation homotaxially equivalent to Olpad Formation, which unconformably overlie, the Deccan Traps (Table 1).

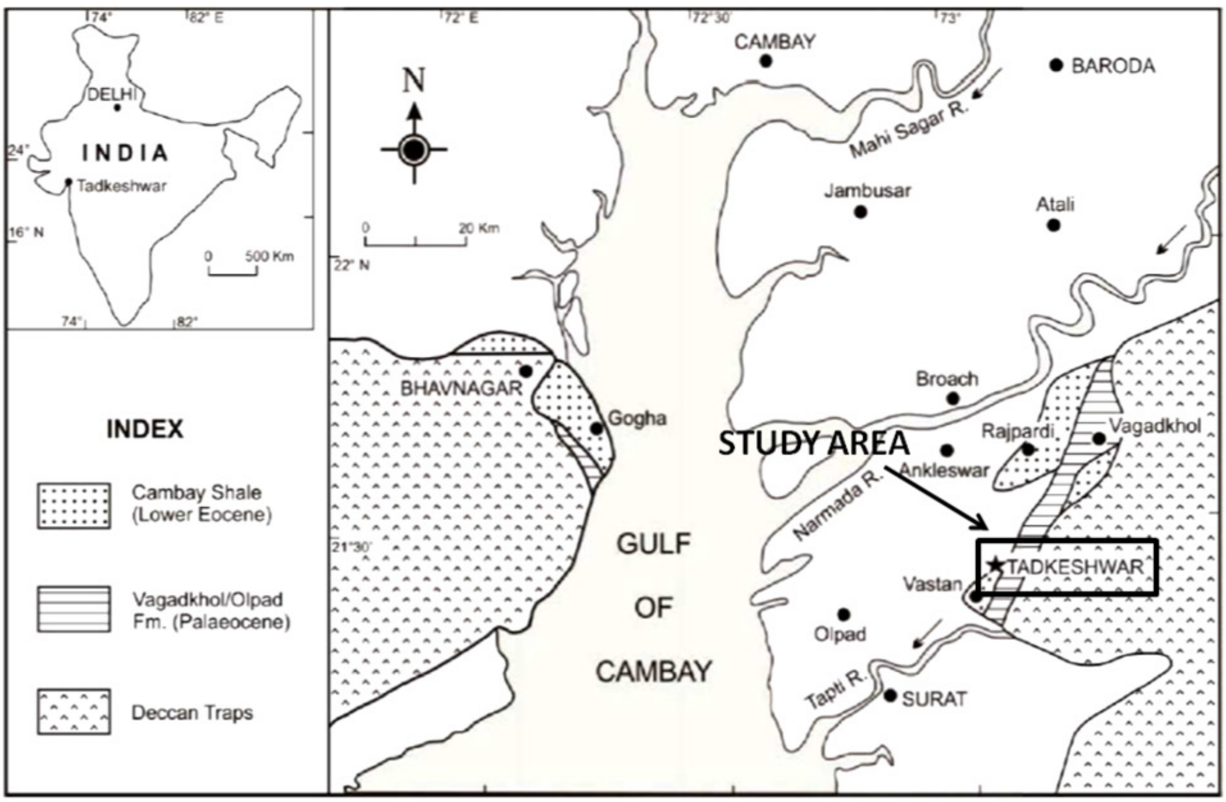

Figure 1. Location and geological map of the area, Tadkeshwar lignite mine, Gujarat [4]

Table 1. Geological succession around Tadkeshwar lignite field, southern Cambay Basin (Source: GMDC Mine report), [4]

AGE	FORMATION	LITHOLOGY (THICKNESS)
Pleistocene to Recent	Alluvium	Varied coloured sands, soil and kankar
Middle Miocene To Pliocene	Jhagadia	Light coloured sandstone, marls, limestone and conglomerate (304 m)
Lower Miocene	Kand	Limestone, marls and clays with sandstone bearing conglomerate (457 m)
Lower Most Miocene	Babaguru	Ferruginous sandstone, agate bearing conglomerate and varied clays, grey sandstone and white sands (152m)
Oligocene to Upper Eocene	Tadkeshwar	Grey, yellow and brown friable sandstone with clay lenses, Bentonitic clays with lignite beds and lenses of carbonaceous clays, sandstone and ignite (152m)
Upper Eocene to Lower Eocene	Nummulite	Numulitic limestone, clays with sandstone lenses (122 m)
Lower Eocene	Vagadkhol	Bentonitic clays, friable sandstone and conglomerates (304 m)
Cretaceous	Deccan Traps	Basalts with basic intrusive

Materials and Methods

Sample collection

Total 10 nos. of coal samples were collected from Tadkeshwar open cast mines being operated by Gujarat Mineral Development Corporation (GMDC). About 500g of rock samples were collected in an air tight aluminium pack, while the information as depth, coal seam, along with the geographic coordinates were noted separately.

