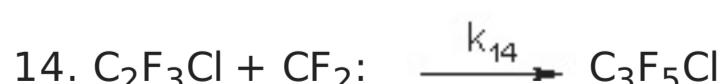
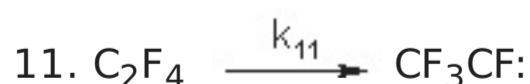
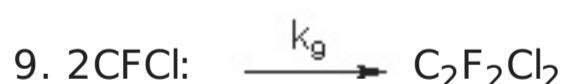
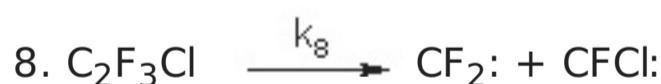
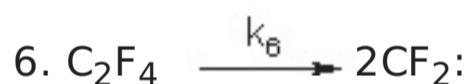
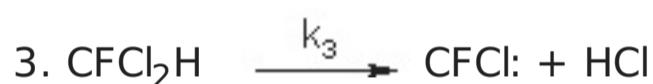
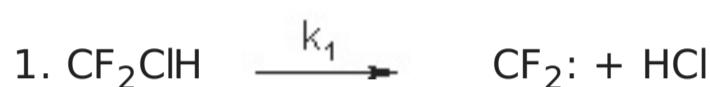
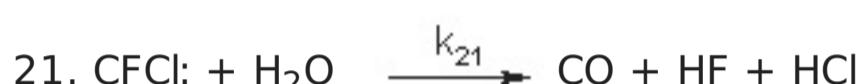
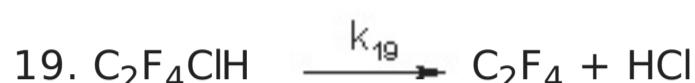
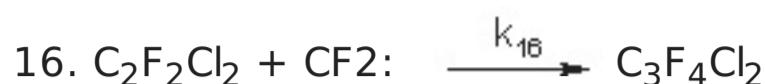
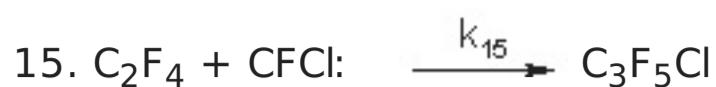


## Study of the process of joint thermal decomposition of chlorodifluoromethane and dichlorofluoromethane. PartII

A.A. Nikolaev, O.V. Rozhdestvenskaya V.G. Barabanov.

In our previous paper [1] we considered the kinetics of dichlorofluoromethane pyrolysis and the mechanism of chlorodifluoromethane and dichlorofluoromethane copyrolysis. Based on the research, the process may be described by following scheme:





For this scheme the kinetic model has been designed and the structural and parametric identification of the model was executed on base of experimental data.

The main task of parametric identification is to find the vector of kinetic constant, the element of which are pre-exponential function and the energies of activation:

$abs(f(p) Y) < Em$ , where

$Y$  - being the generalized vector of the experimental data, i. e. of all the experimental values of molar concentrations related to the present complex reaction;

$f(p)$  - being the generalized vector of the design data for the identified set of kinetic constant  $p$ , the latter being obtained under the same condition as the corresponding elements of the vector  $Y$ ;

$Em$  - being the vector of majorant accuracy estimates of the experiments  $E$ :

$E > sup abs (E)$

The methodology of the parametric identification of the model was based on the method of least squares (MLS). The realization of the MLS for the present model being nonlinear in its parameters was performed on the ground of the Gauss-Newton method [2]. LSODA method designed for the solution of the stable system of differential equation was used as the system's numerical integration method [3].

