Pioneer: Journal of Advanced Research and Scientific Progress (JARSP)
Volume: 01 Issue: 06 | 2022 ISSN: 2751-7551
http://innosci.org

Synthesis of Aliphatic Alcohols on the Base of Natural Gas Processing Product

Khudayberganova Sevara Zokirjonovna
Doctoral student of the National University of Uzbekistan Uzbekistan, Tashkent

Nurmonov Suvonkul Erxonovich
Doctor of Science, Professor of the National University of Uzbekistan Uzbekistan, Tashkent

Abstract

The article describes the method of obtaining isopropyl and isoamyl alcohol from ethylene on the base of telomerization reaction. Which carried out by radical mechanism with methanol in the presence of an initiator at high temperature and pressure? The composition of the obtained product was determined by liquid chromatography.

Keywords: methyl alcohol, ethylene, isopropanol, isoamyl alcohol, temperature, pressure, catalyst, telomerization reaction.

Introduction.

Synthesis of ethylene-based aliphatic alcohols is important. The fact that the starting materials used are derived from local raw materials increases the cost-effectiveness of the process. Alcohols are used as solvents for oils, waxes and oils, and as raw materials in the production of ethers.

Methods.

Alcohols can be synthesized on the basis of many other substances. [1, 2]:

The synthesis of its homologues by adding one or more methylene groups to organic compounds was first carried out in 1940 in the synthesis of alcohols. Ethanol was synthesized catalytically on the basis of methanol under high pressure [3]:

$$CH_3OH + CO + 2H_2 \xrightarrow{Co_2(CO)_8} CH_3CH_2OH + H_2O$$

The mechanism of this reaction is similar to the hydroformylation reaction of alkenes, which can now be achieved by using modified cobalt and ruthenium catalysts and using iodide ions as promoters to form ethanol with a yield of up to 90% [3].

The initial methanol is also derived from carbon monoxide (catalysts based on copper and zinc oxides, pressure 5-10 MPa, temperature 250 ° C) [3], so the general scheme can be expressed as follows:

$$C + H_2O \rightarrow CO + H_2 \rightarrow CH_3OH \xrightarrow[-H_2O]{CO + H_2} CH_3CH_2OH$$

In the process acetaldehyde, ethylene and diethyl esters were formed as by-products.

Gerbe reaction is a high-temperature (200 ° C, pressure 5-6 MPa) process, in which the catalytic condensation of unbranched primary aliphatic alcohols in the a-state is carried out according to the following scheme [4]:

$$2RCH_2CH_2OH \rightarrow RCH_2CH_2CH(R)CH_2OH$$

Complex compounds based on rhenium, nickel, copper, iron salts and other components are used as catalysts. The reaction mechanism is proposed as follows [5]:

$$2RCH_2CH_2OH \rightarrow 2RCH_2CH_2CHO + H_2$$

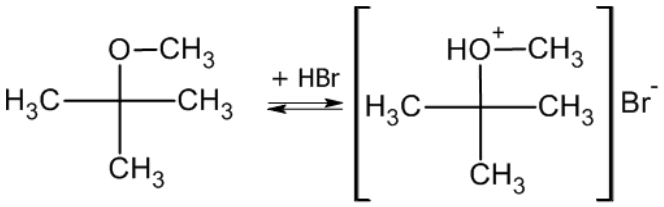
$$2RCH_2CH_2CHO \rightarrow RCH_2CH{=}C(R)CHO + H_2O$$

$$RCH_2CH{=}C(R)CHO + H_2 \rightarrow RCH_2CH_2CH(R)CH_2OH$$

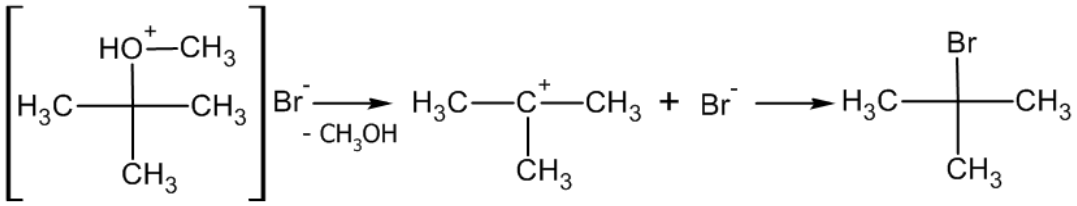
$$RCH_2CH{=}C(R)CHO + 2RCH_2CH_2OH \rightarrow RCH_2CH_2CH(R)CH_2OH + 2RCH_2CHO$$

