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Oxidation of Hexafluoropropylene with Oxygen to Hexafluoropropylene Oxide

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Abstract:

A method for pressure oxidation of hexafluoropropylene (HFP) with oxygen to hexafluoropropylene oxide (HFPO) has been presented. The oxidation was carried out in a periodically operated reactor. The influence of temperature, the nature of the solvent, and the molar ratio of HFP/O_2 on the course of oxidation was investigated during the preliminary studies. The magnitudes describing the process were the conversion of HFP, the selectivity of transformation to HFPO in relation to HFP consumed, and the yield of HFPO in relation to the initial amount of HFP. The optimisation of the technological parameters of oxidation, temperature, HFP/O_2 molar ratio, and the reaction time was performed by the application of a statistical experimental design method. The function describing the process was the yield of HFPO.

1. Introduction

Hexafluoropropylene oxide (HFPO) is a valuable monomer which is subjected to oligomerization in order to prepare the intermediates for the syntheses of highly effective nonionic, ionic, and amphoteric surface active agents. It was found that even small amounts of these compounds cause a significant decrease in the surface tension of water, and for this reason they, among others, are used as the components of the extinguishing agents.[1] The HFPO oligomers are also used as inert solvents and hydraulic fluids.[2] Higher oligomers are important as lubricating oils with regard to high thermostability and chemical resistance.[3,4]

Up to date, HFPO was produced by oxidation with sodium hypochlorite,[5] with oxygen under pressure[6] and with the pressureless method,[4] by means of hydrogen peroxide,[7] and by the electrochemical method.[1] HFPO can be obtained with high efficiency by the epoxidation of HFP with hypochlorite using the method of a phase-transfer catalyst in the system of two phases, water and an organic solvent, in the presence of an inorganic base. Quaternary ammonium salts, quaternary phosphonium salts, and quaternary arsenium salts, and the lipophilic reagents complexed with a sodium cation were used as the phase-transfer catalysts. However, this method is only used for preparative purposes and on a small scale.[5,8]

The oxidation of HFP with oxygen in the gaseous phase in the presence of catalysts such as barium compounds, activated silicagels, metals (Ag, V), supported silicagel, or diatomaceous earth was also investigated.[4,9]

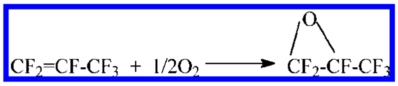
The greatest expectations to realize the commercial production of HFPO are associated with the pressure oxidation of HFP with oxygen in the liquid phase.[10,11]

The investigations on the preparation of this compound by the method of catalyst-free oxidation using hydrogen peroxide in the medium of a water-soluble polar solvent such as acetone or acetonitrile are still on-going.[12]

The electrochemical oxidation was also the subject of interest.[1] An aqueous solution of acetonitrile or its mixture with acetic acid and a compound to improve the conductivity ($NaClO_4$) was used as an electrolyte.

However, the above-mentioned methods created a problem associated with the separation of pure HFPO from the postreactive mixture. This resulted from the similar boiling points of HFP and HFPO. The problem of HFPO purification was solved by conducting the oxidation with oxygen under supercritical carbon dioxide.[13] As a result of irradiation of the reactor by UV light, the produced HFPO immediately underwent polymerization, and perfluoropolyether was formed.

The main reaction of oxidation of hexafluoropropylene with oxygen both in the liquid phase as well as in the gaseous phase can be written as follows:



$$CF_2{=}CF{-}CF_3 + 1/2O_2 \longrightarrow CF_2{-}CF{-}CF_3 \ (\text{epoxide, O bridging } CF_2 \text{ and } CF)$$

According to the assumed reaction mechanism, after the addition of oxygen to the double bond, a biradical is formed with electrons on the oxygen and carbon. Its decomposition and rearrangement as well as the decomposition of HFPO cause the formation of several byproducts such as trifluoroacetic acid fluoride, carbonyl fluoride, 1-trifluoromethyl-perfluorocyclopropane, perfluoroethylene, and perfluorocyclopropane. Temporarily, carbine is also formed. This can be illustrated by the following chemical equations.[14]

