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# SINCLAIR REFINING COMPANY

## Alkylation of n- Butylene With Isobutane Oppau Experiments

Dr. Blumel reports about the alkylation tests at Oppau and about the result of a Raman analysis of the products.

The alkylation of isobutane with propylene or butene in the presence of sulfuric acid, has been carried out in a semi-continuously operating laboratory equipment in the liquid phase at slight gauge pressures. 90-100% sulfuric acid has been used. The best results have been obtained with a concentration of 96-98%.

In the alkylation of isobutane with n- butane, the theoretical output (theory = 204%) could be nearly attained, with 203% (at 0°C, the ratio of the mixture being 10:1) 190%, i.e. 95% of the total output go over at 185°C. This distillate had a specific gravity of 0.714, bromine No. 2, sulfur 0.01, no resinous constituents (acc. to BVM) and an octane No. (motor) of 96.

The following table records output and properties of the fractions up to 185°C.

<u>Column Distillation</u>	<u>%</u>	<u>Octane No/motor of the fraction</u>
53-98°	9.2	93.5
98-102°	23.4	99.5
102-108°	4.2	96.0
108-112°	7.5	94.5
112-115°	47.2	96.0
115-185°	8.5	91.0

The Raman analysis of the individual fractions showed the distillate (up to 185°C) to have a (calculated) composition as follows:

Heptane	5%	2,2 -	Dimethylpentane
	5%	2,4 -	
Octane	27%	2,2,4 -	Trimethylpentane 86% (no
	29.5%	2,3,4 -	2,2,3 trimethylpentane)
	29.5%	2,3,3 -	
Higher Hydrocarbons	4%		

There has not been formed any Dimethylhexane or monomethylheptane.

It is noteworthy that 2,3 - dimethylpentane is formed in the alkylation of isobutane and propylene, whereas 2,2 - dimethylpentane is formed when isobutane is alkylated with n- butane which contains propylene at a lower temperature.

All the three iso-octanes can only be formed by the isomerization of products evolved from n-butene. The outputs are about equal for all the three of them. But 2,2,3-trimethylpentane, which had been expected has not been found. That only the threefold branched octane isomers are formed may be due to the presence of n-butene-2, more than 90% of which are present in the n-butene used and which may appear in its cis and in its trans form.

The test has been run for 120 hours; initially the concentration of the acid was 97%; the test was discontinued when it attained 92%, since the fraction above 185° (polymerization) began to become more important. The consumption of acid amounted thus to 13.5 kg of stabilized alkylate per 1 kg of acid.

In further investigations we have studied the part played by the isobutane in the alkylation. The output obtained in these experiments was the theoretical one. Nevertheless, there are losses of isobutane occurring (3-4%); but these are certainly not due to the alkylation reaction. If we take into consideration the amount of olefins contained in the isobutane used, these losses are still lower.

Leuna had obtained yields which exceeded the theoretical values, in the laboratory as well as in the pilot plant. Copau could not duplicate these results. The discrepancy caused a vivid argument.

In the Oppau tests, particular care has been taken to recover quantitatively all the products which issue from the processing, including isobutane which is frozen out and reintroduced into the process. It had been found that the fresh isobutane used contains always a certain percentage of olefins, in the case in question, e.g. 2.6% butylene. This amount would be sufficient for explaining the fact that outputs exceeded the theoretical expectations. In pilot plant tests at Leuna, with continuous recirculation of isobutane, the outputs have always exceeded the theoretical amount. Leuna thinks that the pilot tests are of greater demonstrative power, because, in contrast to laboratory tests, the losses are not important.

Dr. Rieger states that outputs exceeding the theoretical expectation have been also obtained in U. S. commercial plants.

Hitherto, we cannot explain the outputs which exceed the theoretical expectation. Leuna tests, where isobutane by itself was treated with sulfuric acid, showed apparently the isobutane to contain more olefins after issuing from the sulfuric acid than prior to the treatment; in these tests, the sulfuric acid has been blackened and an oleous layer is separated out on top of the acid. This phenomenon may point to a dehydrogenation action exercised upon the isobutane. But these indications are not plain, as there could not be ascertained whether hydrogen had been formed simultaneously.

This project ought to be studied more carefully. When we operate with split-gas which contains a low percentage of olefins only, this phenomenon might become important, because it means a saving in olefins. Whenever the dehydrogenation product has a high olefin content, it may even be an advantage to obtain only theoretical yields, in order to secure the maximum efficiency of the isobutane available.

Dr. Blusmel reports on rates of output obtained in the n-butylene-isobutane alkylation.

present (the amount of the emulsion) may have been 1000 cm<sup>3</sup>. The optimum charge of the apparatus has been ascertained by determining the yields with increasing charges, whereby the following curve (may be traced, M.B.) resulted.

This curve shows that the optimum charge, using a ratio of isobutane to n-butylene of 10:1, the reaction temperature being 0°, is a through put of ca. 30 and 60 g of olefins per hour.

The O. No. of the product varies with the reaction temperature as follows:

Temperature °C:	-5	±0	+5
Octane No.	95	96	95

The optimum temperature range with respect to the output lies between -2 and +2°C. At -10°C the rate of output goes down steeply, at +20°C it may be estimated to be 160-170%.

The life of the sulfuric acid can be lengthened from 100 to 130 hours by adding emulphor. That means, by adding emulphor, the consumption of sulfuric acid is reduced from 9.2 g per 100 g of alkylate to 7 g.

An important factor is the velocity of the stirrer in the reaction vessel. When the number of rotations per minute made by the stirrer increased from 240 to 680, the output increased 20%.

In the Oppau plant, the hydrocarbons are distributed in the acid by means of a filter plate and the stirrer operates at 680 r. p. m.

M. Beth

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MB:mbt

cc: All Divisions