

The Development and Application of Commercial Technologies for Obtaining Fluorine Compounds Using Elemental Fluorine in FSUE RSC Applied Chemistry

D. S. Pashkevich, V.G. Barabanov, B. N. Maximov

FSUE RSC Applied Chemistry 14, pr. Dobrolubova, St.Petersburg, Russia, 197198,
e-mail: pdsac@peterlink.ru

Russian Scientific Centre (RSC) "Applied Chemistry" was one of the first organizations in Russia, where the fluorine production technology using electrolysis of potassium bifluoride melt was developed and applied [1]. As a result of researches' development in the field of elemental fluorine and its use for the synthesis of different fluorine compounds the fluorine itself has become an available raw material - the world capacity of F₂ production reaches the amount of 25000 tons per year.

During many years the intensive researches regarding using of fluorine for the production of fluorine compounds of different purposes, which are in demand at world market have been being held in RSC "Applied Chemistry". These are so called "electron gases" used for the production of semi-conductors; ozone-friendly chladones (freons); volatile fluorine compounds, which are used for the processes of isotopic enrichment; fluorine compounds for medicine; components of lithium current sources etc.

Fluorinating processes using elemental fluorine are linked up with very high heat isolation and they are easily transferred into the mode of combustion, as a result of which the reaction products may get heated up to several thousands degrees. Under such conditions an overwhelming majority of fluorine compounds are thermolabile. That is why the creation of reactor's unit providing the stable temperature within fluorinating zone, at which the initial, intermediate and target products are thermally stable enough to create a competitive technology is one of the major issues at development of production technology applying fluorine as a fluorinating agent.

In RSC "Applied Chemistry" we have got a unique situation regarding the development of effective reactor units of elemental fluorine fluorination. Under the condition of close collaboration between specialists of fluorine technology and specialists of the theory and practice of combustion processes the reactor's units for a whole series of fluorine compounds productions with application of fluorine were developed.

During the creating of high-performance and safe reactor's unit of fluorine fluorination at first it is necessary to choose thermal conditions for the process: steady or unsteady state. According to [2], exothermal chemical reactions may pass at steady state (the rate of heat-removing is higher or equals the rate of heat-isolation) and unsteady state (the rate of heat-removing is lower than the rate of heat isolation) thermal conditions. A clear border is between those two conditions, it is determined by the combination of energy transfer characteristics and chemical and kinetic and thermodynamic characteristics of the system.

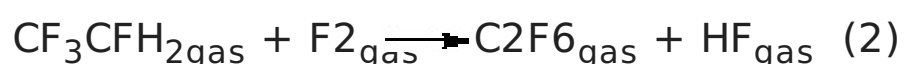
Under the steady state thermal conditions the process is going on under the conditions close to isothermal, the reaction rate is relatively low, the volume of a reaction zone is relatively large. These conditions can be easily formed in reaction systems of high heat-transfer coefficient. If one of the reagents is fluorine, then these are phase systems gas-liquid and gas-solid for dynamic (mixed, moveable) layers of powder.

Under unsteady state thermal conditions a combustion front or thermal explosion is being carried out, the process is going on under conditions close to adiabatic, the reaction rate is relatively high and typical size of the reaction zone is usually significantly smaller than the volume of a whole reactor device (wave localization of reaction zone) [3, 4]. These conditions are formed in phase systems of low heat-transfer coefficient: gas- gas and gas - solid for steady state (immovable, non-mixed) layers of powder.

Usually, the reactor's unit functioning under the unsteady state thermal conditions of fluorination is simpler regarding the lay-out and commercial operation. However, under these conditions it is reasonable either to synthesize compounds thermally stable enough or to carry out the processes of a low productivity.

At the wave localization of a zone of gas-cycle reaction the compounds reacting can be mixed up in advance at molecular level, and then the homogeneous torch is being carried out. In this case the composition of fluorination products depends only on the fluorine concentration. For the reaction systems gas - liquid and gas - solid the diffusion combustion is carried out, at that the chemical reaction often goes in diffusion gas-cycle torch, as the fluorinated liquid and in some cases solid compounds evaporate heated with isolating reaction heat.

