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Assessment of the Performance of Hydrofluoroolefins, Hydrochlorofluoroolefins, and Halogen-Free Foam Blowing Agents in Cellular Plastic Foams

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Building and Transportation Science Division

ASSESSMENT OF THE PERFORMANCE OF HYDROFLUOROOLEFINS, HYDROCHLOROFLUOROOLEFINS, AND HALOGEN-FREE FOAM BLOWING AGENTS IN CELLULAR PLASTIC FOAMS

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ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
CO_2	Carbon Dioxide
CR-100B	Cell Regulator
CFCs	Chlorofluorocarbons
EPA	Environmental Protection Agency
FBA	Foam Blowing Agent
GWP	Global Warming Potential
HIPS	High-impact polystyrene
HP	High Pressure
HCFCs	Hydrochlorofluorocarbons
HFCs	Hydrofluorocarbons
HFOs	Hydrofluoroolefins
HCs	Hydrocarbons
HCFOs	Hydrochlorofluoroolefins
ISO	Isocyanate
LP	Low Pressure
ODP	Ozone Depletion Potential
PU	Polyurethane
PIR	Polyisocyanurate
SNAP	Significant New Alternatives Policy
SPF	Spray Polyurethane Foam
TDCE	Trans-1,2 dichloroethylene
VOCs	Volatile Organic Chemicals

EXECUTIVE SUMMARY

Oak Ridge National Laboratory has conducted a literature search to identify relevant information available on alternative materials and technologies that are proposed for foam blowing agents applications. For comparison, similar information was collected for available hydrofluorocarbons (HFC), hydrofluoroolefin (HFO), and hydrochlorofluoroolefins (HCFO) materials. The publicly available literature was analyzed and assessed for technical accuracy for each alternative, and a gap analysis was conducted to understand if additional studies are required to fully assess the viability of an alternative. In assessing these alternatives, this project focused on relevant performance and safety attributes. The performance attributes collected include insulation value per unit thickness, which impacts energy usage of buildings and insulated equipment such as refrigerators. We also assessed the impact of blowing agents on foam mechanical properties and flammability characteristics, and the ability of current processing equipment and techniques to utilize these alternatives. Diffusion of blowing agents through foam cells and its impact on foam aging was also examined. The applications covered in this study are spray foam, boardstock, panels, and appliances. Some of the most relevant findings are summarized below.

High-Pressure Spray Foam Applications

Hydrochlorofluoroolefins and hydrofluoroolefins are well established foam blowing agents (FBA) in High-Pressure Spray Foam (HP-SPF) applications due to the resulting excellent physical properties and thermal insulation performance. Additionally, they are non-flammable and compatible with spray foam processing equipment, making them suitable for these applications. Methyl formate and methylal can be used as additives. Still, mixtures containing these additives must be non-flammable to be acceptable. Carbon dioxide (CO_2) water based blowing agents for HP-SPF could be suitable where the thermal performance (i.e., thermal resistivity) of foams is not critical. Trans-1,2 dichloroethylene (TDCE) could also be used as additives and in limited quantities due to toxicity issues.

Hydrocarbons (HCs) are not used as blowing agents for High-Pressure Spray Foam applications due to their high flammability. During a typical spray foam application, a fraction of the blowing agent is inevitably released into the atmosphere, which requires additional safety precautions because of the resultant flammability of mixtures containing hydrocarbons. Hence, due to flammability issues and incompatibility with equipment, hydrocarbons are not currently in use for HP-SPF applications.

Low-Pressure Spray Foam Applications

Hydrochlorofluoroolefins and hydrofluoroolefins are widely used blowing agents for low-pressure spray foam (LP-SPF) applications. They are non-flammable, exhibit adequate compressive strength and are compatible with spray foam processing equipment. Liquified CO_2 based blowing agents are non-flammable and can produce adequate compressive strength for closed-cell foams. They could be suitable where thermal performance of foam is not critical. On the other hand, open-cell foams produced using CO_2 (water) based blowing agents do not have good compressive strength, making them not suitable for LP-SPF applications. CO_2 (water) open-cell based FBA are suitable for LP-SPF only when good mechanical properties are not required. In addition, CO_2 (water) blowing agents are only acceptable where closed-cell foams with low thermal conductivity are not critical. Finally, Trans-1,2 dichloroethylene (TDCE) is flammable restricting its use only as an additive for LP-SPF applications.

