

Catalytic Hydrolysis of Chloromethane*

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Abstract

The catalytic methyl in chloride hydrolysis process was investigated. ZnO and Al₂O₃ were used as catalysts. A maximum possible degree of methyl chloride conversion was attained (comparable with the one obtained as a result of thermodynamic calculations). At the initial stage of the catalysts' performance ZnO is washed out (the lack of reflection from the zinc oxide phase on the produced catalyst diffractions after the hydrolysis; after about 3 hours of the process initiation, the degree of methyl chloride into methanol conversion is slightly reduced). The catalytic activity of the examined catalysts does not change in a given time (apart from the result mentioned above). The greatest capacity was achieved at the temperature 220 – 250°C. Above 320°C carbon dioxide can be observed in the products of the reaction (thus there is a decrease of the selectivity)

Key words: methane, methanol, hydrolysis, chloromethane, catalyst, ZnO, Al₂O₃

Introduction

Direct conversion of methane into useful chemicals remains as a big challenge in catalysis in the 21st century. Although there is still no direct process with commercial viability at this moment, many new methods and catalysts have been developed for the direct activation and conversion of methane. One of the solutions is a new method of producing methyl alcohol from methane. Most of the problems connected with employing this technology result from an unfavourable balance of the methyl chloride hydrolysis reaction. In the ambient temperature a reverse reaction is favoured, namely, producing methyl chloride from methyl alcohol and hydrogen chloride. The aim of the work was to find the best catalyst

and examine influence of conditions on methyl chloride hydrolysis. We have found that the catalysts containing ZnO and Al₂O₃ demonstrated a catalytic activity methyl in chloride hydrolysis process. A maximum possible degree of methyl chloride conversion was attained (comparable with the one obtained as a result of thermodynamic calculations). At the initial stage of the catalysts' performance ZnO is washed out. The catalytic activity of the examined catalysts does not change in a given time. The greatest capacity was achieved at the temperature 220 – 250°C. The rapidly changing over the last years ways of life as well as the humans' approach to the existential problems, have considerably affected chemical industry. It is based to a significant extent on the non-

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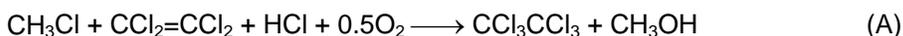
renewable resources, the reserves of which might wear thin in future or their exploitation will become so expensive that the profitability of the technologies applied will be open to doubt. Thus at present technologists are facing the challenge of coming up with new, having better qualities substances and finding new solutions and production technologies that would meet the increasing demand. A frequently occurring problem is the way of transporting such resources as crude oil or natural gas from their mining sites to the remotely situated areas facing the biggest demand.

This issue is particularly acute in the case of methane (the main component of natural gas). The cost of its transport is high and the delivery of the condensed gas is hazardous. Converting methane into products more convenient for transport right at the mining site seems the best solution [1]. A large number of studies have contributed to the direct conversion of methane in the past decade. Although there is still no direct process with commercial viability at this moment, many new methods and catalysts have been developed for the direct activation and conversion of methane. The carried out over the last years investigations regarding the attempts to oxidize methane while a heterogeneous catalysis is applied, have led the researchers to shared conclusions. Carrying out the process is feasible, however, the high selectivity of converting methane into the desired

products is accompanied by a low methane conversion and vice versa which eliminates employing such technologies on an industrial scale. Hence the more promising investigation concerning the process of methane conversion into the liquid phase has been recently emphasised. Methanol is the main product received during the process of methane oxidation while the homogeneous catalysis is being performed.

One of the ways of methane oxidation is the process of using natural methane and ethane halogen derivatives [2]. This process has proved to be interesting from a scientific point of view since some of its stages have difficult to conduct reactions because of unfavourable thermodynamics. From the practical point of view, though, as it has proved to a non-waste technology and while methane and oxygen are introduced into the system, methanol can be obtained as a valuable product.

In 1993 an American researcher, John Stauffer (Greenwich, Ohio), patented a new method of producing methyl alcohol from methane[2]. It is based on applying organic chloride compounds. The process proposed by Stauffer is composed of two stages mutually connected. Perchloroethylene, which initiates the first step, is oxychlorinated with hydrogen chloride with a view to receiving hexachloroethane and methanol.



