

Pollutant emissions management in an existing plant by diminishing the production of undesirable compounds: the case of CHF_3

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Abstract

Changing production patterns towards waste reduction in a globalizing world can be considered a starting point towards sustainable development. It is generally admitted that the aim of a chemical plant designer must be to reduce pollutant emissions, not by cleaning the effluents, but by diminishing the production of the undesirable compounds. This work is focused on reducing the CHF_3 (*HFC-23*) emission of an existing plant, which is a result of over-fluorination during the CHF_2Cl (*HCFC-22*) manufacture. According to European directives very stringent limits are imposed on emissions of *HFC-23*, a volatile gas that has a significant contribution to the greenhouse effect. The aim of this study is to allocate the source of the problem and try to decrease by-product emissions by reducing their production in the first place. To achieve this goal, the design engineer must be able to examine the effect of the various design parameters on the overall output. In this work the effect of the reactor operation conditions on the formation rate of both the product and the by-product of the plant is studied by employing a commercial process simulator (*AspenPlus*[®]). The optimum result is accomplished by reducing the residence time in the fluorination reactor, since *HCFC-22* formation is relatively fast compared to the corresponding slow formation of *HFC-23*. Thus the proposed solution deals with the emissions problem only by influencing the reactor performance, i.e. without the need for extra investment and/or energy consumption. The proposed solution is not only environmental friendly but also more desirable from an economic point of view. The results of the study were applied to an existing plant and found to be very realistic, since the *HFC-23* emission was reduced by 50%.

Keywords: clean technology, VOC emission reduction, process simulation

Introduction

In view of the Kyoto protocol that obliges the worldwide reduction of greenhouse gas emissions (i.e. 5.2% from 1990 levels by 2008/2012), a number of industrialized countries, including the EU, committed themselves to large reductions (Schwarz & Leisewitz, 1999; Anonymous, 2000; Hartikainen et al., 2003). Consequently, the requirement for sustainable development, energy savings and pollution reduction becomes more and more important for the process design engineer (Harmsen, 2004). It is generally admitted that the aim of a chemical plant designer must be to reduce pollutant emissions, not by cleaning the effluents, but by diminishing the production of the undesirable compounds, i.e. the clean technology approach. In existing plants, pollution prevention can be achieved by three main types of clean technology (Belis-Bergouignan et al., 2004), i.e. through:

- process change, which involves the modification of the very nature of the production procedure,

- process modification, where the overall process principle remains essentially the same but some steps (e.g. additional equipment) are added and

- existing process optimisation, leading to an abatement in the emission of pollutants by studying changes in the process operating conditions.

Obviously the first option can be applied only to new plants, whereas the other two options can be also regarded as an appropriate way to reduce pollutant emissions from an existing plant. However, adding new equipment can not be always considered a feasible way to minimize emission impact on the environment, since new apparatus, apart from requiring capital investment, contributes to the greenhouse effect due to the energy consumption increase. It is therefore of great importance to investigate first, whether the same target can be achieved merely by changing some of the process parameters.

The European Union has recently issued directives on Volatile Organic Compounds emissions (VOC's) imposing very stringent limits on VOC's concentrations of gaseous effluents (Vilela et al., 2003). Studies have therefore been conducted in many countries with the aim of identifying the applications of fluorinated greenhouse gases, calculating their present and future consumption and emission levels and appraising emission abatement options (Schwarz & Leisewitz, 1999). A Volatile Organic gas that has a significant contribution to the greenhouse effect is trifluoromethane (HFC-23), an over-fluorination by-product during the production of difluorochloromethane (HCFC-22). The latter is widely used as refrigerant in air-conditioning systems and as a chemical feedstock for the production of synthetic polymers. According to Rand et al. (1999), HFC-23 has a 100-year global warming potential (GWP), i.e. 11,700 times greater than that of carbon dioxide over the same period. To comply with the EU regulations, plants producing HCFC-22 are obliged to rearrange their processes. The common practice is to separate the HFC-23 emitted and destroy or transform it, using a wide range of methods, such as thermal oxidation and pyrolysis (Miotke, 1999; Rand et al., 1999), an approach associated both with additional energy consumption and capital investment. An alternative policy is to reduce the by-product quantity by altering the process parameters.

