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CHARACTERIZATION OF CANADIAN COALS BY SOLID STATE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Characterization of Canadian Coals by Nuclear Magnetic
Resonance Spectroscopy

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ABSTRACT

Apparent aromaticities of a series of Canadian coals of different rank were estimated by solid state nuclear magnetic resonance spectroscopy. The aromaticities varied from 0.57 for a lignite up to 0.86 for a semi-anthracite coal. The aromaticities correlated well with fixed carbon and oxygen content of the coals as well as with the mean reflectance of the coals. Correlations were also established between aromaticities and the H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios of the coals. Uncertainties in calculation of the hypothetical $H_{\text{aru}}/C_{\text{ar}}$ ratios, from experimental data were pointed out.

Structural parameters of the chars derived from the coals by pyrolysis at 535°C were, also, estimated. The H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios of the chars were markedly lower than those of coals. This was complemented by higher apparent aromaticities of the chars compared to the coals.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy has been used extensively in the area of coal characterization. At first only soluble materials derived from coal could be analyzed and the approach proposed by Brown and Ladner, based on ^1H NMR technique found wide application (1). The equation derived by these authors includes several assumptions. Some of these assumptions became unnecessary after ^{13}C NMR technique was introduced, i.e., the distribution of carbon can now be obtained directly. Nevertheless, the results obtained from the equation are in agreement with those obtained directly (2).

Coal as a solid substance could not be effectively studied by conventional NMR techniques. However, when the cross polarization technique (3) combined with magic angle spinning (4) was introduced into ^{13}C NMR technique a significant improvement in the resolution of the aromatic and parafinic carbon regions, was achieved. This resulted in a direct estimate of aromatic carbon content and apparent aromaticity of coal (5).

Numerous attempts to correlate the aromaticity with various parameters of coal have been reported in the scientific literature. For example, a linear correlation between the aromaticity and either volatile matter or fixed carbon content of coal was established on U.S. coals (6). This enables the coal classification to be expressed in structural terms.

Despite extensive research activities in characterization of Canadian coals, the NMR techniques attracted little attention. For example, the aromaticities of a series of Canadian coals of different rank have not yet been reported. Thus, a structural comparison of the coals can not be made. Such comparison may provide additional information on the suitability of the coals as feedstocks for various processing and utilization technologies. To fill this gap, at least partially, is the main purpose of the present study.

The present work includes estimates of several structural parameters of eleven Canadian coals of different rank (from lignite to semi-anthracite). These parameters were then correlated with data obtained from ultimate and proximate analyses. The effects of temperature on the coals' structure were also investigated. For this purpose the coals were pyrolysed according to classical Fischer assay. The residual chars were then evaluated in the same manner as the coal feedstocks. Attempts were made to elucidate the structure of coals from the changes incurred by coals during pyrolysis.

Experimental

Carbon 13 NMR spectra of solid coals and chars were obtained at 45.28 MHz on a Bruker CXP-180 NMR spectrometer by means of cross-polarization dipolar decoupling (3) and magic angle sample spinning techniques (4). A single matched 1 msec cross polarization contact was used with rf field amplitudes of 45KHz. Spin temperature alteration was used, as well as flip-back of the proton magnetization after data acquisition.

A sweep width setting of 20 KHz was employed to acquire 500 pt free induction decays, which were zero filled to 4K before Fourier transformation. Magic angle spinning was performed at 3.4KHz with Kel-F rotors of the Andrew type (7). Intensities of the aliphatic and aromatic bands were corrected for spinning side bands, assuming the 1st order high and low field sides and intensities to be the same.

The proximate analyses of coals and chars were performed on the Fischer coal analyzer model 490. The CHN 240 Perkin Elmer analyzer and Leco sulphur analyser were used for the ultimate analysis.

Sample preparation for petrographic analysis, reflectance and maceral analysis was carried out in accordance with ASTM procedures.

Pyrolysis experiments were performed in a modified Fischer assay retort which was connected directly to a volume calibrated trap, immersed in ice. The retort and its 70 g coal charge were weighed before and after each experiment. After charging, the retort was then heated (12°C/min) to 535°C and held at this temperature for 15 min; the heating was then discontinued.