Reaction (A) is a sum of reactions:



At the next stage (D) methane is chlorinated with hexachloroethane producing methyl chloride and reproducing perchloroethylene and hydrogen chloride.



The diagram of the process proposed by Stauffer is presented in Fig.1.

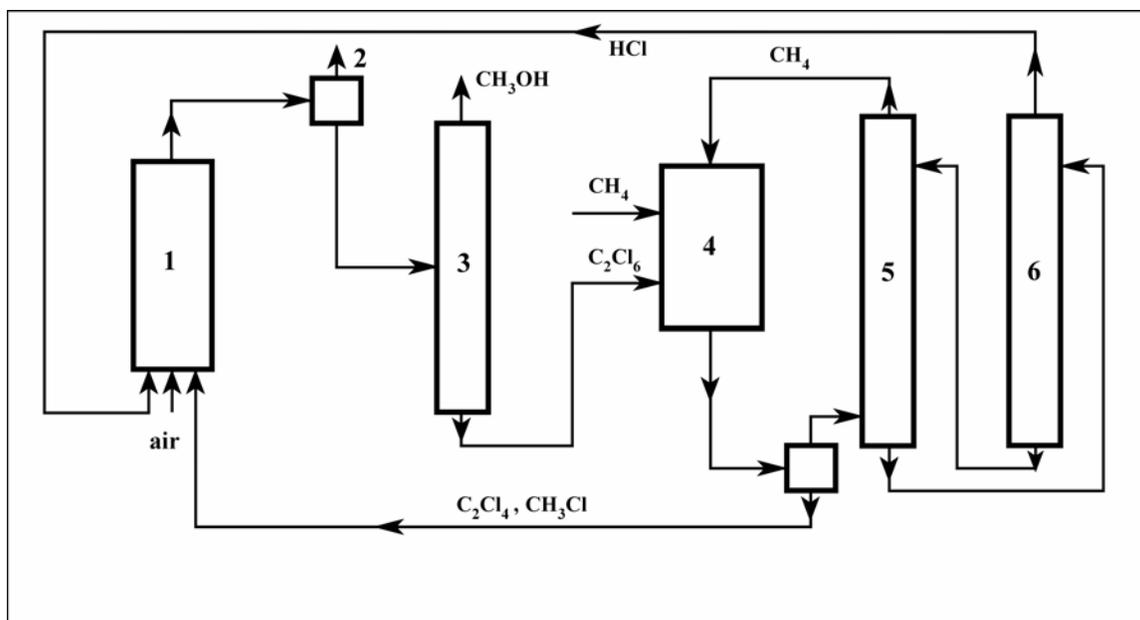


Fig. 1. The diagram of the production of methyl alcohol from methane while the process of perchloroethylene oxychlorination is applied. 1 – Catalytic reactor, 2 – Vent, 3 – Distillation column, 4 – Thermal reactor, 5 – Absorber, 6 – Stripper.

Most of the problems connected with employing this technology result from an unfavourable balance of the methyl chloride hydrolysis reaction. In the ambient temperature a reverse reaction is favoured, namely, producing methyl chloride from methyl alcohol and hydrogen chloride. Due to that a research concerning a catalytic methyl chloride hydrolysis was launched. In order to shift the equilibrium of this reaction towards receiving methanol, increasing the temperature was necessary. However, even then only partial methyl chloride conversion

was possible. Thus, to increase the degree of conversion, the excess of water in relation to stoichiometric quantities is necessary, whereas the unreacted methyl chloride should be directed for the hydrolysis reaction once again. The calculated dependency of the conversion of methyl chloride into methanol on the temperature of the conducted process is presented in Fig. 2.

