A STUDY OF THE PROCESS OF PREPARING γ-ACETOPROPYL ALCOHOL FROM FURFURAL

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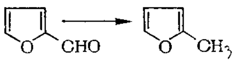
γ-Acetopropyl alcohol is a very expensive intermediate in the synthesis of vitamin B_1 [1]. It can be prepared by the condensation of sodium acetoacetic ester with ethylene oxide [2] or by hydrogenation of sylvan (2-methylfuran) [3, 4], which, in turn, can be synthesized from furfural.

I. Preparation of Sylvan from Furfural

According to the literature [5-18], the most promising method for preparing synthetic sylvan (II) is the hydrogenation of furfural (I) in the vapor phase over a catalyst.



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Nickel, cobalt, copper, silver, iron, chromium, and their alloys, oxides, or salts on various supports (kieselguhr, pumice, charcoal, etc.) are recommended as catalysts. The best results were obtained in hydrogenation over copper catalysts. Thus, by hydrogenation of furfural in the vapor phase at 250° over copper chromite on charcoal, sylvan was obtained in a yield 92% of the theoretical [7]. However, this catalyst is weak mechanically and requires frequent regenerations. Satisfactory results were attained with alloyed copper-aluminum catalysts, which do possess sufficient mechanical strength [6]. A ternary alloy of aluminum, copper, and zinc (50 :13 : 17) has been used for the hydrogenation of furfural to sylvan, and sylvan was obtained in a yield of 86% of the theoretical [8]. The catalyst operated for 12 h without regeneration.

We have conducted work on selecting the most effective catalyst for hydrogenating furfural to sylvan and on determining the optimum conditions for operation in a continuous laboratory unit. Catalyst in an amount of 100-160 ml was charged into the reactor, which was a vertical tube of 25 mm diameter and 1000 mm height. Freshly distilled furfural together with hydrogen was fed into the upper part of the reactor. The hydrogenation was carried out at an excess pressure of 70-360 mm of water. The vapors leaving the reaction column were condensed in a condenser at 10-12°.

The catalyzate was distilled in a column, and the fraction of b.p. 58-65° was collected, which contained the sylvan. The percentage content of sylvan in the product was determined by gas chromatography. Pure sylvan has the following constants: bp 64° (760 mm); d_4^{20} 0.913; n_D^{25} 1.4305. We tested vari-

TABLE 1. Results of Experiments on Preparing Sylvan by Hydrogenating Furfural on Various Catalysts

Catalyst		Yield of sylvan (%)	Duration of operation of a single cycle (in h)
Cu+Al	(50:50)	65	80—120
Cu+Cr+Al	(48:2:50)	43	22
Al+Cu+Zn	(50:33:17)	13	10
Al+Cu+Zn	(50:45:5)	52	14
GIPKh 105		55	100

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*Deceased.

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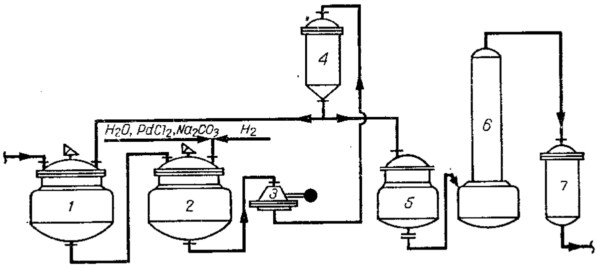

Fig. 1. Scheme in principle for production of γ-acetopropyl alcohol from synthetic sylvan. Explanation in text.

ous catalysts for hydrogenating furfural to sylvan-alloyed catalysts, and catalysts on supports. Experimental results are given in Table 1. The best results were obtained in work with alloyed copper–aluminum catalyst.

Preparation of the catalyst was performed in a catalyst tube by treatment with 0.75 N sodium hydroxide solution. The alkali solution was fed continuously from below upward into the reactor at a rate of 1.2 liters/h for 3.5 h, after which washing of the catalyst from alkali was carried out with water, to pH 6.5. The washed catalyst was dried in a stream of hydrogen at 200-250° until evolution of water ceased and then the hydrogenation process was started.