Hydrocarbons are highly flammable, which prevents their use in some low-pressure spray foam applications. Methyl formate as FBA is flammable, which makes them also not suitable for LP-SPF applications. In the case of mixtures containing methyl formate, they show poor dimensional stability, which creates significant technical challenges. As for Methylal mixtures used as blowing agents, they show acceptable dimensional stability and thermal conductivity properties. However, problems of flammability make them not suitable for LP-SPF applications.

Boardstock

Hydrofluoroolefin blowing agents are adequate alternatives for PU/PIR foam board applications as they are non-flammable and possess excellent insulation and physical properties. Hydrocarbons (HCs) are also acceptable for PU/PIR foam board applications due to their good thermal insulation and physical properties. However, hydrocarbons are highly flammable, which will require general safety precautions to be considered as FBAs for PU/PIR foam applications.

Methyl formate and methylal are not suitable as foam blowing agents for boardstock applications. This is due to poor foam thermal insulation and physical properties. They could be used as additives only. Additionally, CO_2 based FBA for boardstock could potentially be used when thermal performance of foam is not critical. These are compatible with foam processing equipment. Finally, Trans-1,2 dichloroethylene (TDCE) based FBA for boardstock applications could only be used as additive with considerations for toxicity issues.

Panels

Fluorinated materials (HFOs, HCFOs) and hydrocarbons are commercially used as blowing agents for PU and PIR panels. Non-flammable HCFOs are practical when setting up manufacturing plants as they do not require safety mitigation. On the other hand, many large-scale manufacturers can afford to use of hydrocarbons (pentanes), which will require high initial capital investment but lower operating costs.

Appliances and Small Refrigeration Systems

Most of the foam blowing agents used in domestic appliances and small refrigeration systems are either fluorinated (HCFO, HFO) and hydrocarbons materials. Foams produced with these blowing agents have good thermal insulation and physical properties, which are quite important to comply with the energy efficiency standards mandated for these applications. Manufacturers of domestic refrigerators currently use as blowing agents materials such as HCFO-1233zd(E) and HFO-1336mzz(Z), and hydrocarbons such as cyclopentane.

1. SPRAY POLYURETHANE FOAM

1.1 BLOWING AGENTS IN SPRAY POLYURETHANE FOAM

In the history of the polyurethane (PU) foam industry, chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) have been used as blowing agents (see Figure 1). Since the 1990s, HFCs have been widely used as blowing agents in the polyurethane industry because of their excellent physical properties, zero ODP, and nonflammability. HFC-134a (1,1,1,2-tetrafluoroethane) and HFC-245fa (1,1,1,3,3-pentafluoropropane) are used in spray foam systems owing to their excellent insulation performance and good physical properties. Although HFCs do not cause ozone depletion, they absorb infrared radiation in the atmospheric window and have relatively long atmospheric lifetimes [1], which leads to a high GWP. As a result, HFCs are presently being phased out by international protocols. They have been replaced with Hydrofluoroolefins (HFOs) or blowing agents with a lesser environmental impact.

