Studies on Constituents of Coal Carbonization Light Oil. I. On Saturated Hydrocarbons Contained in High-temperature Coal Carbonization Light Oil

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Constituents and their contents of coal carbonization light oil, are influenced by their carbonization temperature. It has been reported, that components contained in high-temperature coal carbonization light oil differ from those in low-temperature coal carbonization light oil, qualitatively and quantitatively[1,2]. Apparently, such constituents of low-temperature coal carbonization light oil are mainly saturated hydrocarbons and less aromatic and unsaturated hydrocarbons. By contrast, those of high temperature coal carbonization light oil are mainly aromatic and less saturated and unsaturated hydrocarbons. In the studies on the constituents of high-temperature coal carbonization, nearly all the aromatic hydrocarbons contained in the light oil have been determined[3-5]. But the saturated hydrocarbons in the light oil are not present in any large quantity, but separation of these saturated hydrocarbons is difficult, resulting data of such separation being scanty. Saturated hydrocarbons contained in the light oil, previously reported, are *n*-heptane[6-8], octane[9], *n*-decane[10,11] as *n*-paraffin, and 2, 2, 4-trimethylpentane[6,7] and 3-ethyl-3-metylpentane[12] as isoparaffin, and cyclopentane[10], methylcyclopentane[8,10] cyclohexane[7,8,10], methylcyclohexane[10], 1, 2-, 1, 3- and 1, 4-dimethylcyclohexane[10], 1, 3, 5-[13] and 1, 2, 4-trimethylcyclohexane[14] and 1, 2, 4, 5-tetramethylcyclohexane[13] as cycloparaffin. While, the presence of *n*-decane, *n*-undecane and 1, 2, 3, 4-tetramethylcyclohexane in solvent naphtha produced from Yawata Iron & Steel Co., Ltd. in 1949, has been already ascertained by S. Kimura and the author[15]. In this research, the author has ascertained and identified the saturated hydrocarbons contained in benzene[16,17], toluene[17,18] and solvent naphtha fractions[19,20] separated from high-temperature coal carbonization light oil (carbonization temperature, 1250°C) of Yawata Iron & Steel Co., Ltd. in 1952.

Experimental

Materials. — Crude Saturated Hydrocarbon Oil Obtained from Benzene Fraction.—A residual oil after chlorination of benzene fractiton (b. p. 79.5~81°C) at Nihon Kayaku Co., Ltd., which is colorless oil and has $d_4^{20}=0.7755$ and $n_D^{20}=1.444$, was used as material.

Toluene Fraction.—Toluene fraction purified by treatment with conc. sulfuric acid, manufactured by Yawata Iron & Steel Co., Ltd. in January, 1952, a colorless oil of b. p. 110.3~111.2°C, $d_4^{20}=0.8633$ and $n_D^{20}=1.493$, was used as material.

Solvent naphtha.—Solvent naphtha prepared at Yawata Iron & Steel Co., Ltd. in January, 1952, consisting of 17.8% of 10°-xylene (136~142°C fraction), 40.5% of solvent naphtha I (125~172°C fraction) and 41.7% of solvent naphtha II (149~203°C fraction) in proportion to each rate of production, a pale yellow oil of $d_4^{20}=0.8698$ and $n_D^{20}=1.496$, was used as material.

Separation of Saturated Hydrocarbon Oil in the Materials.—Saturated Hydrocarbons Contained in Benzene Fraction.—As benzene was expected to be contained in the material from its physical constants, 500 ml. of it was shaken vigorously with the mixture of 50 ml. of conc. nitric acid ($d_4^{20}=1.42$) and 100 ml. of conc. sulfuric acid ($d_4^{20}=1.84$); and aromatic hydrocarbons were removed. The residual oil was washed by water, neutralized with 10% sodium hydroxide solution, rewashed similarly and dried with calcium chloride to obtain 433 ml. of

