

Telomerization reaction of ethylene with ethanol

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Abstract. The research's main aim is to synthesize saturated alcohols containing four or more carbon atoms in the chain from ethylene and ethanol, which are products of natural gas processing. During of investigation, isobutyl and isohexyl alcohols were synthesized, and the optimal conditions for the process were determined. The dependence of the product yield on various factors has been studied.

1 Introduction

Ethylene production has an important role in natural gas processing. Different hydrocarbons, from ethane to gas oil, are used as raw materials in this process. In Uzbekistan, most of the ethylene is produced at Shurtan Mining and Chemical Combine, and the Ustyurt Mining and Chemical Combine is used to produce polyethylene. However, many different compounds can be synthesized on its basis, including alcohols [1].

The synthesis of saturated monoatomic alcohols has great practical importance. For example, isopropyl alcohol is used in medicine, the chemical industry, and acetone production [2-5], and butyl and isobutyl alcohols are used as solvents [4]. Isobutyl alcohol can replace butanol-1 due to its low cost [5] and also is used as a component of varnishes, washes, perfumes, and hydraulic fluids [6]. Iso-amyl alcohol is the main raw material in producing solvents, validol, and carbonic acid; in the perfume industry [2-5], C₆-C₁₁ alcohols are mainly used as plasticizers.

One of the non-traditional methods of obtaining the highest alcohols required for the industry is the production of low molecular alcohols in the process of telomerization, which is a chain reaction consisting of inserting a repeating fragment of the monomer M between two parts of the X-Y compound (telogen), resulting in the formation of homologous telomeres X-M_n-Y (n=2-40). In telomerization, unsaturated compounds are often used as monomers, and peroxides, azocompounds, oxygen, and UV or γ radiation are mainly used as initiators.

The process of telomerization is similar to polymerization reactions in the sense that for process continuation, active particle X must be formed, but it differs by chain transmission and interruption. The reaction between saturated alcohols and ethylene is based on the mechanism of free radical telomerization, which causes the branching of the telomere carbon chain owing to the growing radical homolytic rearrangement. The composition of the telomeric mixture is determined by the values of the chain transfer constant, and the

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process can be optimized by selecting the reagent concentration, pressure, temperature, and initiator for the synthesis of the desired products [8-10].

2 Methods

The synthesis of isobutyl and iso-hexyl alcohols on the base of ethylene was carried out at 10 atm. and 40°C during 2–6 h (Table 1). Yield has increased from 7.2 to 15.1% in 2-5 hours. Increasing the reaction time to 6 hours led to decreasing product yield.

Table 1. Effect of reaction time on the yield of isobutyl alcohol

№	Pressure, atm.	Temperature, °C	Reaction time, h.	Yield, %
1	10	40	2	7.2
2			3	9.0
3			4	12.7
4			5	15.1
5			6	13.9

To determine the effect of temperature on the product yield, the process was carried out in the range of 30-70°C at a pressure of 10 atm and a duration of 5 hours. It was shown that increasing temperature in the range of 30-70 °C positively affected the product yield, and its maximum of 23.4 % was observed at 60 °C (Table 2).

Table 2. Effect of temperature on synthesis of isobutyl alcohol

№	Pressure, atm.	Reaction time, h	Temperature, °C	Yield, %
1	10	5	30	11.7
2			40	15.1
3			50	19.8
4			60	23.4
5			70	21.0

The effect of pressure on the product yield was investigated in the range of 10-40 atm at the optimal temperature of 60 °C and duration of 5 hours (Table 3).

Table 3. Selection of optimal pressure for synthesis of isobutyl alcohol

№	Reaction time, h.	Temperature, °C	Pressure, atm.	Yield, %
1	5	60	10	23,4
2			15	29,2
3			20	35,2
4			25	40,4
5			30	49,6
6			35	53,5
7			40	51,3

Increasing pressure in the range of 10-35 atm has caused an increasing yield of isobutyl alcohol from 23.4 to 53.5%, and it is further increasing led to a decreasing yield of the product.

At a temperature of 60 °C, the reaction time was 5 hours, and the pressure in each experiment was equaled from 5 to 60 atm. It is shown that an increase in pressure from 35

to 60 atm caused increasing the product yield from 23.4 to 58.6%, respectively, and a further extension of pressure practically does not change it; for example, at 60 atm, the yield was 58.2% (Fig. 1).