Results and Discussion

Properties of Canadian coals investigated in the present work are summarized in Table 1. The proximate and ultimate analyses data are expressed on a dry ash free basis (daf). Complete analyses of the materials were published elsewhere (8). The aromaticities of the coals ($f_a = C_{ar}/C$) were obtained by direct integration of the aromatic envelope. The atomic H/C ratios for hypothetical unsubstituted aromatic nuclei (H_{aru}/C_{ar}) were calculated using the equation:

$$H_{aru}/C_{ar} = (H - 3C_{ali}/2 + O)/C_{ar}$$

where ar and ali denote atoms in aromatic and aliphatic groupings, respectively. The calculation is based on the assumption that the O atoms and half of the C_{ali} atoms are attached to an aromatic ring (9).

Aromaticity and Rank of Coals

A general concept of coal maturation and change of rank associated with this, is based on a gradual increase in aromaticity with increasing rank. Thus, the f_a values may be a useful tool in determining the rank of coals. Numerous attempts to correlate various parameters of coal with the f_a have been reviewed recently by Davidson (10). The attention is usually focused on data obtained from proximate (VM and FC contents) and ultimate (C, H and O contents and H/C ratios) analyses. Heating values and petrographic data have been of interest as well.

The O content is known to follow a trend with a change in coal rank, e.g., the O content increases with decreasing rank of coal. At the same time the f_a values increase with increasing rank. The present results show (Fig. 1) that the O content increases dramatically when f_a decreases below about 0.7 (high volatile bituminous coals down to lignites). Thus, a high O content in lignites complemented by low f_a suggests that in the direction of low rank coals, a stage of organic matter (e.g., cellulosic and humic acid structures) is approached, from which coals may originate.

The most common method to rank coals is based on data obtained from proximate analysis. The correlation between the f_a and FC of the Canadian coals investigated in this work, is shown in Fig. 2. Experimental data in the f_a range below 0.45 are not available. It was confirmed by Solomon that the f_a values for the majority of coals are larger than 0.45 (11). Present results agree with this observation. The line, when extrapolated, intersects the zero FC at f_a of about 0.2. In other words, the materials with f_a of 0.2 or less should consist mostly of VM. Surprisingly enough, the f_a of macerals derived from some U.S. coals, published recently by Ziln et al. (12), show little deviation from the extrapolated line. It is then believed that the correlation between f_a and FC of coals or materials derived from coals directly is a rather general one.

Contents of maceral, either reactive or non-reactive, have been shown to correlate with various chemical (13) as well as coal processing parameters (14). Attempts to correlate the H/C ratios with maceral composition of

Canadian coals (Table 2) yielded no correlation (8). The same was observed when the f_a was plotted versus maceral content. This is attributed to the different structure of macerals derived from coals. For example, the reactivity of vitrinites and the aromaticity from different coals is not necessarily the same. On the other hand, the mean reflectance exhibits a progressive trend with increase in f_a as it is shown in Fig. 3. The mean reflectance levels off when the f_a approaches the value of about 0.65.

Other parameters often used for determination of coal rank include contents of C and H as well as the heating value. Some correlations between f_a and these parameters were reported (10). Attempts to correlate the experimental data obtained on Canadian coals resulted in rather poor correlation.

The experimental f_a values alone reflect only qualitatively the difference in coal ranks. The spread of f_a from 0.56 for lignite and sub-bituminous coals up to 0.86 for semi-anthracite are in agreement with the range reported by Miknis et al. for a series of U.S. coals of different rank (6). The f_a for the lignite and sub-bituminous coals seem to overlap. This suggests that the NMR technique can not directly differentiate between low rank materials. The estimate of coal rank in a wide range of rank would, therefore, need some other data in addition to f_a , e.g., such as shown in Figs. 1 to 3. The ranking is, however, based often on heating value of coal, which always depends on moisture and mineral matter contents. Solid state NMR takes into consideration only the organic portion of coal while ignoring moisture and mineral matter. Therefore, two coals when compared on a dry ash free basis may be structurally very similar though having different heating values. The f_a is thus more directly related to coal structure than to rank.

Aromaticity and Structure of Coal

The generally accepted concept of a coal structure is based on an assumption of coal fragments composed of fused aromatic, heteroaromatic and naphthenic rings being linked either by methylene bridges or heteroatoms. Numerous attempts have been made to describe the structure of coal units in more exact terms. It was, for example, proposed by Gerstein et al. that the hypothetical H_{aru}/C_{ar} ratios can be used to estimate the number of fused rings and the extent of ring substitution in coal units (15). This method can, how-

ever, give only an approximate estimate. This is illustrated in Fig. 4 using coronene as an example. Thus, the $H/C(H_{\text{aru}}/C_{\text{ar}})$ ratio of the unsubstituted coronene is 0.5. Fusing additional rings in positions indicated in Fig. 4 by strong lines will increase the ring number from seven to thirteen without affecting the ratio. One can easily recognize that there is a way to add even more rings without changing the ratio. On the other hand, fusing only one additional ring to coronene in a position indicated in Fig. 4 by weak lines will decrease the ratio to 0.47.