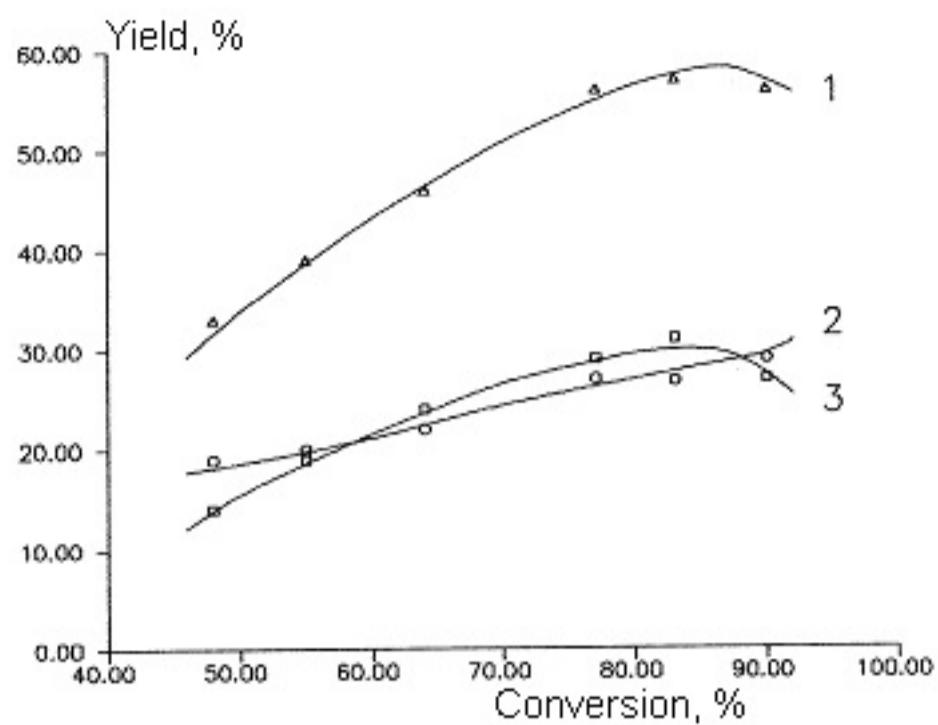
The initial data were the experimental results for copyrolysis of chlorodifluoromethane and dichlorofluoromethane at the temperature of 1008-1073K and residence time of 0,02-0,1c.

The Arrhenius parameters of the rate constants of the analyzed process stages are provided hereby in Table 1.

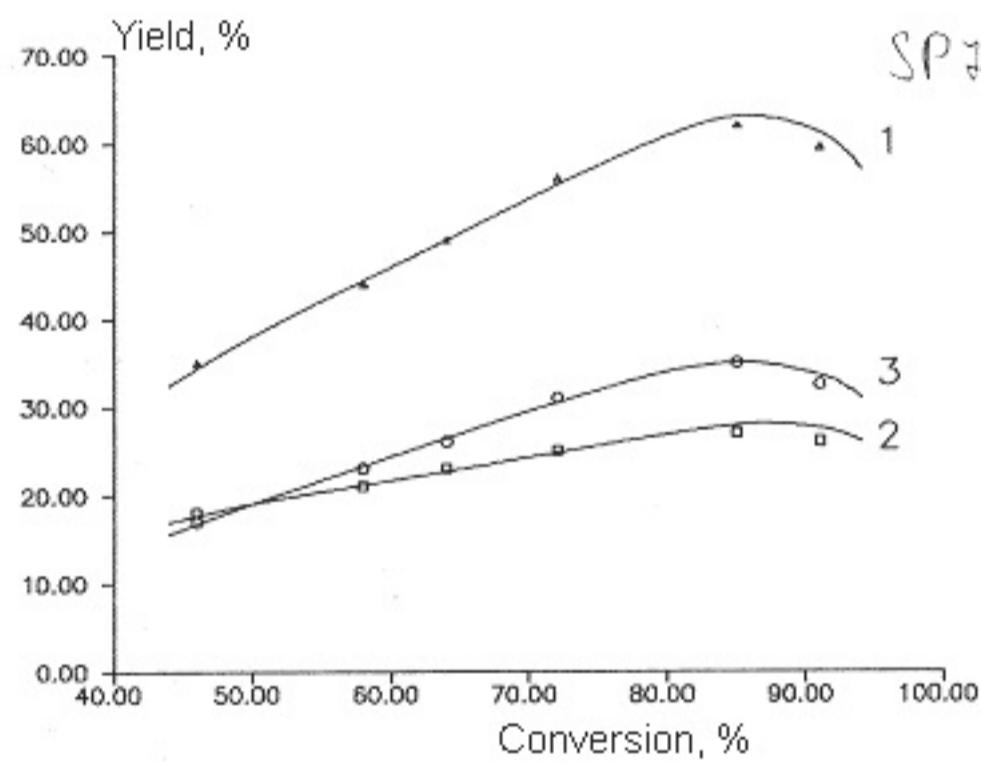
Figures 1-10 provides some of the experimental data (indicated by points ) and designed data (lines), obtained with the use of the aforementioned model. A good correspondence of the design and experimental data confirm the adequacy of the process's model.