Figure 2. Samples were collected from the Tadkeshwar mines of GMDC

Materials and methods

Proximate analysis

Four parameters which have been analysed under this particular method as, (a) moisture content, (b) volatile matter, (c) ash content, (d) fixed carbon [5].

Moisture content analysis

It is the loss of weight of coal when heated at about 105°C in a crucible. A known amount of finely powdered coal sample, in a silica crucible is heated in an electrical hot air oven at 105-110°C for about an hour later cooled in a desiccators and weighed. This process of heating, cooling and weighing is repeated till the weight of the crucible containing anhydrous coal becomes constant. Loss in weight is reported as percentile moisture content.

Moisture (%) = loss in weight due to removal of moisture / weight of coal sample taken x 100

Determination of Volatile Matter

The volatile matter is the loss in weight of moisture free coal when heated at designated temperature and time. The moisture free coal sample is taken in silica crucible covered with lid and placed in muffle furnace, pre-heated at 925° +/- 20° C for 7 minutes. The crucible is then taken out and cooled first in air, then inside desiccators and weighed again. The loss in weight (%) is reported as volatile matter.

Volatile matter (%) = (loss in weight due to removal of volatile matter/wt of coal sample used) x 100

Determination of Ash content

It is weight of residue obtained after burning a known amount of dry coal in an open crucible. The sample is heated at 700-750°C for half an hour in a muffle furnace. Heating cooling and weighing is repeated till a constant weight is obtained. The indication is the lower ash content better the quality of coal.

Ash content (%) = (weight of ash formed / weight of dry coal taken) x 100

Fixed Carbon

After the determination of moisture, volatile matter and ash content, the remaining material is the fixed carbon representing the quality of coal that can be burnt by a primary current of air drawn through the hot bed of a fuel. The fixed carbon analyses require designing of furnace and shape of the fire-box as it burns in solid state. The trend is that higher the fixed carbon greater the calorific value hence the better quality of coal.

Ultimate analysis

The ultimate analysis has been carried out by using CHNSO analyzer (2400 Series II of Perkin Elmer make). The CHN and CHNS modes are based on the classical Pregl-Dumas method where samples are combusted in a pure oxygen environment, with the resultant combustion gases measured automatically. In the combustion zone, samples are encapsulated in tin or aluminium vials and are inserted automatically from the integral 60-position auto sampler or manually using a single-sample auto injector. The analytical procedure comprised with four major zones; combustion zone, gas control zone; separation zone and detection zone.

3. Results and Discussion

3.1. Proximate Analysis

The results of proximate analysis for moisture, volatile matter, fixed carbon, and ash are given in Table 2.

Moisture

The moisture is an important factor of coal as all coals are mined wet. The groundwater and other extraneous moisture known as adventitious moisture is readily evaporated while the moisture held within the coal itself is inherent moisture that is analysed quantitatively. Most coals, as they are dug from the ground, have some amount of moisture associated with them. Generally, the moisture content of coals ranges from 5% to nearly 70% which is an undesirable constituent as it reduces the heating value and adds weight to the transportation cost. The fluid matter of coal comprises moisture, gas, and gas-liquid inclusions associated with both solid organic matter (OM) and inorganic matter (IM) [6, 4]. The increased contents of this physically and chemically adsorbed water are characteristic of lower-rank coals, while the decreased values of this parameter are typical of higher-rank coals [8]. In the present study the moisture content coal samples ranges between 7.25 to 22.17 wt% and arithmetic mean of 12.64 wt% indicating the existence of lignite and partially the above rank coal.

Fixed Carbon (FC)

The fixed carbon content of the coal is the carbon found in the material which is left after volatile materials are driven off. This differs from the ultimate carbon content of the coal because some carbon is lost in hydrocarbons with the volatiles. Fixed carbon is used as an estimate of the amount of coke that will be yielded from a sample of coal. Fixed carbon is determined by removing the mass of volatiles determined by the volatility test, above, from the original mass of the coal sample. The fixed carbon content of coals, not including the moisture and ash, ranges from 50% to about 98%. The FC values are highly dependent on the values of C and OM in coals. It is well known that the FC content increases with coal rank advance [4]. The fixed carbon content the samples of the study area ranges between 41.62 and 62.15 wt% with arithmetic mean of 50.63 wt%.

Ash Content (AC)

The ash content of coal is the non-combustible residue left after the coal is burnt representing the bulk mineral matter after carbon, oxygen, sulphur and water are driven off during combustion indicating the quality of coal. These results reveal that the bulk ash yield itself is a poor informative characteristic of coal if the origin, composition, and abundance not considered resembling the correlation of ash yield as relatively contradictory [9]. The ash content in the lignite and coaly shale samples varies from 7.74 to 29.10 wt% and arithmetic mean of 17.10 wt%.

