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PRODUCTION OF SYNTHETIC FATTY ALCOHOLS BY HYDROGENATION OF FATTY ACIDS

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ABSTRACT
In the article, one of the main objectives is to improve the process of hydrogenation of fatty acids in order to obtain higher fatty alcohols, which can subsequently be used as plasticizers for skin substitutes, using them instead of expensive imported products. The article presents graphs of the dependence of the product yield on various reaction parameters and determines the optimal conditions for the hydrogenation process in order to obtain higher fatty alcohols.
Keywords: higher fatty alcohols (HFAs), process, method, reaction, hydrogenation, parameters, temperature, catalyst, raw materials, degree of conversion, finished product.

Introduction

Higher fatty alcohols (HFAs) are natural and synthetic aliphatic alcohols containing at least 6 carbon atoms per molecule.

In their pure form, VLCs are not found in nature, but are found in a bound state - in the form of esters and organic acids. VLS esters are contained in many waste products of some animals, insects, microorganisms, plants and trees (fat, wax, essential oils). Natural HSLs are predominantly monoatomic, primary, saturated or unsaturated, with an even number of carbon atoms.

Higher fatty alcohols of composition C6–C11 are colorless, flammable liquids with a fruity-floral odor; composition C12 and higher are solids.

Soluble in diethyl ether and ethanol, insoluble in water.

Traditionally, two groups of natural raw materials were used for the production of fatty alcohols:

1) fats and oils of vegetable or animal origin containing fatty acids in the form of triglycerides, which can be hydrogenated after appropriate pre-treatment to produce fatty alcohols;

2) wax esters from whale oil, from which fatty alcohols are obtained by simple hydrolysis or reduction with sodium.

Higher alcohols are now produced commercially from olefins in a multi-step process that involves an oxo-(hydrocarbonylation) reaction and subsequent hydrogenation and separation steps. The HRC market is currently highly dependent on oil prices. The expansion of the plasticizer market would likely accelerate if superior performance and low cost products were demonstrated.

Theoretical basics of the process

Based on the importance of VLS in various industries, it will be advisable to review and compare methods and raw materials for their synthesis.

The most common high-quality liquid resins in production, the physical properties of which are listed in Table 1, depending on the production method, are divided into natural and synthetic. Synthetic alcohols are produced by the synthesis of petrochemical products from paraffins and olefins.

Table 1.1. Physical properties of basic fatty alcohols

Name of alcohols	Chemical formula	**t melting, °C**	**ρ, *г/см***	state
Lauryl alcohol	$C_{12}H_{25}OH$	24-27	0,8201	liquid
Cetyl alcohol	$C_{16}H_{33}OH$	59-60	0,8120	liquid
Oleyl alcohol	$C_{18}H_{35}OH$	14– 19	0,8450	liquid
Stearyl alcohol	$C_{18}H_{37}OH$	59,80	0,8120	liquid
Myricyl alcohol	$C_{31}H_{63}OH$	85-85,5	0,7770	liquid

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

Hydrogenation is a targeted change in the composition of fats and oils in the fatty acid ratio, as a result of the reaction of hydrogen addition to the double bonds of unsaturated fatty acids. For example, hydrogenation of linoleic and linolenic fatty acids to oleic acid glycerides increases the ability of fats to resist oxidation by atmospheric oxygen several times (from 10 to 15) [1-2]

During the catalytic hydrogenation of fatty acids, a reaction occurs that can be expressed by the following equation:

$$RCOOH \xrightarrow{+2H_2} RCH_2OH + H_2O \qquad (1)$$

All schemes proposed for hydrogenation processes are based on a stepwise process. The primary hydrogenation reaction of higher acids is the addition of hydrogen to the acid, where an intermediate product is formed, i.e. a dihydric alcohol with two hydroxyl groups on one carbon atom. The resulting alcohol is unstable and decomposes into aldehyde and water. Subsequent hydrogenation of this aldehyde leads to the release of the target product - alcohol. When enough alcohol accumulates in the reaction mixture, it begins to react with the parent acid to form an ester, which is subsequently converted to alcohol in the hemiacetal stage. This process has a number of disadvantages, one of which is the occurrence of several side and secondary reactions during the process, which, in turn, reduces the yield of the target product and leads to contamination of the synthesized alcohols.

In addition to vegetable oils, such as cottonseed, sunflower, soybean, rapeseed and some others, animal fats, as well as free fatty acids obtained from soap stocks, are subject to hydrogenation [3].

The method of hydrogenating fat in the presence of a catalyst also has its application and is widely used in the industry.

