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ABSORPTION METHOD FOR PURIFYING LOWER PERFLUOROOLEFINS

Olena Matskiv[1,✉]

[1] Lviv Polytechnic National University, 12, S. Bandery str., Lviv, 79013, Ukraine
✉ *olena.o.matskiv@lpnu.ua*

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Abstract. The present study investigates the relevance of producing fluorine-containing polymers based on tetrafluoroethylene (TFE) and TFE-hexafluoropropylene (HFP) compositions. It has been demonstrated that the by-products resulting from the degradation of these polymers are hazardous, and their recycling or disposal is challenging. A thorough analysis of contemporary methods of polytetrafluoroethylene (PTFE) recycling has been conducted, indicating that chemical processing of PTFE results in the generation of substantial quantities of monomers, including TFE, HFP, and cyclooctafluorobutene. These monomers can be utilized in the synthesis of new fluoropolymers, contingent upon the assurance of sufficient purity. The article puts forward a novel absorption-based method for the purification of HFP and TFE from fluorinated hydrocarbon compounds. It has been established that ethyl acetate (EA) is a selective solvent for TFE, HFP, and the associated fluorinated hydrocarbons. The solubility of all components of the gas mixture in EA was investigated within the temperature range of 263–313 K. An analysis was conducted on the temperature dependence of Henry's law constant during dissolution, the results of which indicated an increase in the solubility of fluorinated organic gases in EA with an increase in temperature. The parameters of the absorption purification process for perfluoromonomers were determined, thereby enabling the reduction of fluorinated hydrocarbon compounds by two orders of magnitude and yielding monomer products with a main substance content of no less than 99.99 vol. %.

Keywords: tetrafluoroethylene, hexafluoropropylene, fluorinated hydrocarbon compounds, impurities, absorption, purification.

1. Introduction

Perfluoroolefins, and more specifically their low-molecular-weight homologues, are considered valuable fluorinated organic compounds that are extensively utilized in the synthesis of fluoropolymers, sealants, high-temperature lubricants, and a range of other specialized materials. The inherent properties of these materials, namely their thermal stability, chemical inertness, and exceptional dielectric strength, render them indispensable in a multitude of industrial applications.[1] Fluoropolymer materials derived from tetrafluoroethylene and TFE-hexafluoropropylene copolymers are of particular importance and have become essential materials in the chemical, nuclear, defense, and especially medical industries.[2]

However, as with other fluoropolymers, fluoroplastics are not without their drawbacks. The utilization of polytetrafluoroethylene, which is obtained through the polymerization of TFE, contributes to environmental pollution. This is attributable to its markedly elevated melt viscosity, which engenders processing challenges when employing conventional techniques such as extrusion or injection molding.[3] Furthermore, the incineration of PTFE waste is an energy-intensive process that results in the release of toxic substances, including fluorophosgene, hydrogen fluoride, carbonyl difluoride, and other hazardous compounds classified under hazard classes I and II. A significant limitation of PTFE is its inability to be extruded or molded from the melt. Its high viscosity [1010 Pa·s (10 pP) at 653 K] precludes conventional thermoplastic processing. In addition, the material's exceptional resistance to physical, chemical, thermal, and environmental stressors contributes to the enhanced persistence of the resulting waste. Therefore, due to the technological complexity of fluoropolymer waste disposal, the task of recycling them for reuse is particularly urgent.

A review of the literature indicates that, in contrast to other polymers, the reuse of fluoropolymers has not yet become widespread and remains in the early stages of development. In recent years, there has been an emergence of new studies and technologies focused on the recycling of polytetrafluoroethylene. In particular, the authors of research[4] report the synthesis of tetrafluoroethylene-hexafluoropropylene copolymers, known as fluorinated ethylene propylene (FEP), which retain the key properties of PTFE while exhibiting lower melt viscosity, thereby facilitating processing. FEP demonstrates excellent chemical resistance, a low coefficient of friction, and outstanding dielectric properties, making it suitable for use in electronics, the chemical industry, and medical devices. As demonstrated by the authors in work,[5] the study revealed that surface modification of PTFE-HFP copolymer films can remarkably enhance their adhesion properties, expanding their applicability in composite materials and coatings. In study,[6] the authors investigated the viability of recycling multi-component polymer waste via injection molding, a process that does not necessitate the preliminary separation of components. This research aims to develop a validated technology that maintains the essential performance characteristics of products made from such recycled waste. The present study investigates the impact of blend composition on the rheological, physical, and mechanical properties of the resultant materials, in addition to the stability of the molding process. The findings demonstrate the potential of this approach to reduce polymer waste and enhance the efficiency of plastic manufacturing.