The aim of this study is to decrease HFC-23 emissions by reducing its production through process parameter modification. Alternative scenarios are examined by employing a commercial process simulator (AspenPlus®) and the results are compared to data from an existing plant.

Process Description

The production process of difluorochloromethane (CHClF_2) is based on the catalytic fluorination of chloroform (CHCl_3) by hydrogen fluoride (HF), using antimony pentachloride (SbCl_5) as catalyst (Rand et al., 1999; Santacesaria et al., 1989; Bajzer & Kim, 1996).

A simplified flow diagram of the process is presented in Figure 1.

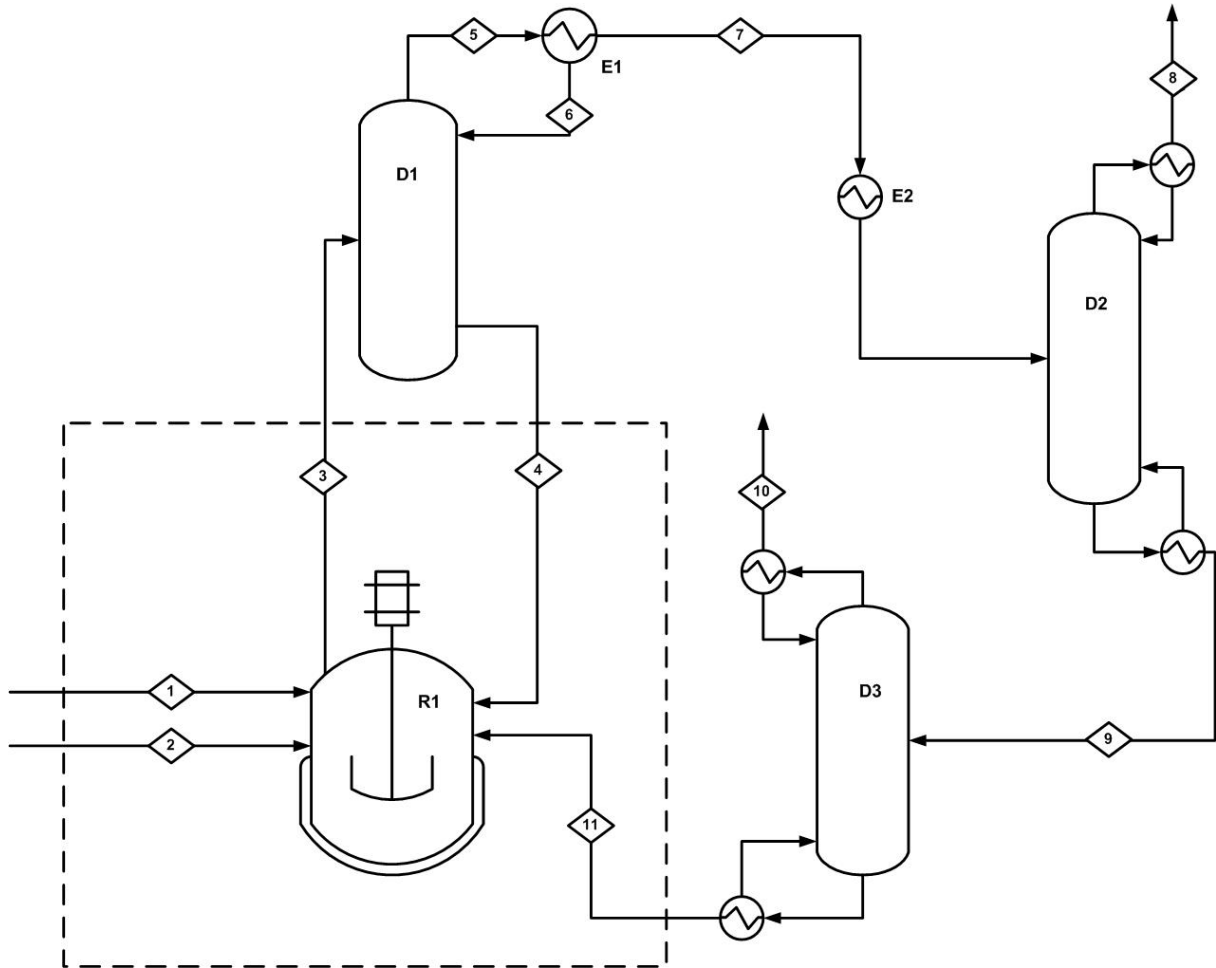


Figure 1: Process flow diagram.

