

Reel 67 API-TOM Ruhrchemie Oberhausen-Holten.

Report by Dr. Grimme - Motor fuel works Rheinpreussen.

About the preparation of isopropyl alcohol and methylethylcarbinol.

The conversion of olefin hydrocarbons to alcohols with the use of sulfuric acid as (as you may know) a large scale process, is used in the United States since the first years after the world war on a growing scale. In Europe this process has not been introduced before we started the investigations, except in small experimental plants that were mostly used for the conversion of ethylene from coke gas to ethyl alcohol. The processing of ethylene to ethyl alcohol by way of sulfuric acid esters differs in many respects very far from the processing of the rest of the olefin hydrocarbons to the corresponding alcohols. Therefore in the following the ethylene processing which is of no importance in the scope of the Fischer-Tropsch products shall be neglected. On the other hand, what we have reported about the processing of propylene or butylene is valid also for higher olefins like pentene and heptene if one neglects small variations. Only with olefins starting with octene upwards does the production of the corresponding alcohols over sulfuric acid esters differ so much that they do not lie in the scope of the present subject. Although the chemistry of dissolving olefins in acids and adjoining hydrolysis of the sulfuric esters to alcohol is relatively simple, the way to obtain good yields in this method is quite difficult. We experienced that during our investigations in the laboratory (partly together with Ruhrchemie) that were started in spring 1937 and that led to the beginning of the operation of the first large scale plant in Europe in the winter 1939-1940 at our motor fuel works. In order to visualize for you the hidden difficulties of the processing of olefins I would like to make a few general statements about the chemistry of the olefin-acid reaction, before we go into the special process as it is carried out by us.

Till today sulfuric acid is the only acid that is used for the technical conversion of olefins to alcohols by way of ester. Other reagents of acid character have been suggested but are without practical importance because they give poor alcohol yields. Probably the basic reaction occurs upon use of all acid admixtures in such a way that the olefin combines first with acid to definite ester-like compounds which are hydrolyzed with formation of alcohol either immediately or in later reactions. Numerous suggestions were made for a "direct" or "catalytic" water addition to olefins for alcohol formation in the attempt to avoid the use of concentrated sulfuric acid in the process. In most of these direct methods dilute acid or an acid salt is used, usually with simultaneous addition of steam and using of high pressure. But one can assume in such processes the function of the acid reagent in the beginning is the same as in the better known reactions with concentrated acid. Thus, intermediate ester formation with following hydrolysis occurs. Three operation conditions are of decisive importance for the alcohol yield in the processing of olefins with sulfuric acid.

1. The acid concentration.
2. The acid-olefin ratio.
3. The temperature during the olefin absorption.

Acid Concentration

The concentration of phosphoric acid is of great importance for the course of the olefin absorption. 100% H_2SO_4 causes charring in all olefins and temperature control in such cases is difficult. The water content of less concentrated acids does not act as simple dilution agent because other homogeneous mixtures of sulfuric acid are inferior to sulfuric acid where water is used as dilution agent. Only 75-80% acid can be utilized practically for the absorption of C_2-C_7 hydrocarbon, such acids in which monohydrate ($H_2SO_4 \cdot H_2O$) is contained in abundant amounts. The stability of the compound $H_2SO_4 \cdot H_2O$ is already indicated by its high formation heat. This monohydrate remains also when it reacts with olefins whereby the equation was $C_nH_{2n} + H_2SO_4 \cdot H_2O = C_nH_{2n} + 1.0SO_2 \cdot H_2O$. The monoalkylsulfate forms without elimination of water. That can be seen from the composition of numerous salts, for instance, the barium salt that can be isolated and contains the corresponding hydration water. This assumption is further confirmed by the fact that by use of pure monohydrates (84% acid,) the reaction with olefins occurs with smallest decline of the reaction velocity during progressing reaction. Thus, no accumulation of water occurs in the excess unreacted acid. If dialkyl sulfate is formed by the reaction of a mono alkyl sulfate with further olefins, the equation is: $C_nH_{2n} + 1.0SO_2 \cdot H_2O + C_nH_{2n} = (C_nH_{2n} + 1)_2 O_2SO_2 + H_2O$. The corresponding dialkyl sulfate is water free. This may explain the fact that the reaction heat of reaction 2 is very small in contrast to the heat development during the mono alkyl sulfate formation.

