Low Temperature Carbonisation of Coal. Part I. Treatment of Coal at 500° in Fischer's Aluminium Retort.

By

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ABSTRACT.

In order to obtain a comparative survey of various coals under low temperature carbonisation, 16 kinds of coals of oriental origin (covering 8 bituminous coals, 4 semi-anthracitic coals and 4 anthracites) were treated in Fischer's aluminium retort at 500° and the quantity and quality of the resulting liquids, gases and the semi-coke, together with the rate of evolution of gases and various relations between the natures of the original coals and those of the products of distillation were studied.

The results of the proximate analyses of coal have usually little value for suggesting the behavior of the coal under low temperature carbonisation as regards the quantity and quality of the resulting liquids and gases, the rate of evolution of gases, the effect of the temperature and the time of carbonisation, and the quality of the resultant coke. The present paper includes the results obtained from subjecting a small quantity of various coals to carbonisation at 500° and studying the products of carbonisation.

For the above purpose, the following apparatus[1], Fig. 1, has been found to serve admirably.

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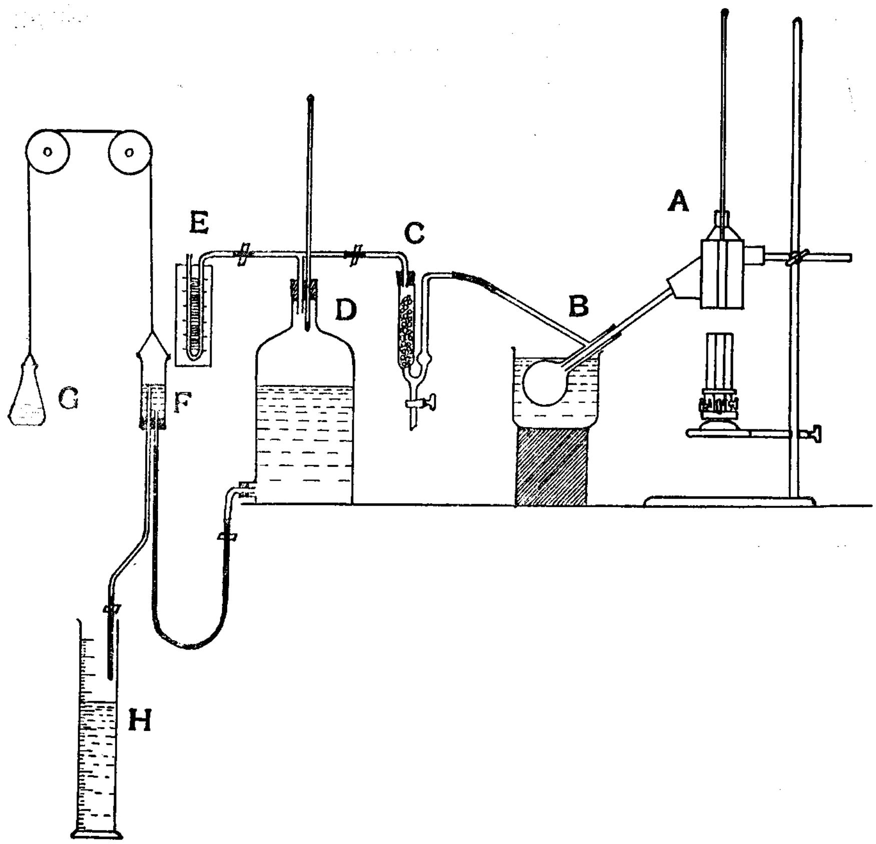
1 Refer to "Interim Report on Methods of Analysis of Coal," Fuel Research Board, London, 1923.

Fig. 1.



A. An aluminium retort[1] to hold 20 gms. of coal.
B. A distilling flask of about 100 c.c. capacity of known weight, dipped in ice-water to condense all the water and tarry product.
C. A U-tube with a cock, containing glass rings drenched with sulphuric acid (1 : 1 by volume) for the absorption of ammonia.
D. A 3-litre bottle to serve as a gas-holder, filled with water previously saturated with low temperature carbonisation gas.
E. A manometer.
F and G. A cylinder with one end open and its counterpoise balancing on pulleys.

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1 Fischer and Schrader, Z. ang. Ch., **33**, 172 (1920); Abh. Kohle, **5**, 55 (1920) Brennstoffchemie, **1**, 31 (1920).

H. A measuring cylinder, 1000 c.c. in capacity, receiving the overflow (= vol. of the gas to be measured) from F, when the gas enters D and displaces the liquid in it.

In the above apparatus it is convenient to have pinch-cocks on all the rubber-tube connections.

Method of Operation:

Finely divided, air-dried coal (which passes through a sieve of 0·25 m.m.), 20 gms. in weight, is put into the retort A; after the gas tightness of the apparatus has been proved, the retort is heated by a triple burner, and the rise of the temperature is read by a high temperature thermometer inserted in the wall of the retort. The pressure in the apparatus can be easily adjusted to one's desire by raising or lowering F. In my experiments, the pressure was kept slightly negative, say 3 - 6 m.m. of the water column throughout the carbonisation. In order to obtain comparative results, the heating of the retort was so adjusted that it took 45 minutes to reach 500°, and at that temperature heating of the retort was kept up for another 45 minutes, and then stopped after the gas-holder was detached.

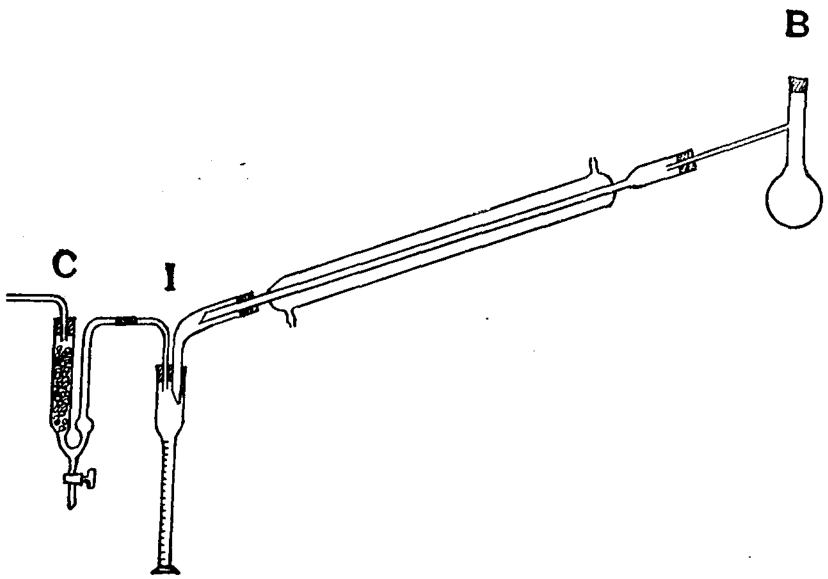
Water and tar condense in B; ammonia is absorbed in C and gas is collected in D. In order to obtain the true volume of gas evolved from the coal, it is necessary to take into account the expansion of the air originally contained in the apparatus, due to heating from the room temperature to 500°.