Experımental part

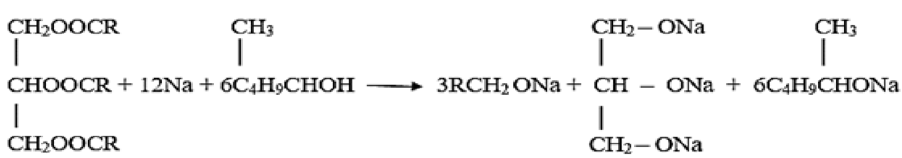
To study the dynamics of the main indicators of the quality of the resulting alcohol during hydrogenation using a powder catalyst, a laboratory installation was used. In an autoclave (the internal diameter of which is 80 mm and a height of 160 mm) equipped with a stirrer, about 500 g of raw materials were loaded, and hydrogen was supplied while stirring with the stirrer very low flow (0.5 l/min). The reactor is equipped with an electric heater, which heats up to 150-200°C. The rheometer served to determine the hydrogen supply 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. At the same time, the hydrogen supply and the stirrer were not turned off.

During the experiment, a constant temperature in the reactor and air flow were maintained, and the volume of water collecting in the Dean and Stark trap was noted. The yield of the target product was 78-88% [5].

Table 2. Shows the consumption of raw materials per 1 ton of alcohols.

Consumable raw materials	**Quantity**
Fatty acids $C_{10} – C_{20}$, t	1,1
Hydrogen, nm^3	285-310
Catalyst, kg	4-6
Electricity, kW*h	300-350
Steam, t	0,5-0,6
Water, m^3	40-50

Among the methods for obtaining higher fatty alcohols, one more should be highlighted - reduction with metallic sodium.



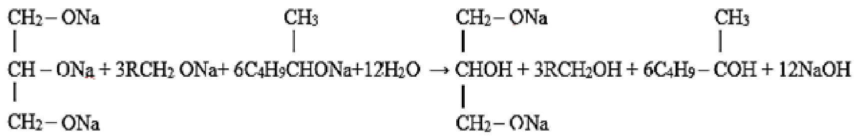
(2)

This method has found wide use in Western Europe for the production of unsaturated alcohols, and reduction with sodium is also used in America [6].

Typically, fatty acid esters are used for this process. The triglyceride (or one of the fatty acid esters) is treated with sodium metal 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. The alcoholic alcohols that are formed during the reaction are subjected to hydrolysis to form an alkaline solution of sodium and alcohols.

Carrying out this process ensures an alcohol yield of about 80-95%.



(3)

The advantages of the method are ease of maintenance, as well as the use of atmospheric pressure. Along with a number of advantages, there are also disadvantages: limited resources and high cost of sodium metal.

When the process conditions and the composition of the raw materials themselves changed, the fractional composition of fatty acids varied over a fairly wide range. in turn, this will make it possible to purposefully change the resources for obtaining higher fatty alcohols (C_7-C_9, C_{10}-C_{16}) used for the production of the most popular industrial materials, such as plasticizers, surfactants, etc. [4].

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

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 here, depending on the catalyst used, the technological parameters of the process, the quality of the resulting product, the yield of alcohols, and therefore the economic parameters of the process change. Table 3 presents the main indicators of the process of hydrogenation of synthetic fatty acids (SFA) on a stationary catalyst [5].

Table 3. Main indicators of the process of hydrogenation of synthetic fatty acids on a stationary catalyst

Indicators	**Copper-chromium catalyst**	**Zinc-chromium catalyst**
Raw materials – synthetic fatty acids	C_{10} – C_{16}	C_{10} – C_{16}
Process pressure, at	284	286
Volumetric velocity of raw materials, m3/m3*h	0,13	0,5
Amount of circulating hydrogen, nm3t of raw materials	16000	80000
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

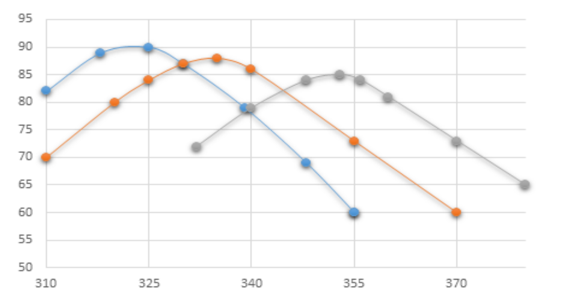
According to the table, we can conclude that in both cases of using catalysts, a high yield of alcohols can be observed in one pass.

