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# CHEMICAL ANALYSES AND CHARACTERIZATION OF SOME ETHIOPIAN COALS

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**ABSTRACT.** A geological and exploratory investigation for possible coal reserves conducted on 5 $km^2$ in Dilbi and on 10 $km^2$ in Moye (Jimma) areas found an identified reserve estimate of coal field of 15-20 million tons of coal and 40-50 million tons of coking coal, respectively. Samples from several bore cores of Mendi (Wollega), Mush Valley (N. Shewa), Kindo Halale (Sidamo), Dilbi (Jimma) were analyzed. The important analytical quality parameters studied were proximate, ultimate, TLC, X-ray diffraction, specific gravity and elemental analyses. In addition, programmed pyrolysis and vitrinite reflectance were performed to evaluate the generative potential, total organic carbon content, type of organic matter, quantity of accumulated or depleted hydrocarbons and degree of maturity of coals. Accordingly, the quality of various coal ranks were determined and categorized as sub-bituminous and high volatile bituminous coals of rank B + C, medium and low volatile bituminous coals or coking coal.

## INTRODUCTION

The availability of energy at reasonable costs has always been a condition of industrial growth, economic and social progress and the improvement of the standard of living of the population. Coal, formed from compaction and induration of fossilized plant debris with aromatic structures [1], was the world's most important fuel for many years. Some authors believe that the world's total coal resources are estimated to be about 17 x $10^{12}$ metric tons (t) [2-4]. Lukaschew [5] commented that by the end of the century, this volume could easily increase to 30 or 40 x $10^{12}$ t as the results of the discovery of further deposits at great depths, particularly in the developing countries. However, some estimates [6,7] suggest the figure may reach 1.5 x $10^{15}$ t when the deposits finally will be delineated by further exploration. Fettweis [8] suggested that coal could serve as a major source of energy supply for about 400 - 500 years to come, lasting until the second half of the next millennium.

Although lignite occurrences and deposits were recognized and reported long ago in Ethiopia, there is no record of commercially exploitable deposit [9]. A program of an extensive and intensive exploration of coal in Ethiopia was set and carried out from 1986-1991. In this study, an attempt is made to evaluate and characterize Ethiopian coals based on some geochemical and chemical parameters.

## ANALYTICAL AND EXPERIMENTAL METHODS

Eighteen bore holes at Dilbi and 8 bore holes at Moye with a total meterage of 3865 and 1570 m, respectively were sunk at the preliminary and detailed drilling scale to determine the lateral and vertical variation of the coal and evaluate the potential reserve [10-17]. Sampling was done according to the thickness of the coal seam. For a coal seam whose thickness was greater than 0.3 m, samples were taken from the upper, middle and lower parts of the seam. For a seam of less than 0.3 m, channel sampling was considered. The locations of coal deposits (the studied area) are shown in Fig. 1.

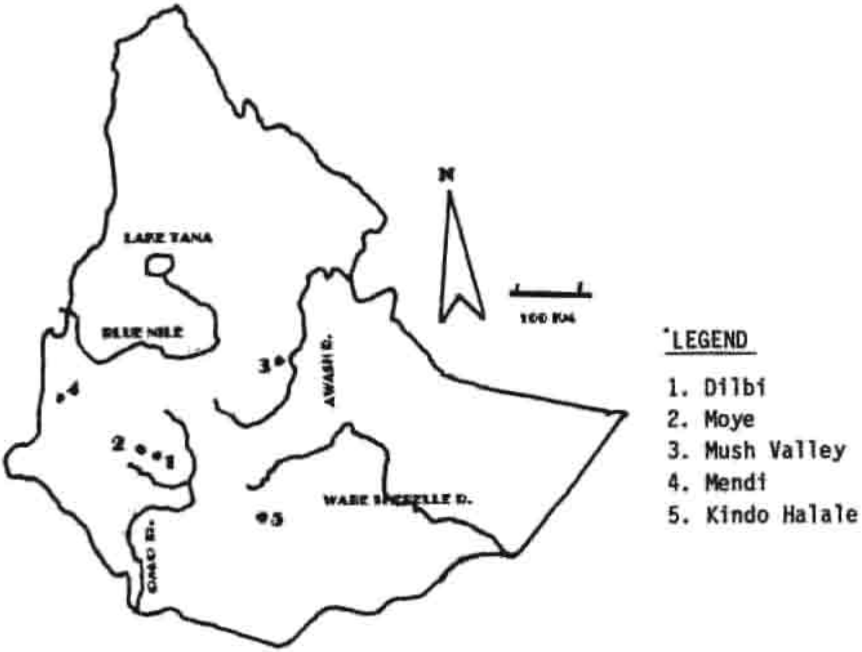

**Fig.1. Loaction of coal fields in Ethiopia.**

In all chemical determinations, coal samples were ground and pulverized to pass 200 mesh. From six consecutive measured replicates, average results were registered. *Proximate Analysis.* This method covers the determination and/or calculation of total moisture ($M_T$), volatile (V), ash (A), fixed carbon (FC), sulfur (S), phosphorus (P), chlorine ($Cl_2$) and calorific value (CV) content in coals and cokes. Proximate analysis was performed on 1 g of a coal sample using Fisher model 490 Coal Analyzer [18].

For the determination of pyrogenetic moisture, a volatile program was used at a temperature of 260°.

The total sulfur in the coal was determined by ASTM standard test method [19]. Sulfate sulfur was determined by extracting a weighed sample of coal (2 g) with dilute hydrochloric acid followed by precipitation with barium chloride and weighing as barium sulfate. Pyritic sulfur was determined by extracting a weighed sample of coal with dilute nitric acid followed by atomic absorption determination of iron in the extract as a measure of pyritic sulfur. The organic sulfur was calculated by the deduction of sulfate-and pyritic-sulfur from the total sulfur.

Phosphorus was determined spectrophotometrically using a Varian DMS 80 spectrophotometer. The stable yellow colored phosphovanadophosphate complex was measured at $\lambda = 880$ nm [20].