Table 1. The rate constants Arrhenius parameters of chlorodifluoromethane and dichlorofluoroethane copyrolysis

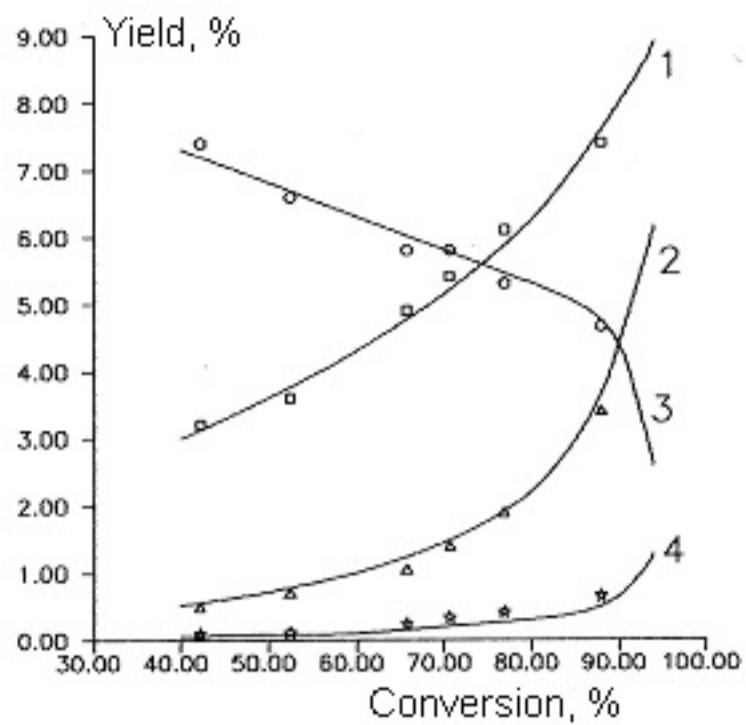
Reaction N	The rate constants Arrhenius meters of reaction		Rate dimention	constants
	lg A	E <sub>act</sub> , kJ/mol		
1	12,4	214,0	sec <sup>-1</sup>	
2	6,8	24,0	l/mol*sec.	
3	13,0	219,0	sec <sup>-1</sup>	
4	8,4	32,0	l/mol*sec.	
5	9,0	4,2	l/mol*sec.	
6	16,7	295,0	sec <sup>-1</sup>	
7	8,5	4,2	l/mol*sec.	
8	13,0	274,0	sec <sup>-1</sup>	
9	7,4	4,2	l/mol*sec.	
10	13,0	285,0	sec <sup>-1</sup>	
11	14,2	135,0	sec <sup>-1</sup>	
12	14,3	6,0	sec <sup>-1</sup>	
13	9,0	8,0	l/mol*sec.	
14	6,5	40,0	l/mol*sec.	
15	6,5	36,0	l/mol*sec.	
16	7,7	24,0	l/mol*sec.	
17	6,5	39,0	l/mol*sec.	
18	7,7	96,0	l/mol*sec.	
19	10,5	193,0	sec <sup>-1</sup>	
20	7,5	46,0	l/mol*sec.	
21	7,5	46,0	l/mol*sec.	



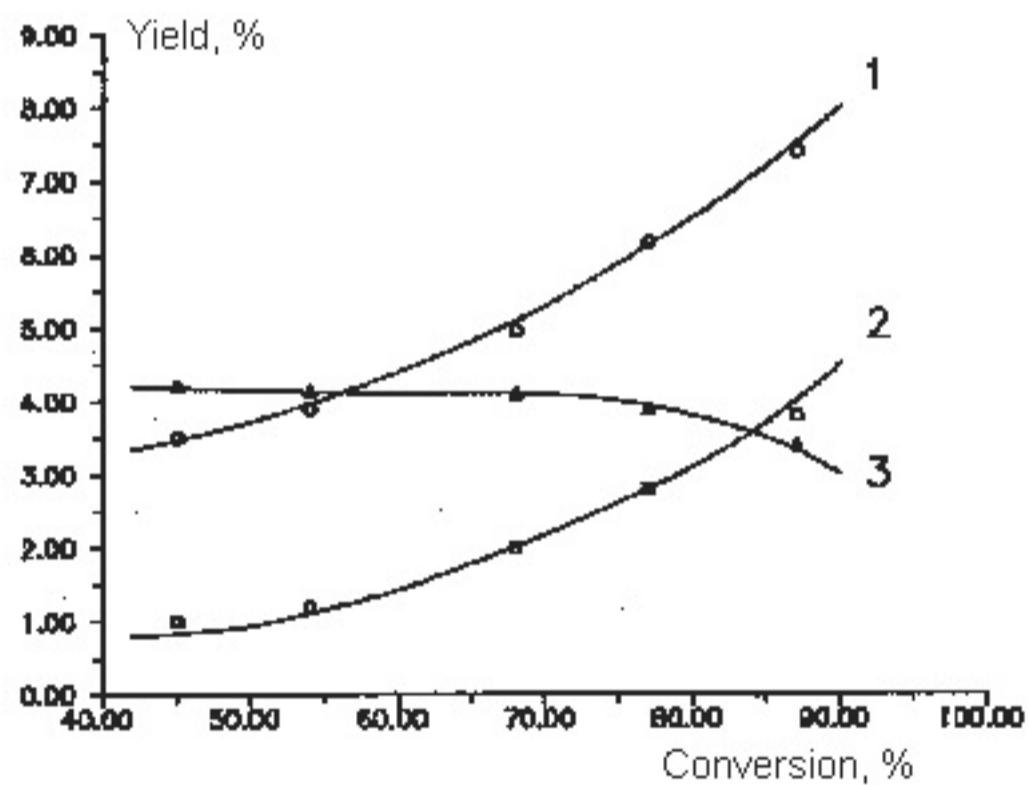
**Fig 1.** Dependence of main products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T = 1008\text{ K}$   
 Molar ratio of  $\text{CF}_2\text{ClH}/\text{CFCl}_2\text{H}$  - 3:1  
 Molar ratio of aqueous vapor/sum of freons - 5:1  
**1**- sum  $\text{C}_2\text{F}_3\text{Cl} + \text{C}_2\text{F}_4$  , **2**-  $\text{C}_2\text{F}_4$ , **3**-  $\text{C}_2\text{F}_3\text{Cl}$



