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The Preparation of Fatty Acids from the Neutralization Alkalies

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Certain amounts of fatty acids are formed in the medium pressure synthesis besides hydrocarbon. These fatty acids are contained in the end gases but leave the oven in vapor form. The condensation of the product and and of the reaction waters occurs in each medium pressure plant because of indirect cooling. The condensed fatty acids that are formed would cause severe corrosion damages in the condensator and in the following installation.

Therefore, it is indispensable to neutralize in vapor form the small amounts of fatty acids before condensation. This is done in the following way. The hot gas is sprayed with soda solution. Thereby the fatty acids which are present in the end gases are formed into fatty acid sodium salt which are present in the used-up sodium hydroxide. A very dilute solution of soda is used for operational reasons particularly in order to avoid unnecessary alkali losses. Working with concentrated solution and its repeated use, i.e. a sodium hydroxide circulation process, is not possible because difficulties occur in the separation of the oil from the hydroxide through emulsion formation. Therefore, the use of very dilute soda solutions for neutralization in medium pressure plants cannot be avoided. These soda solutions contain very low percentages of sodium salt of fatty acids in solution. The concentration of unused alkali in the waste sodium hydroxide amounts to about 0.5% and the concentration of fatty acids about 0.5-1%. The very dilute soda solutions are not used so far, in any of the plants. It has been generally thought that the preparation of these fatty acids would not be economical even if they give good yields.

Although the end gases are neutralized with sodium solution there still remains certain amounts of fatty acids in the condensation product. The residual fatty acids go partly into the reaction water, partly into the condensate oil. Today they are generally removed from the condensed oil by lye washing. The fatty acids quantities that are prepared by means of a lye washing are practically utilized all over. These quantities are small compared with those that are lost in the neutralization alkali solutions.

Because of the shortage of fatty acids that have been caused by the war, we investigated the possibility to recover the fatty acids that are contained in the end hydroxide. Through examination of the conditions we found the workable process which allows to recover the fatty acids on an economical basis with about 90% yield. The investigations that were first carried out in

the laboratory led to the construction of a technical plant in the summer of last year. Since November it has been in uninterrupted operation and has fulfilled all expectations. Before I go into a detailed discussion of this process, I should like to touch upon a few other possibilities which could also be used for the preparation of the fatty acid in the waste hydroxide. I must observe beforehand that the experiments have not given usable results. These processes that were considered only allow a small portion of the available fatty acids to be recovered. In this connection, we tested the possibility to precipitate the fatty acid from the dilute solution with calcium. But we found that the solubility of the fatty acid calcium salt is still too great, respectively the concentration is too small, to attain a practically quantitative preparation. Also, repeated precipitation of the sodium salts of fatty acid with calcium, did not give complete precipitation of the fatty acid. For instance we obtained a precipitation of only 2.3 g. of fatty acid (that is, only 23%) by twice precipitating with sufficient excess of calcium from a hydroxide solution that contains about 10 grams of fatty acid per liter. The investigations show that the fatty acids that have been recovered by this method are primarily high boiling fatty acids. 72.2% from C_8 up has been found. But this method cannot be considered to be an economical recovery.

Further we tried to liberate the fatty acids from the acid dilute solutions by driving them out with carbon dioxide. When the carbon dioxide stream was passed through the acid solution at a temperature of 95°C about 3.6 grams per liter which equals 36% could be recovered from the starting hydroxide of about 10 grams per liter.

Hereby the yield was too small to carry it out economically particularly since in both these methods the precipitation with calcium and driving out with carbon dioxide large amounts of acid are necessary. Partly to split the calcium salt, and partly to acidify the solutions.

Now I shall discuss the actual procedure as it has been used. We tested first the possibility to extract the fatty acids with suitable solvents after they have been liberated by hydrochloric or sulfuric acid from the end solution. The solvent is generally required to be practically insoluble in water. This is necessary in order to keep the acid in the waste water in bearable limits since they deal with considerable amounts of water in the extraction. Suitable extraction agents are trichloroethylene or also the light naphtha that results from this synthesis. We succeeded to accumulate practically all fatty acids in the solvent by choosing suitable operation conditions for the extraction. The solvent that contained the fatty acids can be processed according to various methods. The fatty acids can be recovered by distillation. Thereby the solvent must have a boiling point below that of the lowest fatty acid that is to be recovered. Another method for liberating of the fatty acids from the solvent is by means of sodium hydroxide washing. The sodium

hydroxide can be enriched with fatty acids at will. The fatty acids are then removed by mineral acids. The second method seems more tedious at first. But we have decided in favor of it for various reasons. Its advantage lies in the fact that no corrosion attack by fatty acids is to be expected in the installation parts that come into contact with the solvent. The solvent is freed continuously of the fatty acids that are contained in it by alkali. A distillation would require considerable corrosion resistance in the distillation installation. Also it would be necessary to use an exact and possibly low boiling extraction agent because the lowest fatty acids have low boiling points, e.g. acetic acid at 118°C. A further disadvantage of the distillation separation is the fact that a certain amount of residual oil from the alkali is contained in the solvent and reaches the fatty acids because of the low separation possibilities. Therefore, the distilled fatty acids would always contain a considerable portion of unsaponifiable material. Also this disadvantage is avoided by neutralization of the fatty acids from the solvent with the aid of sodium hydroxide.

