



HFO-1234ze AS BLOWING AGENT IN THE MANUFACTURE OF EXTRUDED POLYSTYRENE FOAM BOARDSTOCK

AN ASSESSMENT FOR APPLICATION IN MLF PROJECTS

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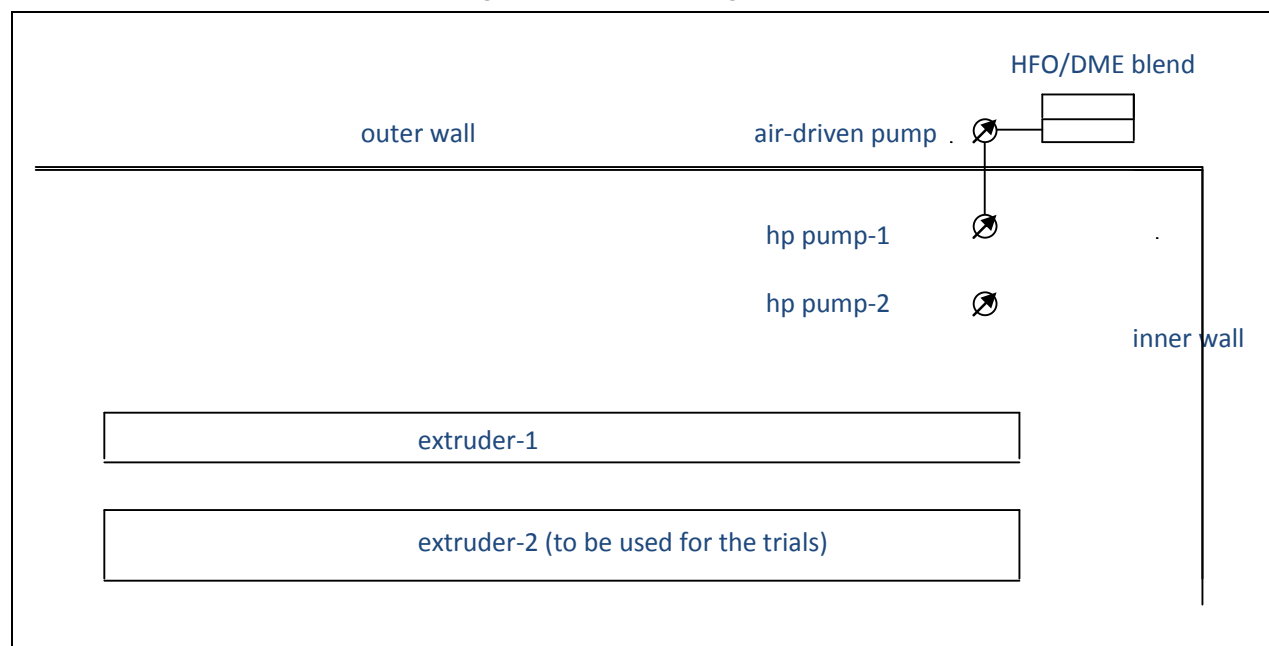
EXECUTIVE SUMMARY

This project is designed to assess the use of HFO-1234ze in a developing country context. HFO-1234ze appears to offer equal climate impact advantages as hydrocarbons without the fire risk and promises improved insulation values compared with other HCFC replacements in extruded polystyrene (XPS) plank.

The project has been divided into

- **Preparatory activities** – which consisted of an implementation Inception Meeting which took place July 6, 2010 and during which the modifications and hardware needed for the trials, the qualities to be trialed, the related testing and the timing were discussed.
- **Trial Preparations** – under which B-PLAS prepared the trial configuration as designed and installed the procured testing equipment. This part is completed as well.
- **Procurement of Testing Equipment and Chemicals** – which included an insulation tester, a closed cell counter and the HFO gas. For cost and processing reasons, HFO-1234ze has been blended by the supplier with DME. At a later stage DME has been directly injected as a co-blowing agent.
- **Trials/Testing** – Before the trials, B-Plas installed an air powered booster pump along the following configuration:

Fig-1: B-Plas Trial Configuration



The products trialed were tested for:

- Thickness
- Density
- Cell Size
- Compressive Strength
- Lambda Value
- Flammability
- Dimensional Stability

- **Assessment** – After the trial results are in, the stakeholders will assess the results and decide how to use these. Follow-up trials and assessments would be conducted as needed. The assessments will then be incorporated in a final assessment report along with recommendations for future use of HFO-1234ze.

The first trials were conducted March 8-11, 2011 and evaluated April 4, 2011. Following observations were made:

- The produced foam sheet's surface properties were pronounced unacceptable
- Physical test results were acceptable

It was decided to conduct a new round of trials on a different production line to eliminate impact of equipment. Because of heavy production commitments these trials could not be made before December 23/24, 2011. The new trials were made starting with the original formulation followed by a new formulation and then again the original formulation. These trials were initially, again, not good in surface and showed large longitudinal pinholes. Adding DME as co-blowing agent improved the product to an acceptable level, although some optimization in density and surface quality will still be needed. Because of the high amount of DME, the blowing agent blend is flammable and proper precautions are needed and outlined in the assessment. An assessment of operating costs could not be completed because of lack of data. From the trials results it was concluded that

- HFO-1234ze XPS foams match HCFC as well as HFC-based foams in insulation and structural properties;
- HFO solubility in the XPS blend appears to be critical. A relatively large amount of co-blowing agent appears necessary to achieve proper processing and cell structure. Alternatively, the equipment used for the trials could be a critical factor;
- Based on the current trials, HFO-1234ze needs 50% co-blowing to be acceptable in processing. If this can be reduced, it is to be expected that the insulation properties of HFO-1234ze will be superior to any other HCFC alternative.

Following recommendations are offered:

1. HFO-1234ze can replace the HCFCs and/or high GWP HFCs in XPS plank while providing acceptable thermal insulation and structural properties;
2. To make this commercially acceptable optimization of density and surface (pinholes!) will be required;
3. The conversion requires equal amounts of DME as co-blowing agent making the blend flammable therefore requiring adequate process safeguards. These are described in the assessment;
4. There is potential to improve thermal insulation performance by reducing the relative amount of DME. This would require further trials for which funding is currently not available. UNDP recommends to continue this project as follows:
 - Duplicate the trials with HFO-1234ze/DME (50/50) on different equipment
 - If these trials are successful, repeat with a 70/30 blend
 - If this is also successful, then there is an equipment compatibility issue at hand with the extruders used in the UNDP trials
 - In that case, continue with an 80/20 blend. The outcome will allow through extrapolation prediction of expected insulation values and provide the manufacturer with a choice between the best insulation (highest amount of HFO) or best cost price (highest amount of DME)

1. Introduction

XPS foam panels have their most important application in buildings to provide thermal insulation. Decisions about thermal insulation are among the most important one will make relative to the environmental impact of buildings. Because insulation reduces energy consumption, it provides ongoing environmental benefits throughout a building's life. However, not all insulation materials are equal environmentally. In assessing the environmental characteristics of insulation materials, one needs to consider a broad range of issues relating to their effectiveness, production and use. This chapter addresses in sequence

- The general principles of heat transfer
- How different insulation materials compare, and
- The impact of blowing agents in thermal insulation

1.1 Thermal Conductivity

Thermal conductivity is defined as the ability of a material to conduct ("transfer") heat. An important function of rigid PU and PS foams is to resist the conduction of heat. Therefore, understanding heat and heat transfer theory is an important factor in understanding thermal conductivity. Heat transfer is a characteristic of a process and is not statically contained in matter. *Heat* is often taken as synonymous to thermal energy. Heat transfer is classified into various mechanisms, such as

- **Conduction** also called diffusion is the transfer of energy between objects that are in physical contact
- **Convection** is the transfer of energy between an object and its environment, due to circular fluid motion
- **Radiation** is the transfer of energy to/from a body through emission or absorption of electromagnetic radiation
- **Mass transfer** is the transfer of energy from one location to another as a side effect of physically moving an object containing that energy.

These mechanisms are explained in more detail below:

Conduction - On a microscopic scale, heat conduction occurs as hot, rapidly moving or vibrating atoms and molecules interact with neighboring atoms and molecules, transferring some of their energy (heat) to these neighboring particles. In other words, heat is transferred by conduction when adjacent atoms vibrate against one another, or as electrons move from one atom to another. Conduction is the most significant means of heat transfer within a solid or between solid objects in thermal contact. Fluids—especially gases—are less conductive. Thermal contact conductance is the study of heat conduction between solid bodies in contact. *Steady state conduction* (see Fourier's law) is a form of conduction that happens when the temperature difference driving the conduction is constant, so that after an equilibration time, the spatial distribution of temperatures in the conducting object does not change any further.^[7] In steady state conduction, the amount of heat entering a section is equal to amount of heat coming out. *Transient conduction* (see Heat equation) occurs when the temperature within an object changes as a function of time. Analysis of transient systems is more complex and often calls for the application of approximation theories or numerical analysis by computer.

Convection - Convective heat transfer, or convection, is the transfer of heat from one place to another by the movement of fluids. (In physics, the term *fluid* means any substance that deforms under shear stress; it includes liquids, gases, plasmas, and some plastic solids). Bulk motion of the fluid enhances the heat transfer between the solid surface and the fluid.^[8] Convection is usually the dominant form of heat transfer in liquids and gases. Although often discussed as a third method of heat transfer, convection actually describes the combined effects of conduction and fluid flow. Free, or natural, convection occurs when the fluid motion is caused by buoyancy forces that result from density variations due to variations of temperature in the fluid. *Forced* convection is when the fluid is forced to flow over the surface by external means—such as fans, stirrers, and pumps—creating an artificially induced convection current. Convective heating or cooling in some circumstances may be described by Newton's law of cooling: "The rate of heat loss of a body is proportional to the difference in temperatures between the body and its surroundings." However, by definition, the validity of Newton's law of cooling requires that the rate of heat loss from convection be a linear function of ("proportional to") the temperature difference that drives heat transfer, and in convective cooling this is sometimes not the case. In general, convection is not linearly dependent on temperature gradients, and in some cases is strongly nonlinear. In these cases, Newton's law does not apply.

Radiation - Thermal radiation is energy emitted by matter as electromagnetic waves due to the pool of thermal energy that all matter possesses that has a temperature above absolute zero. Thermal radiation propagates without the presence of matter through the vacuum of space. Thermal radiation is a direct result of the random movements of atoms and molecules in matter. Since these atoms and molecules are composed of charged particles (protons and electrons), their movement results in the emission of electromagnetic radiation, which carries energy away from the surface. Unlike conductive and convective forms of heat transfer, thermal radiation can be concentrated in a small spot by using reflecting mirrors, which is exploited in concentrating solar power generation. For example, the sunlight reflected from mirrors heats the PS10 solar power tower and during the day it can heat water to 285 °C (545 °F).

Mass Transfer - In mass transfer, energy—including thermal energy—is moved by the physical transfer of a hot or cold object from one place to another. This can be as simple as placing hot water in a bottle and heating a bed, or the movement of an iceberg in changing ocean currents. A practical example is thermal hydraulics.

Applied to the function of XPS foam panels following heat-transfer principles apply:

Insulation - Thermal insulators are materials specifically designed to reduce the flow of heat by limiting conduction, convection, or both. Radiant barriers are materials that reflect radiation, and therefore reduce the flow of heat from radiation sources. Good insulators are not necessarily good radiant barriers, and vice versa. Metal, for instance, is an excellent reflector and a poor insulator. The effectiveness of an insulator is indicated by its **R-value**, or resistance value. The R-value of a material is the inverse of the conduction coefficient (*k*) multiplied by the thickness (*d*) of the insulator. In most of the world, R-values are measured in SI units: square-meter kelvin per watt (m²·K/W). In the United States, R-values are customarily given in units of British thermal units per hour per square-foot degrees Fahrenheit (Btu/h·ft²·°F).

$$R = \frac{d}{k}$$
$$C = \frac{Q}{m\Delta T}$$

Critical insulation thickness - Low thermal conductivity (k) materials reduce heat fluxes. The smaller the k value, the larger the corresponding thermal resistance (R) value. Thermal conductivity is measured in watts-per-meter per kelvin ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), represented as k . As the thickness of insulating material increases, the thermal resistance—or R-value—also increases. However, adding layers of insulation has the potential of increasing the surface area, and hence the thermal convection area. For example, as thicker insulation is added to a cylindrical pipe, the outer radius of the pipe-and-insulation system increases, and therefore surface area increases. The point where the added resistance of increasing insulation thickness becomes overshadowed by the effect of increased surface area is called the critical insulation thickness. In simple cylindrical pipes, this is calculated as a radius:

$$R_{\text{critical}} = \frac{k}{h}$$

Buildings - In cold climates, houses with their heating systems form dissipative systems. In spite of efforts to insulate houses to reduce heat losses via their exteriors, considerable heat is lost, which can make their interiors uncomfortably cool or cold. For the comfort of the inhabitants, the interiors must be maintained out of thermal equilibrium with the external surroundings. In effect, these domestic residences are oases of warmth in a sea of cold, and the thermal gradient between the inside and outside is often quite steep. This can lead to problems such as condensation and uncomfortable air currents, which—if left unaddressed—can cause cosmetic or structural damage to the property. Such issues can be prevented by use of insulation techniques for reducing heat loss. Thermal transmittance is the rate of transfer of heat through a structure divided by the difference in temperature across the structure. It is expressed in watts per square meter per kelvin, or $\text{W}/\text{m}^2\text{K}$. Well-insulated parts of a building have a low thermal transmittance, whereas poorly-insulated parts of a building have a high thermal transmittance. A thermostat is a device capable of starting the heating system when the house's interior falls below a set temperature, and of stopping that same system when another (higher) set temperature has been achieved. Thus, the thermostat controls the flow of energy into the house, that energy eventually being dissipated to the exterior.

1.2 Comparison of Insulation Materials

XPS belongs to the top insulation materials available. While rigid PU foam provides an even more effective insulation, XPS foams, being lower in weight and costs, are frequently preferred. The following comparison shows the performance of the most important insulation materials (thickness in mm to give $0.4 \text{ W}/\text{m}^2\text{K}$ insulation):

Table-2: Comparison of Insulation Materials

MATERIAL	THICKNESS
polyurethane	60
extruded polystyrene	80
expanded polystyrene	90
mineral wool	95
glass fiber	100
light weight block	400

The data provided are approximations. Optimized polystyrene foam may perform better than a non-optimized polyurethane foam. Of importance, apart of—and even more than—the base material is the cell gas applied and the cell size.

1.3 Impact of the Blowing Agent

Blowing agents in XPS are solely physical blowing agents. They are introduced in the production extruder under pressure as a liquid but, upon exiting the extruder they turn into a gas and, in the process, expand the polystyrene blend into a cellular foam and fill the cells. As a cell gas, the blowing agent impacts the conductivity of the foam. For a given foam type, the less the thermal conductivity of the blowing agent, the better the insulation value of the foam is. Other criteria for blowing agents are:

- o solubility in the resin,
- o worker safety (flammability, toxicity),
- o consumer safety (toxicity),
- o thermal and chemical stability,
- o diffusivity,
- o environmental impact.

Extruded polystyrene foams can be categorized into sheet and boardstock. Sheet is mostly used for food applications and insulation requirements are modest. For boardstock, however, good thermal insulation is critical. Therefore, while virtually all CFC that was originally used in sheet has been converted to hydrocarbons, boardstock has initially been converted to more thermal efficient HCFCs and then later, where forced by regulations, to a mixture of the following options:

Table-1: HCFC Replacements for XPS board

Substance	GWP	MW	Δ GWP	Observations
HCFC-142b/22 (75/25)	2185	97	Baseline	Not allowed in MLF projects
HCFC-22	1810	87	-562	
HCF-134a	1430	102	-681	Expensive; performance
HFC-152a	124	66	-2101	Flammable, performance
HFC-152a/DME (75/25)	85	61	-2132	Flammable, performance
(Iso) butane, LPG	4	58	-2183	Flammable , performance
CO ₂ (gas/liquid)	1	44	-2185	In combinations only; performance

It should be noted that

- All options mentioned, except perhaps HFC-134a, are lower (less good) than the baseline in thermal insulation performance
- HFC-134a, however, shows from all replacement options the largest global warming effect
- HFC-152a and hydrocarbons are flammable
- Because of solubility issues, most replacements need a co-blowing agent

The UNEP Foams Technical Options Committee (FTOC) mentions therefore that the phaseout of HCFCs in developed countries *“has been—and continues to be—a problem”*. North American XPS boardstock producers use HFC blends, CO₂ (LCD) and hydrocarbons. The significant variety in products required to serve the North American market (thinner and wider products with different thermal resistance standards and different fire-test-response characteristics) require different solutions than in Europe where the use of HFC-134a, HFC-152a and CO₂ prevails and Japan, where the use of hydrocarbons is significant.

However, recently introduced so called F-Gas regulations in Europe may change the scenario in that region as HFC-134a will have to be phased out. With so many uncertainties it is a challenge to provide guidance to developing countries.

The manufacture of XPS boardstock has traditionally been an insignificant market in the developing world. However, the FTOC mentions that recently production took off in China and Turkey. In addition, there is rapidly increasing production in Argentina, Egypt, Saudi Arabia, Kuwait, Brazil and Mexico. This increase in prominence, in addition to the mentioned lack of comparable performance requires a close look at potential HCFC phaseout options.

Blowing agent manufacturers are diligently working on a new generation of blowing agents that aim to combine zero ODP and good thermal insulation properties with low GWP. However, the horizon for industrialization in industrialized countries is around 2015 which would imply that any phaseout efforts in A5 countries would not initiated before 2016 and therefore not contribute to phase-1 of the HCFC phaseout strategy of these countries ("freeze + 10 %").

There is one exception and that is HFO-1234ze. This substance, which is produced by Honeywell, is already industrially applied by one-component PU foam (OCF) manufacturers in Europe which were in July 2008 struck by a ban on the use of HFC-134a and needed a replacement urgently. Indicative trials show promise for the use of this substance in XPS boardstock as well.

This project was designed to assess the use of HFO-1234ze in a developing country context. HFO-1234ze appears to offer equal climate impact advantages as hydrocarbons without the fire risk and promises improved insulation value compared with other HCFC replacements.

Technology validation is a global task. Experience gained in one country can be applied in MLF-sponsored XPS projects worldwide and could save in this way millions of dollars in addition to making costs more transparent. Past experience in the HCFC phaseout in PU foams has shown this.

2. Project Design

This project has been implemented under the supervision of the Government of Turkey. The UNDP Country Office in Turkey has been in charge of the implementation activities. The activities have been conducted at the facilities of Bursa Plastic Corporation (B-Plas). The company was selected on recommendation by the XPS Association. The implementation consisted of:

1. Preparatory Activities;
2. Trials/Testing
3. Assessment

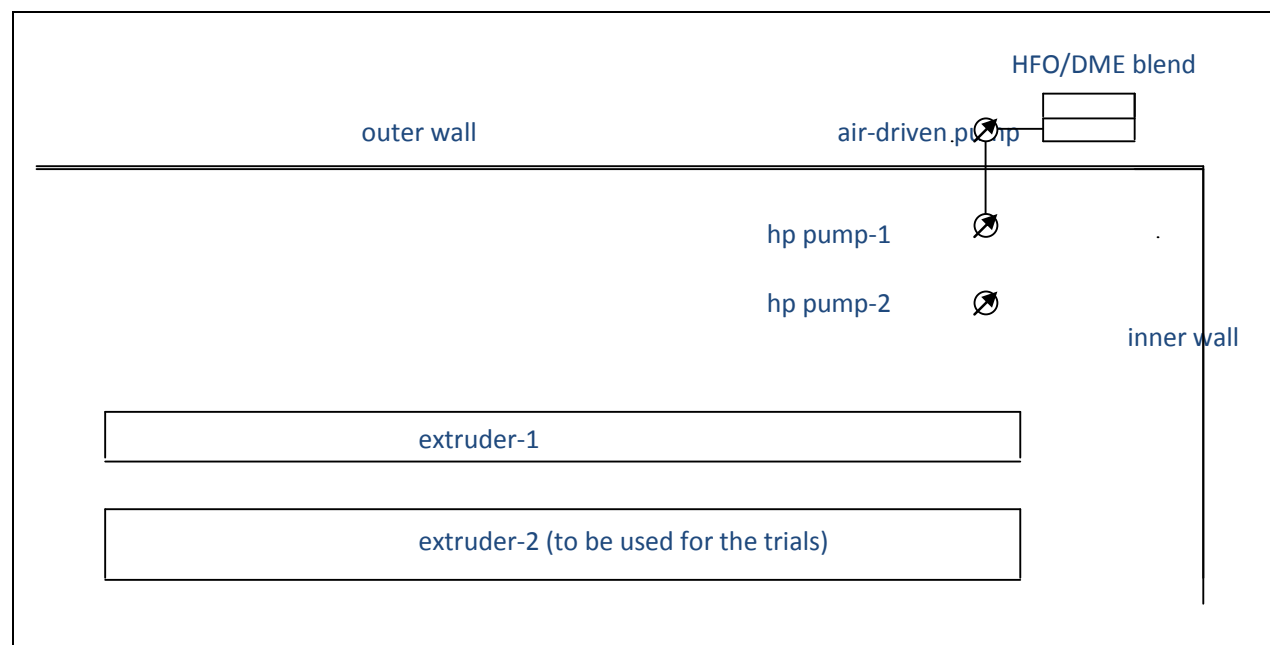
These activities are discussed in detail below.

1. Preparatory activities – these consist of

- **Implementation Inception Meeting** – during this meeting, at BPLAS, which took place July 6, 2010, the modifications and hardware needed for the trials, the qualities to be trialed, the related testing and the timing was discussed.
- **Trial Preparations** – B-PLAS prepared the trial configuration as designed and installed the procured testing equipment. Additional testing was conducted by a certified laboratory.
- **Procurement of Testing Equipment and Chemicals** – these included an insulation tester and the HFO gas. For cost and processing reasons, HFO-1234ze has been blended by the supplier with DME. At a later stage DME has been directly injected as a co-blowing agent.

2. Trials/Testing – Before the trials, B-Plas installed an air powered booster pump along the following configuration:

Fig-1: B-Plas Trial Configuration



Following is the initial formulation, based on a dry rate of 300 kg/hr:

- Sabic Virgin PS MFI 7 97%
- Recycle PS 0.0%
- Flame-retardant 1.5%
- Talcum 1.5%
- Color 0.0%
- Blowing Agent 8.0% (might be varied during trials)

Trial products were continuous planks of 30 mm X 600 mm and 40 mm X 600 mm

The products were tested for:

- Thickness
- Density
- Cell Size
- Compressive Strength
- Lambda Value
- Flammability
- Dimensional Stability

Samples were retained from each trial and tested on:

- Compressive Strength after: 10 days 20 days 30 days
- Lambda values after: 10 days 20 days 30 days
- Dimensional Stability: 1 bundle of each sample

3. Assessment – After the 30 days trial results were assessed by the stakeholders. The outcome of the first trials was not satisfactory and a new set of trials was conducted and assessed. B-Plas prepared extended reports on these trials that are appended to this report.

3. Implementation

3.1 Health, Safety and Environment (HSE)

HFO-1234ze is a hydrofluoroolefin developed by Honeywell as a fourth generation blowing agent aimed to replace HCFCs or HFCs. HFOs are also known as unsaturated HFCs but this name creates confusion as they replace (saturated) HFCs as well. Comparative properties are as follows:

Table-2: Comparative properties of blowing agents

Property	HCFC-142b	HCFC-22	HCFC-142b/-22 (75/25) ¹	Isobutane	DME	HFC-152a	HFC-134a	HFO-1234ze
Molecular Weight	100	86	97	58	46	66	102	114
Boiling Point (°C)	-9	-41	-25 ²	-12	-25	-27	-26	-19
TLV or OEL (ppm)	1000	1000	1000	800	500	1000	1000	1000 ³
LEL/UEL(vol% in air)	6-18	None	8-24	1.8-8.4	3.3-18	3.8-21.8	None	None ⁵
Λ (mW/m ² K @ 10°C)	8.4	9.9	8.7	16 (20°C)	17 (20°C)	14 (25°C)	12.4	13 ⁴
ODP	0.066	0.05	0.063	0	0	0	0	0
GWP	2270	1810	2185	4	2	124	1430	6

Notes: ¹linear weighted averages

²there may be a boiling point range

³recommended

⁴not known at what temperature

⁵however, at 30°C LEL/UEL values of 7.0/9.5 exist

Apart from the molecular weight, the comparison appears favorable for HFO-1234ze. However, it should be kept in mind that the original baseline, CFC-12, has a molecular weight of 121 and that other factors determine the blowing efficiency as well! A safety data sheet and a technical data sheet are attached (**Attachment II, III**).