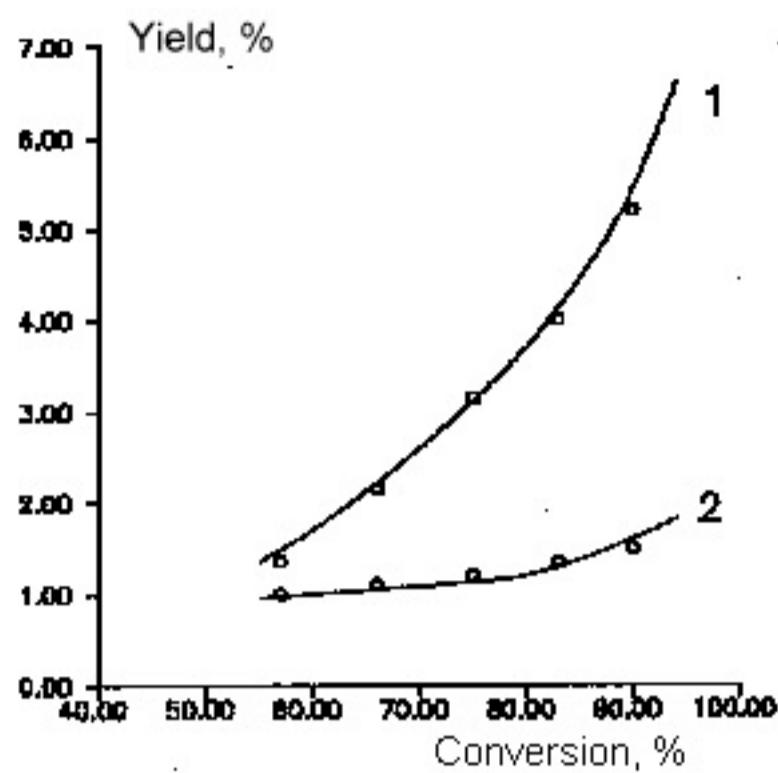
**Fig 2.** Dependence of main products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T = 1053\text{ K}$   
 Molar ratio of  $\text{CF}_2\text{ClH}/\text{CFCl}_2\text{H}$  - 2:1  
 Molar ratio of aqueous vapor/sum of freons - 5:1  
**1**- sum  $\text{C}_2\text{F}_3\text{Cl} + \text{C}_2\text{F}_4$  , **2**-  $\text{C}_2\text{F}_4$ , **3**-  $\text{C}_2\text{F}_3\text{Cl}$



