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# Process for the selective hydrogenolysis of $CCl_2F_2$ (CFC-12) into $CH_2F_2$ (HFC-32)

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## Abstract

The conversion of waste $CCl_2F_2$ (CFC-12) into high added value product $CH_2F_2$ (HFC-32) seems technically and economically feasible with a selected palladium on activated carbon catalyst. This catalyst shows a remarkable constant selectivity to HFC-32 in the range between 70% and 90% at all conversion levels with varying process conditions. Small amount of impurities, like Al, Fe or Cr, present in the activated carbon can have a significant effect on the catalyst performance. These impurities act as Friedel–Crafts catalyst thus catalyzing the unwanted chlorine–fluorine exchange. The chlorine–fluorine exchange can be sufficiently suppressed by removing the impurities from the activated carbon support prior to introduction of the palladium. The mechanism of the reaction follows mainly parallel rather than the expected serial pathways. A reaction scheme is proposed, which explains the high selectivity to HFC-32 by formation of a $CF_2$-carbene, which preferentially desorbs as HFC-32.

*Keywords*: Dichlorodifluoromethane; Difluoromethane; Hydrogenolysis; Palladium; Catalyst; Activated carbon

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## 1. Introduction

The term CFCs is a general abbreviation for chlorofluorocarbons. They have been extensively used since their discovery in the thirties, mainly as refrigerant, foam blowing agents or solvent because of their unique properties (non toxic, non flammable, cheap). However, after the first warning of Rowland and Molina [1] in 1974 that CFCs could destroy the ozone layer, the world has moved rapidly towards a phase-out of CFCs. Because the destruction of stratospheric ozone would lead to an increase of harmful UV-B radiation reaching the earth's surface, the production and use of CFCs will be prohibited (per 1-1-1995 in the European Union and per 1-1-1996 worldwide). However, the depletion of stratospheric ozone will continue in spite of this prohibition. This is caused by the diffusion of CFCs present in the troposphere to the stratosphere and the eventual emission of still used CFCs. In Fig. 1 the expected effect of different CFC phase-out scenarios on the amount of stratospheric chlorine is depicted [2]. This figure shows that additional control options can significantly accelerate the decrease in the stratospheric chlorine concentration. Not only the time during which the chlorine concentration in the stratosphere is above the maximal acceptable level (ca. 2.8 ppb) can be reduced

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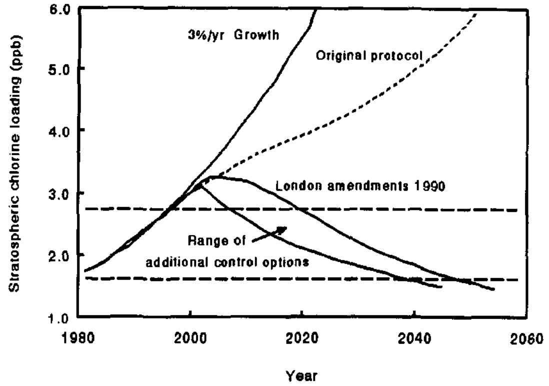

Fig. 1. CFC phase-out scenarios [2].

by more than a factor of 2, but also the no-effect level (ca. 1.8 ppb) can be reached almost 10 years earlier. An important additional control option is to prevent the emission of CFCs still in use. Fig. 2 shows an estimation of banked ozone depleting substances (ODS) [3]. About 95% of the ODS are CFCs. The majority thereof, in use for refrigeration and present in foams, are CFC-12 and CFC-11 respectively, and thus about 84% of the banked ODS are CFC-11 and CFC-12. The recovery of CFC-11 and CFC-12 from their current applications and subsequent destruction thereof is a logical next step.