The authors of research[7] proposed a method of mechanical grinding (Primary Recycling) of PTFE waste into micropowder, which can be reused in manufacturing processes. In particular, the method of secondary recycling of PTFE through thermomechanical degradation involves the use of thermal or radiation treatment to reduce the molecular weight of PTFE, converting it into a micropowder that can serve as an additive to enhance the properties of other materials, for instance, by reducing friction or improving lubrication. The authors of work[8] explored the use of electron beam treatment for processing PTFE, which also yields micropowder applicable in the production of lubricants or paints. The SATOORNIK Gen I technology employs a magnetic field to facilitate the efficient separation of PTFE microparticles from liquid media, thereby reducing environmental impact and enabling the reuse of the material. Another company, Neuman & Esser,[9] has developed a method for grinding PTFE into particles with an average size of approximately 50 μm using a classifier mill. The resultant material can be blended with virgin PTFE to manufacture new products with enhanced performance characteristics. Studies on the processing and modification of polymeric materials, particularly PTFE and composite systems, show that the performance characteristics largely depend on the supramolecular structure of the polymer and its ability to integrate fillers. Mechanical activation of PTFE allows controlling the crystalline domains and improving the physicomechanical properties of the composites.[10] Antifriction polymer composites based on aromatic polyamide with carbon black demonstrate reduced friction and wear at optimal filler content,[11] while composite hydrogels used for tubular products provide high strength and elasticity of structures capable of withstanding internal pressure, opening possibilities for technical and biomedical applications.[12]

The authors of study[13] also present alternative methods for fluoropolymer recycling, including thermoslysis, thermal treatment, flash pyrolysis, smoldering, open burning, air detonation, and other techniques. It is important to note that particular attention is paid to efforts aimed at avoiding the release of low molecular weight oligomers and per- and polyfluoroalkyl substances (PFAS) such as perfluorooctanoic acid (PFOA) and its alternatives. The researches demonstrate complete decomposition of PTFE with the formation of tetrafluoroethylene, and to a lesser extent, other products. Incineration, in particular, is one of the few technologies capable of fully degrading fluoropolymers and other perfluoroalkyl substances (PFAS) at temperatures above 1123 K. In work,[14] the method of pyrolysis and chemical depolymerisation was employed to break down PTFE into monomers, namely tetrafluoroethylene and hexafluoropropylene. These monomers can then be reused for the synthesis of new PTFE. While the method is technically feasible, it requires elevated temperatures and specialized equipment, which limits its broader application. Furthermore, it has been determined that the chemical recycling of PTFE results in high yields of TFE (C_2F_4), HFP (C_3F_6) and cyclooctafluorobutene (c-C_4F_8), which can be reused in the production of new fluoropolymers. This technology facilitates the disposal of PTFE without the prerequisite of reducing the size of the waste, and it enables the recovery of monomers that, once purified, are suitable for repolymerization. Of particular note is the copolymer FEP, synthesized from tetrafluoroethylene (80–90 wt. %) and hexafluoropropylene (10–20 wt. %). This is commercially represented by trademarks such as “Teflon-FEP” (USA), “Hostaflon FEP” (Germany), and “Neoflon” (Japan). These materials are effectively used in the electrical and electronics industries (for insulating coatings and components of electrical and electronic devices), in the chemical industry (as internal linings of processing equipment and industrial piping), as well as in medicine and optical fiber techniques. This fluoropolymer is melt-processable and can be extruded, a property that allows it to retain PTFE’s resistance to corrosive environments, chemical agents, and solvents. The processability of the material through compression molding, injection molding, and powder spraying leads to an expansion of the range of PTFE-based products and permits safe contact with foodstuffs. Therefore, the incorporation of HFP as a comonomer in the synthesis process has been shown to have a significant effect on the performance characteristics of these homopolymers.