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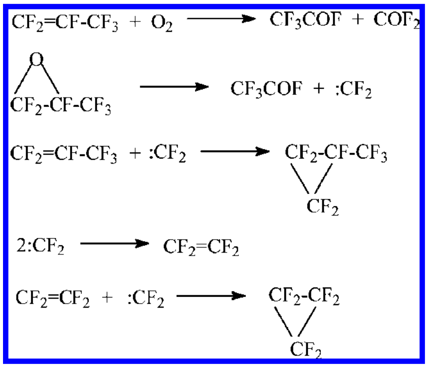

The objective of this work was to investigate the influence of the changes of technological parameters on the course of direct oxidation of HFP with oxygen in the liquid phase under pressure and to establish the most advantageous parameters of process operation.

2. Experimental Section

2.1. Raw Materials. HFP was prepared by the debromination of 1,2-dibromohexafluoropropane. Oxygen was obtained from Messer-Poland. Carbon tetrachloride, methylene chloride, and 1,2,2-trichloro-1,1,2-trifluoroethane (CFC-113) were obtained from POCh, Poland.

2.2. Oxidation Procedure. The oxidation was carried out in the liquid phase in a steel autoclave made by Lampart (Hungary) of 500 cm^3 capacity. The autoclave content was mixed via the swinging movements of a horizontally assembled cradle. This cradle was electrically heated. The autoclave cover was equipped with two metering valves, a manometer, a safety valve, and a sensor for measurement of temperature within the autoclave and on its external wall. The autoclave was purged with nitrogen, and a volumetrically determined amount of solvent was introduced into the autoclave. After closing the cover, the autoclave was cooled in the cryostat to the temperature of about −50 °C. Subsequently, the air was removed from the autoclave with the oil vacuum pump. From a gas cylinder located on the balance, a proper amount of HFP was distilled off to the autoclave through the dosing valve. This amount of HFP was determined by the weight. The autoclave was taken out of the cryostat and was left to achieve ambient temperature. A measured amount of oxygen was introduced using a special pressure feeder. For this purpose a container for oxygen (4, Figure 1) was filled up with carbon tetrachloride.

The oxygen supplied from gas cylinder 3 was introduced into volumetrically calibrated container 4. This container was previously filled up with carbon tetrachloride. After opening valves 8 and 14, container 4 was filled up with oxygen. Simultaneously after opening valve 9, the flow of carbon tetrachloride took place from container 4 to container 5, which was previously filled up with nitrogen under atmospheric pressure. The amount of oxygen in container 4 under the atmospheric pressure was read out on level gauge 7, after closing valves 9 and 14 and opening valve 11. The total amount of oxygen was introduced in three portions, at equal time intervals. The atmospheric pressure and overpressure were measured using mercury-filled manometer 6. After the equalization of pressure in oxygen container 4 with atmospheric pressure, an overpressure was generated in the nitrogen