The increase of the weight of the flask B represents the amount of tar and water. After adding about 15 c.c. of xylene into the flask and giving it a good shaking, the whole was distilled on a direct fire with an arrangement as shown in Fig. 2. The xylene, carrying all the water, distils and collects in I, a 20 c.c. cylinder measured to 0·2 c.c., in which the water settles at the bottom giving a sharp layer from that of the xylene (containing a little low boiling fraction of the tar) floating on the top. The amount of water thus found is substracted from the above value to obtain the quantity of anhydrous tar. Any ammonia which might be driven off by the distillation can be caught by C.

The ammonium sulphate solution from C, combined with the sulphuric acid washing of the distillate in I, is subjected to the ordinary method of ammonia estimation.

The gas collected in the holder was analysed according to the usual method of the Hempel gas analysis, using potassium hydroxide for carbon dioxide and hydrogen sulphide, bromine water for unsaturated hydrocarbons, potassium pyrogallate for oxygen and cuprous chloride

Fig. 2.



(in hydrochloric acid) for carbon monoxide. For the determination of paraffine hydrocarbons and hydrogen at the same time by means of an explosion pipette, it is necessary to make the assumption that the ratio of methane and ethane (and no other higher homologues) is in a definite proportion. This was provisionally taken as 2 : 1, under the experimental conditions, from the results of the foregoing study of low temperature carbonisation gas[1], and it was found that in most cases, the calculated amount of nitrogen from the percentage of oxygen well coincided with the actual value obtained for nitrogen, proving that the above assumption may be satisfactorily used for quick determinations when very rigorous results are not wanted. The quantities of paraffine hydrocarbons ($CH_4 : C_2H_6 = 2 : 1$) and hydrogen are then given by the following equations:

Paraffine hydrocarbons $= \frac{3}{4} y$, and Hydrogen $= \frac{2}{3} (x - \frac{13}{8} y)$,

where x = total contraction of volume after explosion, and y = contraction of volume by the subsequent absorption with KOH.

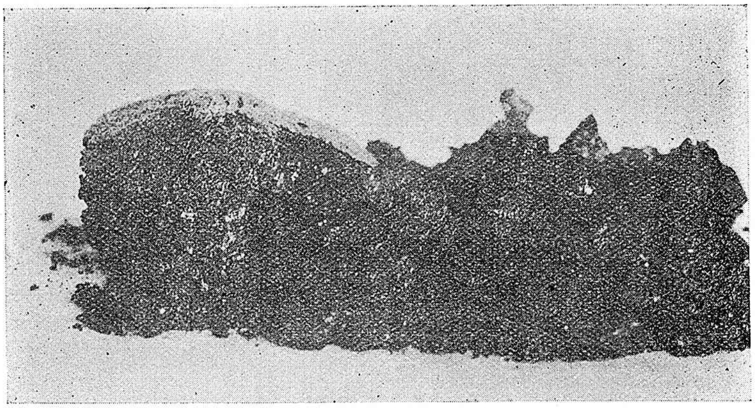
In the present investigation, sixteen kinds of coals of oriental origin, used for blending materials in the manufacture of metallurgical coke

1 Foerster, Brennstoffchemie, **2**, 65 (1921).
Dietz, Grünert and Noack, Brennstoffchemie, **5**, 33 (1924).

were examined. Table I gives their analyses together with other information, being arranged according to their content of volatile matter, the first eight ("Yubari"—"Sasa") belonging to the class of ordinary bituminous coals, the second four ("Kaiping"—"Rogatyi") being the so-called semi-anthracitic coals, while the last four ("Honghè"—"Mallien") fall in the class of anthracites,

The results of the carbonisation effected under as equal conditions as possible are tabulated in Table II.

Semi-coke: – The yield and appearance of the semi-coke vary according to the nature of the coal carbonised. The yields are 70—78 %

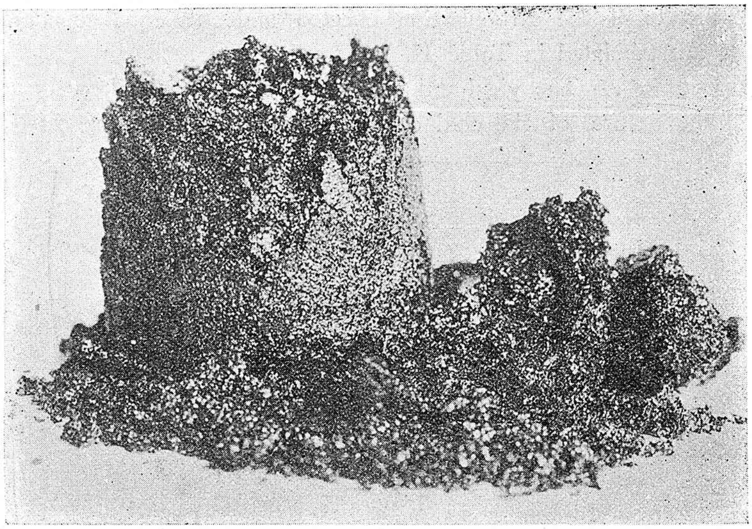


1. Yubari No. 1 Pit

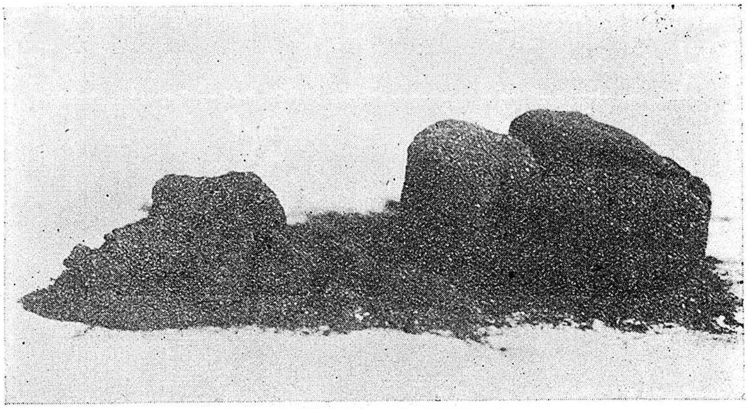
2.