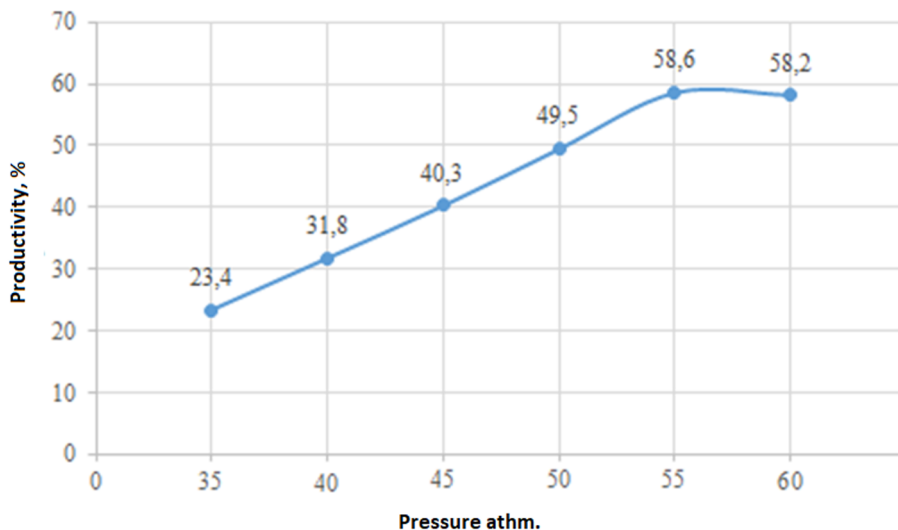


Fig. 1. Effect of pressure on synthesis of isohexyl alcohol

At an optimum pressure of 55 atm and temperature of 60 °C, the effect of a reaction time from 1 to 8 hours was studied. With a duration of 2 to 8 hours, the yield increased from 29.5 to 63.9 %, and a further increase in time caused a decrease in the product yield (Fig. 2).

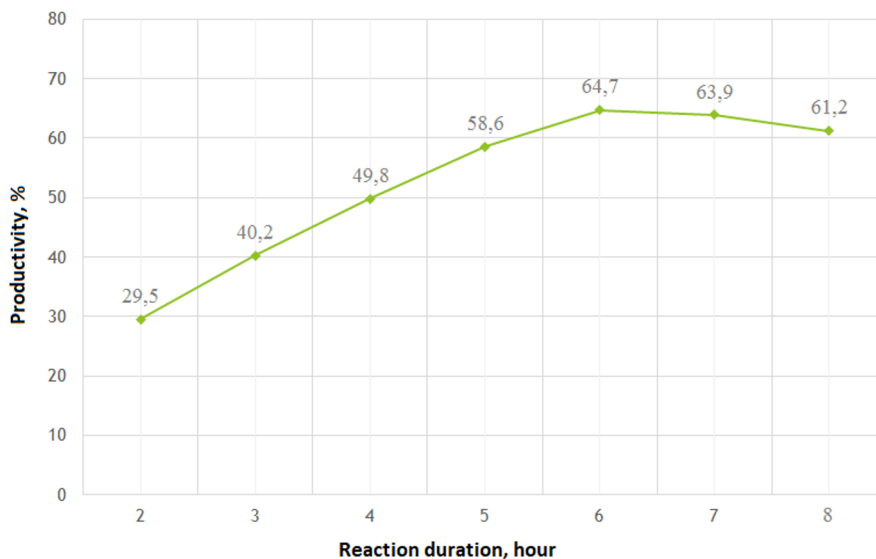


Fig. 2. Effect of reaction time on synthesis of isohexyl alcohol

For investigation of the effect of temperature on the product yield at the optimal pressure - 55 atm and reaction time of 6 hours, experiments were carried out by synthesis of iso-hexyl alcohol in the temperature range 40–90 °C, which was increased stepwise from 40 to 90 °C, and the maximum yield of the product was observed at 80 °C (Fig. 3).

