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Study of the Influence of the Type of the Catalyst on the Technological Process of Hydration of Higher Fatty Acids into Alcohols, Optimal Parameters of the Process, the Industry of Use of Higher Alcohols

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ABSTRACT:One of the main tasks of the authors is to improve the methods of hydrogenation of fatty acids in order to obtain higher fatty alcohols, which can later be used in many branches of our industry, replacing expensive imported products. The article discusses the influence of various types of catalysts on the quality indicators of the initial product, as well as economic indicators. The graphs of the dependence of the product yield on the type of catalyst are presented, the optimal conditions for the hydrogenation of fatty acids in order to obtain higher fatty alcohols are determined.

KEY WORDS: higher fatty alcohols, hydrogenation, fatty acids, catalyst, copper-chromic, zinc-chromic, yield, degree of conversion

I. INTRODUCTION

Higher fatty alcohols (HFA) received practical application in the late thirties of the 20th century, then they entered a number of chemical products that were paramount for consumer consumption and became an object of production on a large scale. Such alcohols are actively used as lubricants, solvents, cosmetics, extractants, and also find application in pharmaceutical production. Based on the importance of HFM in various industries, it will be advisable to consider and compare the methods and raw materials for their synthesis.

Higher alcohols, depending on the method of their production, are subdivided into natural and synthetic. Synthetic alcohols are obtained by the synthesis of petrochemical products from paraffins and olefins [1].

At present, the most common method for producing synthetic fatty alcohols is the hydrogenation of fatty acids and their esters, aldehydes, oils and fats. To obtain alcohols, a hydrocarbon fraction with a boiling point of 275-320 ° C can also serve as raw materials.

II. MATERIALS AND METHODS.

The hydrogenation process is influenced by various factors such as temperature, pressure, as well as the catalyst, its nature and condition.

Catalyst slurries used in hydrogenation reactions pose a number of difficulties in use and installation. Erosion of devices and equipment is a big problem. Here it should also be taken into account that the separation of the catalyst is associated with additional consumption of time, labor, and also the catalyst itself. Therefore, the hydrogenation of acids



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into fatty alcohols on a stationary catalyst is considered a more promising method that meets the modern requirements of technological processes [1].

The process of direct hydrogenation, as studies have shown, with the aim of converting acids into higher alcohols can be successfully carried out on stationary catalysts, and this, in turn, is of great interest at present. In this case, synthetic fatty acids of the C10 - C16 fraction can be used as raw materials. It should be noted that the hydrogenation process in this case is affected by the fractional composition of the raw material. The presence of more than the required amount of acids with a low molecular weight can negatively affect high pressure equipment, while acids with a high molecular weight (over C20) lead to rapid deactivation of the catalyst [2].

Numerous studies have shown that the direct hydrogenation of acids into alcohols can be successfully carried out on zinc-chromium or copper-chromium catalysts. It should be taken into account that, depending on the catalyst used, the technological parameters of the process, the quality of the product obtained, the yield of alcohols, and hence the economic parameters of the process, change.

III. RESULTS.

Table 1 shows the main indicators of the hydrogenation of synthetic fatty acids (FFA) on a stationary catalyst [3].

Table 1
The main indicators of the hydrogenation of synthetic fatty acids on a stationary catalyst

Indicators	Copper-chromium catalyst	Zinc-chromium catalyst
Raw material - synthetic fatty acids	$C_{10} - C_{16}$	$C_{10} - C_{16}$
Hydrogenation temperature, °C	225	335
Process pressure, at	284	286
Volumetric flow rate for raw materials, m ³ /m ³ *h	0,13	0,5
The amount of circulating hydrogen, nm ³ t of raw materials	16000	80000
Hydrogenate yield,% of raw materials		
Hydrogenate composition,% weight	93	93
Higher alcohols	81,2	73,2
Water	8,3	8,6
Free acids	0,62	0,55
Esters	1,48	3,61
Free hydrocarbons	6,2	11,0
Carbonyl compounds	0,78	1,43

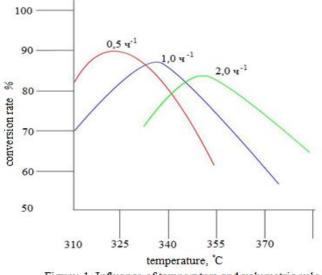


Figure: 1. Influence of temperature and volumetric velocity of raw materials on the depth of ether hydrogenation into alcohol

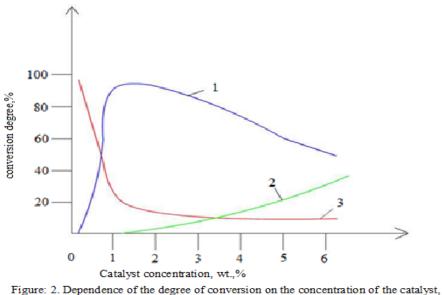


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According to the table, we can conclude that in both cases of using catalysts, a high yield of alcohols in one pass can be observed.