Koyaki

of the dry coal in the case of bituminous coals; 80—88 % with semi-anthracitic coals, and 95—98 % with anthracites. The appearance of the semi-coke seems to fall into four classes as shown in the accompanying photographs, i. e. 1. a fragile mass of spongy texture ("Yubari", "Sakito", "Poshan"); 2. a rather hard, swollen mass of compact texture



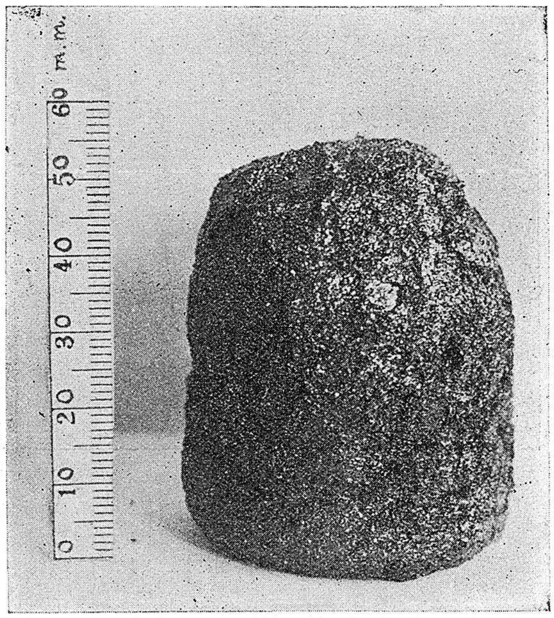
3. Sakito



4. Nansu

("Koyaki", "Hashima", "Besshu", "Kaiping"); 3. a compact dense mass of close structure, showing little or no swelling ("Matsushima", "Sasa", "Dui", "Rogatyi"); and 4. a non-coherent, powdery form ("Nansu", "Honghé", "Tsun-chin", "Kin-tschou", "Mallien"[1]).

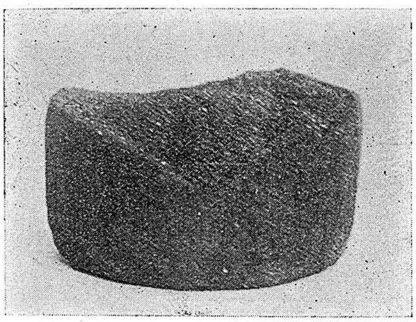
The relation between the volatile matter (dry-basis) of the semi-coke and that of the original coal is given by dotted and dash-line in Fig. 3, the curve having a tendency to rise as the volatile matter of the coal



5. Hashima

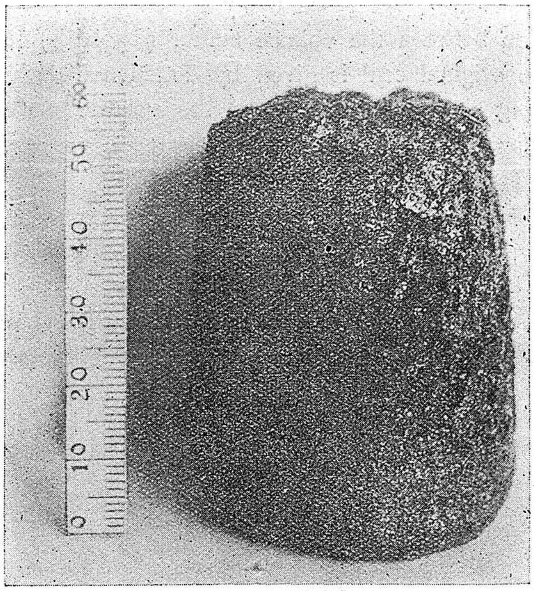
decreases, though with some fluctuations.

The ratios of the contents of C and H (dry, ashless basis) in the semi-coke to those of the original coals are given in the upper two

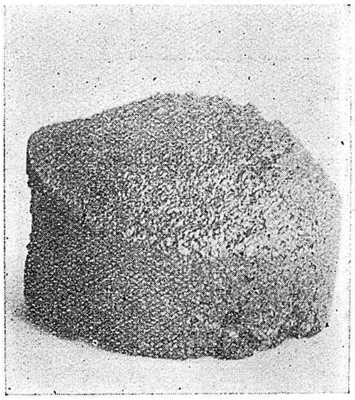


6. Matsushima

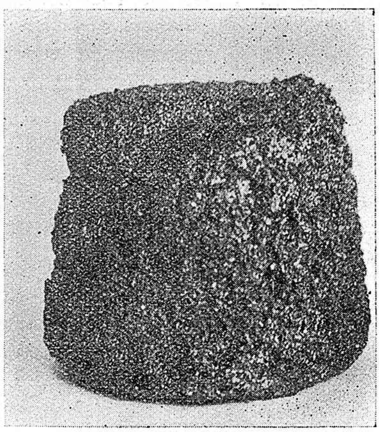
1 The last four are not shown in the photographs, for they have suffered apparently no alteration of appearance by carbonisation.