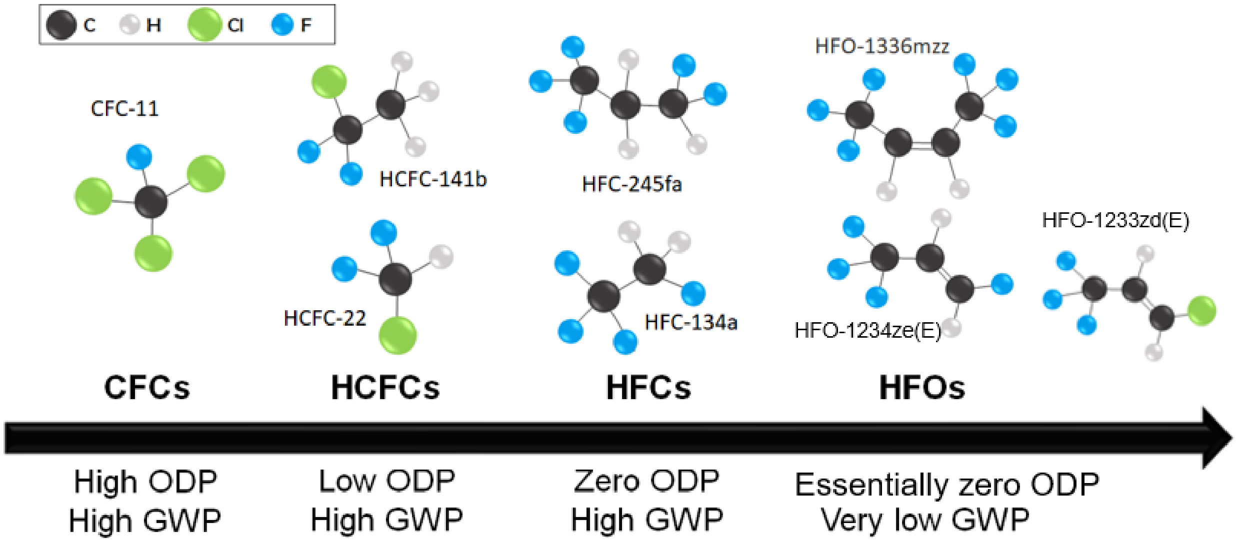


Figure 1. Foam blowing agent generations in the spray PU foam application and their environmental impact.

As illustrated in Figure 2, the gas thermal conductivity accounts for approximately 50%–60% of the total thermal conductivity of closed-cell foams [2, 3]. Blowing agents, which have different molecular weights, boiling points, thermal conductivities, and total content in the cell, directly affect the foam's properties, including density, thermal performance (initial and aged), mechanical properties, and dimensional stability. Understanding the role of the blowing agent and its effect on the final foam's performance is critical when designing spray foam systems. Because all commercial spray foam processing equipment are not rated to handle flammable materials, the blowing agent should be non-flammable in order to produce non-flammable polyol blends (B-side) and, less commonly, if blowing agents are blended with the isocyanate, the A-side blend [4-6]. Blowing agents must have adequate miscibility with isocyanate or polyol resin side components to provide a homogeneous mixture that remains consistent over storage periods, which are typically on the order of 6 months.

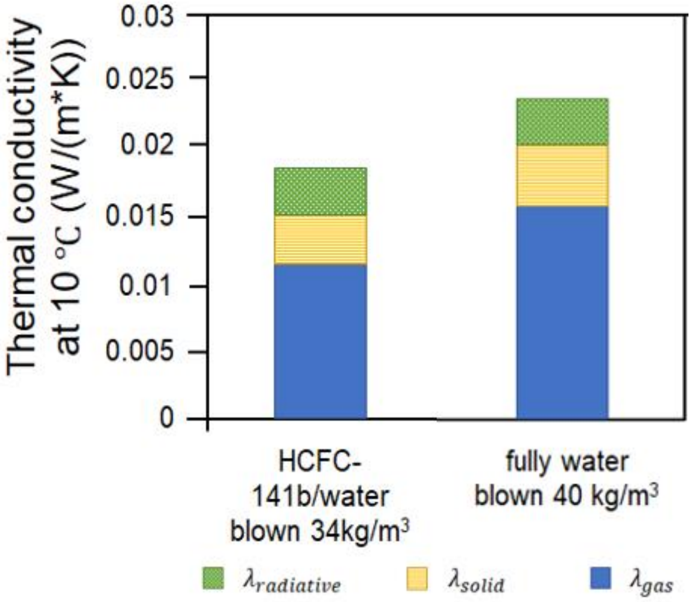


Figure 2. Contributions of solid conduction, gas conduction, and radiation on the thermal conductivity of cellular plastic foams [3].