As can be seen from the curves of the dependence of the transformation on the temperature and feed rate of the raw material, each speed of the volume corresponds to its own special maximum yield of the product, that is, alcohol, and it is achieved with an increase in the temperature and the feed volume.



1 - fatty alcohol, 2 - hydrocarbon, 3 - ether

However, it can also be said that the higher the temperature, the lower the alcohol yield. But basically the yield of the final product up to about 88% depends on the set temperature and the volumetric velocity of the raw material. For an even greater degree of conversion by 1-2%, with an alcohol yield of more than 90%, a significant increase in pressure is required, and this is almost not technologically justified [4].

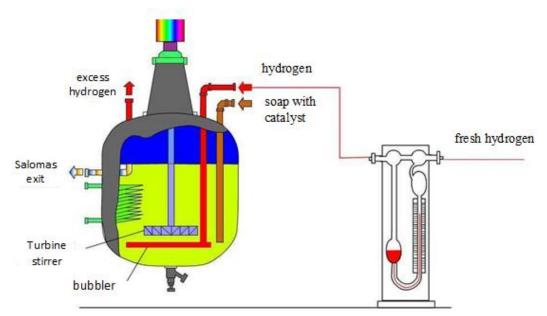


Figure: 3. Laboratory unit for hydrogenation in the presence of a powdered catalyst



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In fig. 2 shows the dependence of the degree of conversion on the catalyst concentration at a process temperature of 335 ° C, a pressure of 250 atm, and a volumetric feed rate of 1 kg / (1 * h) and a gas supply of 1 m3 / (kg * h).

When the values of the last three process parameters change, the shape of the curves practically does not change.

It can be seen from the graph data that each temperature and volumetric concentration has its own optimal catalyst concentration.

The method of fat hydrogenation with a powdery catalyst has the same application and is widely used in the industry. To study the dynamics of the main indicators of the quality of the obtained alcohol during hydrogenation using a powdered catalyst, we used a laboratory setup shown in Fig. 3.

Into the autoclave, (the inner diameter of which is 80 mm, and the height of 160 mm) equipped with a stirrer, about 500 g of raw material was loaded, while stirring with a stirrer, hydrogen was fed in a very weak flow (0.51 / min). The reactor is equipped with an electric heater that heated up to 150-200 ° C. The rheometer was used to determine the hydrogen feed rate. When the temperature in the reactor reached the required value, a sample of the catalyst weighed on a balance was introduced into the reactor, and hydrogen was supplied at the accepted rate. When the mixture in the reactor was heated to the specified temperature, the heating was turned off and from that moment a sample of the resulting substance was taken every 10-15 minutes. In this case, the hydrogen supply and the stirrer were not turned off.

In factories in Europe, there are factories for the production of fatty alcohols, by the method of direct hydrogenation of fatty acids on a suspended catalyst [3]. Initially, a suspension of the catalyst in fatty alcohols is prepared. This process is carried out at a temperature of $300 \degree C$ and a pressure of 325 atm. The hydrogenated product goes to the sump. The lower layer containing 30-40% of the catalyst is recycled. Table 2 shows the consumption of raw materials per 1 ton of alcohols.

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Calculated indicators of raw materials for the hydrogenation of fatty acids to higher fatty alcohols			
Consumable raw materials	amount		
Fatty acid $C_{10} - C_{20}$, m	1,1		
Hydrogen, <i>nm</i> ³	285-310		
Catalyst, kg	4-6		
Electricity, kW * h	300-350		
Steam, t	0,5-0,6		
Water, m ³	40-50		

IV. **DISCUSSION**.

The tendency to replace suspended catalysts with stationary ones manifested itself precisely in the production of higher fatty alcohols by catalytic hydrogenation. The use of catalysts on a stationary basis makes it possible to exclude complex primary processes for preparing a suspension, removing catalyst sludge. The disadvantage here is the periodic shutdown of the process to overload the catalyst. And in order to maximize the life of the catalyst, it is necessary to pay special attention to the preparation of the raw materials. Raw materials of the same quality can halve the catalyst consumption [5].

Among the methods for obtaining higher fatty alcohols, one more should be distinguished - reduction with the help of metallic sodium. This method has found wide application in Western European countries in order to obtain unsaturated alcohols, as well as recovery with sodium is used in America [3].

Typically, fatty acid esters are used for this process. The triglyceride (or one of the fatty acid esters) is treated with



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metallic sodium in the presence of a secondary alcohol.

This reaction is carried out at a temperature of about 40 ° C, there is a slight excess of sodium. Alcoholates of alcohols that are formed during the reaction are hydrolyzed to form an alkaline solution of sodium and alcohols.