Atmospheric Chemistry

In general, hydrofluoroolefins—being unsaturated hydrofluorocarbons—will have shorter atmospheric life times than saturated hydrofluorocarbons. This is evident from their much lower GWPs. However, the issue of decomposition products may be brought up. The University of Copenhagen conducted a study on the atmospheric chemistry of HFO-1234ze¹. While trifluoroacetic acid (HFA) is mentioned as a major final breakdown product, this is a natural component of the background oceanic environment and any environmental burden associated with trans CF₃CH=CHF oxidation will be of negligible environmental significance. The study concludes “that the products of the atmospheric oxidation of trans-CF₃CH=CHF will have negligible environmental impact.” (**Attachment IV**)

The USEPA (**Attachment-V**) came to the same conclusion when evaluating HFO-1234ze under the Significant New Alternatives Policy (SNAP) program². EPA’s decision states that:

Hydrofluoroolefin (HFO)–1234ze is acceptable as a substitute for CFCs and HCFCs in:

- **Rigid Polyurethane Appliance Foam.**
- **Rigid Polyurethane Spray, Commercial Refrigeration, and Sandwich Panels.**
- **Polystyrene Extruded Boardstock & Billet.**

¹ M.S. Javadi et al, Atmospheric chemistry of trans-CF₃CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation

² Federal register / Vol. 74, No 188 / Wednesday, September 30, 2009 / rules and regulations, pg 50129 ev

Toxicity

The toxicity of HFO-1234ze has been relatively extensively researched. Following table summarizes current information—which shows low toxicity levels:

Table-3: HFO-1234ze Toxicology Assessment

Test		Results
Cardiac Sensitization		No Effect to 120,000 ppm
Genetic Testing:	Mouse micronucleus Ames assay	Not Active at 100,000 Not Active at 50,000 ppm
Acute Inhalation		LC50>400,000 ppm
Chromosome Aberration Test:	Inhalation: 2 week Inhalation 4 week	Test Complete Test Complete
Unscheduled DNA Synthesis	rat; 4 week @15,000	Not Active
Bone Marrow Micronucleus Formation rat; 4 week@ 15,000		Not Active
Carcinogenicity Screen Test		Complete
Metabolism Study		Underway
Inhalation	13 week	Test Complete
Developmental Toxicity Pilot Test		Complete

Based on these data as well as other data mentioned in Attachments III-V, HFO-1234fa is assumed to be a non-ODP/insignificant GWP substance with low toxicity and valid for XPS applications—as is already the case in one component PU foams.

3.2 System Processability

HFO-1234ze needs to be shipped in pressurized containers (1,000 kPa or 10 Bar), identical to CFC-11, HCFC-142a and HCFC-22 ones. When kept out of sunlight and a room temperatures (<25⁰ C), the substance is stable for at least one year. No data on solubility in the polystyrene matrix are known but in all tested plastics except PTFE, absorption is less than 1% (PTFE 2%).

Because the gas is not chemically aggressive or flammable, it can be processed on the same equipment as currently used for HCFC-142b, HCFC-22 and HFC-134a.

3.3 Process Trials and Evaluation

Several challenges caused delays in conducting the trials, such as

- Picking a time that the production at B-Plas would allow freeing up an extruder for three days
- Finding a contractor that would blend HFO-1234ze with DME
- Shipping/receiving HFC-1234ze, which was never before imported in Turkey
- Getting the test equipment lined up

Trials were finally conducted March 8-11, 2011 and evaluated April 4, 2011.

B-Plas prepared an extensive report on these trials (**Attachment-V**) that included:

- Information on formulations and processing conditions
- Test results, on 10 and 20 days age of the trial materials

Following observations were made:

- The produced foam sheet's surface properties are not meeting standards and pronounced unacceptable
- Physical test results are acceptable

It was decided that a new round of trials would be needed. This was done on B-Plas' second production line to assess impact of equipment. Because of heavy production commitments these trials could not be conducted until December 23/24, 2011. The new trials were made starting with the original formulation followed by revised formulations. An extended report, prepared by B-Plas, can be found in **Attachment-VI**. These trials were initially, again, not good in surface and showed large longitudinal pinholes. An additional DME supply was then rigged to the extruder and the amount of DME was increased to 50%. Following observations were made:

- At HFO-1234ze/DME 50/50 , a good product was obtained
- Some further surface optimization would be needed. However, material was short and budget depleted, so that further optimization could not be taken on
- Physical test results are acceptable with the k-value equal to the base line (HCFC-142b/-22) and better than the current blowing agent as shown below:

Table-4: Comparison of Past and Current Blowing Agents at B-Plas

Tests	Standard	Unit	50/50% HFO1234ze/DME	75/25% 152a/DME	¹ 50/50% 152a/DME	² 75/25 142b/22a
Thermal conductivity	TS EN 12667	W/mK	0.030	0.035	0.032	0.028

¹ Current blowing agent

² Original blowing agent

Attachment VIII provides a more detailed comparison.

4. Conversion Costs

4.1 Incremental Capital Costs

HFO-1234ze can be metered with the same dosing pump and from the same tank as HCFC-142b/-22. Therefore, conversion can basically be made without any capital costs apart from trials and testing. However, with the higher costs of HFOs, it would be advisable to meter DME separately so that its use can be optimized depending on the customers' specifications. This would imply that a separate stream—tank, booster pump, metering pump, connecting piping—would have to be installed. As DME is flammable (but not explosive!), proper precautions need to be incorporated. A very tentative budget for such a conversion would be:

• Pressurized Tank	US\$ 50,000 – 60,000
• Booster pump	US\$ 5,000 – 5,000
• Metering pump	US\$ 30,000 – 50,000
• Miscellaneous safety (grounding, ventilation, sensors)	US\$ 15,000 – 25,000
• Laboratory equipment (k-tester, pycnometer)	US\$ 25,000 – 40,000
• Technology Assistance, Trials, Testing	US\$ 30,000 – 30,000
• Contingencies (~10%)	US\$ 15,000 – 20,000
• Total	US\$170,000 – 210,000

4.1 Incremental Operating Costs

UNDP prepared the following comparison of HFO-1234ze/DME 50/50 with HFC-152a/DME 50/50:

Table 5: cost comparison between different blowing agents

Chemical	Formulation (%)	Costing HFC-152/DME		Costing HFO-1234ze/DME	
		Price (€/kg)	Price (€)	Price (€/kg)	Costs (€)
Resin	90.0	1.40	1.26	1.40	1.26
Flame Retardant	1.4	8.50	0.12	8.50	0.12
Nucleating Agent	1.4	2.2	0.03	2.2	0.03
Blowing agent	7.2	2.65	0.19	7.35	0.53
Costs (€/kg)			1.60		1.94
Difference (%)					21

The difference is substantially and probably more than the market can bear. However, the difference with the baseline (HCFC-142b/-22) and the most prevalent replacement (HFC-134a) is much less. UNDP does not have sufficient process and cost information to calculate these.

5. Conclusions

Based on the information presented in this report and its attachments it is concluded that:

5.1 Health, Safety, Environment

- The use of HFO-1234ze does not create incremental health concerns;
- HFO-1234ze is inert, not flammable and in itself does not require any related safety precautions;
- HFO-based blowing agent blends do not pose an environmental hazard based on current knowledge. Its atmospheric profile is benign, there is no ODP and its global warming potential is negligible.

5.2 System Processability

- Based on blowing potential at equimolecular comparison, HFO 1234ze requires almost the same mass as CFC-12 but 15% more than HCFC-142b and HFC-134a and 70% more than HFC-152a. The customary co-blowing with DME will flatten these differences to some extent;
- Shipment and storage of HFO-1234ze must take place in pressurized containers—which is the case for all other competing blowing agents as well and therefore no incremental burden;
- The shelf life for HFC-1234ze is at par with most other alternatives;
- Flammability of HFO-1234ze/DME 50/50 requires process safeguards. However, the blend is not explosive.

5.3 Foam Properties

- HFO-1234ze-based XPS foams match HCFC as well as HFC-based foams in insulation properties and structural properties;
- The resulting foam from the assessment trials will need surface and density optimization to be commercially acceptable;
- The amount of co-blowing agent appears critical for processing and cell structure. Alternatively, the equipment used for the trials could be a critical factor. Further trials will be needed on other equipment to assess the impact of the extruder;
- **Based on the current trials, HFO-1234ze needs 50% co-blowing with DME to be acceptable in processing. If this can be reduced, it is to be expected that the insulation properties of HFO-1234ze will be superior to other HCFC alternatives and can match those of HCFC-142b/-22.**

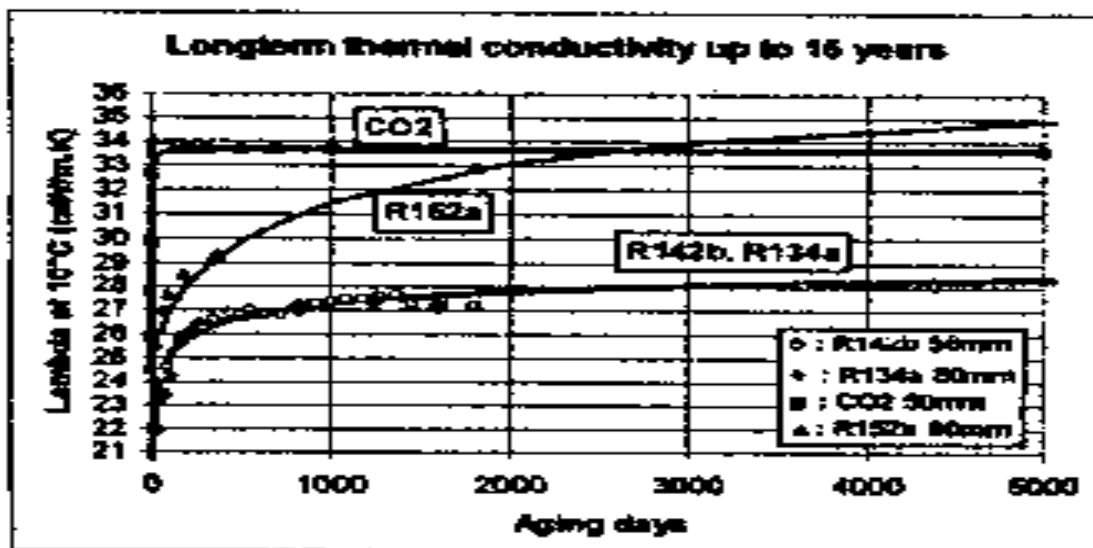
5.4 Conversion Costs

- HFO-1234ze is non-flammable and can be used with the same equipment as HCFC-142b/-22. However, the large amount of DME as co-blowing agent will make the blend flammable. UNDP estimates investment conversion costs therefore around US\$ 200,000, as detailed under 4.1;
- Most other current non-ODS/low GWP, however, show very similar or even more severe flammability characteristics;
- A preliminary operational costs analysis indicates a substantial increase of up to 21% compared to using HFC-152a/DME 50/50.

6. Recommendations

6.1 Preface

HFO-1234ze is the only non-ODP/low GWP blowing agent that shows the potential to replace HCFCs in XPS foam without compromising insulation performance. The following graph, showing other alternatives, illustrates this:



However, the price of HFO-1234ze might only justify its use in high performance higher end of the market while the less demanding lower end of the market might be served with HFC-152a and/or CO2—both with a co-blowing agent. In at least one case an MLF project reflects option this already.

The solubility of HFO-1234ze in the polymer blend requires incorporation of a co-blowing agent—which reduces the insulation performance. Alternatively, a retrofit of the extruder to improve solubility or to decrease its impact might allow the full benefit of the inherent insulation performance of HFO-1234ze. The project budget did not allow investigating the latter option.

The project budget also did not allow full optimization of product surface and density. The result is that a potential user of HFO-1234ze still has to conduct optimization trials that can reach from product fine-tuning all the way through extruder retrofit. Rather than having every company coping with this on an individual basis, an extension of the current pilot project to include these items would be a more cost-effective option

Based on these observations, UNDP recommends to continue this project as follows:

- Retrofit the current extruder to improve the solubility of the blowing agent;
- Do trials with the HFO-1234ze/DME 50/50 to optimize surface and density;
- If these trials are successful, conduct repeat trials with a 70/30 blend;
- If this is also successful, then the equipment compatibility issue is proven.
- In that case, continue with an 80/20 blend. The outcome will allow through extrapolation prediction of expected insulation values and provide the manufacturer with a choice between the best insulation (highest amount of HFO) or best cost price (highest amount of DME);

- If the retrial with a 70/30 blend is not successful, another co-blowing agent might be needed. This could be methyl formate and UNDP will look into the results of the Chinese MF project before taking any action;
- Processability for thinner board such as below 30 mm will be studied as well in more detail to apply the results to those countries which operate within these ranges.

It is expected that for this follow-up assessment following costs will be incurred

1. Retrofit of existing extruder	US\$ 65,000
2. Surface/density trials	US\$ 25,000
3. 70/30 blend trials	US\$ 25,000
4. 80/20 blend trials	US\$ 25,000
5. Final optimization trials	US\$ 25,000
6. Contribution Honeywell (provision of HFO-1234ze at no costs)	US\$ -15,000
<u>Total</u>	<u>US\$ 150,000</u>

The Executive Committee may wish to consider whether to grant UNDP additional funding based on the above justification or accept the assessment “as is” and allow UNDP to discontinue its work on this HFO demo project.

60th Meeting of the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol

COUNTRY:	Turkey	IMPLEMENTING AGENCY:	UNDP
PROJECT TITLE:	Validation of the use of HFO-1234ze as Blowing Agent in the Manufacture of Extruded Polystyrene Foam Boardstock (Phase-I)		
PROJECT IN CURRENT BUSINESS PLAN:	Yes (added, based on ExCom Decision 55/43e i-iii)		
SECTOR:	Foams		
Sub-Sector:	Extruded Polystyrene Boardstock Foam		
ODS USE IN SECTOR			
Baseline:	Not yet determined		
Current (2007):	923 ODP t HCFCs, as per Government reporting		
BASELINE ODS USE:	N/A		
PROJECT IMPACT (ODP targeted):	N/A for this phase		
PROJECT DURATION:	10 months		
PROJECT COSTS:	US\$ 165,000 (Phase-I only)		
LOCAL OWNERSHIP:	100 %		
EXPORT COMPONENT:	0 %		
REQUESTED MLF GRANT:	US\$ 165,000		
IMPLEMENTING AGENCY SUPPORT COST:	US\$ 12,375 (7.5 %)		
TOTAL COST OF PROJECT TO MLF:	US\$ 177,375		
COST-EFFECTIVENESS:	N/A		
PROJECT MONITORING MILESTONES:	Included		
NATIONAL COORDINATING AGENCY:	Ministry of Environment and Forestry		

PROJECT SUMMARY

Turkey is a Party to the Vienna Convention and the Montreal Protocol. It also ratified the London, Copenhagen, Montreal and Beijing amendments to the Protocol. The country is committed to an early phaseout of HCFCs (2015) and willing to take the lead in assessing and implementing new HCFC phaseout approaches to achieve that goal. The objective of this project is to validate the use of a recently industrialized hydrofluoroolefin, HFO-1234ze, in the production of extruded polystyrene foam boardstock. This substance has no ODP and a very low GWP. Turkey hosts 12 local manufacturers of extruded polystyrene boardstock, most using a mixture of HCFC-142b and -22 because of safety (non-flammable) and performance (good thermal insulation). These producers tested already several HCFC replacement options with mixed results and are eager to round off their evaluations with the testing of this HFO that may make the use of high-GWP HFCs unnecessary. The project is divided into two phases:

Phase I: validate on existing equipment the use of HFO-1234ze and determine conditions under which commercial conversion could be implemented.

Phase-II: in case of a positive outcome, conversion of the existing operation to HFO-1234ze

At this stage funding only for Phase-I is requested. The costs of Phase-II cannot be determined at this stage and will be calculated after completion of Phase-I and then submitted for approval.

IMPACT OF PROJECT ON COUNTRY'S MONTREAL PROTOCOL OBLIGATIONS

Phase-I of this project is a pilot project and will not directly contribute to the fulfillment of Turkey's Montreal Protocol obligations. However, if successfully validated, the technology will contribute to availability of cost-effective options that are urgently needed to implement HCFC phase-out in extruded polystyrene boardstock. Such options can be applied in all XPS manufacturers in Turkey and world-wide. **Gaining experience through just one project rather than 12 (in Turkey) or in excess of 50 (worldwide A2 countries only) may save millions of dollars on actual phaseout costs compared to just over US\$ 200,000 for one pilot project.**

Prepared by: Rappa, Inc.

Date: February, 2010

60th Meeting of the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol

PROJECT OF THE GOVERNMENT OF TURKEY

VALIDATION OF USE OF HFO-1234ze AS BLOWING AGENT IN THE MANUFACTURE OF EXTRUDED POLYSTYRENE (XPS) FOAM BOARDSTOCK (PHASE-I)

1. PROJECT OBJECTIVES

The objective of this project is to validate the use of HFO-1234ze in the manufacture of XPS foam boardstock and, if the outcome is positive, apply the technology subsequently in a sector phaseout project. Lessons learned may be of use for similar manufacturing plants worldwide.

2. INTRODUCTION

2.1 GENERAL

Extruded polystyrene foams can be categorized into sheet and boardstock. Sheet is mostly used for food applications and thermal insulation requirements are modest. For boardstock, however, which is mostly used for construction applications, good thermal insulation is critical. Therefore, while virtually all CFC use in sheet has been converted to hydrocarbons, boardstock has initially been converted to HCFCs and then later, where forced by regulations, to a mixture of options that all are less than desired from a performance point of view. The UNEP Foams Technical Options Committee (FTOC) mentions that the phaseout of HCFCs in non-A5 countries “*has been—and continues to be—a problem*”. North American XPS boardstock producers are on course to phaseout HCFC use by the end of 2009. Phaseout choices will be HFC blends, CO₂ (LCD) and hydrocarbons. The significant variety in products required to serve the North American market (thinner and wider products with different thermal resistance standards and different fire-test-response characteristics) require different solutions than in Europe and Japan, who have already phased out HCFCs with HFC-134a, HFC-152a and CO₂ in Europe and significant use of hydrocarbons in Japan. However, recently introduced so called F-Gas regulations in Europe may change the scenario in that region as HFC-134a will have to be phased out.” With so many uncertainties in non-A5 countries, it is a challenge to provide guidance to A5 countries.

The manufacture of XPS boardstock has been traditionally an A2 market. There has been minor production in A5 countries but the FTOC states that recently production took off in China and Turkey. In addition, there is production in Argentina, Egypt and Saudi Arabia, while Kuwait, Brazil and Mexico are starting up new production lines. This increase in prominence, combined with the urgency caused by Turkey’s decision to early HCFC phaseout, requires a close look at HCFC phaseout options.

Blowing agent manufacturers are working diligently on a new generation of blowing agents that aim to combine zero ODP and good thermal insulation properties with low GWP. However, the horizon for industrialization in industrialized countries is 2-4 years which would imply that any phaseout efforts in A5 countries would not contribute to the period through 2016 (“freeze + 10 %”). There is one exception and that is HFO-1234ze. This chemical which is produced by Honeywell is already industrially applied in one component PU foam (OCF) manufacturers in Europe which were struck by a ban on the use of HFC-134a in July 2008 and needed a replacement urgently. The properties of this chemical as well as preliminary trials show promise for use in XPS boardstock but there has been no formal validation so far. If the MLF desires a full range of HCFC phaseout options for XPS boardstock that are not sub-standard in performance or unwanted in climate impact, evaluation of HFO-1234ze will be needed. This substance appears to offer the same climate impact advantages as hydrocarbons without the fire risk and to promise improved insulation value compared with other HCFC replacements.

But, with no diffusion data available, this is a very preliminary statement. UNDP is in contact with its manufacturer, Honeywell, which has agreed to support a validation project.

Technology validation is a global task. Experience gained can be applied in all MLF project dealing with XPS (estimated to exceed 50) and could save in this way millions of dollars in addition to making costs more transparent. Past experience in CFC phaseout has shown this. However, it has to be executed in one particular country. Because of the global impact, deduction of the first phase, which deals with development, optimization and validation from the national aggregate HCFC consumption would not be considered fair and it is requested to treat phase-1 in this way.

2.2 THE USE OF HCFCs IN XPS BOARDSTOCK APPLICATIONS IN TURKEY

The XPS Boardstock industry in Turkey consumed in 2008 about 4,100 t blowing agents from which ~70% (2,860 t) consisted of HCFCs. Growth in this industry has been impressive as the following overview shows:

Table-1: production of XPS Boardstock in Turkey

	2006	2007	2008	2009
XPS Boardstock Capacity (m ³)	1.200.000	1.900.000	2.200.000	2.400.000
Capacity Use (%)	75	75	75	
XPS Boardstock production	900,000	1,425,000	1,650,000	
Average Density (kg/m ³)	~31	~31	~31	
Annual production (t)	28,000	44,200	51,000	
Blowing Agent (%)	8	8	8	
Blowing agent use	2,240	3,540	4,080	
HCFC Share (%)	100	80	70	
HCFC Consumption (t)	2,240	2,830	2,860	

The industry is under pressure from the Government—that wants to phaseout the use of HCFCs by the end of 2015—and has been testing alternatives with the following outcome:

- HFC-134a trials have been successful but the high GWP makes it less attractive
- HFC-152a most trials have been in combination with dimethylether (DME) and have been Successful, albeit with a penalty in insulation value of around 10%. There is current commercial production using this approach
- Hydrocarbons trials are imminent, pending the finalization of safety measures
- CO₂ trials have been so far unsuccessful (inconsistent product)

See paragraph 5 below for a detailed discussion of these options.

3. RECIPIENT INFORMATION

This pilot project has been prepared around B-Plas, a Turkish manufacturer of extruded polystyrene foam boardstock. Contact information is as follows:

Company: B-Plas Bursa Plastic, Metal ve Turizm San. Ve Tic. A.S.
 Contact: Levent Ceylan
 Address: Yeni Yalova Yolu 5. km No: 365 Bursa, Turkey
 Ph/Fx: +90-224-261-0900/+90-224-261-0918
 Email: leventc@bplas.com.tr

B-Plas was established in 1987 and is owned by Celal and Memduh Gökçen, both Turkish nationals and residents of Osmangazi/Bursa. The XPS plant is located in Bursa, about 170 km from the port of Istanbul and 25 km from the port of Gemlik. It employs 36 and produces XPS on three twin screw extruders. Production has developed as follows:

Table 2: XPS Boardstock Production at B-Plas

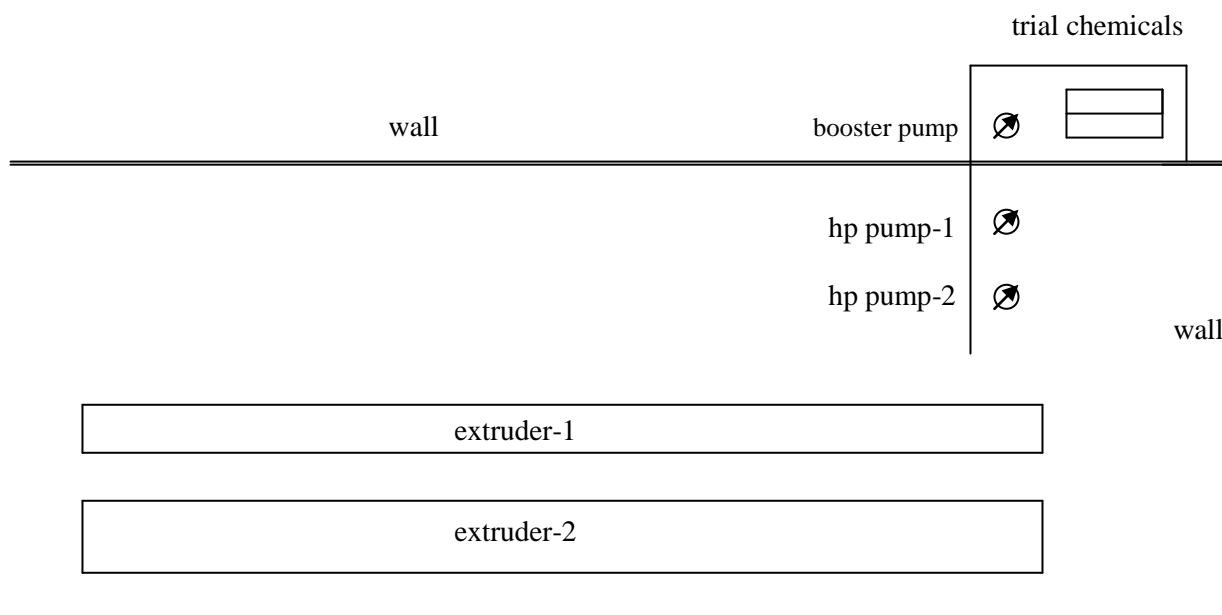
	2006	2007	2008	Comments
Production (m ³)	38,000	44,000	79,000	Increase through higher sales and lower density
Sales (m ³)	38,000	44,000	75,000	
Resin use (kg)	1,550,000	1,600,000	2,350,000	
Blowing agent use (kg)	220,000	240,000	369,000	

There is no export to other countries. The operation belongs to the B-Plas Bursa Plastic Group which employs about 1,600, had in 2007 sales of over US\$ 200 million.

