The Nature of Athabasca Tar Sand (Canada) and Tar Sand Derivatives. A Comparison with Coal-hydrogenolysis Products

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(Received September 21, 1978)

Solvent extracts of Athabasca tar sand were analyzed by the Brown-Ladner method, the Takeya *et al.* method, and the Speight method on the basis of the ^{1}H-NMR data and by ^{13}C-NMR spectroscopy. The structural characteristics of Athabasca tar sand derivatives were also compared with those of coal-hydrogenolysis products. The results show that the structural characteristics of hexane solubles, monomers consisting of one aromatic ring substituted highly with C_6 aliphatic chains, resemble those of the oil fraction produced during the initial stage of the hydrogenolysis of Taiheiyo coal. However, the structural characteristics of the hexane insoluble-benzene solubles, oligomers consisting of 2 aromatic rings substituted highly with C_{4-5} aliphatic chains, are different from those of any coal-hydrogenolysis products. In addition, the close agreement between the f_a value obtained by the Brown-Ladner method and ^{13}C-NMR may indicate that, for solvent extracts of Athabasca tar sand, the assumption in the Brown-Ladner method that the atomic H/C ratio of aliphatic structures is 2 is proper.

From the standpoint of developing alternative resources to petroleum, studies of the chemical structures of coal, tar sand bitumen, and shale oil have been carried out with the view of utilizing these materials as raw material for energy. Studies of the chemical structure of tar sand bitumen have been carried out by the Speight method[2-5] using the data of ultimate analysis, ^{1}H-NMR, and molecular weight. The present authors have previously studied coal-hydrogenolysis products[6-9] using the Brown-Ladner method[10] and the Takeya *et al.* method,[11] which determined the structural parameters for structural units from the data of ultimate analysis and ^{1}H-NMR. Therefore, in the present investigation solvent extracts of Athabasca tar sand were analyzed by the Brown-Ladner method and the Takeya *et al.* method, and the results were compared with the chemical structures of coal-hydrogenolysis products. The aromaticity(f_a) determined by ^{13}C-NMR analysis was compared with the value obtained on the basis of the Brown-Ladner method. The Speight method is also discussed.

Experimental

Solvent Separation. As solvents, hexane and benzene used in the separation of coal-hydrogenolysis products[8,9] were adopted. A portion of about 10—20 g of tar sand was weighed accurately and they extracted with 5 vol of hexane per weight of tar sand. The solution was filtered after it had been stirred for 1 h at room temperature. The residue was again extracted with hexane in the same manner as the first extraction. The yield of hexane solubles (oil) was defined as the sum of the yields of the two hexane extractions. The hexane-insoluble residue was extracted with benzene in the same manner as in the hexane extraction. The yield of the hexane insoluble-benzene solubles (asphaltene) was obtained as the sum of two benzene extractions. Bitumen prepared from tar sand at the Research Council of Alberta was also separated in the same manner as the tar sand.

Analysis of the Hexane Solubles and the Hexane Insoluble-Benzene Solubles. The ultimate analysis,[8,9] ^{1}H-NMR analysis (solvent:$CDCl_3$),[8,9] ^{13}C-NMR analysis(solvent:$CDCl_3$),[12] molecular-weight determination (solvent:$CHCl_3$),[8,9] GPC (solvent:THF),[8] and determination of the hydroxyl-group content by trimethylsilylation[13] were carried out on both fractions in the manners previously reported.[8,9,12,13]

Results and Discussion

The yields of the hexane solubles and the hexane insoluble-benzene solubles are 9.5—10.3% and 2.0—2.2% respectively on the basis of tar sand, and the yield of bitumen is 11.5—12.5%. Consequently, the yields of the hexane solubles and the hexane insoluble-benzene solubles are 82.4—82.6% and 17.4—17.6% respectively on the basis of bitumen. The yield of benzene-insoluble matter, namely sand, is 87.6—88.5% on the basis of tar sand. The ash content of tar sand determined by high-temperature ashing techniques (815 °C) is 87.2%, which is almost equal to the yield of benzene-insoluble matter. These results indicate that the sand obtained here does not contain any organic matter. This fact was confirmed by the TGA of the benzene-insoluble matter. The weight loss of benzene-insoluble matter up to 800 °C is 0.2%.