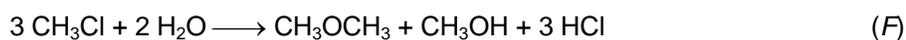
ΔG of the methyl chloride hydrolysis are as follows.



$$\Delta G_{298} = 31.66 \text{ kJ mol}^{-1}$$

$$\Delta G_{423} = 31.39 \text{ kJ mol}^{-1}$$

$$\Delta G_{973} = 28.44 \text{ kJ mol}^{-1}$$



$$\Delta G_{298} = -158.63 \text{ kJ mol}^{-1}$$

$$\Delta G_{423} = -183.72 \text{ kJ mol}^{-1}$$

$$\Delta G_{973} = -540.29 \text{ kJ mol}^{-1}$$

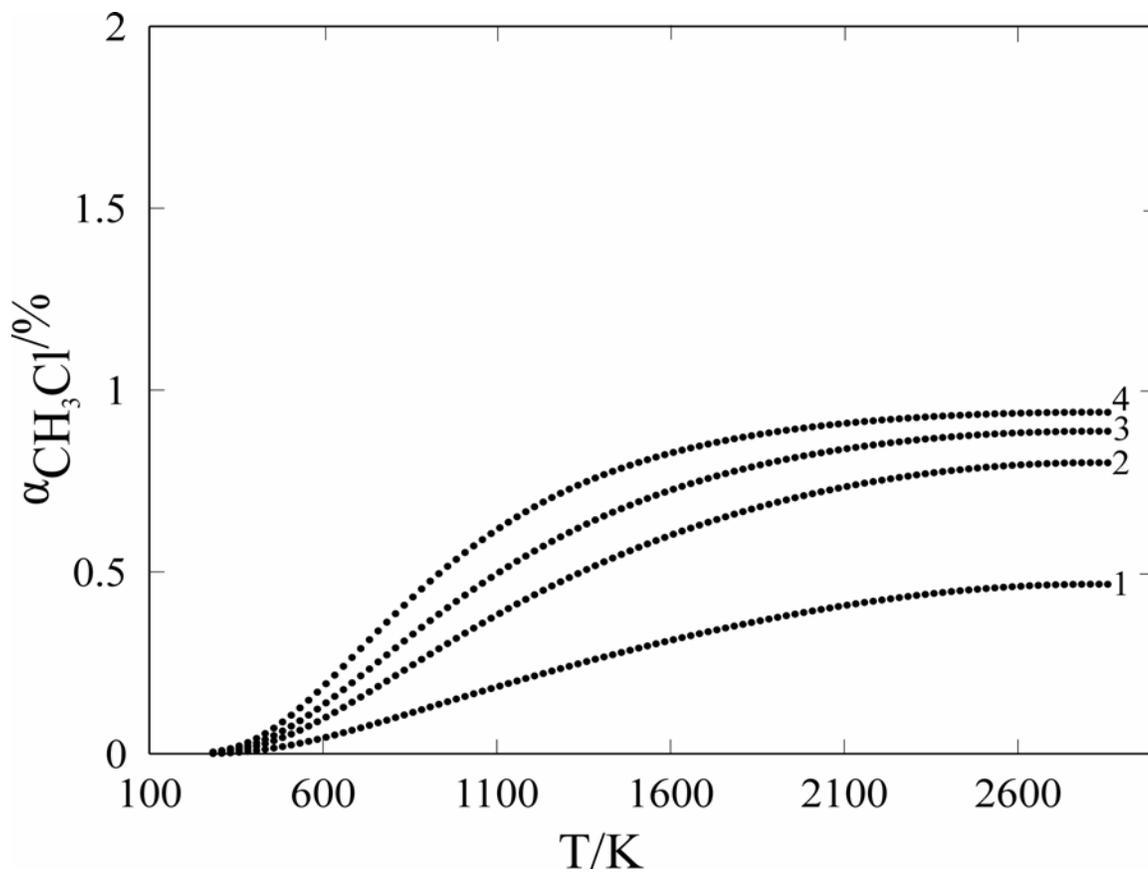


Fig. 2. The dependency of the conversion of methyl chloride into methanol on the temperature of the conducted process. 1 – $\text{CH}_3\text{Cl} : \text{H}_2\text{O} = 1 : 1$; 2 – $\text{CH}_3\text{Cl} : \text{H}_2\text{O} = 1 : 5$; 3 – $\text{CH}_3\text{Cl} : \text{H}_2\text{O} = 1 : 10$; 4 – $\text{CH}_3\text{Cl} : \text{H}_2\text{O} = 1 : 20$.