4. PROJECT DESCRIPTION

The aim of the trials proposed under this pilot project will be to validate the use of HFO-1234ze and in this way to determine processability and cost impact when replacing current HCFC-142b/-22 blends. It is expected that such trials can be conducted with unchanged production equipment. However, a separate storage/feed operation for the trial chemical will have to be installed, because the existing feed system is too remotely located and would incur substantial contamination if used (see layout below).

FIG-1: B-PLAS TRIAL CONFIGURATION



It is emphasized that this trial configuration is unique for this being a pilot project that needs to keep the existing flow of blowing agents to other extruders than the one used for the trial to avoid costly business interruption. It will not need to be repeated in other XPS conversions. Apart from using HFO-1234ze as sole blowing agent, combinations with co-blowing agents will be tested as well.

During the trial, process conditions will be checked against baseline. Boards with several thicknesses will be produced. The baseline and the trial material will be tested for:

- board density
- appearance
- compression strength
- thermal performance
- water absorption
- diffusivity

Properties testing will be conducted at B-Plas and the HFO-1234ze manufacturer, Honeywell. However, final validation testing will be certified through an independent testing laboratory in Turkey. Honeywell and an independent expert recommended by Honeywell will attend and advise with the trials. A report will be prepared for the ExCom, outlining the quality of the product, changes recommended to equipment—if any—for future commercial production and cost analyses. Based on these trials and other trials conducted by the Turkish XPS manufacturers—independently and on their own costs—a phase-II proposal for the entire Turkish XPS boardstock industry (12 plants) will be prepared for commercial conversion from HCFCs to non ODP/low GWP alternatives – if agreed with by the Government.

5. TECHNICAL OPTIONS FOR HCFC REPLACEMENT IN XPS FOAMS

5.1 GENERAL INFORMATION

Extruded polystyrene foam can be categorized into sheet and boardstock applications. In virtually all sheet applications CFCs have been replaced by hydrocarbons—butane, isobutane, LNG or LPG. In boardstock, most of the replacement has been a blend of HCFC-142b and HCFC-22 in a 70-80%/30-20% ratio. The use of HCFC-22 was aimed at countering HCFC-142b's (modest) flammability. With the prices of HCFC-22 ever decreasing, many manufacturers—mainly in China—converted to HCFC-22 alone. This had its toll on product quality as the use of HCFC-22 only is prone to shrinkage.

The FTOC 2006 report offers following overview of past and expected conversions:

Table-3: Past and expected Blowing Agents for XPS Boardstock

XPS Type	CFC Alternatives		
	Currently in Use (2005/2006)	Anticipated in 2010-2015 period	
		Developed Countries	Developing Countries
Sheet	Primarily hydrocarbons, HCFCs are not technically required for this end use	CO ₂ (LCD), hydrocarbons, inert gases, HFC-134a, -152a	Hydrocarbons, CO ₂ (LCD)
Boardstock	CO ₂ (LCD) or with HC blends, hydrocarbons (Japan only), HFC-134a, HFC-152a, HCFC-22, HCFC-142b	CO ₂ (LCD) or with HC blends, hydrocarbons (Japan only), HFC-134a, HFC-152a and HC blends	HCFC-142b, HCFC-22

As already mentioned in the introduction, the 2008 FTOC update reports that *“the phaseout of HCFCs in non Article 5 countries has been—and continues to be—a problem”*. North American XPS boardstock producers are scheduled to phaseout HCFC use by the end of 2009 through HFC blends, CO₂ (LCD) and

hydrocarbons. The significant variety in products required to serve the North American market (thinner and wider products with different thermal resistance standards and different fire-test-response characteristics) will result in different solutions than in Europe and Japan, who have already phased out HCFCs. In Europe, this has been achieved with HFC-134a, HFC-152a and CO₂ (sometimes with a co-blowing agent or blended with an additives) while in Japan there has been significant use of hydrocarbons. Recently introduced so-called F-Gas regulations in Europe may change the scenario in that region as this regulation introduces limits on allowed GWPs.

Following is the current commercial/technical status on potential replacement for HCFCs:

Table-4: Status of HCFC replacements in XPS Boardstock

SUBSTANCE	COMMENTS
HFC-134a	Considered expensive; high GWP
HFC-152a	Moderately flammable and considered expensive
(Iso)butane	Highly flammable; high investment
CO ₂	As gas only capable to replace 30% of the blowing agent. As liquid, high in investment and not fully mature
HFO-1234ze	Non-flammable, ideal boiling point, but still experimental

It will be important to assess for all technologies their climate impact. Using GWP and MW data as provided by the FTOC (2006), following indicative GWP changes are to be expected for the replacement of HCFC-141b in PU foam applications:

Table-5: Indicative GWP Changes when Replacing HCFC-142b/-22

SUBSTANCE	GWP	MOLECULAR WEIGHT	INCREMENTAL GWP	COMMENTS
HCFC-142b/-22 (75/25)	2,185	97	Baseline	
HCFC-22	1,810	87	-562	Non flammable
HFC-134a	1,430	102	-681	Non flammable
HFC-152a	124	66	-2,101	Moderately flammable
(Iso)butane	4	58	-2,183	Flammable
CO ₂ (LCD)	1	44	-2,185	Non Flammable
HFO-1234ze	6	114	-2,178	Non flammable

Green = favorable GWP effect; red = favorable comparable GWP effect but higher than the EU F gas limit (150)

Based on these data, it appears that HCs, CO₂ (LCD) and HFO-1234ze have by far the lowest climate impact based on GWP.

HFC-152a may also be an acceptable alternative from a climate change perspective.

While HFC-134a reduces the comparable global warming effect, it will be disallowed in the future in the EU and its use is therefore discouraged. An HCFC substitution program for XPS boardstock may therefore include HFC-152a, Hydrocarbons, Carbon Dioxide and HFO-1234ze

5.2 PROPERTIES OF HFO-1234ze

General

HFO-1234ze is a hydrofluoroolefin developed by Honeywell as a fourth generation blowing agent to replace HFCs in non-A5 countries. Comparative properties are as follows:

Table-6: Comparative properties of blowing agents

Property	HCFC-142b	HCFC-22	HCFC-142b/-22 (75/25) ¹	Isobutane	HFC-152a	HFC-134a	HFO-1234ze
Molecular Weight	100	86	97	58	66	102	114
Boiling Point (°C)	-9	-41	-25²	-12	-27	-26	-19
TLV or OEL (ppm)	1000	1000	1000	800	1000	1000	1000³
LEL/UEL (vol% in air)	6-18	None	8-24	1.8-8.4	3.8-21.8	None	None³
λ (mW/m ² K @ 10°C)	8.4	9.9	8.7	16 (20°C)	14 (25°C)	12.4	13⁴
ODP	0.066	0.05	0.063	0	0	0	0
GWP	2270	1810	2185	4	124	1430	6

¹linear weighted averages.

²there may be a boiling point range

³recommended

⁴not known at what temperature

⁵however, at 30°C LEL/UEL values of 7.0/9.5 exist

The two gases that will be compared in these trials are shown in bold. Apart from the molecular weight, the comparison appears favorable for HFO-1234ze. However, it should be kept in mind that the original baseline, CFC-12, has a molecular weight of 121!

Atmospheric Chemistry

In general, hydrofluoroolefins—being unsaturated hydrofluorocarbons—will have shorter atmospheric life times than saturated hydrofluorocarbons. This is evident from their much lower GWPs. However, the issue of decomposition products may be brought up. The University of Copenhagen conducted a study on the atmospheric chemistry of HFO-1234ze¹. While trifluoroacetic acid (HFA) is mentioned as a major final breakdown product, this is a natural component of the background oceanic environment and any environmental burden associated with trans CF₃CH=CHF oxidation will be of negligible environmental significance. The study concludes *“that the products of the atmospheric oxidation of trans-CF₃CH=CHF will have negligible environmental impact.”*

The USEPA came to the same conclusion when evaluating HFO-1234ze under the Significant New Alternatives Policy (SNAP) program². EPA’s decision states that:

Hydrofluoroolefin (HFO)–1234ze is acceptable as a substitute for CFCs and HCFCs in:

- *Rigid Polyurethane Appliance Foam.*
- *Rigid Polyurethane Spray, Commercial Refrigeration, and Sandwich Panels.*
- *Polystyrene Extruded Boardstock & Billet.*

Toxicity

The toxicity of HFO-1234ze has been relatively extensively researched. Following table summarizes current information—which shows low toxicity levels:

¹ M.S. Javadi et al, Atmospheric chemistry of trans-CF₃CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation

² Federal register / Vol. 74, No 188 / Wednesday, September 30, 2009 / rules and regulations, pg 50129 ev

Table-7: HFO-1234ze Toxicology Assessment

Test		Results
Cardiac Sensitization		No Effect to 120,000 ppm
Genetic Testing:	Mouse micronucleus	Not Active at 100,000
	Ames assay	Not Active at 50,000 ppm
Acute Inhalation		LC50>400,000 ppm
Chromosome Aberration Test:	Inhalation: 2 week	Test Complete
	Inhalation 4 week	Test Complete
Unscheduled DNA Synthesis	rat; 4 week @ 15,000	Not Active
Bone Marrow Micronucleus Formation	rat; 4 week @ 15,000	Not Active
Carcinogenicity Screen Test		Complete
Metabolism Study		Underway
Inhalation	13 week	Test Complete
Developmental Toxicity Pilot Test		Complete

In conclusion, the outcome of toxicity and atmospheric studies confirm that HFO-1234fa is a non-ODP/insignificant GWP substance with low toxicity and valid for XPS applications—as is already the case in one component PU foams.

6. PROJECT COSTS

Following are the summarized cost expectations:

Table-8: Project Budget

#	ACTIVITY	COSTS (US\$)		
		INDIVIDUAL	SUB-TOTAL	TOTAL
PHASE-I – CONDUCTION OF TRIALS AND TESTING				
1	Preparative work Project Preparation (incl. second phase) Technology Transfer, Training	40,000 30,000	70,000	165,000
2	Trials Purchase of materials (see Annex-1) Testing Retrofit	40,000 10,000 20,000	70,000	
3	Validation	10,000	10,000	
4	Contingencies/Rounding (~10%)	15,000	15,000	

The costs for phase-1 of this project are relatively limited compared to most other pilot projects because cooperation with the manufacturer of HFO-1234fa, Honeywell, makes it possible to have most tests performed in existing facilities, avoiding in this way expensive equipment purchases and the trials can be performed on existing production equipment with only minor retrofits. No costs for phase-II have been calculated at this point. While it is assumed that existing production equipment can be used with few—if any—changes, phase-I will have to confirm this.

UNDP requests a grant for the first phase of this project amounting to

US\$ 165,000.

7. IMLEMENTATION/MONITORING

Table-9: Implementation Schedule

TASKS	2009				2010			
	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q
Project Start-up								
MF Project Approval			X					
Receipt of Funds			X					
Grant Signature				X				
Procurement arrangement				X				
Phase I								
-Arrival of chemicals					X			
-Trials					X			
-Testing					X			
-Analysis/Reporting/preparation phase II					X			

Table-10: MILESTONES FOR PROJECT MONITORING

TASK	MONTH*
(a) Project document submitted to beneficiaries	2
(b) Project document signatures	3
(c) Procurement	4, 5
(e) Chemicals delivered	5
(f) Trial Runs	6
(g) Testing/analysis/reporting	7
(h) Project closure/start Phase II	12

* As measured from project approval

7. ANNEXES

Annex 1: Budget Details

ANNEX-1

BUDGET DETAILS

Assumptions:

- Chemical prices: Crystalline Polystyrene US\$ 2.50/kg
 Talcum US\$ 1.00/kg
 HFO 1234ze US\$ 20.00/kg (US\$ 12.00 +freight & logistics)
- Output: 200 kg/hr total
 180 kg/hr PS
 20 kg/hr gas
- Trial duration: 6 hours total per thickness

Trial costs:

Trials	Duration [hours]	PS Crystal [kg]	Cost [US\$]	Talcum [kg]	Cost [US\$]	HFO-1234ze [kg]	Cost [US\$]	Total Cost
20 mm	6	1,080	2,700	11	11	150	3,000	5,711
25 mm	6	1,350	3,375	14	14	187.5	7,500	7,139
40 mm	6	2,160	5,400	22	22	300	6,000	11,422
50 mm	6	2,700	6,750	28	28	375	7,500	14,278
Calibration	n/a	n/a	n/a	n/a	n/a	50	1,000	1,000
Total	24	7,290	18,225	75	75	1,012.5	21,250	39,550

* Say US\$ 40,000

Total Budget:

#	ACTIVITY	COSTS (US\$)		
		INDIVIDUAL	SUB-TOTAL	TOTAL
PHASE-I – CONDUCTION OF TRIALS AND TESTING				
1	Preparative work Project Preparation (incl. second phase) Technology Transfer, Training	40,000 30,000	70,000	165,000
2	Trials Purchase of materials (see Annex-1) Testing Retrofit	40,000 10,000 20,000	70,000	
3	Validation	10,000	10,000	
4	Contingencies/Rounding (~10%)	15,000	15,000	

SAFETY DATA SHEET
according to Regulation (EC) No. 1907/2006

Honeywell

HFO-1234ze, HBA-1

Version 1.6

Revision Date 13.08.2008

Print Date 15.09.2008

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

Product information

Trade name : HFO-1234ze, HBA-1

Use of the : Aerosol propellant
Substance/Preparation : Foam blowing agent
Refrigerant

Company/Undertaking Identification

Company : Honeywell Fluorine Products Europe B.V.
Laarderhoogtweg 18
1101 EA Amsterdam
Telephone : (31) 020 5656911
Telefax : (31) 020 5656600
Emergency telephone : (32) 14584545
For further information, : SafetyDataSheet@Honeywell.com
please contact:

2. HAZARDS IDENTIFICATION

Risk advice to man and the environment

Not a hazardous substance or preparation according to EC-directives 67/548/EEC or 1999/45/EC.
Additional advice : Rapid evaporation of the liquid may cause frostbite.

See Section 11 for more detailed information on health effects and symptoms.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical characterization

Chemical Name : trans-1,3,3,3-Tetrafluoroprop-1-ene
CAS-No. : 1645-83-6
EC-No. : 471-480-0

Occupational Exposure Limit(s), if available, are listed in Section 8.

4. FIRST AID MEASURES

General advice : Show this safety data sheet to the doctor in attendance.
Keep warm and in a quiet place.
Inhalation : If inhaled, remove to fresh air.
Get medical attention if irritation develops and persists.
Skin contact : Rapid evaporation of the liquid may cause frostbite.
If there is evidence of frostbite, bathe (do not rub) with lukewarm (not hot) water. If water is not available, cover with a clean, soft cloth or similar covering.
Call a physician if irritation develops or persists.
Eye contact : If eye irritation persists, consult a specialist.

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Notes to physician

Symptoms : headache
Dizziness
Nausea
Palpitation
Respiratory disorders
Rapid respiration

See Section 11 for more detailed information on health effects and symptoms.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media : Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.
Water mist
Dry powder
Foam
Carbon dioxide (CO₂)

Specific hazards during fire fighting : Heating will cause pressure rise with risk of bursting
Some risk may be expected of corrosive and toxic decomposition products.
Fire may cause evolution of:
Hydrogen fluoride
However, this material can ignite when mixed with air under pressure and exposed to strong ignition sources.

Special protective equipment for fire-fighters : Wear self-contained breathing apparatus and protective suit.
Exposure to decomposition products may be a hazard to health.

Further information : In the event of fire, cool tanks with water spray.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions : Provide adequate ventilation.
Vapours are heavier than air and can cause suffocation by reducing oxygen available for breathing.
Avoid skin contact with leaking liquid (danger of frostbite).
Use personal protective equipment.
Keep people away from and upwind of spill/leak.

Environmental precautions : Prevent further leakage or spillage if safe to do so.
The product evaporates readily.
Prevent spreading over a wide area (e.g. by containment or oil barriers).

Methods for cleaning up : Do not direct water spray at the point of leakage.
Allow to evaporate.

For personal protection see section 8.

7. HANDLING AND STORAGE

Handling

Advice on safe handling : Pressurized container: Protect from sunlight and do not expose to temperatures exceeding 50 °C. Do not pierce or burn, even after use.
Do not burn.

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Exhaust ventilation at the object is necessary.

Advice on protection against fire and explosion : Do not spray on a naked flame or any other incandescent material.
Keep away from direct sunlight.
Fire or intense heat may cause violent rupture of packages.
Vapours may form explosive mixtures with air.
The product is not easily combustible.

Storage

Further information on storage conditions : Keep containers tightly closed in a cool, well-ventilated place.
Keep only in the original container at temperature not exceeding 50°C
Keep away from direct sunlight.

Advice on common storage : Do not store together with:
Oxidizing agents

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational exposure controls

Components	Basis	Value type	Control parameters	Exceeding Factor	Form of exposure	Remarks
trans-1,3,3,3-Tetrafluoroprop-1-ene	HONEYWELL	Time Weighted Average (TWA):	1.000 ppm			We are not aware of any national exposure limit.

Engineering measures

Local exhaust

Personal protective equipment

Respiratory protection : Remarks: In case of insufficient ventilation wear suitable respiratory equipment.
Wear a positive-pressure supplied-air respirator.

Hand protection : Glove material: Viton (R)
Heat insulating gloves

Eye protection : Goggles

Skin and body protection : impervious clothing
Wear cold insulating gloves/face shield/eye protection.

Hygiene measures : Avoid breathing vapors, mist or gas.
Keep working clothes separately.
Do not smoke.

Protective measures : The Personal Protective Equipment must be in accordance

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with EN standards:respirator EN 136, 140, 149; safety glasses EN 166; protective suit: EN 340, 463, 468, 943-1, 943-2; gloves EN 374, safety shoes EN-ISO 20345.
The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.
Avoid inhalation of vapour or mist.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form : compressed liquefied gas
Colour : colourless
Odour : slight, original odour

Safety data

Boiling point/boiling range : -19 °C
Flash point : Remarks: does not flash
Ignition temperature : 288 - 293 °C
Vapour pressure : 4.192 hPa
at 20 °C
Vapour pressure : 10.998 hPa
at 54,4 °C
Density : 1,12 g/cm3
at 21,1 °C
Water solubility : 0,373 g/l
Partition coefficient: n-
octanol/water : log Pow estimated 2,01
Relative vapour density : 4
Remarks: (Air = 1.0)

10. STABILITY AND REACTIVITY

Conditions to avoid : Some risk may be expected of corrosive and toxic decomposition products.
Heat, flames and sparks.
Materials to avoid : Reactions with alkali metals.
Hazardous decomposition products : Pyrolysis products containing fluoride
Fluorocarbons
Hydrogen fluoride

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Thermal decomposition : Note: Hazardous decomposition products formed under fire conditions., To avoid thermal decomposition, do not overheat.

11. TOXICOLOGICAL INFORMATION

Acute inhalation toxicity : LC50
Species: rat
Dose: > 965 mg/l
> 207000 ppm
Exposure time: 4 h

Further information : Remarks: Not mutagenic in Ames Test. May cause headache and dizziness. No experimental indications on genotoxicity in vivo found. Detailed toxicological data and examinations, exceeding the data set in the MSDS are available for professional users on request.

12. ECOLOGICAL INFORMATION

Elimination information (persistence and degradability)

Biodegradability : aerobic
Result: Not readily biodegradable.

Ecotoxicity effects

Toxicity to fish : NOEC
Species: Cyprinus carpio (Carp)
Value: > 117 mg/l
Exposure time: 96 h

Toxicity to aquatic plants : NOEC
Growth inhibition
Species: Algae
Value: > 170 mg/l
Exposure time: 72 h

Acute toxicity to aquatic invertebrates : EC50
Species: Daphnia magna (Water flea)
Value: > 160 mg/l
Exposure time: 48 h

13. DISPOSAL CONSIDERATIONS

Product : Dispose according to legal requirements.
Contact manufacturer.

Packaging : Legal requirements are to be considered in regard of reuse or disposal of used packaging materials

14. TRANSPORT INFORMATION

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ADR

UN Number : 3163
Description of the goods : LIQUEFIED GAS, N.O.S.
(TRANS-1,3,3,3-TETRAFLUOROPROP-1-ENE)
Class : 2
Classification Code : 2A
Hazard identification No : 20
Hazard Label : 2.2

IATA

UN Number : 3163
Description of the goods : Liquefied gas, n.o.s.
(trans-1,3,3,3-Tetrafluoroprop-1-ene)
Class : 2.2
Hazard Label : 2.2
Packing instruction (cargo aircraft) : 200
Packing instruction (passenger aircraft) : 200

IMDG

UN Number : 3163
Description of the goods : LIQUEFIED GAS, N.O.S.
(TRANS-1,3,3,3-TETRAFLUOROPROP-1-ENE)
Class : 2.2
Hazard Label : 2.2
EmS Number : F-C
Marine pollutant : no

RID

UN Number : 3163
Description of the goods : LIQUEFIED GAS, N.O.S.
(TRANS-1,3,3,3-TETRAFLUOROPROP-1-ENE)
Class : 2
Classification Code : 2A
Hazard identification No : 20
Hazard Label : 2.2

15. REGULATORY INFORMATION

Labelling according to EC Directives 67/548/EEC

Further information : Not a hazardous substance or preparation according to EC-directives 67/548/EEC or 1999/45/EC.
The product does not need to be labelled in accordance with EC directives or respective national laws.

National legislation

16. OTHER INFORMATION

Further information

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The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text. Final determination of suitability of any material is the sole responsibility of the user.

This information should not constitute a guarantee for any specific product properties.

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1. Identification of the substance / preparation and company / undertaking

Product name	Harp® DME
REACH registration number	01-2119472128-37-0000
Company	Harp International Ltd Gellihirion Industrial Estate Pontypridd Rhondda Cynon Taff CF37 5SX Tel: +44 (0) 1443 842255 Fax: +44 (0) 1443 841805 Email: harp@harpintl.com
Emergency phone number	+44 (0) 1270 502891 (24 hour)
Use	Aerosol propellant

2. Hazards identification

EC Classification of the substance or mixture

Hazard Class & category code:

Regulation (EC) No. 1272/2008 (CLP):

- Physical hazards**
Flammable gases - Category 1 – Extremely flammable gas (H220)
Gases under pressure - Contains gas under pressure; may explode if heated (H280)

Classification EC67/548 or EC 1999/45 : R12 – Extremely flammable.

Label Elements

Labelling Regulation EC 1272/2008 (CLP)

- Hazard pictogram(s)**



GHS02



GHS04

- Hazard pictograms code**
GHS02 (Flame) - GHS04 (Gas cylinder).
- Signal word**
Danger
- Hazard statements**
H220 : Extremely flammable gas
H280 : Contains gas under pressure; may explode if heated.
- Precautionary statements**
 - Prevention**
P210 : Keep away from heat/sparks/open flames/hot surfaces - No smoking.
 - Response**
P377 : Leaking gas fire : Do not extinguish unless leak can be stopped safely.
 - Storage**
P381 : Eliminate all ignition sources if safe to do so.
P403 : Store in a well ventilated place.
P410 : Protect from sunlight.

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2. Hazards identification continued

Labelling EC 67/548 or EC 1999/45

Symbol(s)

F+ : Extremely flammable.



R Phrase(s)

R12 : Extremely flammable.

S Safety phrase(s)

S9 : Keep container in a well-ventilated place.

S16 : Keep away from sources of ignition.

Other hazards

This substance is not considered to be persistent., bio-accumulating nor toxic (PBT).

This substance is not considered to be very persistent., nor very bio-accumulating nor toxic (vPvB).

May form explosive peroxides.

Rapid evaporation of the liquid may cause frostbite.