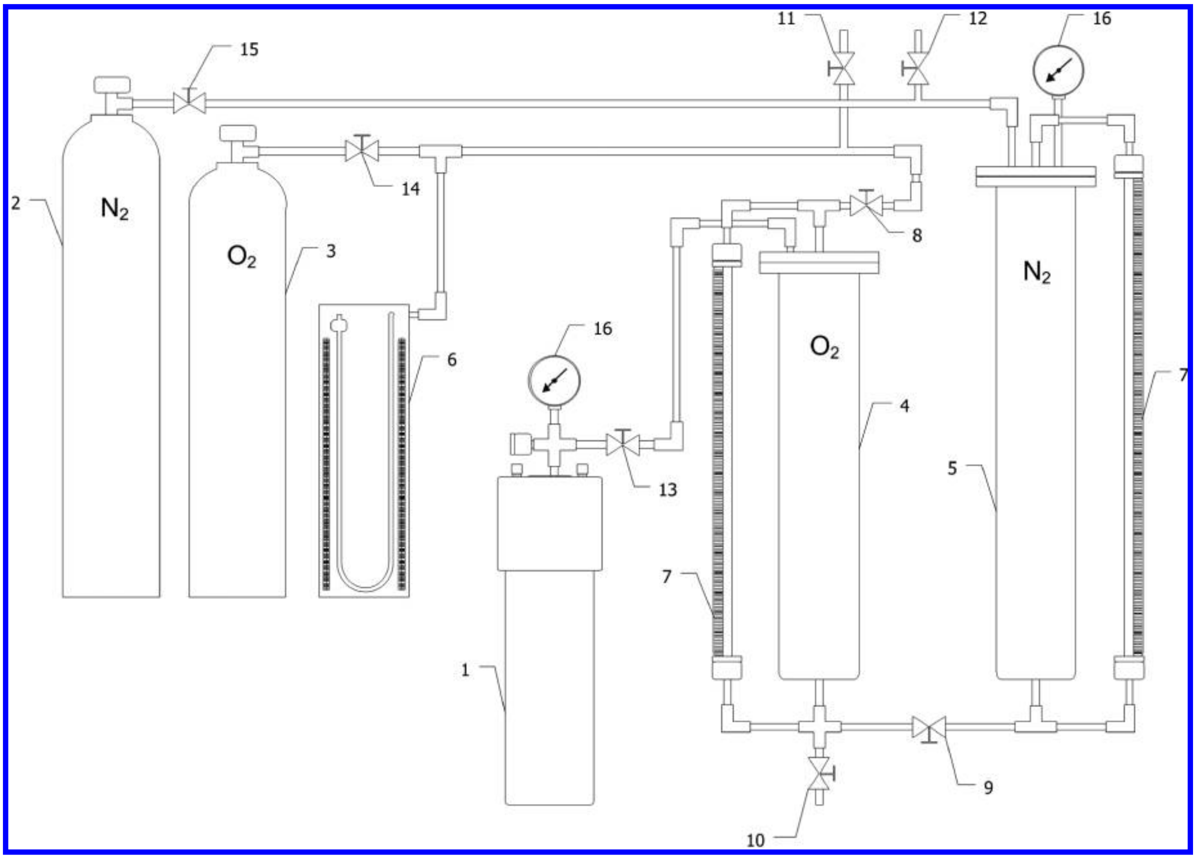

Figure 1. **Scheme of the equipment for HFP oxidation: 1-autoclave, 2-nitrogen cylinder, 3-oxygen cylinder, 4-oxygen pressure container, 5-nitrogen pressure container, 6-mercury manometer, 7-level gauge, 9−15-valves, 16-manometer.**

container 5 that exceeded the pressure in the autoclave 1 by about 3 MPa. Nitrogen from cylinder 2 was utilized for this purpose. Under this overpressure oxygen was dosed to the autoclave 1. The oxidation was carried out using an initially established temperature for the determined HFP/O_2 molar ratio at the fixed residence time.

The mass balance was performed for each synthesis after completing the reaction. The following magnitudes describe the process determined: conversion of HFP (C_{HFP}), selectivity of transformation to HFPO (S_{HFPO}), and the yield of HFPO (Y_{HFPO}). They are calculated according to the following equations:

$$C_{HFP} = \frac{\text{amount of HFP consumed (mol)}}{\text{initial amount of HFP (mol)}} \cdot 100\%$$

$$S_{HFPO} = \frac{\text{amount of HFPO obtained (mol)}}{\text{amount of HFP consumed (mol)}} \cdot 100\%$$

$$Y_{HFPO} = \frac{\text{amount of HFPO obtained (mol)}}{\text{initial amount of HFP (mol)}} \cdot 100\%$$

2.3. Separation of HFPO. Due to the similar volatilities of HFP (bp −29.4 °C) and HFPO (bp −27.4 °C) these compounds cannot be separated by the distillation methods. With regard to close boiling points, another method for the separation of oxidation products has been developed. The reaction products in the gaseous form were directed to a scrubber sprinkled with a 5 wt % aqueous solution of sodium hydroxide. During the absorption there proceeded the hydrolysis of trifluoroacetic acid fluoride and carbonyl fluoride, followed by the neutralization of the products. A formed eluate was analyzed for the content of fluoride ion. Gas that did not undergo absorption was directed to the photobromination. As a result of HFP photobromination there was formed 1,2-dibromohexafluoropropane that remained in the reactor as a compound having a higher boiling point, whereas the gases leaving the reactor were subjected to the treatment in the scrubber with an aqueous solution containing 5 wt % of NaOH and 10 wt % of $NaHSO_3$. The treated gases were condensed in the freezer and cooled to a temperature of −40 °C. The product after the condensation contained at least 99.8 wt % of HFPO. The analyses were carried out with a GC method according to the procedure presented below.