The gross calorific value was determined according to ASTM method [19], by burning a 0.5 - 1.1 g coal sample in oxygen in a calibrated Parr adiabatic bomb calorimeter. The gross calorific value of the coal sample was computed from temperature observations made before, during and after combustion.

The total chlorine content of coal was determined by oxidizing about 1 g of sample through combustion in a bomb with oxygen. The chlorine was absorbed in a small amount of ammonium carbonate solution and determined by a modified Volhard procedure [19].

*Ultimate analysis.* The determination of carbon and hydrogen was carried out by burning a weighed quantity of sample (100-200 mg) at 850-900° in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances.

Organic nitrogen was converted into ammonia by the Kjeldahl method. The ammonia was distilled off and determined spectrophotometrically at $\lambda = 410$ nm [21,22]. Oxygen was calculated by subtracting from 100 the sum of the percentages of carbon, hydrogen, nitrogen, sulfur, moisture and ash [23].

*Elemental analysis.* The coal or coke was ashed under standard conditions and ignited to a constant weight. Trace elements were determined by optical emission spectrometry (OES) semi-quantitatively at a confidence level of 61%. The ashed coal samples were placed in a carbon electrode and arced by a direct current on a Rank Hilger OES. Detection limits of In, La and Nb were 3, 30 and 3 ppm, respectively. All major elements, except P and Ti, were analyzed by atomic absorption spectrophotometer (Varian Spectr AA-20 model) after fusion of the ash with lithium metaborate ($LiBO_2$), and final dissolution of the melt in dilute nitric acid (1,19). Confidence level of the instrument for most of the major elements was 95%.

*TLC separation.* The coal sample from Dilbi surficial (DS), Dilbi borehole (DBH), Moye surficial (YS) and Moye borehole (YBH) was column chromatographed. The crude coal sample (0.5-1.0 g) was mixed with 3.0 g of neutral alumina (Brockman Activity I, 80-200 mesh, Fisher No. A 950) and the mixture was placed on the top of an 11 mm i.d. column containing about 9 g of $SiO_2$. The sample was eluted with the following chromatographic grade solvents: fraction-1, aliphatic hydrocarbons, 100 ml of hexane; fraction-2, neutral-polycyclic aromatic compounds (Neutral-PAC), 200 ml of benzene; fraction-3, nitrogen containing polycyclic aromatic compounds (N-PAC), 300 ml of chloroform containing 0.75% ethyl alcohol; and fraction-4, hydroxy polyaromatic hydrocarbons (HPAH), 200 ml of tetrahydrofuran containing 20% ethyl alcohol [24].

*X-ray diffraction.* Major and minor minerals were identified using an HZG-4 universal X-ray diffractometer (XRD). Coal samples were filled into holders with cavities and examined by X-rays as disordered aggregates. X-ray diffraction peak heights at 3.34, 7.15, 2.8, 2.71, 3.48, 3.03 and 7.6 Å were used as a comparative measure of the amounts of quartz, kaolinite, siderite, pyrite, mordenite, calcite and gypsum, respectively [25]. It should be noted that for determining the ratio of the minerals, the adiabatic x-ray diffraction quantitative method of Peter Kalman is advantageous when standards are not used [26].

*Programmed pyrolysis.* Samples of coal rock weighing 10 - 100 mg were placed in a crucible which itself was inserted into one of the holders of the automatic sampler carriage and was pyrolyzed at 300° for 3 min, followed by programmed pyrolysis at a rate of 25 °/min to an optimum temperature of 600°, both in a helium atmosphere. Simultaneously, the crucible which had been in the pyrolysis oven was moved to the oxidation oven. Pyrolysis takes place in three stages, during which free gaseous ($S_0$), liquid ($S_1$) and heavy ($S_2$) hydrocarbons held in the coal are volatilized and detected by means of a flame ionization detector (FID). Oxidation also takes place in two stages, during which the carbon dioxide is adsorbed and desorbed on a molecular sieve ($S_4$) and detected by the thermal conductivity detector (TCD) [27].

*Type of Kerogen.* Palynomorphs were freed from 30 g of the original coal samples by digestion with hydrochloric acid, followed by removal of silicates using hydrofluoric acid. Total content of kerogen was determined gravimetrically. After heavy liquid separation, centrifuging and sieving the unoxidised and oxidized kerogen was mounted onto the microscope slide using petropoxy resin. Then the visible solid organic matter in coals was microscopically identified using a Leitz Wetzlar microscope with a UV light which changes within yellow-black range [25,28].

*Specific Gravity.* 7 - 10 g of coal samples were dried to a constant mass in a drying oven at a temperature of 105± 5°, cooled and weighed ($m_1$). Then it was pelleted under a pressure of 40 MPa for ten minutes using a Carl Zeiss Jena Pellet Pressor. The pelleted sample was covered with liquid paraffin heated to 60 ± 3° and weighed in air ($m_2$). The paraffin covered sample was weighed under water ($m_3$) with a gravity balance. The dry density in g/cm$^3$ was calculated [29].

## RESULTS AND DISCUSSION

A review of Dilbi and Moye drilling activities and the result attained are summarized in Tables 1 and 2 [10-11].

Jimma area consists of trap volcanics and sedimentary rocks. In this area, the K/Ar ages of one basalt and rhyolite are 31 and 26 million years, respectively, and suggested the existence of volcanic sequence coeval with the Aiba and Oligocene-Alaji formation [12]. The coal bearing formations of Dilbi-Moye are interbedded between two volcanics. The probable age of Dilbi -Moye area was determined by Amoco Production Company [13] to be Oligocene-Miocene.

The fluvio-lacustrine sedimentary formation of Dilbi is composed of mudstone, siltstone, sandstone, conglomerate, carbargillite, volcanic ash beds, coal (humic and sapropelic), oilshale, ederitic beds with concretions. The formation is composed of 30% fine and 70% coarser clasts. Deposition of the sediments took place within a large asymmetrical graben controlled by NNW-SSE fault system. The sedimentary formations attain a maximum thickness of 192 m, and are characterized by fluviatile, unstable lacustrine, stable lacustrine and swampy facies.