As demonstrated, fluoropolymers based on TFE and its copolymers with HFP remain key materials for a wide range of applications due to their unique properties and potential for modification. The utilization of monomers that are characterized by appropriate purity levels is of paramount importance in the context of the production of fluoropolymer materials that exhibit superior quality characteristics. The quality of monomeric TFE and HFP is regulated by the presence of certain harmful impurities such as vinylidene fluoride, trifluoroethylene, and fluoromethane in TFE, and tetrafluoro-($C_3H_2F_4$) and pentafluoropropylene (C_3HF_5) in HFP. These compounds have been observed to catalyze undesirable side reactions, reduce the molecular weight of the resulting polymer, or introduce structural defects. It is imperative that these monomers are of the highest purity in order to guarantee the stability of the polymerization processes and to ensure that the final materials exhibit superior performance characteristics. Specifically, the international standard ASTM D2116-16 (2021)[15] defines the requirements for fluoropolymer materials obtained by the copolymerization of tetrafluoroethylene with hexafluoropropylene, including the provision for a high-purity commercial-grade product.

A paucity of contemporary studies has been observed with regard to the purification of these fluoroolefins. Recent sources indicate that the purification of TFE is typically carried out via multistage rectification. It is noteworthy that the modernization of a five-stage purification system to a four-stage one using Aspen Plus software enabled the achievement of a TFE purity of 99.999 %, while simultaneously reducing energy consumption by 112.9 kW.[16] However, the multi-stage nature of the process renders it economically inefficient.

The purification of HFP presents particular challenges due to the difficulty of separating it from compounds with similar physical and chemical properties, such as octafluoropropane (C_3F_8). A recent study[17] demonstrated that the use of metal-organic frameworks (MOFs), specifically the material JXNU-21, allows for high selectivity towards HFP, with a selectivity coefficient of 15.6 and product purity exceeding 99.999 % after a single sorption stage. In addition to laboratory-scale approaches, industrial solutions are increasingly being implemented. For instance, Yuji Materials has developed a process for purification of HFP to a 4N (99.99 %) grade, tailored for use in the electronics industry, where purity requirements are exceptionally stringent.[8] Yuji employs state-of-the-art filtration techniques and impurity control systems, including the removal of fluorine-containing by-products that have the potential to exert a detrimental effect on polymer properties. Consequently, their HFP product is deemed suitable for sensitive applications, particularly in the semiconductor industry.

Thus, contemporary practices in the purification of TFE and HFP are undergoing active development with regard to both energy-efficient rectification methods and the application of highly selective sorbent materials, thereby enabling a high level of purification. Nevertheless, the challenge of selecting the most efficient, economically justified, and environmentally safe method for purifying low-molecular-weight perfluoroolefins remains highly relevant. Therefore, this study aims to ascertain the most efficient method for purification of TFE and HFP, with a view to ensuring product purity, whilst minimizing costs and environmental impact. The efficient separation of components with close boiling points *via* rectification is a technologically complicated process. This is due to the physical and chemical properties of the mixture components (such as the presence of azeotropes or similar volatilities). Significant losses of valuable monomers often accompany this process. Purification can also be carried out utilizing alternative mass exchange processes. Specifically, gas-liquid absorption or extractive rectification using a selective solvent offers promising alternatives for efficient separation.

2. Experimental

The object of this study is the optimization of the process for obtaining HFP to increase the selectivity of its formation at the stage of TFE pyrolysis and to improve the yield of high-grade HFP grade 1 by using absorption purification of HFP grade 2 (99.95 vol. %) from fluorocarbon impurities.

