

used several times, or the separation might be effected by the addition of acid tars from other sources. For it is probable that the acid tar produced, has a greater solvent power for the oxygenated constituents of primary tar, than for the hydrocarbons. A separation might also be attempted by dissolving other solids in the tar which are soluble in the phenols, but insoluble in the hydrocarbons. The hydrocarbons would then be replaced in their solution in the phenols by the other solute.

It has been found⁹⁷ that solutions of sodium sulphide may also be used for extracting the phenols from the low-temperature oils, and that this extraction will take place without an appreciable liberation of hydrogen sulphide. On passing hydrogen sulphide into the extract, phenols are precipitated, and a solution of sodium hydrosulphide (NaHS) is formed. This solution, on boiling with phenolic oils, dissolves the phenols with evolution of hydrogen sulphide. A combination of the two processes would therefore allow us to utilise the NaHS solution, over and over again, for extracting the phenols. Simple as this method appears, there is the disturbing influence of some other substance present in a small proportion in the tar oils, evidently of polybasic character (perhaps a penta- or hexa-phenol), and of an extraordinarily strong reducing power.

*The Recovery of the Phenols by Means of Superheated Water*⁹⁸

Whilst carbolic acid can be readily extracted from oils by means of hot water, this is not possible with the phenols in primary tar, as they are homologues of phenol which are little or not at all soluble in water. If a phenol containing fraction of primary tar, *e.g.*, fraction 200° to 300°, of gas flame coal tar which contains nearly 50 per cent. of phenols, is heated in an autoclave with an equal quantity of water to 200°, with or without stirring, the cresols and the xylenols are largely dissolved in the superheated water, the oil having given up part of its phenols to the water forming a layer above the aqueous solution. This shows that the cresols and xylenols, which are scarcely soluble in water below 100°, are soluble to a considerable extent in water superheated to 200°.

On cooling the autoclave, the phenols separate again from the aqueous layer as their solubility diminishes with falling temperature. The drops of phenols forming in the oil do not sink to the bottom but rise, being still hot and specifically lighter than the aqueous layer. In consequence they redissolve in the layer of oil floating on top. If this is not taken into account and the contents of the autoclave are drawn off at the bottom, one must not be surprised to find no indication of separation, as expected on the strength of the higher specific gravity of cresols and xylenols at ordinary temperature.

The failure of the separation is, therefore, due to the difference in the coefficients of expansion of cresols and water,⁹⁹ cresols being lighter than water at temperatures of 200° to 300°. Another method was therefore tried.

The autoclave was so modified that the aqueous layer could be withdrawn at a temperature of 200°. For this purpose a high-pressure water-cooled condenser made of steel was fixed at the bottom of the autoclave, having a reducing valve at its outlet. The autoclave was again charged with the same quantities of primary tar oil and water; it was then closed and heated to 200° for 15 minutes. The autoclave was not allowed to cool, as in the first experiment, but connection was made with the high-pressure condenser, and the reducing valve was opened. A milky liquid was discharged, from which some drops of phenols began to separate and accumulate at the bottom of the receiver, as a heavy oily layer below the water. A test showed that the phenols were almost entirely soluble in caustic soda, proving that it should be possible to extract almost pure phenols from primary tar oils by means of superheated water.

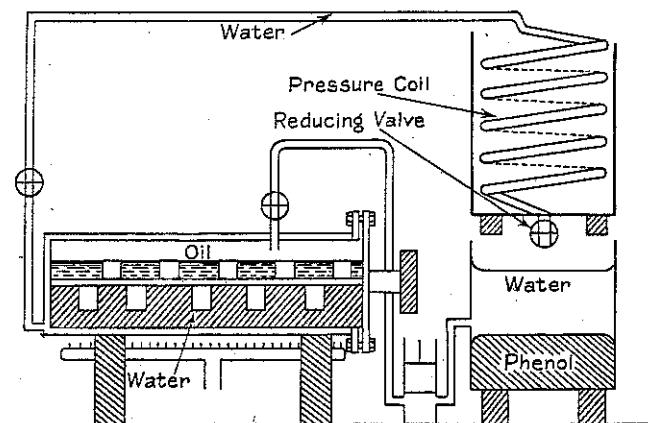


FIG. 52.

For works use, the process must, of course, be made continuous as regards both the feed and the discharge of the oils, water and the solution of phenols. We have been able to solve this problem on the small scale on which we were working with respect to the water feed.