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crude saturated hydrocarbon, which has b. p. 85∼105°C, $d_4^{20}=0.7711$ and $n_D^{20}=1.430$. Now 300 ml. of this oil was submitted to fractional distillation with metallic sodium and 120 ml. of 78∼90°C fraction ($d_4^{20}=0.8059$, $n_D^{20}=1.458$), and 150 ml. of 90∼103°C fraction ($d_4^{20}=0.7290$, $n_D^{20}=1.406$) were obtained. But, in the 78∼90°C fraction, residual benzene was still expected from its physical constants and ultraviolet spectrum[17]. The residual benzene in this fraction, therefore, was again removed with a mixture of conc. sulfuric acid and conc. nitric acid, and the residual oil and 90∼103°C fraction were fractionated by Podbielniak distillation equipment, and 4 per cent by weight of 78∼90°C fraction ($d_4^{20}=0.7067$, $n_D^{20}=1.398$) and 96 per cent by weight of 96∼100°C fraction ($d_4^{20}=0.7170$, $n_D^{20}=1.405$), were obtained.

Saturated Hydrocarbons Contained in Toluene Fraction.—In an iron-pot provided with a stirrer, toluene contained in 169 kg. of toluene fraction, was extracted with 361.7 kg. of conc. sulfuric acid and 2.1 kg. of crude saturated hydrocarbon oil, and about 1.2% by weight of toluene fraction was obtained. Residual toluene in 756 g. of this oil was again removed completely with conc. sulfuric acid. 709 g. of saturated hydrocarbon oil, amounting to about 1.1% of toluene fraction, was obtained. This oil was distilled with metallic sodium and 120∼126°C fraction, which has $d_4^{20}=0.7234$ and $n_D^{20}=1.406$, was obtained.

Saturated Hydrocarbons Contained in Solvent Naphtha.—In an iron-pot provided with a stirrer, aromatic hydrocarbons contained in 200 kg. of the material, were extracted four times with conc. sulfuric acid (total of 197.34 kg.), and 6.44 kg. of crude saturated hydrocarbon oil, was obtained. Moreover, the residual aromatic hydrocarbon in 760 g. of this oil was removed with conc. sulfuric acid repeatedly and 708 g. of saturated hydrocarbon oil, amounting to about 3% by weight of the material, was obtained. This oil has b. p. 132∼198°C, $d_4^{20}=0.7632$ and $n_D^{20}=1.425$. 616 g. of this oil was submitted to the fractional distillation with metallic sodium and six fractions shown in Table I, were obtained.

Total of 118∼147°C and 147∼161°C fractions were fractionated by Podbielniak distillation equipment, and five fractions shown in Table II were obtained.

Moreover, total of 155∼162°C fraction in Table II and 161∼172°C, 172∼177°C fractions in Table I, were fractionated and three fractions shown in Table III were obtained.

Analyses were carried out on the main fractions of 143.5∼155°C in Table II and of 165∼174°C in Table III.

TABLE I. FRACTIONS OBTAINED BY FRACTIONAL DISTILLATION OF 616 g. OF 132∼198°C FRACTION

Frac. °C	g.	d_4^{20}	n_D^{20}
118∼147	126	0.7492	1.419
147∼161	180	0.7551	1.421
161∼172	97	0.7629	1.424
172∼177	73	0.7705	1.428
177∼184	54	0.7749	1.431
184∼	—	0.7889	1.439

TABLE II. FRACTIONS OBTAINED BY FRACTIONAL DISTILLATION OF A TOTAL OF 118∼147°C AND 147∼161°C FRACTIONS

Frac. °C	g.	d_4^{20}	n_D^{20}
111.5∼132.5	19	0.7368	1.412
132.5∼139	20	0.7461	1.416
139 ∼143.5	8	0.7486	1.416
143.5∼155	156	0.7502	1.418
155 ∼162	28	0.7605	1.422

TABLE III. FRACTIONS OBTAINED BY FRACTIONAL DISTILLATION OF A TOTAL OF 155∼162°C IN TABLE II AND 161∼172°C, 172∼177°C FRACTIONS IN TABLE I

Frac. °C	g.	d_4^{20}	n_D^{20}
145∼147	7.5	0.7571	1.420
147∼165	36	0.7596	1.422
165∼174	83	0.7643	1.425