The coal seams are interbedded in non-fossiliferous indurated mudstone, carbargillites and ash beds. The thickness of the coal seams ranges between 0.1 - 2 m. Maximum thickness of the coal seams is recorded at Legamese stream (Borehole 1 and 2). The seam thickness decreases to 0.4 m at the north and 0.3 m at the southern extremes. The coal bearing horizon at the eastern part is represented by many seams. The coal bearing formation reaches a thickness of 100 m at the western part and 50 m at the eastern part of Dilbi. Genetically, the coal seams of Dilbi are classified under humic and sapropelic litho type. In general the beds are horizontal-gentle dipping to SW (10° - 13°) [10-11]. Total reserve of humic coal in the Dilbi coal field is 3.8 x $10^6$ tons and of sapropelic coal 15 x $10^6$ tons.

Table 1. Summary of Drilling Activities and Results at Dilbi.

| Bore hole No | Total depth (m) | Borehole Elev. (m) | Depth range , Thickness (Sediment Type) | Number of Coal Seams > 0.5 m and its Depth | Bottom Edge Lithology |
|---|---|---|---|---|---|
| 1 | 264.3 | 2158.6 | 62-68 m, 6 m (MS & pebbles);<br>81-246 m, 165 m (MS, coal seams, oil shale bearing horizon; SS, silty MS) | 5 seams at 64 m, 2.2 m; 91.4-94.4 m, 3 seams (tot. thick. of 2.9 m); 109.9 -113.7 m, 2 seams (tot. thick. = 1.6 m) | basalt |
| 2 | 229.9 | 2195 | 18-22 m, 4 m (SS)<br>46-219 m, 173 m (MS,coal seams, oilshale SS, C Sh, clay) | 3 coal seams<br>50.55-51.90 m=1.35 m;<br>58.7-59.70 m=2.00 m;<br>202-204 m, 1.95 m | basalt |
| 4 | 105.2 | 2160 | 3.25-67 m, 63.7 m (oilshale, MS,clay and coal seam) | 1 seam at 69.5 m, 0.5 m thick | trachyte |
| 5 | 200.2 | 2191.9 | 23.4-174.8 m, 151.4 m (MS, oil shale, coal seam, C Sh, SS) | 1 seam at 89.5 m,0.5 m thick | basalt |
| 6 | 247.4 | 2252.4 | 158.6-234.7 m, 76.1 m (MS, coal seams, C Sh, oilshale) | 3 coal seams at 168.3 m, 0.5 m; 175-180.6 m (two seams tot. thick.= 2.1 m) | basalt |
| 7 | 283.3 | 2206.6 | 123.4-283.5 m, 160.1 m (MS,C Sh, coal seam, SS, oilshale) | 1 coal seam at 183.5 m, 0.5 m thick | mudstone |
| 8 | 297.0 | 2304.3 | 43.1 m, 5 m (C Sh,MS & SS); 57-66 m, 9 m (claystone, C Sh, MS); 82.4-98.6 m, 16.2 m (C Sh); 149-225 m, 76 m (oilshale, MS, coal seams, SS, clay stone) | 1 coal seam at 183.5 m, 0.5 m thick | basalt |
| 101 | 101.7 | 2124.0 | 21-101.7 m, 81.7 m (C Sh, oilshale, MS and coal) | 1 coal seam at= 77 m 0.55 m thick | mudstone |
| 102 | 101.6 | 2136.4 | 14-101.6 m, 87.6 m (oil shale MS, C Sh and coal seam) | 1 coal seam at =31 m, 0.52 m thick | mudstone |
| 11 | 267.1 | 2240 | 65.7-71.7 m, 6 m(MS); 98.9-102.8m, 3.9 m (MS); 119.9-243.7m, 123.8 m (MS, coal, oilshale, C Sh, silty SS) | 2 coal seams at 90-90.5 m, 0.5 m; 133.8-134.8 m, 1 m | basaltic tuff |

MS = mudstone; C Sh = Carbonaceous Shale; SS = Sandstone.

The sedimentary formation of Moye, composed of mudstones, sand stones, sandy conglomerate, carbargillites, coal (humic) and small amounts of oil shale, rests on a basaltic substratum. The sedimentary sequence is deposited in a tectonically or/and paleotopographically controlled basin and characterized by stable lacustrine, unstable lacustrine and fluviatile facies. The lower part of the sequence is deposited under unstable lacustrine environment fed by high energy fluviatile coarse clastic sediment from the rift wall. As a result of block adjustment through fault, a series of horst and graben complex were developed. The intense tectonic activities were followed by a calm period which led to the deposition of coal seams in the lacustrine facies under stable environment. Three humic coal bearing sedimentary cycles were registered at different levels of the sedimentary formation. The coal seams range between 0.5 - 2 m. Megascopically, the coal seams are characterized by vitrain, subordinated by clarian macro-litho type [11]. Total reserve of humic coal in Moye coal field is 40-50 x $10^6$ tons.

The sedimentary sequence of Mendi overlies the Precambrian basement rock and is capped by trap volcanic of 70-80 m thick. The fluviatile facies comprise alternating strata of conglomerates, sands, silts, clays, sandstone, siltstone, claystone, shale,

Table 2. Moye Drilling Activities.