A small high-pressure pump was fixed at one end of the horizontal autoclave by means of a copper capillary tube; by this, water was forced into the apparatus during the experiments. If the stirrer was used, the apparatus was mounted at an angle of about 6°, the pump being at the higher end, and the outlet valve at the lower end. In order to allow layers to form at this end, while stirring, the three last blades of the stirrer (see fig., *Abh. Kohle*, 1919, 4, 19) were removed. In the same way, oil might be introduced continuously from the other side and withdrawn from the water inlet side. In the industrial adaptation of such an apparatus the question of heat economy must be considered, and provision should be made for preheating the water entering the apparatus by means of the hot liquid discharged.

(1) *Experiments with Stirring.*—For these experiments rotary retort tar

from gas flame coal of Graf Bismarck Colliery was used, the fraction selected being 200° to 300°, containing 55.3 per cent. of phenols. The autoclave was charged with 1.5 litres of oil and 1.5 litres of water, heated to 225° and kept at that temperature for 10 minutes with agitation. The water for extraction was pumped in at the rate of 2 litres per hour; a total of 4.5 litres of pure water was used and circulated, after the phenols were settled and had been withdrawn. The aqueous solution of phenols was collected in portions of 1 litre. The temperature was maintained as far as possible at 250°; the speed of stirring

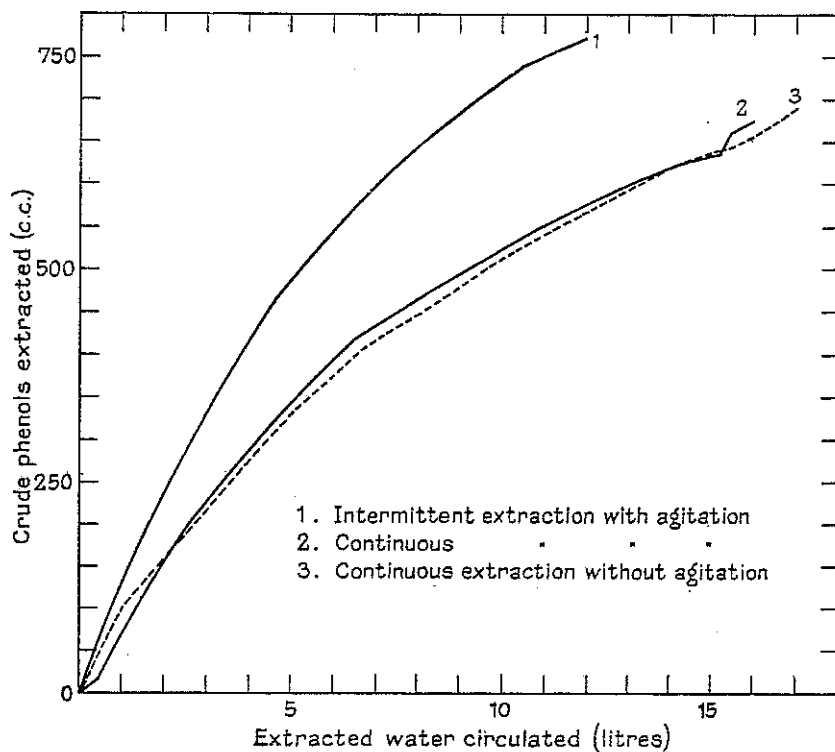


FIG. 53.

was about 120 r.p.m. After 7½ hours' extraction, during which altogether 15 portions of 1 litre each were collected, 635 c.c. of crude phenols had been extracted with a phenol content ranging from 86 to 96 per cent. The 1.5 litres of aqueous phenol solution still remaining in the autoclave were then withdrawn, yielding a further 30 c.c. of phenols. Renewed extraction with 1.5 litres of fresh water, with stirring, yielded another 12 c.c. of phenols, so that a total of 677 c.c. was obtained. In the autoclave 660 c.c. of oil now remained, containing only 16.1 per cent. of phenols. Of the 1.5 litres of oil used, there were 163 c.c. missing. Most of that remained dissolved in the water used for extraction; the rest was lost. The specific gravity of the oil had dropped from 0.984 down to 0.943, owing to the elimination of the relatively heavy phenols.