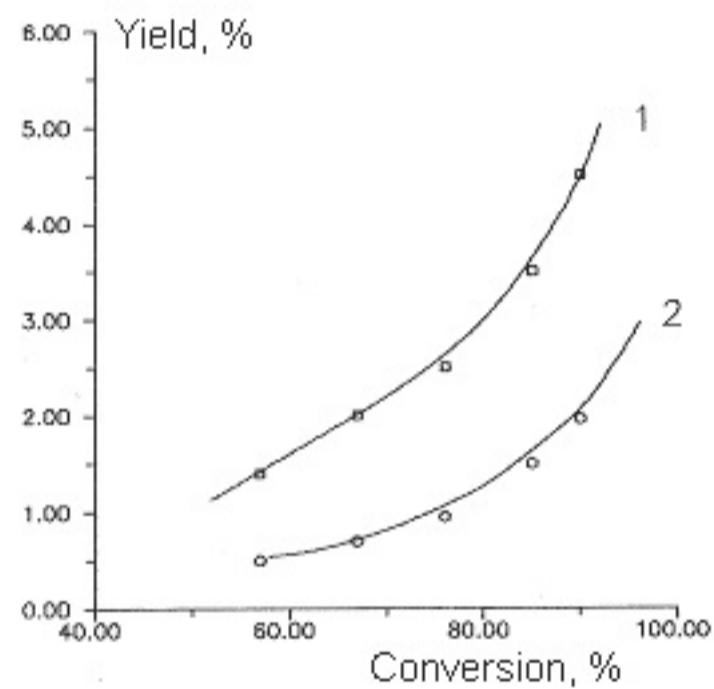
**Fig 3.** Dependence of by- products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T=1053\text{ K}$   
 Molar ratio of  $CF_2ClH/NFCI_2H$  - 3:1  
 Molar ratio of aqueous vapor/sum of freons - 5:1  
**1**-  $CO$  , **2**-  $C_3F_6$ , **3**-  $C_2F_2Cl_2$ , **4**-  $C_2F_4ClH$



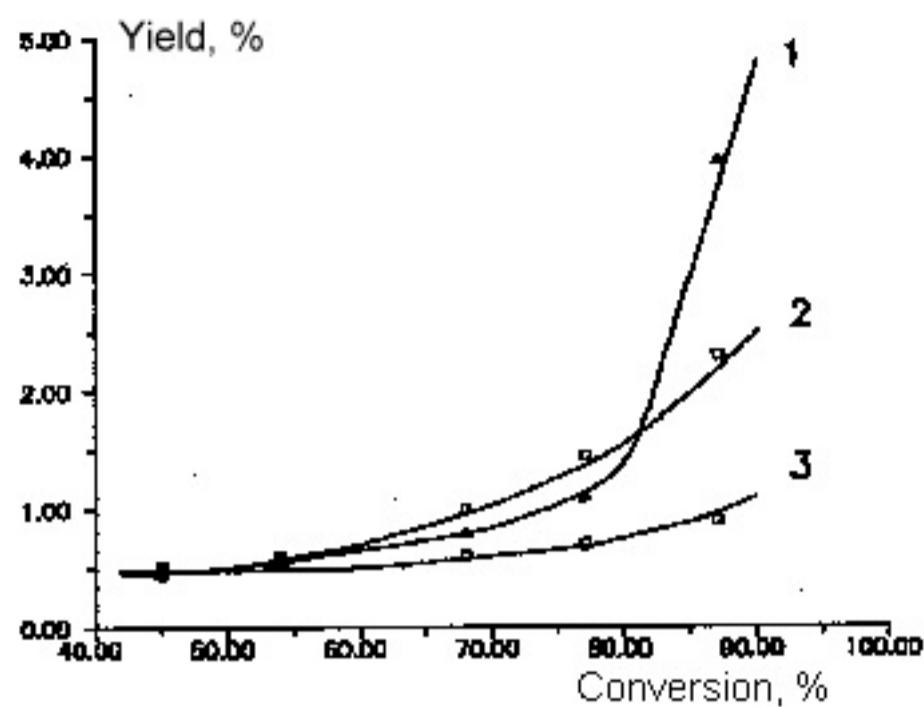
**Fig 4.** Dependence of by- products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T=1008\text{ K}$   
 Molar ratio of  $CF_2ClH/CFCI_2H$  - 3:1  
 Molar ratio of aqueous vapor/sum of freons - 5:1  
**1**-  $CO$  , **2**-  $C_3F_6$ , **3**-  $C_2F_2Cl_2$