2.1. Investigation of Perfluorocarbon Compounds Solubility and Fluorinated Hydrocarbons

In our earlier studies, it was established that among the most effective organic solvents, DMFA, NMP, and ethyl acetate (EA) were the most suitable.[19, 20] The solubility of perfluorocarbon compounds and fluorocarbons was studied using a dynamic method combined with chromatographic analysis of the gas and liquid phases, which ensures efficient and complete dissolution of the gas in the liquid. The solubility was calculated using the empirical equation (1):[21]

$$\gamma_i = \left[1 + \frac{\Delta V(1 - {}^{P_p}/_{P_{bar}})}{\Delta V_p}\right] \cdot \frac{273.2 \cdot P_{bar}}{760 \cdot T_b}, \qquad (1)$$

where γ_i – apparent solubility, cm^3 of gas/cm^3 of solvent; ΔV – measured difference between the volume of gas passed through and that collected, cm³; ΔV_p – measured volume of solvent introduced for absorption, adjusted for density ρ_4^{20}, cm³; P_p – vapour pressure of the solvent at the temperature of the burette walls T_b; P – barometric pressure.

Table 1 presents the solubility data for selected perfluorocarbon and fluorinated hydrocarbon (FHC) compounds in DMFA, NMP, and EA.

As can be seen from Table 1, the two most effective solvents in this process are DMFA and EA. Considering the solubility of the key gaseous components, namely C_2HF_3 and C_3F_6, DMFA is inferior to EA not only in terms of solubility but also in other important parameters, namely:

1. Under conditions of elevated humidity and temperatures approaching the boiling point of the substance, DMFA undergoes hydrolysis, resulting in the formation of corrosive formic acid. In contrast, EA has been demonstrated to be non-corrosive.

2. In contrast to DMFA, EA exhibits limited solubility in water and consequently forms a heteroazeotrope.

3. EA has been demonstrated to exhibit a higher absorption capacity in comparison to DMFA.

4. It is evident that EA is non-toxic, with a threshold limit value (TLV) in workplace air of 200 mg/m³. In contrast, for DMFA, this value is reduced to 10 mg/m³.

5. EA can be regenerated under comparatively milder conditions than those required for DMFA (the boiling point of EA is 350 K, while that of DMFA is 426 K).

Table 1. Solubility of selected fluorinated gases in DMFA, NMP, and EA at 293 K and 0.1 MPa, L of gas / L of solvent

Solvent	Gaseous Component							
	C_2F_4	C_2F_3H	$C_2F_2H_2$	C_3F_6	cyclo-C_4F_8	C_3F_5H	$C_3F_4H_2$	CF_3H
DMFA	0.9	6.3	2.86	2.4	0.7	16.4	20.5	11.0
NMP	0.7	3.5	–	1.36	0.37	2.4	2.9	–
EA	1.35	16.5	3.9	8.1	6.8	42.2	62.0	20.6

Therefore, EA was selected as the most effective solvent for the absorption-based purification of C_3F_6. Since the purification of low molecular weight perfluoroolefins (such as C_3F_6 or C_2F_4) from fluorinated hydrocarbons (FHCs) involves working with specific fractions of these perfluoroolefins, it is important to consider the potential impurities based on their boiling points. For C_2F_4 (boiling point = 196.6 K), typical impurities may include $C_2H_2F_2$ (boiling point = 189.4 K), CHF_3 (boiling point = 190.9 K), and C_2HF_3 (boiling point = 212.7 K). For C_3F_6 (boiling point = 244 K), possible impurities include C_3HF_5 (boiling point = 252.4 K), $C_3H_2F_4$ (boiling point = 244.8 K), and C_3HF_7 (boiling point = 255.1 K).

The solubility of perfluorocarbon and fluorinated hydrocarbon compounds that are present (or may be present) in C_3F_6 and C_2F_4, based on the technology of C_3F_6 production *via* C_2F_4 pyrolysis, was studied within the temperature range of 263–313 K and at a pressure of 0.1 MPa (Table 2). The technology of C_3F_6 production via C_2F_4, pyrolysis was used to produce the compounds.