| B.Hole No. and Elev.(m) | Total Depth (m) | Depth, Thickness and Sedimentary Formation | Number of Coal Seams >.5m & its Depth | Bottom Edge Lithology |
|---|---|---|---|---|
| 10<br>2015.7 | 222.2 | 10-200.4 m, 190.4 m (clay-stone, C Sh, coal seams, MS and silt stone) | 2 seams, at 63.2 m , about 1m; at 131.1 m about 1.1 m | basaltic tuff |
| 18<br>1810 | 179.72 | 36.4-156.2 m, 119.8 m (MS, C Sh.,coal, carbonaceous clay, SS and silty SS ) | 4 seams, at 58.6 m, 1.7 m; at 70.2 m, 1.8 m;at 78.1 m, 2 m; at 80.2 m , 6 m | pyroclastic rocks |
| 19<br>1917 | 278.0 | 0-278 m, 278 m (MS, C Sh, coal seam, carbonaceous clay, SS, silt stone, berccio conglomerate ) | 10 seams, at 30 m ,Φ 6 m; at 39 m, 55 m; at 81 m, 1.05 m; at 97 m, 2.3 m; at 102 m , 1 m; at 105 m, 7 m; at 126 m, 5 m; at 126 m, 5 m; at 155 m, 7 m; at 165 m, 7 m; at 171 m, 1.2 m;<br>at 195 m = 7m | basalt |
| 20<br>1745 | 106 | 18.7-93.8 m, 75.1 m (MS, silty MS, C Sh & clay) | one seam at 50 m = 0.65 m | volcanic breccia |
| 21<br>1660 | 196.2 | 6-196.2 m, 190.2 m (coal seam, C Sh, clay, MS, silt stone) | 11 seams at 6-7 m, 1 m, 8-9.4 m, 1.4 m; 59-60.6 m, 1.25 m; 5 seams at ≈60-80.85 m(0.8,0.4,0.5,0.5,2 m); 3 seams at ≈142.2-147.18 m(1.3, 0.5, 1.2 m); 2 seams at ≈160.48-168 at (0.5, 0.9 m) | basaltic tuff |

carbonaceous shale and the associated lignite seams. Genetically these lithotypes are classified under three major groups: monomictic extra-formational conglomerate, convoluted and cross-laminated fine-medium grained quartz arenite and coal bearing strata. Patches of lignite bearing sediments of distinctly continental type are confined to northern, southern and central parts of the studied area.

The coal bearing horizons are exposed at:

a) Babuleka in the stream valley of Galisa ( Gerba); two coal seams with a thickness of 0.5 m each, horizontally extend 10-12 m;

b) Ombosa Yesus (9 km SE of Mendi) coal bearing horizons exposed at the valley of Jarsa, Lega Supo, Abo Guma and Shegilla, and

c) Teyba (17 km west of Mendi) the sediment attains a thickness of 4 m, four beds of carbonaceous materials ranging between 0.3-0.8 m overlain by thick pile of basalt which facilitated the degree of carbonification [14].

The intertrappean coal bearing sedimentary formation of Mush Valley is predominantly composed of sand, sandstone, siltstone, shale, carbonaceous shale and coal seams. The succession of Mush Valley lies upon the Miocene Pliocene basaltic substratum [15]. The sedimentation took place in a structurally controlled basin. The coal bearing sedimentary formation is exposed at the banks of Mush Stream. The first seam is 1.75 m thick, and characterized by black, lustrous, conchoidal cleavage. The second seam, ranging in thickness from 1 cm - 1 m, is widely dispersed in the sedimentary formation. The surface area of the reserve is estimated to be 0.15 - 0.26 km$^2$, and the reserve to be 300,000 tons [16]. Genetically, the coal seam of Mush is grouped under humic lithotype.

The sedimentary succession of Kindo Halale is predominantly composed of terrigeneous clasts (clay and shale); volcanogenic deposits (tuffite); organo-genic carbargillite [17]. The sediment blankets an area of 1-5 km$^2$ and is characteristic of shallow basin deposit of continental type. Jelenc [16] indicates the presence of the carbonaceous sediment of Challe and Kindo valleys. A lenticular bed consisting of higher rank coal at Challe is interbedded in carbonaceous shale, which strikes 12° east and dipping west by 25-65°. The sediment of Challe Valley extends 75 m and is characterized by thin deltaic deposit. The upper bed (2-8 m thick) of carbonaceous shale with an intercalation of thin lenses of high rank coal. The lower bed is composed mainly of unconsolidated black shale. At Kindo valley, the upper part of the formation is composed of a 3 m alternating beds of shale, carbonaceous shale and 20 cm thick coal seam. The lower part of the sequence is mainly made of 1 - 2 m thick carbonaceous shale [16].

Table 3. Proximate analysis of Ethiopian coals.

| Locality | Total moisture, MT(%) | Volatile matter VM, (%) | Ash, A(%) | Fixed carbon FC(%) | Calorific value, CV Kcal/kg | Total sulfur $S_t$ (%) | $P_2O_5$ % | $Cl_t$ (%) |
|---|---|---|---|---|---|---|---|---|
| Mendi, M (Wollega) | 10.6 | 35.8 | 22.5 | 27.9 | 4025 | 2.5 | 0.2 | 1.4 |
| Mush Valley, MV (N. Shoa) | 11.4 | 32.7 | 20.4 | 31.1 | 4075 | 4.3 | 0.2 | 1.4 |
| Kindo Halale, KH (Sidamo) | 2.9 | 21.5 | 31.8 | 42.8 | 5140 | 0.4 | 0.2 | 1.4 |
| Dilbi- surficial, DS (Jimma) | 4.6 | 25.1 | 33.6 | 34.5 | 3900 | 0.7 | 0.2 | 1.5 |
| Dilbi- borehole, DBH (Jimma) | 17.4 | 20.0 | 26.6 | 35.6 | 4700 | 1.1 | 0.2 | 1.5 |
| Moye - surficial, YS (Jimma) | 3.5 | 22.5 | 43.7 | 30.1 | 3265 | 0.4 | 0.2 | 1.5 |
| Moye - borehole, YBH (Jimma) | 1.5 | 18.9 | 18.3 | 60.1 | 6900 | 0.5 | 0.2 | 1.4 |

Proximate analysis for the composite coal samples obtained from various places in Ethiopia is given in Table 3. It appears that in general Ethiopian coals are of low moisture, volatile matter and sulfur and high ash, chlorine, average fixed carbon and phosphorous contents when compared to similar rank of coals from Russia, Poland, U.K, U.S.A and Australia [30-33]. Comparing outcrop samples from Dilbi (DS) and Moye (YS) with their respective Dilbi borehole (DBH) and Moye borehole (YBH), moisture content for Dilbi increases with depth, while that of Moye decreases. This is most probably due to the type of rock, temperature gradient during coalification, the thickness of sedimentary formation and oxic environments [34]. The content of ash decreases with depth for both coals. Volatile matter content of coals decreases rather regularly with depth [35].