Vapours are heavier than air and can cause suffocation by reducing oxygen available for breathing.

May cause cardiac arrhythmia.

3. Composition / information on ingredients

Substance / Preparation

Chemical name

Substance.

Chemical formula

Dimethyl ether.

(CH₃)₂O

Substance name	Contents	CAS no.	EC No	Registration no.	Classification According to Directive 67/548/EEC	Classification According to Regulation 1272/2008 (CLP)
Dimethyl ether	100%	115-10-6	204-065-8	01-2119472128- 37-0000	F+; R12	Flam. Gas; H220 Press. Gas; H280

4. First aid measures



The first aid advice given for skin contact, eye contact and ingestion is applicable following exposures to the liquid or spray. Also see section 11.

Inhalation

Remove patient from exposure, keep warm and at rest. Administer oxygen if necessary. Apply artificial respiration if breathing has ceased or shows signs of failing. In the event of cardiac arrest apply external cardiac massage. Obtain immediate medical attention.

Skin contact

Thaw affected areas with water. Remove contaminated clothing. Caution: clothing may adhere to the skin in the case of freeze burns. After contact with skin, wash immediately with plenty of warm water. If irritation or blistering occur, obtain medical attention.

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4. First aid measures continued

Eye contact	Immediately irrigate with eyewash solution or clean water, holding the eyelids apart for at least 15 minutes. Obtain immediate medical attention.
Ingestion	Unlikely route of exposure. Do not induce vomiting. Provided the patient is conscious, wash out mouth with water and give 200-300ml (half a pint) of water to drink. Obtain immediate medical attention.
Most important symptoms and effects both acute and delayed.	Skin contact may produce the following symptoms : Frostbite Inhalation may produce the following symptoms : Shortness of breath, dizziness, weakness, nausea, headache, narcosis, irregular cardiac activity.
Indication of any immediate medical attention and special treatment needed	Do not give adrenaline or similar drugs.

5. Fire-fighting measures

Specific hazards	Exposure to fire may cause containers to rupture/explode.
Hazardous combustion products	Incomplete combustion may form carbon monoxide.
Extinguishing media -Suitable extinguishing media Specific methods	All known extinguishants can be used. If possible, stop flow of product. Move away from the container and cool with water from a protected position. Do not extinguish a leaking gas flame unless absolutely necessary. Spontaneous/explosive re-ignition may occur. Extinguish any other fire.
Special protective equipment for fire fighters	In confined space use self-contained breathing apparatus.

6. Accidental release measures

Personal precautions	Evacuate personnel to safe areas. Ventilate area.. Refer to protective measures listed in sections 7 and 8.
Environmental precautions	Should not be released into the environment.
Clean up measures	Evaporates.

7. Handling and storage

Precautions for safe handling
Advice for safe handling

Avoid breathing vapours or mist. Avoid contact with skin, eyes and clothing. Provide sufficient air exchange and/or exhaust in work rooms.
For personal protection see section 8. See Annex – Section 2.2

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7. Handling and storage continued

Advice on protection against fire and explosion

Vapours are heavier than air and may spread along floors. Vapours may form explosive mixtures with air. The products should only be used in areas from which all naked lights and other sources of ignition have been excluded. Electrical equipment should be protected to the appropriate standard. No sparking tools should be used. Take measures to prevent the build of electrostatic charge. Keep away from heat and sources of ignition. Keep away from open flames., hot surfaces and sources of ignition. When using do not smoke. Avoid breathing vapours or mist. Avoid contact with skin, eyes and clothing.

Conditions for safe storage, including any incompatibilities Requirements for storage areas and Containers

Keep containers tightly closed in a cool, well ventilated place. Store in original container.

Specific end uses

No data available.

8. Exposure controls / personal protection

Control parameters

Components with workplace control parameters

Components	CAS-No.	Type form of exposure	Control parameters	Update	Basis
Dimethyl ether	115-10-6	TWA	766mg/m ³ , 400ppm	2007	EH40 WEL
		STEL	985mg/m ³ , 500ppm	2007	
		TWA	1920mg/m ³ , 1000ppm	02 2006	

Derived No Effect Level

- Dimethyl ether

Type of Application (Use): Workers exposure routes: Inhalation health effect: Chronic effects, systematic toxicity value: 1894mg/m³

Type of Application (Use): Consumers exposure routes: Inhalation health effect: Chronic effects, systematic toxicity value: 471mg/m³

Predicted No Effect Concentration

- Dimethyl ether

Value: 0,155 mg/l

Compartment: Fresh water

Value: 0,016 mg/l

Compartment: Marine water

Value: 1,549 mg/l

Compartment: Water

Remarks: Intermittent use/release

Value: 160 mg/l

Compartment: Water

Remarks: sewage treatment plants

Value: 0,681 mg/l

Compartment: Fresh water sediment

Value: 0,069 mg/l

Compartment: Marine sediment

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8. Exposure controls / personal protection continued

Value: 0,045 mg/l

Compartment: Soil

Personal protection

Wear suitable protective clothing, gloves and eye/face protection.
Wear thermal insulating gloves when handling liquefied gases. In cases of insufficient ventilation, where exposure to high concentrations of vapour is possible, suitable respiratory protective equipment with positive air supply should be used.
Do not smoke while handling product.



Safety glasses. Additionally wear a face shield where the possibility exists for face contact due to splashing, spraying or airborne contact with this material.



Heat insulating gloves

9. Physical and chemical properties

Form	Liquefied gas
Physical state at 20°C	Gas
Colour	Colourless
Odour	Slight ether-like.
Molecular weight [g/mol]	46.07
Solubility in water [g/l]	45.6 at 25°C at 1013 hPa
Boiling point/boiling range (°C)	-24.8 at 1013 hPa
Melting point/range (°C)	-141.5 at 1013 hPa
Relative density	1.88 at 25°C
Vapour pressure (25°C)	5132,9 hPa
Flammability range [vol% in air]	3.3 to 26.2
Auto ignition temperature [°C]	226 at 1013 hPa
Explosive properties	Not explosive
Partition coefficient: n-octanol/water	POW 0.07 at 25°C
Other data	No data available.

10. Stability and reactivity

Reactivity	Extremely flammable gas.
Chemical Stability	The product is chemically stable
Possibility of hazardous reactions	Vapours may form explosive mixture with air.
Conditions to avoid	Temperatures > 52°C
Incompatible materials	Oxygen, oxidising agents, acid anhydrides, strong acids, Carbon monoxide, acetic anhydride, powdered metals.
Hazardous decomposition products	Hazardous thermal decomposition products may include: Formaldehyde, carbon dioxide, Carbon monoxide, Methanol.

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11. Toxicological information

Information on toxicological effects

Acute oral toxicity

- Dimethyl ether Not applicable

Acute inhalation toxicity

- Dimethyl ether LC50/rat: 164000 ppm
Respiratory effects, anaesthetic effects, central nervous system depression, narcosis, cardiac irregularities, coma.

/ dog
Cardiac sensitization.

Acute dermal toxicity

- Dimethyl ether Not applicable

Skin irritation

- Dimethyl ether Not tested on animals.
Classification: Not classified as irritant.
Result: No skin irritation.
Not expected to cause skin irritation based on expert review of the properties of the substance.

Eye irritation

- Dimethyl ether Not tested on animals.
Classification: Not classified as irritant.
Result: No eye irritation.
Not expected to cause eye irritation based on expert review of the properties of the substance.

Sensitisation

- Dimethyl ether Not tested on animals.
Classification: Not classified as skin sensitizer.
Not expected to cause sensitization based on expert review of the properties of the substance.

- Dimethyl ether There are no reports of human skin sensitization.

There are no reports of human respiratory sensitization.

Repeated dose toxicity

- Dimethyl ether Inhalation rat: No toxicologically significant effects were found.

Mutagenicity assessment

- Dimethyl ether Animal testing did not show mutagenic effects. Tests on bacterial or mammalian cell cultures did not show mutagenic effects.

Carcinogenicity assessment

- Dimethyl ether Animal testing did not show any carcinogenic effects.

Toxicity to reproduction assessment

- Dimethyl ether No toxicity to reproduction.

Further information

May cause cardiac arrhythmia. Rapid evaporation of the liquid may cause frostbite.

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12. Ecological information

Toxicity

Toxicity to fish

- Dimethyl ether LC50/96 h/Poecilia reticulata (guppy): >4000 mg/l

Toxicity to aquatic invertebrates

- Dimethyl ether EC50/48 h/Daphnia: >4000 mg/l
LC50/48 h/Daphnia: 755,549 mg/l

Chronic toxicity to fish

- Dimethyl ether Due to its physical properties, there is no potential for adverse effects.

Persistence and degradability

Biodegradability

Method: Closed bottle test. According to the results of tests of biodegradability this product is not readily biodegradable.

Physio-chemical removability

The product can be degraded by abiotic (e.g. chemical or photolytic) processes.

Bio-accumulative potential

Bio-accumulation

No data available.

Mobility in soil

Mobility in soil

Koc: 7,759

Results of PBT and vPvB assessment

Results of PBT and vPvB Assessment

This substance is not considered to be persistent, bio-accumulating nor toxic (PBT). This substance is not considered to be very persistent nor very bio-accumulating (vPvB).

Other adverse effects

Ozone depletion potential

0

Global warming potential (GWP)

1

13. Disposal information

Waste treatment methods

Product

Can be used after re-conditioning. In accordance with local and national regulations. Must be incinerated in suitable incineration plant holding a permit delivered by the competent authorities.
See Annex – Section 2.1

Contaminated packaging

Empty pressure vessels should be returned to the supplier.

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14. Transport information

UN No. 1033

Labelling ADR, IMDG, IATA



2.1 : flammable gas

Land transport

ADR/RID

H.I.nr 23

UN No. 1033

UN Proper shipping name Dimethyl ether

Labelling No. 2.1

Transport hazard class(es) 2

DR/RID Classification code 2 F

Tunnel instructions (B/D)

Sea transport

IMO-IMDG code

Proper shipping name Dimethyl ether

Class 2.1

UN No. 1033

Labelling No. 2.1

Air transport

IATA_C

-Proper shipping name Dimethyl ether

Class 2.1

UN No. 1033

Labelling No. 2.1

Further information ICAO/IATA cargo aircraft only.

15. Regulatory information

Safety, health and environmental regulations/legislation specific for the substance or mixture No data available.

Chemical safety Assessment A chemical Safety Assessment has been carried out for this substance.

16. Other information

Text of R-phrases mentioned in Section 3

R12 Extremely flammable

Full text of H-Statements referred to Under Section 3

H220 - Extremely flammable gas.

H280 - Contains gas under pressure; may explode if heated.

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16. Other information continued

Further information

For further information contact Harp International Limited.

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Annex:

1 Exposure Scenario (2)			
Formulation and repacking			
SU 3, 10 PC1, 3, 4, 8, 9a, 14, 15, 21, 23, 24, 25, 26, 27, 29, 31, 32, 34, 35, 38, 39 PROC 1, 2, 3, 4, 5, 8b, 9 ERC 2			
Formulation/blending in batch processes, transfers and packaging will describe the group of contributing scenarios listed below:			
Scenario name	Process Category (PROC)	Type of setting	Short name
Use in closed process	PROC 1	Industrial	CS 1
Use in closed continuous process w/occasional controlled exposure	PROC 2	Industrial	CS 2
Use in closed batch process	PROC 3	Industrial	CS 3
Use in batch and other process where opportunity for exposure	PROC 4	Industrial	CS 4
Mixing and blending	PROC 5	Industrial	CS 5
Transfer to small containers	PROC 9	Industrial	CS 6
Transfer at dedicated facilities	PROC 8b	Industrial	CS 7
2.1 Contributing scenario (1) controlling environmental exposure for formulation/blending in batch processes and packaging			
Product characteristics			
Physical state: gas/liquefied gas Concentration: max, 100%			
Amounts used			
Max. 6000 t/year or 20 t/day [largest site tonnage]			
Frequency and duration of use			
300 days/year			
Environment factors not influenced by risk management			
Dilution factor river: 10 Dilution factor marine: 100			
Other given operational conditions affecting environmental exposure			
None			
Technical conditions and measures at process level (source) to prevent release			
Containment in process			
Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil			
None			
Organisational measures to prevent/limit release from site			
None			
Conditions and measures related to municipal sewage treatment			
Effluent rate of municipal STP: 2000 m ³ /days River flow rate: 18000 m ³ /days			
Conditions and measures related to external treatment of waste disposal			
No waste generated as substance is a gas and will evaporate to air.			
Conditions and measures related to external recovery of waste			
None.			
2.2 Contributing scenario (2) controlling worker exposure for Formulation/blending in batch processes, transfers and packaging			
Product characteristic			
Physical state: gas/liquefied gas Concentration: max. 100%			

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Amounts used

Not relevant

Frequency & duration of exposure

Exposure frequency: daily for all PROCs

Scenario name	Duration of activity [hours/day]
CS1	>4 hours
CS2	>4 hours
CS3	>4 hours
CS4	>4 hours
CS5	>4 hours
CS6	>4 hours
CS7	>4 hours

Human factors not influenced by risk management

None

Other given operational conditions affecting workers exposure

Scenario name	Use of ventilation
CS1	Indoors without LEV
CS2	Indoors without LEV
CS3	Indoors without LEV
CS4	Indoors without LEV
CS5	Indoors without LEV
CS6	Indoors without LEV
CS7	Indoors without LEV

Technical conditions and measures at process level (source) to prevent release

Handling in industrial settings.
Containment according to definition of PROCs for liquefied gas.
See SDS section 7.

Technical conditions and measures to control dispersion from source towards the worker

None

Organisational measures to prevent/limit release, dispersion and exposure

See SDS.

Conditions and measures related to personal protection, hygiene and health evaluation

See SDS section 8.

3. Exposure estimation and reference to its source

Scenario name	Inhalative Exposure Estimate (mg/m ³)
CS1	0.0192
CS2	96.0
CS3	192
CS4	192
CS5	480
CS6	384
CS7	288

Comment: Tables below are reporting worst case values for PROC 5 – CS 5:

(Semi) Quantitative risk characterisation for workers

	Leading toxic end point/critical effect	Risk characterisation ratio
Long term- systematic effects - inhalation	Anaesthetic	0.3

(Semi) Quantitative risk characterisation for humans exposed via environment

Route	Leading toxic end point/critical effect	Risk characterisation ratio (RCR)
Long term- systematic effects - inhalation	Anaesthetic	0.00002

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Risk characterisation for the aquatic compartment

Compartments	RCR
Freshwater	0.00001
Marine water	0.00006
Sediment	0.00001
Marine sediment	0.00006

Risk characterisation for the terrestrial compartment

Compartments	RCR
Agricultural soil	0.07
Grassland	0.07

Microbiological activity in sewage treatment systems

Compartments	RCR	Discussion
STRP (mg/l)	0.003	No release to STP

Assessment method:

Worker inhalation: ECETOC TRAM worker (May 2010 release)

Man via Environment: ECETOC TRAM Environment (May 2010 release)

Consumer: ECETOC TRAM Consumer (May 2010 release)

Environment: ECETOC TRAM Environment (May 2010 release)

Release factors:

Air: 0.2%, max release rate of 40 kg/day per site

Wastewater: no release to wastewater

Soil: no processes/process steps leading to direct release to soil

4. Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Worker exposure

Input parameters resulting in highest exposure estimates (worst-case) were used to evaluate worker exposures (see section 3). If the downstream user reduces exposure duration each activity/process to less than 8 hours, it may be necessary to consider summing exposure estimates if the same worker may be engaged in multiple tasks during the day.

For DNELs, see SDS section 8.

Environmental exposure

Downstream users should check whether they are still within the boundaries of the ES if:

- Release factors exceed those listed (see Section 3),
- Number of operating days is less than the frequency and duration of use (see Section 2.1), or
- Actual tonnage (one location) exceeds amount used (see Section 2.1)

ECETOC/TRAM basic input parameters

Molecular weight: 46.07 g/mol

Vapour pressure, water solubility, octanol-water partition coefficient [Kow] (see SDS Section 9), organic-carbon adsorption coefficient [Koc], bio-degradability (see SDS Section 12)

For PNECs, see SDS Section 8.

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1 Exposure Scenario (6)

Industrial/professional use of propellants

SU 3, 19, 22

PC1, 3, 4, 8, 9a, 14, 15, 21, 23, 24, 25, 26, 27, 29, 31, 32, 34, 35, 39

PROC 7, 11, 15

PC1, 3, 4, 8, 9a, 14, 15, 21, 23, 24, 25, 26, 27, 29, 31, 32, 34, 35, 39

ERC 8a, 8d

Spraying of propellant and laboratory use as a chemical will describe the group contributing scenarios listed below:

Scenario name	Process Category (PROC)	Type of setting	Short name
Industrial spraying	PROC 7	Industrial	CS 1
Industrial spraying	PROC 7	Industrial	CS 2
Professional spraying	PROC 11	Professional	CS 3
Professional spraying	PROC 11	Professional	CS 4
Use of laboratory in small scale laboratory	PROC 15	Professional	CS 5

2.1 Contributing scenario (1) controlling environmental exposure for spraying of propellant and laboratory use as a chemical

Product characteristics

Physical state: gas/liquefied gas

Concentration: >25% (ECETOC TRAM does not modify exposure estimates for substances in mixtures if >25%)

Amounts used

Max. 15000 t/year

Fraction to region 0.1 (default for wide dispersive use)

Fraction used at main local source: 0.002 (default for wide dispersive use)

Frequency and duration of use

Continuous release, 365 days/year (default for wide dispersive use)

Environment factors not influenced by risk management

Dilution factor river: 10

Dilution factor marine: 100

Other given operational conditions affecting environmental exposure

None

Technical conditions and measures at process level (source) to prevent release

None

Technical onsite conditions and measures to reduce or limit discharges, air emissions and releases to soil

None

Organisational measures to prevent/limit release from site

None

Conditions and measures related to municipal sewage treatment

Effluent rate of municipal STP: 2000 m³/days

River flow rate: 18000 m³/days

Conditions and measures related to external treatment of waste disposal

No waste generated as substance is a gas and will evaporate to air.

Conditions and measures related to external recovery of waste

None.

2.2 Contributing scenario (2) controlling worker exposure for spraying of propellant and laboratory use as a chemical

Product characteristic

Physical state: gas/liquefied gas

Concentration: >25% (ECETOC TRAM does not modify exposure estimates for substances in mixtures if >25%)

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Amounts used

Not applicable

Frequency & duration of exposure

Exposure frequency: daily for all PROCs

Scenario name	Duration of activity [hours/day]
CS1	>4 hours
CS2	>4 hours
CS3	>4 hours
CS4	1-4 hours
CS5	>4 hours

Human factors not influenced by risk management

None

Other given operational conditions affecting workers exposure

Scenario name	Use of ventilation
CS1	Outdoors
CS2	Indoors without LEV
CS3	Outdoors
CS4	Indoors without LEV
CS5	Indoors without LEV

Technical conditions and measures at process level (source) to prevent release

Handling in industrial settings.
Containment according to definition of PROCs for liquefied gas.
See SDS section 7.

Technical conditions and measures to control dispersion from source towards the worker

None

Organisational measures to prevent/limit release, dispersion and exposure

See SDS.

Conditions and measures related to personal protection, hygiene and health evaluation

See SDS section 8.

3. Exposure estimation and reference to its source

Scenario name	Inhalative Exposure Estimate (mg/m ³)
CS1	672
CS2	960
CS3	1340
CS4	1150
CS5	96

Comment: Tables below are reporting worst case values for PROC 5 – CS 3:

(Semi) Quantitative risk characterisation for workers

	Leading toxic end point/critical effect	Risk characterisation ratio
Long term- systematic effects - inhalation	Anaesthetic	0.7

(Semi) Quantitative risk characterisation for humans exposed via environment

Route	Leading toxic end point/critical effect	Risk characterisation ratio (RCR)
Long term- systematic effects - inhalation	Anaesthetic	0.0000005

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Risk characterisation for the aquatic compartment

Compartments	RCR
Freshwater	0.00001
Marine water	0.00006
Sediment	0.00001
Marine sediment	0.00006

Risk characterisation for the terrestrial compartment

Compartments	RCR
Agricultural soil	0.03
Grassland	0.004

Assessment method:

Worker inhalation: ECETOC TRAM worker (May 2010 release)

Man via Environment: ECETOC TRAM Environment (May 2010 release)

Consumer: ECETOC TRAM Consumer (May 2010 release)

Environment: ECETOC TRAM Environment (May 2010 release)

Release factors:

Air: 100%, max release rate of 4110 kg/day (regional release)

Wastewater: no release to STP

Soil: no direct release to soil

4. Guidance to DU to evaluate whether he works inside the boundaries set by the ES

Worker exposure

Input parameters resulting in highest exposure estimates (worst-case) were used for all activities/processes except for professional spraying (PROC 11), which is limited to 4 hours or less where the activity occurs indoors without LEV. If operating conditions differ, exposure estimates can be scaled using ECETOC TRAM exposure modifiers as follows:

$$RCR_s = RCR_o \times \sum_{i=1}^n CF_{s,i} \div CF_o$$

RCR_o = original exposure prediction

RCR_s = scaled exposure prediction

$CF_{s,i}$ = original correction factor

$CF_{o,i}$ = correction factor for the i th determinant scaling

Correction factor for professional spraying (PROC 11) indoors without LEV = 1 (CF_o)

Correction factor for professional spraying indoors with LEV = 0.2 (CF_s)

Other notes

If the downstream user reduces the exposure duration for each activity/process to less than 8 hours, it may be necessary to consider summing exposure estimates if the same worker may be engaged in multiple tasks during the day.

For DNELs, see SDS section 8.

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Environmental exposure

If conditions differ significantly from those listed in Section 2.1, downstream user (DU) should check whether they are still within the boundaries of the ES. For wide-dispersive releases, DU should check that the RCR from all wide-dispersive releases are below one. This is shown in column ET of the “datasheets” worksheet in ECETOC TRAM.

Basic input parameters required for the environmental assessment using ECETOC TRAM are:

ECETOC/TRAM basic input parameters

Molecular weight: 46.07 g/mol

Vapour pressure, water solubility, octanol-water partition coefficient [Kow] (see SDS Section 9), organic-carbon adsorption coefficient [Koc], bio-degradability (see SDS Section 12)

For PNECs, see SDS Section 8.

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1 Exposure Scenario (7)

Consumer use of propellants

SU 21

PC1, 3, 4, 8, 9a, 24, 39

ERC 8a, 8d (ERC 8a covered by ERC 8d)

Scenario name	Product Category (PC)	Type of setting	Short name
Spraying of propellants indoors and outdoors	PROC1, 3, 4, 8 9a, 24, 39	Consumer	CS 1

2.1 Contributing scenario (1) controlling environmental exposure for spraying of propellant indoors and outdoors

Product characteristics

Concentration: typically <50% substance in preparation

Physical state: gas/liquefied gas

Amounts used

3000 t/year

Fraction to region 0.1 (default for wide dispersive use)

Fraction used at main local source: 0.002 (ESVOC spERC 8.23b.v1 [ESVOC 22]))

Frequency and duration of use

Continuous release, 365 days/year (default for wide dispersive use)

Environment factors not influenced by risk management

Dilution factor river: 10

Dilution factor marine: 100

Other given operational conditions affecting environmental exposure

None

Conditions and measures related to municipal sewage treatment plant

Effluent rate of municipal STP: 2000m³/day

River flow rate: 18000m³/day

Conditions and measures related to external treatment of waste disposal

None

Conditions and measures related to external recovery of waste

None.

2.2 Contributing scenario (2) controlling worker exposure for spraying of propellants indoors and outdoors

Product characteristic

Concentration: typically <50% substance in preparation

Physical state: gas/liquefied gas

Amounts used

Up to 10g per application

Frequency & duration of exposure

Frequency: 4 times/day

Duration [for contact]: 15 minutes

Human factors not influenced by risk management

None

Other given operational conditions affecting workers exposure

This product is used indoors and outdoors. Only indoors is considered since it leads to worst case potential exposure.

Indoor air volume: min. >2.5m³, 1.5/hr air exchange rate

Conditions and measures related to information and behavioural advice to consumers

Label advices on safe use.

Conditions and measures related to personal protection and hygiene

Label advices on safe use.