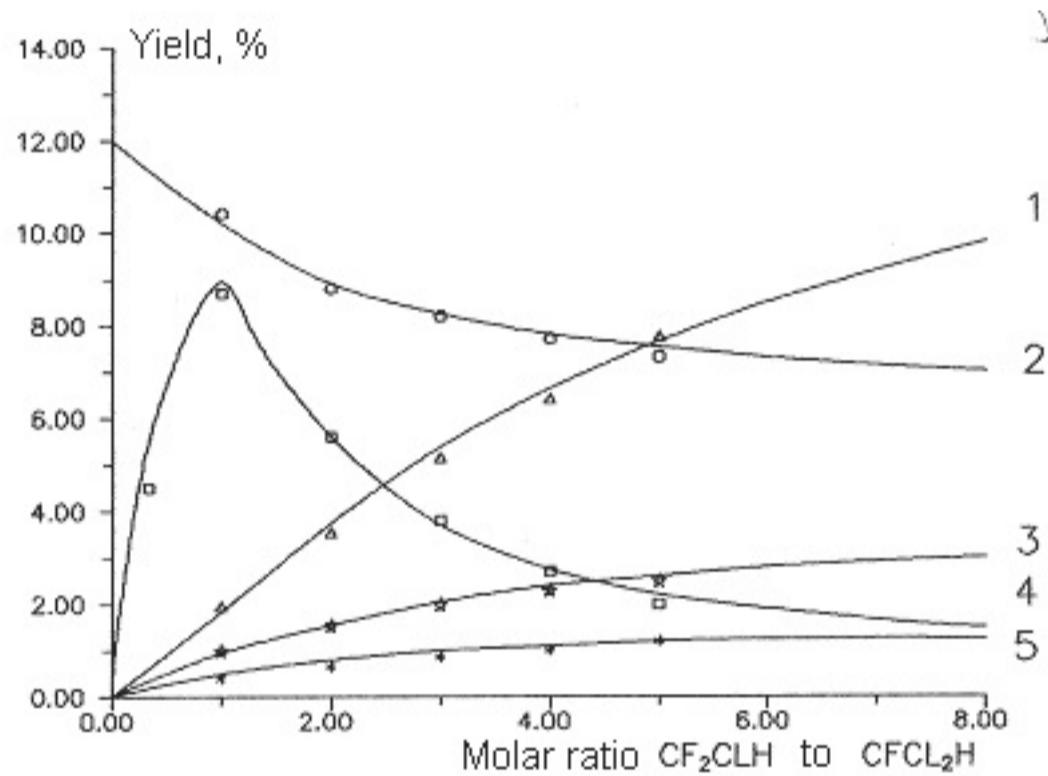
**Fig 5.** Dependence of by- products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T=1053\text{ K}$   
 Molar ratio of  $CF_2ClH/ CFCl_2H$  - 2:1  
 Molar ratio of aqueous vapor/sum of freons - 5:1  
**1**-  $C_3F_4Cl_2$  , **2**-  $C_3F_5Cl$



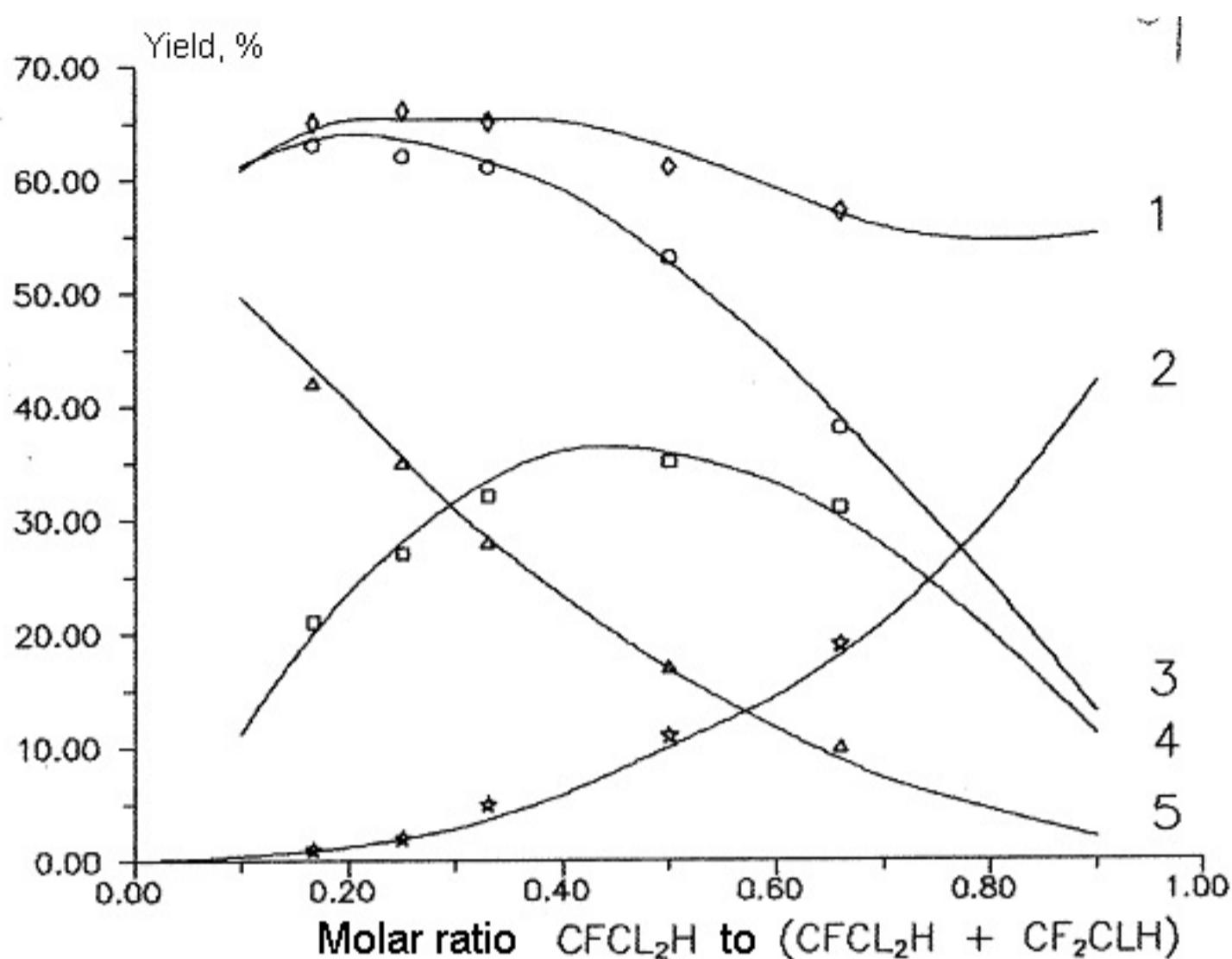
**Fig 6.** Dependence of by- products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T=1008\text{ K}$   
 Molar ratio of aqueous vapor/sum of freons - 5:1