The long term replacements for CFCs in their applications are most probably HFCs. Especially HFC-134a is often mentioned, but the total number of possible replacements still increases. HFC-32 or a mixture thereof is a good replacement in heavy duty cooling applications because it has excellent cooling properties and in addition a lower global warming potential than HFC-134a. Combining the fact that there is not enough destruction capacity for the banked CFCs and that the market for CFC-replacements such as HFC-32 is growing, a challenging task is to convert the waste CFCs into valuable HFCs.

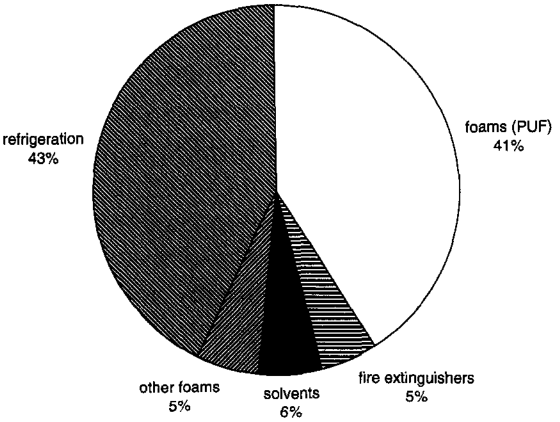

Fig. 2. Estimation of 2.25 Mton banked ODS [3].

At the Delft University of Technology a catalytic process is under development in which the harmful CFC-12 is converted into the valuable, ozone friendly HFC-32 ($CH_2F_2$). With this process both the waste materials CFC-11, which can be converted into CFC-12 by use of HF, and CFC-12 can be converted.

This paper deals with the performance of a selected palladium on activated carbon catalyst with varying process conditions and the mechanism of the hydrogenolysis reaction. A preliminary process design for the conversion of recovered CFC-12 into high value added HFC-32 will be discussed. Because of the limited time available a close cooperation between catalyst development and process design is crucial.

## 2. Background

The catalytic hydrogenolysis can be represented as the reaction of CFC-12 via HCFC-22 ($CHClF_2$) to HFC-32. A high selectivity to HFC-32 can be expected because fluorine is more difficult to replace with hydrogen than chlorine as has been found, among others, by Lacher and coworkers [4–7]. All hydrogenolysis reactions starting from CFC-12 are exothermic, irreversible reactions and the formation of methane is thermodynamically most favoured. The reaction enthalpies are for the selective hydrogenolysis to HFC-32 −150 kJ/mol and for the complete hydrogenolysis to methane −320 kJ/mol. Besides hydrogenolysis also Cl–F exchange (e.g. to HFC-23) could take place. Also coupled products like ethane and propane can be formed. The complete reaction scheme for one carbon containing CFCs is depicted in Fig. 3. Several activated carbon supported noble metals have been tested. Activated carbon is chosen as support material for

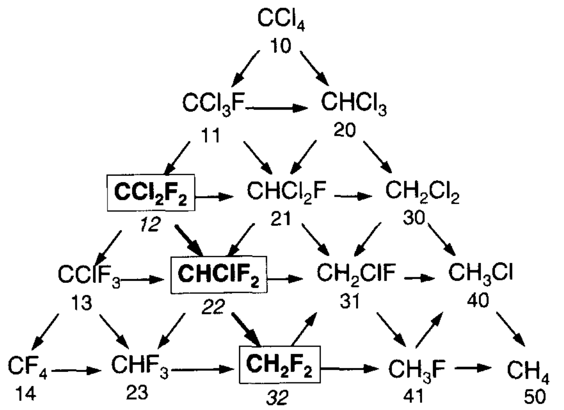

Fig. 3. Reaction scheme of $C_1$-type CFCs. The bold arrows represent the reactions aimed for.

its inertness under the corrosive reaction conditions (HF and HCl). Palladium from the group VIII elements was found to be a very suitable metal for the reaction.

