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High Pressure Experiments

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# PRODUCTION OF PYRIDINE FROM THE LIQUID PHASE PRODUCTS FROM BROWN COAL

## Preliminary Experiments

## Summary

Bases and phenols from brown coal liquefaction products were washed out in glass columns with 10 percent sulfuric acid and 10 percent sodium hydroxide. The bases were set free by neutralization with gaseous ammonia, separated, and pyridine determined in them analytically.

The amount in the different products were as follows:

Liquid phase gasoline, - 165°, from Lu. Catchpot
0.012 - 0.014 percent pyridine

- 200°, from Rhenish brown coal
0.019 - 0.022 percent pyridine

Liquid phase middle oil, + 165°, Lu. Catchpot
0.042 - 0.056 percent pyridine

According to information in literature, pyridine forms compounds with the phenols present in solution, and it is to be suspected that it will be found in higher fractions than corresponds to its boiling point

(116°). This fact seems to be confirmed in the higher percentage of pyridine content of the middle oil.

No reduction in quality of the products is to be feared from the removal of the bases. The experiments are being continued.

/s/ Botter

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Apparatus and Recovery of Bases (Phenols).

For the scrubbing of the liquid phase products from bases and phenols glass columns about 160 cm long (135 cm with Raschig rings about 3 x 6 mm) and 6 cm diameter were used. The products were fed from below countercurrently to the 10 percent sulfuric acid or sodium hydroxide (fed dropwise from above). Between the two scrubbers and behind them was a water scrubber consisting of a 85 cm column, also filled with Raschig rings.

Attempts to distribute the feed as fine as possible by using fritted glass inlets were successful only with gasoline; with middle oil there was a plugging up.

At first the breaking up of the double compounds of phenols and pyridine was done by means of sodium hydroxide solution. Water scrubbing was followed with sulfuric acid wash, and then again with water. A thruput was maintained of 1000/g of the feed, 200 g 10 percent NaOH, 200 g water, 200 g 10 percent $H_2SO_4$ and 200 g w ater.

The total wash acid (the alkali was only studied once) was separated from the entrained oil in a separatory funnel, and distilled for the separation of alcohol, etc. Gaseous ammonia from a steel cylinder was fed under cooling (below 15° C) into the acid so lution until the solution reacted alkaline. The liberated bases were recovered in part by separation in a separatory funnel and in part by extraction with ether.

Pyridine was determined by titration (Astruc, C.R. vol. 129, 1899, p. 1021) in the 70 - 160° fraction after distilling off the ether and fractionization, or by the precipitation method with cadmium chloride (Malatesta and Germain, Bull chim. et farm., vol. 53, 1914, p. 225).

Changes in the product are shown in table 1, the results of the determination of bases in table 2.

Table 1 shows that only the bases and the phenol contents have changed (no figures given). The washing has not however been sufficiently thorough to remove all the bases.

Table 2 shows that the crude base contents of the products was more reduced in the higher boiling point range, - about two to three times as much in the middle oil than in gasoline, - , and that the three products contained similar proportions of pyridine in the crude bases.

Table 1.

| | Liquid phase gas. Leuna, P 1251 -165° | | Liquid phase m.o. Leuna, P 1251 + 165° | | Liquid phase gasoline from Rhenish brown coal K 229, -200° | |
|---|---|---|---|---|---|---|
| | before scrubbing | after scrubbing | before scrubbing | after scrubbing | before scrubbing | after |
| Spec. grav, 20° | 0.750 | 0.753 | 0.936 | 0.927 | 0.781 | - |
| Aniline point, °C | 26.5 | 27 | 9.5 | 12.5 | 18 | - |
| Start. b.p. °C | 53 | 66 | 178 | 158 | 70 | - |
| percent - 100° | 46 | 41.5-200° | 4 | 7-100° | 19 | - |
| - 150° | 95 | 95.5-250° | 52.5 | 51.5-150° | 80 | - |
| - 170° | - | --300° | 90.0 | 88.5-170° | 95 | |
| Final b.p. | 164/98 | 163/98.5 | 321/99 | 320/98 | 233/99 | |
| Phenols | 0.125 | - | 24.43 | - | 0.92 | |
| Bases(mg $NH_3$/li) | 984.0 | 56.6 | 978.0(? | 76.5 | 168 | 40.8 |

Table 2.

Analyses of the recovered crude bases

| | P1251, -165°C | | P1251+165° | | K 229 S gas-200° | |
|---|---|---|---|---|---|---|
| kg starting matter | 95 | | 18 | | 80 | |
| g crude bases, ether-free, moist, | 135 | | 194 | | 189 | |
| Decomposition of crude bases | | | | | | |
| 70-160° fract,: upper layer, percent $H_2O$ | 66.3 | (89.5) | 39.0 | (75.5) | 77.0 | (145.6) |
| percent pyridine (titrat.) | 19.2 | (26.0) | - | | 1.1 | (2.0) |
| percent pyridine ($CdCl_2$) | 14.5 | (19.5) | 61.0 | (118.5) | 21.8 | (41.4) |
| Lower layer: | | | | | | |
| percent pyridine (titr.) | 3.7 | (1.0) | - | - | 9.0 | (0.2) |
| g crude bases, dry | 118.2 | | 141.1 | | 171.8 | |
| percent crude bases in orig, product | 0.125 | | 0.786 | | 0.215 | |
| g pyridine in crude bases after titration | 12.8 | | 10 | | 17.2 | |
| after $CdCl_2$ pption | 10.8 | | 7.5 | | 14.9 | |
| percent pyridine in crude bas. | 9.1-10.8 | | 5.3-7.1 | | 8.7-10.0 | |
| percent pyridine in original product | 0.012-0.014 | | 0.042-0.056 | | 0.019-0.022 | |