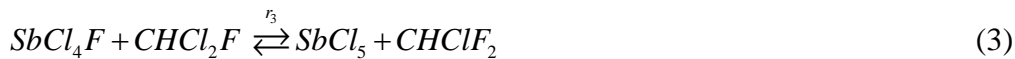
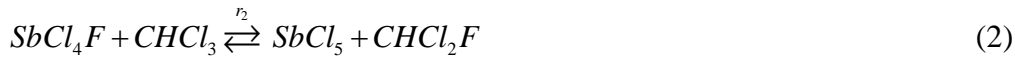
Stream	Components
1	HF
2	CHCl_3
3	HCFC-21, HCFC-22, HFC-23, HCl, HF, CHCl_3 ,
4	HCFC-21, HCFC-22, HFC-23, HCl, HF, CHCl_3 ,
5	HCFC-21, HCFC-22, HFC-23, HCl, HF, CHCl_3
6	HCFC-21, HCFC-22, HFC-23, HCl, HF, CHCl_3 ,
7	HCFC-21, HCFC-22, HFC-23, HCl, HF, CHCl_3
8	HCFC-22, HFC-23 , HCl, HF
9	HCFC-21, HCFC-22, HFC-23, HF, CHCl_3
10	HCFC-22 , HFC-23, HCl, HF
11	HCFC-21, HCFC-22

The overall reactions leading to the formation of the chloroform fluorination products are:



The reactions take place in a continuous stirred tank reactor (*CSTR*), *R1*, in the liquid phase, while the fluorinated reaction products, referred to as *HCFC-21* ($CHCl_2F$), *HCFC-22* ($CHClF_2$) and *HFC-23* (CHF_3), are gaseous and are withdrawn from the top of the reactor. Consequently, the reactor, whose pressure is around 17 bar, contains a liquid phase, i.e. a catalyst solution in chloroform ($CHCl_3$), and a gas phase comprising of the reaction products, the non reacting *HF* as well as a small amount of $CHCl_3$ determined by the thermodynamic equilibrium. The gas phase from the reactor (*stream 3*) is fed to the distillation column *D1*. The column bottom product (*stream 4*) is recycled to the reactor, whereas the distillate (*stream 7*), containing mainly the volatile reaction products i.e. *HCl*, *HCFC-22* and *HFC-23*, is cooled and directed to the next distillation column *D2*. There the by-product *HFC-23*, is separated and withdrawn (*stream 8*), whereas the bottom outlet (*stream 9*) is fed to the distillation column *D3*, where the product *HCFC-22* is finally obtained as distillate (*stream 10*). The residue (*stream 11*) containing *HCFC-21* and *HCFC-22* is recycled to the reactor.

In order to simulate the operation of the reactor, the kinetic model proposed by Santacesaria et al. (1989) is adopted. According to this model the catalyst ($SbCl_5$) is reacting first with the *HF* forming an intermediate reagent ($SbCl_4F$), which in turn reacts with the $CHCl_3$. Consequently, the actual reactions leading to the formation of the fluorinated compounds are as follows:



According to the aforementioned model all the reactions take place in the liquid phase at a temperature range of 80-120°C. The reaction rates depend on the reagent concentrations in the liquid phase, whose volume is strongly affected by the vapor-liquid equilibrium. Reaction (1), i.e. $SbCl_4F$ formation, is fast and reversible. Considering the formation rate of the main product (*HCFC-22*) as reference, the relative rates of the reactions (1) to (4) are 150:7:1:0.03 respectively. Some very slow side reactions resulting in the formation of several catalyst by-products are also observed and considered the main reason leading to the gradual catalyst deactivation. The reaction kinetics is assumed to be second order for all the reactions. The reaction rates as well as the consumption and production rates are represented by the Equations (5) to (8) and (9) to (14) respectively.