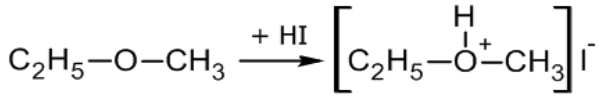
The application of this method is relatively limited due to the complexity of the reaction conditions, the relatively low yield of the product and the formation of acids and aldehydes as by-products [5].

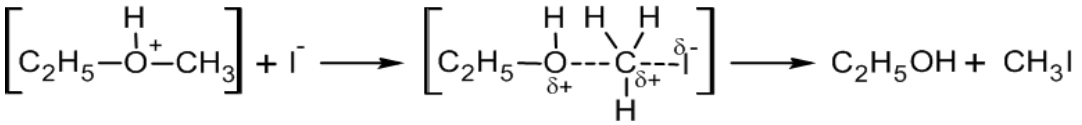
This method of production in the laboratory is used very rare, because alcohols serve as the primary raw material for the synthesis of esters. Typically, the reaction is carried out by heating an ether and a concentrated solution of hydrogen bromide or hydrogen iodide acid, while the decomposition can proceed through the mechanism of S_N1 and S_N2



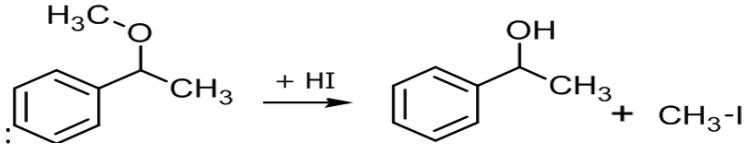
[6]:



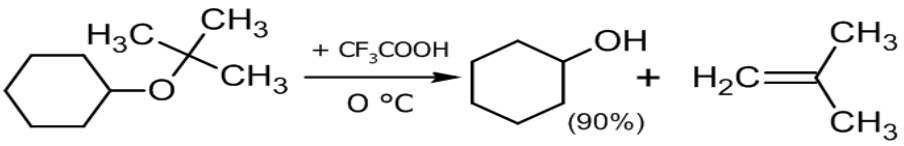




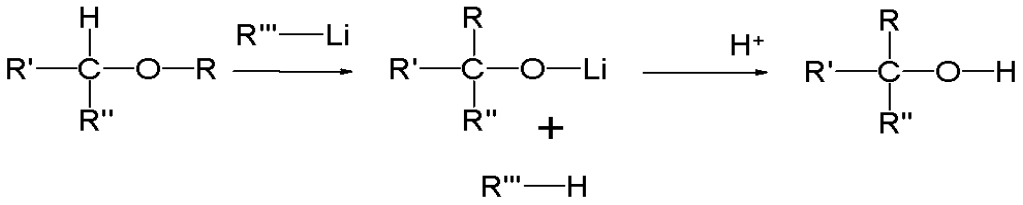
In case of symmetric esters, two different alcohols and two different halogenated products were obtained, but in the case of methyl ether the reaction product consists of alcohol and methyliodide or methyl bromide [7]