2.4. Analytical Methods. The fluoride ions were determined potentiometrically in the eluate after the absorption of gaseous products of oxidation. A Radelkis OP-108 apparatus with a fluoride electrode Orion 9403 was used for measurements.

The quantitative analyses of HFPO and the gaseous products of HFP oxidation were performed chromatographically on a Chrom 5 apparatus equipped with a thermal conductivity detector (TCD). The concentrations of the following compounds in this gas were determined: HFP, HFPO, perfluoroethylene, perfluorocyclopropane, trifluoroacetic acid fluoride. A stainless steel column 2.5 m × 0.4 cm packed with silica gel ASTM-E 80/100 mesh was used. The remaining conditions of detection were as follows: carrier gas $H_2 = 20$ cm^3/min, oven temperature = 150 °C, injection sample = 100 μL.

Table 1. **Influence of temperature on the conversion of HFP, selectivity of transformation to HFPO, and the yield of HFPO**[a]

reaction temperature °C	temperature of the autoclave wall (±5 °C)	C_{HFP} mol %	S_{HFPO} mol %	Y_{HFPO} mol %
130	150	12	83	10
140	160	32	81	26
145	165	57	77	44
150	170	81	68	55
155	175	99	62	62
160	180	99	59	58
170	185	99	50	49

[a] Constant parameters: HFP = 0.766 mol; total O_2 = 9 dm^3 - 3 dm^3 of O_2 was introduced 3 times after 0, 60, 120 min; molar ratio HFP/O_2 = 1.91:1; solvent - carbon tetrachloride 385 cm^3; reaction time 3 h. C_{HFP} - conversion, S_{HFPO} - selectivity, Y_{HFPO} - yield.

The liquid products of photobromination were analysed quantitatively with the same apparatus under the following conditions: detector FID, stainless steel packed column (3 m × 0.4 cm) with 3% silicone oil SE-30 on Chromosorb G 80/100 mesh. The column temperature was programmed isothermally at 60 °C for 4 min, followed by an increase at a rate of 8 °C/min to 170 °C, isothermally 170 °C for 10 min, injection sample 0.1 μL.

The mass balance of experiments was performed on the basis of these analyses.

3. Results and Discussion

3.1. Preliminary Investigations. The influences of temperature, the nature of the solvent, and the molar ratio of HFP to oxygen on the HFP conversion, the selectivity of transformation to HFPO, and the yield of HFPO have been determined during the preliminary investigations. The results of studies on the effect of temperature are presented in Table 1.

The results presented in Table 1 indicate that an increase in the reaction temperature in the range of 130−170 °C increases the conversion of HFP from 12 mol % at a temperature 130 °C to practically the complete conversion in the temperature range 155−170 °C. An inverse tendency of the changes in the regarded temperature range takes place in the case of the selectivity of conversion to HFPO. The highest selectivities at a level of 80 mol % are achieved in the range of temperatures 130−140 °C; subsequently, the selectivities decrease to 50 mol % at a temperature of 170 °C. Hence, the highest yield is a choice between a high selectivity of transformation to HFPO and a high conversion of HFP. It was found that, under the specified technological conditions, a high selectivity of transformation to HFPO in relation to HFP consumed corresponds to a lower conversion of HFP and vice versa.

The studies on the effect of the nature of the solvent (Table 2) under the remaining conditions being comparable indicate that the highest conversion of HFP, selectivity of transformation to HFPO, and the yield of HFPO is achieved with carbon tetrachloride.

Table 3 presents data on the influence of the molar ratio of HFP to oxygen on the selectivity and conversion of HFP. It results from these data that high selectivity of transformation to HFPO in relation to HFP consumed can be obtained in case

Table 2. **Influence of solvent on the conversion of HFP, selectivity of transformation to HFPO, and the yield of HFPO**[a]

solvent[b]	cm^3	temperature °C	HFP mol	oxygen dm^3	C_{HFP} mol %	S_{HFPO} mol %	Y_{HFPO} mol %
CCl_4	380	150	0.766	9	85	64	55
CH_2Cl_2	380	155	0.766	9	64	72	46
CFC-113	380	152	0.766	9	76	58	44

[a] Constant parameters: molar ratio $HFP/O_2 = 1.91:1$, 3 dm^3 of oxygen was introduced three times: after 0, 60, and 120 min. [b] The amount of solvent was constant in all experiments.