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3. Exposure estimation and reference to its source

Scenario name Inhalative Exposure Estimate (mg/m³)
CS1 57.1

Comment: Tables below are reporting worst case values for PC 9a:

(Semi) Quantitative risk characterisation for workers

	Leading toxic end point/critical effect	Risk characterisation ratio
Long term- systematic effects – inhalation	Anaesthetic	0.4

(Semi) Quantitative risk characterisation for humans exposed via environment

Route	Leading toxic end point/critical effect	Risk characterisation ratio (RCR)
Long term- systematic effects – inhalation	Anaesthetic	0.0000005

Risk characterisation for the aquatic compartment

Compartments	RCR
Freshwater	0.00001
Marine water	0.00006
Sediment	0.00001
Marine sediment	0.00006

Risk characterisation for the terrestrial compartment

Compartments	RCR
Agricultural soil	0.00005
Grassland	0.00005

Assessment method:

Consumer: ECETOC TRAM Consumer (May 2010 release), ConsExpo 4.1, and AISE REACT

Man via Environment: ECETOC TRAM Environment (May 2010 release)

Environment: ECETOC TRAM Environment (May 2010 release)

Release factors:

Air: spERC ESVOC 22 (refinement of ERC 8a): release to air is 100%, max release rate of 8220 kg/day (regional release)

Wastewater: No release to wastewater as 100% goes to air

Soil: no direct release to soil as 100% goes to air

4. Guidance to DU to evaluate whether he works inside the boundaries set by the ES

If conditions differ significantly from those listed in Section 2, downstream user (DU) should check whether they are still within the boundaries of the ES. This evaluation may be based on expert judgement or on the risk assessment tools that are recommended by ECHA.

Honeywell HFO-1234ze Blowing Agent

trans – 1,3,3,3-tetrafluoropropene

Honeywell HFO-1234ze blowing agent is the Honeywell trade name for trans – 1,3,3,3-tetrafluoropropene, Honeywell's new low global warming potential (GWP), fourth generation blowing agent and propellant. The low GWP molecule is the first hydrofluoroolefin (HFO) to be commercialised into these industries. This molecule has low environmental impact, as measured by its ultra-low global warming potential and zero ozone depletion potential (ODP). Honeywell HFO-1234ze blowing agent is fully compliant with the EU F-Gas regulation. As a gas material at room temperature, this molecule has diverse applications including as a blowing agent for polyurethanes, polystyrene and other polymers; as well as an aerosol propellant.

Honeywell HFO-1234ze blowing agent has received Notification VIII, Level 1 by the EU Competent Authority for quantities to 1000 tonnes/annum, allowing commercialisation in the EU, as of October 2008.

Honeywell remains committed to developing new innovative low environmental impact technology to meet ever exacting market needs for products that have low GWP and zero ODP properties, plus are safe to use and impart energy saving benefits due to thermal conductivity performance in insulation foams. Honeywell HFO-1234ze blowing agent is non-flammable by ASTM E-681 and EU A11 test methods. However, the material does exhibit flame limits at elevated temperatures.

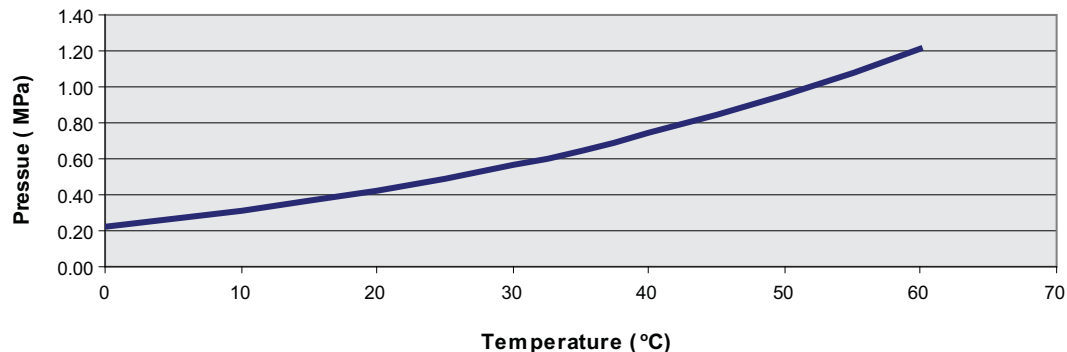
HONEYWELL HFO-1234ZE BLOWING AGENT SALES SPECIFICATION

Parameter	Limit
Assay as trans – 1,3,3,3-tetrafluoropropene	99.5 wt. % min.
Moisture	0.0050 wt.% max.
Acidity	
as HCl	0.0001 wt.% max.
as mg KOH/gm.	0.0015, max.
Non-volatile residue	0.0050 wt.% max

GENERAL PROPERTIES

Molecule	Honeywell HFO-1234ze Blowing Agent trans – 1,3,3,3-tetrafluoropropene
CAS #	1645 – 83 – 6
ELINCS # (EU)	471 – 480 – 0
Formula	trans – CHF=CHCF ₃
Molecular Weight	114
Boiling Point	- 19° C
Vapor Pressure @ 25° C	490 kPa
Vapor Pressure @ 55° C	1080 kPa
Liquid Density @ 25° C	1.18 gm/cm ³
Vapour Thermal Conductivity	13.0 mW / m• °K (@ 25°C)
Flame Limits	None to 30° C
Ozone Depletion Potential	Zero (non-ODS)
Global Warming Potential	6 (100 yr time horizon)

TRANS-1,3,3,3-TETRAFLUOROPROPENE VAPOUR PRESSURE



MATERIALS COMPATIBILITY WITH HONEYWELL HFO-1234ZE BLOWING AGENT

Substrate	Hardness	Avg Percentage Change Weight	Volume
Plastics			
HDPE		+0.82	-3.74
Polypropylene		+0.83	0.0
PVC – Type 1		+0.01	-0.44
PET		-0.01	0.0
Polyetherimide		-0.04	0.0
Nylon 6,6		-0.26	0.0
PVDF		+0.21	0.0
PTFE		+2.03	-2.43
Elastomers			
Fluoroelastomer	-11.29	+4.43	+5.71
Nitrile Rubber	+8.91	-4.95	-7.18
EPDM	-1.50	-2.00	-2.49
Butyl Rubber	-1.13	+1.27	+0.88
Neoprene	+7.32	-7.70	-11.47

HEALTH, SAFETY AND ENVIRONMENTAL

Honeywell HFO-1234ze blowing agent has progressed through a battery of toxicity testing for human health effects (data for which EU Competent Authority uses for Notification Status). The Honeywell material safety data sheet (MSDS) for HFO-1234ze(E) contains comprehensive and the most current detail for the health, safety and environmental aspects and considerations.

EU ELINCS Number: 471 – 480 – 0

Flammability Characteristics

Honeywell HFO-1234ze blowing agent is a non-flammable gas by test methods ASTM E-681, and by EU Test method A-11. Flammability characterization of Honeywell HFO-1234ze blowing agent was performed by Chilworth Technologies Ltd – UK, with the finding, “It has been concluded beyond reasonable doubt that the material (Honeywell HFO-1234ze blowing agent) will not possess oxidizing or explosive properties.”

It should be noted that flammability characterization and flammability regulations for gaseous materials are evaluated at room temperature ~21°C. Honeywell HFO-1234ze blowing agent exhibits narrow vapour flame limits at elevated temperatures (>28°C). At 30°C, Honeywell HFO-1234ze blowing agent exhibits flame limits LEL/UFL at 7.0/9.5 volume percent in air.

Further investigation into the flammability characterization of Honeywell HFO-1234ze blowing agent has yielded evidence that (at elevated temperatures, 60°C) the minimum ignition energy is significantly high – 61,000 mJ. This is several orders of

magnitude higher than other commonly used low GWP blowing agents, such as hydrocarbons, meaning HFO-1234ze is more difficult to ignite.

Safe handling and use in processes utilizing Honeywell HFO-1234ze blowing agent, as well as any other halogenated materials, include avoidance of fire, open flame, smoking, and hot surfaces in the vicinity of these materials.

STORAGE AND HANDLING

Honeywell HFO-1234ze blowing agent should be handled in a manner consistent with materials categorized as 'liquefied gases under pressure.' As illustrated by the vapour pressure data, Honeywell HFO-1234ze blowing agent is a moderate pressure gas, and containers (bulk storage tanks or packages) should be pressure rated to Honeywell HFO-1234ze blowing agent vapour pressure at the ambient temperature, or nominally (minimally) at 1000 kPa (10 Bar).

Honeywell HFO-1234ze blowing agent, in approved packages (containers), should be stored in a cool, well-ventilated area. Honeywell HFO-1234ze blowing agent packages (containers) should neither be punctured or dropped, nor exposed to open flames, excessive heat or direct sunlight. The package (container) valves should be tightly closed after use and when the container is empty.

Based on industry experience, Honeywell HFO-1234ze blowing agent should not be mixed with oxygen or air at elevated pressures. Applications necessitating pressurization – exceeding the vapour pressure of Honeywell HFO-1234ze blowing agent– should use dry nitrogen.

Honeywell Fluorine Products

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Atmospheric chemistry of trans-CF₃CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation

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Abstract

Smog chamber/FTIR techniques were used to study the products and mechanisms of OH radical and Cl atom initiated oxidation of trans-CF₃CH=CHF in 700 Torr of N₂/O₂ diluent at 295±1 K. Hydroxyl radical initiated oxidation leads to the formation of CF₃CHO and HC(O)F in yields which were indistinguishable from 100% and were not dependent on the O₂ partial pressure. Chlorine atom initiated oxidation gives HC(O)F, CF₃CHO, CF₃C(O)Cl, and CF₃C(O)CHFCl. The yields of CF₃C(O)Cl and CF₃C(O)CHFCl increased at the expense of HC(O)F and CF₃CHO as the O₂ partial pressure was increased over the range 5–700 Torr. The results are discussed with respect to the atmospheric chemistry and environmental impact of trans-CF₃CH=CHF.

1 Introduction

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere (Molina et al., 1974; Farman et al., 1985) has led to an international effort to replace these compounds with environmentally acceptable alternatives. Saturated hydrofluorocarbons (HFCs) have become widely used CFC replacements. For example, CF₃CH₂F (HFC-134a) is used as the working fluid in all modern vehicle air conditioning systems. Hydrofluorocarbons do not contain chlorine and hence do not contribute to the well established chlorine based catalytic ozone destruction cycles (Wallington et al., 1994). The atmospheric lifetime of HFCs is determined by their reactivity towards OH radicals. HFC-134a has a direct global warming potential of 1440 over a 100 y time horizon; a factor of 8 lower than the CFC-12 that it replaced (World Meteorological Organization, 2007).

Unsaturated hydrofluorocarbons are a class of compounds, which are potential replacements for CFCs and saturated HFCs in air conditioning units. In general, unsaturated hydrofluorocarbons react more rapidly with OH radicals, have shorter atmospheric lifetimes, and have lower global warming potentials than saturated hy-

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drofluorocarbons. Prior to their large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of these compounds is needed. The present paper provides information concerning the atmospheric oxidation products of trans-CF₃CH=CHF. Specifically, smog chamber/FTIR techniques
 5 were used to determine the products of the OH radical and Cl atom initiated oxidation of trans-CF₃CH=CHF. The present work builds upon a recent kinetic study in which values of $k(\text{Cl}+\text{trans-CF}_3\text{CH=CHF})=(4.64\pm0.59)\times10^{-11}$ and $k(\text{OH}+\text{trans-CF}_3\text{CH=CHF})=(9.25\pm1.72)\times10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ in 700 Torr total pressure at 296 K were determined (Søndergaard et al., 2007).

10 2 Experimental

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer (Wallington and Japar, 1989). The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. The products of the atmospheric oxidation of trans-
 15 CF₃CH=CHF were investigated by irradiating trans-CF₃CH=CHF/CH₃ONO/O₂/N₂ and trans-CF₃CH=CHF/Cl₂/O₂/N₂ mixtures. All samples of trans-CF₃CH=CHF used in this work were supplied by Honeywell International Inc. at a purity >99.9% and were used without further purification.

Chlorine atoms were produced by photolysis of molecular chlorine,



OH radicals were produced by photolysis of CH₃ONO in the presence of NO in air,



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CH₃ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of NaNO₂ in methanol. Other reagents were obtained from commercial sources at purities >99%. Experiments were conducted in 700 Torr total pressure of N₂/O₂, or air diluent at 295±1 K.

- 5 Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm⁻¹ and an analytical path length of 27.1 m. Unless stated otherwise, quoted uncertainties are two standard deviations from least squares regressions.

3 Results

10 3.1 Products of OH radical initiated oxidation of trans-CF₃CH=CHF

- To investigate the products and mechanism of the reaction of OH radicals with trans-CF₃CH=CHF reaction mixtures consisting of 8.3–34.9 mTorr trans-CF₃CH=CHF, 82.3–117.3 mTorr CH₃ONO, 15.1–19.6 mTorr NO, and 126–700 Torr O₂ in 700 Torr total pressure of N₂ diluent were introduced into the chamber and subjected to UV irradiation. Figure 1 shows IR spectra at 1750–1950 cm⁻¹ obtained before (a) and after (b) 15
subjecting a mixture containing 34.9 mTorr trans-CF₃CH=CHF, 82.3 mTorr CH₃ONO, 19.6 mTorr NO, and 126 Torr O₂ in 700 Torr of N₂ diluent to 6 min of UV irradiation. The consumption of trans-CF₃CH=CHF was 6%. Subtraction of IR features attributable to CF₃CH=CHF, H₂O, NO, and HCHO (product of CH₃ONO photolysis) from panel (b) 20
gives the product spectrum shown in panel (c). Comparison of the IR features in panel (c) with the reference spectra of HC(O)F and CF₃CHO in panels (d) and (e) shows the formation of these products.

- HC(O)F and CF₃CHO were the only identified carbon containing products of the OH radical initiated oxidation of trans-CF₃CH=CHF. Figure 2 shows a plot of the observed 25
formation of HC(O)F and CF₃CHO versus loss of trans-CF₃CH=CHF. The yields of HC(O)F and CF₃CHO were indistinguishable. For low consumptions (<1 mTorr) the

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linear least squares fit to the combined data sets has a slope $=0.93 \pm 0.08$ indistinguishable from 100%. For consumptions of $\text{CF}_3\text{CH}=\text{CHF}$ greater than 1 mTorr the observed yields of $\text{HC}(\text{O})\text{F}$ and CF_3CHO are less than 100% indicating that either the efficiency of conversion of $\text{trans-CF}_3\text{CH}=\text{CHF}$ into $\text{HC}(\text{O})\text{F}$ and CF_3CHO is lower, or there are significant losses of these products at higher $\text{trans-CF}_3\text{CH}=\text{CHF}$ conversions, or both. To test for heterogeneous loss of $\text{HC}(\text{O})\text{F}$ and CF_3CHO , reaction mixtures were allowed to stand in the dark for 15 min; there was no discernable loss ($<2\%$) of either compound. For the 2–14% conversions of $\text{trans-CF}_3\text{CH}=\text{CHF}$ in the data shown in Fig. 2, loss of $\text{HC}(\text{O})\text{F}$ and CF_3CHO via secondary reactions with OH radicals should be of minor importance as their reactivity with OH is less than that of $\text{trans-CF}_3\text{CH}=\text{CHF}$; $k(\text{OH}+\text{trans-CF}_3\text{CH}=\text{CHF})=(9.25 \pm 1.72) \times 10^{-13}$ (Søndergaard et al., 2007), $k(\text{OH}+\text{HC}(\text{O})\text{F})<4 \times 10^{-15}$ (Wallington et al., 1993), and $k(\text{OH}+\text{CF}_3\text{CHO})=(6 \pm 1.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2007). It seems likely that the curvature in Fig. 2 reflects a lower yield of both $\text{HC}(\text{O})\text{F}$ and CF_3CHO with increased consumption of $\text{CF}_3\text{CH}=\text{CHF}$. A possible explanation of this effect is the reaction of NO_2 (which increases in concentration with consumption of $\text{trans-CF}_3\text{CH}=\text{CHF}$) with the alkoxy radicals formed in the system leading to the formation of small amounts of nitrates. In the atmosphere such reactions will not be of any significance and we did not pursue the origin of the curvature further.

By analogy to the well established oxidation mechanism of propene (IUPAC, 2007), the reaction of OH radicals with $\text{trans-CF}_3\text{CH}=\text{CHF}$ is expected to proceed via addition to the $>\text{C}=\text{C}<$ double bond. The mechanism of the OH radical initiated oxidation of $\text{trans-CF}_3\text{CH}=\text{CHF}$ which explains the observed formation of $\text{HC}(\text{O})\text{F}$ and CF_3CHO as shown in Fig. 3. The results from the present work indicate that irrespective of whether the OH radicals add to the terminal, or central carbon atom, the subsequent reactions lead to the formation of one molecule of both $\text{HC}(\text{O})\text{F}$ and CF_3CHO .

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3.2 Products of Cl atom initiated oxidation of trans-CF₃CH=CHF

The products of the Cl atom initiated oxidation of trans-CF₃CH=CHF were studied using the UV irradiation of trans-CF₃CH=CHF/Cl₂/O₂/N₂ mixtures. Mixtures consisting of 6.6–8.4 mTorr trans-CF₃CH=CHF, 102.9–134 mTorr Cl₂ and 5–700 Torr of O₂ in 5
700 Torr total pressure of N₂ diluent were introduced into the reaction chamber and subjected to UV irradiation. Figures 4 and 5 show IR spectra at 675–1000 cm⁻¹ and 1650–2000 cm⁻¹, respectively, obtained before (a) and after (b) subjecting a mixture containing 6.6 mTorr trans-CF₃CH=CHF and 109 mTorr Cl₂ in 700 Torr air diluent to 20 s of UV irradiation. Comparison of the IR features formed in low and high [O₂] experiments revealed that four products were formed in the chamber; HC(O)F, CF₃CHO, 10
CF₃C(O)Cl, and a product with a broad absorption feature in the carbonyl stretching region centered at 1801 cm⁻¹ which we attribute to the ketone CF₃C(O)CHFCl. We do not have a calibrated reference spectrum for CF₃C(O)CHFCl. The concentration of this compound in the chamber was estimated by assuming that the carbonyl stretching band integrated absorption cross section at 1780–1820 cm⁻¹ is the same as that in 15
CF₃C(O)CH₂Cl (1.06×10^{-17} cm molecule⁻¹, Nakayama et al., 2007).

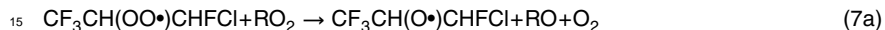
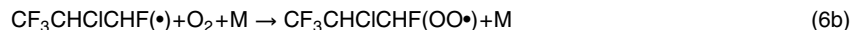
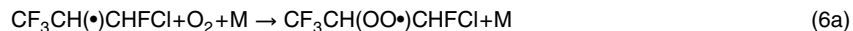
Figure 6 shows a plot of the concentrations of HC(O)F, CF₃CHO, CF₃C(O)Cl, and CF₃C(O)CHFCl versus the loss of trans-CF₃CH=CHF observed following the UV irradiation of a mixture of 6.61 mTorr trans-CF₃CH=CHF and 109 mTorr Cl₂ in 700 Torr of air diluent. As seen from Fig. 6 the formation of HC(O)F, CF₃C(O)H, CF₃C(O)Cl and CF₃C(O)CHFCl scaled linearly with the loss of trans-CF₃CH=CHF over the range of 20
trans-CF₃CH=CHF consumption of 10–95%. The linearity of the formation of HC(O)F, CF₃CHO, CF₃C(O)Cl and CF₃C(O)CHFCl suggests that loss of these compounds via secondary reactions is not significant. This observation is consistent with the fact that Cl atoms react much more slowly with these products than with the parent trans-CF₃CH=CHF compound; $k(\text{Cl} + \text{trans-CF}_3\text{CH=CHF}) = (4.64 \pm 0.59) \times 10^{-11}$ (Søndergaard et al., 2007), $k(\text{Cl} + \text{HC(O)F}) = (1.9 \pm 0.2) \times 10^{-15}$ (Meagher et al., 1997), and $k(\text{Cl} + \text{CF}_3\text{CHO}) = (1.85 \pm 0.26) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Sulbaek Andersen et al., 25

2004). Previous work has shown that $\text{CF}_3\text{C}(\text{O})\text{Cl}$ is not lost by heterogeneous processes, photolysis, or reaction with Cl atoms in the chamber (Møgelberg et al., 1995).

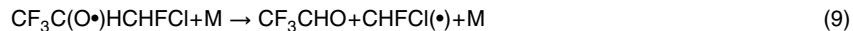
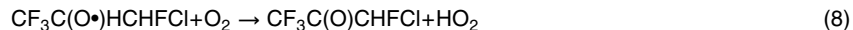
As shown in Fig. 7, the yields of $\text{HC}(\text{O})\text{F}$, CF_3CHO , $\text{CF}_3\text{C}(\text{O})\text{Cl}$ and $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ varied with $[\text{O}_2]$. In experiments with high $[\text{O}_2]$ the yields of $\text{CF}_3\text{C}(\text{O})\text{Cl}$ and $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ increased at the expense of $\text{HC}(\text{O})\text{F}$ and CF_3CHO . As in the case of the OH radical attack, the reaction of Cl atoms with $\text{trans-CF}_3\text{CH=CHF}$ is expected to proceed via electrophilic addition to the terminal and central carbon atoms:



The radicals produced in Reaction (5) will react with O_2 to give peroxy radicals which will undergo self- and cross-reaction to give the corresponding alkoxy radicals (in the equations below M represents a third body):



Decomposition via C-C bond scission or reaction with O_2 are likely fates of the alkoxy radicals. The observed formation of the ketone $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ in a yield which varies with $[\text{O}_2]$ shows that $\text{CF}_3\text{C}(\text{O}\bullet)\text{HCHFCl}$ radicals undergo reaction with O_2 and decomposition via C-C bond scission:



The $\text{CHFCI}(\bullet)$ radicals formed in Reaction (9) will add O_2 , undergo reaction with other peroxy radicals in the system to give $\text{CHFCI}(\text{O}\bullet)$ radicals, and decompose via Cl atom elimination to give $\text{HC}(\text{O})\text{F}$ (Tuazon et al., 1993). The data in Fig. 7 contain information concerning the rate constant ratio k_8/k_9 . The yield of $\text{CF}_3\text{C}(\text{O})\text{CHFCI}$, $Y_{\text{CF}_3\text{C}(\text{O})\text{CHFCI}}$, can be described by the expression $Y_{\text{CF}_3\text{C}(\text{O})\text{CHFCI}} = Y_{\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCI}} (k_8[\text{O}_2]/(k_8[\text{O}_2] + k_9)) + C$, where $Y_{\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCI}}$ is the yield of $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCI}$ radicals in the system, k_8 and k_9 are the rate constants for Reactions (8) and (9), and C is the $[\text{O}_2]$ independent yield of $\text{CF}_3\text{C}(\text{O})\text{CHFCI}$ (e.g., from self-reaction of $\text{CF}_3\text{CH}(\text{OO}\bullet)\text{CHFCI}$ peroxy radicals).

The curve through the $\text{CF}_3\text{C}(\text{O})\text{CHFCI}$ data in Fig. 7 is a fit of the expression above to the data which gives $k_8/k_9 = (8.0 \pm 2.6) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$. This value can be compared to the analogous rate constant ratio $k_{\text{O}_2}/k_{\text{diss}} = (3.8 \pm 1.8) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ measured for $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CH}_2\text{Cl}$ radicals (Nakayama et al., 2007). The increased importance of decomposition as an atmospheric fate of $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCI}$ compared to $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CH}_2\text{Cl}$ radicals is consistent with theoretical work showing that the barrier to C-C bond scission decreases as the degree of fluorine substitution on the two carbon atoms becomes more even and the bond becomes less polar (Somnitz et al., 2001). The limiting value for the $\text{CF}_3\text{C}(\text{O})\text{CHFCI}$ yield reached at high $[\text{O}_2]$ provides a measure of $k_{5a}/(k_{5a} + k_{5b}) = 47 \pm 7\%$.