$$r_1 = k_1 C_{HF} C_{SbCl_5} - \frac{k_1}{K_{e1}} C_{CHCl_2F} C_{HCl} \quad (5)$$

$$r_2 = k_2 C_{SbCl_4F} C_{CHCl_3} - \frac{k_2}{K_{e2}} C_{CHClF_2} C_{HCl} \quad (6)$$

$$r_3 = k_3 C_{SbCl_4F} C_{CHCl_2F} \quad (7)$$

$$r_4 = k_4 C_{SbCl_4F} C_{CHClF_2} \quad (8)$$

$$dC_{HF}/dt = -dC_{HCl}/dt = -r_1 \quad (9)$$

$$dC_{SbCl_5}/dt = -dC_{SbCl_4F}/dt = -r_1 + r_2 + r_3 + r_4 \quad (10)$$

$$dC_{CHCl_3}/dt = -r_2 \quad (11)$$

$$dC_{CHCl_2F}/dt = r_2 - r_3 \quad (12)$$

$$dC_{CHClF_2}/dt = r_3 - r_4 \quad (13)$$

$$dC_{CHF_3}/dt = r_4 \quad (14)$$

where

- r_i : reaction rate of reaction i ($kmole/m^3 \cdot s$)
- k_i : kinetic constant of reaction i ($m^3/kmole \cdot s$)
- K_{ei} : equilibrium constant of reaction i (-)
- C_j : concentration of component j ($kmole/m^3$)
- t : time (s)

The kinetic parameters and equilibrium constants proposed by Santacesaria et al. (1989) based on experimental data, are summarized in **Table 1**.

Table 1: Reaction constants (Santacesaria et al., 1989)

T	K_{e1}	K_{e2}	k_1	k_2	k_3	k_4
$^{\circ}C$	equilibrium constants (-)		kinetic constants ($m^3/kmole \cdot s$)			
85	-	0.267	-	-	$7 \times 10^{-4} \pm 4 \times 10^{-5}$	$3 \times 10^{-5} \pm 3 \times 10^{-6}$
100	0.45	0.152	0.1	0.009	$1.3 \times 10^{-3} \pm 7 \times 10^{-5}$	$5 \times 10^{-5} \pm 4 \times 10^{-6}$
115	-	0.09	-	-	$2 \times 10^{-3} \pm 1 \times 10^{-3}$	$8 \times 10^{-5} \pm 8 \times 10^{-6}$

Process Simulation

The main concern of the design engineer must be to decrease the undesirable by-product formation, without considerably reducing the amount of the plant main product. In this work the effect of the reactor and separation column operating conditions on both the product and by-products production rate is studied, using a commercial process simulator (*AspenPlus*[®]).

In the actual plant the reaction vessel (*RI*) serves both as a continuous stirred tank reactor and a phase separator, since the gaseous reaction products are withdrawn from the top of the vessel. This notion is introduced in the simulation by including both a *CSTR* and a phase separator operating under the same pressure and temperature conditions (**Figure 2**). Thus in the simulation the two-phase product stream from the reactor is directed to the phase separator, whose gas phase represents the actual reactor outlet, while the liquid phase is recycled to the reactor. The reactor size as well as the reaction conditions (i.e. $T=92^{\circ}C$ and $P=17.5bar$) correspond to those of an existing plant. The physical properties are calculated using the Han-Starling modification of Benedict-Webb-Rubin equation of state (*BWR-HS*), a method considered suitable for organic compounds (Assael et al., 1996).