## 3. Experimental

Catalysts were prepared by impregnation of a noble metal compound on an activated carbon support. The activated carbon support was treated with acid- and alkaline solution in a flow set-up prior to introduction of the noble metal. The activity tests of the CFC-12 hydrogenolysis catalysts were carried out in a Hastelloy-C microflow reactor connected to an on-line gas chromatograph with a Poraplot Q column (50 m × 0.53 mm) and a thermal conductivity detector. Reaction conditions, such as temperature, hydrogen to CFC-12 ratio, pressure and space velocity, were varied during a catalytic test. The influence of possible recycled compounds, such as HF, HCl, HCFC-22 ($CHClF_2$) and methane were tested by adding these components to the feed.

## 4. Results

An important step in the catalyst preparation is the purification of the activated carbon support. The effect of the purification procedure on the performance of a catalyst is summarized in Table 1. After purification of the activated carbon not only the conversion of CFC-12, but also the selectivity to HFC-32 is higher. The results show that the removal of impurities like Fe, Al and Cr clearly suppresses both the formation of HFC-23, which can only be formed by chlorine–fluorine exchange, and the formation of coupled products by total hydrogenolysis.

The influence of the palladium loading on the catalyst performance is shown in Fig. 4. The conversion of CFC-12 increases with increasing palladium loading. However, the selectivity to HFC-32 slightly decreases and in equal amounts more methane is produced, whereas the selectivity to HCFC-22 remains almost the same. Thus, the best palladium loading is an optimum between high conversion of CFC-12 and high selectivity to HFC-32. In our process design the choice has been made for low loading and, thus, high selectivity to HFC-32.

The catalytic behaviour of the selected palladium catalyst in the hydrogenolysis is given in Fig. 5 as a function of temperature. The results show that the palladium on activated carbon is an excellent catalyst for the selective hydrogenolysis. Over a range of temperatures, in which the conversion changes from 0% to 100%, the selectivity to HFC-32 only drops from 85% to 75%. The selectivity of the catalyst is much higher than has been reported in literature [8], where a selectivity of 60% to 70% for palladium on graphite at low CFC-12 conversions is mentioned. The minor change in selectivity is remarkable and inconsistent with kinetics of a serial reaction. The behav-

Table 1
Influence of the purification of carbon on the catalyst performance in the hydrogenolysis of CFC-12

| | Not purified | Purified |
|---|---|---|
| Conversion of CFC-12 | 78 | 85 |
| Selectivity to HFC-32 | 64 | 78 |
| Selectivity to HCFC-22 | 8 | 5 |
| Selectivity to methane | 21 | 15 |
| Selectivity to HFC-23 | 3 | 0 |
| Selectivity to ethane and propane | 3 | < 1 |

Values are in mol-%.

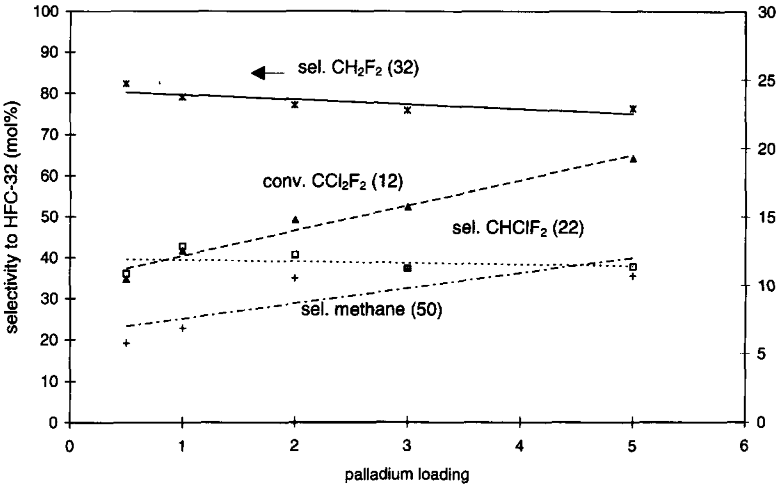

Fig. 4. Influence of palladium loading on performance.