**Fig 7.** Dependence of by- products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T=1023\text{ K}$   
 Molar ratio of  $\text{CF}_2\text{ClH}/\text{CFCl}_2\text{H}$  - 3:1  
 Molar ratio of aqueous vapor/sum of freons - 5:1  
**1**-  $\text{C}_3\text{F}_6$  , **2**-  $\text{C}_3\text{F}_5\text{Cl}$ , **3**-  $\text{C}_2\text{F}_4\text{ClH}$



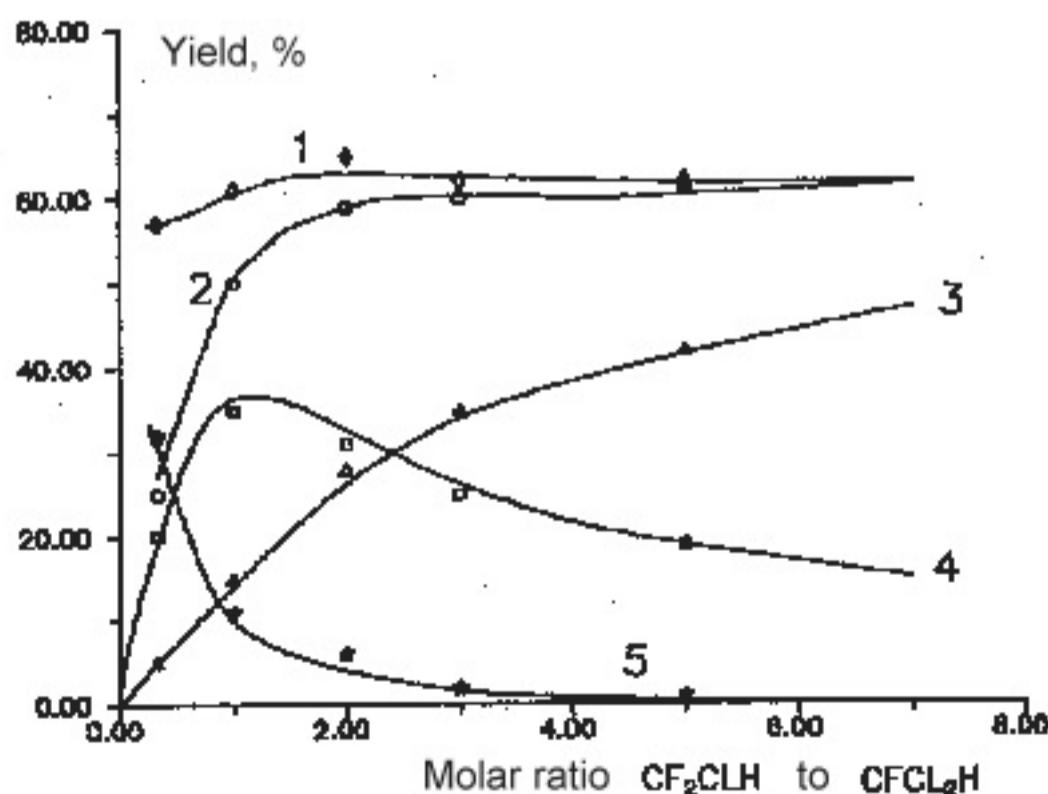
**Fig 8.** Dependence of by- products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from initial product conversion.  $T=1023\text{ K}$   
 Molar ratio of  $\text{CF}_2\text{ClH}/\text{CFCl}_2\text{H}$  - 2:1  
 Molar ratio of aqueous vapor/sum of freons - 5:1. Conversion 87%  
**1**-  $\text{C}_3\text{F}_6$  , **2**-  $\text{CO}$ , **3**-  $\text{C}_3\text{F}_5\text{Cl}$ , **4**-  $\text{C}_3\text{F}_4\text{Cl}_2$ , **5**-  $\text{C}_2\text{F}_4\text{ClH}$