The high ash yield is normally a marked by the relatively abundant supply of detrital materials in swamp, wherein; the authigenic minerals dominate mostly with low-ash (8-10%) coals, whereas the proportion of detrital minerals increases [10] and the concentration of organically bound elements decreases [11] with increased ash yield. However, these observations seem valid mainly for higher-rank coals as the high-ash (24–49%) lignite, found abundant with moisture, authigenic mineralization, calcite, pyrite and gypsum and organically bound Ca and S are common [9]. The latter observation is also in agreement with the statement that some low-ash (<10%) coals contain mainly authigenic and biogenic inorganic matter, whereas those with higher ash yield (>10%) show simultaneous enrichment in detrital and authigenic inorganics [4].

Volatile matter (VM)

The volatile matter (VM) in coal refers to the components of coal, except for moisture, that are liberated at high temperature in the absence of air which is usually a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulphur. The VM content is measured in the absence of moisture and ash ranging from 2% to about 50%. In domestic stoves and furnaces or in small industrial appliances the coals that contain large amounts of volatile matter are easy to ignite it burns quickly and often burn with a long, smoky flame. The increased VM content is more characteristic of low-rank coals, while the decreased value is more typical of higher-rank coals Table 2 and [8]. The high VM yield is also indicative for the enrichment in liptinite, hydrocarbons, CO, CO_2, and chemically combined water, and for the depletion in inertinite [13]. The volatile carbon content in the samples of the study area ranges between 37.85 to 57.69 wt% with arithmetic mean of 54.39 wt%.

Table 2. Descriptive statistics of proximate analysis of Tadkeshwar coal samples

	M (wt.%)	AC (wt.%)	VM (wt.%)	FC (wt.%)
Minimum	7.25	7.74	37.85	41.62
Maximum	22.17	29.10	57.69	62.15
Mean	12.64	17.10	54.39	50.63
Median	12.69	15.5	54.05	50.69
Stdev.	3.92	8.69	10.19	9.21

M: Moisture; VM: Volatile Matter, AC: Ash Content, FC: Fixed Carbon

3.2. Ultimate Analysis

The results of analyzed parameters Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen are tabulated in Table-3. The results of each element are discussed below in detail.

Carbon (C)

The Carbon content in the collected coal samples from the study area varies from 42.65 to 72.52 wt% with an arithmetic mean of 58.55 wt%. The high concentrations of C are normally characteristic of vitrinite macerals [8, 13]. It is also well known that the C content in coal increases steadily with increasing coal rank Table 4 and [8, 13, 14]. The measurement of C concentration in coal is still the leading and most accurate parameter among other chemical characteristics for evaluation of coal rank despite some limitations [6, 8, 13-17].

Oxygen (O)

The Oxygen content in the samples ranges between 20.02 and 42.16 wt% with an arithmetic mean of 28.81 wt%. The increased content of O is characteristic of low rank coals, while the decreased concentration is typical of higher-rank coals Table 4 [8, 14]. The increased O concentration is in accordance with greater contents of moisture and hydrated minerals or as a result of advanced coal weathering. While the loss of O occurs in the later stages of metamorphic development of coal due to the well-known decrease in oxy-containing functional groups as carboxylates and increase in aromaticity [8, 13].

Hydrogen (H)

The Hydrogen content is found varying from 1.80 to 7.77 wt% with an arithmetic mean of 5.11 wt%. The increased content of H is normally more characteristic of low rank coals, while the decreased values are commonly more typical of higher-rank coals Table 4. The H concentrations increase with increasing liptinite, alginite, resinite, sporinite, cutinite and degree of bituminization, as well as residual moisture, hydrated minerals, and methane in coals [13, 16]. Wherein; liptinites have the highest H content among all macerals [18]. The enhanced H concentration is also a characteristic feature of sapropelic coals [13].

Sulphur (S)

The Sulphur content in the lignite samples ranges between 0.84 and 6.31 wt% with an arithmetic mean of 3.67 wt%. The increased content of S is more characteristic of lignites, while the decreased values of this element is more typical of higher-rank coals with some exceptions Table 4. High-S coals are known to derive most of their S from reduction of sulphate ions to H_2S in sea or brackish water in the coal beds by microbial processes [19]. The penetration of sea water in the peat bog has been a major source of sulphate ion in the Donbas basin [20].