Closed-cell foams' thermal performance changes over time because of the gas diffusion in and out of the cell, which can be identified using the following stages: 1) Outgassing of CO_2 from the foam, 2) Diffusion of air into the foam, 3) Outgassing of other low–thermal conductivity gases used as blowing agents. Diffused atmospheric gases in the foam increase the thermal conductivity [2, 7]. These changes occur over a long period of time and lead to gradual increase in thermal conductivity (or degradation of insulation properties). Moreover, as seen in Figure 3, the blowing agent will also diffuse out of the foam until the partial pressure of each blowing agent reaches a steady state between the ambient air and air inside the foam cells. This process can take extended periods of time, which may exceed the useful life of the foam. A portion of the blowing agent will also be absorbed in the solid polymer [8]. Thus, measuring initial and aged thermal conductivities is needed to estimate the thermal performance of foam insulation over its service life.

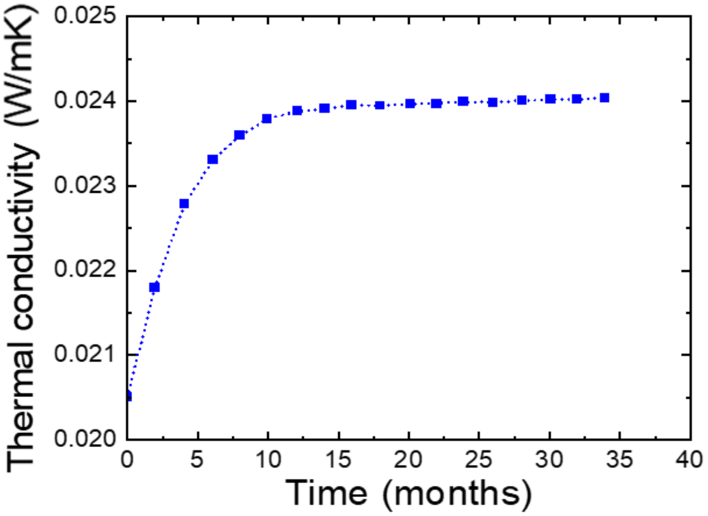


Figure 3. Typical foam thermal conductivity as a function of foam age [2].

Table 1 depicts a grouping that differentiates between low-pressure (LP) and high-pressure (HP) spray polyurethane foam (SPF) products, further segmented by product density [9]. Two-component LP-SPF products are suitable for professional and do-it-yourself applicators, catering to weatherization and small-scale insulation needs [10]. In contrast, two-component HP-SPF products are exclusively accessible to professionals, serving larger-scale insulation purposes such as roofing, filling interior wall cavities, and facilitating continuous insulation (e.g., exterior insulation without gaps from studs, joists). For HP-SPF, each component is delivered through a set of metering pumps (traditionally the pumps are equal volume in displacement), through a heat exchanger and then through heated hoses into a mixing chamber in a handheld spray gun, where the two components begin to react and are spray-applied.

Table 1. Grouping of priority products by product type [9]

Group name	Applications
Low pressure (various densities)	Typically used as air sealants and for small-scale insulation applications
High pressure 0.5 lb/ft^3, open-cell	Typically used as insulation for above-grade interior wall cavities and unvented attics and crawlspaces
High pressure 2 lb/ft^3, closed-cell	Typically used for exterior continuous insulation, insulation for above- and below-grade, and unvented attics
High pressure >3 lb/ft^3, closed-cell	Typically used in roofing or where high loads are placed on the foam surface

1.2 BLOWING AGENT CURRENTLY IN USE IN HIGH-PRESSURE SPRAY FOAM (HP-SPF)

1.2.1 HFOs

All commercially available HFOs, includingHFO-1224yd(Z) , HFO-1234ze(E), HFO-1336mzz(E), HFO-1233zd(E) and HFO-1336mzz(Z), are non-ODP (i.e., negligible), low-GWP foam blowing agents that provide the desired characteristics of current HFCs: non-volatile organic chemicals (VOCs), suitable boiling point, low vapor thermal conductivity, and nonflammability [2, 11, 12]. Owing to these characteristics of HFOs, the material has been used/tested as a foam blowing agent (FBA) in HP-SPF.