During the diffusion combustion the composition of products can be changed by altering the rate of fluorine introduction into the zone of reaction. The process of pentafluoroethane (ozone-friendly chladone and fire-extinguishing agent) and hexafluoroethane (electrone gas) obtaining by gas-cycle fluorination of 1,1,1,2-tetrafluoroethane [5, 6] is a characterizing example of gas-cycle fluorination in homogeneous torch:



These processes were put into practice at reactor of a "tunnel burner" type with preliminary components mixing and flame stabilization, at that a conversion of fluorine had been reached, the selectivity by pentafluoroethane reached 80%. A destructive fluorination of fluoroethane molecule with the forming of fluoromethanes is the main side process. At conversion of initial 1,1,1,2-tetrafluoroethane to 30% the concentration of fluoromethanes in synthesis gas does not exceed 1 %. The raw materials which had not come into reaction are directed into recycle.

The developed method had undergone the stage of pilot plant at the unit of reactor of tunnel burner type of 20mm diameter and length of 2.5m and tentative capacity of approximately 50 tons per year by pentafluoroethane and hexafluoroethane.

Nowadays some producers of semi-conductors consider a carbonyl bifluoride as an alternative to nitrogen trifluoride and perfluorocarbons for the silicone etching due to simplicity of utilization of its waste. That's why the technology to synthesize this compound had been developed, it is based on the process of carbon monoxide diffusion burning in fluorine [7]:



The yield of target product in the process (3) at equimolecular rate of the initial components exceeds 70% and at the excess of fluorine - 90%. Tetrafluoromethane, carbon dioxide and the traces of trifluoromethylhypofluorite as well are presented as admixtures.

The synthesis of sulphur hexafluoride (dielectric for electrical and technical articles) is being carried out in diffusion gas-cycle sulphur evaporating in fluorine burning torch:

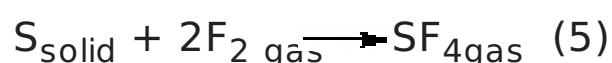


It is known, that during the fluorination of sulphur its other fluorides can be formed along with SF_6 , the yield of which should be minimized. Based on thermodynamic calculations carried out [8] the conditions have been determined, at which sulphur hexafluoride is the main product and a reactor has been developed, in which the diffusion sulphur burning in fluorine torch is formed by supply of fluorine flow to the surface of sulphur melted [9]. At the conversion of fluorine equal to 90% the yield of SF_6 reached 95%. SF_4 and S_2F_{10} were the main admixtures.

Reactor of 400mm diameter and 3m length allowed obtaining of 30 tons of sulphur hexafluoride per year. According to the technology developed two large sulphur hexafluoride commercial plants were created in Russia - One with the production capacity equal to 500 tons per year at JS Halogen (Perm region)) and another with the production capacity equal to 450 tons per year at Kirovo-Chepetsk Chemical Combine.

Another commercially important sulphur fluoride, which is obtained out of elements is SF_4 , fluorinating agent for substituting oxygen in carbonyl groups. According to thermodynamic calculations [8] maximum content of sulphur tetrafluoride is observed at temperature around 1500K.

A reactor of falling layer, in which the interaction of sulphur and fluorine goes at thermal explosion under conditions close to adiabatic [10, 11] had been developed for the implementing of this process. This reactor is a vertical tube, to which upper part the solid fluorinated material and fluorine are being put with the help of a screw:



At pilot unit equipped with the reactor of 60mm diameter created at Pilot Plant of RSC of "Applied Chemistry" sulphur was mixed with calcium difluoride, which consumed the heat of reaction. At this plant they managed to obtain the yield of

sulphur tetrafluoride equal to 80% compare from theoretic one at a full fluorine conversion and reactor's capacity of around 10 tons per year. Sulphur hexafluoride was the main by-product.