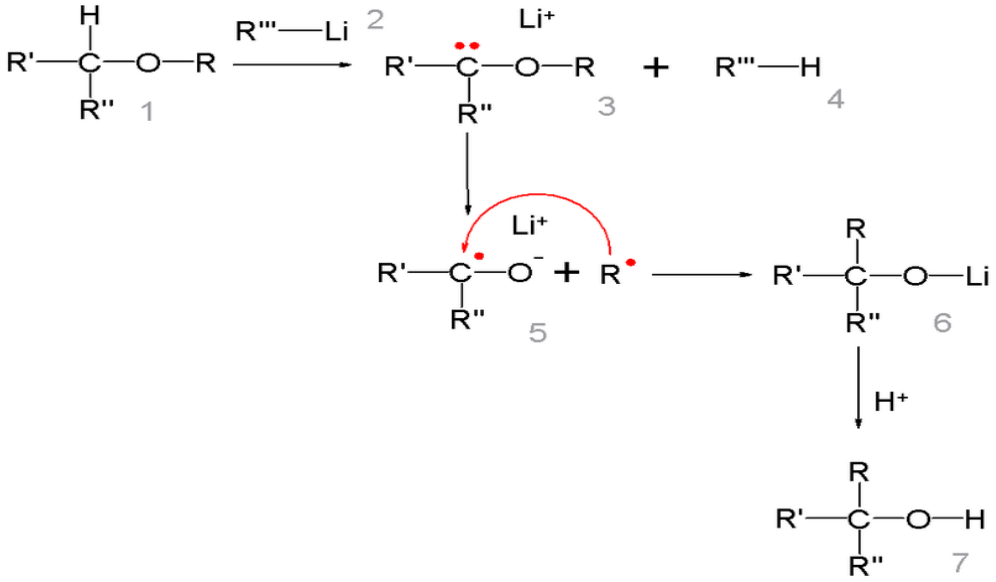
BF3, BCl3, AlCl3 and other similar Lewis acids as well as strong organic acids can also be used to decompose esters. For example, the reaction of quaternary butylcyclohexyl ester with triphosphoric acid occurs through the mechanism of S_N1 with the formation of cyclohexanol and 2-methylpropene [8]:



Ordinary esters are regrouped into alcohols under the influence of phenylthite (Georg Vittig reaction):



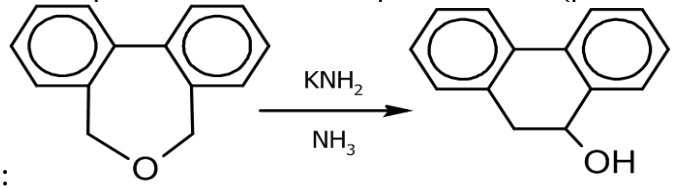
The carbonyl regrouping can be expressed as the reaction occured by separation-recombination through radical mechanism [8]:



Since new C-C bonds are formed very rapidly in the Vittig regrouping the R-radical does not have time to reverse, so that the initial configurations are usually retained in the reaction . The study of regrouping on the example of b-alkoxyalkylalyl esters shows that the selectivity of tsin-1,3-diol derivatives reaches 90-95% with a yield of 14-32% [8].

Vittig regrouping occurs not only with alkyl- but also arrhythmic compounds (phenylthite, butylithium, methyllythium, lithium diethylamide, etc.), as well as under the influence of other strong bases, such as potassium amide in liquid ammonia (product yield 90%)

[8]:



Study method.

Homogeneous-catalytic methods, gas treatment methods, liquid chromatography, IR-spectroscopy, physicochemical methods were used in the research. The production of isopropyl and isoamyl alcohols as a result of the telomerization reaction of ethylene in the presence of

methanol was studied. The process was mainly carried out at 40^{0}-100^{0}C, pressure of 1.0 - 5.0 MPa and a duration of 2-8 h.