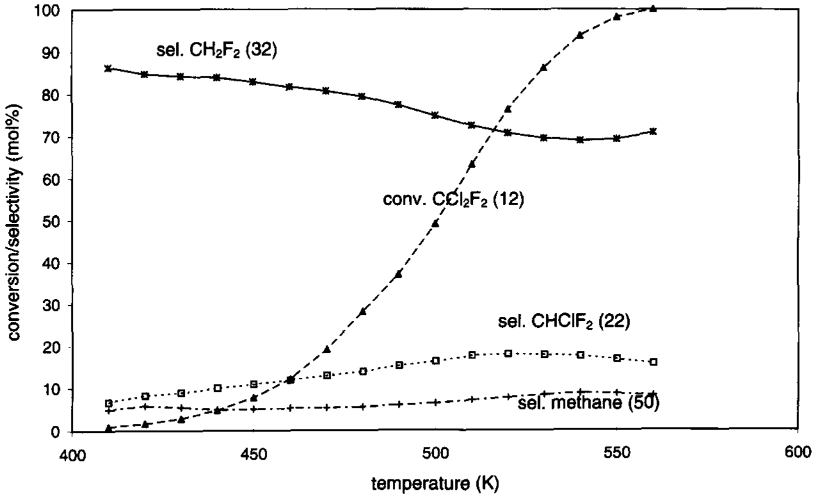

Fig. 5. Influence of temperature.

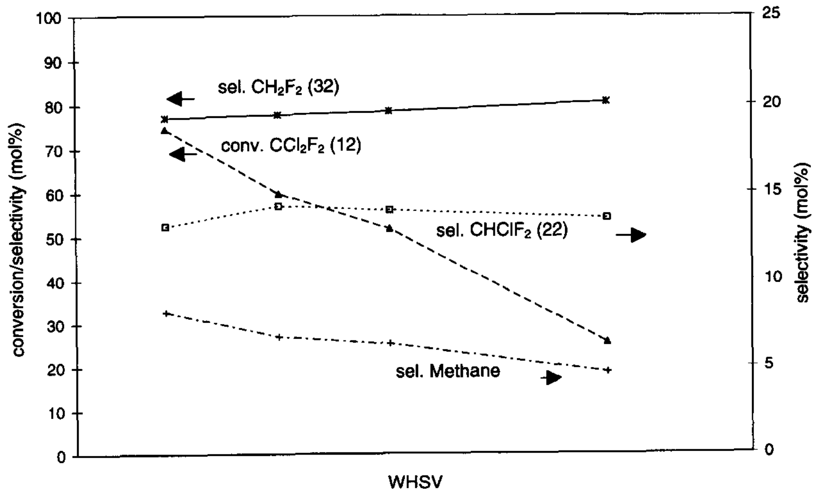

Fig. 6. Influence of WHSV.

iour of the catalyst becomes even more remarkable as one looks at the influence of the space velocity on the catalyst performance, as depicted in Fig. 6. When the space velocity is decreased, the conversion increases linearly as might have been expected. However, the selectivities to HFC-32, HCFC-22 as well as methane do not change profoundly.

For normal serial reactions the selectivity to the end product, methane, should increase with decreasing space velocity and the selectivity to the intermediate product HCFC-22 should also decrease. The results suggest different kinetics from a normal serial kinetics. The reaction rates of HCFC-22 and HFC-32 have, therefore, been compared under the same conditions at $T=540$ K. The results show that the reaction rates for CFC-12/HCFC-22 compare to 100:5. The main products of the HCFC-22 hydrogenolysis are HFC-32 (90%) and methane (10%). Hydrogenolysis of HFC-32 was not observed under those conditions.