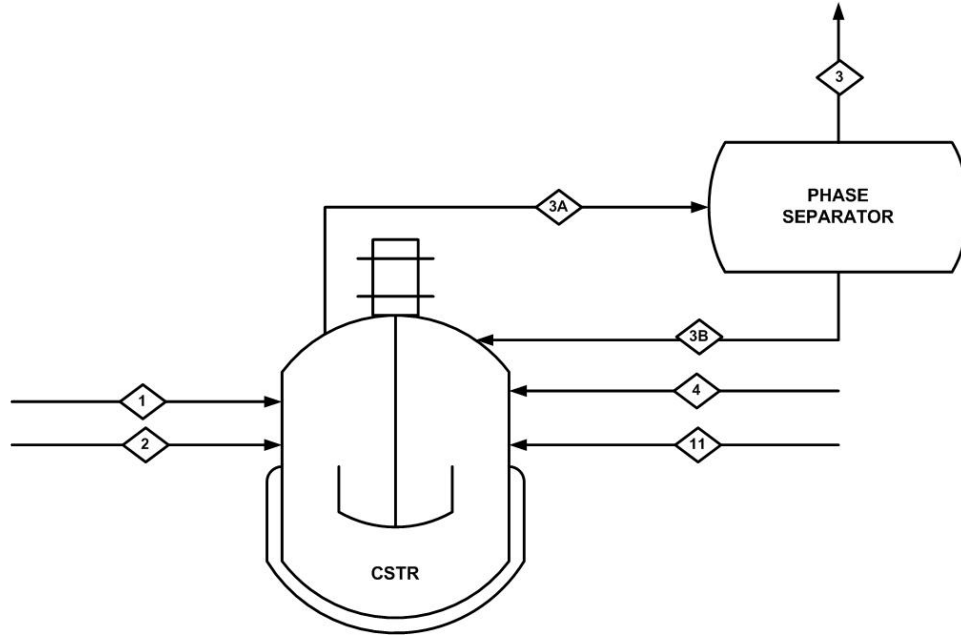


Figure 2: Simulation reactor

The main objective, i.e. to inhibit the by-product formation in the reactor, can be better accomplished by individually studying all the parameters influencing the reactor performance. As it is already mentioned, the catalyst, SbCl_5 , reacts with HF to form SbCl_4F (Eq. 1), an intermediate reactant, which is involved in the main fluorination reactions (Eqs. 2-4) simply as a fluorine carrier and reacts back to SbCl_5 . Given that SbCl_4F formation is very fast compared to the other reactions, it can be assumed that it does not affect the total production rate. Thus SbCl_4F can be excluded from the simulation and HF can be considered as the fluorination agent. Furthermore, SbCl_4F is an unstable compound, whose physical properties can not easily be specified and are also not included in the simulator databank. Consequently the reactions introduced into the simulator model are the overall reactions (Eqs. I-III).

Phase equilibrium is another factor that must be taken into account, as the reactions occur in the liquid phase, while the reaction products are in the gas phase. Therefore SbCl_5 , even though it is considered not to participate in the fluorination reactions, is included in the phase equilibrium calculations.

Although the catalyst does not participate in the simulation reactions, its influence on the reaction rate is taken into account by assuming that the kinetic parameters for the reaction Eqs. (I) to (III) are the same as those for Eqs. (2) to (4). The reaction rates are represented by Eqs. (15) to (17).

$$r_I = k_2 C_{\text{HF}} C_{\text{CHCl}_3} - \frac{k_2}{K_{e2}} C_{\text{CHClF}_2} C_{\text{HCl}} \quad (15)$$

$$r_{II} = k_3 C_{\text{HF}} C_{\text{CHCl}_2\text{F}} \quad (16)$$

$$r_{III} = k_4 C_{\text{HF}} C_{\text{CHClF}_2} \quad (17)$$

The reaction constants proposed by Santacesaria et al. (1989), were used slightly modified to conform to the data obtained from the existing plant (**Table 2**). It must be noted that, since the formation reaction of SbCl_4F (Eq. 1) is not included in the model applied to the simulator, K_{e1} and k_1 that refer to reaction (I) are not calculated.

Table 2: Reaction constants based on an existing plant data

T	K_{e1}	K_{e2}	k_1	k_2	k_3	k_4
$^{\circ}C$	equilibrium constants (-)		kinetic constants ($m^3/kmole \cdot s$)			
92	-	0.23	-	0.01	11×10^{-4}	4.3×10^{-5}

The initial approach was to include the entire flow sheet in the process model and this was necessary in order to validate the simulation model using data (e.g. conditions, stream composition etc) from an existing plant. The results are found to be in very good agreement with the plant data, which, however, as proprietary information can not be published. For the same reason the various parameters examined, are referred to as percent variation with respect to the operating conditions of the existing plant.

Results

The base case mentioned here corresponds to the data (i.e. operating conditions, stream flow rates and composition, catalyst composition etc) acquired from the existing plant. The solution involving *HFC-23* separation and destruction is not examined, since it requires both additional capital investment and energy consumption. The various cases analyzed correspond merely to operational parameter variation with respect to the base case, i.e. without adding new equipment. The aim is to study the effect of the various parameters on the amount of the *HFC-23* formed in the reactor and for this reason a sensitivity analysis was conducted involving the parameters that influence the performance of the “simulation reactor”, i.e. the model containing the reactor and the phase separator (**Figure 2**). For the presentation of the results, the parameters are presented as **percent deviation** from the corresponding base case value; a positive deviation indicates an increase, while a negative a decrease. The examination of simply the reactor performance helps reducing the computational demands (memory, CPU time).