At a mode of graphite burning in fluorine the process of tetrafluoromethane (electrone gas) synthesis was carried out [12, 13]:



Tetrafluoromethane is one of the most thermostable fluorine compounds, that is why it is reasonable to use the mode of filtration burning of carbon immobile layer in fluorine for its synthesis. The reactor equipped with immersed two-component nozzle of a special structure, by which fluorine and gaseous hydrocarbon was fed into reactor to form the high-temperature reaction zone at a start up of reaction was developed especially for this process. Thermostabilization of the reaction zone was being carried out selecting in an experimental manner the fluorine consumption in such way, that all the heat being isolated was to be offset based on radiation heat onto cooled nozzle.

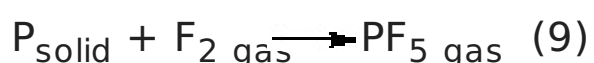
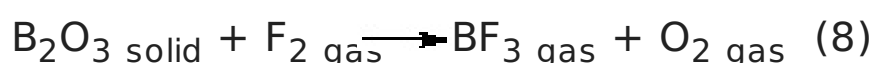
In FSUE "Angarsk Electrolysis Chemical Complex" the production of tetrafluoromethane of 450 tons per year capacity equipped with 3 reactors operating in the mode of inverse wave of filtration burning using the above described method of the reactors' start-up was created based on the developing of RSC "Applied Chemistry". Tetrafluoromethane is the only product of implemented synthesis method.

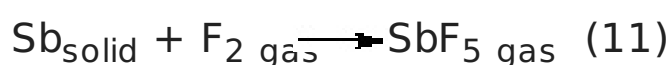
In the mode of filtration burning and the phase system of gas-solid compound the fluorinating processes of high-melting metals: tungsten, molybdenum, rhenium were carried out, their hexafluorides: WF_6 (forming of tungsten films for microelectronics), MoF_6 (isotope industry) and ReF_6 are rather thermostable [14]:



The thermostabilization of the reaction zone is being carried out based on the radiation of heat the same way as during the tetrafluoromethane synthesis, though the reactor's start-up is simpler, because there is no need of special techniques for forming the high-temperature reaction zone. The pilot production of WF_6 and MoF_6 was created at pilot plant of RSC "Applied Chemistry", the production of WF_6 of the capacity of 50 tons per year - at JS "Halogen" (Perm).

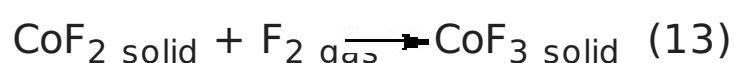
At the mode of burning the synthesis of boron trifluoride (catalyst for alkylation processes, polymerization and isomerization processes; volatile compound of boron, which is used for rectification enrichment of boron by isotope ^{10}B), the synthesis of phosphorus pentafluoride (raw material for the production of electrolyte for lithium sources of current), the synthesis of silicon tetrafluoride (forming of silicon films for microelectronics) and antimony pentafluoride (fluorinating agent) were carried [1, 11]:





Such feed rate of fluorine was chosen that the solid raw materials would not melt. The boron trifluoride commercial production of 15 tons per year was created at JS "Halogen", and pilot units for the synthesis of phosphorus and antimony pentafluorides and SiF_4 - at pilot plant of RSC "Applied Chemistry".

In the mode of wave localization of the reaction zone a few industrial obtaining processes of perfluorocarbons out of hydrocarbons and fluorocarbons by fluorinating the latter using cobalt trifluoride were carried out [15]:



where R_H - initial compound, R_F - target perfluorocarbon compound.

Fluorination processes using cobalt trifluoride and regeneration of cobalt difluoride by fluorine are accompanied by high heat emission. That's why in the commercial units covered with stationary layer of CoF_3 they were carried out at the mode of wave of filtration burning regulating temperature within reaction zone by the feed rate of fluorinated gaseous compound or fluorine at regeneration.