The influence of the total pressure on the catalyst performance is weak (not shown). The conversion of CFC-12 slightly increases with increasing pressure. The highest selectivity to HFC-32 is obtained at low pressures at the expense of the formation of HCFC-22. The hydrogen to CFC-12 ratio also has a small influence on the catalyst performance (not shown). The conversion of CFC-12 slightly increases with increasing hydrogen to CFC-12 ratio, whereas the selectivity to HFC-32 increases at the expense of the formation of HCFC-22. When the amount of hydrogen is limiting, the CFC-12 conversion is proportional to the amount of hydrogen in the feed and the effect on the selectivities is more pronounced. The influences of both pressure and hydrogen to CFC ratio on the performance are the same at all conversion levels.

## 5. Discussion

Starting from CFC-12 a number of different serial reactions which in the end leads to the formation of methane are possible. In spite of the number of possible reactions only small changes in selectivity with varying process conditions are observed. These minor changes in selectivity indicate a mechanism different from serial kinetics. The large difference in reactivity between CFC-12, HCFC-22 and HFC-32 observed, leads to the conclusions that formation of HFC-32 does not take place via HCFC-22, and the methane formation not via HFC-32. Thus, it can be concluded that all the hydrogenolysis products are mainly formed by parallel reaction pathways. A possible reaction mechanism for catalytic hydrogenolysis has been proposed in literature [8]. This mechanism, which is depicted in Fig. 7a, explains many of the observations. However, it is, in our view, too complicated. We propose a less complicated mechanism, depicted in Fig. 7b, which can also explain the observed phenomena. In our proposed mechanism the first step in the hydrogenolysis of CFC-12 is dissociative adsorption of CFC-12, followed by a fast surface reaction to a $CF_2$-carbene. This carbene can be desorbed by reaction with hydrogen to give HFC-32 or can react further to $CH_2$, which gives methane. The rate determining step is the dissociative adsorption of CFC-12,

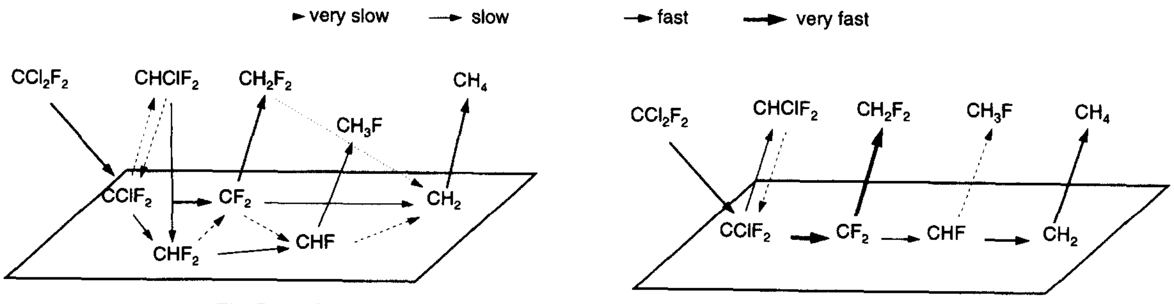

Fig. 7. (a) Suggested mechanism by Coq et al. [8]. (b) Proposed reaction mechanism.

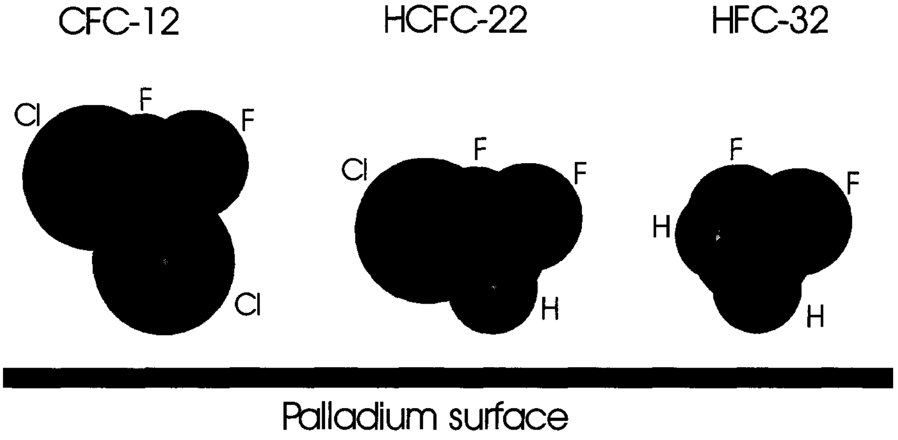

Fig. 8. Schematic model for the adsorption of CFCs on the palladium surface.