Sulfuric Acid-Olefin Ratio

The ratio of sulfuric acid:olefin determines to a large extent the formation of mono and dialkyl sulfates according to equations 1 and 2. It is true to some extent the two reactions occur simultaneously. With high temperatures there occurs a conversion of mono into dialkyl sulfates with splitting off of sulfuric acid. If one would only have to watch for the good utilization of the used sulfuric acid then one would try for extensive formation of dialkyl sulfate. But a number of disadvantages are connected with it in the further processing of the ester. The higher dialkyl sulfates of butyl sulfate, amino sulfate, etc., are noticeably soluble in liquid hydrocarbons so that during the formation of dialkyl sulfates part of them goes into the residual hydrocarbon. For the same reason naphthas that have been refined with sulfuric acid always contain primarily dialkylsulfate.

The presence of dialkyl sulfates is also important for the formation of ether as we shall see immediately.

Temperature

The polymerization of olefins to unsaturated hydrocarbons of double or triple molecular size is possible under the influence of sulfuric acid. The occurrence of such polymerization reactions depends on the acid strength and on the temperature. Propylene is relatively little inclined to polymerization so the temperature and acid strength can be kept in wide limits for the absorption. N-butylene on the other hand is considerably more sensitive, and temperatures over 60°C have to be absolutely avoided during absorption. Isobutylene is even more sensitive. Only with particular precautions and with acid strength not more than 65% can it be converted into the sulfuric acid esters of the tertiary butyl alcohol, otherwise there forms almost exclusively

polymerizate. Amylene requires temperatures of less than 40°C if polymerization is to be avoided. For most of the high olefins the permissible adsorption temperatures declines steadily. Higher olefins from C₆ up can only be treated with sulfuric acid at temperatures of 0°C and lower without predominant polymerization. In a mixture of different olefins one olefin can be polymerized with another which would not polymerize alone. Also, ethyl sulfuric acid ester that has been formed already can split off the added olefin in polymerized condition by prolonged storage or by heating.

The polymerization reaction influences the alcohol yield considerably, and because of this undesirable secondary reaction the operation conditions for a good alcohol yield have to be determined very exactly.

The other reaction possibilities in the action of sulfuric acid on olefins in which saturated hydrocarbons, further unsaponifiable sulfur compounds like carbysulfate, sulfones, etc., are formed, shall only be mentioned.

Saponification of the Ester

The reactions that were just described occur in the absorption of hydrocarbons in acids. In the adjoining processing stage of hydrolysis of the sulfuric acid ester other secondary reactions that influence alcohol yield have to be watched.

Mono and dialkyl sulfates are quite stable in presence of water at normal temperature. Upon heating with water they are hydrolyzed slightly if hydrogen-ion is present in excess. Therefore, the influence of excess sulfuric acid on the hydrolysis of alkyl sulfate is very important. The hydrolysis is complicated by the possibility that ether is formed in place of alcohol.

Ether Formation

These ethers are formed by the reaction of dialkyl sulfates with alcohol according to equation 3.



Special provisions are necessary to suppress the ether formation in a normal ester mixture in which dialkyl esters are always present. On the other hand, by the knowledge of the reaction conditions of the ether formation, one can obtain high ether yields directly from the ester.

Olefin Cleavage

The reaction according to equation 1 can run in both directions; that is, under circumstances olefins that have been taken up by ester formation can be split off again as such. The decomposition of the ester that has been formed from alcohol and sulfuric acid is a long-known method for preparation of olefin hydrocarbons. In order to avoid this undesirable decomposition in the alcohol synthesis, the hydrolysis has to be done only with dilute esters. In the case of propyl ester the olefin splitting is practically eliminated by dilution

to 40% acid content. For esters of the higher alcohols the dilution with water before heating must be increased considerably.

The hydrolysis of sulfuric acid esters leads to secondary or tertiary alcohols. Primary alcohols (whose OH group is terminal) do not occur in this method of preparation. The other properties of alcohols that are prepared by the present method will be named soon.