(2) *Experiment without Stirring.*—1.5 litres of the fraction 200° to 300° of primary tar from Graf Bismarck Colliery and 1.5 litres of water were heated to 225° in the horizontal autoclave, and kept at this temperature for 40 minutes. Water was then circulated. The volume of fresh water this time amounted to 3.5 litres. After collecting 16 lots of 1 litre each, the 1.5 litres of water left in the autoclave were drawn off. A total of 695 c.c. of crude phenols was thus extracted, containing 94 to 98 per cent. of phenol, *i.e.*, considerably more than in the experiment with stirring. 730 c.c. of oil remained in the autoclave; this had a phenol content of 18.8 per cent. The specific gravity had dropped from 0.984 to 0.947.

Fig. 53 shows clearly that in continuous experiments at the selected rate of circulation, the extraction proceeds just as quickly without stirring as with stirring. Curve 1 further shows that extraction in steps with equal quantities of water yielded a somewhat larger amount of phenols. Therefore, in the continuous extraction, the solution withdrawn was not quite saturated. This drawback might be obviated either by working at a slower rate, or by making the pressure-tube longer.

(3) *Further Experiments without Stirring.*—We then applied continuous extraction to a number of commercial phenolic oils, particulars of which are tabulated below. Experimental arrangements and rate of circulation were the same as in the previous experiment.

TABLE XXVII

Continuous Extraction of Commercial Oils without Stirring

Used: 1.5 litres oil, 4.5 litres water

1	2	3	4	5	6	7		8
Expt. No.	Kind of oil.	Phenol in oil before extraction. %	Number of Extracts.	Total crude phenols extracted. c.c.	Phenol in individual crude extracts. Vol. %.	Oil residue in autoclave.		Phenol content. % by Vol.
						c.c.		
1	Fraction 200–300° from primary tar of Graf Bismarck Colliery.	55.3	16 × 1 l. 1 × 1.5 l.	695	94–98	730		18.8
2	Fuel oil 180–310° from primary brown coal tar, Rositz.	19.8	10 × 1 l. 1 × 1.5 l.	156	95.5–97.5	1245		9.8

In the extraction of fraction 200° to 300° of the primary tar from gas flame coal (Experiment 1),* the phenol content, after pumping-through 12 times its volume of water, was reduced from 55 to 19 per cent. The extracted crude phenols contained hardly any hydrocarbons. A similarly favourable result was obtained in the extraction of the fuel oil fraction 180° to 300° from Rositz primary brown coal tar. In that case only one-half of the 20 per cent. of phenols remained in the oil. It should be pointed out at this stage that for most

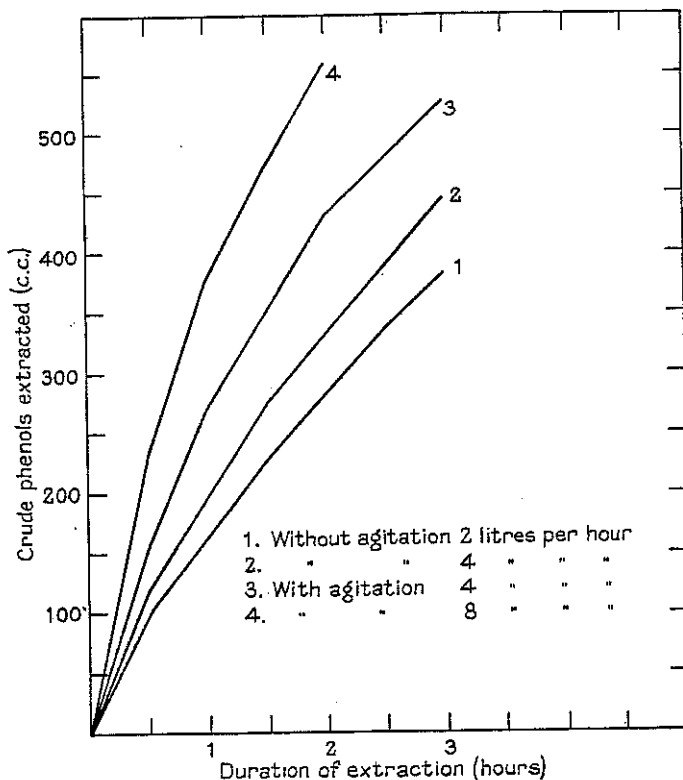


FIG. 54.

purposes a complete removal of the phenols from the oils will not be necessary. It will be sufficient to remove those tar acids which are corrosive or otherwise deleterious, that is to say, only those more readily soluble in water, since the corrosive acid properties depend upon their solubility in water.