Figure 8 shows the mechanism of Cl atom initiated oxidation of $\text{trans-CF}_3\text{CH=CHF}$ which is consistent with our experimental observations. From $k_8/k_9 = (8.0 \pm 2.6) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ it can be calculated that in 700 Torr of O_2 the reaction with O_2 accounts for 92% of the $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CH}_2\text{Cl}$ radicals with decomposition accounting for the remaining 8%. Given the estimate of $k_{5a}/(k_{5a} + k_{5b}) = 47 \pm 7\%$ we then expect a 4% $\text{HC}(\text{O})\text{F}$ yield resulting from addition of Cl atoms to the terminal carbon atom (left hand side of Fig. 8). Hence, we can attribute the bulk of the approximately 40% $\text{HC}(\text{O})\text{F}$ yield in experiments in 700 Torr of O_2 to the decomposition of $\text{CF}_3\text{CHClCHF}(\text{O}\bullet)$ radicals. Decomposition via C-C bond scission is the dominant fate of $\text{CF}_3\text{CHClCHF}(\text{O}\bullet)$ radicals. Finally, the increase in the yield of $\text{CF}_3\text{C}(\text{O})\text{Cl}$

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with $[O_2]$ evident in Fig. 7 is consistent with the expected competition between reaction with O_2 and decomposition for the available $CF_3CHCl(O\bullet)$ radicals. The yield of $CF_3C(O)Cl$, $Y_{CF_3C(O)Cl}$, can be described by the expression $Y_{CF_3C(O)Cl} = Y_{CF_3CHCl(O\bullet)} (k_{10}[O_2]/(k_{10}[O_2] + k_{11})) + C$, where $Y_{CF_3CHCl(O\bullet)}$ is the yield of $CF_3CHCl(O\bullet)$ radicals in the system, k_{10} and k_{11} are the rate constants for Reactions (10) and (11), and C is the $[O_2]$ independent yield of $CF_3C(O)Cl$.



The curve through the $CF_3C(O)Cl$ data in Fig. 7 is a fit of the expression above to the data which gives $k_{10}/k_{11} = (4.6 \pm 1.9) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$. This result is larger than the previous more direct determination of $k_{10}/k_{11} = (2.1 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ (Møgelberg et al., 1995). A likely explanation for this discrepancy lies in the indirect and complex route by which $CF_3CHCl(O\bullet)$ radicals are formed in the present system. As indicated in Fig. 8, decomposition and reaction with O_2 are possible competing fates for $CF_3CHClCHF(O\bullet)$ radicals. Increased loss of $CF_3CHClCHF(O\bullet)$ via reaction with O_2 at high $[O_2]$ will lead to a decreased yield of $CF_3CHCl(O\bullet)$ radicals and hence $CF_3C(O)Cl$. The net effect will be to cause the $CF_3C(O)Cl$ yield to plateau at a lower $[O_2]$ which will lead to an overestimation of k_{10}/k_{11} . To investigate this effect further would require the use of $[O_2]$ levels higher than 700 Torr where a decrease in the yield of $CF_3C(O)Cl$ would be expected with increased loss of $CF_3CHClCHF(O\bullet)$ via reaction with O_2 . Such experiments are beyond the scope of the present work.

4 Atmospheric chemistry and environmental impact of trans- $CF_3CH=CHF$

The present work improves our understanding of the atmospheric chemistry of trans- $CF_3CH=CHF$. The atmospheric lifetime of trans- $CF_3CH=CHF$ is dictated by its reaction with OH radicals (Søndergaard et al., 2007) and has been estimated at approximately 2

weeks. The OH initiated oxidation of trans-CF₃CH=CHF gives CF₃CHO and HC(O)F in yields of approximately 100%. CF₃CHO is removed from the atmosphere via photolysis and, to lesser extents, reaction with OH radicals (Chiappero et al., 2006) and addition of water to give the hydrate (Sulbaek Andersen et al., 2006). Photolysis gives CF₃ and HCO radicals (Chiappero et al., 2006) while reaction with OH gives CF₃CO radicals. CF₃ radicals will add O₂ to give CF₃O₂ radicals which are then converted into COF₂ (Wallington et al., 1994) which hydrolyzes to give CO₂ and HF. CF₃CO radicals will add O₂ to give CF₃C(O)O₂ radicals, the majority of which will be converted into COF₂, with a small fraction converted into CF₃C(O)OH (Hurley et al., 2006) via reaction with HO₂ radicals. The hydrate, CF₃CH(OH)₂ is lost via reaction with OH radicals to give CF₃C(O)OH (Sulbaek Andersen et al., 2006). The available data suggest that while CF₃C(O)OH is not a natural component of the freshwater environment (Nielsen et al., 2001), it is a natural component of the background oceanic environment (Frank et al., 2002), and any additional burden associated with trans-CF₃CH=CHF oxidation will be of negligible environmental significance. We conclude that the products of the atmospheric oxidation of trans-CF₃CH=CHF will have negligible environmental impact.

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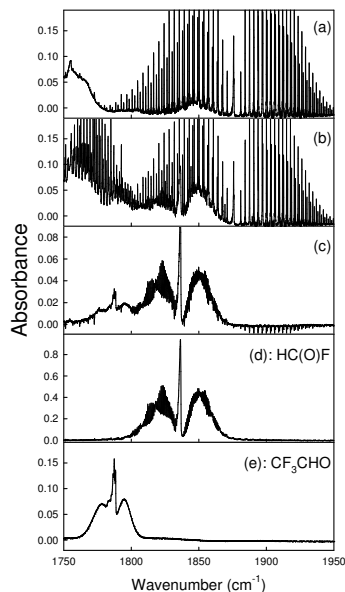


Fig. 1. Infrared spectra acquired before **(a)** and after **(b)** UV irradiation of mixtures 34.9 mTorr $\text{trans-CF}_3\text{CH=CHF}$, 82.3 mTorr CH_3ONO , 19.6 mTorr NO and 126 Torr O_2 in 700 Torr total pressure of N_2 diluent. Panel **(c)** show the residual IR features after subtraction of features attributable to $\text{trans-CF}_3\text{CH=CHF}$, H_2O , NO , and HCHO from panel (b). Panels **(d)** and **(e)** show reference spectra of HC(O)F and CF_3CHO , respectively.

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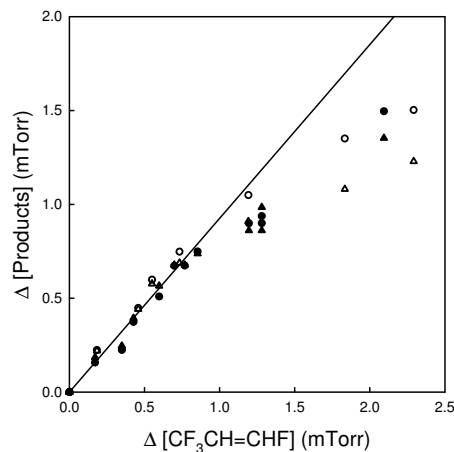


Fig. 2. Formation of HC(O)F (triangles) and CF₃CHO (circles) versus loss of trans-CF₃CH=CHF observed following the UV irradiation of mixtures of 8.32–9.18 mTorr trans-CF₃CH=CHF and 109.1–113.8 mTorr CH₃ONO in 700 Torr total pressure of air diluent at 296±1 K. The open symbols are results obtained in the absence of NO.

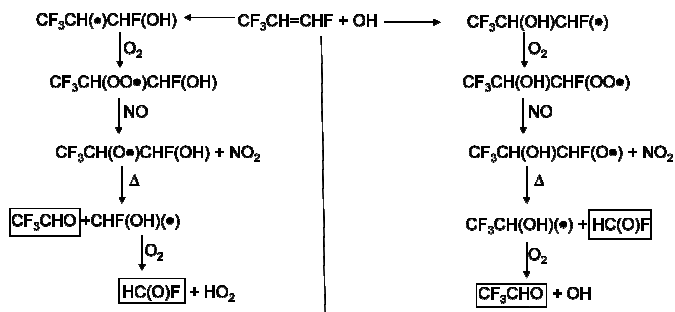


Fig. 3. Mechanism of OH radical initiated oxidation of trans-CF₃CH=CHF, boxes indicate observed products.

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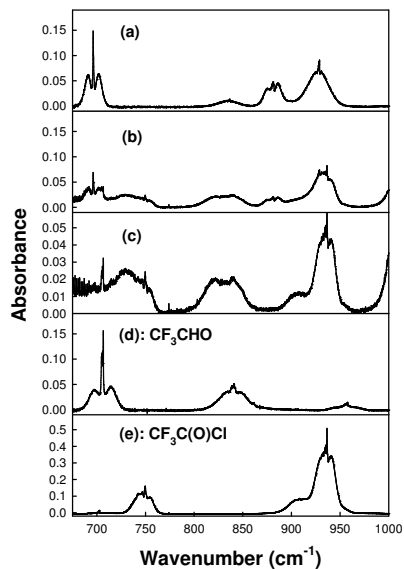


Fig. 4. Infrared spectra acquired before **(a)** and after **(b)** UV irradiation of 6.6 mTorr trans- $\text{CF}_3\text{CH}=\text{CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent. Panel **(c)** show the residual IR features after subtraction of trans- $\text{CF}_3\text{CH}=\text{CHF}$ from panel **(b)**. Panels **(d)** and **(e)** show reference spectra of CF_3CHO and $\text{CF}_3\text{C}(\text{O})\text{Cl}$, respectively.

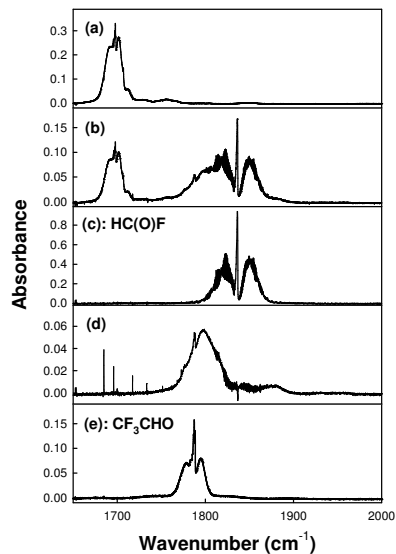


Fig. 5. Infrared spectra acquired before **(a)** and after **(b)** UV irradiation of 6.6 mTorr $\text{trans-CF}_3\text{CH=CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent. Panel **(c)** show a reference spectrum of HC(O)F . Panel **(d)** show the residual IR features after subtraction of $\text{trans-CF}_3\text{CH=CHF}$ and HC(O)F from panel **(b)**. Panel **(e)** shows a reference spectrum of CF_3CHO .

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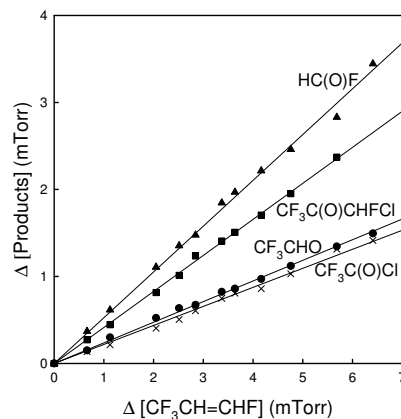


Fig. 6. Formation of HC(O)F (triangles), $\text{CF}_3\text{C(O)CHFCl}$ (squares), CF_3CHO (circles) and, $\text{CF}_3\text{C(O)Cl}$ (crosses) versus loss of $\text{trans-CF}_3\text{CH=CHF}$ observed following the UV irradiation of a mixture of 6.6 mTorr $\text{trans-CF}_3\text{CH=CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent.

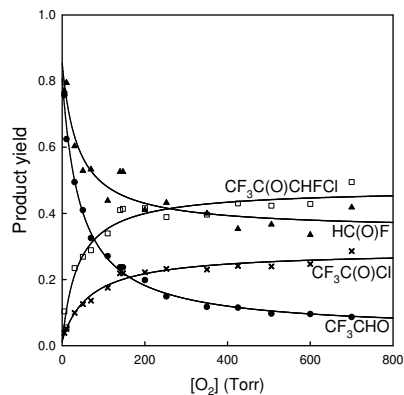


Fig. 7. Observed molar yields of HC(O)F (triangles), CF₃CHO (circles), CF₃C(O)Cl (crosses) and CF₃C(O)CHFCI (squares) versus the O₂ partial pressure following the UV irradiation of trans-CF₃CH=CHF/Cl₂/N₂/O₂ mixtures at 700 Torr total pressure. Curves through the CF₃C(O)CHFCI and CF₃C(O)Cl are fits to the data using the expressions described in the text. The curves through the HC(O)F and CF₃CHO data are polynomial fits to aid visual inspection of data trends.

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Atmospheric chemistry of trans-CF₃CH=CHF

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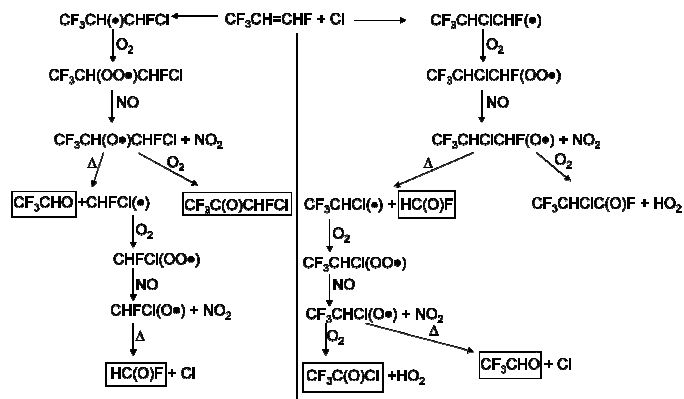


Fig. 8. Mechanism of Cl atom initiated oxidation of trans- $\text{CF}_3\text{CH=CHF}$, boxes indicate observed products.

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Atmospheric chemistry of trans-CF₃CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation

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Abstract

Smog chamber/FTIR techniques were used to study the products and mechanisms of OH radical and Cl atom initiated oxidation of trans-CF₃CH=CHF in 700 Torr of N₂/O₂ diluent at 295±1 K. Hydroxyl radical initiated oxidation leads to the formation of CF₃CHO and HC(O)F in yields which were indistinguishable from 100% and were not dependent on the O₂ partial pressure. Chlorine atom initiated oxidation gives HC(O)F, CF₃CHO, CF₃C(O)Cl, and CF₃C(O)CHFCl. The yields of CF₃C(O)Cl and CF₃C(O)CHFCl increased at the expense of HC(O)F and CF₃CHO as the O₂ partial pressure was increased over the range 5–700 Torr. The results are discussed with respect to the atmospheric chemistry and environmental impact of trans-CF₃CH=CHF.

1 Introduction

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere (Molina et al., 1974; Farman et al., 1985) has led to an international effort to replace these compounds with environmentally acceptable alternatives. Saturated hydrofluorocarbons (HFCs) have become widely used CFC replacements. For example, CF₃CH₂F (HFC-134a) is used as the working fluid in all modern vehicle air conditioning systems. Hydrofluorocarbons do not contain chlorine and hence do not contribute to the well established chlorine based catalytic ozone destruction cycles (Wallington et al., 1994). The atmospheric lifetime of HFCs is determined by their reactivity towards OH radicals. HFC-134a has a direct global warming potential of 1440 over a 100 y time horizon; a factor of 8 lower than the CFC-12 that it replaced (World Meteorological Organization, 2007).

Unsaturated hydrofluorocarbons are a class of compounds, which are potential replacements for CFCs and saturated HFCs in air conditioning units. In general, unsaturated hydrofluorocarbons react more rapidly with OH radicals, have shorter atmospheric lifetimes, and have lower global warming potentials than saturated hy-

drofluorocarbons. Prior to their large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of these compounds is needed. The present paper provides information concerning the atmospheric oxidation products of trans-CF₃CH=CHF. Specifically, smog chamber/FTIR techniques were used to determine the products of the OH radical and Cl atom initiated oxidation of trans-CF₃CH=CHF. The present work builds upon a recent kinetic study in which values of $k(\text{Cl}+\text{trans-CF}_3\text{CH=CHF})=(4.64\pm0.59)\times10^{-11}$ and $k(\text{OH}+\text{trans-CF}_3\text{CH=CHF})=(9.25\pm1.72)\times10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ in 700 Torr total pressure at 296 K were determined (Søndergaard et al., 2007).

2 Experimental

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer (Wallington and Japar, 1989). The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. The products of the atmospheric oxidation of trans-CF₃CH=CHF were investigated by irradiating trans-CF₃CH=CHF/CH₃ONO/O₂/N₂ and trans-CF₃CH=CHF/Cl₂/O₂/N₂ mixtures. All samples of trans-CF₃CH=CHF used in this work were supplied by Honeywell International Inc. at a purity >99.9% and were used without further purification.

Chlorine atoms were produced by photolysis of molecular chlorine,



OH radicals were produced by photolysis of CH₃ONO in the presence of NO in air,



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CH₃ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of NaNO₂ in methanol. Other reagents were obtained from commercial sources at purities >99%. Experiments were conducted in 700 Torr total pressure of N₂/O₂, or air diluent at 295±1 K.

Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm⁻¹ and an analytical path length of 27.1 m. Unless stated otherwise, quoted uncertainties are two standard deviations from least squares regressions.

3 Results

3.1 Products of OH radical initiated oxidation of trans-CF₃CH=CHF

To investigate the products and mechanism of the reaction of OH radicals with trans-CF₃CH=CHF reaction mixtures consisting of 8.3–34.9 mTorr trans-CF₃CH=CHF, 82.3–117.3 mTorr CH₃ONO, 15.1–19.6 mTorr NO, and 126–700 Torr O₂ in 700 Torr total pressure of N₂ diluent were introduced into the chamber and subjected to UV irradiation. Figure 1 shows IR spectra at 1750–1950 cm⁻¹ obtained before (a) and after (b) subjecting a mixture containing 34.9 mTorr trans-CF₃CH=CHF, 82.3 mTorr CH₃ONO, 19.6 mTorr NO, and 126 Torr O₂ in 700 Torr of N₂ diluent to 6 min of UV irradiation. The consumption of trans-CF₃CH=CHF was 6%. Subtraction of IR features attributable to CF₃CH=CHF, H₂O, NO, and HCHO (product of CH₃ONO photolysis) from panel (b) gives the product spectrum shown in panel (c). Comparison of the IR features in panel (c) with the reference spectra of HC(O)F and CF₃CHO in panels (d) and (e) shows the formation of these products.

HC(O)F and CF₃CHO were the only identified carbon containing products of the OH radical initiated oxidation of trans-CF₃CH=CHF. Figure 2 shows a plot of the observed formation of HC(O)F and CF₃CHO versus loss of trans-CF₃CH=CHF. The yields of HC(O)F and CF₃CHO were indistinguishable. For low consumptions (<1 mTorr) the

linear least squares fit to the combined data sets has a slope $=0.93\pm0.08$ indistinguishable from 100%. For consumptions of $\text{CF}_3\text{CH=CHF}$ greater than 1 mTorr the observed yields of HC(O)F and CF_3CHO are less than 100% indicating that either the efficiency of conversion of $\text{trans-CF}_3\text{CH=CHF}$ into HC(O)F and CF_3CHO is lower, or there are significant losses of these products at higher $\text{trans-CF}_3\text{CH=CHF}$ conversions, or both. To test for heterogeneous loss of HC(O)F and CF_3CHO , reaction mixtures were allowed to stand in the dark for 15 min; there was no discernable loss ($<2\%$) of either compound. For the 2–14% conversions of $\text{trans-CF}_3\text{CH=CHF}$ in the data shown in Fig. 2, loss of HC(O)F and CF_3CHO via secondary reactions with OH radicals should be of minor importance as their reactivity with OH is less than that of $\text{trans-CF}_3\text{CH=CHF}$; $k(\text{OH}+\text{trans-CF}_3\text{CH=CHF})=(9.25\pm1.72)\times10^{-13}$ (Søndergaard et al., 2007), $k(\text{OH}+\text{HC(O)F})<4\times10^{-15}$ (Wallington et al., 1993), and $k(\text{OH}+\text{CF}_3\text{CHO})=(6\pm1.2)\times10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, 2007). It seems likely that the curvature in Fig. 2 reflects a lower yield of both HC(O)F and CF_3CHO with increased consumption of $\text{CF}_3\text{CH=CHF}$. A possible explanation of this effect is the reaction of NO_2 (which increases in concentration with consumption of $\text{trans-CF}_3\text{CH=CHF}$) with the alkoxy radicals formed in the system leading to the formation of small amounts of nitrates. In the atmosphere such reactions will not be of any significance and we did not pursue the origin of the curvature further.

By analogy to the well established oxidation mechanism of propene (IUPAC, 2007), the reaction of OH radicals with $\text{trans-CF}_3\text{CH=CHF}$ is expected to proceed via addition to the $>\text{C}=\text{C}<$ double bond. The mechanism of the OH radical initiated oxidation of $\text{trans-CF}_3\text{CH=CHF}$ which explains the observed formation of HC(O)F and CF_3CHO as shown in Fig. 3. The results from the present work indicate that irrespective of whether the OH radicals add to the terminal, or central carbon atom, the subsequent reactions lead to the formation of one molecule of both HC(O)F and CF_3CHO .

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3.2 Products of Cl atom initiated oxidation of $\text{trans-CF}_3\text{CH=CHF}$

The products of the Cl atom initiated oxidation of $\text{trans-CF}_3\text{CH=CHF}$ were studied using the UV irradiation of $\text{trans-CF}_3\text{CH=CHF}/\text{Cl}_2/\text{O}_2/\text{N}_2$ mixtures. Mixtures consisting of 6.6–8.4 mTorr $\text{trans-CF}_3\text{CH=CHF}$, 102.9–134 mTorr Cl_2 and 5–700 Torr of O_2 in 700 Torr total pressure of N_2 diluent were introduced into the reaction chamber and subjected to UV irradiation. Figures 4 and 5 show IR spectra at $675\text{--}1000\text{ cm}^{-1}$ and $1650\text{--}2000\text{ cm}^{-1}$, respectively, obtained before (a) and after (b) subjecting a mixture containing 6.6 mTorr $\text{trans-CF}_3\text{CH=CHF}$ and 109 mTorr Cl_2 in 700 Torr air diluent to 20 s of UV irradiation. Comparison of the IR features formed in low and high $[\text{O}_2]$ experiments revealed that four products were formed in the chamber; HC(O)F , CF_3CHO , $\text{CF}_3\text{C(O)Cl}$, and a product with a broad absorption feature in the carbonyl stretching region centered at 1801 cm^{-1} which we attribute to the ketone $\text{CF}_3\text{C(O)CHFCl}$. We do not have a calibrated reference spectrum for $\text{CF}_3\text{C(O)CHFCl}$. The concentration of this compound in the chamber was estimated by assuming that the carbonyl stretching band integrated absorption cross section at $1780\text{--}1820\text{ cm}^{-1}$ is the same as that in $\text{CF}_3\text{C(O)CH}_2\text{Cl}$ ($1.06\times10^{-17}\text{ cm molecule}^{-1}$, Nakayama et al., 2007).

Figure 6 shows a plot of the concentrations of HC(O)F , CF_3CHO , $\text{CF}_3\text{C(O)Cl}$, and $\text{CF}_3\text{C(O)CHFCl}$ versus the loss of $\text{trans-CF}_3\text{CH=CHF}$ observed following the UV irradiation of a mixture of 6.61 mTorr $\text{trans-CF}_3\text{CH=CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent. As seen from Fig. 6 the formation of HC(O)F , $\text{CF}_3\text{C(O)H}$, $\text{CF}_3\text{C(O)Cl}$ and $\text{CF}_3\text{C(O)CHFCl}$ scaled linearly with the loss of $\text{trans-CF}_3\text{CH=CHF}$ over the range of $\text{trans-CF}_3\text{CH=CHF}$ consumption of 10–95%. The linearity of the formation of HC(O)F , CF_3CHO , $\text{CF}_3\text{C(O)Cl}$ and $\text{CF}_3\text{C(O)CHFCl}$ suggests that loss of these compounds via secondary reactions is not significant. This observation is consistent with the fact that Cl atoms react much more slowly with these products than with the parent $\text{trans-CF}_3\text{CH=CHF}$ compound; $k(\text{Cl}+\text{trans-CF}_3\text{CH=CHF})=(4.64\pm0.59)\times10^{-11}$ (Søndergaard et al., 2007), $k(\text{Cl}+\text{HC(O)F})=(1.9\pm0.2)\times10^{-15}$ (Meagher et al., 1997), and $k(\text{Cl}+\text{CF}_3\text{CHO})=(1.85\pm0.26)\times10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (Sulbaek Andersen et al.,

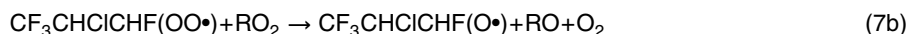
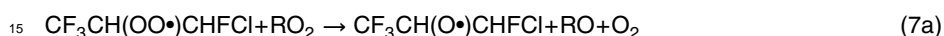
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2004). Previous work has shown that $\text{CF}_3\text{C}(\text{O})\text{Cl}$ is not lost by heterogeneous processes, photolysis, or reaction with Cl atoms in the chamber (Møgelberg et al., 1995).