TABLE 2. Preparation of γ-Acetopropyl Alcohol by Hydrogenation of Sylvan

Charged						Yield of γ-acetopropyl alcohol	
sylvan (g)	water (ml)	hydrochloric acid (ml)	acetone	$PdCl_2$	Pd/c	g	% of theor.
			g				
100	50	1,0	—	0,25	—	62,9	50,7
100	50	1,0	—	0,25	—	63,0	50,8
100	50	1,0	—	0,25	—	64,2	51,8
100	35	1,0	100	—	0,1	80,6	65,8
100	35	0,7	100	—	0,1	78,7	63,5
100	35	0,7	100		0,1	78,0	62,9

The following optimum conditions for the process of hydrogenating furfural to sylvan were established experimentally: temperature, 200-250°; molar ratio of hydrogen to furfural, (5-6) : 1; optimum space velocity with respect to furfural, 0.2-0.3 h^{-1}. Under these conditions, the mean sylvan yield was 60% of the theoretical. However, the duration of active catalyst action did not exceed 14 h. Restoration of activity by repeated treatment of the catalyst with alkali solution did not give useful results. In this connection we have used the method of catalyst activation with a stream of air at a velocity of 80 liters/h at 300-350° for 3-4 h, until evolution of carbon dioxide ceased. After the oxidative roasting, the catalyst was cooled and subjected to treatment with hydrogen at 250° with the objective of reducing the copper oxides on the contact mass. Reduction was continued until evolution of water ceased. After such treatment, the duration of active catalyst action rose to 83 h, and the mean sylvan yield rose to 64.5% of theory.

A check of the data obtained was conducted on a large-scale laboratory unit with a catalyst volume of 480 ml. Here it was observed that the catalyst can operate for 500 h under conditions of periodic regeneration by oxidative roasting after 80-120 h of continuous hydrogenation. The yield of sylvan in individual hydrogenation process cycles fluctuated in the limits of 82-60%; and on the average was 65% of the theoretical. As is evident from Table 1, the other hydrogenation catalysts which we tested proved less effective. Catalyst GIPKh-105, which contained 47 to 51% CuO, not less than 2% CaO; 40 to 46% Cr_2O_3; and about 2% graphite, placed on a brass screen permitted obtaining a mean sylvan yield of 55% of theory in hydrogenating furfural, and operated for 100 h without regeneration. Here the copper–aluminum alloy catalyst in the ratio of 50 : 50 parts by weight was distinguished by simplicity of preparation and regeneration, good mechanical strength, and low cost.

II. Preparation of γ-Acetopropyl Alcohol from Sylvan

The mechanism of formation of acetopropyl alcohol from sylvan has been studied by many investigators [3, 10, 19-24], and the following scheme has been proposed to explain it:

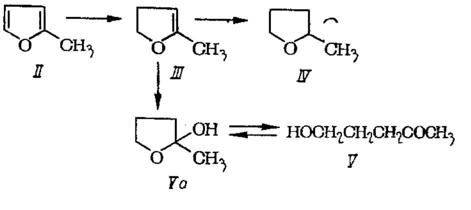

TABLE 3. Results of Preparing γ-Acetopropyl Alcohol under Production Conditions

Temp. (in deg)	Pressure (in atm)	Yield of acetopropyl alcohol (% of theory)
58	1,0	45,0
60	1,2	46,0
60	1,5	46,8
60	2,5	53,8
59	2,5	53,7
60	2,5	53,8
58	2,0	52,3
59	2,0	52,2
60	2,5	53,7

Sylvan goes over to 2-methyl-4,5-dihydrofuran (III) on incomplete hydrogenation; the latter is hydrogenated in anhydrous medium to tetrahydrosylvan (IV), but in acidic aqueous medium gives 2-hydroxy-2-methyltetrahydrofuran (Va) – the cyclic form of γ-acetopropyl alcohol, which is present in equilibrium with the acyclic form (V). On further hydrogenation, γ-acetopropyl alcohol affords 1,4-pentanediol.

There are indications in the literature of the possibility of preparing γ-acetopropyl alcohol by hydrogenating of sylvan under different conditions. By the method proposed by K. S. Topchiev and L. N. Pavlov [4], hydrogenation of sylvan is carried out in aqueous medium over palladium black in the presence of hydrochloric acid. This method has found industrial use. According to manufacturing data, the yield of γ-acetopropyl alcohol by this method is 40-44% of theory.

According to another method [10], γ-acetopropyl alcohol is prepared by hydrogenation of sylvan in dioxane medium in the presence of water, small amounts of formic acid, and a catalyst–nickel on zeolite. The reaction takes place at 150° and a pressure of 75 atm, over a period of 15 h. The yield of γ-acetopropyl alcohol is 30.9% of the theoretical. The yield of γ-acetopropyl alcohol under these conditions, but without a solvent, was 30% of the theoretical [22-24].

We made tests of catalysts (nickel–chromium, nickel on kieselguhr, nickel–aluminum) under continuous conditions, with addition of formic acid or water. The data obtained confirmed the yield of 30% of theory for γ-acetopropyl alcohol which was given above. A method has been patented for preparing γ-acetopropyl alcohol by hydrogenating sylvan in acetone using palladium on charcoal; the yield of acetopropyl alcohol being 75% of the theoretical [25]. We have checked out this process on this catalyst under continuous conditions. The yield given was not corroborated.

