Treatment of HFC-23 by conversion to environmentally benign chemicals

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Production of HCFC-22 and HFC-23

\[ \text{CHCl}_3 + \text{HF} \rightarrow \text{CHClF}_2 + 2\text{HCl} \]

\[ \text{CHClF}_2 + \text{HF} \rightarrow \text{CHF}_3 + \text{HCl} \]

- HFC-23 is the only carbon-containing byproduct
- High purity
- One Man’s Trash, Another Man’s Treasure

# 1. Introduction

## Treatment of HFC-23

<table>
<thead>
<tr>
<th>Process optimization</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Low cost</td>
</tr>
<tr>
<td>× Difficult</td>
</tr>
<tr>
<td>× Formation of HFC-23 unavoidable</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Incineration (AM001, CDM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Non-specific</td>
</tr>
<tr>
<td>× High temperature</td>
</tr>
<tr>
<td>× Relatively expensive and diluted HF</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conversion technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Minimise C-F bond breakage</td>
</tr>
<tr>
<td>✓ Relatively low energy process</td>
</tr>
<tr>
<td>✓ Produces a useful product</td>
</tr>
</tbody>
</table>

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Jianxin Hu et al., Environmental Science & Technology, 2014, 48, 4056−4062
2. Conversion to HCFC-22

Process I: Conversion to HCFC-22

\[ \text{CHCl}_3 + \text{CHF}_3 \rightarrow \text{CHClF}_2 + \text{CHCl}_2\text{F} \]

(HFC-23) (HCFC-22) (HCFC-21)

Atmospheric pressure, <400 °C
2. Conversion to HCFC-22

Process I: Conversion to HCFC-22

Industrial production of HCFC-22

Conversion of HFC-23 to HCFC-22
2. Conversion to HCFC-22

Reaction results

Reaction of CHF$_3$ with CHCl$_3$ over catalyst developed by our team

(Atmospheric pressure, CHF$_3$/CHCl$_3$=1, 900 h$^{-1}$)
2. Conversion to HCFC-22

Reaction results

Reaction of CHF$_3$ with CHCl$_3$ over catalyst developed by our team

(Atmospheric pressure, CHF$_3$/CHCl$_3$=1, 900 h$^{-1}$)
2. Conversion to HCFC-22

Exploration of catalysts

**Catalysts**

- Conversion of CHF$_3$ (%)
  - Cr-based
  - Al-Based
  - Cr-Al based

- Selectivity of CHClF$_2$ (%)
  - Cr-based
  - Al-Based
  - Cr-Al based

**Preparation**

- Conversion of CHF$_3$ (%)
  - Mixing
  - New method
  - Precipitation

- Selectivity of CHClF$_2$ (%)
  - Mixing
  - New method
  - Precipitation
2. Conversion to HCFC-22

Reaction mechanism

Reaction of CHF$_3$ with CH$_x$Cl$_{4-x}$

Reaction of CHCl$_3$ with fluorinated carbons
3. Conversion to VDF

Process II: Conversion to VDF

\[ \text{CH}_4 + \text{CHF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{C}_2\text{F}_4 \]

(HFC-23) (VDF) (TFE)

Atmospheric pressure, 700~900°C
3. Conversion to VDF

Process II : Conversion to VDF

Rate of formation of VDF and TFE during reaction of CHF$_3$ with CH$_4$ (1:1) at 1 bar and with a residence time of 0.5 s

**At 900 °C**

- Conversion of HFC-23: 77%
- Selectivity to VDF: 27%, yield of 21%

- Byproducts: HF, TFE, CH$_2$F$_2$, C$_3$F$_6$, CH$_2$=CHF, C$_2$H$_2$, CHF$_2$CHF$_2$ and CHF=CF$_2$
- Coke formation

Wenfeng Han, et al. J. Fluorine Chem., 131(7), 2010, 752-761
3. Conversion to VDF

**CaBr₂**

**Halon 1301**

**O₂**

**Catalyst**

**CaBr₂促进作用：**

\[
\text{CHF}_3 + \text{CH}_4 \rightarrow \text{CH}_2\text{CF}_2
\]

