

Proximate Analysis

Determination of

- Moisture
- Volatile matter
- Fixed carbon
- Ash content

Moisture :-

Moisture in a coal occur in four possible forms

- (a) Surface moisture - water held as films on the surface of coal particles.
- (b) Hygroscopic moisture - water held inside the capillaries of coal substances.
- (c) Decomposition moisture → water incorporated in some of the coal organic compound.
- (d) Mineral moisture → water which forms part of the crystal structure of clays and other minerals present in the coal.

Adventitious Moisture → Sample collected from a mine or stockpile is usually wet with a variable amount of 'adventitious moisture' from seepage, water sprays, rain and other sources.

Inherent moisture → like moisture in pores of the coal, which is driven off by 100°C, but some mineral and decomposition moisture may not be liberated until temperature exceed 500°C.

$$\text{Total moisture} = \text{Adventitious moisture} + \text{Inherent moisture.}$$

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Methodology: -

For determination of inherent moisture.

1 gm of air dried coal is ground to (212 micron)

is taken in a silica dish and heated to a temperature of $108 \pm 2^\circ\text{C}$ in an oven. The sample is cooled at room temperature and weighed again.

The loss in weight before and after the heating is taken as moisture.

- The moisture content of low rank coal is greater than 20% whereas in the highest rank coal anthracite moisture is less than 2%.
- Sometimes free moisture is of added advantage specially for firing boilers. For optimal thermal efficiency about 5% total moisture in coal is required.
- For making coke about 3 to 5% of free moisture is essential for best result.

Measurement of Volatile Matter

Volatile matters are the methane, hydrocarbons, hydrogen and carbon monoxide and incombustible gases like carbon dioxide and nitrogen found in coal.

VM is the index of the gaseous fuel present.

Measurement-

Volatile matter of 1 gm of air dried coal is heated under controlled crucible with a lid. The crucible is placed in a furnace and heated to $900 \pm 10^\circ\text{C}$ for seven minutes.

For example:

1 gm sample taken for V.M

1 gm sample $\xrightarrow[\text{7 min}]{\text{heated } 900 \pm 10^\circ \text{C}}$ residue 0.75 gm

Loss in weight due to escape of moisture + V.M = 0.25 gm

% loss due to V.M + moisture = 25%

Moisture as determined = 2%

Therefore V.M = 25% - 2% = 23%

→ After heating for 7 minute to $900 \pm 10^\circ \text{C}$ it is to be noted whether the residue is forming a coherent agglutinating mass or not. If the residue is a coherent mass the coal is said to be caking.

→ Lower rank coal (Lignite) contain 50% volatile matter. Highest rank coal (Anthracite) is less than 10%.

→ Proportionately increases.

→ From amount of volatile matter content in a coal, behaviour of the coal on combustion, carbonization and gasification can be judged.

→ The prime coking coals on carbonisation yield coke of sufficient strength which can be used for metallurgical purpose.

→ Sometimes due to scarcity of prime coking coal usually prime coals are mixed with high volatile coals or semi-coking coals and the mixture is used for steel making. The blend or mixture generally contains 25-29% volatile matter.

Ash →

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- The non-combustible inorganic residue that remains after coal is burned is Ash of Coal.

It represents bulk of mineral matter in the coal, after volatile component such as CO_2 (from carbonate), SO_2 (from sulphate) and H_2O (from clays) have been driven off.

Determination of Ash

1 gm of air dried coal grounded and pass through 212 micron IS sieve, ~~is~~ taken in silica dish. The dish with thinly spread coal is heated in a muffle furnace. First the temp is given is 500°C for 30 minutes followed by the temperature of $815 \pm 10^\circ\text{C}$ for another 30 to 60 minutes. The dish is taken out and cooled in a desiccator and weighed.

Ash weight → The difference between weight of ash before and after heating.

- An excess of ash deterrent for the combustion of coal as it clogs the grate of the boiler and restricted the passage of air.
- ~~As~~ A low ash coal in which the ash is easily fusible may be less valuable than a high ash coal in which the ash is of infusible character.
- Ash is the inorganic residue left after the complete combustion of coal. For industrial purpose ash in coal plays a vital role.

Fixed Carbon :-

- The fixed carbon content of coal is the carbon found in the material that remains after the volatile matter has been expelled.
- It represents the decomposition residue of the coal's organic components, and ~~carries~~ carries with it small amount of nitrogen, sulphur, hydrogen and possibly oxygen as absorbed or chemically combined material (Rees 1966)

- The fixed carbon content is not directly determined but is the difference in an air dried coal, between the sum of other components (moisture, volatile matter, ash) and 100%.

$$F.C = 100 - (M + V.M + A)$$

F.C = Fixed Carbon

M = Moisture

V.M = Volatile matter

A = Ash.

