Biochemical Studies on Pityrol, II. Distillation of Rice Bran

By

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1. Analysis of Rice Bran

The rice bran which was used in the preparation of the tar was obtained from the rice named Shinriki which is grown near Osaka, and was taken to the laboratory immediately after being milled in a milling machine designed by Mr. Tsuge. The bran was subjected to a dry heat of about 80°C for one hour to destroy any enzymes in it.[1] It was divided into two parts, and the one part (B) was treated with petroleum ether in an oil extractor[2] of Wegelin and Huebner A-G, Hall, to extract the rice oil, and dried in the open air, and both samples were analysed with the following results:

1. Water-content.

A sample taken in a weighing-bottle was kept at 105° to a constant weight, the loss in weight is the assumed water-content.

2. Ash-content.

Crude ash prepared by burning in a porcelain crucible with an alcohol lamp, and then incinerated at about 400°C in an electric oven, and weighed.

3. Elementary analysis.

The dried sample was analysed and the results, calculated on ash-free and dry bases, are shown in the table.

4. Crude fat.

1 C. A. Browne: J. Am. Chem. Soc., **25**, 948 (1903)

2 Ullmann: Encyclopedia Bd. **5**, 375 (1914)

Table I

	A	B
C	46.2	39.9
H	7.4	6.0
N	2.4	3.0
S	1.5	2.0
Water	14.7	14.1
Ash	9.3	12.0
Crude fat	22.4	0.7
Protein	12.9	16.5
Cellulose	11.4	14.6
Pentosans	8.7	11.1
Reducing sugar	1.3	1.5
Sucrose	10.6	13.6

The fatty substance in the sample was extracted with ether in Soxlet's extractor, and the residue obtained by expelling the solvent by distillation, was estimated of itsacid and iodine values in the usual manner: A.V.=160; I.V.=118.

5. Crude protein.

The total nitrogen content was estimated by Kjeldahl's method and the crude protein was calculated by multiplying the total nitrogen by 6.25.

6. Pentosan.

The content of pentosans was estimated by Tollens aud Kruger's method as usual.

7. Sucrose.

According to Dr. S. Hirai[1], reducing and non-reducing sugars which occur in the bran were composed mostly of d-glucose, and sucrose, respectively, and were isolated from the aqueous extract.

The bran, after being deffated, was treated with 50% hot ethyl alcohol in presence of calcium carbonate, and the content of d-glucose and sucrose in the extracted solution was estimated by means of Fehling's solution.

8. Cellulose.

The cellulose content was determined of the dried sample by Cross-Bevan's method modified by Renker.[2]

1 Acta Scholae Medi. Univ. Imp. Kyoto, **7**, 463 (1925)

2 J. Soc. Chem. Ind., **28**, 1269 (1910)

2. Dry Distillation

30 grm. each of samples (A and B), were distilled in Fischer's aluminium retort, and the tar with aqueous distillate was condensed in a flask connected directly with the retort, which carried a delivery tube by which the generated gas was permitted freely into the gas holder. The apparatus used in this experiment is similar in arrangement to the low temperature assay apparatus for coal of the Fuel Research Board[1].

The gas began to evolve at 200°, a tarry substance of a light yellow colour distilled and at 350° the generation of gas and tar of a dark colour increased equally with the temperature rise, a violent decomposition of the contstituents of the rice bran taking place at about 400° and the reactions as will be seen in the temperatures-volume curve of the gas, were completed at 450°.

Repeating the same operation, 2500 grm. of one or the other samples (A and B) were distilled and the following results were obtained:

Table II

	A	B
Tar	600 grm.	375 grm.
Coke	700 „	775 „
Aqueous liquor	900 „	1000 „

The yields of these reaction products are shown in percentage.

The yield of the reaction products, as may be seen in the foregoing table, will vary with the chemical composition of the raw material, though the conditions under which the sample were treated were the same in both cases.

In order to see what difference in chemical and physical properties will be found between the reaction products-gas and the tar, which was obtained from the two materials, the tar was divided into two portions—volatile, and non-volatile by steam distillation and each fraction was then subdivided into acidic, basic and neutral parts. The oil-containing bran yields, as may be seen in Table IV, a neutral tarry matter in a greater amount than the other, while the content of the basic and acidic parts is greater in the tar from the oil-free material. The physical constants

1 C. H. Lander and R. F. McKay: Low temperature carbonisation (1924), P. 61

Table III

	A	B
Tar	24 %	15 %
Coke	28 „	31 „
Aqueous liquor	36 „	40 „
Gas	12 „	14 „

	Tar	
	A	B
d_4^{25}	0.967	0.981
Volatile part	13 %	17 %
	d_4^{25}=0.871	d_4^{25}=0.919
Non-volatile	87 „	83 „

	Aqueous liquor	
	A	B
Density	1.021	1.035
Organic matter	22	19

	Coke	
	A	B
Moisture	0.80	1.23
Ash	32.67	34.56
Volatile carbon	19.42	19.06
Non-volatile carbon	47.11	45.15
Elementary analysis		
C	49.79	51.73
H	2.82	3.24
N	3.58	3.74
S	0.02	0.03
Ash	33.46	35.30