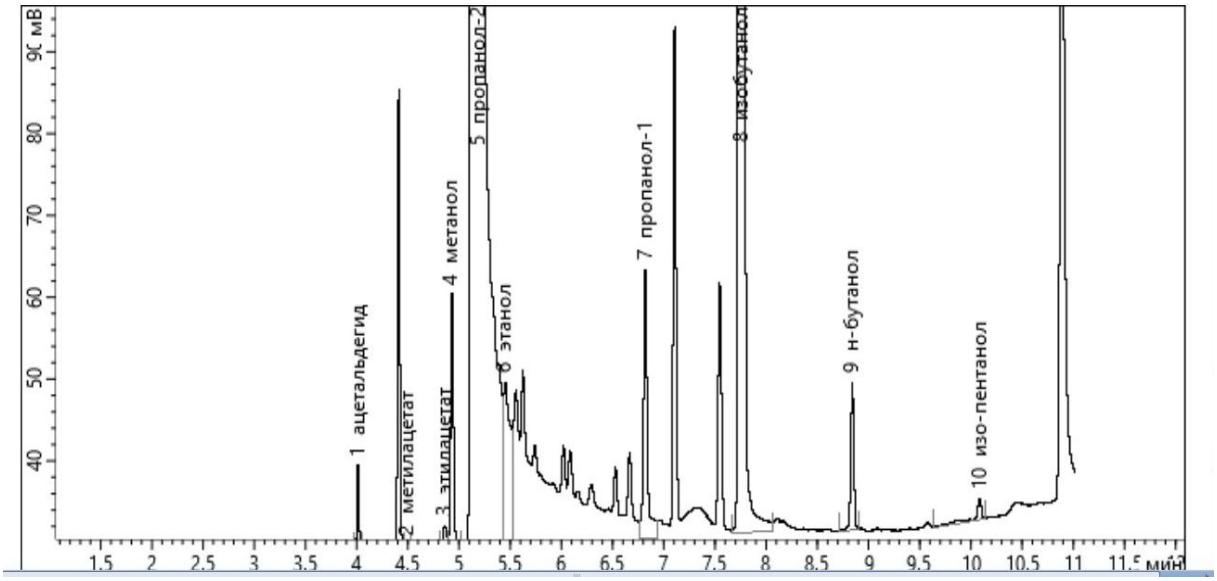
The discussion of the results.

The production of isopropyl and isoamyl alcohols during of the telomerization of ethylene in the presence of methanol was studied. The telomerization reaction takes place in the presence of methanol and ethylene on the basis of the following steps:

$$CH_3{-}OH + CH_2{=}CH_2 \rightarrow C_3H_7OH \xrightarrow{CH_2=CH_2} C_5H_{11}OH$$

The method of synthesis involves the telomerization of ethylene with methanol in the presence of a radical initiator at high temperature and pressure.

The synthesis process was carried out in a high-pressure resistant hermetic reactor. The composition of the reaction mixture was determined by liquid chromatography (Fig 1.).