Conversion of \( \text{CH}_4 \) and formation rate of VDF during Reaction of \( \text{CHF}_3 \) and \( \text{CH}_4 \) (1:1) on \( \text{CaBr}_2 \)

3. Conversion to VDF

**CaBr$_2$ | Halon 1301 | O$_2$ | Catalyst**

CaBr$_2$ reacts with CHF$_3$ forming CBrF$_3$ selectively.

\[ \text{CaBr}_2 + \text{CHF}_3 \rightarrow \text{CBrF}_3 \]
3. Conversion to VDF

| CaBr$_2$ | Halon 1301 | O$_2$ | Catalyst |

**Promotion of CBrF$_3$**

\[
\text{CHF}_3 + \text{CH}_4 \rightarrow \text{CH}_2\text{CF}_2
\]

At 850 °C, selectivity and yield to VDF jump to 55% and 16%, almost doubled. At 900 °C, selectivity and yield to VDF are 77% and 26.6%.

3. Conversion to VDF

<table>
<thead>
<tr>
<th>CaBr₂</th>
<th>Halon 1301</th>
<th>O₂</th>
<th>Catalyst</th>
</tr>
</thead>
</table>

Promotion of O₂

\[
\text{CHF}_3 + \text{CH}_4 \rightarrow \text{CH}_2\text{CF}_2
\]

- Conversion levels of CHF₃ and CH₄ increase with O₂/CH₄.
- At 800°C, conversion of CH₄ is increased from 4% to 45%, and while that of CHF₃ is increased from 12% to 42%.
- Yield of VDF is increased by 3 times.

Han WF, Greenhouse Gases: Science and Technology, 2017
3. Conversion to VDF

Catalytic reaction

- Transition metal oxides with variable valence possess lattice oxygen. They can function as oxygen buffer, transferring O from O\(_2\) to reaction pool. Hence, they are adopted as the catalyst for oxidative coupling of methane (OCM):

\[
\text{CH}_4 \xrightarrow{O} \text{CH}_3\cdot + \text{H}_2\text{O} \xrightarrow{O} \text{CH}_3\text{CH}_3 + \text{CH}_2=\text{CH}_2
\]

\[
\text{O} \rightarrow \text{CO, CO}_2
\]

- Similarly, catalyst of OCM can be used to co-pyrolysis of CHF\(_3\) and CH\(_4\) forming VDF:

\[
\text{CH}_4 \xrightarrow{O} \text{CH}_3\cdot + \text{CF}_2 \xrightarrow{O} \text{CF}_2\cdot \xrightarrow{O} \text{VDF} + \text{H}
\]

\[
\text{O} \rightarrow \text{CO, CO}_2
\]
3. Conversion to VDF

- Conversions over CeO$_2$ are improved significantly.

- At 860 °C, conversion of CHF$_3$ is higher than 90%, and selectivity of VDF is 83%.

- With further investigation of catalyst, reaction temperature is expected to be reduced.

Effect of CeO$_2$ on the co-pyrolysis of CH$_4$ and CHF$_3$ in the presence of O$_2$. 

Han WF, Journal of hazardous materials, submitted
3. Conversion to VDF

CaBr\textsubscript{2}  |  Halon 1301  |  O\textsubscript{2}  |  Catalyst

**OCM**

\[
\begin{align*}
&\text{CHF}_3 \xrightarrow{\text{La}_2\text{O}_3} \text{LaOF} \xrightarrow{\text{O}_2} \text{LaOF} \cdot \text{O}_2 \xrightarrow{\text{CH}_4} \text{CH}_3 \\
&H \xrightarrow{\text{CH}_4} \text{CH}_3 \\
&\text{CH}_2=\text{CF}_2 \ (\text{VDF})
\end{align*}
\]

**Co-pyrolysis**

\[
\begin{align*}
&\text{CHF}_3 \xrightarrow{\text{HF}} : \text{CF}_2 \\
&\text{H} \xrightarrow{\text{CH}_4} \text{CH}_3 \\
&\text{CH}_2=\text{CF}_2 \ (\text{VDF})
\end{align*}
\]