Experiments at Increased Rate of Pumping.—We proceeded to experiment on the influence of an increased pumping rate on the efficacy of the extraction. Theoretically, it is to be presumed that the absorption of the phenols by the aqueous liquid will, with increasing water feed, more and more recede from

* Only 3.5 litres of water were used in Expt. I.

the saturation point. In this series of experiments the fraction 200–300° of the primary tar from Graf Bismarck Colliery was used. The experimental arrangements were the same as before at slower rates of pumping. In the first instance we worked with a rate of pumping of 4 litres per hour, without stirring; we then extracted 19 per cent. more phenols in the same time as before. Since the high rate of pumping might not leave the water in contact with the oil for a sufficiently long period, mixing of the liquid by stirring was tried. Thus the amount of phenols extracted was increased by about 4 per cent. when pumping at the rate of 4 litres per hour, compared with the experiment at 2 litres per hour without stirring. In a third experiment in which the rate of pumping was increased to 8 litres per hour, we extracted in two hours 560 c.c., against 280 c.c. in the first experiment at 2 litres per hour without stirring. The rate of extraction had therefore been doubled.

TABLE XXVIII

Extraction Experiment with Fraction 200—300° from Primary Tar of Graf Bismarck Colliery.

Duration of extraction.	Total crude phenols extracted.			
	1.	2.	3.	4.
	Without stirring.		With stirring.	
	Rate of pumping.			
	2 litres per hr.	4 litres per hr.	4 litres per hr.	8 litres per hr.
1 hr.	164	195	270	379
2 hrs.	280	335	433	560
3 hrs.	377	448	531	—

The curves of Fig. 54 will make these relations still clearer.

The phenol content of the extract did not vary noticeably in these four experiments; it ranged from 94 to 98 per cent. In Expt. 4, the heating gas had to be increased considerably owing to the high rate of pumping, in order to maintain a temperature at 225°. It was therefore of interest to inquire whether the phenol extraction could not be rendered more complete and rapid by raising the temperature. To decide this question in the easiest way an oil, which contained relatively little phenol and which yet had not been completely exhausted by treatment at 225°, was submitted to extraction.

Extraction Experiment at 300°.—Since the solubility in water of phenols increases with rising temperature, it was to be anticipated that the extraction

would become more efficient at higher temperatures. It was also to be expected that the phenol content of the extract would fall off markedly after a few operations. We had in particular to ascertain whether the proportion of hydrocarbons in the extracted crude phenols would rise with higher temperature. With a view to the industrial application of the process, it should be noted that a plant operating at higher temperatures would be more expensive and less safe on account of the increased pressure. At 225° the vapour pressure of liquid water is about 25 atm., a pressure which is not unusual in boiler practice; at 300° it is 85 atm. The question would therefore arise whether the advantages of operating at 300° would compensate for the difficulties which the construction and manipulation of the plant involve.

For this experiment we used a fuel oil from the primary brown coal tar of the Rositz works of the Deutsche Erdöl A.-G. We extracted the oil with water in the first instance four times at 225°, as in the previous experiments, and continued the extraction afterwards at 300°. Table XXIX shows the results.

In the first four extractions the quantity of crude phenols extracted dropped from 55 to 26 c.c. In the next extraction, at 300°, it rose to 100 c.c.; in the

TABLE XXIX

*Extraction of Fuel Oil from Rositz Brown Coal Primary Tar
(boiling 180° to 310°) at 225° and 300°*

	Extracted at							Total phenols separated.
	225°.				300°.			
Extract No. . . .	1	2	3	4	5	6	7	
Phenols (c.c.) . . .	55	45	34	26	100	108	56	424
Purity %	about 95				55.5	47.5	36.5	

sixth, even to 108 c.c., but dropped off in the last to 56 c.c. There had thus been a very considerable increase in the quantity extracted. It is true that the phenols recovered at 300° showed an extraordinarily high percentage of hydrocarbons; this was indicated by the circumstance that the extracted phenols on separation from the aqueous solution did not sink to the bottom, but collected in a surface layer. The quantity of oil residue amounted to 950 c.c., and it contained only 3.3 per cent. of phenols.

These experiments, therefore, demonstrate that one can by the use of higher temperature reduce the phenol content to a greater degree than at