Identification of *n*-Paraffin.—*n*-Paraffin was isolated by means of urea adduct[21]. According to an estimation *n*-paraffin contained was about 30% in each fraction. It was added to urea (about 4 mol.) moistened with methanol (about 1 mol.). The suspension was stirred for 30 min. at 25°C and filtered, removing unreacted oil. The mixture of urea adduct and residual urea, were washed with anhydrous ether, which was removed under reduced pressure, and decomposed with water, and oil (*n*-paraffin) was obtained. And, unreacted oil was added to urea moistened with methanol, and treated as mentioned above, repeatedly until oil (*n*-paraffin) was no longer obtained by decomposition with water of urea adduct.

78∼90°C and 96∼100°C Fractions.—These fractions were treated as mentioned above, but oil was not obtained by decomposition with water of the urea adduct[17], suggesting difficulty by means of urea adduct, to separate *n*-paraffin expected to be contained in these fractions as stated by Kuwata and co-workers previously[22].

TABLE IV. ISOLATION OF *n*-PARAFFINS BY MEANS OF UREA ADDUCTS IN 120°∼126C, 143.5∼155°C AND 165∼174°C FRACTIONS

Frac.		Oil isolated by means of urea adduct				Residual oil	
°C	g.	g.	% for frac.	b. p. °C	d_4^{20}	g.	% for frac.
120 ∼126	100	30	30	124∼125.5	0.7035	51	51
143.5∼155	30	7.6	25	149∼151	0.720	18	60
165 ∼174	30	12	40	165∼178	0.7306	12	40

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120～126°C[18], 143.5～155°C[19] and 165～174°C[20] Fractions.—*n*-Paraffin contained in the three fractions were isolated by means of urea adduct and the result was shown in Table IV.

Oil Isolated by Means of Urea Adduct in 120～126°C Fraction. — Physical constants (Table IV) of this oil are identical with those of *n*-octane[23] (b. p. 125.6°C, $d_4^{20}=0.703$, $n_D^{20}=1.397$). IR spectrum bands[18] (wavelengths; 7.68, 7.87, 8.16, 8.33, 8.8, 9.27, 9.65, 9.95, 10.34, 10.92, 11.4, 11.84, 12.6, 13.08, 13.32, 13.85 μ) of this oil are analogous to those of *n*-octane.

Oil Isolated by Means of Urea Adduct in 149～151°C Fraction.—Physical constants (Table IV) of this oil are identical with those of *n*-nonane[23] (b. p. 150.7°C, $d_4^{20}=0.718$, $n_D^{20}=1.406$) and IR spectrum bands[19] (wavelengths; 7.67, 7.94, 8.22, 8.41, 8.81, 9.2, 9.41, 9.58, 10.14, 10.29, 10.79, 11.22, 11.84, 12.05, 12.89, 13.29, 13.86 μ) of this oil are analogous to those of *n*-nonane.

Oil Isolated by Means of Urea Adduct in 165～174°C Fraction.—Physical constants (Table IV) of this oil are identical with those of *n*-decane[23] (b. p. 174°C, $d_4^{20}=0.7298$, $n_D^{20}=1.412$). IR spectrum bands[20] (wavelengths; 7.67, 8.01, 8.25, 8.42, 8.81, 9.16, 9.29, 9.92, 10.05, 10.86, 11.15, 11.83, 12.28, 13.0, 13.85 μ) of this oil are analogous to those of *n*-decane.

Identification of Cycloparaffin.—Dehydrogenation of the residual oil free from *n*-paraffin, was carried out with Pt-C catalyst at 300～310°C.

Dehydrogenation[24,25] Catalyst. — Pt-C catalyst was prepared by Berl's method[24]. About 10 g. of granulated active carbon was mixed with 1 g. of platinum chloride ($PtCl_2 \cdot 2HCl + 6HCl$) dissolved in 25 ml. of water acidified with hydrochloric acid, and the mixture was dried at 110°C with frequent stirring. These were put in a quartz reaction tube (dia., 2 cm., length, 80 cm.) and kept in position by a stopper of glass wool. They were heated to 200°C by electric furnace and the platinum compound was decomposed. Hydrogen was sent to the tube from the entrance until no more hydrochloric acid was formed and a treatment with hydrogen at 300°C was carried out for 30 min.

