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Concerning Cleavage of Pressure

Paraffins

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Ruhrchemie- Addressed to Prof. Martin, Dr. Alberts, Dr. Velde
and Engineer Wilkie.

In the following we describe a few experiments which have the aim to carry out the cleavage of paraffins from pressure synthesis in such a manner that as little gas and naphtha (up to 200°C boiling) and as much as possible of Diesel oil fractions (200-320°C) would result.

The cracking experiments were carried out in the following manner.:

The pressure paraffin was forced from a heated steel bottle by compressed hydrogen or nitrogen through two (in series) pressure pipes of 16.5 mm diameter and 1.5 meter length. These pipes are surrounded by a electrically heated lead bath in a length of each 70 centimeters whose temperature is measured. After passing through these pipes the product is relieved to normal pressure. Whereby the cracked gas that has been formed escapes. In a low cooled condenser the light naphtha is separated from the gas. The cracking temperatures that are recorded in the table are lead bath temperatures.

The experiments 1 to 12 that are summarized in table I were carried out under the direction of Dr. Speitmann. The so-called "pressure paraffin" from the experimental plant of Ruhrbenzin serve as starting product for the cracking process. It contains 1-2 wt.% of components that boil below 200°C, and about 26 wt% of Diesel oil fraction (200-320°C compare Figure I). The values "percent cleavage", "percent gas", "percent naphtha" and "percent Diesel oil" are calculated in such a manner that the naphtha and Diesel oil amounts already contained in the starting product were subtracted from the amounts that were determined in the end product by boiling analysis. The numbers "percent cleavage" gives therefore the percentage of newly formed products from the total charged amount. The statements "percent gas", "percent naphtha" and "percent Diesel oil" express the distribution of the newly-formed product in wt. %

The numbers in Table I show that in the experiments 1-12 the principal amount of the cracked product did not consist of Diesel oil as was planned. A considerably larger portion of the pressure paraffin was split into gas and naphtha. This is caused by too large a cleavage at one throughput (pass). In continuously operating cracking plants this cleavage percentage amounts to about 10-20%, here the values were about 30-57%. Further one needs to consider that at least a part of the Diesel oil quantities that are already contained in the starting product are split into gas and naphtha, that therefore the newly-formed naphtha and gas portions do not originate only from the cleavage of the true solid paraffins.

One cannot see a considerable dependence upon pressure from the statements in table I. This is also not very probable since in all the used pressures there occurs a cracking of the liquid phase.

One needs to add to the results of Table I that the naphtha that is contained has an octane number of 58 (research) at a boiling point of 140°C.

The experiments 13-21 (compare Table 2) differ from the experiments so far in that the naphtha and Diesel oil amounts that were present in the pressure paraffin of Ruhrbenzin were removed before cracking by distillation.

For the cleavage experiments 13-27 and 19-21 the Diesel oil fractions were taken out through distillation at a normal pressure in a pilot distillation apparatus. The distillation residue however contains 8% of the fraction 200-320°C (compare figure 2).

For cleavage test 18 we used a starting product that was still more sharply cut. At a pressure of 15 mm mercury about 25 wt.% were distilled off from the pressure paraffin. The boiling curves of distillate and residues are presented in Figure 3. The residue contained only 1 wt.% of fraction 200-320°.

The boiling analysis of the mixture that contained much solid paraffin was carried out at a pressure of 15 mm mercury. The conversion of boiling temperature from vacuum to normal pressure was done on the basis of literature claims for paraffin hydrocarbons.

Experiments 13-21 were carried out at 100 atm. absolute pressure and at 1.0 atm. absolute pressure. These two pressures were chosen on purpose as extreme conditions. 450°C to 1629°C pressure paraffin were put thru the apparatus per hour which correspond to a residence time in the cracking of 11 minutes to 40 minutes if one considers the total pipe space that is surrounded by the lead bath as the reaction space.

In calculation of numbers "percent cleavage", "percent gas", etc. one considers also here the Diesel oil amounts that are contained in the charge product.

Since these experiments also were conducted only once through for the product through the cracking pipes, one cannot say with certainty that the numbers that are summarized in Table II are valid also for cracking in continuous operation. It is uncertain whether material that has already passed through the apparatus once but is still uncracked would behave just like fresh starting products in the later cracking. But one can assume with great probability that no considerable difference exists. If one compares the boiling curves of starting material and end product of experiment 18 (Figure 3 and 5) and those of starting material for experiments 13-17 and 19-21 (Figure 2) then one can see that this latter product (Figure 2) could represent with regard to boiling positions an end product of experiment 18 that has been freed of cracked fractions. But since the cracking of the starting product of experiment 18 proceeds just like those of the other experiments the above assumption has been justified.

The following should be mentioned with regard to the solidifying point of the Diesel oil that is obtained. The solidifying point of fraction 200-320°C were about $+2^{\circ}$ to $+4^{\circ}$ C. This poor solidifying point is probably caused by poor sharpness of separation in the distillation. As can be seen from Figure 5 the various numbers that are found in the various fractions correspond to the values that were obtained in the distillation of normal Kogasin.

If the Diesel oil (200-320°C) that was separated by vacuum distillation is subjected to a second vacuum distillation, the solidifying point of the distillates were: at 70 wt.% distillates of minus 11° C, at 90 wt.% distillate at -4° C.

A number of gas analyses of the cracked gases that were contained are summarized in Table III. The cracked gas contained various amounts (partly up to 30%) of gas that was used as compression gas with hydrogen or nitrogen. The analysis results and the liter numbers for the cracked gas collections were corrected in such a manner that the first experiment an H_2 content of 2% was assumed in the other experiments a nitrogen content of 2% was assumed on that basis.

If one compares the results of experiments 13-21 (Table II) with the numbers of the experiments 1-12 (Table I) one can recognize the distribution of cracked products has been shifted considerably mainly through depression of cleavage percentage from about 35% to about 15%. The Diesel oil portions could be increased on an average from 30% to about 75% to 80%.

At a pressure of 100 atm. absolute pressure a temperature of 440°C and a charge of 600-900 cc per hour (corresponding to about 20-30 min. residence time in the reaction zone) is most favorable.

If one works at a pressure of 10 atm. absolute pressure then the temperature is about 470°C, and a charge of 500-600 cc per hour is most favorable (corresponding to about 30-36 min. charge residence time in the reaction zone). One no longer reaches the favorable gas-liquid ratio of the experiment of 100 atm. absolute pressure. The gas that is obtained here obtains more unsaturated hydrocarbon. It corresponds now in composition almost to the cracking gas that results from cleavage of Kogasin II to lubricating oil cracked naphtha (gas phase cleavage).

At 10 atm. absolute pressure and 470°C part of the pressure paraffin is present as gas, while at 100 atm. absolute pressure and 440°C there exists for certainty only liquid phase cleavage.

/s/ Kolling

Tables and Graphs follow in Original

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