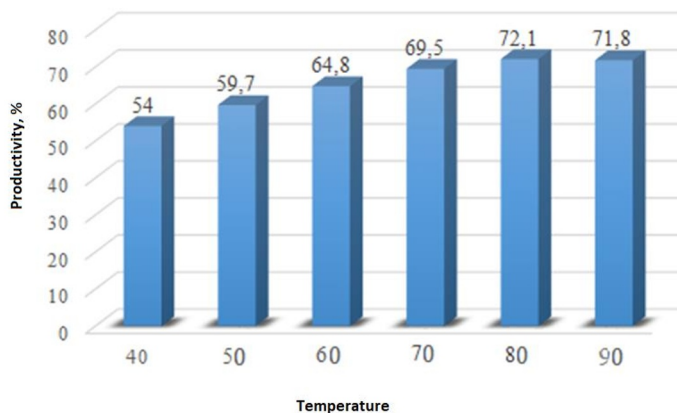


Fig. 3. Effect of temperature on synthesis of isohexyl alcohol

3 Results and discussion

The structure of the synthesized isobutyl alcohol was confirmed by the chromato-mass spectrum. For investigation and analysis of synthesized products' composition and structure, such methods as chemical, quantum-chemical, physical, physico-chemical, and mathematical modeling were used. The mass-spectrums of the obtained substances were obtained in the liquid phase on a standard HP-5MS column, control parameters in the range of 0-320°C, Agilent MSD 5975C-GC7890A chromato-mass spectrometers with an initial temperature from 50 to 120°C. In the chromato-mass spectrum of isobutyl alcohol, the formation of ions corresponding to the molecular mass and the masses of fragmented ions formed during it is decomposition determined. In this case, the molecular-ion peak of isobutyl alcohol is 74. Below, the chromato-mass spectrum of ions forming from the molecular ion of initial isobutyl alcohol is presented (Fig. 4).

Unknown: Average of 1.621 to 1.644 min.: 195_10_1.D\data.ms
Compound in Library Factor = 273

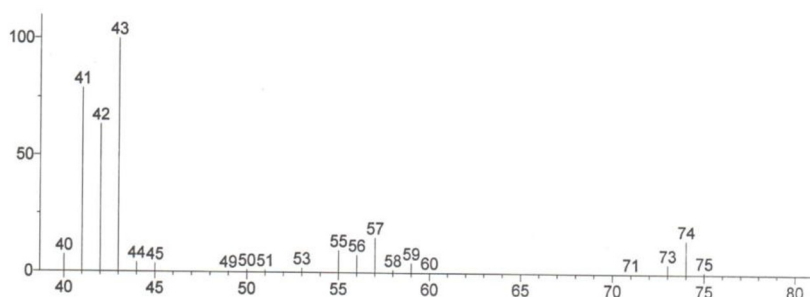
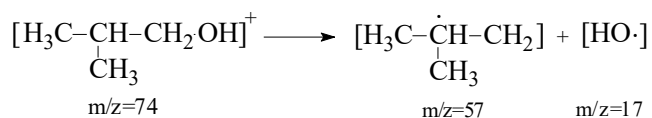
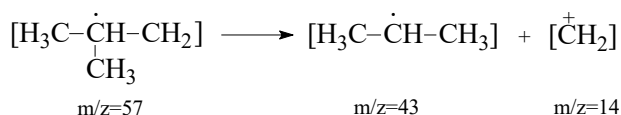


Fig. 4. Chromato-mass spectrum of isobutyl alcohol

In addition, the formation of fragment ions with masses m/z 57, m/z 56, m/z 55, m/z 43, m/z 42, and m/z 41 was found in the spectrum. The release of the hydroxyl radical from the isobutyl alcohol ion during 1644 min resulted in the release of isobutyl with m/z 57.



The release of the methylene ($=\text{CH}_2$) group of the isobutyl ion leads to the release of the isopropyl ion with m/z 43.



Thus the optimal conditions for the synthesis of isobutyl alcohol based on ethylene are the following: reaction time of 5 hours, temperature of 60°C , and pressure of 35 atm. The yield was 53.5%. The structure of isobutyl alcohol has been proven using mass chromatography, Raman, and IR spectrums.

For the analysis of the synthesized isobutyl and iso-hexyl alcohols, IR spectrums together with the method of chromato-mass spectroscopy were used (Fig. 5).

IR Spectra The Agilent Technologies Cary 640 Series FTIR spectrometer has an optical spectral range of the IR-Fure spectrometer $<0.25 \text{ cm}^{-1}$, an IR spectral range of $7900\text{-}400 \text{ cm}^{-1}$ and an extended spectral range of $4000\text{-}400 \text{ cm}^{-1}$. The IR-Fure spectrophotometer with a $50\text{-}13500 \text{ cm}^{-1}$ range was obtained on Nicolet iS50 spectrometers [11-12].