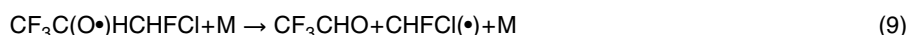
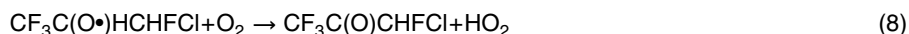
As shown in Fig. 7, the yields of $\text{HC}(\text{O})\text{F}$, CF_3CHO , $\text{CF}_3\text{C}(\text{O})\text{Cl}$ and $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ varied with $[\text{O}_2]$. In experiments with high $[\text{O}_2]$ the yields of $\text{CF}_3\text{C}(\text{O})\text{Cl}$ and $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ increased at the expense of $\text{HC}(\text{O})\text{F}$ and CF_3CHO . As in the case of the OH radical attack, the reaction of Cl atoms with trans- $\text{CF}_3\text{CH}=\text{CHF}$ is expected to proceed via electrophilic addition to the terminal and central carbon atoms:



The radicals produced in Reaction (5) will react with O_2 to give peroxy radicals which will undergo self- and cross-reaction to give the corresponding alkoxy radicals (in the equations below M represents a third body):



Decomposition via C-C bond scission or reaction with O_2 are likely fates of the alkoxy radicals. The observed formation of the ketone $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ in a yield which varies with $[\text{O}_2]$ shows that $\text{CF}_3\text{C}(\text{O}\bullet)\text{HCHFCl}$ radicals undergo reaction with O_2 and decomposition via C-C bond scission:



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The $\text{CHFCl}(\bullet)$ radicals formed in Reaction (9) will add O_2 , undergo reaction with other peroxy radicals in the system to give $\text{CHFCl}(\text{O}\bullet)$ radicals, and decompose via Cl atom elimination to give $\text{HC}(\text{O})\text{F}$ (Tuazon et al., 1993). The data in Fig. 7 contain information concerning the rate constant ratio k_8/k_9 . The yield of $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$, $Y_{\text{CF}_3\text{C}(\text{O})\text{CHFCl}}$, can be described by the expression $Y_{\text{CF}_3\text{C}(\text{O})\text{CHFCl}} = Y_{\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCl}} (k_8[\text{O}_2]/(k_8[\text{O}_2]+k_9)) + C$, where $Y_{\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCl}}$ is the yield of $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCl}$ radicals in the system, k_8 and k_9 are the rate constants for Reactions (8) and (9), and C is the $[\text{O}_2]$ independent yield of $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ (e.g., from self-reaction of $\text{CF}_3\text{CH}(\text{OO}\bullet)\text{CHFCl}$ peroxy radicals).

The curve through the $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ data in Fig. 7 is a fit of the expression above to the data which gives $k_8/k_9 = (8.0 \pm 2.6) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$. This value can be compared to the analogous rate constant ratio $k_{\text{O}_2}/k_{\text{diss}} = (3.8 \pm 1.8) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ measured for $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CH}_2\text{Cl}$ radicals (Nakayama et al., 2007). The increased importance of decomposition as an atmospheric fate of $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCl}$ compared to $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CH}_2\text{Cl}$ radicals is consistent with theoretical work showing that the barrier to C-C bond scission decreases as the degree of fluorine substitution on the two carbon atoms becomes more even and the bond becomes less polar (Somnitz et al., 2001). The limiting value for the $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ yield reached at high $[\text{O}_2]$ provides a measure of $k_{5a}/(k_{5a}+k_{5b}) = 47 \pm 7\%$.

Figure 8 shows the mechanism of Cl atom initiated oxidation of trans- $\text{CF}_3\text{CH}=\text{CHF}$ which is consistent with our experimental observations. From $k_8/k_9 = (8.0 \pm 2.6) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ it can be calculated that in 700 Torr of O_2 the reaction with O_2 accounts for 92% of the $\text{CF}_3\text{CH}(\text{O}\bullet)\text{CH}_2\text{Cl}$ radicals with decomposition accounting for the remaining 8%. Given the estimate of $k_{5a}/(k_{5a}+k_{5b}) = 47 \pm 7\%$ we then expect a 4% $\text{HC}(\text{O})\text{F}$ yield resulting from addition of Cl atoms to the terminal carbon atom (left hand side of Fig. 8). Hence, we can attribute the bulk of the approximately 40% $\text{HC}(\text{O})\text{F}$ yield in experiments in 700 Torr of O_2 to the decomposition of $\text{CF}_3\text{CHClCHF}(\text{O}\bullet)$ radicals. Decomposition via C-C bond scission is the dominant fate of $\text{CF}_3\text{CHClCHF}(\text{O}\bullet)$ radicals. Finally, the increase in the yield of $\text{CF}_3\text{C}(\text{O})\text{Cl}$

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with $[O_2]$ evident in Fig. 7 is consistent with the expected competition between reaction with O_2 and decomposition for the available $CF_3CHCl(O\bullet)$ radicals. The yield of $CF_3C(O)Cl$, $Y_{CF_3C(O)Cl}$, can be described by the expression $Y_{CF_3C(O)Cl} = Y_{CF_3CHCl(O\bullet)} (k_{10}[O_2]/(k_{10}[O_2] + k_{11})) + C$, where $Y_{CF_3CHCl(O\bullet)}$ is the yield of $CF_3CHCl(O\bullet)$ radicals in the system, k_{10} and k_{11} are the rate constants for Reactions (10) and (11), and C is the $[O_2]$ independent yield of $CF_3C(O)Cl$.



The curve through the $CF_3C(O)Cl$ data in Fig. 7 is a fit of the expression above to the data which gives $k_{10}/k_{11} = (4.6 \pm 1.9) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$. This result is larger than the previous more direct determination of $k_{10}/k_{11} = (2.1 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ (Møgelberg et al., 1995). A likely explanation for this discrepancy lies in the indirect and complex route by which $CF_3CHCl(O\bullet)$ radicals are formed in the present system. As indicated in Fig. 8, decomposition and reaction with O_2 are possible competing fates for $CF_3CHClCHF(O\bullet)$ radicals. Increased loss of $CF_3CHClCHF(O\bullet)$ via reaction with O_2 at high $[O_2]$ will lead to a decreased yield of $CF_3CHCl(O\bullet)$ radicals and hence $CF_3C(O)Cl$. The net effect will be to cause the $CF_3C(O)Cl$ yield to plateau at a lower $[O_2]$ which will lead to an overestimation of k_{10}/k_{11} . To investigate this effect further would require the use of $[O_2]$ levels higher than 700 Torr where a decrease in the yield of $CF_3C(O)Cl$ would be expected with increased loss of $CF_3CHClCHF(O\bullet)$ via reaction with O_2 . Such experiments are beyond the scope of the present work.

4 Atmospheric chemistry and environmental impact of trans- $CF_3CH=CHF$

The present work improves our understanding of the atmospheric chemistry of trans- $CF_3CH=CHF$. The atmospheric lifetime of trans- $CF_3CH=CHF$ is dictated by its reaction with OH radicals (Søndergaard et al., 2007) and has been estimated at approximately 2

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weeks. The OH initiated oxidation of trans- $CF_3CH=CHF$ gives CF_3CHO and $HC(O)F$ in yields of approximately 100%. CF_3CHO is removed from the atmosphere via photolysis and, to lesser extents, reaction with OH radicals (Chiappero et al., 2006) and addition of water to give the hydrate (Sulbaek Andersen et al., 2006). Photolysis gives CF_3 and HCO radicals (Chiappero et al., 2006) while reaction with OH gives CF_3CO radicals. CF_3 radicals will add O_2 to give CF_3O_2 radicals which are then converted into COF_2 (Wallington et al., 1994) which hydrolyzes to give CO_2 and HF. CF_3CO radicals will add O_2 to give $CF_3C(O)O_2$ radicals, the majority of which will be converted into COF_2 , with a small fraction converted into $CF_3C(O)OH$ (Hurley et al., 2006) via reaction with HO_2 radicals. The hydrate, $CF_3CH(OH)_2$ is lost via reaction with OH radicals to give $CF_3C(O)OH$ (Sulbaek Andersen et al., 2006). The available data suggest that while $CF_3C(O)OH$ is not a natural component of the freshwater environment (Nielsen et al., 2001), it is a natural component of the background oceanic environment (Frank et al., 2002), and any additional burden associated with trans- $CF_3CH=CHF$ oxidation will be of negligible environmental significance. We conclude that the products of the atmospheric oxidation of trans- $CF_3CH=CHF$ will have negligible environmental impact.

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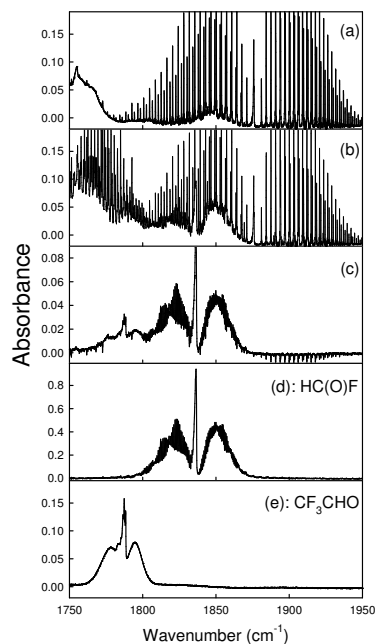


Fig. 1. Infrared spectra acquired before **(a)** and after **(b)** UV irradiation of mixtures 34.9 mTorr trans- $\text{CF}_3\text{CH=CHF}$, 82.3 mTorr CH_3ONO , 19.6 mTorr NO and 126 Torr O_2 in 700 Torr total pressure of N_2 diluent. Panel **(c)** show the residual IR features after subtraction of features attributable to trans- $\text{CF}_3\text{CH=CHF}$, H_2O , NO, and HCHO from panel (b). Panels **(d)** and **(e)** show reference spectra of HC(O)F and CF_3CHO , respectively.

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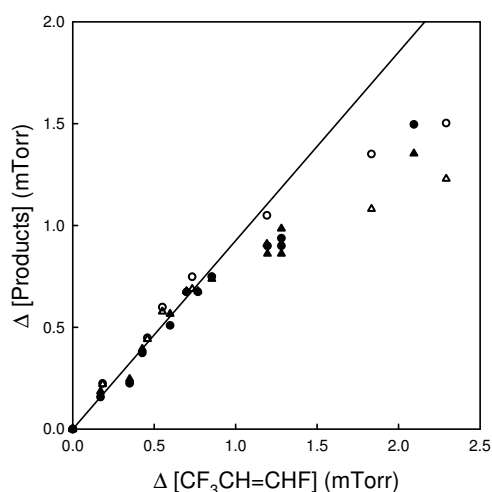


Fig. 2. Formation of HC(O)F (triangles) and CF_3CHO (circles) versus loss of trans- $\text{CF}_3\text{CH=CHF}$ observed following the UV irradiation of mixtures of 8.32–9.18 mTorr trans- $\text{CF}_3\text{CH=CHF}$ and 109.1–113.8 mTorr CH_3ONO in 700 Torr total pressure of air diluent at 296 ± 1 K. The open symbols are results obtained in the absence of NO.

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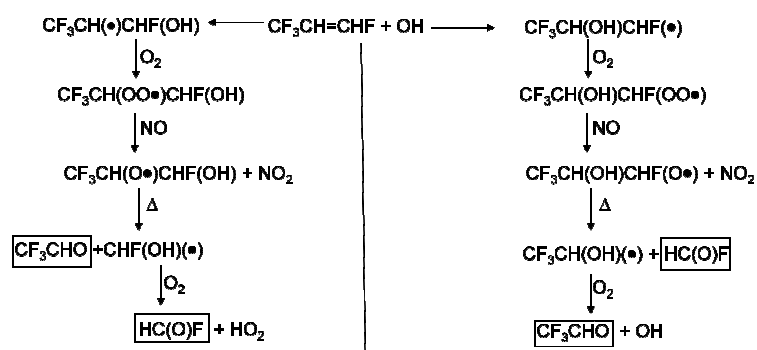


Fig. 3. Mechanism of OH radical initiated oxidation of trans- $\text{CF}_3\text{CH}=\text{CHF}$, boxes indicate observed products.

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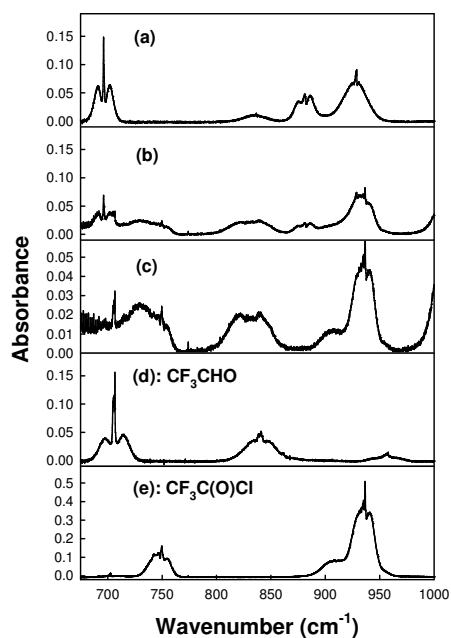


Fig. 4. Infrared spectra acquired before (a) and after (b) UV irradiation of 6.6 mTorr trans- $\text{CF}_3\text{CH}=\text{CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent. Panel (c) show the residual IR features after subtraction of trans- $\text{CF}_3\text{CH}=\text{CHF}$ from panel (b). Panels (d) and (e) show reference spectra of CF_3CHO and $\text{CF}_3\text{C}(\text{O})\text{Cl}$, respectively.

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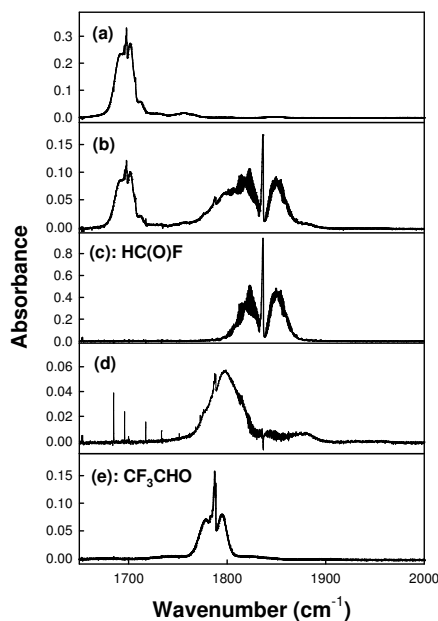


Fig. 5. Infrared spectra acquired before (a) and after (b) UV irradiation of 6.6 mTorr trans- $\text{CF}_3\text{CH}=\text{CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent. Panel (c) show a reference spectrum of HC(O)F . Panel (d) show the residual IR features after subtraction of trans- $\text{CF}_3\text{CH}=\text{CHF}$ and HC(O)F from panel (b). Panel (e) shows a reference spectrum of CF_3CHO .

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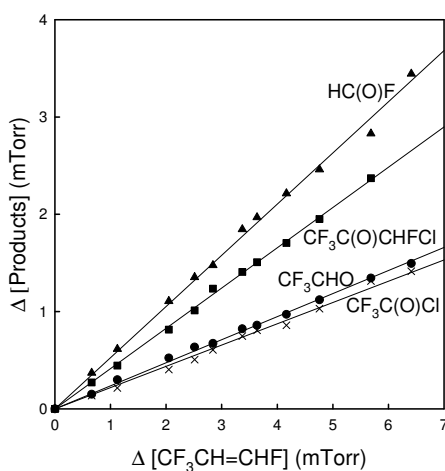


Fig. 6. Formation of HC(O)F (triangles), $\text{CF}_3\text{C(O)CHFCl}$ (squares), CF_3CHO (circles) and $\text{CF}_3\text{C(O)Cl}$ (crosses) versus loss of trans- $\text{CF}_3\text{CH}=\text{CHF}$ observed following the UV irradiation of a mixture of 6.6 mTorr trans- $\text{CF}_3\text{CH}=\text{CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent.

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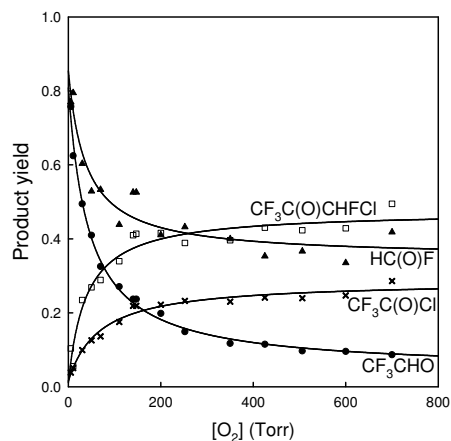


Fig. 7. Observed molar yields of HC(O)F (triangles), CF₃CHO (circles), CF₃C(O)Cl (crosses) and CF₃C(O)CHFCl (squares) versus the O₂ partial pressure following the UV irradiation of trans-CF₃CH=CHF/Cl₂/N₂/O₂ mixtures at 700 Torr total pressure. Curves through the CF₃C(O)CHFCl and CF₃C(O)Cl are fits to the data using the expressions described in the text. The curves through the HC(O)F and CF₃CHO data are polynomial fits to aid visual inspection of data trends.

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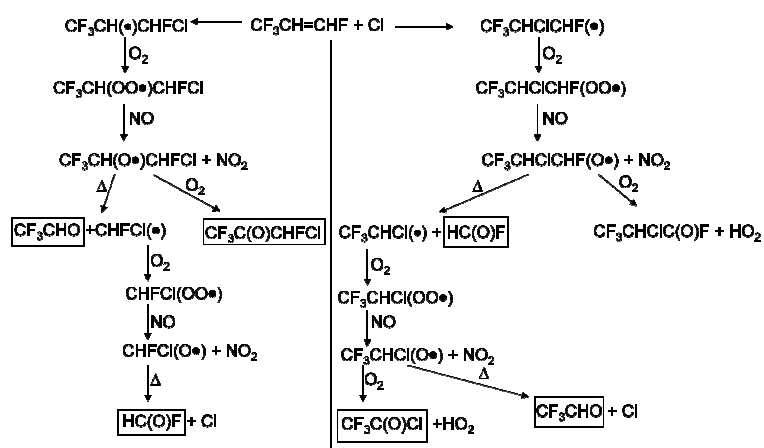


Fig. 8. Mechanism of Cl atom initiated oxidation of trans-CF₃CH=CHF, boxes indicate observed products.

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EPA's decision: Hydrofluoroolefin (HFO)–1234ze is acceptable as a substitute for CFCs and HCFCs in:

- Rigid Polyurethane Appliance Foam.
- Rigid Polyurethane Spray, Commercial Refrigeration, and Sandwich Panels.
- Polystyrene Extruded Boardstock & Billet.

HFO–1234ze is also known as HFC– 1234ze or trans-1,3,3,3-tetrafluoroprop-1-ene (CAS Reg. No.29118–24–9). You may find the submission under Docket item EPA–HQ–OAR–2003–0118–0222 at <http://www.regulations.gov>.

Environmental information: HFO– 1234ze has no ODP. HFO–1234ze has a GWP of 6 and an atmospheric lifetime of approximately 2 weeks (“Atmospheric chemistry of trans-CF₃CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation,” M.S. Javadi, R. Sondergaard, O.J. Nielsen, M.D. Hurley, and T.J. Wellington, *Atmospheric Chemistry and Physics Discussions* 8, 1069–1088, 2008). HFO–1234ze is currently defined as a VOC as defined under Clean Air Act regulations (*see* 40 CFR 51.100(s)) addressing the development of SIPs to attain and maintain the national ambient air quality standards. Hydrofluoroolefins are a subset of hydrofluorocarbons that contain double bonds between carbon atoms.

Flammability information: HFO– 12. HFO–1234ze

EPA's decision: Hydrofluoroolefin¹ (HFO)–1234ze is acceptable as a substitute for CFCs and HCFCs in:

- Rigid Polyurethane Appliance Foam.
- Rigid Polyurethane Spray, Commercial Refrigeration, and Sandwich Panels.
- Polystyrene Extruded Boardstock & Billet.

HFO–1234ze is also known as HFC– 1234ze or trans-1,3,3,3-tetrafluoroprop-1-ene (CAS Reg. No.29118–24–9). You may find the submission under Docket item EPA–HQ–OAR–2003–0118–0222 at <http://www.regulations.gov>.

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Flammability information: HFO– 1234ze is non-flammable.

Toxicity and exposure data: Potential health effects of this substitute at lower concentrations include drowsiness and dizziness. The substitute may also irritate the skin or eyes or cause frostbite. At sufficiently high concentrations, it may cause central nervous system depression or irregular heartbeat. The substitute could cause asphyxiation, if air is displaced by vapors in a confined space. The substitute may also irritate the lungs, skin or eyes or cause frostbite. These potential health effects are common to many foam blowing agents.

EPA anticipates that HFO–1234ze will be used consistent with the recommendations specified in the manufacturer's MSDSs. EPA recommends a preliminary workplace exposure limit of 375 ppm for HFO– 1234ze. EPA anticipates that users will be able to meet this recommended workplace exposure limit and will be able to address potential health risks by following requirements and recommendations in the MSDSs and other safety precautions common in the foam blowing industry. Further, EPA is reviewing this substance as a Pre-manufacture Notice under the Toxic Substances Control Act (TSCA). Therefore, use of HFO–1234ze must be in accord with EPA's final decision under TSCA.

Comparison to other foam blowing agents: HFO–1234ze is not ozone depleting in contrast to the ozone depleting substances which it replaces. In its lack of risk for ozone depletion, HFO–1234ze is comparable to other substitutes for HCFC–22 and HCFC– 142b, such as HFC–134a and HFC– 245fa. (HCFC–22 and HCFC–142b have ODPs of 0.05 and 0.07, respectively (WMO, 2006).) HFO–1234ze's GWP is 6, comparable to or lower than that of other substitutes for HCFC–22 and HCFC–142b. For example, the GWP of HFC–134a is about 1430 and the GWP of HFC–245fa is about 1030. Additionally, the GWP for HFO–1234ze is significantly lower than the GWPs for the ozone-depleting substances it will replace. (The GWPs of HCFC–22 and HCFC–142b are 1810 and 2310, respectively (WMO, 2006).) Flammability risks can be addressed by procedures common in the industry. The toxicity risks are low, as discussed above. Thus, we find that HFO–1234ze is acceptable because it does not pose a greater overall risk to public health and the environment than the other substitutes acceptable in the end uses listed above.

THE USE OF HFO-1234ze BLOWING AGENT IN THE PRODUCTION OF XPS (EXTRUDED POLYSTYRENE FOAM BOARD) PHASE 1

Prepared by
Yasemin Gündoğdu Ceylan
Project Manager

18 March 2011



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1- ABSTRACT

The purpose of this project is; use of HFO-1234ze blowing agent in XPS foam with Standard production equipment (all ingredients are same except blowing agent) to phaseout of HCFCs in XPS. If the new gas is acceptable according to test results this gas can be use all of XPS production in the world.

This gas was approved by the U.S. Environmental Protection Agency to use in foam and aerosol applications. This gas was used with other co blowing agents like acetone, ethyl alcohol. These tryouts are the first use of DME (dimethyl ether) co blowing agent with HFO 1234ze in XPS foam production. This month the tryouts were made at B-PLAS factory on 8th – 11th of March 2011 in Bursa, Turkey.

The tryouts were made according to project implementation plan.

The product thickness was 30mm, the equipment was twin screw corotating extruder. The other details can be seen at related chapters.

2- THE ACTIVITIES IN THE PERIOD OF 08/02/2011 – 18/03/2011

2.1- PURCHASING OF HFO 1234ze

The gas tanks arrived to B-PLAS on 23rd of February. There were 2 gas tanks on the production side, one of them was belonging to 70/30 HFO 1234ze/DME blend, other was belonging to 80/20 HFO 1234ze/DME blend. The photographs of the gas tanks are below.

Picture 1- 80/20 HFO 1234ze/DME blend



Picture 2- 70/30 HFO 1234ze/DME blend



Picture 3- The whole gas tank



2.2- PURCHASING OF THE THERMAL CONDUCTIVITY TESTER

The tester will be choiced through below suppliers. The alternative equipments and suppliers are;

- * QuickLine™-30 (Anter)
- * C-Therm TCi (C Therm Technology)
- * Lambda (F 5 Techmology GmbH)

2.3- THE TRYOUTS

2.3.1- THE GAS DELIVERY TO B-PLAS

The gas tanks were sent from France by Honeywell. The tryouts will have made at the end of year 2010. But the gas wasn't supplied on time. So the tryouts were postponed to end of February 2011. The documents of gas delivery can be seen at Annex 1.

2.3.2- FINAL PREPARATIONS

2.3.2.1- B-PLAS supplied below safety equipments before the tryouts. These safety equipments conform to CE standards which can be seen in MSDS documents and data sheet of gases (Annex 2).