EXPERIMENTAL

The catalyst deposit was placed on the grate in the reactor. A mixture of aluminium hydroxide and zinc oxide mounted on the carrier was used as a catalyst. Alpha or gamma aluminium oxide served as a carrier. The reactor was placed in the tubular furnace. Behind the furnace was the condenser and receiver of the reaction products. This system allowed separating the mixture products and analysing them considering their quantity and quality. The diagram of the apparatus is shown in Fig. 3.

Gas methyl chloride contained in the steel bottle was directed through the micrometric valve and flow meter to a round-bottomed flask filled with water. The round-bottomed flask was placed in the heating jacket which made it possible to maintain constant temperature of the water contained in it. The

substrates from the flask were directed to a glass reactor through a tube wrapped in a heating tape. Halfway through the height of the reactor there was a grate

with the deposit of the hydrolysis reaction catalyst placed on it. From the reactor the products as well as the unreacted substrates were fed to the condenser and the receiver.

During the experimental part, water was supplied with the help of the peristaltic pump and evaporated directly at the reactor inlet. It allowed its precise dosage as well as increasing the ratio of water to the methyl chloride in the substrates, which was supposed to shift the equilibrium of the reaction to the right, towards generating methanol.

The reaction was run at 120 – 350°C. The substrates' residence time in the reactor was changed as well as their mutual relation. Different kinds of catalysts were applied. At first, the catalytic activity of the catalysts prepared for the contact apparatus in the process of hydrolysis, was examined. There the hydrolysis was to be conducted simultaneously with perchloroethylene oxychlorination. The mentioned catalysts did not demonstrate catalytic activity in the examined process. Zinc oxide and aluminium hydroxide mounted on the aluminium oxide were introduced into the process. So prepared catalyst turned out to be active in the conducted procedure.

A 8610C (SRI) type gas chromatograph equipped with a katharometer was used to analyse the obtained products. Hydrogen served here as a carrier gas. The volume of the injected gas samples was 1ml, whereas with the liquid ones, it amounted to 1 μ l. The following analysis conditions were introduced:

- methanol, water and methyl chloride were analysed on the 4m length column filled with

HayeSepT with a diameter $\Phi=3$ mm: the temperature of the process was 100°C

- carbon dioxide was analysed on the 4m length column with a diameter $\Phi=3$ mm and filled with HayeSep T. The temperature was 50°C

- carbon oxide was analysed on the 1m length column filled with 5A molecular sieves with a diameter $\Phi=3$ mm. The temperature of the column's work was 50°C.

In order to prepare the catalysts ZnO and Al(OH)₃ were used. The substrates were dissolved in the deionised water, next placed in the round-bottomed flask and applied on the carrier in the vacuum pan where while the solvent was being mixed and heated (the temperature was 50°C), it was subjected to evaporation. α -Al₂O₃ and γ -Al₂O₃ served as carriers. Following the process of impregnation, the catalysts were dried at 110°C, next they were calcinated in the tubular furnace at 400°C for 6 hours in the nitrogen atmosphere, and for the further 2 hours in the air flow.