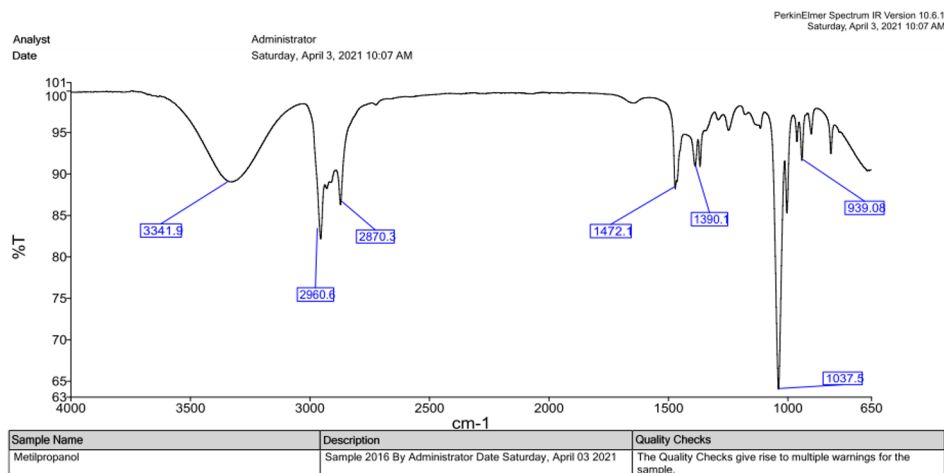


Fig. 5. IR spectrum of isobutyl alcohol.

In the IR spectrum of isobutyl alcohol, hydrogen bonds of the hydroxyl group were observed in a wide and intense region of the stretching vibration signal at 3341 cm^{-1} , and an intense signal of the stretching vibrations of the carbon-bonded hydroxyl group (C-OH) at 1037 cm^{-1} . The vibrational signal of the methylene group (CH_2) was observed in the region 1390 cm^{-1} ; stretching vibrations of the text group (CH) were observed in the region

cm^{-1} ; asymmetric stretching vibrations of the methyl group (CH_3) with high intensity were observed at 2960 cm^{-1} , while the signal of asymmetric bending vibrations observed in the region 1472 cm^{-1} .

The Raman spectrums of the synthesized products were obtained at room temperature on an InViaRaman Renishaw Spectrometer designed to obtain fingerprints of molecules and monitor changes in the structure of molecular bonds (changes in state, stress, and strain). The following methods were used as a source of excitation:

- laser Cobolt CW 532 nm DPSS with a wavelength of 532 nm, nominal power 100 mW., Renishaw CCD camera with a standard detector with periodic diffraction grating 1800 lines/mm and as a recording device;

- spectrum Stabilized Laser Module 785 nm laser, rated power 100 mW, Renishaw CCD camera with standard 1200 lines/mm periodic grating detector and recorder.

At measurements, the laser beam was focused on the surface of samples with a diameter of $10 \mu\text{m}$ and at this intensity of radiation on it's varies depending on the value of the output signal on the detector; a magnifying lens x50 was used to focus the moving light, as well as a collection of scattered light. Measurements in the advanced regime of exposure time are 10 seconds, which has allowed to carried out measurements in the desired wavelength range.