The ratios can, also, be decreased by a substitution of hydrogens in coronene molecules. This may be accomplished in several ways, e.g., by linking two such molecules either directly or via a heteroatom. Thus, linking the two molecules by O gives the formula $C_{48}H_{22}O$ having the ratio of 0.46 as compared to 0.5 in the original species. This structure contains 93.8% C, 3.6% H and 2.6% O. The estimate of the $H_{\text{aru}}/C_{\text{ar}}$ ratio from these contents, using the above equation yields the value of 0.48.

The low $H_{\text{aru}}/C_{\text{ar}}$ ratio can be, also attained in structures containing less fused rings than in coronene. This may be achieved by a high degree of linking and H atom substitution. Then, the estimate of the number of fused rings is rather tentative.

In the series of investigated coals the $H_{\text{aru}}/C_{\text{ar}}$ and H/C ratios exhibit some trends when correlated with f_a (Fig. 5a and 5b). Thus, the decrease of both H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios with increasing f_a towards high rank coals is predictable. On the other hand contents of heteroatoms and paraffinic carbon decrease with coal rank. This diminishes chances for linking and ring substitution. The observed trends are more likely the result of increased ring polycondensation than ring substitution with increasing coal rank. The increase in the average molecular weight of coal units with increasing rank as observed by Wachowska (16) is also in favor of ring polycondensation. This suggest that complementing the trends shown in Fig. 5a and 5b by some additional data may improve merit of structural information obtained from $H_{\text{aru}}/C_{\text{ar}}$ ratios.

The extrapolation of the curves in Fig. 5a and 5b to $f_a = 1.0$ leads to an interesting observation, i.e., the extrapolated H/C and $H_{\text{aru}}/C_{\text{ar}}$ are about 0.45 and 0.25, respectively. At this level of f_a one would expect the ratios to be similar. The Pennsylvania anthracite (93.3% C, 3.0% H and 2.0% O all on daf), for which the f_a was estimated to be 1.0 (18), has similar

H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios (0.39 and 0.40 respectively). It is believed that an underestimate in the f_a values, especially at the high rank end of the coal series, may be one of the reasons for the difference. For example, the $H_{\text{aru}}/C_{\text{ar}}$ ratio of the Canmore semi-anthracite would increase from 0.40 to 0.45 if one assumes the C_{ar} content to be 90% instead of 86%, as determined experimentally. Such uncertainty in the NMR analysis is not unusual. For example, for coals having C content between 80 to 90% the f_a value of the same coal, determined by different NMR techniques was observed to differ by as much as 10% (17). Conditions of NMR analysis are also important and may affect the experimental f_a values (6).

Structural parameters obtained from determination of coal aromaticity are further affected by assumptions used in calculations of $H_{\text{aru}}/C_{\text{ar}}$ ratios. It is believed that these assumptions are becoming less valid when approaching either high or low rank coals. Thus, the probability of one O atom linking together two aromatic structures may increase with increasing coal rank. On the other hand, an important portion of O in low rank coals may be attached to paraffinic carbon.

The correlation between the H/C and $H_{\text{aru}}/C_{\text{ar}}$ shown in Fig. 6 is another confirmation of expected trends. This suggests that structural information obtained from f_a and $H_{\text{aru}}/C_{\text{ar}}$ are valid for a comparison in a series of coals. This is supported by the gradual increase of f_a from the Bienfait lignite up to Canmore semi-anthracite.

Some data for the low rank coals of the series appear to be inconsistent. The large difference in the H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios for the Poor Eagle and Eastern Blackfoot coals complemented by identical f_a is rather intricate. This may, however, be reconciled by assuming etheric groups to be predominant in the former while hydroxyl groups are attached to aromatic rings in the latter. The higher hydrogen content in the Eastern Blackfoot coal is in support of this assumption. Further, on pyrolysis of these two coals the yield of liquid hydrocarbons from the Poor Eagle Blackfoot coal was markedly higher (8). It is believed that the cleavage of etheric links is an important route leading to the liquid formation (19).