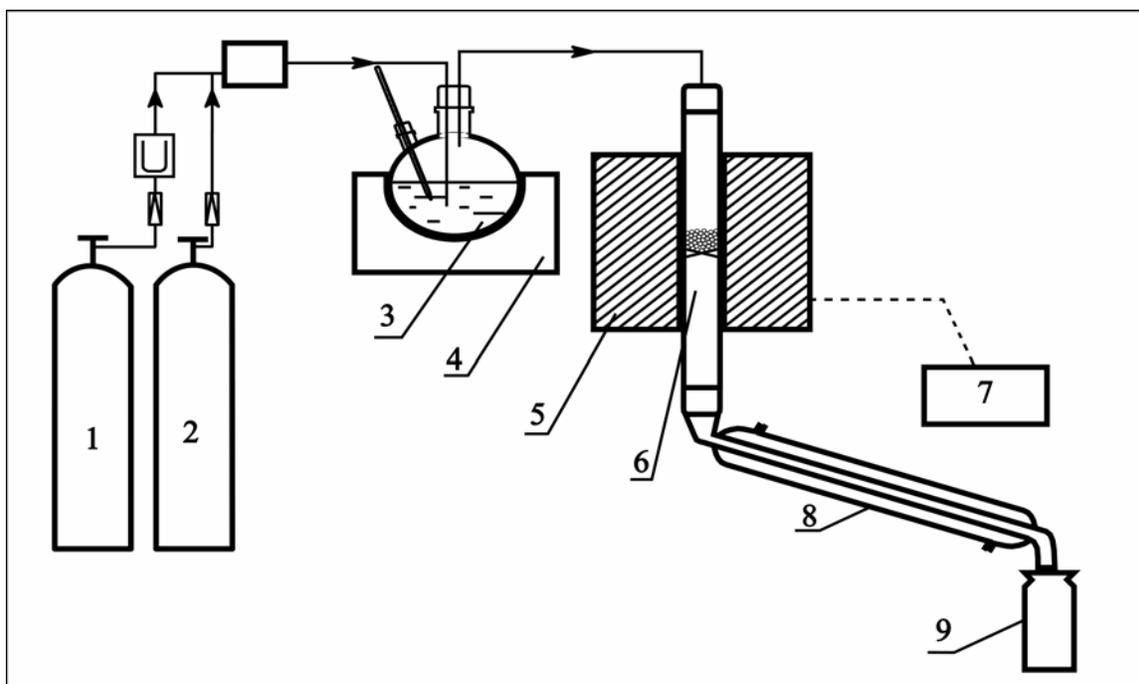


Fig. 3. The diagram of the apparatus used for conducting the reaction of methyl chloride hydrolysis. 1 – CH₃Cl, 2 – N₂, 3 – A flask with H₂O, 4 – A heating jacket, 5 – Furnace, 6 – Reactor, 7 – The temperature control system, 8 – Water cooler, 9 – Products receiver.

RESULTS AND DISCUSSION

The catalysts which were prepared in this manner were introduced into the process of methyl chloride hydrolysis. The catalysts in which aluminium oxide alpha varieties were used, failed to demonstrate any catalytic activities in the investigated process. The catalysts prepared on γ - Al_2O_3 proved active.

With a view to describing the phase content of the received catalysts and examining how their structure is affected by the process of hydrolysis, their samples were scrutinized using the X-Ray diffraction. Diffractions of the samples at an angle range 2 θ from 10° to 90° were made while a diffractometer with $\text{CoK}\alpha$ lamp (Phillips) was employed. The measurement was done every 0.05°. Next the diffractions were analysed and the layout of the reflections against the diffraction patterns included in the Phillips data base, was compared (Fig. 4). It was stated on the basis of the analyses that during the hydrolysis, zinc oxide is rinsed out. That partially caused the decrease of its catalytic activity, yet does not deactivate the catalyst completely.

The dependence of the degree of methyl chloride conversion into methanol on the time (Fig. 5) and temperature (Fig. 6) of the hydrolysis was investigated. We have found that conducting methyl chloride hydrolysis is possible in laboratory conditions. The catalysts containing ZnO and Al_2O_3 demonstrated a catalytic activity in the examined process. A maximum possible degree of methyl chloride conversion was attained (comparable with the one obtained as a result of thermodynamic calculations). At the initial stage of the catalysts' performance ZnO is washed out (the lack of reflection from the zinc oxide phase on the produced catalyst diffractions after the hydrolysis; after about 3 hours of the process initiation, the degree of methyl chloride into methanol conversion is slightly reduced). The catalytic activity of the examined catalysts does not change in a given time (apart from the result mentioned above). The greatest capacity was achieved at the temperature 220–250°C. Above 320°C carbon dioxide can be observed in the products of the reaction (thus there is a decrease of the selectivity