Carrying out such a process provides an alcohol yield of about 80-95%. The advantages of the method are ease of maintenance and the use of atmospheric pressure. Along with a number of advantages, there are also disadvantages:

$$\begin{array}{cccc} CH_2-ONa & CH_3 & CH_2-ONa & CH_3 \\ | & | & | & | \\ CH-ONa+3RCH_2 \ ONa+6C_4H_9CHONa+12H_2O & \rightarrow CHOH+3RCH_2OH+6C_4H_9-COH+12NaOH \\ | & | \\ CH_2-ONa & CH_2-ONa \end{array}$$

limited resources and the high cost of metallic sodium.

When the conditions for the process and the composition of the raw material itself change, the fractional composition of fatty acids varies within a fairly wide range. in turn, this will make it possible to purposefully change the resources for obtaining higher fatty alcohols (C7-C9, C10-C16) used in the production of the most demanded industrial materials, such as plasticizers, surfactants, etc.

V. CONCLUSION.

At present, the use of animal and vegetable fats in the leather industry has been almost completely replaced by the use of synthetic fatty material for fatliquoring leather, which has not only the same properties, but significant advantages over natural ones.

Product quality and issues related to it are inextricably linked to technology issues. The use of natural fats and oils for fatliquoring chrome tanned leathers, as well as emulsifiers based on them, provides high elastic - plastic and operational properties of the leather. However, the lack of natural fats, high cost, and often low quality set the task of replacing them with synthetic fatty materials that are not inferior in technological properties to natural ones [7].

The process of processing leather and hides includes about 25 technological and physical operations that require certain raw materials costs, which include a large number of chemicals. Surfactants play an important role in a number of them and are widely used in the leather industry. Both anionic and nonionic types are used quite widely, while cations have more specialized uses. The main anionic surfactants used are sulfate oils, soaps, sulfated higher alcohols and alkyl benzene sulfonates. Nonionic compounds are mainly condensation products of ethylene oxide with a secondary alcohol containing 11-15 carbon atoms, or with octyl- and nonylphenol, with the introduction of 7-10 oxyethylene units. Surfactants are used in various stages of leather production. They are used in soaking, dehairing, herb, tanning and dyeing, where they serve primarily as processing aids. They find more important use in fatliquoring, impregnation and finishing, where they become part of the finishing composition. Several surfactants, namely chromium complexes of fatty acids and perfluoric acids and alkenyl succinic acid, have been used to render the skin water repellent. Research in this area shows promising new uses for surfactants in the leather industry [8].

One of the most pressing challenges of the twenty-first century is to meet the growing demand for fuels for transportation, agricultural use, industrial processes and domestic use, as well as to ensure their sustainable production due to the inevitable depletion of the world's fossil fuel resources, as highlighted by high oil prices.

VI. ACKNOWLEDGEMENT.

Ethanol is now the main biofuel worldwide and is produced from sugar and starch based feedstocks such as sugar cane, corn, and sugar beets. However, ethanol has significant drawbacks that prevent its full use as an additive to fuels. For example, its energy density is less than that of gasoline, and it tends to absorb water from the environment, making it more corrosive when stored or transported. In comparison with ethanol, higher alcohols have a number of advantages, the main ones being higher specific energy and lower hygroscopicity. Moreover, higher alcohols are flexible oxygen-containing compounds with properties that can be mixed with both gasoline and diesel fuel [9, 10]. When used as a product blend, higher alcohols can reduce harmful emissions such as CO2, NOx, SOx and smog-



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causing particles, making them attractive alternatives. In addition, branched chain higher fatty alcohols (BCFATs) have higher octane numbers than their straight chain counterparts, resulting in less engine noise [11]. As excellent organic solvents and indispensable chemical materials, HRCPs are also widely used in plastics, cosmetics, perfumery, fragrances, paints and resins, and organic synthesis. For example, isobutanol is converted to an acetate ester, which is widely used as a varnish solvent, and isopropanol is widely used in herbicide synthesis and as a solvent for coatings and paints.

Higher alcohols, including HLCRC, are currently produced commercially from olefins in a multi-stage process that includes an oxo (hydrocarbonylation) reaction and subsequent hydrogenation and separation steps. The HFA market is currently highly dependent on oil prices. The expansion of the fuel additives market would probably accelerate if superior performance and low cost of production were demonstrated [12].

Based on the foregoing, the process of hydrogenation of fatty acids in the presence of a catalyst and their derivatives will in the near future retain its priority importance in the production of C10 - C20 higher fatty alcohols.

Making a conclusion, we can say that in the process of determining the optimal parameters for the synthesis of synthetic fatty alcohols by hydrogenation, the efficiency of the catalysts used in this process was determined. As a result, an analysis was made of the yield and fractional composition, as well as the physicochemical parameters of fatty alcohols. A laboratory setup for the synthesis of fatty alcohols by hydrogenation was recommended. The obtained higher fatty alcohols can be used in various areas of the chemical industry.

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