Table 2. Solubility of fluoroorganic gaseous components in ethyl acetate at 0.1 MPa, L of gas / L of solvent

Fluoroorganic gaseous components	Solubility γ_i at the temperatures, K					
	263	273	283	293	303	313
CF_3H	93.7	54.5	32.9	20.6	13.3	8.8
C_2F_4	5.4	3.6	2.5	1.35	1.0	0.6
C_2F_3H	44.9	31.6	23.4	16.5	12.6	8.0
$C_2F_2H_2$	10.4	7.4	5.3	3.9	2.8	2.1
C_3F_6	27.6	18.2	12.1	8.2	5.7	4.0
C_3F_5H	250.0	128.0	77.0	42.2	24.3	15.5
$C_3F_4H_2$	320.0	180.0	110.0	62.0	36.0	25.0
C_3F_7H	–	356.0	175.0	91.0	50.0	38.0
cyclo-C_4F_8	–	21.0	12.4	6.8	4.6	3.0
C_4F_6	–	22.4	15.7	11.0	7.57	5.17

It has been demonstrated that the solubility of perfluorocarbon compounds containing an equivalent number of carbon atoms in EA is lower than that of their fluorinated hydrocarbon analogues. The maximum solubility of a fluorinated hydrocarbon in EA was observed for the saturated compound, namely heptafluoropropane, at 273 K, while the minimum solubility was recorded for tetrafluoroethylene, which decreases significantly with increasing temperature. Consequently, EA can be employed for the purification of both C_3F_6 and C_2F_4 from fluorinated hydrocarbon impurities present in the respective perfluoroolefin fractions.

The determination of Henry's law constants was achieved through the utilisation of Eq. (2).

$$P = K \cdot N, \qquad (2)$$

where P – partial pressure of the gas above the solvent, mmHg; N – concentration of gas in the solution (in mole fractions); K – Henry's law constant, in mmHg.

The mole fraction of the dissolved gas component per mole of solvent (N) was calculated using Eq. (3):

$$N = \frac{\frac{\gamma_i}{22.4}}{\frac{\gamma_i}{22.4} + \frac{1000d}{M}}, \text{ mol of gas / mol of solvent} \qquad (3)$$

where γ – solubility of the gaseous component, L of gas / L of solvent; d – density of the solvent, g/cm^3; M – molar mass of the solvent, g/mol.

The density of EA was determined using Eq. (4):

$$d_t = 0.93 \cdot (1 - 0.0013t), \mathrm{g/cm^3} \qquad (4)$$

where: t – temperature of the solvent in °C.

Table 3 presents the dependence of the Henry's law constants (K) and the molar fractions (N) of the dissolved gaseous components in the solvent on temperature, demonstrating that the solubility of fluorinated organic gases in EA increases with rising temperature.

The calculation of the absorption-based purification process was achieved through the utilization of a method that employs parametric Antoine-type Equations ((5), (6)) to describe the temperature dependence of gas solubility in an organic solvent, as developed by the authors of study [22].

$$K = \frac{1}{\gamma}(p - P)(\gamma + B); \qquad (5)$$

$$\gamma = exp(D + \frac{E}{F+t}); \qquad (6)$$

where K – Henry's law solubility constant; γ – volumetric solubility of the gas, L of gas/ L of solvent; p and P – total system pressure and solvent vapour pressure, respectively, in mmHg; D, E, F – dimensionless coefficients determined from three experimental data points of corresponding γ and t values; t – dimensionless parameter numerically equal to the dissolution temperature in °C; B – a coefficient dependent on the ratio of the volumetric solubility γ to the unit volume or mass of the solvent, calculated in accordance with equations (7, 8):

$$B = 22.41\frac{\rho_0}{M}(1 - \alpha t), \text{ to unit of volume} \qquad (7)$$

$$B = 22410/M \text{ to unit of mass,} \qquad (8)$$

ρ_0 – density of the solvent under standard conditions, g/cm^3; α – volumetric expansion coefficient of the solvent, α = 0.0013; M – molar mass of the solvent, g/mol; t – temperature, °C.