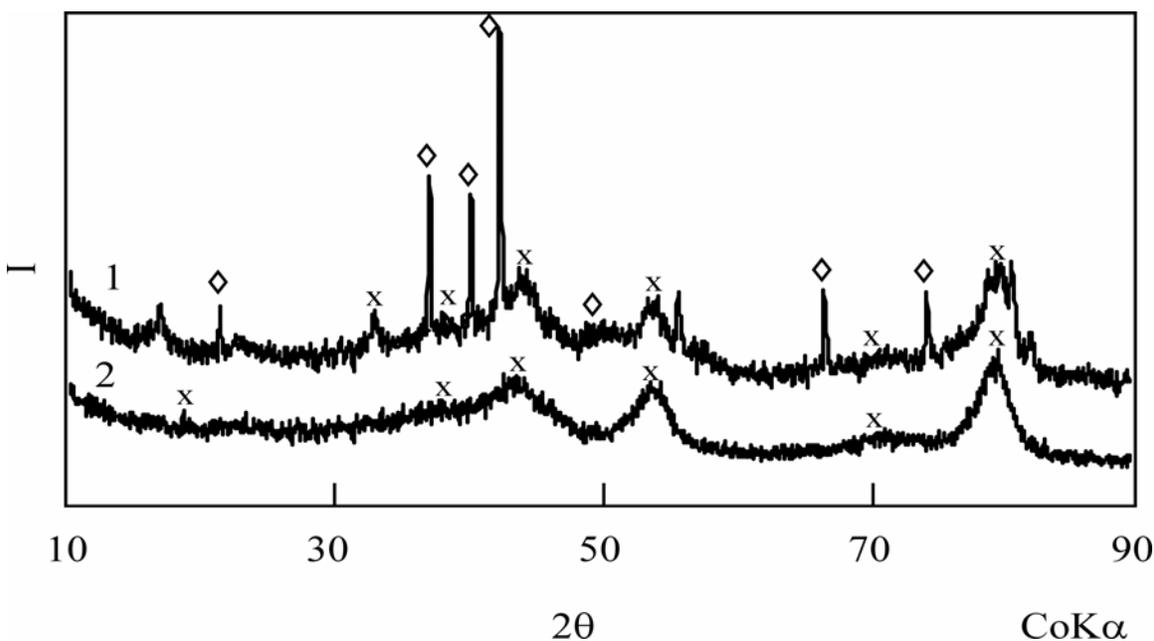


Fig. 4. Comparison of the catalysts diffractions before (1) and after (2) the process of methyl chloride hydrolysis was conducted. ◇ – ZnO , × – Al_2O_3 , I – the number of counting.