In particular, production technologies of octafluoropropane out of hexafluoropropylene [16] and of perfluorodecaline out of naphthalene [17] were developed:



The productions of octafluoropropane with the reactors covered with the stationary layer of powder were set at pilot plant of FSUE RSC "Applied Chemistry", which capacity accounted to 10 tons per year and at JS "Halogen" of 25 tons per year capacity. Perfluorodecaline synthesis technology was introduced at pilot plant of FSUE RSC "Applied Chemistry", the production capacity reached 1 ton per year.

The obtaining technology for carbonyl bifluoride was developed too [7]:



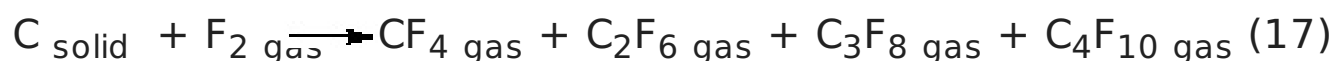
Virtually full conversion of carbon monoxide was observed within self-spreading reaction zone at maximum temperature of 400-500°C in a mode of filtration burning. The yield of target product exceeded 90%, tetrafluoromethane, carbon dioxide and trifluoromethylhypofluorite traces were the main admixtures.

The examples above demonstrate the effectiveness of production of rather thermostable fluorine compounds using fluorine in the mode of burning. At this mode even complicated compounds can be obtained, for example perfluorodecaline, however the productivity of reactor's unit is relatively low in this case.

The more thermolabile fluorine compounds can be obtained with rather high productivity using fluorine as well. It is practical to use stationary heating (close to isothermal) synthesis rate for that, not allowing the wave localization of high-

temperature zone of reaction to occur. At that, the more effective method of heat removal out of the reaction zone is being carried out in apparatus under development, the higher productivity of that apparatus will be.

In the reaction system of gas-solid we can provide a close to isothermal synthesis rate using dynamic (movable, mixable) layer of powder. For example, for the reaction system of fluorine-carbon a commercial synthesis method for the lowest perfluoroalkanes (electron gases) has been developed:



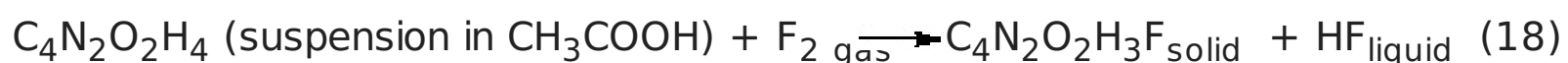
When using reactors with circulating aerated graphite layer, ascending gas-dust flow and a reactor with freely descending layer of powder we managed to obtain the mixture of named products of the following composition: CF_4 40-45 mass.%, C_2F_6 20-25 mass.%, C_3F_8 15-20 mass.%, C_4F_{10} 10 mass.% [18-20].

At that in first case a close to isothermal rate was formed removing the heat of reaction into the wall of reactor. And in the reactors with freely descending powder layer and with ascending gas-dust flow graphite was used not only as a reagent but also as a heat content for consumption of the reaction heat, controlling the powder heat-up altering its flow rate.

At Pilot Plant of RSC "Applied Chemistry" a number of small-capacity technologies for fluorination of solid compounds using elemental fluorine obtaining corresponding fluorides - carbon polyfluoride (a component of cathode composite of lithium sources of current, antifriction material) [21], selenium, tellurium, iridium (isotopic enrichment) hexafluorides [11, 27], selenium tetrafluoride (fluorinating agent for replacement of oxygen in carbonyl groups) [22], iodide pentafluoride (laser techniques) [23], manganese tetrafluoride and potassium hexafluoronickelate (hardbody fluorine generators) [24], germanium tetrafluoride (isotopic enrichment) [25] was implemented.

Fluorination processes were carried out at the mode close to isothermal in multiply-shell reactors, which productivity accounted to hundreds kilograms a year. The heat extraction out of the reaction zone was carried out based on natural convection. Commercial production of carbon polyfluoride based on that technology of capacity of up to 10 tons per year was created at FSUE of "Angarsk Electrolysis Chemical Complex".