Analysıs of results

Let us study the influence of the copper-chromium catalyst on the process in conjunction with other factors. Curves in Fig. 1 shows the effect of temperature and supply of liquid feedstock at constant hydrogen flow and pressure, where the catalyst concentration was 2 wt.%.

As can be seen from the curves of the dependence of the conversion on the temperature and feed rate of raw materials, each volume speed corresponds to its own special maximum yield of the product, that is, alcohol, and it is achieved with increasing temperature and feed volume. However, it can also be said that the higher the temperature, the lower the alcohol yield.

Conversion rate %

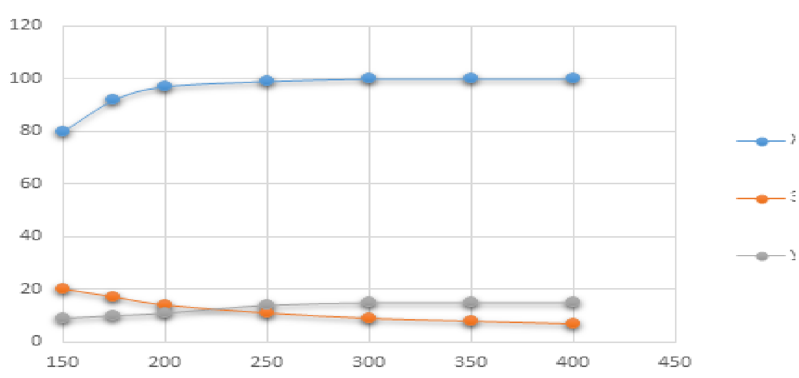


temperature

Fig. 1. Dependence of the hydrogenation process on temperature and volumetric velocity

In Fig. Figure 2 shows the dependence of the hydrogenation process on pressure. If we compare the graphs, we can see that increasing the pressure to some extent increases the selectivity of the process.

Conversion rate %



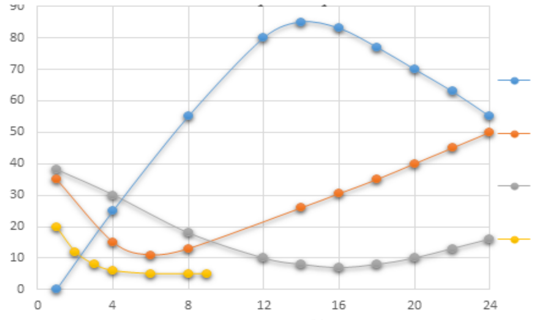
pressure

Fig. 2. Dependence of the hydrogenation process on pressure

But basically, the yield of the final product up to a value of about 88% depends on the given temperature and volumetric velocity of the raw material. For an even greater conversion rate of 1-2%, with an alcohol yield of more than 90%, a significant increase in pressure is required, and this is almost technologically unjustified.

Figure 3 shows graphs of the influence of the gas: liquid ratio at a process temperature of 3400C, a pressure of 250 atm and a volumetric velocity of 0.5 kg/(l*h).

Conversion rate %



mole ratio

Fig. 3. Dependence of the hydrogenation process on the ratio of hydrogen - raw materials

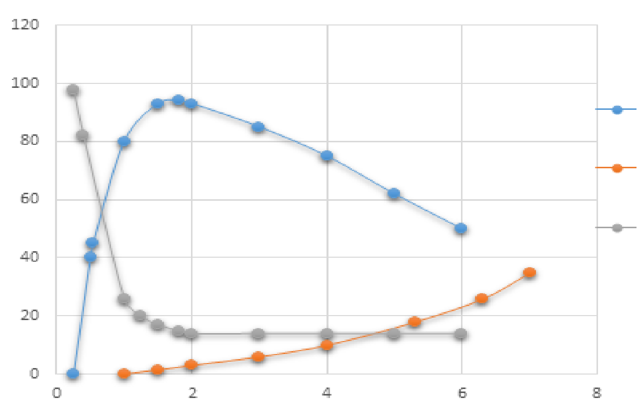
As can be seen, with an increase in this ratio, the yield of the final product reaches a maximum. With small hydrogen supplies, acid is formed due to the thermal decomposition of the ether:

$$RCOO - CH_2 - CH_2\acute{R} \rightarrow RCOOH + CH_2 = CH\acute{R} \qquad (3)$$

This judgment can be proven by the fact that when the gas supply is small, the amount of hydrocarbons increases sharply, and as the gas supply increases, the yield of hydrocarbons and acid decreases in parallel. At the moment when the acid completely disappears from the reaction products, the yield of hydrocarbons decreases to a minimum, and then increases again. Here it must be taken into account that with a gas:liquid ratio, the linear velocity of the gas in the reactor increases, as a result, the flow turbulizes and the hydrogen pressure increases to some extent.