The content of $S_T$ (Table 3) tends to increase, but that of phosphorous and chlorine is constant with depth. When the amount of the three types of sulfur are compared with each other, sulfate-sulfur (Table 5) predominates in the outcrop and borehole samples from Dilbi and Moye.

Table 4. Ultimate analysis of Ethiopian coals (%).

| Locality | C | H | Atomic H/C | N | O | Atomic O/C | $S_T$ |
|---|---|---|---|---|---|---|---|
| M | 72.0 | 5.5 | 0.92 | 1.7 | 18.3 | 0.19 | 2.5 |
| MV | 77.0 | 5.6 | 0.87 | 1.6 | 11.9 | 0.12 | 6.7 |
| KH | 78.5 | 5.6 | 0.86 | 2.0 | 14.0 | 0.13 | 0.6 |
| DS | 74.6 | 5.9 | 0.95 | 1.9 | 17.4 | 0.18 | 0.7 |
| DBH | 81.0 | 5.5 | 0.82 | 1.7 | 10.7 | 0.10 | 1.1 |
| YS | 74.4 | 5.9 | 0.96 | 1.8 | 17.5 | 0.19 | 0.4 |
| YBH | 87.9 | 4.4 | 0.61 | 1.4 | 6.0 | 0.05 | 0.5 |

The results of the latest investigation confirmed that the carbonaceous materials are deposited on a tectonic block of 0.4-1.5 km$^2$ and are characterized by high angle dip. The organic matter of coal is a complex and multiform aggregate which includes chemical compounds of C, H, N, O and S [36]. Proportional content of these elements in coal (Table 4) is established by ultimate analysis. Elemental composition is mainly useful for classifying kerogens according to the material originally responsible for their formation and structure. Comparison of outcrop samples from Dilbi and Moye with its respective borehole shows that the content of carbon increases while that of oxygen decreases in the chemical composition of the coal. It may be explained that during the transition from sub-bituminous to high-rank coals (coking coal), the content of H and O decrease. This is because H and O are taken up by the removal of $H_20$ and $CO_2$. The content of chemical compounds of C, H, N and O for most of Ethiopian coals is in good agreement with the content of these elements for some of the foreign coals [30,32]. A very simple and rapid means of obtaining an insight into the course of the processes occurring during coalification is the atomic H/C *vs* O/C ratio (Fig. 2).

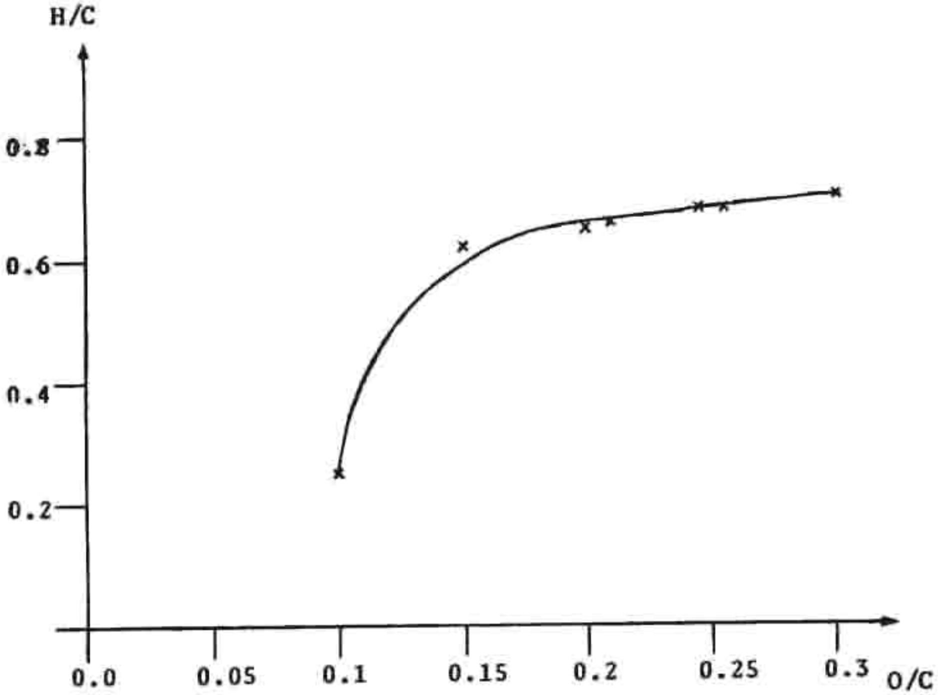

**Fig.2. Plot of Kerogen Atomic H/C vs O/C.**

In the burning of coal in boiler furnaces or in coke producers, a significant role is played by the fusibility of its ash. This quality depends mainly on its chemical composition. Increased silica or alumina content tends to raise this point, while that of iron, calcium and magnesium compounds lowers it. That is why major element analysis of coals is very essential (Table 5). When the outcrop samples from Dilbi and Moye are compared with respective boreholes, there is a trend for Ca, Fe, Mg, Mn, Ti and organic carbon contents to increase and Al, Si, compound water and organic carbon contents to decrease with depth.

There are various trace elements in coal (Table 6). Their concentration does not exceed 1%.

As shown in Table 6, contents of Ag, Ge, and Ga in studied coals can have a value of industrial significance. The presence of such elements as Be, Cu, Cr, Mo, Ni, Pb, U, V and Zn even in small amounts cause high toxicity. These trace elements are not enriched above normal abundance levels in Ethiopian coals. This presumably reflects more of lacustrine environment of coal formation.