while the selectivity is determined by the reactions on the catalyst surface. Thus, the observed high selectivity to HFC-32 can be explained by rapid formation of a $CF_2$-carbene, which preferentially desorbs as HFC-32. Because of the low reactivity of HCFC-22 readsorption of HCFC-22 on the catalyst surface is a slow reaction. Readsorption of HFC-32 can also be neglected.

The large differences in reactivity of CFC-12, HCFC-22 and HFC-32 are remarkable. Because the observed selectivities in the CFC-12 and HCFC-22 hydrogenolysis to HFC-32 and methane are the same, the reactions follow most probably the same reaction pathway on the catalyst surface and the difference in the reactivity can be explained by a difference in the rate determining adsorption step. This difference might be due to a difference in bonding strength of the reacting molecule or a difference in the kinetics of the adsorption, or a combination of both.

Generally the order of the bonding strengths is $C–Cl < C–H \ll C–F$. Dissociative adsorption would, therefore, preferably include breakage of the carbon–chlorine bond. The strength of the carbon–chlorine bond in HCFC-22 is expected to be stronger than the carbon–chlorine bond in CFC-12 and, thus, the order in reactivity found is consistent with the differences in bonding strength. However, although the differences in bonding strength obviously play a role, the question remains if the large reactivity difference between CFC-12 and HCFC-22 can be explained only by this small difference in bonding strength.

Another explanation would be a difference in the kinetics of the adsorption. HCFC-22 might preferable be adsorbed with the hydrogen directed to the surface of the catalyst. The first step in the dissociative adsorption is then the breakage of the carbon–hydrogen bond, which could be a more cumbersome step. This is illustrated in Fig. 8. As can be seen form this figure the HCFC-22 and HFC-32 have to get closer to the catalyst surface than a CFC-12 molecule for sufficient interaction. Both the differences in bond strength and the steric considerations can explain the observed differences in reactivity.

The influence of the process parameters support the proposed mechanism. The rate determining step of the reaction is different from the selectivity determining steps and, therefore, selectivity and conversion are independent. Thus, the selectivity with increasing reaction temperatures hardly changes while the conversion varies between 0% and 100%. A higher total pressure leads to a higher concentration of intermediates on the catalyst surface, resulting in a decrease in the total number of vacant sites. The dissociation rate of $CClF_2$ to $CF_2$ is then decreased because this step requires an additional free site. With respect to the selectivity it is understandable that at high surface coverage the surface concentration of hydrogen is relatively low and, as a consequence, at higher pressures the selectivity to HCFC-22 increases whereas the selectivity to HFC-32 decreased.

A higher hydrogen to CFC ratio leads to a higher hydrogen concentration on the catalyst surface. This favours the desorption steps in which more hydrogen atoms are involved. Therefore, the selectivities to HFC-32 and methane increases, whereas the selectivity to HCFC-22 declines. The formation of both ethane and propane indicates the presence of both $CH_2$- and $CH_3$-intermediates on the catalyst surface. This indicates that the desorption of methane probably occurs in two steps via a $CH_3$-intermediate on the catalyst surface (not shown in the proposed mechanism).

It should be noted that in the proposed mechanism the adsorbed chlorine and fluorine atoms are not taken into account in spite of the fact that a lot of chlorine is released from CFC-12. Also the formation of coupled products like ethane and propane, is not yet described in the mechanism. More measurements have to be performed in order to determine whether chlorine and fluorine play a role in the desorption reactions and to determine whether and which other coupled products besides ethane and propane will be formed.