Table 3. **Influence of molar ratio HFP/O_2 on the conversion of HFP, selectivity of transformation to HFPO, and the yield of HFPO**[a]

HFP mol	oxygen dm^3	HFP/O_2 mol/mol	C_{HFP} mol %	S_{HFPO} mol %	Y_{HFPO} mol %
0.766	14	0.62:1	99	32	32
0.766	11	0.78:1	99	36	36
0.766	9	0.96:1	86	62	54
0.766	7	1.24:1	82	65	53
0.766	5	1.74:1	62	72	45

[a] Constant parameters: temperature 155°C, carbon tetrachloride 385 cm^3, reaction time 3 h, oxygen was introduced in 3 portions, after 0, 60, 120 min.

Table 4. **Real and normalized values of the technological parameters**

level	normalized factor X_i	real factors temperature, x_1 °C	 HFP/O_2, x_2 mol/mol	 reaction time, x_3 h
lower	−1.682	150	0.4	1
basic	0	165	1.7	3
higher	1.682	180	3.0	5

The design matrix utilized for the experiment realization, the experimentally obtained values of HFPO yields, and the results of statistical analysis were compiled in Table 5.

Table 5. **Design matrix, the yield of HFPO, and results of statistical analysis**[a]

	X_1 temperature	X_2 HFP/O_2	X_3 reaction time	Y_{HFPO} mol %
1	−1.682	−1	−1	16
2	+1.682	−1	−1	18
3	−1.682	+1	−1	25
4	+1.682	+1	−1	28
5	−1.682	−1	+1	29
6	+1.682	−1	+1	28
7	−1.682	+1	+1	35
8	+1.682	+1	+1	32
9	0	0	0	44
10	0	0	0	44
11	0	0	0	43

[a] $R^2 = 99.83$, $S^2{}_{adeq} = 1.8218$, $S^2{}_{repeat} = 18200$, $f_{repeat} = 2$, $F = 1.000989$, $\Delta z_{max} = 1.35$.

of excessive HFP in relation to oxygen. However, this causes a decrease of the conversion of HFP as well as the yield of the HFPO.

3.2. Optimization of Oxidation Process of HFP. The following ranges of changes in the parameters describing the oxidation process of HFP were established on the basis of the preliminary studies: temperature 150−180 °C, molar ratio of HFP/O_2 0.4−3.0 mol/mol, and the reaction time 1−5 h. The amount of carbon tetrachloride used as a solvent was equal to 400 cm^3 in all the experiments. The optimization was performed for the function of HFPO yield. The optimization of the technological parameters of HFP oxidation was performed according to the mathematical method of experiment design.[15,16] The plan was realized for three technological parameters (input variables x_1−x_3): x_1 = temperature, x_2 = molar ratio of HFP/O_2, x_3 = the reaction time and for two levels. The number of possible combinations for the above-mentioned system amounted to $2^3 = 8$. The total number of experiments amounted to 11, whereas there were 3 in the plan centre. The real and normalized values of the technological parameters (input variables) at levels resulting from experimental design are presented in Table 4.

Experimental design and the calculation results were performed by computer, applying the program Cadex: Esdet 2.2.