Table 3. Dependence of Henry's law constant (K, mmHg) on temperature (T, K) for the dissolution of fluorinated organic gases in EA (N, mol of gas / mol of solvent)

Gaseous Component	263 K		273 K		283 K		293 K		303 K		313 K	
	N	K	N	K	N	K	N	K	N	K	N	K
CF_3H	0.281	2669	0.187	4011	0.123	6097	0.082	9146	0.055	13636	0.038	19894
C_2F_4	0.022	34091	0.015	50000	0.011	70755	0.058	129310	0.004	170454	0.003	280899
C_2F_3H	0.158	4756	0.118	6372	0.091	8242	0.067	11227	0.053	14291	0.034	21802
$C_2F_2H_2$	0.042	18072	0.030	24752	0.022	33784	0.017	45181	0.012	61475	0.009	80906
C_3F_6	0.103	7267	0.071	10504	0.049	15244	0.034	21866	0.024	30738	0.018	42857
C_3F_5H	0.510	1470	0.351	2137	0.248	3024	0.155	4839	0.096	7772	0.065	11610
$C_3F_4H_2$	0.571	1313	0.432	1736	0.320	2344	0.212	3538	0.137	5430	0.100	7500
C_3F_7H	–	–	0.601	1248	0.428	1751	0.283	2650	0.180	4167	0.113	6637
cyclo-C_4F_8	–	–	0.082	9205	0.050	14881	0.029	26224	0.020	37879	0.0132	56818
C_4F_6	–	–	0.086	8680	0.063	11905	0.046	16483	0.032	23292	0.023	33333

This method enables the temperature range of gas solubility in the solvent to be extended by approximately 20 %. The temperature dependence of the solubility of fluorinated organic components in EA, calculated using Antoine's equation, is presented in Table 4.

The empirical equations system was employed to determine the parameters and material balance of the absorption-based purification process of HFP from fluorinated hydrocarbon impurities.

Table 4. Temperature dependence of the solubility of fluorinated organic components in EA

Fluorinated organic component	Temperature dependence of solubility
1	2
CF_3H	$\gamma_{CF_3H} = \exp(-10.4 + \frac{3974}{t + 276})$
C_2F_4	$\gamma_{C_2F_4} = \exp(31.38 + \frac{22123}{t - 735})$

Table 4. (*Continuation*)Temperature dependence of the solubility of fluorinated organic components in EA

1	2
C_2F_3H	$\gamma_{C_2F_3H} = \exp(35.72 + \frac{34430}{t-1067})$
$C_2F_2H_2$	$\gamma_{C_2F_2H_2} = \exp(-14.57 + \frac{8136}{t+491})$
C_3F_6	$\gamma_{C_3F_6} = \exp(-20.05 + \frac{12922}{t+563})$
C_3F_5H	$\gamma_{C_3F_5H} = \exp(15.57 + \frac{2377}{t-222})$
$C_3F_4H_2$	$\gamma_{C_3F_4H_2} = \exp(14.59 + \frac{1971}{t-210})$
C_3F_7H	$\gamma_{C_3F_7H} = \exp(-10.5 + \frac{3603}{t+220})$
$cyclo-C_4F_8$	$\gamma_{cyclo-C_4F_8} = \exp(-8.49 + \frac{2262}{t+196})$
C_4F_6	$\gamma_{C_4F_6} = \exp(30.97 + \frac{22304}{t-800})$

2.2. Absorption Purification of HFP and TFE from Fluorinated Hydrocarbon Impurities.

HFP (grade 2) with a purity of 99.95 vol. % was utilized for the absorption purification from fluorinated hydrocarbon compounds, as well as off-spec TFE (containing less than 99.93 vol. % of TFE). As previously stated, TFE functions as a feedstock in the production of HFP. It is therefore imperative to ensure that fluorinated hydrocarbon impurities present in TFE do not enter the pyrolysis mixture from which monomeric HFP is extracted.