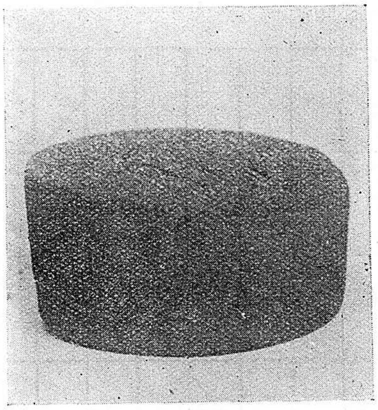
7. Besshu



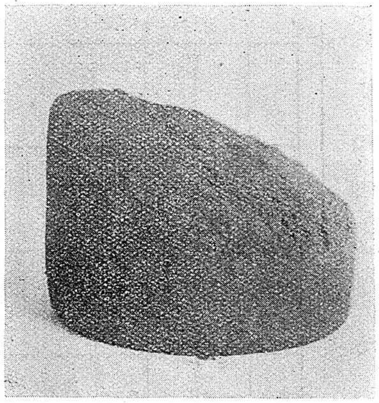
8. Sasa



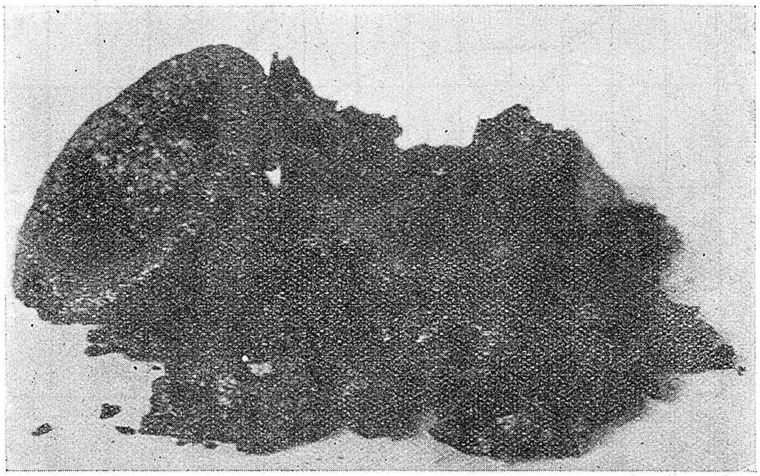
9. Kaiping



10. Dui



12. Rogatyi



11. Poshan

curves in Fig. 4. The curve of the C-relation have a tendency to fall, while that of the H-relation to rise, both nearing unity as the volatile matter of the coal decreases. It is interesting to note that the latter curve shows some similarity in its general form to that of the CH_4 and C_2H_6-curve in Fig. 6, which indicates the content of these hydrocarbons in the gas produced.

Water: – So-called water of constitution is driven off at comparatively low temperatures in varying degrees.

Tar: – The yield of tar was found to be roughly proportional to the content of the volatile matter of the original coal, except, of course, in

Fig. 3.

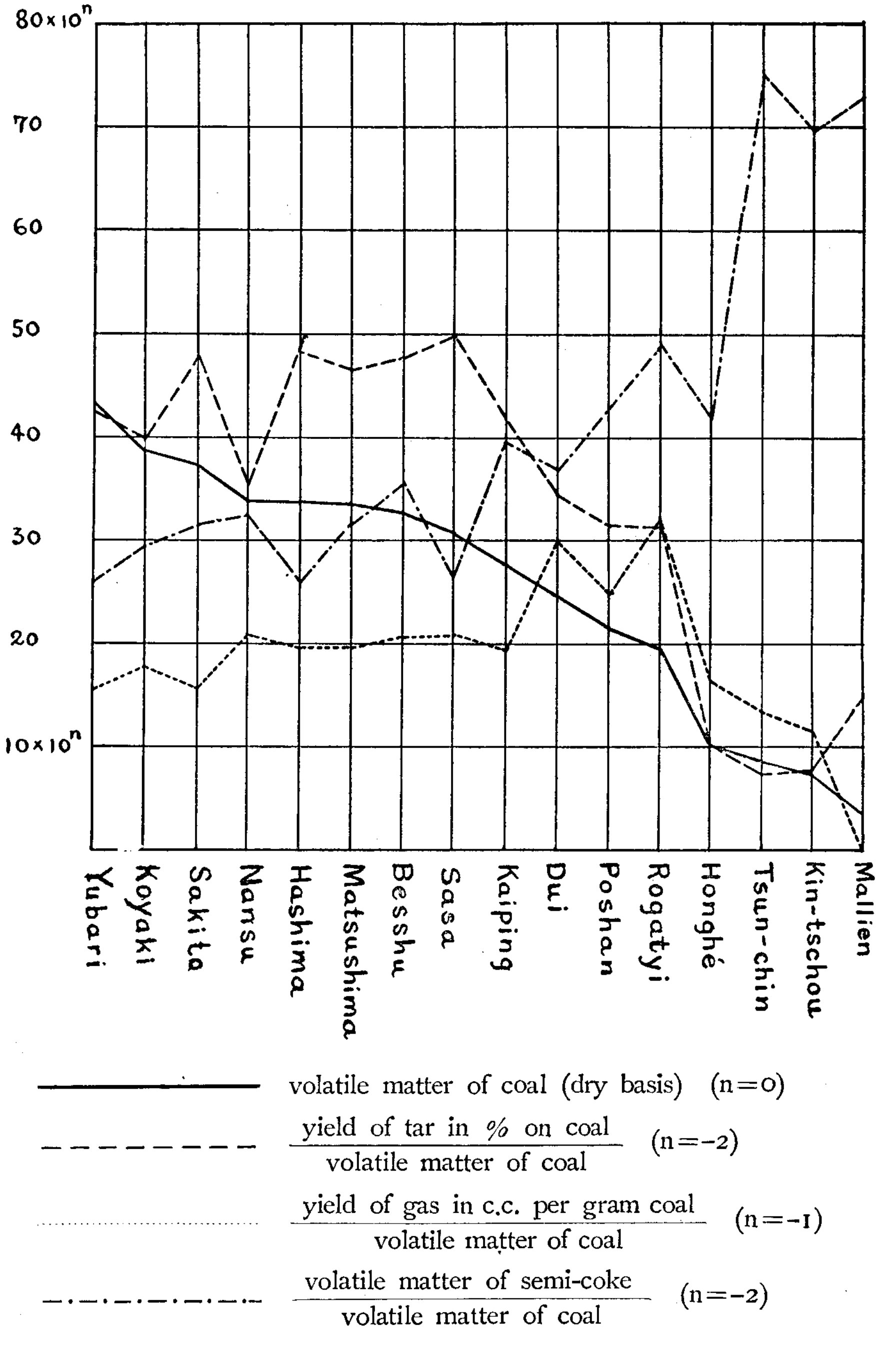
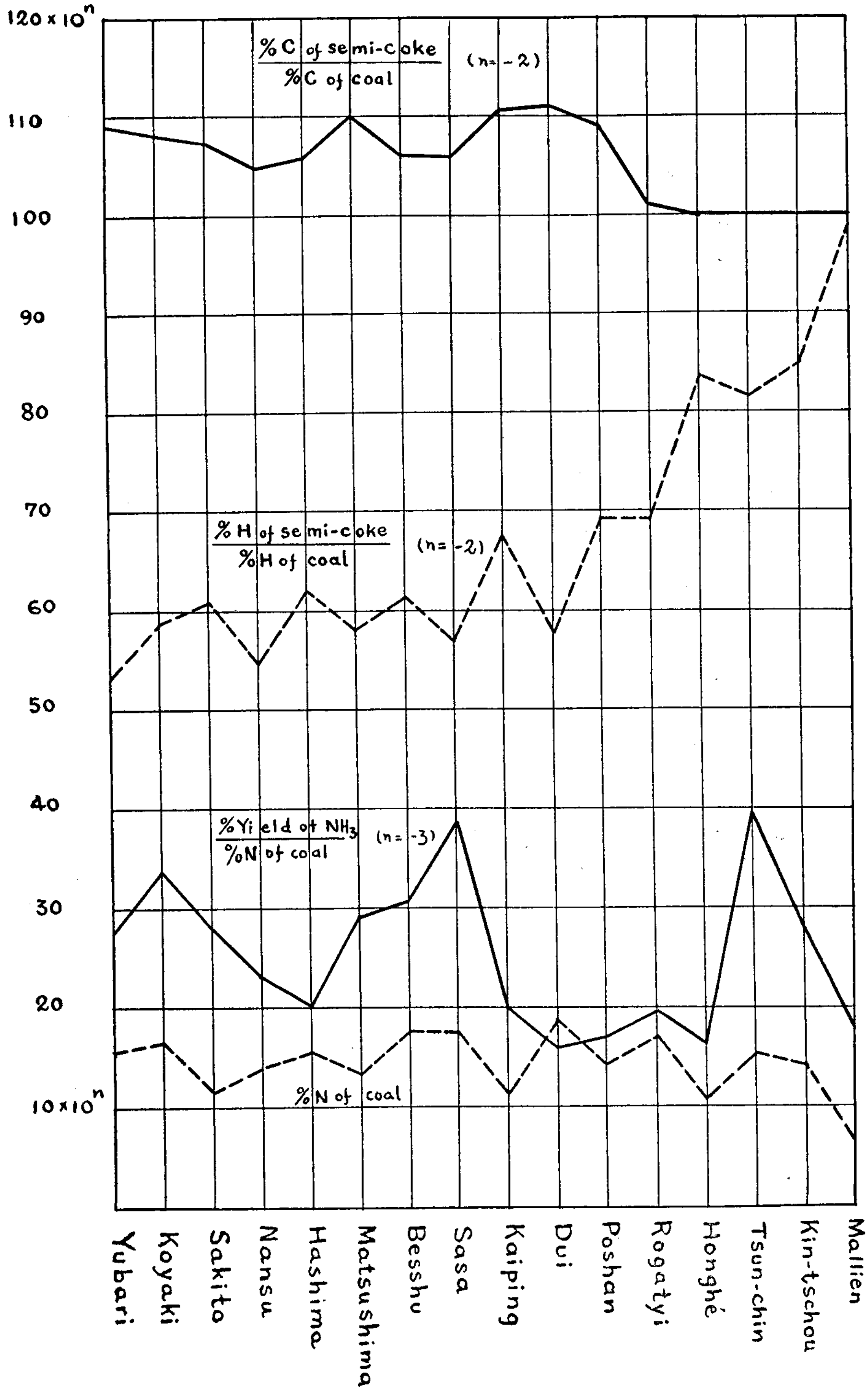