Apparatus.—The sample was dropped into one end of a reaction tube from the sample flask, the dropping velocity regulated by the opening of the cock provided at the lower part of the sample flask, and the oil produced was received from the other end by a receiving flask with an ice-cooled condenser and the gas produced was collected in a gas collector, its pressure being controlled by a pressure

TABLE V. DEHYDROGENATION

Reac. temp. 300～310°C; Dropping velocity 5～6 g./hr.

Sample	g.	Dehydrogenated oil g.	Gas produced ml. (N. T. P.)	H_2* ml. (N. T. P.)
(a)	7	4.5	828.8	812.2
(b)	10	6	1906.0	1815.2
(c)	11	5.5	1261.1	1171.0
(d)	13	9.5	1330.1	1210.6
(e)	10	8.5	455.4	439.6

* The gas produced by dehydrogenation was analyzed by the Hempel method, and the volume of hydrogen produced by dehydrogenation was calculated from the gas produced.

TABLE VI. NITRO-COMPOUNDS OBTAINED BY NITRATION OF DEHYDROGENATED OILS

	Dehydroganated oil	Nitro-compound				
		Obtained			Referred[26]	
		Crude	Recrystal.		Comp.	
	g.	g.	g.	m. p. °C		m. p., °C
(a)	0.7	0.5	0.05	88 ～ 90	*m*-Dinitrobenzene	90
			0.18	69 ～ 70	2,4-Dinitrotoluene	70
(b)	0.7	0.7	0.4	69.5～ 70	〃	〃
(c)	2	0.4	0.31	179 ～181	2,4,6-Trinitro-*m*-xylene	180
			0.02	138 ～141	2,3,5-Trinitro-*p*-xylene	140
(d)	1.5	0.8	0.45	169 ～171	3,5-Dinitro-1,2,4-trimethylbenzene	172
			0.05	99 ～100	Dinitro-1,2,3-trimethylbenzene	100
(e)	2	0.3	0.03	230 ～232	2,4,6-Trinitro-1,3,5-trimethlybenzene	232
			0.1	179 ～181	4,6-Dinitro-1,2,3,5-tetramethylbenzene	180

* All melting points are uncorrected.

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control device. 78~90°C (a) and 96~100°C fractions (b) and each residual oils (c), (d), (e) free from *n*-paraffin in 120~126°C, 143.5~155°C and 165~174°C fractions were dehydrogenated as mentioned above, and the oil condensed in the receiver were subjected to dehydrogenation repeatedly, and the results, shown in Table V, were obtained.

Identification of Aromatic Hydrocarbons Produced by Dehydrogenation — UV Spectrum of Dehydrogenated Oil[15-20]. — UV spectra of dehydrogenated oils dissolved in purified cyclohexane, was measured with a Beckman spectrophotometer, model DU and the aromatic hydrocarbons produced by dehydrogenation were estimated from their UV spectra.

Nitration of Dehydrogenated Oil[15-20].—Dehydrogenated oil was added to a mixture of 1 vol. of conc. nitric acid and 2 vol. of conc. sulfuric acid and the mixture was heated to boil for five minutes and poured into cold water, and crude nitro-compounds were obtained. These compounds were purified or separated by recrystallization from ethyl alcohol solution, obtaining pure nitro-compounds. The results were shown in Table VI.

The aromatic hydrocarbons contained in each dehydrogenated oil, were determined from UV spectra and Table VI, and the original cycloparaffins contained in (a), (b), (c), (d) and (e) were estimated. The result was shown in Table VII.

TABLE VII. CYCLOPARAFFINS CONTAINED IN (a), (b), (c), (d) AND (e)

	Cycloparaffin	Ratio*
(a)	Cyclohexane	1
	Methylcyclohexane	: 4
(b)	Methylcyclohexane	
(c)	1,3-Dimethylcyclohexane	15
	1,4-Dimethylcyclohexane	: 1
(d)	1,2,4-Trimethylcyclohexane	9
	1,2,3-Trimethylcyclohexane	: 1
(e)	1,3,5-Trimethylcyclohexane	1
	1,2,3,5-Tetramethylcyclohexane	: 3

* The ratio of cycloparaffins contained in each fraction was calculated from weights of nitro-compounds obtained.