The data on the ultimate analysis of hexane solubles and the hexane insoluble-benzene solubles are shown in Table 1, along with the data for the coal-hydrogen-

Table 1. Elementary analysis (%)

	C	H	O	N	S
Tar sand					
Hexane solubles	83.9	11.3	0.7	1.1	4.2
Benzene solubles	80.5	9.0	3.4	0.9	7.8
Tar-sand bitumen[a]					
Hexane solubles	84.4	11.4	0.5	1.8	4.2
Benzene solubles	80.4	8.5	2.3	1.0	8.1
Coal-hydrogenolysis products (Taiheiyo coal)					
Hexane solubles	86.4	9.2	3.5	0.7	0.2
Benzene solubles	86.5	6.7	5.0	1.8	0.2

a) This sample was obtained from the Research Council of Alberta.

Table 2. Chemical structure of Athabasca tar-sand bitumen (Brown-Ladner method)

	Hydrogen distribution			Structural parameter							
	H_a	H_α	H_o	f_a[c]	f_a	σ	H_{au}/C_a	H_o/H_α	M_n[d]	M_v[e]	M_v/M_n
Tar sand											
Hexane solubles	0.057	0.166	0.777	0.25	0.24	0.69	1.07	4.9	320	440	1.4
Benzene solubles	0.082	0.202	0.716	0.37	0.39	0.68	0.86	3.5	320	2130	6.7
Tar-sand bitumen[a]											
Hexane solubles	0.049	0.156	0.794	0.26	0.23	0.67	1.07	5.1	330	410	1.2
Benzene solubles	0.101	0.178	0.721	0.44	0.43	0.65	0.79	4.1	360	2250	6.3
Coal-hydrogenolysis products[b]											
Hexane solubles											
Oil(S_1) Taiheiyo coal	0.05—0.13	0.15—0.18	0.69—0.79		0.25—0.40	0.50—0.69	0.90—1.00	3.8—5.2	270—350	220—260	0.7—1.0
Oil(S_1) Oyubari coal	0.15—0.21	0.24—0.29	0.50—0.60		0.42—0.57	0.44—0.50	0.76—0.97	1.7—2.4	260—280	280—300	1.0—1.1
Oil(S_2) Taiheiyo coal	0.15—0.28	0.32—0.34	0.39—0.42		0.57—0.62	0.40—0.45	0.81—0.88	1.2—1.3	190—220	220—260	1.0—1.3
Oil(S_2) Oyubari coal	0.25—0.30	0.31—0.35	0.37—0.40		0.60—0.65	0.38—0.45	0.79—0.84	1.1—1.3	190—230	260—280	1.2—1.5
Benzene solubles											
Taiheiyo coal	0.34—0.39	0.30—0.36	0.30—0.33		0.67—0.71	0.38—0.41	0.77—0.90	0.8—1.0	160	420—470	2.9
Oyubari coal	0.29—0.36	0.30—0.32	0.34—0.40		0.66—0.71	0.39—0.44	0.64—0.75	1.0—1.3	260	490—830	3.2

a) This sample was obtained from the Research Council of Alberta. b) Quoted from the papers of Yoshida *et al.* (1974, 1976):[8,9] Coal → Oil(S_1); Coal → Asphaltene → Oil(S_2)

c) Calculated from the data of ^{13}C-NMR. d) Weight of the average structural unit calculated numerically from the value of the structural parameter. e) Molecular weight determined by vapor-pressure osmometry.

Table 3. Comparison of the results obtained by the Speight method with the results obtained by the Brown-Ladner method

	R_a[b]	R'_a[c]	C_{sa}/C_p	σ	C_s/C_{sa}	H_o/H_α	C_p/C_a	H_{au}/C_a	*M.W.*
Hexane solubles	1.2—1.4	*ca.* 1.2—1.4	0.59—0.61	0.67—0.69	5.7—6.2	4.9—5.1	0.89—0.94	1.07	410—440[d]
Oil (Speight, 1970)[a]	1.4		0.58		4.7		0.92		424[e]
Benzene solubles	10.9—15.3	*ca.* 13.4	0.47—0.55	0.63—0.68	4.5—5.1	3.5—4.1	0.56—0.64	0.79—0.86	2130—2250[d]
Asphaltene (Speight, 1970)[a]	57.4		0.52		4.8		0.40		5489[e]
									(2492)[f]

a) Quoted from the paper of Speight (1970).[2] b) Aromatic rings per molecule: $(C_i+2)/2$. c) Aromatic rings per molecule: calculated from H_{au}/C_a and M_v/M_n. d) Solvent: chloroform. e) Solvent: benzene. f) Quoted from the paper of Boyd *et al.* (1962).[16]