80×10ⁿ
70
60
50
40
30
20
10×10ⁿ
Yubari
Koyaki
Sakita
Nansu
Hashima
Matsushima
Besshu
Sasa
Kaiping
Dui
Poshan
Rogatyi
Honghé
Tsun-chin
Kin-tschou
Mallien
volatile matter of coal (dry basis) (n=0)
yield of tar in % on coal / volatile matter of coal (n=−2)
yield of gas in c.c. per gram coal / volatile matter of coal (n=−1)
volatile matter of semi-coke / volatile matter of coal (n=−2)

Fig. 4.


120 × 10ⁿ
110
100
90
80
70
60
50
40
30
20
10 × 10ⁿ
% C of semi-coke / % C of coal (n = -2)
% H of semi-coke / % H of coal (n = -2)
% Yield of NH3 / % N of coal (n = -3)
% N of coal
Yubari
Koyaki
Sakito
Nansu
Hashima
Matsushima
Besshu
Sasa
Kaiping
Dui
Poshan
Rogatyi
Honghé
Tsun-chin
Kin-tschou
Mallien

anthracites which yield only an insignificant quantity of tar. The relation between the yield of tar and the volatile matter of the coal (dry-basis) is given in Fig. 3.

The bituminous coals yield usually 15 – 19 % of anhydrous tar on the dried coal used, among which "Nansu" shows a rather low figure (11·89%) in spite of its high percentage of volatile matter. This reduction, however, is made up by its high yield of gas as shown in Table II.

The semi-anthracitic coals give 6 – 12 % of anhydrous tar, while almost no tar distils from the anthracites.

Ammonia :- The yield of ammonia was found very small in comparison to the results obtained in the usual practice in high temperature carbonisation, varying from 0·02 to 0·07 % as ammonia or 0·06 – 0·3 % in the form of ammonium sulphate on the coal carbonised. It will be seen in Fig. 4 that generally the yield of ammonia is not concordant with the nitrogen content of the original coal, e. g. "Hashima," "Dui" and "Honghè" yield a rather low percentage of ammonia in spite of their high content of nitrogen, while "Koyaki", "Sasa" and "Tsun-chin" give very high yields. The variation seems due to the different natures of nitrogen compounds originally contained in the coals.