TABLE VIII. PHYSICAL CONSTANTS OF OILS, REMOVED AROMATIC HYDROCARBONS CONTAINED IN DEHYDROGENATED OILS

	Dehydrogenated oil	Oil (saturated hydrocarbon)			
	g.	g.	b. p., °C	d_4^{20}	n_D^{20}
(a)	2.1	1.7	93 ~ 96	0.6865	1.389
(b)	2.2	1.5	98.5~ 99.5	0.6942	1.393
(c)	1.6	1.35	114 ~116	0.7221	1.405
(d)	2.0	1.5	140 ~145	0.7265	1.407
(e)	1.6	1.3	164 ~166	0.7340	1.413

Identification of Isoparaffin.—Aromatic hydrocarbons produced by dehydrogenation were removed from dehydrogenated oils by mixture of 2 vol. of conc. sulfuric acid and 1 vol. of conc. nitric acid or by conc. sulfuric acid[15-20]. The residual oils were washed by water and neutralized with alkaline solution. Similarly rewashed and dried with calcium chloride and distilled with metallic sodium, and the oils, having the physical constants shown in Table VIII were obtained.

IR spectra of these oils were measured with a Baird infrared spectrophotometer and isoparaffins contained in each oil were determined. IR spectrum bands of oil of (a) (wavelengths; 7.45, 7.68, 8.78, 9.30, 9.79, 10.4, 10.74, 11.1, 11.42, 11.57, 12.01, 12.91, 13.54, 13.83 μ) are analogous to those of *n*-heptane. In IR spectrum bands of oil of (b), those of *n*-heptane and 2,2,4-trimethylpentane (wavelengths; 7.7, 8.01, 8.30, 8.56, 9.84, 10.2, 10.82, 11.58, 13.4 μ) were observed. It was observed that IR spectrum bands of oil of (c) contain the bands of the spectrum for 2-methylheptane (wavelengths; 7.45, 7.68, 7.9, 8.55, 9.28, 10.42, 10.56, 10.74, 12.3, 13.06, 13.82 μ) and those of the spectrum for 3-methylheptane (wavelengths; 7.68, 7.9, 9.28, 10.42, 10.95, 11.43, 12.3 μ). In IR spectrum bands of oil of (d), those of 3-methyloctane (wavelengths; 8.7, 9.97, 10.3, 10.48, 10.72, 10.94, 11.22, 11.43, 12.3 μ) and 4-methyloctane (wavelengths; 8.7, 9.26, 10.48, 10.72, 10.94, 11.22, 12.94, 13.5, 13.8 μ) were observed. In IR spectrum of bands of oil of (e), those of 3-methylnonane (wavelengths; 8.6, 9.43, 9.77, 9.96, 10.34, 10.95, 11.2, 13.0, 13.8 μ) and 4-methylnonane (wavelengths; 8.6, 9.24, 10.47, 11.2, 11.86, 12.3, 13.0, 13.6, 13.8 μ) were observed.

Results and Discussion

The saturated hydrocarbons identified from each fraction and the proportion of *n*-paraffin, isoparaffin and cycloparaffin to each fraction, are shown in Table IX.

It is obvious that saturated hydrocarbons contained in benzene fraction consist of *n*-heptane (about 74.5%), cyclohexane (about 0.1%), methylcyclohexane (about 25.4%) and 2, 2, 4-trimethylpentane (trace). In the saturated hydrocarbons contained in toluene fraction, *n*-octane (30%), mixture of 2-methylheptane and 3-methylheptane (42%) and 1, 3-dimethylcyclohexane (9%) and 1, 4-dimethylcyclohexane (0.5%) were determined. Saturated hydrocarbons contained in solvent naphtha fraction were determined to contain *n*-nonane (about 5.4%), *n*-decane (about 4.7%), mixture of 3-methyloctane and 4-methyloctane (about 10.8%), mixture of 3-methylnonane and 4-methylnonane (about 4.3%), 1,2,4-trimethylcyclohexane (about 0.2%), 1, 2, 4-trimethylcyclohexane (about 2%), 1, 3, 5-trimethylcyclohexane (about 0.1%) and 1, 2, 3, 5-tetramethylcyclohexane (about 0.4%).