In Fig. 4 shows the dependence of the degree of conversion on the catalyst concentration at a process temperature of 335^{0}C, a pressure of 250 at, and a volumetric feed rate of 1 kg/(l*h) and a gas supply of 1m3/(kg*h). When changing the values of the last three process parameters, the appearance of the curves practically does not change. From the graph data it is clear that each temperature and volumetric concentration corresponds to its own optimal catalyst concentration [4].

Conversion rate %



concentration of the catalyst

Fig. 4. Dependence of the hydrogenation process on the catalyst concentration

To summarize, the optimal parameters for the hydrogenation process of fatty acid esters have been established, which can be presented in the following table:

Table 1.4. Optimal mode for carrying out the process of hydrogenation of fatty acid esters in order to obtain VLS

№	Parameters	Value
1	Temperature, 0C	318-340
2	Hydrogen pressure, at	325
3	Volumetric velocity of liquid raw materials, kg/(l*h)	1
4	Hydrogen: raw material ratio, m3/kg	2-5
5	Catalyst concentration, wt.%	1,5

With the specified parameters, the product yield will be about 88%, when converted to processed raw materials, where the composition of the final product will be:

Table 1.5. Composition of the mixture formed during the hydrogenation reaction of fatty acid esters

№	Product formed	Per 100 mol ester	Per 33.3 mol triglyceride
1	Higher fatty alcohols	91-95	91-95
2	Paraffin hydrocarbons	3-7	3-7
3	Fatty acids, no more	0,12	0,12
4	Isopropyl alcohol	-	30-31
5	Water	3-6	65-70
	Unconverted esters	1-2	0,6 -0,9

Conclusion.

Based on the results of the article, we can say that the production of fatty alcohols from secondary petroleum products undoubtedly has economic efficiency and scientific significance, which means the process of hydrogenation of fatty acids in the presence of a catalyst and their derivatives will in the near future retain its priority in the production of C_6 higher fatty alcohols – C_{10}.

1. Raw materials for organic additives to PVC, namely higher fatty alcohols, are synthesized by hydrogenation of higher acids obtained from local raw materials, namely secondary petroleum products in the presence of a catalyst. The optimal process parameters were studied and identified, where the yield of the final product was 78-88% relative to the weight of the raw material.
2. In the process of determining the optimal parameters for the synthesis of synthetic fatty alcohols by hydrogenation, the effectiveness of the powdered catalyst 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.

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ПРОИЗВОДСТВО СИНТЕТИЧЕСКИХ ЖИРНЫХ СПИРТОВ ПУТЕМ ГИДРИРОВАНИЯ ЖИРНЫХ КИСЛОТ

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РЕЗЮМЕ

В статье одной из основных задач является совершенствование процесса гидрирования жирных кислот с целью получения высших жирных спиртов, которые в дальнейшем можно использовать в качестве присадок и пластификаторов заменителей кожи, используя их вместо дорогостоящих импортных продуктов. В статье представлены графики зависимости выхода продуктов от различных параметров реакции и определены оптимальные условия проведения процесса гидрирования с целью получения высших жирных спиртов.

Ключевые слова: высшие жирные спирты (ВЖС), процесс, метод, реакция, гидрирование, параметры, температура, катализатор, сырье, степень конверсии, готовый продукт.

YAĞ TURŞULARININ HİDROGENASYON YOLU İLƏ SİNTETİK YAĞLI SPORQOLLARIN İSTEHSALI

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XÜLASƏ

Məqalədə əsas məqsədlərdən biri daha yüksək yağlı spirtlər əldə etmək üçün yağ turşularının hidrogenləşməsi prosesini təkmilləşdirməkdən ibarətdir ki, bu da sonradan aşqar kimi dəri əvəzediciləri üçün plastikləşdirici kimi istifadə oluna bilər, onlardan bahalı idxal məhsulları əvəzinə istifadə oluna bilər. Məqalədə məqsədli məhsulun çıxımının müxtəlif reaksiya parametrlərindən asılılığının qrafikləri verilmiş və yüksək yağ spirtlərin alınması üçün hidrogenləşmə prosesinin optimal şərtləri müəyyən edilmişdir.

Açar sözlər: yüksək yağlı spirtlər (HFA), proses, üsul, reaksiya, hidrogenləşmə, parametrlər, temperatur, katalizator, xammal, çevrilmə dərəcəsi, hazır məhsul.