Solvolysis or solvent extraction has always been one of the most commonly used techniques for studying the composition of a coal. Practically all organic solvents can be tried for this purpose. But as far as rapidity, reproducibility, economy and efficiency are concerned many separation schemes are hindered by incomplete chemical class separation and overlap of compound types into adjacent fractions. Therefore, for the achievement of faster analysis and better evaluation of the numerous types of coal products, improved techniques were used. These methods consume not more than 1000 ml solvent, 12 g adsorbent and need only 6 hours [37].

The resolved fractions on a plate and on a column chromatography were quantified gravimetrically. From the results displayed in Table 7, it can be concluded that with increasing depth (compare DS *vs* DBH and YS *vs* YBH) the content of extractable hydrocarbons increases, free hydrocarbons are enriched by saturates and aromatics, and polars are depleted. The maximum yield of extractable products is obtained from coal with 88% carbon and an atomic H/C ratio of 0.6 (Table 4). Beyond this rank, the yield decreases.

The chemical variations noted above are reflected in the distribution of the important mineral components kaolinite, quartz, gypsum, calcite, siderite, pyrite and mordenite (Table 8). Kaolinite and quartz abundences predominate in most coals of Mendi, Kindo Halale, Dilbi and Moye and show little variation with depth. Calcite and siderite are present everywhere. The content of kerogen increases with depth too. For Mush Valley, pyrite contents tend to be highest within the zone of minimum oil yields. So all these data show a general geochemical association with the alumino-silicate minerals.

Pyrolysis is defined as the heating of organic matter in the absence of oxygen, to yield organic compounds. Using the Rock Eval pyrolysis method, the petroleum-generative potential and thermal maturity of coals was rapidly evaluated [38]. Parameters determined by Rock-Eval III (oil show analyzer) for Dilbi coal are given in Table 9.

Higher TOC samples typically generate more pyro-products ($S_2$+$S_4$). When $S_2$ >6 mg/g, the rock has commercially exploitable accumulations, and such is the case of Dilbi coal where $S_2$> 20 mg/g. But GPI/OPI values are too low and this shows a hydrocarbon deficiency. Therefore, high values of $S_2$ and $S_4$ is due to the "false shows" which corresponds to oil and gas influxes into the coal rock during diageneses and metamorphism. It is indicated that Dilbi coal contain type III Kerogen (gas - prone) and these results were verified by atomic H/C ratios and by microscopy of the macerals of the Kerogen. For most coals $S_4/S_2 < 5$ and HI values are less than 300 mg HC/g $C_{org}$ [38]. These conditions are fulfilled for Dilbi coals. In the coal zones of Dilbi T max increases and TOC decreases. When pyro products of DBH in the coal zones are compared with that of DS, the values $S_1$, $S_2$, $S_4$, OPI and HI increase while that of T max and TOC decrease as kerogen matures.

Table 5. Major Element Analysis of Ethiopian Coals (%)

| Locality | $Al_2O_3$ | CaO | $Fe_2O_3$ | $K_2O$ | MgO | $MnO_2$ | $P_2O_5$ | $SiO_2$ | $TiO_2$ | $H_2O^a$ | $H_2O^b$ | $C_{org}$ | $CO_2$ | H | $N_t$ | $N_{org}$ | $N_{inorg}$ | $S_t$ | $S_{org}$ | $S_{pyrite}$ | $S_{SO4}$ | Cl2 | Fusibility of Ash |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M | 8.0 | 1.0 | 3.2 | 0.2 | 0.2 | 0.1 | 0.2 | 11.6 | 0.5 | 10.8 | 10.0 | 38.9 | 8.6 | 5.5 | 0.8 | 0.6 | 0.2 | 2.5 | 0.5 | 1.2 | 0.8 | 1.4 | fusible |
| MV | 4.8 | 1.4 | 3.3 | 0.2 | 0.2 | 0.2 | 0.2 | 9.2 | 0.8 | 11.4 | 9.8 | 36.7 | 11.1 | 5.8 | 0.7 | 0.6 | 0.1 | 4.3 | 1.3 | 1.7 | 1.0 | 1.4 | fusible |
| KH | 11.0 | 0.8 | 1.3 | 0.3 | 0.2 | 0.01 | 0.2 | 16.5 | 0.8 | 2.8 | 7.8 | 45.4 | 4.8 | 5.8 | 0.8 | 0.7 | 0.2 | 0.4 | 0.1 | 0.2 | 0.1 | 1.4 | medium fusible |
| DS | 8.8 | 0.4 | 0.7 | 0.3 | 0.1 | 0.01 | 0.2 | 28.8 | 0.6 | 4.7 | 5.0 | 43.5 | 5.6 | 5.8 | 1.3 | 1.0 | 0.3 | 0.7 | 0.2 | 0.2 | 0.3 | 1.5 | low fusible |
| DBH | 7.0 | 2.0 | 1.5 | 0.5 | 0.5 | 0.3 | 0.2 | 15.0 | 0.8 | 17.4 | 3.0 | 41.1 | 4.1 | 5.5 | 1.1 | 0.8 | 0.2 | 1.1 | 0.3 | 0.3 | 0.5 | 1.5 | medium fusible |
| YS | 15.0 | 0.2 | 0.7 | 0.4 | 0.2 | 0.01 | 0.2 | 28.0 | 0.8 | 3.5 | 7.2 | 32.4 | 5.1 | 5.8 | 0.8 | 0.7 | 0.2 | 0.5 | 0.2 | 0.2 | 0.1 | 1.5 | very low fusible |
| YBH | 7.1 | 0.2 | 1.0 | 0.3 | 0.3 | 0.1 | 0.2 | 8.4 | 1.0 | 1.5 | 2.4 | 47.8 | 3.5 | 4.4 | 0.8 | 0.4 | 0.2 | 0.8 | 0.2 | 0.2 | 0.2 | 1.5 | medium fusible |

$H_2O^a$ - Hydrated Moisture at 108° , $H_2O^b$ - Pyrogenetic Moisture at 260°.