The conducting of fluorination process in a mode close isothermal one is convenient to carry out in a reaction scheme of gas-liquid, as in that system it is rather simple to reach a high intensiveness of transfer processes. The synthesis of 5-fluorouracile (carcinolytic preparation), which was obtained by fluorination of powdery uracil using fluorine in the medium of acetic acid, was carried out in this phase system [26]:



Pilot unit was created at Pilot Plant of FSUE RSC "Applied Chemistry". Its capacity was about several tons a year. In recent years in RSC "Applied Chemistry" the synthesis technology of nitrogen trifluoride by fluorination of $\text{NH}_4\text{F} \cdot n\text{HF}$ melt using gaseous fluorine [28-30] was developed according to the contracts with NewChem LLC:



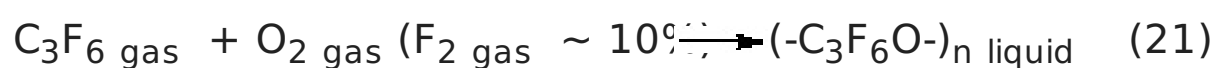


The fluorination is being carried out in non-gradient reactor equipped with high-speed mixer in circulation loop, which allows effective heat extracting based on forced convection and keeping isothermal rate of the process carrying out, and also it provides maximum contact area of gaseous fluorine and melt. At such method of the process carrying out the fluorination reactor's output reaches 30 g of $\text{NF}_3/(\text{dm}^3 \cdot \text{hour})$ at fluorine conversion up to 95%.

This technology is being put into practice at FSUE "Siberian Chemical Plant" today. So, when creating commercial productions of fluorine compounds using fluorine as fluorinating agent depending on thermostability of target and initial compounds, and also productivity of commercial technology the process of synthesis can be put into practice in the mode of burning or under conditions close to isothermal.

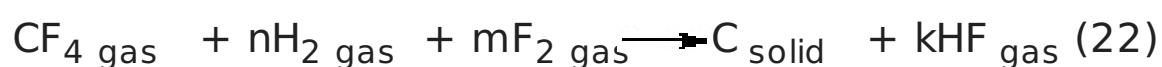
It should be noted, that elemental fluorine is being used for chemical and technological processes not only as a main fluorinating agent but for some other purposes as well. Thus, at Pilot Plant of RSC "Applied Chemistry" the process of obtaining of perfluoropolyetherpolyperoxide (a component for antifriction liquids) by isothermal low-temperature liquid phase oxidation of hexafluoropropylene using oxygen was put into practice.

When using fluorine as an initiator of the oxidation process, which in a quantity of a few percents is added to oxygen, the simple polyether chains prevail in the structure of this compound [31]:



n value was being altered, varying the fluorine concentration in oxygen and the method of gas feed into reactor [32]. At that there were virtually no gasiform products of destruction in the process of oxidation.

Fluorine finds its another application as a reagent for flame processing of tetrafluoromethane waste obtaining anhydrous hydrogen fluorine [33]:



Tetrafluoromethane is one of the most thermodynamically stable fluorine compounds and its survival in the atmosphere reaches 50000 years. At that its potential of global warming is very high and amounts to 6500 [1]. That's why the development of its extermination methods for the purpose of termination of its dispersion in the atmosphere is an urgent matter. As a results of a work completed it was proved, that it was manageable to reach the tetrafluoromethane conversion of more than 80% when value of $n=0.5$ and value of $m=2.5$. At that the discharge coefficient of fluorine is about 0.2 when obtaining anhydrous hydrogen fluoride. It should be said, that at some modes of the process (22) the high content of tetrafluoroethylene in the reaction products was observed [33, 34], which may become a matter of a separate research in the future. Fluorine is also used for replacement of residual oxygen in perfluodecaline [35], in tertiary fluorinated amines [36] obtained by electrochemical fluorination etc., which allows improving of chemical stability and some other operational characteristics of mentioned compounds. As a conclusion we can say, that elemental fluorine is being widely used in Russian industry for production of a whole range of commercially important fluorine compounds.

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