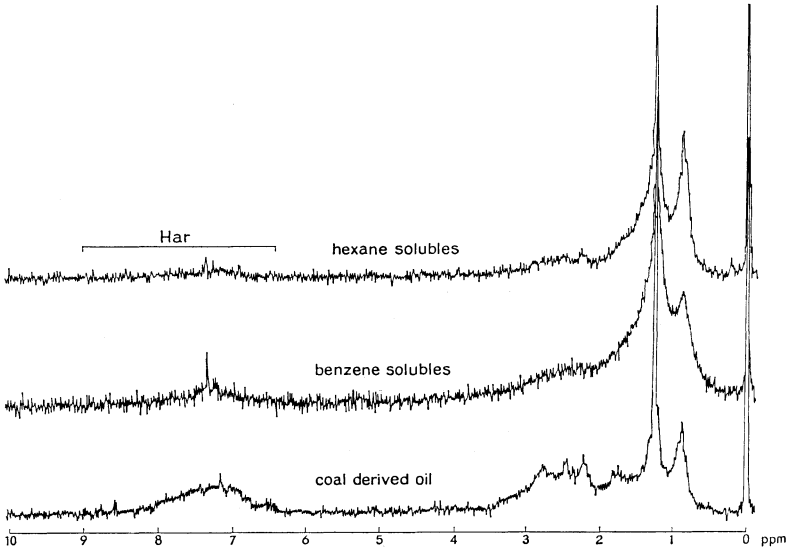

Fig. 1 ^{1}H-NMR spectra of tar sand extracts and coal-hydrogenolysis product.

olysis products. For both fractions of tar sand, the carbon content is lower and the hydrogen content is higher than those of the coal-hydrogenolysis products. The most remarkable differences in ultimate composition between the tar-sand derivatives and the coal-hydrogenloysis products is that the oxygen content of the coal-hydrogenolysis products is higher, while the sulfur content of the tar-sand derivatives is higher. The hydroxyl oxygen content of tar-sand bitumen is 0.3%, lower than that of the coal-hydrogenolysis products(1.1—3.3%).[8] In Figs. 1 and 2 the spectra of the ^{1}H-NMR and ^{13}C-NMR of tar-sand derivatives are compared with those of coal-hydrogenolysis products. In Table 2 the hydrogen distributions determined by means of ^{1}H-NMR, the structural parameters calculated on the basis of the Brown-Ladner method and ^{13}C-NMR, the weights of the average structural units calculated from the values of the

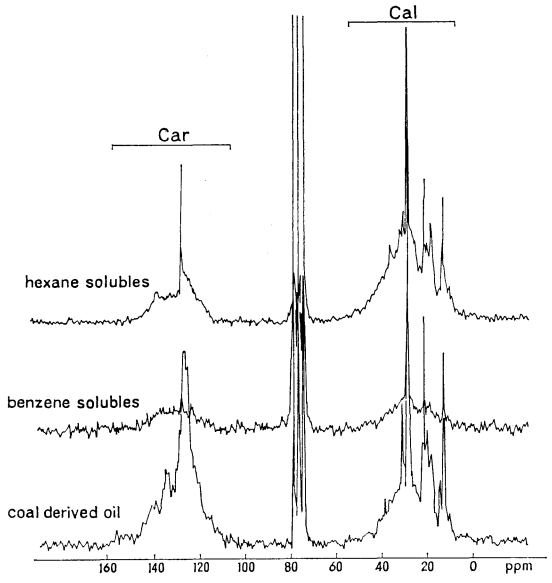

Fig. 2. ^{13}C-NMR spectra of tar sand extracts and coal-hydrogenolysis product.

structural parameters(M_n), and the molecular weights determined by the vapor-pressure osmometry(M_v) of tar-sand derivatives are compared with those of coal-hydrogenolysis products. Regarding the hexane solubles, the aromaticity(f_a) is low, and the f_a values based on the Brown-Ladner method and on ^{13}C-NMR agree closely. The measure of the substitution of the aromatic system(σ) is high, the size of the aromatic rings in the structural unit is 1 ring (H_{au}/C_a : 1.07), and the measure of the aliphatic chain length (H_o/H_α) is about 5, which means that the length of the aliphatic chain is C_6. The molecular weight(M_v) is 410—440, and the degree of polymerization(M_v/M_n) is 1.2—1.4. This shows that hexane solubles consist mostly of monomers. These structural characteristics resemble those of Oil(S_1) from Taiheiyo coal. They are however, different from those of Oil(S_1) from Oyubari coal(C:85.6%), which is of a higher rank than Taiheiyo coal(C : 76.9%), from those of Oil(S_2), and from those of benzene solubles, Asphaltene(R). The following reaction scheme for coal hydrogenolysis has been proposed:[14,15]

$$\text{Coal} \begin{cases} \nearrow \text{Oil}(S_1) \\ \searrow \text{Asphaltene(R)} \longrightarrow \text{Oil}(S_2) \end{cases}$$