	Gas	
	A	B
Bases	22 %	23 %
C_nH_{2n}	25.4 „	17.4 „
C_2H_4	0.4 „	0.4 „
C_nH_{2n+2}	2 „	3 „
CO	17.3 „	20.6 „
CO_2	31.8 „	31.6 „

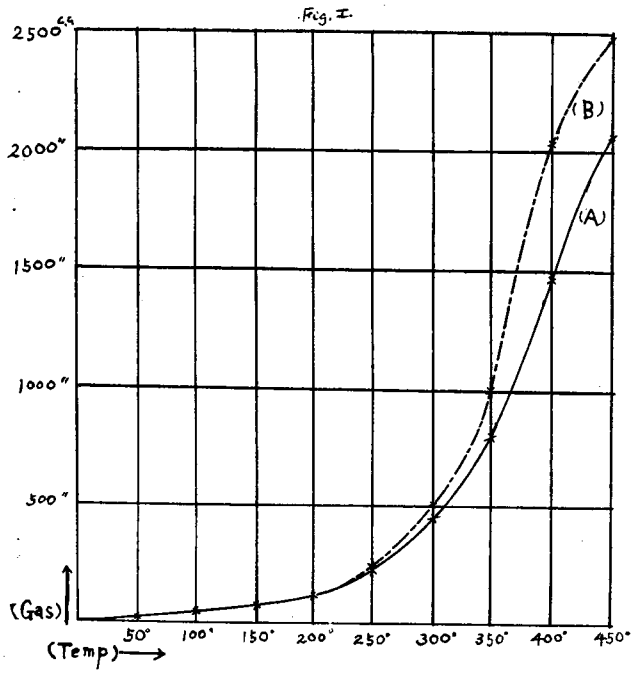

Table IV

		A	B
	Neutral part	68 %	53 %
	Acidic „	29 „	35 „
	Basic „	3 „	11 „
V. part	Neutral part	66	46
	Acidic „	30	39
	Basic „	4	16
N. V. part	Neutral part	68	55
	Acidic „	29	35
	Basic „	3	10

and the analytical results of the aqueous liquor and coke are similar in both cases, while the chemical composition of the tar and the gas is different as may be seen from the table IV.

The neutral oil from bran A. is lower in density and index of refraction than the oil from B, the difference in the physical properties

Table V

	Fraction (5–10 mm)	A	B
Neutral Oil.	60°—100°	1.9 grm (25%)	2.3 (37%)
	d_4^{25}	0.8021	0.8377
	n_D^{25}	1.4476	1.4617
	I.V.	201	200
	C.	83.48	82.28
	H.	11.86	11.11
	100°—150°	3.1 grm (41%)	2.3 grm. (37%)
	d_4^{25}	0.8486	0.8889
	n_D^{25}	1.4715	1.4893
	I.V.	167	202
	C.	83.60	82.25
	H.	11.94	10.98
	150°—180°	1.1 grm (14%)	0.6 grm. (10%)
	d_4^{25}	0.8516	0.8935
	n_D^{25}	1.4734	1.4912
	I.V.	164	183
	C.	83.21	82.55
	H.	12.44	11.06
	Residue	1.5 grm.	1.1 grm.
Acidic Oil.	60°—100°	1.1 grm (22%)	2.1 grm. (38%)
	d_4^{25}	0.9757	0.9949
	n_D^{25}	1.4892	1.5020
	C.	71.03	72.20
	H.	9.05	8.41
	100°—150°	1.5 grm (31%)	1.8 grm. (32%)
	d_4^{25}	0.9785	1.006
	n_D^{25}	1.4863	1.5073
	C.	69.93	72.30
	H.	9.35	9.13
	Residue	1.3 grm.	1.7 grm.

	760 mm.	A	B
Basic Oil.	100°—200°	0.5 grm (17%)	0.6 grm. (14%)
	d_4^{25}	0.9981	0.9785
	n_D^{25}	1.4853	1.4791
	C.	66.00	66.25
	H.	8.46	8.83
	N.	8.51	7.05
	200°—255°	0.9 grm. (31%)	1.6 grm. (38%)
	d_4^{25}	1.0265	1.0470
	n_D^{25}	1.5241	1.5292
	C.	71.03	71.00
	H.	7.78	7.30
	N.	7.73	6.60
	Residue	1.4 grm.	2.0 grm.

indicates that of the chemical nature in both tars. The lighter oil should be saturated in chemical structure, and the analytical results of carbon, & the hydrogen content of the fractions, show a fair agreement with the indication of the physical constants. The relation in the physical and the chemical natures, which was observed in the natural oils, was also noticed in the acidic oils from the two different origins, but not in the two basic oils, and the explanation for the difference in the properties of the neutral and the acidic oils from two different origins would be learned when we take the difference in the constituents of the brans into consideration.