The influence of independent parameters: temperature, HFP/O_2 molar ratio, reaction time on the response function, HFPO yield, was presented in the form of second-order polynomial (regression equations) containing the linear and square components and the double products (interactions):

$$Y_{HFPO} = -893.579 + 10.834x_1 + 12.12x_2 + 17.93x_3 + 0.00705x_1x_2 - 0.0437x_1x_3 - 0.361x_2x_3 - 0.0325x_1^2 - 2.797x_2^2 - 2.31x_3^2$$

The coefficients of the regression equation for the normalized input variables (parameters) were determined by the least-squares method with the application of matrix calculations. After the determination of the function approximating the experimental results, a verification of the adequacy of the equation based on the Fisher−Snedecor test on significance level $\alpha = 0.05$ was proved as $F < F(\alpha)$. This function is adequate because it has a lower value than that read out from $F(\alpha)$ tables. The values of R^2, the coefficient of multiple correlation, $S^2{}_{adeq}$, the variance of adequacy, $S^2{}_{repeat}$, the variance of inaccuracy, f_{repeat}, the freedom degrees number of variance of inaccuracy, F, the value of the quotient of the test of Fisher−Snedecor, and Δz_{max}, the maximum error of approximation, are given in Table 5.

The obtained equation of HFPO yield is adequate and has a high value of the multiple correlation coefficient $R^2 = 99.83$.

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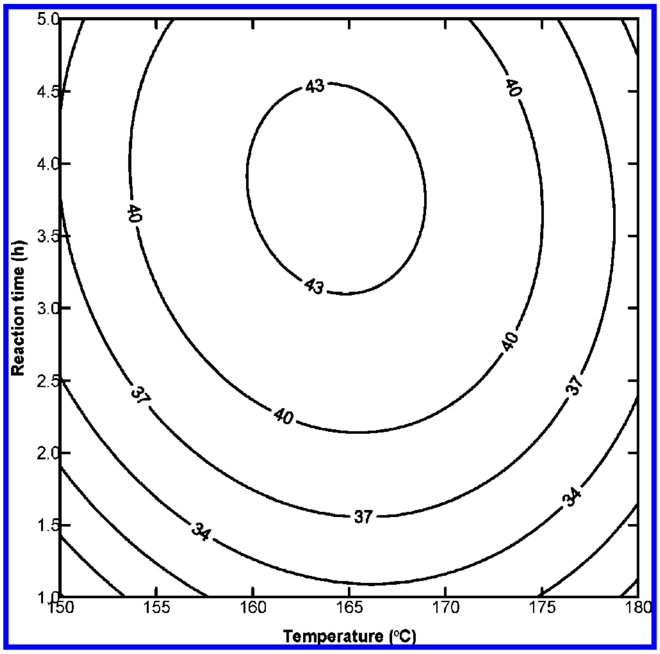

Figure 2. **Influence of temperature and reaction time on the yield of HFPO, $HFP/O_2 = 1.7:1$.**

The yields calculated from this equation correlate well with values obtained experimentally for the particular points of rotatable uniform design.

The course of variations in the function of HFPO yield (Y_{HFPO}) at the constant molar ratio of $HFP/O_2 = 1.7:1$ during the changes of temperature, and time is shown in Figure 2.

Figure 2 shows that the highest yield of HFPO on a level of $Y_{HFPO} = 43$ mol % is achieved during the changes of temperature in the range 160−170 °C for the reaction times 3.1−4.5 h. The prolongation of the reaction time over 4.5 h does not cause significant changes in the value of the yield function of HFPO. A decrease of temperature below 160 °C or its increase above 170 °C causes a decrease of value of this function by a 12 mol %. This results from the rate of the epoxidation reaction being lower when the temperature is below 160 °C. However, above 170 °C the reactions lead to the formation of byproducts, including the reaction associated with the decomposition of HFPO to trifluoroacetic acid fluoride. It was found in several experiments carried out at temperatures above 170 °C that the epoxidation process proceeded rapidly and even explosively. This was visualized by a rapid increase of both pressure and temperature. In this case, the major product of reaction was carbonyl fluoride together with a small amount of trifluoroacetic acid fluoride.

A combined effect of the molar ratio HFP/O_2 and the reaction time (Figure 3) at the temperature of 165 °C indicates that the highest yield can be achieved during the changes of the molar ratio in the range of 1.6−2.6, after reaction time of 3.1−4.5 h.

A decrease of the molar ratio HFP/O_2 below 1.6, while the reaction times were shorter than 3 h, causes a significant decrease of HFPO yield. For the reaction times below 3 h the HFPO yield is shown to undergo decreases over the entire examined range of molar ratios.