Oil(S_1) is the product produced during the initial stage of coal hydrogenolysis. Oil(S_2) is the product produced through the reaction of Coal→Asphaltene(R)→Oil(S_2). Regarding the hexane insoluble-benzene solubles, f_a is higher than for hexane solubles, while the f_a values based on the Brown-Ladner method and on ^{13}C-NMR agree closely. The size of the aromatic rings is larger(about 2 rings, H_{au}/C_a: 0.76—0.86), H_o/H_α is smaller, and M_v and M_v/M_n are much larger than those for the hexane solubles. This is also obvious from the GPC chromatogram in Fig. 3. The structural unit of this fraction resembles Oil(S_1) from Oyubari coal as to f_a and H_{au}/C_a, but compared with Oil(S_2) and Asphaltene(R) f_a is much lower and H_o/H_α is much larger. M_v and M_v/M_n are much larger than those of coal-hydrogenolysis products.

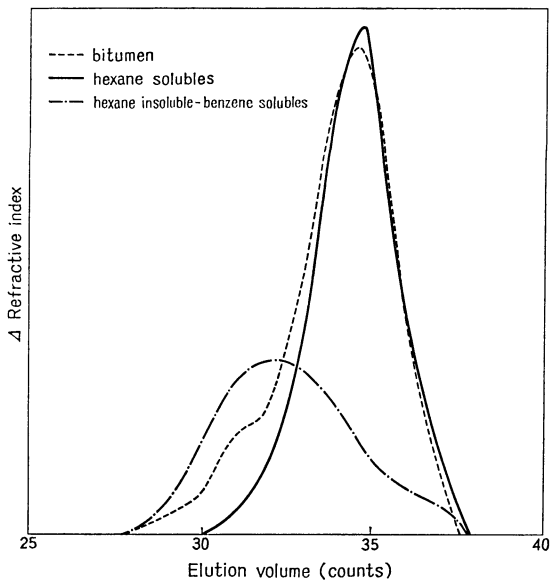

Fig. 3. GPC chromatograms of tar-sand extracts.

This fraction is an oligomer(M_v/M_n: 6.3—6.7) consisting of 2 aromatic rings substituted highly with the C_{4-5} aliphatic chain. In Table 3, a comparison of the results obtained by the Speight method with the results obtained by the Brown-Ladner method is shown. Theoretically, R_a, C_{sa}/C_p, C_s/C_{sa}, and C_p/C_a in the Speight method have the same meaning as R_a'(aromatic rings per molecule, they can be calculated from the values of H_{au}/C_a and M_v/M_n), σ, H_o/H_α, and H_{au}/C_a respectively. Comparing the analytical results obtained by the two methods, R_a and R_a', and C_s/C_{sa} and H_o/H_α, agree precisely, but C_{sa}/C_p and σ, and C_p/C_a and H_{au}/C_a, differ slightly. This may be due to the lack of consideration of heteroatoms in the Speight method. Comparing the present data with Speight's data[2] obtained by the Speight method for the hexane solubles, similar values for molecular weight and R_a are obtained. However, for the hexane insoluble-benzene solubles the molecular weights are remarkably different from each other. There is also a large difference between the values of R_a. The present data on the molecular weight of the hexane insoluble-benzene solubles(2130—2250) agree closely with the data of Boyd *et al.*(2492).[16] The value of R_a in the Speight method varies with the value of the molecular weight according to $R_a=(C_i+1)/2$, where C_i is a function of the molecular weight. In addition, the close agreement between the f_a values obtained by the Brown-Ladner method and by ^{13}C-NMR may indicate that, for Athabasca tar-sand derivatives, the assumption in the Brown-Ladner method of 2 for the atomic H/C ratio of aliphatic structures is correct.

The authors are grateful to Dr. Yosuke Maekawa of the Government Industrial Development Laboratory, Hokkaido, for samples, and would like to thank Prof. D. M. Bodily of the University of Utah for his helpful discussion.

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