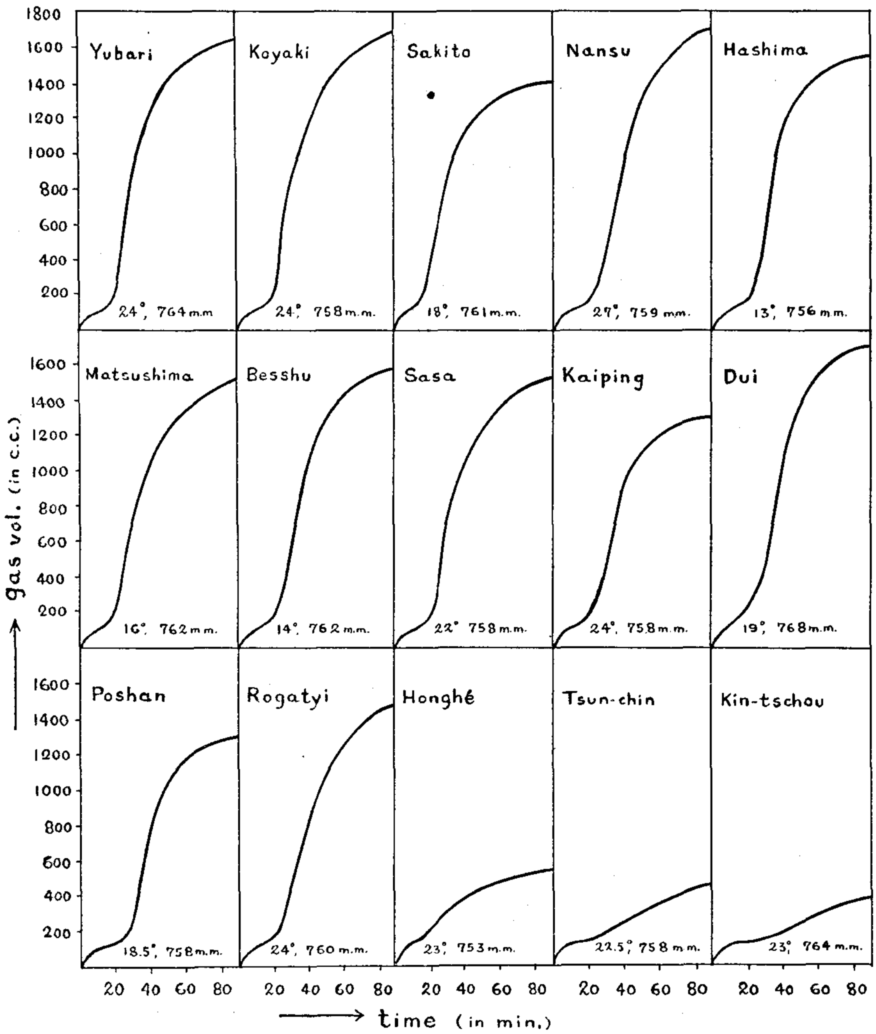
Gas :- Fig. 5 indicates the rate of gas evolution of various coals as taken in the experiments including the volume due to expansion of the air originally contained in the apparatus in the process of heating from the room temperature to 500°.

The gas volume produced by distillation at 500° varies according to the nature of the original coal, ranging from 50 c.c. to 70 c.c. (at N. T. P.) per gram coal carbonised with bituminous and semi-anthracitic coals, and nil to 16 c.c. with anthracites.

It is remarkable that the semi-anthracitic coals yield a fairly large amount of gas, contrary to the yield of tar, in spite of a much smaller content of volatile matter in comparison with the ordinary bituminous coals, although the gas so obtained has less calorific value than that from the bituminous coals. In the case of low temperature carbonisation, therefore, it is unwise to foretell the gas yield simply from the content of volatile matter of the coal.

In the case of bituminous and semi-anthracitic coals, it is interesting to note that the higher the yield of tar, the less the volume of gas produced, provided the two coals have similar contents of volatile matter. Thus the curves of "yield of tar in % on coal/volatile matter of coal" and "yield of gas in c.c. per gram coal/volatile matter of coal" (Fig. 3) take a fairly symmetrical form against an imaginary horizontal line which

Fig. 5.

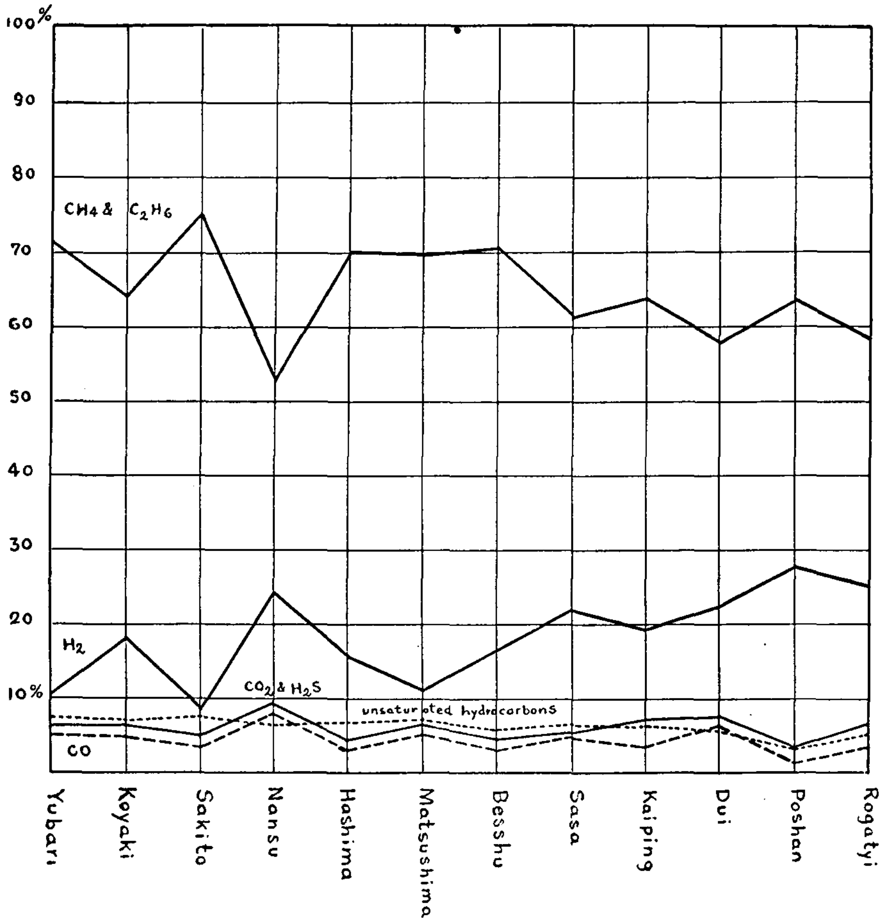


Apparent rate of evolution of gases.

may be drawn between them, as far as the bituminous and semi-anthracitic coals are concerned.