Considering the described facts we have arranged our present plant as follows:

The terminal alkali solutions of the I, II and III stage are acidified with sulfuric acid or hydrochloric acid up to a certain pH value about 6-5.5 with the aid of a simple dosage installation. Then they are extracted with light naphtha that is formed in the synthesis proper. This light naphtha is always in a closed cycle. In order to obtain sufficient extraction of the water a very simple apparatus is necessary which consists practically of a mixing pipe and a separator. The extraction naphtha is forced through an extraction installation and immediately after extraction through a sodium hydroxide wash as it is customary in the normal naphtha extraction. Thus only one pump is necessary for the circulation of the naphtha.

The sodium hydroxide is also conducted in a cycle, and is changed after accumulation of the desired amount of soap. After changing the sodium hydroxide that has been enriched with sodium soap it is decomposed by sulfuric acid. Thereby the fatty acids that are now present in concentrated form separate into a distinct layer. The emulsion formation of naphtha with the soap solution that is to be feared can be controlled entirely by minor tricks.

The following is an interesting phenomenon of the extraction of the waste water with naphtha. With suitable choice of the ratio of waste hydroxide; naphtha it is possible within certain limits to influence the composition of fatty acids that are to be prepared. With a high excess of naphtha over the waste hydroxide it is possible to extract also the low fatty acids like acetic acid, propionic acid without residue. With low naphtha excess the water-soluble fatty acids are only extracted to a certain degree. Since the low fatty acids are practically equally soluble in naphtha and water these fatty acids are distributed according to their distribution coefficient, to naphtha and hydroxide.

The more naphtha I use the more fatty acids I can wash out. This fact can be used when the fatty acids are to be used for a certain purpose. If for a certain reason the portion of low fatty acids is to be kept small then I will extract with small amounts of naphtha. If it is of value to recover all fatty acids, I will use a correspondingly larger naphtha excess. The fatty acid composition that has been obtained in our operation with various amounts of naphtha was, e.g. as follows:

In one case to one part of hydroxide, 0.5 parts of naphtha were used. It was found that up to C_4 inclusive only 7.5% were contained. The rest were higher fatty acids. Another case in which four parts of naphtha were used to one part of hydroxide, the portion of low fatty acids up to C_4 inclusive was 29.6%. When naphtha amounts were used that lie between these figures also the portions of low fatty acids were between the limits stated.

One can also obtain by this method the separated recovery of predominantly higher or predominantly lower fatty acids. One has to operate with two separate extraction naphtha cycles, whereby in the circulation naphtha of the first extraction there are extracted primarily high fatty acids, while in the second cycle adjoining the first, one recovers the low fatty acids. In this manner one can recover easily 95% of the available fatty acids with two extraction stages or with corresponding higher naphtha excess in one extraction stage.

If one considers the fatty acids amount on the absolute basis, they are relatively small. They are only 0.2-0.3% of the total primary production. Thus, they can hardly carry much weight in consideration of a complete plant. But if one considers the extreme shortage of fatty acids and also considers that the supplement of fatty acids for certain finished products is often relatively small, then it becomes obvious that the recovery of the small amount of fatty acids make it possible to produce considerably more of the products that are prepared from it.

Finally, it should be mentioned that the recovery of these fatty acids even in such small amounts can be carried out economically because the installation costs and the operation costs are so low that they can hardly be considered. Practically no personnel is necessary. The two pumps that are necessary can be put into another pump house, as it is done in our case. The pure operation costs of acid and alkali lie so that they are bearable in every way, even if it looks at first as if the use of acid and alkali corresponding to the large amount of water that has to be processed is to be expensive. The operation reagent costs for the plant per kg of fatty acids are about 0.16-0.17 R. Marks.

These costs are bearable since the price for fatty acids from C10 upward is about 0.74 R. Marks. The portion of fatty acids of C_{10}- C_{20} lies between 55-60% of the recovered fatty acid.

As has been mentioned before the construction costs are extremely low since we have used normal iron for the whole plant. In normal times one would probably produce the pipes and separators of acid resistant material. But we have preferred to finish the construction as quickly as possible and to risk possible corrosion attacks. We would change an elbow or similar parts that are used very much. Until now we have not had any considerable corrosion damage. For transferring the acidified alkali solution we used a pump with a pressed material casing.

Summarizing I can say that it is possible to erect such an installation which makes it possible to recover the fatty acids which result in the neutralization waste lyes of pressure synthesis with small means and in a short time. Thereby one utilizes all the possibilities which the Fischer synthesis offers.

signed Ohme

10/15/46 - Rochelle H. Bondy

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