Table 6. Trace Element Analysis of Ethiopian Coals ( PPM )

| Locality | $Ag^a$ | $B^b$ | $Ba^b$ | $Be^b$ | $Co^a$ | $Cr^a$ | $Cu^a$ | $Ga^b$ | $Ge^b$ | $In^b$ | $La^b$ | $Li^b$ | $Mo^a$ | $Na^a$ | $Nb^b$ | $Ni^a$ | $Pb^a$ | $Sc^b$ | $Sn^b$ | $V^a$ | $W^b$ | $Y^b$ | $Zn^a$ | $Zr^b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M | 1.5 | 180 | - | 60 | 200 | 50 | 300 | 15 | 85 | 10 | - | - | 10 | 10 | - | 100 | 20 | - | 4 | 50 | 40 | 85 | 850 | 35 |
| MV | 1.0 | 180 | - | 20 | 100 | 60 | 100 | 20 | 30 | - | - | - | 10 | 10 | - | 60 | 20 | - | 4 | 50 | 125 | 25 | 80 | 25 |
| KH | 2.0 | 180 | - | 60 | 25 | 150 | 200 | 80 | 70 | - | - | - | 30 | 50 | 30 | 100 | 60 | 10 | 25 | 56 | - | 40 | 200 | 135 |
| DS | 2.0 | 100 | - | 55 | 40 | 45 | 50 | 40 | 30 | - | 100 | - | 15 | 40 | 30 | 80 | 30 | 5 | 15 | 40 | 40 | 85 | 60 | 135 |
| DBH | 8.0 | 180 | 220 | 80 | 60 | 290 | 60 | 40 | 15 | 18 | 100 | 10 | 25 | 80 | 30 | 40 | 20 | - | 10 | 90 | 80 | 40 | 200 | 70 |
| YS | 2.5 | 100 | - | 40 | 10 | 30 | 45 | 70 | - | - | 100 | - | 10 | 40 | 20 | 35 | 35 | 10 | 20 | 40 | - | 65 | 65 | 135 |
| YBH | 3.0 | 100 | 220 | 60 | 30 | 150 | 90 | 80 | 120 | 10 | - | 20 | 20 | 80 | 40 | 80 | 50 | 20 | 30 | 60 | - | 50 | 300 | 140 |

a. Determined by Atomic Absorption Spectrophotometry. b. Determined by Optical Emission Spectrometry.

Table 7. Chemical class separation of Ethiopian coals.

| Locality | Extractable hydrocarbon mg/g | Saturates (S) % | Aromatics (A) % | Polars (P) % | Aliphatic HC % | Neutral PAC % | N-PAC % | HPAH % |
|---|---|---|---|---|---|---|---|---|
| M | 22.7 | 11.0 | 22.9 | 66.1 | - | - | - | - |
| MV | 18.8 | 13.8 | 27.7 | 58.5 | - | - | - | - |
| KH | 30.3 | 9.6 | 26.1 | 64.3 | - | - | - | - |
| DS | 50.7 | 8.6 | 19.1 | 72.3 | 8.6 | 13.3 | 42.5 | 35.6 |
| DBH | 65.5 | 12.0 | 25.2 | 62.8 | 12.0 | 27.0 | 18.4 | 42.6 |
| YS | 32.8 | 13.0 | 24.2 | 62.8 | 13.0 | 20.0 | 47.6 | 19.4 |
| YBH | 72.7 | 15.9 | 32.3 | 51.8 | 15.9 | 28.0 | 33.1 | 23.0 |

Table 8. X-ray diffraction analysis of Ethiopian coals (%).

| Locality | Kaolinite | Quartz | Gypsum | Pyrite | Calcite | Siderite | Mordenite | Kerogen |
|---|---|---|---|---|---|---|---|---|
| M | 22 | 4 | 3 | - | 1 | 2 | - | 68 |
| MV | - | 1 | 8 | 17 | 1 | 1 | - | 72 |
| KH | 25 | 6 | - | - | 0.1 | 1 | - | 68 |
| DS | 21 | 13 | - | - | 0.2 | 0.3 | - | 66 |
| DBH | - | - | - | - | 1 | 0.4 | 32 | 66 |
| YS | 32 | 15 | - | - | 0.3 | 1 | - | 52 |
| YBH | 19 | 4 | - | - | 0.4 | 1 | - | 76 |

Rank analysis of Moye coal is given in Table 10. Moye is the place where an identified coking coal field was reported. From 8 studied boreholes of Moye, 5 are in the coking coal zone, 2 in the HVBT and 1 in the SBT coal zone. This shows that in the Moye coal field the original plant accumulations from which coal is derived progressed through successive stages of coalification from sub-bituminous coal to bituminous coal and to coking coal. Coking coal is formed from LVBT and MVBT. Each classification denotes a different degree or rank in the progress of coalification. The carbon of coal, and thermal value tend to increase progressively with increasing rank [39].

Characterization of all coals in the studied areas are based on the rank analysis (Table 11). These results were obtained by the van Krevelen method or atomic ratios H/C *vs* O/C diagram (Fig. 2) of characterizing organic matter type [40].

Dilbi, Mendi, Mush Valley and Kindo Halale are sources for mixed coal containing kerogen derived from huminite and vitrinite [type III (woody) overlapping type II (herbaceous)]. Kerogen contents are highest in the borehole than the out-crop samples. Moye is a source for humic coal containing kerogen derived from inertinite type III (woody) overlapping type IV (coaly). Kerogens of coals in the studied areas have a low H/C and O/C ratio. It shows that macromolecular structures of the coal

Table 9. Pyrolysis of DS and DBH coals.