Absorption purification was conducted under atmospheric pressure and a specified gas-to-solvent ratio, which was determined based on the solubility of a key component in the gas mixture. That is defined as the component whose solubility is closest to that of the target perfluorolefin being purified. In the context of HFP purification from fluorinated hydrocarbon compounds, the key component pertaining to C_3F_6 was identified as C_3HF_5. Similarly, for C_2F_4, the key component was determined to be $C_2H_2F_2$ (Table 2). The purification mode was then adjusted (gas-to-liquid ratio, absorber top temperature, desorber bottom temperature) based on the results of the chromatographic analysis. The selection of the optimal mode was made to ensure the near-complete absorption of the highly soluble FHC impurities present in the perfluoroolefin.

In order to refine the gas-to-absorbent ratio, the consumption of EA during the absorption-based separation was calculated under conditions approximating ideal interphase equilibrium. The total absorbent flow rate (L) was determined using Eq. (9):[23]

$$L = G_h \frac{y_{init}-y_{fin}}{N_{fin}-N_{init}}, \qquad (9)$$

where Gh – total gas flow into the absorber (feed plus recycled gas), mol/h; y_{init} and y_{fin} – initial and final concentrations of the distributed component in the overall gas mixture and in the purified gas, respectively, mol of gas/mol of solvent; N_{init} and N_{fin} – initial and final concentrations of the distributed component in the initial (regenerated) and final (spent) absorbent, respectively, mol of gas/mol of solvent.

3. Results and Discussion

The results of the purification of off-spec TFE by absorption in ethyl acetate over the course of one hour, under atmospheric pressure, with an absorber top temperature of 253 K and a desorber bottom temperature ranging from 303 to 313 K, at a gas-to-absorbent ratio of 11.6:1 L of gas: L of solvent, are presented in Table 5. In the context of stable operating conditions, 18000 mL of off-spec TFE and 1550 mL of EA were introduced into the absorber. A total of 16,300 mL of purified TFE was obtained, with a content of 99.99 vol. %. The total consumption of EA, calculated according to Eq. (1), amounted to 1258 mL/h. During the absorption-based purification process, 1550 mL of EA was introduced into the absorber, which exceeds the amount required to achieve interphase equilibrium by 23 %.

In addition, grade 2 HFP was subjected to purification under atmospheric pressure, with an absorber top temperature of 268 K, a desorber bottom temperature in the range of 313–323 K, and a gas-to-absorbent ratio of 32:1 L of gas: L of solvent, as demonstrated in Table 6.

Over the course of one hour under stable purification conditions, 22,400 mL of HFP grade 2 was fed to the absorber, and 19,040 mL of purified HFP with a content of at least 99.99 vol. % (grade 1) was obtained. Fluorinated hydrocarbon compounds, including $C_3H_5F_3$, $C_3H_2F_4$, and $C_3H_7F_7$, which possess boiling points in proximity to that of C_3F_6, were efficiently extracted from the mixture. The total EA consumption, calculated according to Eq. (1), was 542 mL/h. During the absorption purification of grade 2 HFP, 700 mL of EA was fed into the absorber. This constitutes 29 % of the calculated amount required to ensure interphase equilibrium in the purification process. Consequently, the purification of grade 2 HFP resulted in a 70 % increase in the yield of grade 1 HFP (99.99 vol. %). A loss of 15 % of the gas mixture, relative to the initial volume of HFP, was primarily attributed to the residual solubility of gases in the non-regenerated absorbent.

Table 5. Data on the purification of off-spec TFE from fluorinated hydrocarbon compounds by absorption in EA

Fed to Absorption			Obtained after Absorption*		
Initial Components	Flow rate, mL/h	Composition, vol. %	Final Components	Recovered Volume, mL/h	Composition, vol. %
1. Gas mixture:	18000	100	Purified TFE:	16300	100
C_2F_4	17942	99.68	incl.: C_2F_4	16298	99.99
$C_2F_2H_2$	18	0.10	$C_2F_2H_2$	1,0	0.005
C_2F_3H	11	0.06	C_2F_3H	–	<0.001
CF_3H	29	0.16	CF_3H	–	<0.001
2. Ethyl acetate	1550	99.8 wt. %	EA with absorbed gases	1530	

*– and purified from EA impurities by adsorption on activated carbon.