The gas is distinctly different from the ordinary coal-gas in its remarkable high content of paraffine hydrocarbons, its calorific value (air-free basis) calculated from the results of the gas analysis, being about 820–1090 B. Th. U. per cubic foot.

Fig. 6.



Analyses of gases produced by low temperature carbonisation.

The results of the analyses of gases from gas-yielding coals are given in Fig. 6, in which it will be noticed that in general, the higher the volatile matter of the original coal, the less hydrogen, or the more paraffine hydrocarbons are evolved. By comparing the results of the gas analysis with the rate of gas evolution, Fig. 5, it will be seen that the gas from coals which yield it comparatively easily, is richer in paraffine hydrocarbons, or in other words, the coal which yields most of the gas before it is heated to 500°, or in less than 45 minutes, produces gas comparatively high in paraffine hydrocarbons, proving that these hydrocarbons are evolved at relatively low temperatures, while hydrogen only appears when the coal is heated at higher temperatures. The above relation is well explained in the cases of "Sakito" and "Nansu" (see Figs. 5 and 6). The former yields about 85% of the total gas in less than 45 minutes (or below 500°), while the latter only 65% in the same interval; the contents of paraffine hydrocarbons and hydrogen are 75·2% and 8·6% respectively in the former, and 52·3% and 24·1% in the latter.

Conclusion:– The coal, which is itself a highly intricate mixture of extremely complex compounds, whose natures are far from being clear, yields on carbonisation numerous products of equally complicated nature. The yields and natures of these products are influenced not only by the nature of the original coal, but also by various conditions at the time of carbonisation, among which the temperature plays the most important rôle.

The above results are only true of the carbonisation up to and at 500° and in the apparatus used. The same material may, of course, give different results if carbonised at different temperatures or in different apparatus, especially in a plant on a large scale, which generally has a tendency to give less tar and more gas and ammonia whatever the structure of the retort may be, than experimental apparatus in a laboratory. In the circumstances, the above results are useful in giving a *comparative* survey of various coals under low temperature carbonisation.

In conclusion, I want to thank cordially Professor M. Chikashige and Dr. Kotaro Shimomura for their interest, and Messrs. Kenji Nakamura and Koji Shimomura for their kind assistance in the work.

Table I.

Analyses of coals etc.

No.	Coal	Treatment		moisture	volatile matter less moisture	ash	Colour of ash	Fixed carbon	C	H	S	N	Place of mine
1	YUBARI No. 1 PIT	washed at mine, as delivered.	A	1·34	42·81	10·56	greyish brown	45·29			0·30	1·53	Yubari, Hokkaidō
	夕張一坑炭		B		43·39	10·69		45·92	71·61	5·66	0·31	1·55	
			C						80·19	6·33		1·74	
2	KOYAKI	washed at mine, crushed.	A	1·52	38·24	8·65	light brown	51·47			0·78	1·64	Nagasaki Pr.
	香焼五尺粉炭		B		38·88	8·78		52·34	73·94	5·65	0·79	1·67	
			C						81·12	6·20		1·83	
3	SAKITO	washed at mine, as delivered.	A	1·54	36·66	11·95	grey	49·85			2·03	1·15	Nagasaki Pr.
	崎戸粉炭		B		37·23	12·14		50·63	71·29	5·20	2·07	1·17	
			C						81·13	5·91		1·33	
4	NANSU	not washed, as delivered.	A	3·42	32·72	4·03	reddish brown	59·83			0·61	1·35	Sumatra
	南蘇炭		B		33·88	4·17		61·95	78·58	5·40	0·64	1·40	
			C						82·01	5·63		1·46	
5	HASHIMA	not washed, as delivered.	A	1·72	33·16	6·63	light brown	58·49			1·03	1·51	Nagasaki Pr.
	端島炭		B		33·74	6·75		59·51	77·39	5·39	1·05	1·54	
			C						83·27	5·80		1·66	
6	MATSUSHIMA	washed at mine, as delivered.	A	2·25	32·81	12·34	brown	52·59			1·42	1·33	Nagasaki Pr.
	松島四尺粉炭		B		33·57	12·63		53·80	69·53	5·18	1·46	1·36	
			C						79·58	5·93		1·56	
7	BESSHU	not washed, as delivered.	A	1·93	32·18	11·47	light greyish	54·42			0·51	1·75	Nagasaki Pr.
	別種炭		B		32·81	11·70	brown	55·49	75·65	5·32	0·52	1·78	
			C						85·42	6·01		2·01	
8	SASA	washed at mine, as delivered.	A	2·66	29·98	13·62	pale brown	53·74			0·51	1·72	Nagasaki Pr.
	佐々炭		B		30·80	13·99		55·21	71·17	5·39	0·52	1·77	
			C						82·75	6·27		2·06	
9	KAIPING	washed at mine, as delivered.	A	1·42	27·10	13·24	grey	58·24			0·95	1·16	China
	開平粉炭		B		27·49	13·43		59·08	69·52	4·43	0·96	1·18	
			C						80·30	5·12		1·36	
10	DUI	not washed, as delivered.	A	2·33	24·11	4·91	orange brown	68·65			0·39	1·80	Sakhalin
	土威切込炭		B		24·69	5·03		70·28	76·41	5·83	0·40	1·84	
			C						80·46	6·14		1·94	
11	POSHAN	not washed, as delivered.	A	0·74	21·58	11·30	pale greyish	66·39			0·61	1·44	China
	博山炭		B		21·74	11·39	brown	66·87	72·89	4·58	0·62	1·45	
			C						82·25	5·17		1·64	
12	ROGATYI	not washed, as delivered.	A	1·32	18·92	9·40	yellowish brown	70·23			0·46	1·69	Sakhalin
	ロガトイ		B		19·17	9·56		71·27	78·83	4·79	0·47	1·71	
			C						87·18	5·29		1·89	
13	HONGHÉ	not washed, as delivered.	A	4·24	9·56	12·29	greyish brown	73·91			0·45	1·03	Indo-China
	鴻基細粉炭		B		10·00	12·83		77·77	79·52	3·48	0·47	1·08	
			C						91·24	4·00		1·24	
14	TSUN-CHIN	not washed, as delivered.	A	1·84	8·59	11·63	pale greyish	77·94			0·67	1·49	China
	振興炭		B		8·75	11·85	brown	79·40	77·85	3·60	0·68	1·52	
			C						88·35	4·09		1·73	
15	KIN-TSHOU	not washed, as delivered.	A	1·68	7·55	13·75	greyish brown	77·02			0·87	1·41	China
	金州炭		B		7·68	13·95		78·37	78·48	3·34	0·89	1·43	
			C						91·24	3·89		1·66	
16	MALLIEN	washed at mine, as delivered.	A	3·99	3·41	15·95	reddish brown	76·65			0·83	0·66	India
	マリエン		B		3·52	16·61		79·87	78·89	1·48	0·87	0·69	
			C						94·65	1·78		0·83	