We have investigated the possibility of preparing γ-acetopropyl alcohol by hydrogenating sylvan either in weakly acidic aqueous medium or in organic solvent media: acetone, dichloroethane, chloroform, or carbon tetrachloride. Before hydrogenation the sylvan was subjected to hydrodistillation in a set-up provided with a fractionating column of 10 theoretical plates efficiency. In the hydrodistillation stage the yield of sylvan from technical sylvan was 93-95%.

The hydrogenation of the sylvan was carried out in a glass bottle of 0.75 liter capacity, which was set in a rocker (250-260 oscillations per min), at a pressure in the system of 1.7-2.5 atm, and with continuous hydrogen feed. Hydrogenation was continued for about 5 h. At the end of the process the reaction mixture was neutralized to pH 7.0 and was subjected to fractional distillation, initially at normal pressure and then under vacuum. Pure γ-acetopropyl alcohol has the following physical constants: bp 75° (3 mm); d_4^{25} 0.993; n_D^{25} 1.4350.

Results of experiments on preparation of γ-acetopropyl alcohol by hydrogenation of sylvan, which were performed under the optimum regime developed, are given in Table 2. In hydrogenation of sylvan in weakly acidic aqueous medium using palladium chloride, the mean yield of acetopropyl alcohol was 51% of theory. Hydrogenating sylvan in aqueous acetone medium using an aqueous palladium suspension increased the mean yield of acetopropyl alcohol to 64% of theory. The increase in yield of γ-acetopropyl alcohol apparently takes place in this case due to a reduction in the amount of by-products which are higher-boiling than acetopropyl alcohol. Hydrogenation of sylvan in a medium of a chlorinated hydrocarbon (dichloroethane, chloroform, or carbon tetrachloride) leads to obtaining low yields of acetopropyl alcohol.

III. Preparation of γ-Acetopropyl Alcohol from Sylvan under Production Conditions

The technological process of manufacturing γ-acetopropyl alcohol from synthetic sylvan is accomplished by the following technological scheme in principle (see Fig. 1). Hydrodistillation of sylvan is carried out in reactor 1 at a liquid temperature of not over 105° and a vapor temperature of not over 95°; after this the sylvan is routed to hydrogenation in reactor 2. To the enameled reactor 2 are charged 100 liters of freshly-distilled sylvan, 60 liters of distilled water, and 100-300 g of 15-20% palladium chloride solution in hydrochloric acid; and the hydrogenation and hydration of the sylvan to γ-acetopropyl alcohol is conducted at a pressure of 1.0-2.5 kg/cm^2, a temperature of 58-60°, and with constant stirring, for 9-12 h.

At the end of the process the reaction mixture is cooled to 30-40°, the pressure is lowered to atmospheric, and 55 liters of distilled water is added; then the reaction mixture is neutralized with a 7-10% calcined soda solution to pH 7.5-9.0, it is separated from the catalyst on pressure filter 3, and is routed to separatory funnel 4 for separation of the layers. After settling for 6-7 h, the upper layer, which consists mainly of unreacted sylvan, is collected, washed with water, and routed to hydrodistillation with subsequent transfer of the sylvan to hydrogenation. The lower, aqueous layer, which contains the main part of the acetopropyl alcohol, is collected and is transferred in an amount of 550 liters to a vacuum-evaporating apparatus 5, where at a vapor temperature not over 90° and a liquid temperature not over 120° the easily volatile compounds and water are distilled off at a residual pressure of 300-400 mm.

Concentration of the aqueous γ-acetopropyl alcohol solution in apparatus 5 is carried out to a content of main product in the pot residue of not less than 85%, and a water content of no more than 0.5%. The pot residue, which is raw acetopropyl alcohol, is routed to fractionation in apparatus 6, where a first fraction in the amount of up to 20%, containing traces of acetopropyl alcohol, is collected at a temperature of not over 92° and a residual pressure of 10-15 mm. The desired product, which makes up about 65%, is distilled at 92-145° and a residual pressure of 10-15 mm, into collector 7. The γ-acetopropyl alcohol prepared,containing not less than 95% of the main compound, is used for the synthesis of the thiazole component in vitamin B_1 production.

The technology developed for preparation of acetopropyl alcohol has been introduced and mastered in the Belgorod vitamin combine. The yield of γ-acetopropyl alcohol from synthetic sylvan is 53.8%(Table 3).

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