## 6. Process design

A preliminary process design has been made, which is based on this catalytic system. Important design considerations are the exothermicity of the reaction, a capacity of 5 kton/year, the low mechanical strength of the catalyst, and the need for the removal of HF and HCl from the products. The technical feasibility of the complete process design looks promising; there were no unavoidable barriers encountered. A scheme of the designed process is depicted in Fig. 9. In this preliminary design several assumptions in particular with respect to the reactivity of recycled products have been made.

The feed of the plant consists of recovered waste CFC-12, and therefore a pretreatment section is necessary, in which possible contaminants such as oil or water are removed, before the feed enters the reactor. Because of the highly exothermic reaction a multi-tube liquid cooled fixed bed reactor has been chosen. The product purification is divided into two steps. First the acids (HCl and HF) are removed from the product stream and subsequently the rest of the mixture is divided into three main streams: The product HFC-32, a waste stream containing methane, ethane and other byproducts, and a recycle stream. Because of the large difference in the reactivity between CFC-12 and HCFC-22, a recycling of the intermediate product HCFC-22 is perhaps not useful and possibly a once through operation with 100% CFC-12 conversion is preferred and makes the process scheme even more simple. The produced HCFC-22 could then be used for other purposes such as the production of tetrafluorethene, the monomer of PTFE. The advantage of a recycle stream is the possibility of more efficient heat control of the reactor and more flexibility in the operation conditions.

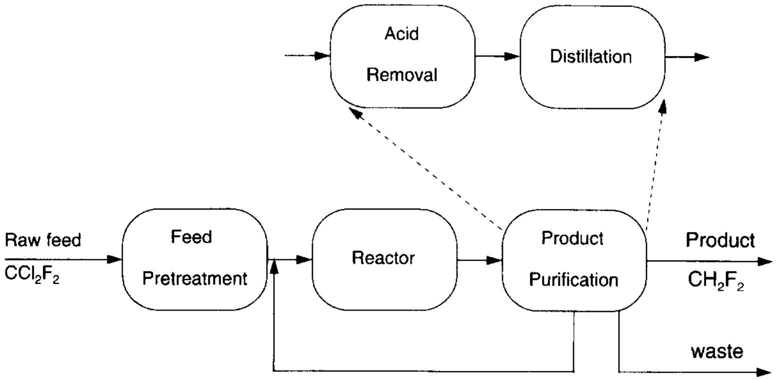

Fig. 9. Scheme of the preliminary process design.

Compared to other CFC destruction techniques, which all charge for the conversion of CFC-12, the catalytic hydrogenolysis process yields a valuable product and, therefore, has economic potential. This preliminary design can be extended to CFC-11 as feedstock because CFC-11 can be easily converted into CFC-12 in the presence of HF, using proven technology. Therefore, both CFC-11 and CFC-12 can be used as starting materials for the production of HFC-32.

## 7. Conclusions

The main products in the hydrogenolysis of CFC-12 over a selected palladium on activated carbon catalyst are HCFC-22, HFC-32 and methane. A high selectivity to HFC-32 can be combined with a high conversion (75% selectivity at 100% CFC-12 conversion). A preliminary process design has shown that the conversion of CFC-12 into high added value product HFC-32 is both technically and economically feasible. The design can be easily extended to a process for conversion of both CFC-11 and CFC-12 into HFC-32. The activated carbon support has to be purified prior to introduction of the palladium because small amounts of impurities can act as Friedel–Crafts catalyst. The mechanism of the reaction follows mainly parallel pathways. The reactivity of a component is determined by its adsorption, while the selectivity is determined by the surface reactions. The high selectivity to HFC-32 can be explained by the formation of a $CF_2$-carbene. A process based on this catalytic system could be an important tool in the protection of the ozone layer.

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