A = % on air-dried sample. B = % on dry-basis. C = % on dry-, ashless-basis.

Table II.

Results of Low Temperature Carbonisation.

No.	Coal		Yields of Carbonisation Products						Analyses of Semi-Coke			Analyses of Gas (on air-free basis)					
			Semi-Coke %	Water %	Tar %	NH_3 %	$(NH_4)_2SO_4$ %	Gas c.c./gr. coal (N.T.P.)	volatile matter	C	H	CO_2 & H_2S	Unsaturated Hydrocarbons	CO	$CH_4+C_2H_6$ (2 : 1)	H_2	Calorific value (gross).
1	YUBARI No. 1 PIT 夕張一坑炭	A	68·48	5·5	18·29	0·0426	0·165	67·4									B. Th. U. per cub ft
		B	69·41	4·2	18·54	0·0432	0·167	68·3	11·20	75·75	2·90	6·4	7·2	4·8	71·2	10·4	1041
		C								87·62	3·35						
2	KOYAKI 香焼五尺粉炭	A	71·89	5·5	15·28	0·0558	0·217	68·6									
		B	73·00	4·0	15·52	0·0567	0·221	69·7	11·33	77·62	3·18	6·2	6·8	4·9	64·1	18·0	1016
		C								88·14	3·61						
3	SAKITO 崎戸粉炭	A	68·85	4·0	17·42	0·0324	0·125	56·7									
		B	69·93	2·5	17·69	0·0329	0·127	57·6	11·60	75·90	3·13	5·0	7·8	3·4	75·2	8·6	1091
		C								87·40	3·60						
4	NANSU 南蘇炭	A	75·68	6·0	11·48	0·0315	0·122	68·6									
		B	78·37	2·6	11·89	0·0326	0·126	71·0	11·17	82·17	2·92	9·1	6·4	8·1	52·3	24·1	824
		C								86·34	3·07						
5	HASHIMA 端島炭	A	72·03	3·5	16·15	0·0310	0·120	65·6									
		B	73·29	1·8	16·43	0·0315	0·122	66·8	9·61	80·93	3·29	4·4	6·9	3·4	70·0	15·3	1041
		C								88·49	3·60						
6	MATSUSHIMA 松島四尺粉炭	A	71·91	6·4	15·22	0·0388	0·151	63·7									
		B	73·57	4·1	15·57	0·0397	0·155	65·2	10·50	73·57	2·89	6·8	7·0	5·5	69·7	11·0	1029
		C								87·84	3·45						
7	BESSHU 別種炭	A	72·06	4·8	15·26	0·0536	0·208	66·8									
		B	73·48	2·9	15·55	0·0547	0·212	68·1	10·16	78·38	3·24	4·8	5·8	3·0	70·2	16·2	1027
		C								90·72	3·75						
8	SASA 佐々炭	A	73·13	5·5	14·88	0·0666	0·258	62·4									
		B	75·13	2·8	15·29	0·0684	0·265	64·1	8·04	70·08	2·88	5·8	6·1	5·0	61·0	22·1	938
		C								87·14	3·58						
9	KAIPING 開平粉炭	A	80·25	2·0	11·35	0·0233	0·090	51·7									
		B	81·41	0·6	11·51	0·0236	0·091	52·5	10·85	71·03	2·83	7·2	6·2	3·6	63·6	19·4	956
		C								88·90	3·46						
10	DUI 土威切込炭	A	79·92	3·6	8·37	0·0287	0·113	71·6									
		B	81·83	1·3	8·57	0·0294	0·116	73·3	9·35	85·94	3·33	7·6	5·6	6·8	57·8	22·2	894
		C								89·45	3·54						
11	POSHAN 博山炭	A	85·34	1·7	6·85	0·0244	0·095	52·2									
		B	85·97	1·0	6·90	0·0246	0·096	52·9	9·30	76·93	3·08	3·5	3·2	1·8	63·7	27·8	933
		C								89·45	3·58						
12	ROGATYI ロガトイ	A	87·08	1·5	5·97	0·0333	0·129	60·2									
		B	88·24	0·2	6·05	0·0338	0·131	61·0	9·35	77·93	3·25	6·6	5·6	3·8	58·8	25·2	908
		C								88·18	3·68						
13	HONGHÉ 鴻基紅粉炭	A	91·63	4·5	1·09	0·0170	0·055	15·5									
		B	95·69	0·3	1·14	0·0178	0·057	16·2	4·28	77·93	3·25						
		C								88·18	3·68						
14	TSUN-CHIN 振興炭	A	95·50	2·5	0·64	0·0596	0·231	12·0									
		B	97·29	0·7	0·65	0·0607	0·235	12·2	6·60	77·84	2·89						
		C								89·73	3·32						
15	KIN-TSHOU 金州炭	A	96·25	2·3	0·57	0·0396	0·154	8·9									
		B	97·89	0·6	0·58	0·0403	0·157	9·1	5·36	78·84	2·77						
		C								91·64	3·30						
16	MALLIEN マリエン	A	94·84	4·0	0·55	0·0118	0·045	0									
		B	98·78	0	0·57	0·0129	0·048	0	2·58	81·51	1·43						
		C								94·69	1·72						

A = % on air-dried sample. B = % on dry-basis. C = % on dry-, ashless-basis.