The main parameters studied are:

- **The amount of *HCFC-22* or *HCFC-21* entering the reactor**

The simulation results prove that the amount of *HCFC-22* recycled to the reactor does not significantly affect the amount of *HFC-23* formed (**Figure 3**). For example, the *HFC-23* generated in the reactor is reduced by less than 10% when the amount of *HCFC-22* recycled to the reactor is eliminated, i.e. 100% decrease. On the other hand, reducing the amount of *HCFC-21* entering the reactor would mostly affect the main product formation without a considerable reduction of the amount of *HFC-23* produced (**Figure 4**). In conclusion, changing the distillation system in order to minimize the amount of *HCFC-22* or *HCFC-21* recycled to the reactor can not be considered an effective solution.

- **The reactor operating conditions**

The reactor operating conditions (i.e. temperature and pressure) affect both the reaction constants and the phase equilibrium. Since the reactions take place in the liquid phase, while all the components involved are volatile, the reactor conditions must be selected, so as to ensure the existence of the liquid phase in the reactor. Thus drastic changes of the reactor operating conditions would cause problems to its performance. The simulation reveals that, by varying the reactor temperature and/or pressure within the permitted limits, the amount of *HFC-23* produced remains practically constant. This is in accor-

dance with the literature (Santacesaria et al., 1989), where it is stated that the composition of the vapor stream from the reactor is little affected by temperature.