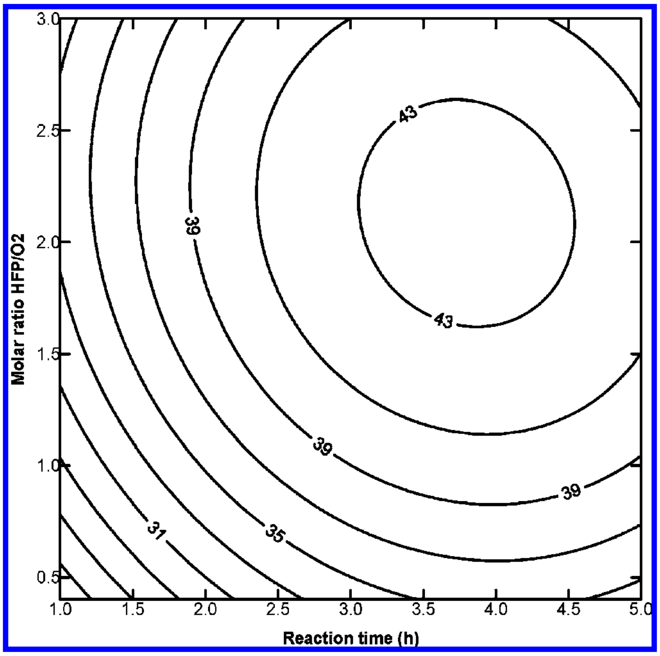

Figure 3. **Influence of HFP/O_2 molar ratio and the reaction time on the yield of HFPO, temperature 165 °C.**

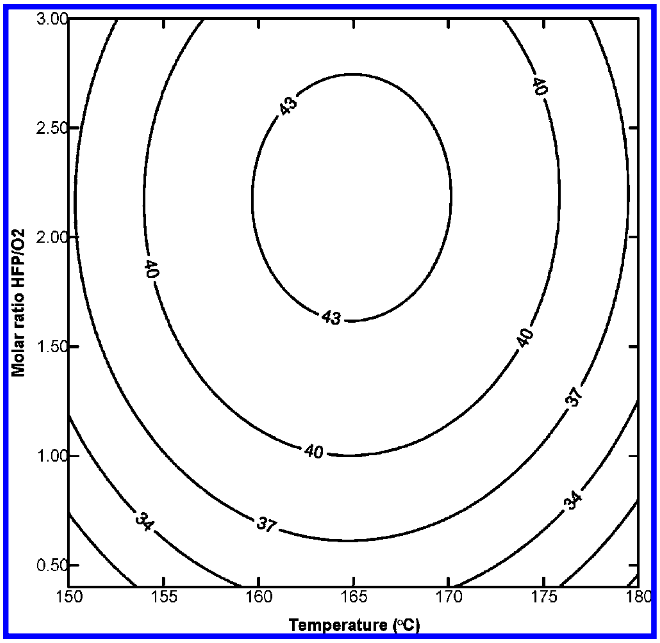

Figure 4. **Influence of temperature and HFP/O_2 molar ratio on the yield of HFPO, reaction time 3 h.**

It results from a combined effect of the molar ratio HFP/O_2 and temperature, that after the reaction time of 3 h (Figure 4) the highest yields of HFPO are achieved in the range of temperature 160−170 °C.

The temperature is here an essential technological parameter; its lowering or increasing by 5 °C beyond the optimal range causes a decrease of HFPO yield of the order of a few or a dozen percentage points.

Conclusions

The performed studies on the influence of temperature, the molar ratio of HFP/O_2, and the reaction time showed that the

HFPO yield achieves the highest value of 43 mol % at temperature of 165 °C, at the molar ratio of HFP/O_2 = 2.2, after the reaction time of 3.1 h, in the medium of carbon tetrachloride as a solvent. The same value of the yield is obtained when the molar ratio of HFP/O_2 is lowered to a value of 1.6, while the remaining parameters maintain their values. The highest yield of HFPO can be also achieved by lowering the temperature to 160 °C. However, this requires maintaining the HFP/O_2 molar ratio of about 2.2 mol/mol and the reaction time 3 h. The presented method enables to run the process on a small scale. In the case of technical scale a continuous dosage of oxygen is required. This will prevent rapidly growing pressure and temperature and exclude the possibility of explosion.

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