Table 3. Descriptive statistics of ultimate analysis of coal samples

Parameter	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)
Minimum	42.65	1.80	0.08	0.84	20.02
Maximum	72.52	7.77	0.90	6.31	42.16
Mean	58.55	5.11	0.51	3.67	28.81
Median	57.27	5.07	0.45	3.70	29.17
Std. Dev	11.06	2.43	0.31	2.64	8.76

Std. Dev: Standard Deviation

Table 4. Variation of selected coal properties with coal rank [22]

	< -----------Low Rank--------------->		< -----------High Rank--------->	
Rank:	**Lignite**	**Sub-bituminous**	**Bituminous**	**Anthracite**
Age:	--Increase-->			
% Carbon:	65-72	72-76	76-90	90-95
% Hydrogen:	~5---------------------------------------decreases-- ~2			
% Nitrogen:	< -- ~1-2 -->			
% Oxygen:	~30-------------------------------------decreases--- ~1			
% Sulphur:	~0----------------------increase---------- ~4 ----------- decreases---------------------- ~0			
% Water:	70-30	30-10	10-5	~5
Heating value (BTU/lb) :	~7000	~10,000	12,000-15,000	~15,000

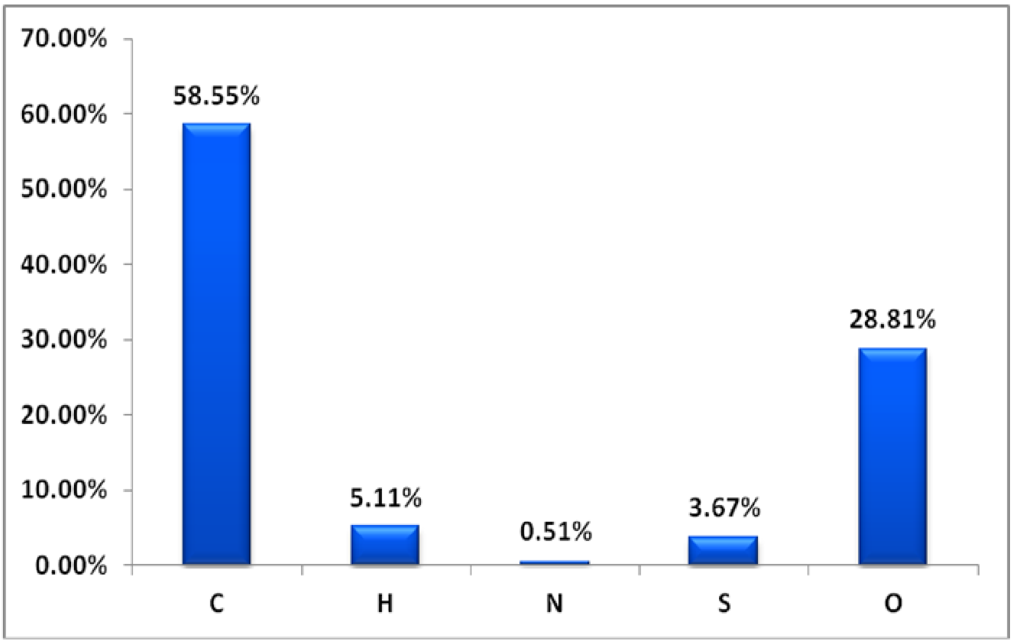

Figure 3. The average CHNSO concentration in coal samples

Nitrogen (N)

The Nitrogen content in the coal samples of the study area ranges between 0.08 to 0.90 wt% with an arithmetic mean of 0.51 wt%. The increased contents of N are normally more characteristic of higher-rank coals, while the decreased values of this element are commonly more typical of lignites Table 4. The reference data show that coal deposits laid down in marine areas are usually rich in N, S and Ash [21].

4. Conclusions

The present study aimed to characterize the coal in the area under study through chemical composition utilizing the parameters through proximate and ultimate analyses. The analytical results show that the Carbon content ranges between 42.65 and 72.52 wt%, Oxygen content varies from 20.02 and 42.16 wt%, the hydrogen content ranges from 1.80 and 7.77 wt%, the sulphur ranges between 0.84 and 6.31 wt%, the Nitrogen content ranges between 0.08 and 0.90 wt%. The analytical results suggest the existing coal with varying thickness spread all over the region is of lignite rank. Moreover proximate and ultimate analyses when interpreted in detail may form an effective tool to characterize the coals of any area. The proximate and ultimate analyses of coals show typical characteristics properties of lignite. The present study helps to characterize the coal type. The interpretation of laboratory data shows that there exists predominantly lignite while the area is occasionally marked with the bit higher rank. Finally, the study highlights the importance of chemical parameters in characterizing the coal besides, tracing the depositional environment in the geological past.

ACKNOWLEDGEMENTS

The authors are thankful to the Dr. D. U. Vyas, General Manager-Geology of Gujarat Mineral Development

Corporation Limited for granting permission and extending necessary support to carry out the field work in Tadkeshwar and other mines. Thanks are due to Dr. T. Harinarayana, Director, Gujarat Energy Research and Management Institute for moral encouragement and guidance leading to the successful completion of this research work and preparation of manuscript.

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