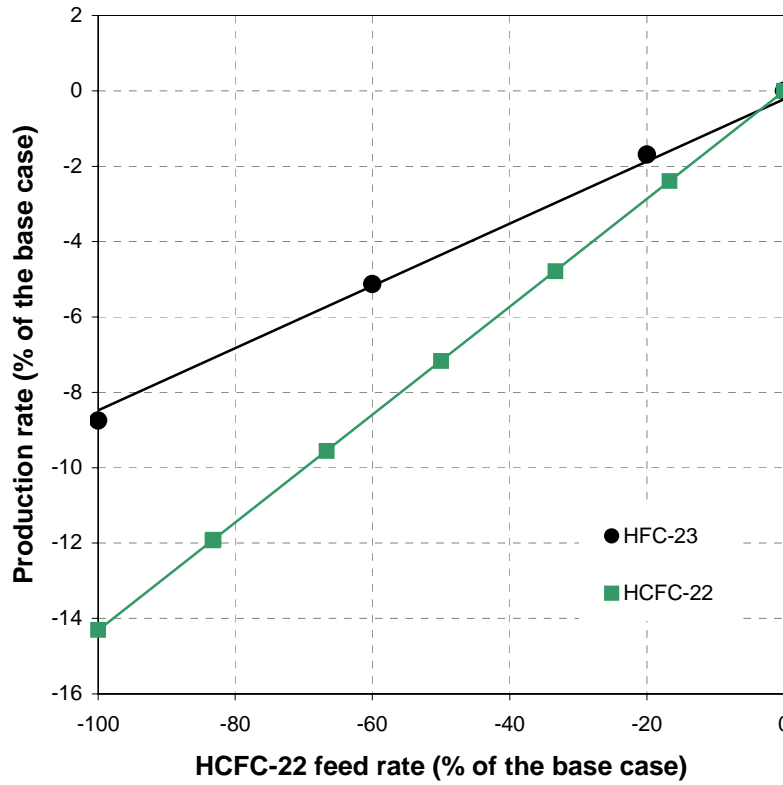


Figure 3: Effect of the *HCFC-22* reactor feed rate

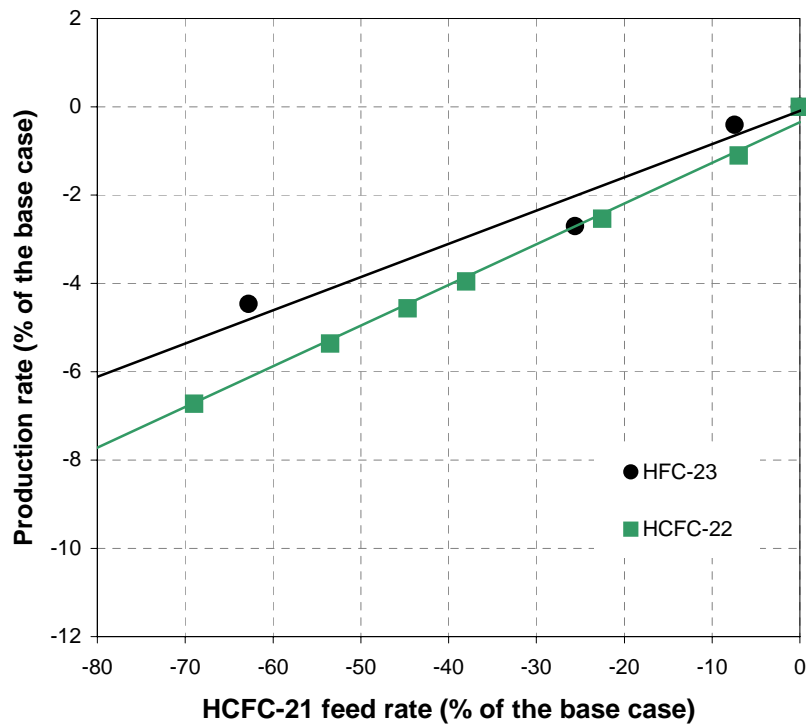


Figure 4: Effect of the *HCFC-21* reactor feed rate

- **The HF and CHCl₃ feed rate**

HF is the main fluorinating agent and consequently its amount affects all the reactions. As expected, HCFC-22 production increases linearly with HF feed rate (Figure 5). Inevitably, HFC-23 production rate will also increase linearly with HF feed rate, but after a certain HF feed rate the slope of the curve exhibits a sudden change, i.e. the HFC-23 increases faster with the HF feed rate (Figure 5). The above change corresponds to the HF feed rate of the base case, which is proved to be the optimum. On the other hand, CHCl₃ is the limiting reagent, and consequently decreasing or increasing its feed rate would reduce or increase accordingly the amount of all the reaction products, both desirable and undesirable ones. For a constant liquid phase level, CHCl₃ feed rate variation also affects the reactants residence time, an option examined in the next paragraph.