Table 6. Purification of grade 2 HFP from fluorinated hydrocarbon compounds by absorption in EA

Fed to Absorption			Obtained after Absorption*		
Initial Components	Flow rate, mL/h	Composition, vol.%	Final Components	Recovered Volume, mL/h	Composition, vol. %
1. Gas mixture:	22400	100	Purified TFE:	19040	100
C_3F_6	22388	99.946	incl.: C_3F_6	19038	99.99
C_3F_5H	4.6	0.020	C_3F_5H	–	~0.0001
$C_3F_4H_2$	3.6	0.016	$C_3F_4H_2$	–	<0.0001
C_3F_7H	3.4	0.015	C_3F_7H	–	<0.0001
2. Ethyl acetate	700	99.8 wt.%	EA with absorbed gases	695	

*– and purified from EA impurities by adsorption on activated carbon.

A comparison of the results of the absorption purification of TFE and HFP from fluorinated hydrocarbon compounds indicates that achieving an equivalent level of purification (main component content of 99.99 vol. %) occurs at a lower gas-to-absorbent ratio (11.6:1) and a lower absorption temperature (253 K) during TFE purification than during HFP purification (32:1) and an absorption temperature of 268 K.

This phenomenon can be attributed to the higher selectivity of EA towards C_3F_6 and its key component C_3HF_5, compared to its selectivity for C_2F_4 and its key component $C_2H_2F_2$ (Table 2). Furthermore, EA has been demonstrated to exhibit a greater absorption capacity for C_3-type fluorinated organic compounds in comparison to those of the C_1-C_2 type.

4. Conclusions

Following a rigorous series of investigations, it was determined that EA would be utilized as a selective organic solvent for the absorption purification of HFP and TFE from fluorinated hydrocarbon compounds. The solubility of components such as CHF_3, C_2F_4, C_2HF_3, $C_2H_2F_2$, C_3F_6, C_3HF_5, $C_3H_2F_4$, C_3HF_7, cyclo-C_4F_8, and C_4F_6 in EA was determined within the temperature range of 263–313 K. The temperature dependence of this substance was characterized using Antoine-type equations. Laboratory-scale absorption-desorption separation experiments have demonstrated that the content of the main substance in the purified perfluoroolefins exceeds 99.99 vol. % (grade 1). The application of the absorption purification method using EA for HFP from fluorinated hydrocarbon compounds is expected to increase the yield of monomeric HFP grade 1 by approximately 70 %. Thus, this absorption purification technique effectively achieves near-complete removal of fluorinated hydrocarbon compounds from both HFP and TFE, which regulate the quality of these monomer products.

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ВИЗНАЧЕННЯ ЕФЕКТИВНОГО СПОСОБУ ОЧИЩЕННЯ НИЖЧИХ ПЕРФТОРОЛЕФІНІВ

Анотація. *Вивчено актуальність виробництва фторовмісних полімерів, отриманих на основі тетрафторетилену (ТФЕ) та композиції ТФЕ із гексафторпропіленом (ГФП). Показано, що їхні відходи небезпечні та складні для повторного перероблення та утилізації. Проаналізовано сучасні методи перероблення політетрафторетилену (ПТФЕ). Запропоновано абсорбційний спосіб очищення ГФП і ТФЕ від фторвуглеводневих сполук. Визначено селективний розчинник для ТФЕ і ГФП та інших фторвуглеводнів, що містяться у них. В інтервалі температур 263–313 К досліджено розчинність в етилацетаті всіх компонентів газової суміші, вивчено залежність константи розчинності Генрі від температури. Визначено параметри процесу абсорбційного очищення перфтормономерів, що дає змогу одержати мономерні продукти з вмістом основної речовини не менше ніж 99,99 об. %.*

Ключові слова: *тетрафторетилен, гексафторпропілен, фторвуглеводневі сполуки, домішки, абсорбція, очищення.*