- The fixed carbon content is used as an Index of the yield of coke expected from a coal on carbonization or as a measure of the solid combustible material that remains in coal-burning equipment after the volatile fraction has been liberated.

- Appropriate correction

Most analyses of coals are carried out on air dried samples, and the percentage of the various constituents calculated in proportion to the mass of that material.

(a) 'As received' or 'as sampled'

The data are expressed as percentage of the coal including the total moisture content, i.e. including both the surface and the air dried moisture content of the coal.

(b) 'Air-dried' basis (a.d.b) → (6)

Data expressed as percentage of air-dried coal which include air dried moisture but not the surface moisture of the coal.

(c) 'Dry' basis (dry) →

Data expressed as percentage of the coal after all the moisture has been removed.

(d) 'Dry, ash-free' basis (d.a.f) →

The coal is considered to consist of volatile matter and fixed carbon on the basis of recalculation with moisture and ash removed. It should be noted that this does not allow for the volatile matter derived from minerals present in the air-dried coal.

$$\text{V.M. (d.a.f) in \%} = \frac{\text{V.M. (air dried)} \times 100}{100 - (M + A)}$$

M = Moisture % on air dried coal.

A = Ash % on air dried coal.

V.M. (air dried) = volatile matter in air dried coal

(e) 'Dry, mineral matter-free' basis (d.m.m.f)

The total amount of mineral matter rather than ash is determined, so that the volatile matter content in the mineral matter can be removed.

$$\text{V.M. (dry mineral matter free or d.m.m.f. basis)} = \frac{\text{V.M. (air dried)} \times 100}{100 - (M + 1.1 A)}$$

M = Moisture % on air dried coal.

A = Ash % on air dried coal.

V.M. (air dried) = volatile matter % on air dried coal.

This may be done directly or indirectly (7)

$$MM = 1.13A + 0.8CO_2 + 0.5S_{pyr} + 2.85S_{SO_4} - 2.85S_{Ash} + 0.5Cl$$

Where MM = percentage mineral matter.

A = percentage ash.

CO₂ = percentage Carbonate CO₂

S_{pyr} = percentage pyritic sulphur.

S_{SO₄} = percentage sulphate sulphur.

Cl = percentage chlorine (all in air dried coal).

The percentage of volatile matter, on a dry mineral matter free basis,

$$\% VM_{d.m.f.} = \frac{100 \times (\% VM_{air\ dried} - \Delta VM)}{100 - \% moisture - \% mineral\ matter}$$

ULTIMATE ANALYSIS

Ultimate analysis of coal consist of the determination of Carbon and hydrogen as gaseous product of its complete Combustion

The determination of sulphur, nitrogen and ash in the material as whole.

The estimation of oxygen by difference.

The details of procedure are given in
IS : 1350, Pt IV/Sec 1 : 1974, IS 1350, Pt III, 1969;
IS : 1350 (Part IV/Sec. 2) - 1975.

(i) Carbon and Hydrogen

When coal is burnt in a current of oxygen, all the carbon is converted into Carbon dioxide and hydrogen into water (H₂O)

These CO₂ is liberated from carbonate minerals that may be present.

H₂O is derived from water in clay or other hydro- minerals. Hydrogen is also found in the inherent moisture of the air-dried coal, and thus any measure of the 'total' carbon and hydrogen includes certain amount of material derived from inorganic sources.

Determination

are based on heating the air-dried coal in a stream of dry oxygen, and collecting the CO₂ and H₂O produced in a series of absorption tube.

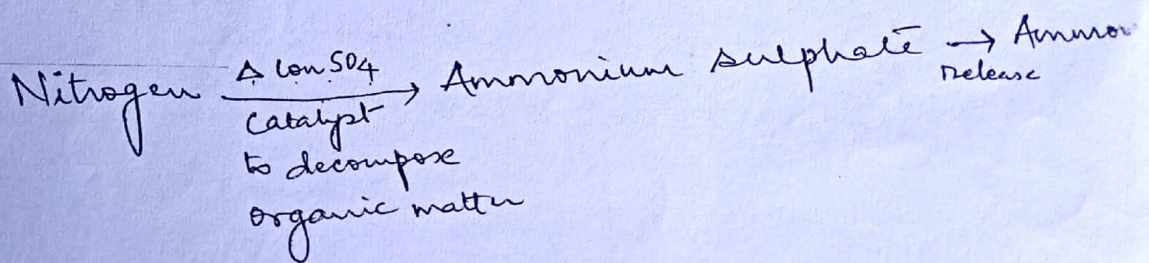
$$C(d.a.f) = \frac{C(\text{air dried}) \times 100}{100 - (M+A)}, \quad H(d.a.f) = \frac{H(\text{air dried}) \times 100}{100 - (M+A)}$$

(ii) Nitrogen

- The nitrogen compound found in coals appears to be mainly confined to the organic compound
- Some nitrogen compounds may occur in pore waters, especially in brown coal.