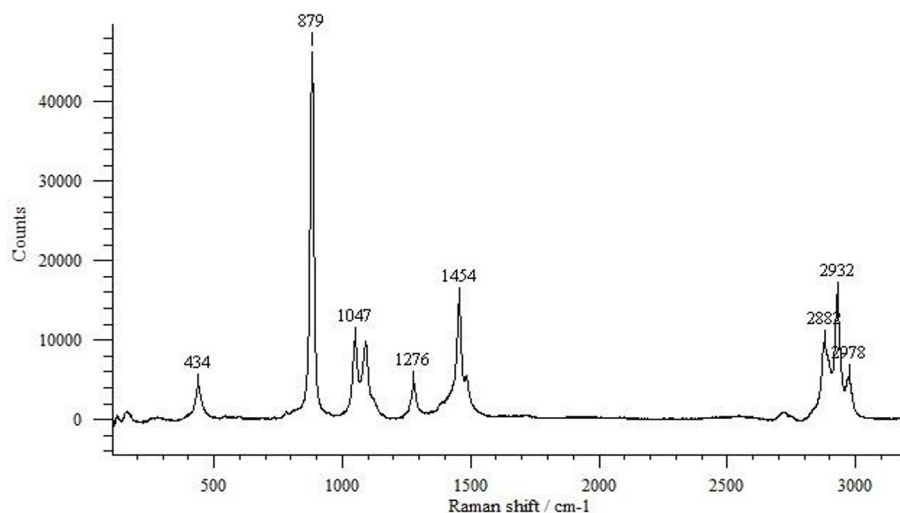
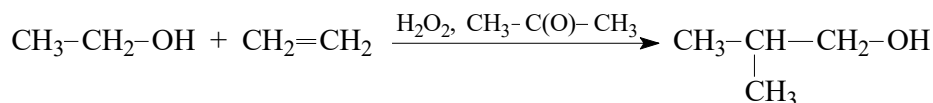
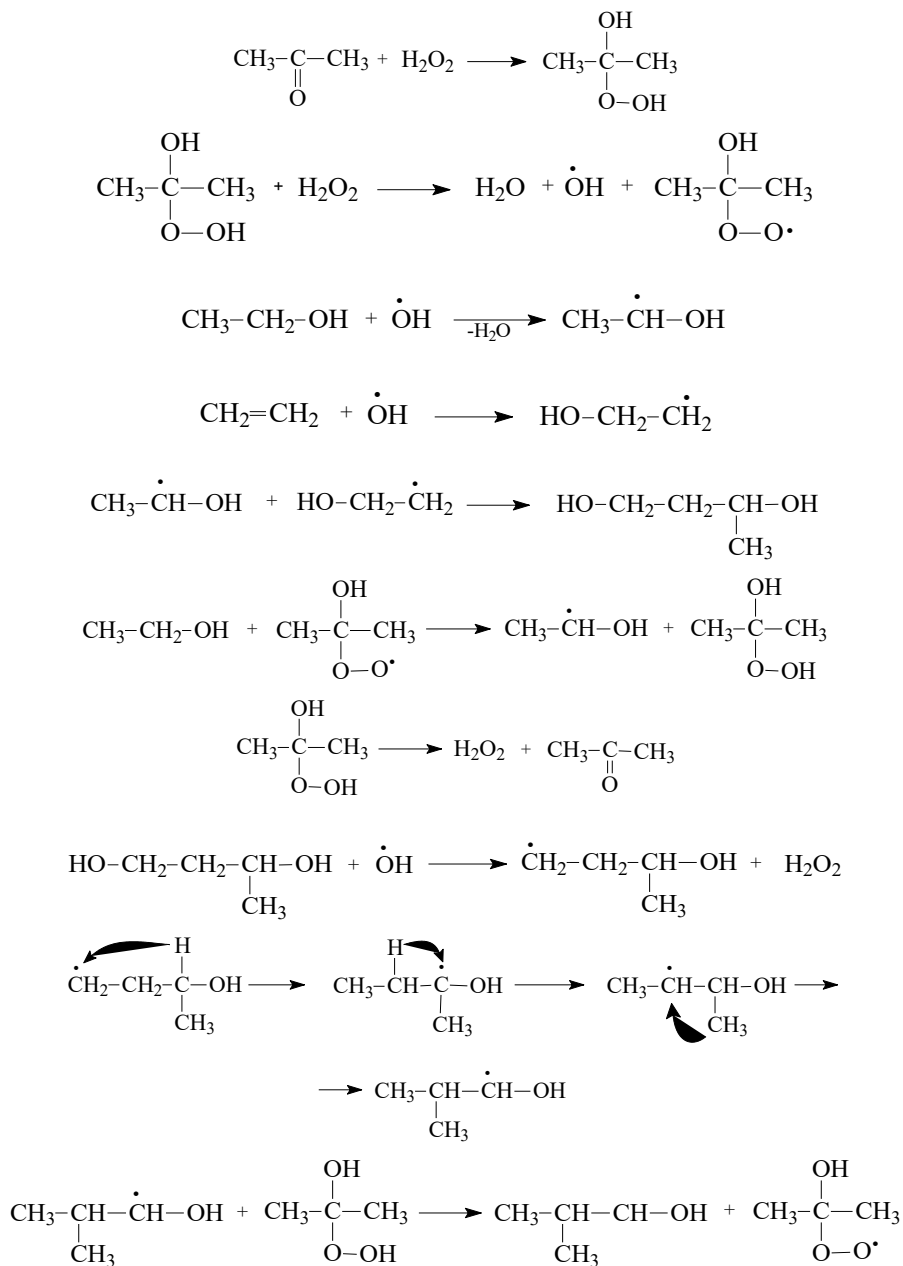


Fig. 6. Raman spectrum of isobutyl alcohol

The formation of isobutyl alcohol during ethylene telomeration in the presence of ethanol occurs as follows:



In the process, acetone acts as a catalyst and hydrogen peroxide was used as an initiator; with their interaction, the initiation stage begins. The reaction mechanism can be presented as follows:



By selecting the technological parameters of the process, it was established that isohexyl alcohol is also formed during the telomeration of ethylene and ethyl alcohol; and the influence of various factors on its yield was also investigated.