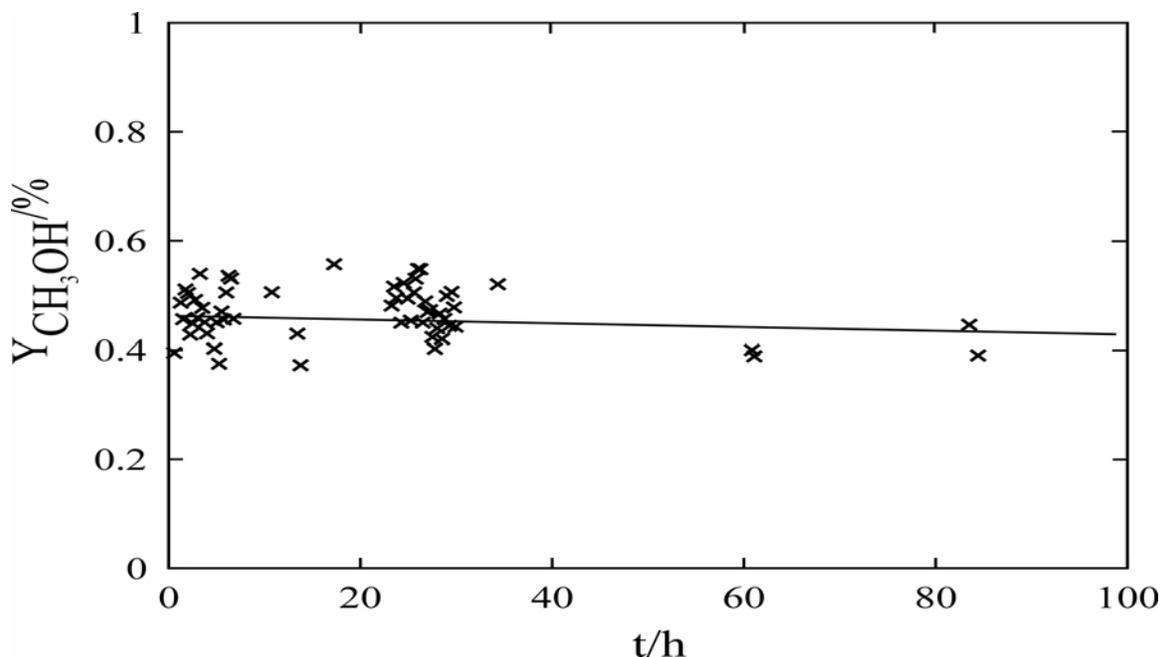


Fig. 5. The dependence of the degree of methyl chloride conversion into methanol on the time of the hydrolysis. The conditions of the conducted process: the temperature – 300°C; the flow ratio CH_3Cl to H_2O – 1:5.

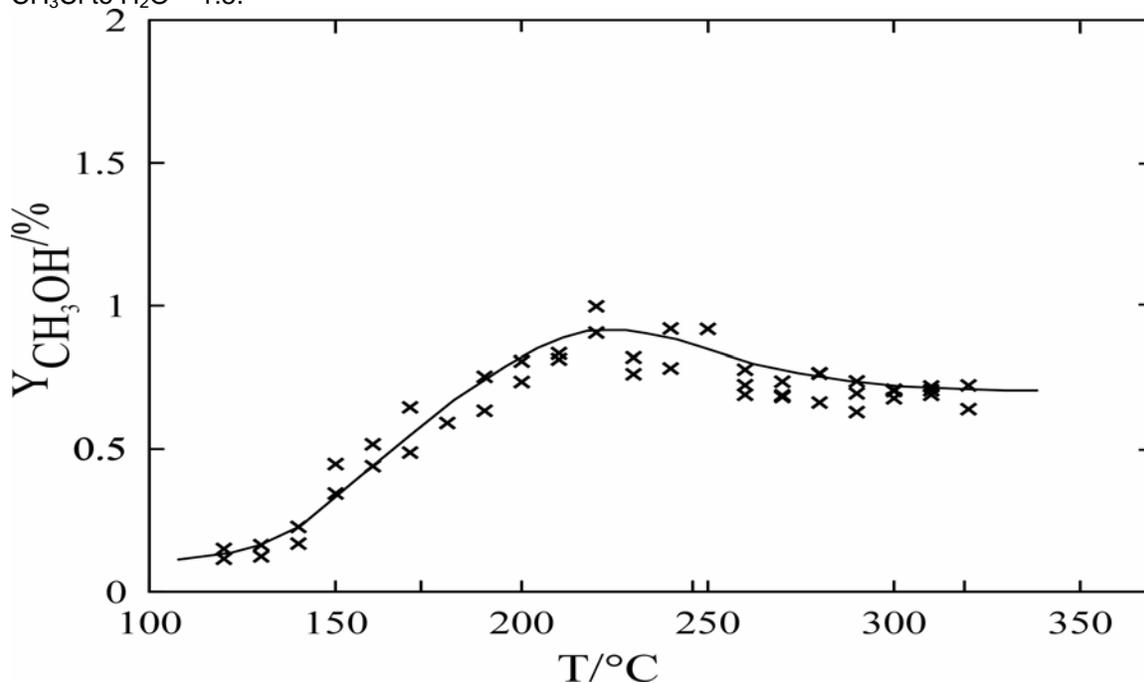


Fig. 6. The dependence of the degree of methyl chloride conversion to methanol on the temperature of the conducted hydrolysis. The conditions of the process being run: the flow ratio of CH_3Cl to H_2O – 1:5.

References

- [1] Taniewski M., *Przem. Chem.*, 74/11, 403 (1995).
- [2] Stauffer, J. E., U.S. Patent 5,185,479, (1993).