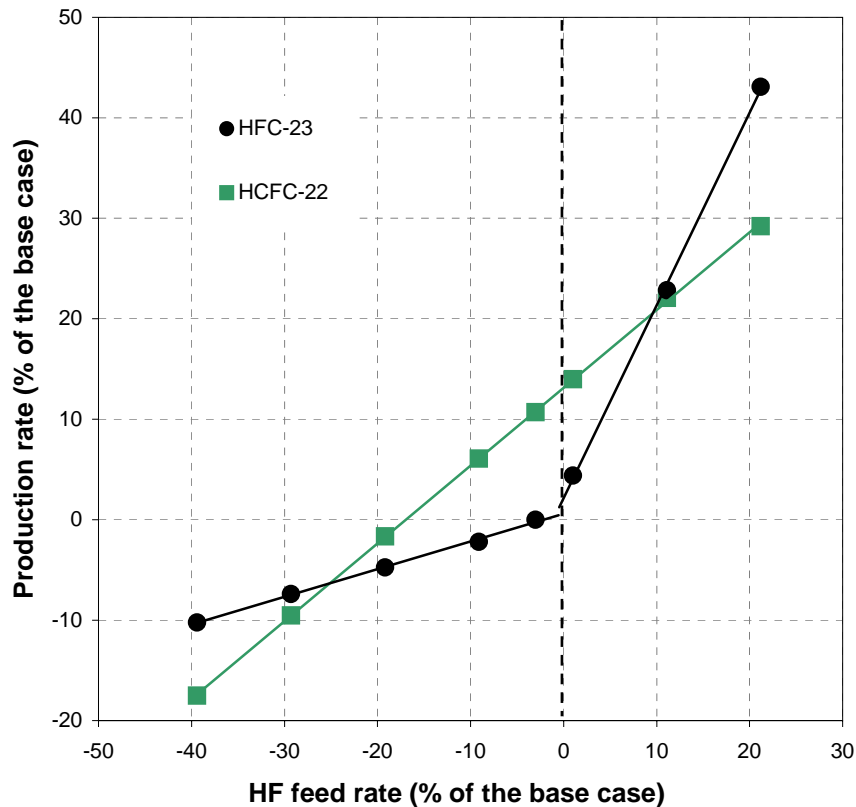


Figure 5: Effect of the HF reactor feed rate variation

- **The reaction residence time**

The reaction rate for the formation of the undesirable by-product HFC-23 (Eq. 4) is low compared to that of the other two reactions (Table 2). Thus, a decrease in the reaction residence time would reduce the amount of the HFC-23 formed, although this would probably affect the amount of the main product, too. As the reactions take place in the liquid phase but the reaction products are gaseous, the reduction of the residence time can be accomplished simply by reducing the volume of the liquid phase, or equally by lowering the liquid phase level of a given reactor. The simulation results reveal that by reducing the liquid phase level a significant reduction of the HFC-23 produced can be achieved for almost constant HCFC-22 production (Figure 6). For example, if the liquid phase level in the existing reactor is lowered by 40%, the HFC-23 production will be reduced by 60%, while the reduction in the amount of HCFC-22 produced is less than 1%, compared to the base case.

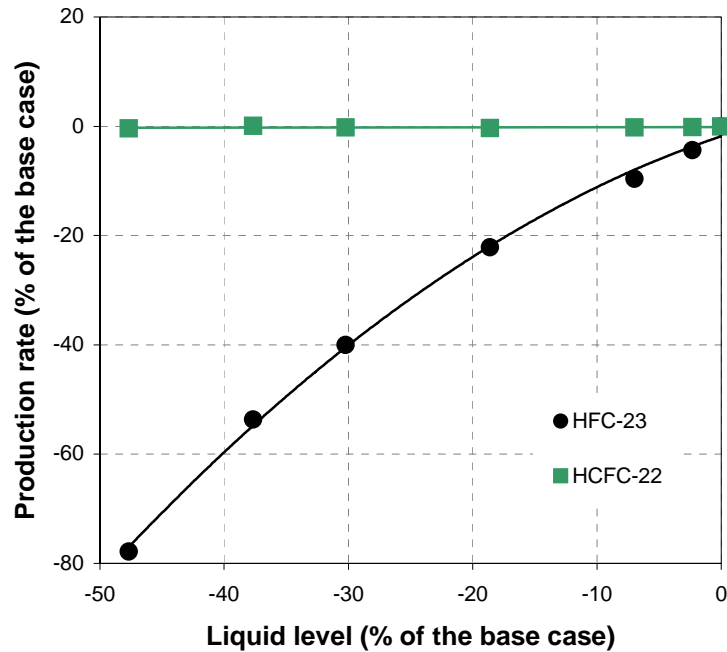


Figure 6: Effect of the reactor liquid level

In conclusion, of all the parameters studied, the reactor residence time is proved to be the most appropriate one, as its variation significantly affects the amount of the undesirable by-product, without practically influencing the rate of the main product formation. Its application also fulfills the imposed constraints, i.e. it requires no capital investment or additional energy consumption. The proposed solution (i.e. the liquid level decrease by 35%) was tested in the existing plant and the results were fully satisfactory (i.e. more than 50% *HFC-23* reduction) permitting the plant to comply with the EU regulations.

Concluding remarks

In view of sustainable development and environmental consideration the clean technology conception was implemented in an existing plant, whose by-product is the undesirable pollutant *HFC-23*. Finding the root of the problem and trying to deal with it where it is established, offers a really simple and attractive solution. Thus, before adopting the solution involving *HFC-23* separation and destruction, which would lead to additional capital investment and further energy consumption, it is examined whether the same target could be achieved merely by changing some of the process parameters, an approach that complies with the clean technology notion.

In this respect, the process simulator has been proved a powerful tool to study alternative solutions, since a sensitivity analysis performed with the aid of the simulator helps the process engineer locate the most crucial parameters, whose variation would have a considerable effect on the results. Consequently the reactor parameters are studied individually, in order to define the optimum reactor conditions that would maximize *HCFC-22* production while keeping the *HFC-23* emissions at the lowest possible level.

The proposed solution deals with the emissions problem only by influencing the reactor performance, i.e. without the need for extra investment and/or energy consumption. The optimum result is accomplished simply by reducing the reactants residence time or equally the liquid phase volume in the reactor. This alternative solution is not only environmental friendly but also more desirable from an economic point of view. The results of the study were applied

to an existing *HCFC-22* plant and found to be very realistic, since the *HFC-23* emission was reduced by 50%, without additional energy consumption and/or capital investment.

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