The structure of the synthesized iso-hexyl alcohol was studied by Raman and IR spectroscopic methods (Fig. 7, 8).

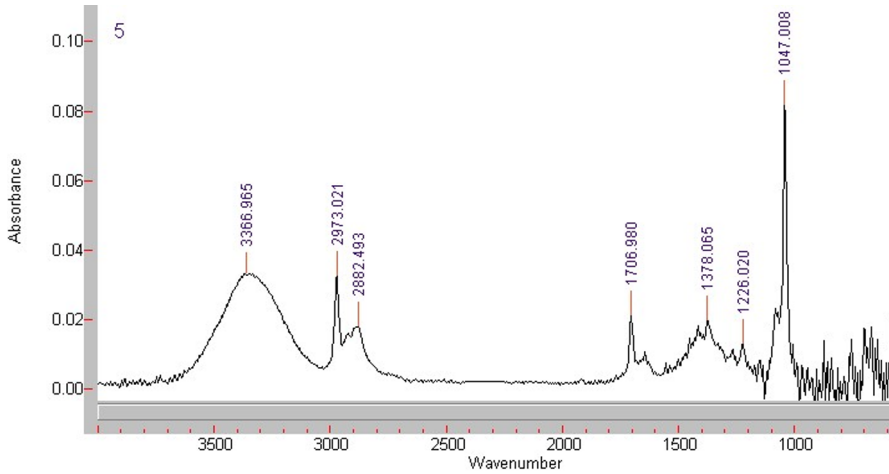


Fig. 7. IR spectrum of isohexyl alcohol

In the IR spectrum of isohexyl alcohol, the hydrogen bond of the hydroxyl group is in the region 3366 cm^{-1} , the carbon hydroxyl group (C-OH) is in the region 1047 cm^{-1} , and the methylene group (CH_2) is manifested by an asymmetric valence signal in the region 2973 cm^{-1} and a signal with solder fluctuations in the region 1378 cm^{-1} ; stretching vibration of the text (CH) group - in the region 2882 cm^{-1} ; an asymmetric signal of deformational vibrations of the methyl group (CH_3) was observed in the region 1378 cm^{-1} .

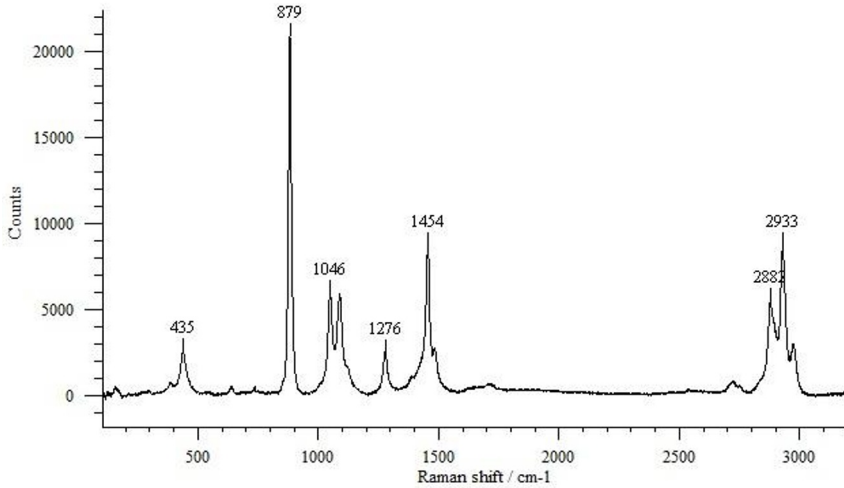


Fig. 8. Raman spectrum of iso-hexyl alcohol

4 Conclusions

The studies showed that at measurements, the laser beam focuses on the surface of samples with a diameter of $10\ \mu\text{m}$ and at this intensity, radiation varied depending on the value of the output signal on the detector. A magnifying lens $\times 50$ was used to focus the moving light, as well as a collection of scattered light. Measurements in the advanced regime of

exposure time were 10 seconds, which has allowed to carry out measurements in the desired wavelength range.

By selecting the technological parameters of the process, it was established that isohexyl alcohol is also formed during the telomeration of ethylene and ethyl alcohol; and the influence of various factors on its yield was also investigated.

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