**Fig 9.** Dependence of main products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from molar ratio chlorodifluoromethane to sum of chlorodifluoromethane and dichlorofluoromethane.  $T = 1023\text{ K}$   
Conversion 87%.

Molar ratio of aqueous vapor/sum of freons - 5:1

**1**- sum  $\text{C}_2\text{F}_3\text{Cl}, \text{C}_2\text{F}_4$  and  $\text{C}_2\text{F}_2\text{Cl}_2$ , **2**- sum  $\text{C}_2\text{F}_3\text{Cl}$  and  $\text{C}_2\text{F}_4$ , **3**-  $\text{C}_2\text{F}_4$ , **4** -  $\text{C}_2\text{F}_3\text{Cl}$ , **5**-  $\text{C}_2\text{F}_2\text{Cl}_2$



**Fig 10.** Dependence of main products yields of chlorodifluoromethane and dichlorofluoromethane copyrolysis from molar ratio chlorodifluoromethane to dichlorofluoromethane.  $T = 1023\text{ K}$   
Conversion 87%.

*Molar ratio of aqueous vapor/sum of freons - 5:1*

**1**- sum  $C_2F_3Cl, C_2F_4$  and  $C_2F_2Cl_2$  , **2**- sum  $C_2F_3Cl$  and  $C_2F_4$  , **3**-  $C_2F_4$  , **4** -  $C_2F_3Cl$  , **5**-  $C_2F_2Cl_2$

Some general conclusion can be drawn based on the calculation results:

1. Yield of chlorotrifluoroethylene is 95% under conversion of 85-87%
2. Maximum yield of basic monomer sum is under conversion of 83-87% as well
3. The molar ratio if chlorodifluoromethane to dichlorofluoromethane have main influence on yield of chlorotrifluoroethylene and other products
4. Maximum selectivity of chlorotrifluoroethylene is 42,5 %, it reaches under this ratio is about 1,2 ( $x_0=1,2$ )
5. It is possible to produce chlorotrifluoroethylene, tetrafluoroethylene and 1,2-dichlorodifluoroethylene over a wide range of concentration in pyrolyzed product

The experiments on joint thermal decomposition in the presence of water vapor were carried out in a continuous reactor made of nickel-chromium corrosion-proof alloy , 4mm diameter, 500mm length of the working zone. To avoid cracking of protective oxide film on the reactor surface the heating of the latter was carried out linearly at a rate below 100K/hour. The pyrolysis was held within a temperature range of 973-1173K at a mole ratio of vapor/ freon 10:1-1.5:1.

The analysis of gas mixtures after purification from acid admixtures was made on a "Tsvet-100M" chromatograph with using a flame ionization detector and a heat conductivity detector (helium as a gas carrier, 3m column length, 2mm column diameter, 293-323K column temperature, tricrezylphosphate ( 15% on silochrome-80)). The identification of the pyrolysis products was made by a spectrometry method on a HP-5995 instrument ( 70eV energy of ionizing electrons, 553K separator temperature, 423 temperature of the ion source)

## **Literature**

1. Nikolaev A.A., Barabanov V.G. Study of the process of joint thermal decomposition of chlorodifluoromethane and dichlorofluoromethane. // Fluorine notes - 2002-Vol.4.
2. Gill P.E., Murroy W., Wright M.H. Practical Optimization. - London, New-York,1981.-371 p.
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