| Depth m | $S_1$ mg HC/g rock | $S_2$ mg HC/g rock | $S_s$ mg/g | $T_{max}$ * | OPI/GPI | TOC %* | HI mg HC/g $C_{org}$ | Oil & Gas Potential $(S_1+S_2)$ | Type of $C_{org}$ |
|---|---|---|---|---|---|---|---|---|---|
| 30-50 | 0.6 | 20.5 | 112 | 437 | 0.03 | 13 | 155 | 21.1 | II |
| 51-65 | 0.9 | 27.4 | 128.4 | 435 | 0.03 | 15.6 | 150 | 28.3 | II |
| 66-93 | 1.9 | 53.9 | 94.3 | 434.5 | 0.03 | 16.7 | 386 | 55.8 | III |
| 94-150 | 2.0 | 60.7 | 138.7 | 433.5 | 0.03 | 19.4 | 355 | 62.7 | III |
| 30-150 | 1.4 | 40.6 | 120.1 | 435 | 0.03 | 16 | 262 | 42 | III |
| 57 | 2.7 | 107.0 | 381.9 | 427 | 0.03 | 47.3 | 221 | 109.7 | II* |
| 89-93 | 6.0 | 137.9 | 338.6 | 431 | 0.04 | 45.8 | 300 | 143.9 | III* |
| 145-150 | 3.5 | 80.7 | 347.5 | 433 | 0.07 | 36 | 304 | 84.2 | III* |
| $\Sigma_{(av)}$ | 4.1 | 108.5 | 356 | 430 | 0.05 | 43 | 275 | 112.6 | III |
| S(o) | 1.4 | 35.6 | 47.9 | 437 | 0.07 | 7.5 | 422.4 | 37 | II |
| $\Sigma_{(av)}+S_{(o)}$ | 3 | 2 | 8 |  | 1.4 | 6 | 1.5 | 3.0 |  |

OPI = Oil Production Index; GPI = Gas Production Index; TOC = Total Organic Carbon ; HI = Hydrogen Index
* = Average Coal Zone.

Table 10. Rank analysis of Moye coal.

| Depth (m) | V M (%) daf | F C (%) daf | C V (kcal/kg) maf | Rank |
|---|---|---|---|---|
| 190 | 18.1 | 81.9 | - | LVBT |
| 162 | 21.0 | 79.0 | - | LVBT |
| 7 | 26.6 | 73.4 | - | MVBT |
| 41 | 28.0 | 72.0 | - | MVBT |
| 60 | 30.4 | 69.6 | - | MVBT |
| 71 | 28.9 | 71.1 | - | MVBT |
| 77 | 29.7 | 70.3 | - | MVBT |
| 90 | 25.1 | 74.9 | - | MVBT |
| 117 | 28.1 | 71.9 | - | MVBT |
| 141 | 23.7 | 76.3 | - | MVBT |
| 147 | 24.7 | 75.3 | - | MVBT |
| 165 | 30.3 | 69.7 | - | MVBT |
| 30 | 35 | 65.0 | 8148 | HVBTA |
| 40 | 34.9 | 65.1 | 8218 | HVBTA |
| 51 | 35 | 65.0 | 8384 | HVBTA |
| 82 | 35.8 | 64.2 | 7942 | HVBTA |
| 102 | 38.2 | 61.8 | 8169 | HVBTA |
| 105 | 33.4 | 66.6 | 7910 | HVBTA |
| 132 | 35.8 | 64.2 | 8328 | HVBTA |
| 67 | - | - | 6864 | HVBTC |
| 69 | - | - | 6941 | HVBTC |
| 63 | - | - | 5735 | SBTB |
| 80 | - | - | 5672 | SBTB |

daf = dry ash free; maf = moist ash free; SBT (B+C) = Sub-bituminous coal of rank B and C; HVBT(A,B,C) = High volatile bituminous coal of rank A, B and C; MVBT(CC) = Medium volatile bituminous - coking coal; LVBT(CC) = Low volatile bituminous - coking coal.

Table 11. Rank analysis of Ethiopian coals.

| Locality | VM(%) daf | FC(%) daf | Sp Gr (g/cc) | S (%) | CV Kcal/Kg maf | Ro (%) | C (%) | H/C | O/C | TGA % | Type* | Rank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M | 53.6 | 46.4 | 1.4 | 2.5 | 5379 | 0.42 | 70.6 | 0.70 | 0.26 | 23.1 | IIIa(H) | SBTC |
| MV | 41.3 | 58.7 | 1.3 | 2.0 | 5311 | 0.40 | 71.7 | 0.67 | 0.21 | 22.1 | IIIa(H) | SBTC |
| KH | 29.9 | 70.1 | 1.4 | 2.0 | 8900 | 1.0 | 78.1 | 0.57 | 0.19 | 30.0 | IIIb(V) | MVBT |
| DS | 35.3 | 64.7 | 1.3 | 2.2 | 6991 | 0.7 | 74.6 | 0.66 | 0.23 | 31.7 | IIIb(V) | HVBTC |
| DBH | 39.6 | 60.4 | 1.4 | 1.2 | 7361 | 0.75 | 81.0 | 0.57 | 0.12 | 21.8 | IIIb(V) | HVBTB |
| YS | 38.2 | 61.8 | 1.2 | 2.3 | 6035 | 0.5 | 74.4 | 0.68 | 0.23 | 35.0 | IIIb(V) | SBTB |
| YBH | 18.1 | 81.9 | 1.4 | 1.6 | 8950 | 1.2 | 88.2 | 0.27 | 0.09 | 18.1 | IV(inert) | CC |

* H = Huminite, V = Vitrinite.

also become increasingly aromatic with increasing rank of the coal. Vitrinitic kerogen is comparable in composition to humic and the type of hydrocarbon is mostly gaseous (gas-prone) [41]. This results from abundant contributions of higher plants and terrestrial humic material accumulated in non-marine or paralic environments [38]. Using CV, Ro, C, H/C, O/C and TGA data, Mendi and Mush Valley coals are characterized as sub-bituminous C coal with huminitic macerals (Type IIIa - gas prone). Kindo Halale, Dilbi surficial, Dilbi borehole and Moye surficial are classified as MVBT, HVBTC, and SBTB coals respectively with vitrinitic macerals (type IIIb- gas-prone).

From Tables 10 and 11, most of Moye coal is characterized as LVBT and MVBT coal (coking coal) with inertinitic macerals (type IV-gas prone). Type IV (inert) kerogen of Moye contains very little hydrogen. All coals in the studied areas have H/C less than 0.95.

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