Determination :-

- Determined by Kjeldahl method (15-1975)
- Converts nitrogen in the coal to ammonium sulphate when coal is heated with concentrated sulphuric acid in the presence of a catalyst to decompose the organic matter.



- Ammonia is absorbed in boric acid solution and titrated with 0.05 N sulphuric acid.

$$N(d.a.f) = \frac{N(\text{air dried}) \times 100}{100 - (M+A)}$$

- Combustion of the coal, nitrogen helps to form oxide, which may be released as flue gases and thereby pollute atmosphere,
- Low in nitrogen are preferred by industry.

SULPHUR

Sulphur may occur in coal in a number of ways:-

- Organic Sulphur → incorporated ~~with~~ into hydrocarbon compounds of coal substance.
- As sulphide mineral → such as pyrite, in the inorganic fraction (pyritic sulphur).
- As sulphate mineral - mostly hydrous iron or calcium sulphate, usually produced by atmospheric oxidation of iron sulphide.

Determination

TOTAL SULPHUR

Eschka Method → involves oxidation of coal at 800°C in magnesium oxide and sodium carbonate, followed by addition of barium chloride to form insoluble barium sulphate. The mass of barium sulphate formed gives the total sulphur content of the coal.

Sulphate Sulphur → determined by extracting coal with dilute sulphuric acid and determining the amount of sulphur in the extract.

Pyritic Sulphur →

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Indirectly estimated by determining the amount of iron combined in the pyritic state and calculating the amount of sulphur associated with this iron.

Organic sulphur → is calculated by deducing the sum of sulphate and pyritic sulphur from the total sulphur of coal i.e.

$$\text{Organic sulphur} = \text{Total sulphur} - (\text{Sulphate Sulphur} + \text{Pyritic sulphur}).$$

- High sulphur is dangerous from the point of view of mining as it produces acidic mine water.
- An unacceptably high level of sulphur may be passed on to the iron and steel produced using coke from high sulphur coal, resulting in material which is brittle or difficult to weld.
- The sulphur may be removed in the blast furnace by producing additional volume of slag, or by oxidation in the subsequent steel-making process.

Oxygen :-

(11)

- Oxygen is a component of many ~~mineral~~ organic and inorganic compounds in coal as well as the moisture content.
- When coal is oxidised, oxygen may be present in oxides, hydroxides and sulfate mineral,
- Oxygen is an important indicator of rank ⁱⁿ of coal.

Determination

by subtracting sum total of carbon, hydrogen and nitrogen from 100.

$$\text{Oxygen \%} = 100 - (\text{C\%} + \text{H\%} + \text{N\%})$$

$$\text{O(d.o.a.f)} = 100 - (\text{C(d.a.f)} + \text{H(d.a.f)} + \text{N(d.a.f)})$$

Phosphorous :-

- Phosphorous may be present in coal, usually concentrated in the mineral apatite.
- It is undesirable for large amount of phosphorous to be present in coking coals to be used in the metallurgical industry, as it contributes to producing brittle steel.
- Coking coal should have maximum phosphorous content of 0.4% (air dried)

CALORIFIC VALUE

(12)

- The calorific value of a coal is the amount of heat per unit mass of coal when combusted.
- Calorific value is often referred to specific energy (SE), particularly in Australia.

The calorific value is expressed in two ways -

- (1) The gross calorific or higher heating value
- (2) Net calorific value or lower heating value.

Gross calorific → In laboratory combustion take place under confined condition, and most of the products are allowed to condense after ignition. The gross value include all the heat available from the heat of condensation of moisture in the coal and moisture formed by combustion of the hydrogen in coal.

Net calorific or lower heating value →

During the actual combustion in furnace, the gross calorific value is never achieved because some products, especially water, are lost with their associated latent heat of vaporization.

The maximum achievable calorific value under these condition is the net calorific value at constant pressure.

Determination

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A small amount of coal is ignited electrically in an oxygen atmosphere, within a pressure-resistant metal cylinder or 'bomb'. This cylinder is immersed before firing, in a known mass of water, and the increase in temperature of this water is monitored after combustion takes place. The amount of heat given off by the sample is determined from the temperature rise by reference to previous calibration run with a thermochemical standard such as benzoic acid in place of the coal.

Calculation of calorific value from Goulet's formula

$$\text{Calorific value} = 82 \text{ F.C} + \alpha \text{ V.M.}$$

F.C = fixed carbon on air dried coal

V.M = volatile matter " air dried coal

$$\alpha = \frac{100 \times \text{V.M.}}{\text{F.C} + \text{V.M.}}$$

- Important Parameter for the assessment of quality of coal because the use of coal is based on the available heat.