- 1- Safety glass, 3M 2740 (EN 166:2001)
- 2- Mask with filter 3M 6800 filtreli (EN 136 CL1) and the filter 3M 6059 (EN 14387:2004)
- 3- Glove Rytill hot
- 4- Glove for chemicals Rytill CE 0321 (Soleyn 33)
- 5- Safety shoes (B-PLAS requirement)

2.3.2.2- The MSDS documents were explained to the workers.

2.3.2.3- The production line was controlled by Production department.

2.3.2.4- The tryout plan was prepared and send to all tryout participants.

From: Yasemin Gündoğdu Ceylan

Sent: Tuesday, February 15, 2011 10:41 AM

To: 'Katalin Zaim'; Mehmet AŞKINER; Mehmet Askiner

Cc: Berkan Toros; Maksim Surkov; Jacques Van Engel; William Buchanan; Bowman, Jim; Bert Veenendaal; Lucarelli, Francesco; Ulrika Richardson-Golinski; Levent Ceylan;

yaseminc@gmail.com; Yasemin Gündoğdu Ceylan

Subject: HFO 1234ze TRIALS

Importance: High

Dear All,

I kindly inform you that I have prepared a time table for HFO 1234ze gas trials. Please send me your opinions . Today I will send you to do list for trials. Please inform me Is there any other participant ?

The participants are ;

Katalin Zaim

Jim Bowman

Bert Veenendaal

William Buchanan

Berkan Toros

Mehmet Aşkiner

TIME TABLE OF HFO 1234 ze PROJECT at B-PLAS A.Ş.

<i>07 March 2011, Monday</i>	<i>Travelling and arrive to Bursa</i>
<i>08 March 2011, Tuesday</i>	<i>Discussion about the trials, control of the production line, safety requirements and trials</i>
<i>09 March 2011, Wednesday</i>	<i>Trials</i>
<i>10 March 2011, Thursday</i>	<i>Trials</i>
<i>11 March 2011 ,Friday</i>	<i>Discussion, meeting</i>

2.3.3- THE TRYOUTS

The experts and other participants arrived to Bursa on 7th of March. All participants and B-PLAS management have a dinner at an authentic restaurant of Bursa.

2.3.3.1- THE RAW MATERIALS AND PRODUCT

A- Polystyrene (PS) (Melt flow rate is: 10 g/10min , 200⁰C, 5 kg)

B- Nucleating agent

C- Flame retardant

D- Gas d1- **70/30 HFO1234ze/DME blend (750 kg)**

d2- **80/20 HFO1234ze/DME blend (750kg)**

The proposal formulation according to Project implementation plan is;

- Sabic Virgin PS MFI 7 97%
- Recycle PS 0.0%
- Flame-retardant 1.5%
- Talcum 1.5%
- Color 0.0%

The product thickness is 30 mm

2.3.3.2- FIRST DAY OF THE TRYOUT (08 March 2011)

The below participants had a meeting about the tryout organisation. The participants are;

Jim Bowman	Honeywell Gas Expert
William Buchanan	IFC Process Expert
Berkan Toros	UNDP Turkey
Mehmet Aşkiner	Expert at National Ozone Office of T.C Ministry of Environment and Forests
Levent Ceylan	B-PLAS Recipient Coordinator
Vahit Babacan	B-PLAS Production Responsible
Yasemin Gündoğdu Ceylan	Project Manager

Picture 4- The participants



From left to right; Mehmet Aşkiner, Berkan Toros, Jim Bowman, Vahit Babacan, Levent Ceylan, William Buchanan, Yasemin G.Ceylan.

The below tryout plan was recommended by Process expert.

Table 1 Draft tryout plan

Date	Explanation
08.03.2011	STEP 1- B-PLAS production will be continued, the thickness is 30 mm
09.03.2011	STEP 2- Production with UNDP Project formule (%97 PS+%1,5 Flame retardant+%1,5 Nucleating agent)+ with B-PLAS gas. STEP 3- After the production stable conditions the gas will be changed with same formule (Production with UNDP Project formule (%97 PS+%1,5 Flame retardant+%1,5 Nucleating agent)+ with %70/30 HFO1234ze/DME gas blend).
10.03.2011	STEP 4- Repeat 1st and 2nd steps. STEP 5- then change gas blend to %80/20 HFO1234ze/DME
11.03.2011	STEP 5- Meeting and discussion on tryouts.

The production line and safety precautions were controlled by experts

The production was continued until 09 March morning with STEP 1.

2.3.3.3- SECOND DAY OF THE TRYOUT (09 March 2011)

The STEP 2 was began at 09 March morning and all Project team was participated this tryout. The Processing conditions which are screw velocity, barrel temperatures, pressures, gas velocity,... were recorded (Annex 3 processing conditions of STEP 2). The product was good surface properties, No waves no some holes. STEP 3 was begun after 3-4 hours later. The product surface was no good. too much waves and some holes. The width of the panel was decreased to 58 cm and the panel density increased to 40 g/cm³. When the gas was fed to the production equipment the die pressure was decreased until 19 bar. Later the screw velocity was decreased by process expert to increase the die pressure (If the die pressure is increased the foaming level will be homogene and small cell size). Because of surface waves and holes, the process expert decreased the nucleating agent ratio by order of % 1.25 and % 1, increased the gas feeding ratio from % 7 to % 7.75 and increased the temperatures. But the surface properties didn't change. The process expert's opinion that latest product with %1 nucleating agent ratio was succesfull (Annex 4 processing conditions).

Picture 5- The photograps of the product which the gas blend is 70/30 HFO1234ze/DME, %1 Nucleating agent.

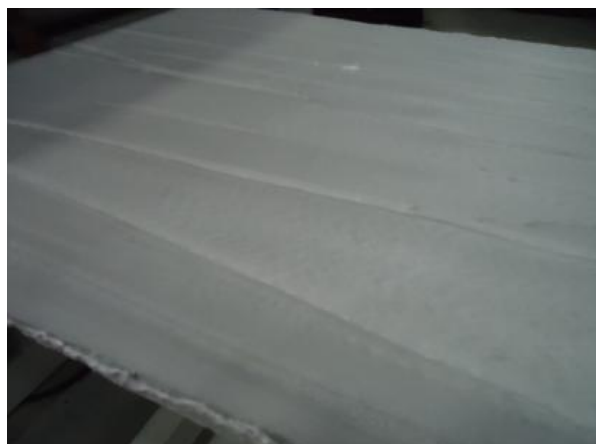


2.3.3.3- THIRD DAY OF THE TRYOUT (10 March 2011)

The STEP 4 wasn't applied on processing, STEP 5 was began at 10 March morning. But the production formule was changed ; (**%97,5 PS+%1,5 Flame retardant+%1 Nucleating agent**)+ with %80/20 HFO1234ze/DME gas blend).

The product surface was no good, too much waves and some holes on the surface. The gas feeding ratio was increased from %7 to % 8,5 to avoid these problems. But there was't been any solution (Annex 5 processing conditions)

Picture 6- The photograpgs of the product which the gas blend is 80/20 HFO1234ze/DME %1 Nucleating agent.



2.3.3.4- THE FINAL FORMULAS

% 70/30 HFO 1234ze/DME	% 80/20 HFO 1234ze/DME
% 97,5 PS	% 97,5 PS
% 1,5 Flame Retardant	% 1,5 Flame Retardant
% 1 Nucleating agent	% 1 Nucleating agent

2.4- DISCUSSIONS, RESULTS (11 March 2011)

2.4.1- THE PROCESSING RESULTS

The results were evaluated by all tryout participants;

2.4.1.1- B-PLAS evaluation; B-PLAS participants said that the produced product wasn't good according to their expectations. The surface properties weren't good to sell on the market.

The density was 40 – 45 g/cm³ this value is high according to XPS which is on the market. The price of HFO gas is high.

HFO-1234ze gas couldn't use alone on XPS product, must be used with other co blowing agents like, DME, ethyl alchole, acetone.

2.4.1.2- T.C Ministry of Environment and Forests evaluation;

He was happy to see this gas can be used for XPS production. But need other try outs for stable processing conditions, homogeneous flat surface.

2.4.1.3- Process expert's evaluation;

The tryouts were made according to Project implementation plan. He observed this gas blend (with DME co blowing agent) can be used for XPS production with B-PLAS machinery technology. The surface of product can be improved with optimum process conditions. So this gas must be tried with other HFO1234ze/DME ratios, other Polystyrenes with lower melt flow ratio and with optimum processing conditions (temperatures, velocity, pressures, ...).

The die pressure couldn't be increased to 45 bar. If the pressure can be increased, the surface can be homogeneous and with no holes. This gas must be tried with other

machinery technologies. The other requirements can be determined according to other tryouts results.

2.4.2- THE USED MATERIALS

Polystyrene : 5566 kg

Flame retardant: 86 kg

Nucleating agent: 86 kg

B-PLAS gas: 103 kg

2.4.3- THE TESTS

The tests (except cell size) will be applied according to Project plan and EN 13164 XPS Standard at TEBAR laboratory which is an accredited laboratory. The cell size will be tested by Process Expert Mr. William Buchanan. The TEBAR price offer is attached (Annex 6)

Table 2- The tests

The test name	Explanation
Thickness	-
Density	-
Cell size	-
Compressive strength	will be made 10 days, 20 days, 30 days and 45 days after the production date
Thermal conductivity	will be made 10 days, 20 days, 30 days and 90 days after the production date
Flammability	-
Dimensional Stability (will be explained by Bill on day one)	These tests were cancelled by Process expert. Because the dimensions of product were not good to measure.

The test results will be issued in next report

2.5- GENERAL EVALUATION

All tryout results will be discussed at the meeting which will be held on 4th April, 2011.

THE USE OF HFO-1234ze BLOWING AGENT IN THE PRODUCTION OF XPS (EXTRUDED POLYSTYRENE FOAM BOARD) PHASE 1

Prepared by
Yasemin Gündoğdu Ceylan
Project Manager

05 January 2012
Report on the second trials
December 23/24, 2011



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1. THE SECOND TRYOUTS

Mr Bill Buchanan and Mr. Berkan Toros arrived to Bursa and B-PLAS on 22th of December. A pre-meeting was made with the Project Manager and Production Responsible at BPLAS production sites and details for the trials discussed.

2. THE MEETING NOTES

- 1- The gas is 70/30 HFO1234ze/DME
- 2- The used XPS line has much capacity than the first tryouts' line.
- 3- The used PS (The MF is 2g/10dk) has lower melt flow value than the first tryouts' PS (The MF is 10g/10dk)
- 4- The formulation is 97% PS (because of lower MF value and to get easy processing the recycled material will be added into the raw material; later the recycle material ratio will be decreased). The formulation will use 1.5% nucleating agent and 1,5% Flame retardant
- 5- First the BPLAS gas (152a/DME) will be used with formulation later gas will be changed to 70/30 HFO1234ze/DME later turn to BPLAS gas.
- 6- The expected die pressure with 70/30 HFO1234ze/DME is approximately 50-60 bar, with 152a/DME is approximately 30 bar.

3. THE TRYOUTS on 23th of DECEMBER

The tryouts were started with 152a/DME blend with above formulation but the PS contain recycle material (%97 PS (%32 Recycle +%65 Orj PS)). We get good product with this gas. Later the gas was changed to 70/30 HFO1234ze/DME blend. We didn't get a good product with this gas blend. The product surface has no pinholes but too much longitudinally waves.

The below formulations have been tried and the processing conditions were not changed too much.

High Original PS ratio with lower gas feeding ratio,
High Original PS ratio with higher gas feeding ratio

Gas 1	152a	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze	HFO 1234ze
Gas 2	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME	DME
Gas1/gas2 ratio, %	-	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30	70/30
Gas feeding ratio, %	7,9	7,9	6,5	6,5	6,5	6,5	6,5	6,5	5,7	7,3	7,6	8,9	9,6	9,6	9,6	9,6	9,6
Capacity, kg/h	375	375	375	375	375	375	375	375	375	375	375	375	375	375	375	375	375
PS, %	65	65	65	70	77	80	82	82	82	57	62	62	62	82	97	67	67
Recyle, %	32	32	32	27	20	17	15	15	15	40	35	35	35	15	0	30	30
Nucleante, %	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5
Flame retardant, %	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5
Die, bar	35	45	47	42	41	43	47	49	49	51	43	43	39	40-41	38	38	66

The photographs;





4. THE PREPARATIONS FOR THE SECOND DAY TRYOUT

The below preparations were made:

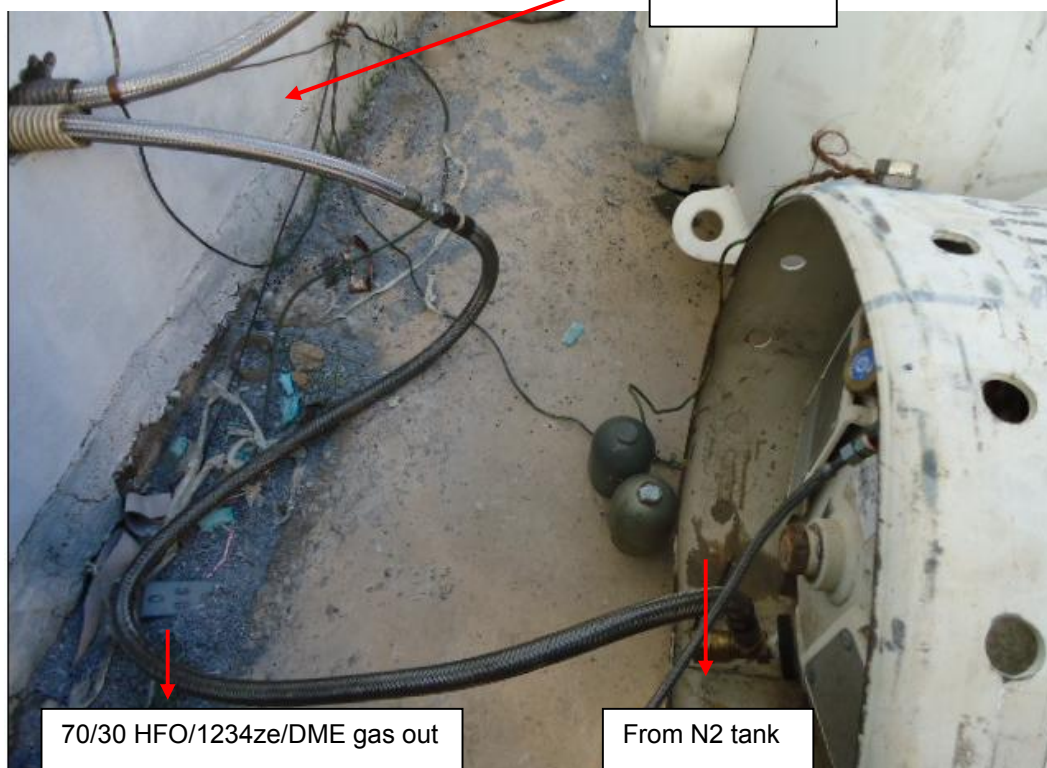
- 180 lt tanks were filled with DME
- The high pressure pump which belongs to the lower capacity line was connected to other high capacity line to pump the DME gas into the extruder.
- Nitrogen gas was used to pressure 70/30 HFO1234ze/DME blend into the extruder.

The photographs of the connections;



DME
tanks

DME tanks
connection



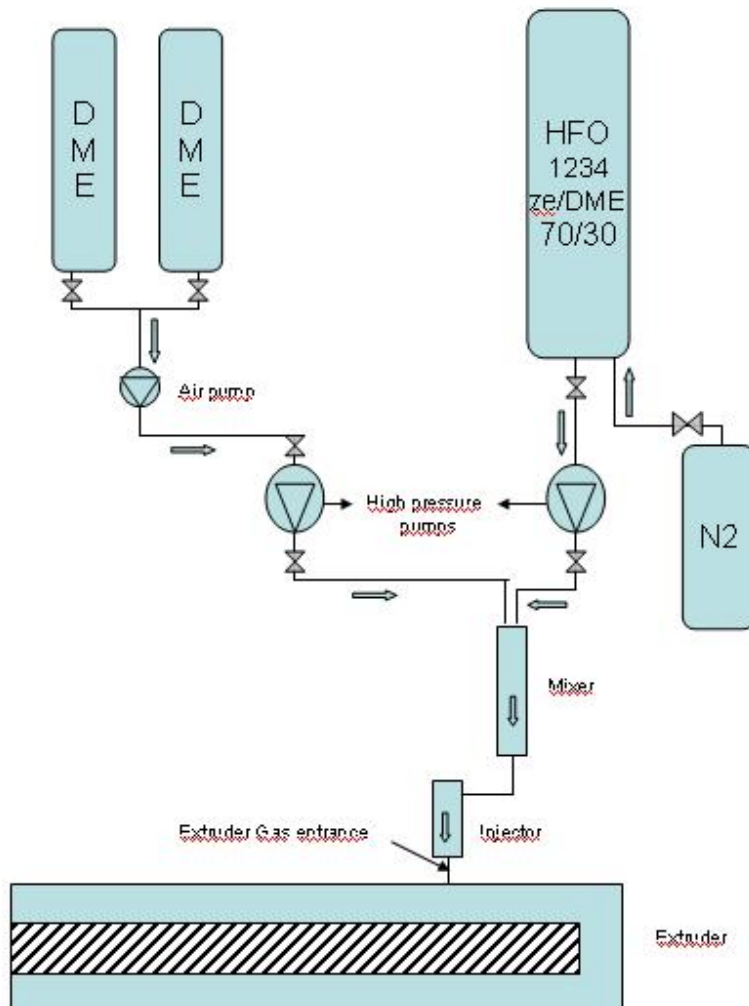
70/30 HFO/1234ze/DME gas out

From N2 tank



From N2 tank

The flow chart of the connections,



5. THE TRYOUTS on 27th of DECEMBER

The tryouts were started with 152a/DME blend the surface of the product is good. Later change to the gas DME and 70/30 HFO1234ze/DME blend. The line capacity is 350kg/h, the total gas feeding is 28 kg/h (total gas ratio is %8).

First the gas ratio is adjusted to 55/45 HFO1234ze/DME blend. The surface of the product is good, with no pinholes, but too much of longitudinally waves.



Later the gas ratio is adjusted to get 50/50 HFO1234ze/DME blend. The surface of the product is good, no pinholes, no waves. But there are some pinholes in the product which is cut for aged thermal conductivity test.

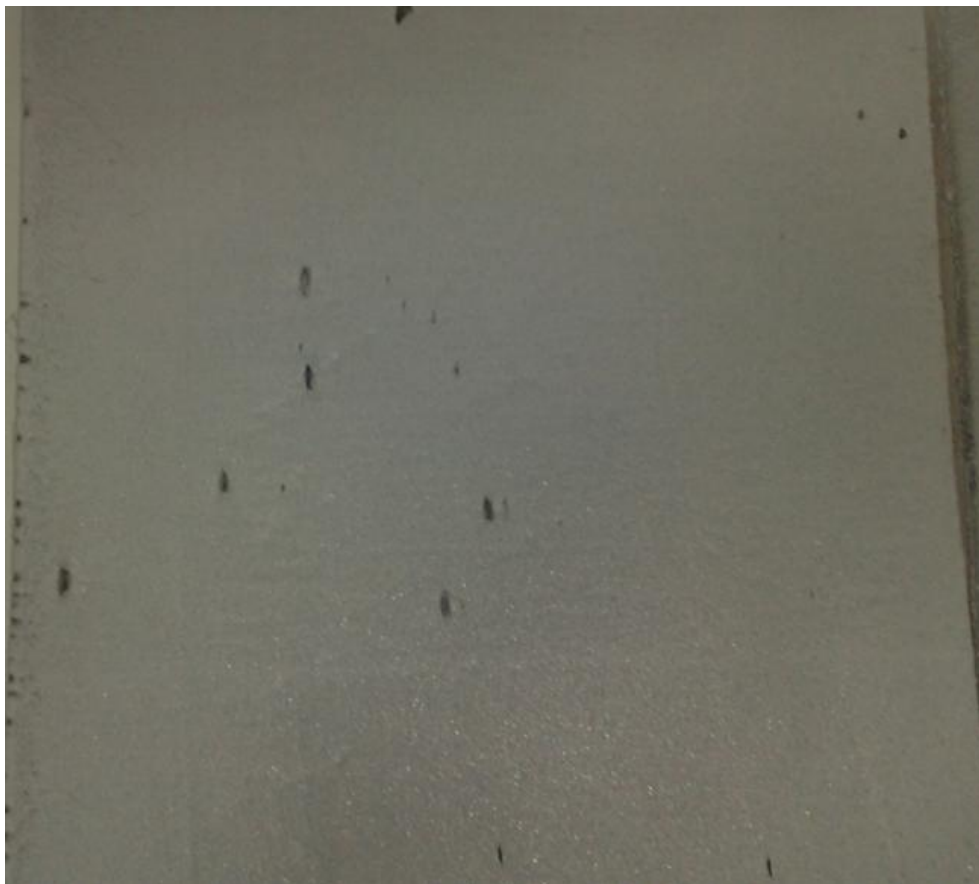
The outer surface of the product which is produced with 50/50 HFO1234ze/DME gas;



The inner surface of the product which is produced with 50/50 HFO1234ze/DME gas;



The inner surface of the product which is produced with 50/50 HFO1234ze/DME gas;



The processing conditions are:

Gas 1	HFO/DME (70/30)	HFO/DME (70/30)
Gas 2	DME	DME
Gas1/gas2 ratio, %	55/45 (HFO/DME)	50/50 (HFO/DME)
Gaz feeding ratio, %	7,4	8,0
Capacity, kg/h	350	350
PS, %	56	56
Recyle, %	41	41
Nucleante, %	1,5	1,5
Flame retardant, %	1,5	1,5
Die, bar	42	37
Zone1, °C	215	215
Zone2, °C	220	220
Zone3, °C	210	210
Zone4, °C	180	180
Zone5, °C	110	110
Zone6, °C	105	105
Zone7, °C	96	96

6. THE MEETING NOTES AFTER THE TRYOUTS

Generally the product is good according to the first tryout sample. If the new tryout is scheduled, the below equipments will be required to attain good gas blend ratio and processing conditions.

- 1- DME pump
- 2- Air pump
- 3- High pressure pump
- 4- DME tank
- 5- HFO 1234 ze tank
- 6- Tryout 3-4 days.

7. THE USED MATERIALS

Polystyrene	:	5411 kg
Flame retardant	:	84 kg
Nucleating agent	:	84 kg
B-PLAS gas	:	379 kg

8. THE TESTS AND RESULTS

The tests will be applied according to Project plan and EN 13164 XPS Standard at B-PLAS laboratory.

The tests

The test name	Explanation
Thickness	-
Density	-
Cell size	-
Compressive strength	will be made 10 days, 20 days, 30 days and 45 days after the production date
Thermal conductivity	will be made 10 days, 20 days, 30 days and 90 days after the production date
Flammability	-

The test results are;

TEST	TEST DATE	UNIT	VALUE
Density	the test were made at the production date	kg/m ³	35
Max Compressive strength		kPa	217,87
Thermal conductivity		W/mK	0,02268
Thermal conductivity	The samples were cut into slices and waited 10 days at laboratory conditions	W/mK	0,02899

COMPARATIVE TEST RESULTS FOR BLOWING AGENTS USED IN TURKEY

Tests	Standard	Unit	80/20% HFO1234ze/DME 18-21/03/2011	70/30% HFO1234ze/DME 18-21/03/2011	50/50% HFO1234ze/DME 12/27/2011	75/25% 152a/DME 3/16/2010	50/50% 152a/DME 9/28/2011	75/25 142b/22a 7/12/2004	Standard Requirement
Length	TS EN 822	mm	1201	1201	1201	1200.3	1200	1250	*1200
Width		mm	599	573	601	598	600	603	*600
Thickness		mm	28.61	31.65	30.6	31.6	29.78	30.66	*30
Density	TS EN 1602	kg/m ³	44.22	38.64	35	33.8	29.8	32	*30 – 32
Thermal conductivity 90 days	TS EN 12667	W/mK	0.03371	0.02889	0.02987	0.035	0.03168	0.028	*0,029-0,031
Aged Thermal conductivity 90 days			0.03309	0.02908	0.03097	n/a	0.03178	n/a	
Compressive strength 45 days	TS EN 826	kPa (N/m ²)	380	276	298	257.4	250	248.36	*>=200
Flammability	TS EN ISO 11925-2	-	E	E	E	E	E	B1	E
Open cell ratio		%	31.69	3.41	10	-	-	-	No value

*Depends on producer declaration