The following observations are based on a study of the data presented in this research.

TABLE IX. SATURATED HYDROCARBONS IDENTIFIED AND THE PROPORTION OF *n*-PARAFFIN, ISOPARAFFIN AND CYCLOPARAFFIN TO EACH FRACTION

Frac.	*n*-Paraffin (%)	Isoparaffin	(%)	Cycloparaffin	(%)	Aromatic*
78 ~ 90	*n*-Heptane (87)	None		Cyclohexane	(3)	Benzene
				Methylcyclohexane	(10)	
96 ~100	*n*-Heptane (74)			Methylcyclohexane	(26)	
120 ~126	*n*-Octane (30)	2-Methylheptane	(42)	1,3-Dimethylcyclohexane	(9)	Toluene
		3-Methylheptane		1,4-Dimethylcyclohexane	(0.5)	
143.5~155	*n*-Nonane (25)	3-Methyloctane	(50)	1,2,3-Trimethylcyclohexane	(1)	*o*-Xylene *m*-Xylene *p*-Xylene *o*-Ethyltoluene *m*-Ethyltoluene *p*-Ethyltoluene 1,2,4-Trimethylbenzene 1,2,3-Trimethylbenzene 1,3,5-Trimethylbenzene
		4-Methyloctane		1,2,4-Trimethylcyclohexane	(9)	
165 ~174	*n*-Decane (40)	3-Methylnonane	(37)	1,3,5-Trimethylcyclohexane	(1)	
		4-Methylnonane		1,2,3,5-Tetramethylcyclohexane	(3)	

* Aromatic hydrocarbons in high-temperature coal carbonization light oil prepared at Yawata Iron & Steel Co., Ltd. as identified previously by S. Kimura, H. Suzumura and the author[3].

1) The saturated hydrocarbons contained in benzene, toluene and solvent naphtha fractions are all composed of saturated aliphatic hydrocarbon, about 85%, and cycloparaffinic hydrocarbon, about 15%.

2) The saturated aliphatic hydrocarbons contained in benzene fraction are nearly all *n*-paraffins and the corresponding isoparaffins are expected to be contained in the forerunnings. In the saturated aliphatic hydrocarbons contained in toluene and solvent naphtha fractions, the proportion of contents of *n*-paraffins and isoparaffins are about 1 : 1.5.

3) The isoparaffins, contained in the three fractions mentioned above, are all monomethylparaffins.

4) Comparing cycloparaffins with aromatics, cyclohexane corresponding to benzene, methylcyclohexane to toluene, dimethylcyclohexane to dimethylbenzene and trimethylcyclohexane to trimethylbenzene, are present respectively. In dimethylbenzene isomer, *m*-xylene is the highest in contents, *p*-xylene, half as much as *m*-xylene and *o*-xylene is of trace[3]. Similar tendency is observed in the contents of dimethylcyclohexane isomers, but 1, 2-dimethylcyclohexane can not be identified in this investigation. It is recognized that in trimethylbenzene isomers, much of 1, 2, 4- and 1, 3, 5-isomers are contained, and almost equally[3]. But it has become clear that in trimethylcyclohexane, the content of 1, 2, 4-isomer is more than that of 1, 3, 5-isomer and 1, 2, 3-isomer is of trace. Thereafter a presence of 1, 2, 3, 5- and 1, 2, 3, 4-isomers[15] in tetramethylcyclohexane isomer is observed. They cannot be compared, however, with the corresponding tetramethylbenzene since it is not analyzed yet by the author. It was reported[27] that 1, 2, 4, 5-tetramethylcyclohexane is contained in high-temperature carbonization tar, but the result obtained in this research presents a different result. Moreover, *p*- and *m*-methylethylcyclohexane[3], which correspond to ethyltoluene isomers, are not found.

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