Some parameters of the coals on the high rank side of the series appear to be inconsistent as well. For example, similar H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios for Balmer and Byron Creek coals are unexpected. In view of higher volatility and markedly lower mean reflectance of the Byron Creek coal, one would expect these ratios to be higher. The content of reactive macerals in

this coal compared to that in Balmer coal is, however, lower. It was established that such macerals have both high H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios (12). The difference in maceral contents in Canmore and McIntyre coals may be responsible for almost identical $H_{\text{aru}}/C_{\text{ar}}$ ratios, though again the volatility and mean reflectance of the coals are markedly different.

Aromaticity and Structure of Chars

Properties of chars shown in Table 3 reflect the treatment to which the coal feedstocks have been subjected. For example, the loss of VM content is complemented by increased carbon and decreased hydrogen and oxygen contents in chars. In other words, the VM removed from coals is richer in hydrogen and oxygen than the chars. This is in agreement with some previous experimental observations (19). Apparent aromaticities are higher for all chars with the exception of that obtained from Balmer coal. The lower f_a of the char compared to that of the Balmer coal may be due to the deviation in the experimental technique, discussed above. The lower f_a values of the chars compared to that of coals are in line with the loss of VM and the decrease in the H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratios. Thus, the differences in properties of coals and chars are rather predictable.

The trends which might exist in the series of the chars are of interest as well. Unfortunately, only one correlation, i.e., between the VM contents of coals and chars, shown in Fig. 7, could be established. Otherwise, only qualitative observations could be made, e.g., predictable increasing yield of chars from coals with decreasing VM contents. Contents, of O change sporadically though the chars obtained from the low rank materials contained markedly larger amounts. The f_a values and H/C ratios do not exhibit any significant differences which would indicate on different chemical structures of chars. The determination of f_a values of the chars were, however, complicated by larger broadening of the aromatic envelope compared to the analysis of the coals. It is believed that this had a direct effect on the $H_{\text{aru}}/C_{\text{ar}}$ ratios.

The structure of chars is expected to differ from the structure of coals from which the chars were produced. This was confirmed by a markedly different H/C and $H_{\text{aru}}/C_{\text{ar}}$ ratio of chars and coals (Tables 1 and 3). The $H_{\text{aru}}/C_{\text{ar}}$ ratios do not show any trend in the series of the chars. Thus, a structural comparison between individual chars. This contradicts with similar H/C ratios as well as a small difference in f_a values of the chars.

Therefore, the interpretation of the data can not go beyond the comparison of the structural parameters of chars and coals. Even in such a case only qualitative information on the hypothetical parameters of the chars can be obtained. For example, the markedly lower value of $H_{\text{aru}}/C_{\text{ar}}$ of chars compared to coals indicate either an increasing ring substitution or ring polycondensation. Decreased contents of heteroatoms and C_{ali} in the chars diminish chances for ring substitution the extent of which depends on the presence of methylene and heteroatom bridges. The low $H_{\text{aru}}/C_{\text{ar}}$ ratios of the chars especially those obtained from bituminous coals are more likely the result of the presence of large polycondensed structures. This suggests that the number of fused aromatic rings in the non-volatile portion of coal is significantly larger than that in the VM assuming that the chemical structure of the non-volatile matter changed little during the coal treatment. Such a qualitative observation of the hypothetical structures of chars appears to be valid despite uncertainties in the $H_{\text{aru}}/C_{\text{ar}}$ estimates, mentioned above. Thus, the markedly lower $H_{\text{aru}}/C_{\text{ar}}$ ratios of chars compared to coals are always complemented by lower H/C ratios and higher f_a of the chars.

CONCLUSIONS

The range of the apparent aromaticities of the series of Canadian coals investigated in the present work agree well with that determined for U.S. coals. The f_a correlate well with some parameters used for coal ranking, e.g., fixed carbon, oxygen content and mean reflectance.

In a series of coals the predictable trends such as decrease of the hypothetical $H_{\text{aru}}/C_{\text{ar}}$ and H/C ratios and the increase of f_a with increasing coal rank, were confirmed. It was proposed that the increased level of aromatic rings fusion is responsible for the observed trends.