You will have noticed from what has been said so far, that there exist noticeable differences between the various olefin hydrocarbons propylene, butylene, amylene which are noticeable in the sulfuric acid treatment. But even between various isomers of the same carbon number one can determine very different behavior under constant conditions. Propylene (which occurs only in one modification) can be very easily reacted with acid. For butylene with the three structure isomers the conditions are more complicated. Isobutylene is inclined to very ready formation of polymerizates and only under certain conditions a tertiary butyl alcohol can be prepared. 1-butylene is most easily processed to alcohol and is similar in its reaction conditions to propylene. 2-butylene is more difficult to convert into butyl sulfuric acid esters. The differences in the various isomers in their behaviour in sulfuric acid is even more distinct in the higher olefins.

Therefore, the usability and the yield in the alcohol process cannot be stated right away. An exact knowledge of all particulars about the mutual relationship of the various isomers is necessary. According to our present observation there exists even among the gasol mixtures of the various Fischer-Tropsch Works considerable differences in this relationship.

Because of the differences in reaction behaviour of propylene, butylene, and amylene one proceeded in the existing plants in America by first separating the various hydrocarbon groups, and then only the uniform fractions, only C₇ or only C₁₁, are put into the sulfuric acid in order to obtain optimum alcohol yields. In contrast to this we went purposely along another path. We tried to react a combined olefin mixture with careful observation of reaction conditions for the conversion of sulfuric acid and only the finished alcohols are separated from each other. We obtained thereby (by maintenance of good alcohol yields) a number of advantages particularly in the field of operating requirements.

Operating requirements for one tonne alcohol

	Absorption Saponification	Dehydration Separation of the various alcohols	H ₂ SO ₄ Concentration	Total
Electric Current	200 Kw/h	40 Kw/h	60 Kw/h	300 Kw/h
Water	85 cu m	135 cu m	300 cu m	520 cu m
Steam	3 tonnes	5 tonnes	10 tonnes	18 tonnes
Sulfuric Acid	10-40 kg		10 kg	

/s/ Grimme

Martini: The development which the aliphatic large scale industry in the U.S.A. has gone through is caused by the abundance of raw materials which are available for the petroleum industry. Only the Fischer-Tropsch-Ruhrchemie process made these materials available to us. This started the development of new processes

in this field. In America the sulfuric acid problem needs to be considered very little. Here part of the acid is processed to ammonium sulfate or it is given off unutilized as waste products. It is the merit of Grimme that the costly (to us) agent in the process has been made usable over again by overcoming the operative difficulties of concentration of the acid.

There exists the question whether primary alcohols are formed besides the secondary and tertiary alcohols which are very important for the war as starting materials for explosives and artificial resins. If these could not be perfected in operation till now, it would be investigated on laboratory scale whether the formation of primary alcohols could not be reached by some change of reaction conditions.

Ziegler reports that primary alcohols have been found in a small scale experiment of Hoesch-Benzin. Grimme could not isolate primary alcohols in large scale operations, even though the detection should be easier to carry out there.

Weittenhiller asks why sulfuric acid is not used in coking plants. Grimme explained it is possible but in the case of Rheinpreussen the operation of alcohol plant is to be put on its own so far as possible.

Löpmann points out the high concentration differences of the sulfuric acid which fluctuates between 72 and 86%. He asks whether the differences are caused by differences in the gasol concentration or through the fluctuation of the olefin content. Grimme explained that the concentration of olefins is primarily the cause. The content of C_3 and C_4 hydrocarbons or of 1- or 2- butylene has some influence. Difficulties occur in too high acid concentration by vigorous heat development which favors undesirable secondary reactions.

Schwenke asks how large the costs of the process are. Grimme states that for one tonne alcohol there is necessary 60 kilowatt hours, 300 cu. meters water, 10 tonnes steam, 10 kgs sulfuric acid. The whole plant needs 3 men per shift as attendants. Thus the operation costs are not high.

Werre asks whether special building materials are necessary. Grimme answers that the lead admixture in the sulfuric acid concentration could be reduced considerably. In the saponification, acid-stable stoneware (which is available) can be used. One can forego the use of copper for coolers and condensers because normal steel is of good use.

Translated October 21, 1946 - Rochelle H. Bondy

Checked November 12, CCM

EG