**Technical indicators**
- At 860 °C and 1 bar, over catalysts,
- Conversion of CHF\textsubscript{3}: 80%
- Selectivity to VDF: 83%

**Economic indicators**
- Conversion cost: 1,700 US $/ton
- Value of product: 2,700 US $/ton
- Profit: 1,000 US $/ton
Process III: Conversion to TFE and HFP

\[ \text{CHF}_3 \rightarrow \text{CF}_2=\text{CF}_2 + \text{CF}_2=\text{CFCF}_3 + 5\text{HF} \]

(HFC-23) (TFE) (HFP)

Atmospheric pressure, 750~900°C
4. Conversion to TFE and HFP

Generally, HCFC-22 is used for the production of TFE and HFP via pyrolysis. Similarly, HFC-23 can be applied.

**Reaction:**

\[
\begin{align*}
\text{CHF}_3 & \rightarrow \text{CF}_2 + \text{HF} \\
\text{CHClF}_2 & \rightarrow \text{CF}_2 + \text{HCl}
\end{align*}
\]

**Products:**

\[
\begin{align*}
\text{CF}_2 + \text{CF}_2 & \rightarrow \text{C}_2\text{F}_4 \quad ; \\
\text{CF}_2 + \text{CF}_2 + \text{CF}_2 & \rightarrow \text{C}_3\text{F}_6
\end{align*}
\]

- (TFE)
- (HFP)

**Reaction rate constant:**

\[
\begin{align*}
\text{R23: } & \quad k = 5.2 \times 10^{13} \ [\text{s}^{-1}] \ e^{-295 \pm 46 \ [\text{kJ/mol}] / RT} \\
\text{R22: } & \quad k = 3.2 \times 10^{12} \ [\text{s}^{-1}] \ e^{-220 \ [\text{kJ/mol}] / RT}
\end{align*}
\]

- HFC-23, 1 bar, >750 °C;
- HCFC-22, 1 bar, 600-900 °C
- HCFC-22 pyrolysis plant can adapt to HFC-23 pyrolysis
4. Conversion to TFE and HFP

Pyrolysis of HFC-23

- At 860 °C, TFE yield (Max.):
  - TFE: 31%
  - HFP: 16%

- Selectivity of HFP increases with temperature.
  - Yield at 900 °C:
    - TFE: 17%
    - HFP: 41%

- Coke at high temperatures:
  - At 900 °C
  - Carbon balance: 75%

4. Conversion to TFE and HFP

KF/AC catalyst enhances the conversion of CHF$_3$, yield of TFE and HFP significantly.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CHF$_3$ conversion, %</th>
<th>Selectivity, %$^c$</th>
<th>Yield, %$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-catalytic$^a$</td>
<td>15.1</td>
<td>55.9</td>
<td>8.03</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>8.45</td>
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<td></td>
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<td>1.21</td>
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<td></td>
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<td>9.66</td>
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<tr>
<td>Catalytic$^b$</td>
<td>61.1</td>
<td>33.3</td>
<td>23.6</td>
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<tr>
<td></td>
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<td>16.1</td>
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<td>14.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>34.7</td>
</tr>
</tbody>
</table>

## 5. Summary

### I. Conversion to HCFC-22
- Reaction temperature: $< 400 \, ^\circ C$
- Conversion of CHF$_3$: $> 30\%$
- Selectivity of HCFC-21 and HCFC-22: $> 95\%$
- Treatment profit: $\geq 450$ USD/ton

### II. Conversion to VDF
- Reaction temperature: 700-900$^\circ$C
- Conversion of CHF$_3$: 80% (860 $^\circ$C)
- Selectivity of VDF: $> 83\%$ (860 $^\circ$C)
- Treatment profit: $\geq 1,000$ USD/ton

### III. Conversion to TFE and HFP
- Reaction temperature: 750-900$^\circ$C
- Conversion of CHF$_3$: 60% (800 $^\circ$C)
- Selectivity of TFE: $> 33\%$ (800 $^\circ$C)
- Selectivity of HFP: $> 23\%$ (800 $^\circ$C)
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Thanks for your attention!

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