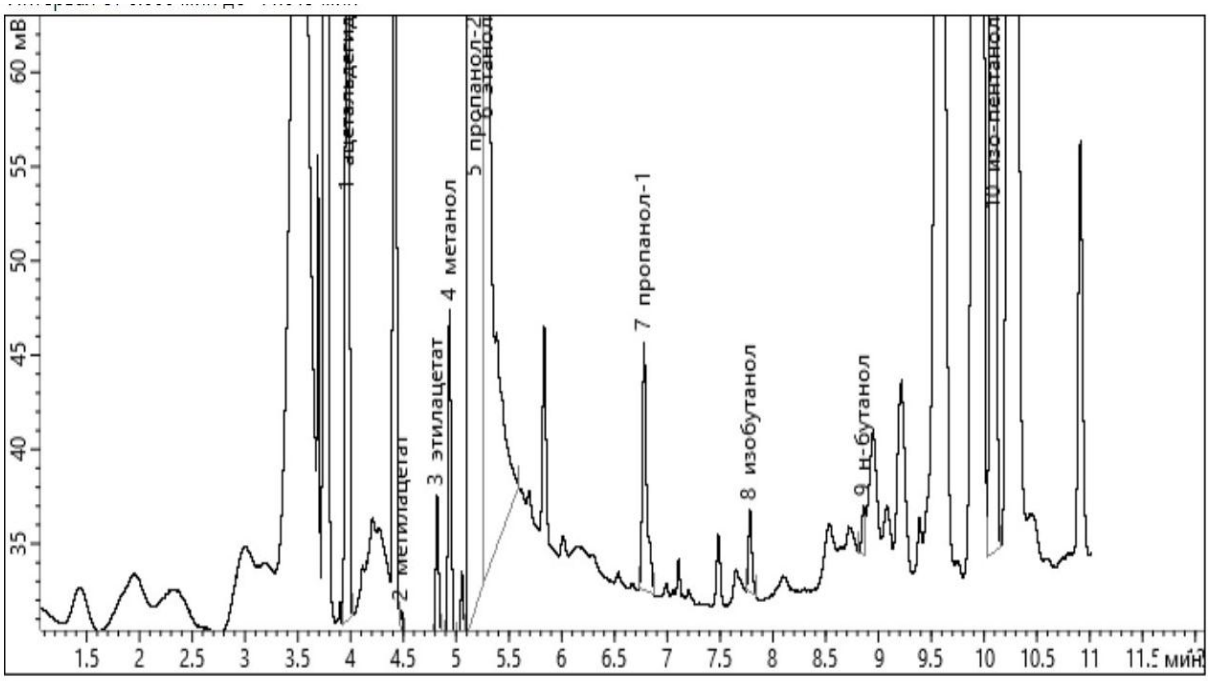


Результат анализа

Компонент	Время (мин)	Площадь (мВ*с)	Высота (мВ)	Концентрация	Ед. измер.	Детектор
ацетальдегид	3.948	6.624	3.729	9.9534	мг/л	ПИД-1
метилацетат	4.393	64425.469	38213.525	1.4665E+05	мг/л	ПИД-1
этилацетат	4.838	284224.509	62574.606	3.0394E+05	мг/л	ПИД-1
метанол	4.741	5.854	3.578	0.00086103	об.%	ПИД-1
пропанол-2	5.152	382.594	96.972	411.6	мг/л	ПИД-1
этанол	5.280	1757.332	662.137	0	мг/л	ПИД-1
пропанол-1	6.827	38.441	4.820	30.826	мг/л	ПИД-1
изобутанол	7.774	4.110	1.433	3.055	мг/л	ПИД-1
н-бутанол	8.848	1.949	0.837	1.4672	мг/л	ПИД-1
изо-пентанол	10.075	2.293	0.528	1.5655	мг/л	ПИД-1

Fig. 1. Liquid chromatogram of ethylene telomeration reaction products in the presence of Methanol

The process was mainly carried out at 60^{0}C, pressure of 4.0 MPa and a duration of 4 h.



Результат анализа

Компонент	Время (мин)	Площадь (мВ*с)	Высота (мВ)	Концентрация	Ед. измер.	Детектор
ацетальдегид	3.969	596.908	450.459	896.89	мг/л	ПИД-1
метилацетат	4.487	1.282	0.942	2.9187	мг/л	ПИД-1
этилацетат	4.820	14.946	7.689	15.983	мг/л	ПИД-1
метанол	4.937	37.165	17.592	0.0054664	об.%	ПИД-1
пропанол-2	5.186	392832.889	133364.133	4.2262E+05	мг/л	ПИД-1
этанол	5.292	763.841	368.326	0	мг/л	ПИД-1
пропанол-1	6.781	38.708	13.180	31.041	мг/л	ПИД-1
изобутанол	7.784	10.143	4.424	7.54	мг/л	ПИД-1
н-бутанол	8.863	5.582	2.567	4.2018	мг/л	ПИД-1
изо-пентанол	10.091	611.972	241.155	417.84	мг/л	ПИД-1

Fig. 2. Liquid chromatogram of ethylene telomeration reaction products in the presence of methanol. The process was mainly carried out at 80^0C, pressure of 4.0 MPa and a duration of 4 h.

Conclusion

The analysis of the results has shown that the main products of the telomeration reaction of ethylene in the presence of methanol are isopropyl and isoamyl alcohols, as well as acetaldehyde, methylacetate, ethyl acetate, butanol, isobutanol, propanols.

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