Chemical compositions of chars produced by pyrolysis of the coals at 535°C are markedly different than those of the coal feedstocks, e.g., higher f_a values, lower $H_{\text{aru}}/C_{\text{ar}}$ and H/C ratios. This is again attributed to a higher average number of fused aromatic rings in char units compared to that in coal units. The results were not consistent enough to draw any conclusions on the structure of individual chars. This was explained in terms of known uncertainties in obtaining accurate data by the NMR technique.

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Table 1 - Properties of Coals, daf

Coal	Rank	FC	C	H	O	fa	H/C	H _{aru} / Car
Canmore	sa	86.0	91.4	4.1	1.8	0.86	0.55	0.40
Balmer	m vb	77.3	90.1	4.9	3.0	0.80	0.66	0.47
McIntyre	m vb	79.3	90.4	4.7	2.8	0.77	0.62	0.39
Byron Creek	m vb	69.7	85.7	4.9	7.7	0.74	0.69	0.49
Devco	h vb	61.4	87.3	6.1	5.6	0.69	0.83	0.60
Prince	h vb	57.1	80.0	5.6	5.9	0.71	0.83	0.65
Coal Spur	h vb	59.0	79.5	5.1	14.0	0.67	0.76	0.61
Shauhnessey	h vb	56.2	76.1	5.4	15.6	0.65	0.85	0.74
Poor Eagle Blackfoot	sb	51.3	69.5	5.0	23.0	0.58	0.86	0.83
Eastern Blackfoot	sb	48.0	70.8	5.8	21.3	0.58	0.99	1.00
Bienfait	1	51.6	72.6	5.3	20.2	0.57	0.80	0.77

sa - semi-anthracite

m vb - meduim volatile bituminous

h vb - high volatile bituminous

sb - sub-bituminous

1 - lignite

Table 2 - Maceral Composition of Coals

Coal	Vitrinite	Exinite	Semi-		Micrinite	Mean Reflectance
			Fusinite	Fusinite		
Canmore	67.3	0.0	28.4	3.6	0.7	2.12
Balmer	52.6	0.0	38.8	7.4	1.2	1.38
McIntyre	50.0	0.0	38.4	8.8	2.8	1.49
Byron Creek	35.3	3.2	53.0	4.5	4.0	0.93
Devco	79.5	7.1	4.3	3.4	5.7	0.93
Prince	79.2	5.8	7.7	4.3	3.0	0.67
Coal Spur	70.3	3.0	13.9	7.5	5.3	0.57
Shauhnessy	89.7	3.1	1.8	2.6	2.8	0.50
Poor Eagle Blackfoot	89.8	1.0	4.6	3.2	1.4	0.48
Eastern Blackfoot	87.6	2.6	5.2	3.0	1.4	0.49
Bienfait	81.4	5.2	7.4	1.8	4.2	0.40

Table 3 - Properties of Chars, daf

Coal	Yield	VM	C	H	O	fa	H/C	H _{aru} /Car
Canmore	95.7	9.5	93.1	3.8	.8	.87	.48	.35
Balmer	93.6	11.8	91.3	3.7	3.4	.78	.50	.24
McIntyre	96.3	12.2	93.1	3.8	1.1	.83	.49	.29
Byron Creek	91.0	17.4	90.8	3.3	3.6	.88	.47	.34
Devco	85.8	12.1	91.8	3.5	1.8	.83	.45	.26
Prince	87.5	14.8	88.1	3.2	4.1	.79	.47	.20
Coal Spur	89.6	18.3	90.6	3.6	4.5	.84	.47	.33
Shauhnessey	87.9	19.6	86.4	3.7	7.1	.86	.47	.46
Poor Eagle Blackfoot	66.5	26.1	75.1	3.2	19.8	.78	.52	.49
Eastern Blackfoot	68.6	24.5	75.4	3.1	19.5	.79	.49	.47
Bienfait	65.3	20.9	83.5	3.2	11.0	.77	.46	.28

FIGURE CAPTIONS

Fig. 1 - Oxygen content in coals versus f_a of coals

Fig. 2 - Fixed carbon (FC) of coal versus f_a of coals

Fig. 3 - Mean reflectance of coals versus f_a of coals

Fig. 4 - Effects of fusion of additional aromatic rings to coronene molecules on the H_{arU}/C_{ar} ratio

Fig. 5 - Correlations between H_{arU}/C_{ar} (5a) and H/C (5b) and f_a , respectively

Fig. 6 - Correlation between H/C and H_{arU}/C_{ar} of coals

Fig. 7 - Content of volatile matter (VM) of coal versus that of chars