Both HFO-1336mzz(Z) and HFO-1336mzz(E) were tested in HP-SPF as FBA [12-14]. All foams using HFOs in their formulations exhibit an initial foam thermal conductivity within the range of 21.4 to 21.6 mW/mK, contingent upon the specific formulations. Variations in thermal performance over a span of 90 days is approximately 10%. Additionally, all samples possess densities ranging from 33.64 to 40.05 kg/m^3 (2.1 to 2.5 lb/ft^3), and they show satisfactory dimensional stability.

As a typical example, Table 2 shows the results of the properties of HP-SPFs blown with HFO-1336mzz(Z). Higher water levels were applied in the HFO-1336mzz(Z) controls to ensure a consistent density. All foam samples blown with HFO-1336mzz(Z) and water demonstrate favorable thermal conductivity, dimensional stability, density, and notable closed-cell content, and they are within an acceptable density range. The only exception is the sample containing a high proportion of water. This high amount of water could potentially be attributed to the combination of a low isocyanate (ISO) index and a significant amount of heat and CO_2 generation.

It should be mentioned that the polyol blend containing these materials must be non-flammable, that to be considered commercially acceptable the closed cell content must be higher than 90%. Additionally, none of the samples met the closed cell criteria besides HFO-1336mzz(Z) foams. The findings illustrate the use of a consistent water level of 2.55% for the methyl formate and methylal blends. Conversely, higher water levels were applied in the controls to ensure a consistent density [15].

Table 2. Comparison of foam's characteristics on various chemical compositions of HFO-1336mzz(Z), methyl formate, and methylal blends.

Water (wt %)	Methyl formate (wt %)	Methylal (wt %)	HFO 1336mzz (Z) (wt %)	Thermal conductivity (W/mK)	Closed-cell content (%)	Density (lb/ft^3)	ISO index	Dimensional stability (70°C humid and −20°C)
2.55	0	4.27	9.21	0.0210	76.5	1.81	105	Poor
2.55	0	3	11.95	0.0207	83.93	1.87	105	Fair
2.55	0	2	14.11	0.0203	88.83	1.86	105	Fair
2.55	4.27	0	6.75	0.0211	63.8	1.84	105	Poor
2.55	3	0	10.22	0.0206	72.19	1.82	105	Poor
2.55	2	0	12.96	0.0204	86.74	1.81	105	Fair
3.56	0	0	9.21	0.0226	>95	1.89	90	Poor
2.98	0	0	14.5	0.0205	>95	1.83	100	Good
2.75	0	0	16.5	0.0202	>95	1.84	105	Good

1.2.2 Methyl Formate

Methyl formate, whether in its pure form or as a blend with HFOs, could be used in HP-SPF with restrictions, owing to certain difficulties in specific formulations and its flammability (Table 2). These challenges involve issues regarding the stability of blends and the potential for compromised long-term dimensional stability. Ensuring that manufacturing equipment and the final product are compatible is crucial to prevent occurrences of chemical deterioration, especially when compared with FBAs. On the other hand, when the concentrations of methyl formate are elevated, they are categorized as flammable according to transportation regulations, as well as for the purposes of handling and processing. Nonetheless, because of its affordability and widespread availability, small- and medium-sized enterprises are revisiting the possibility of incorporating methyl formate into blends alongside HFCs or hydrochlorofluoroolefins (HCFOs).

Regarding the consideration of using methyl formate in HFO blends, a series of studies have been presented by Wysong [15]. As the concentrations of flammable methyl formate increase, the associated flash points decrease. Table 2 explains the effect of methyl formate and HFO-1336mzz(Z) blends on the final foam's characteristics. Elevating the concentration of methyl formate in the formulation leads to detrimental effects on the foam's thermal performance, closed-cell content, and dimensional stability.

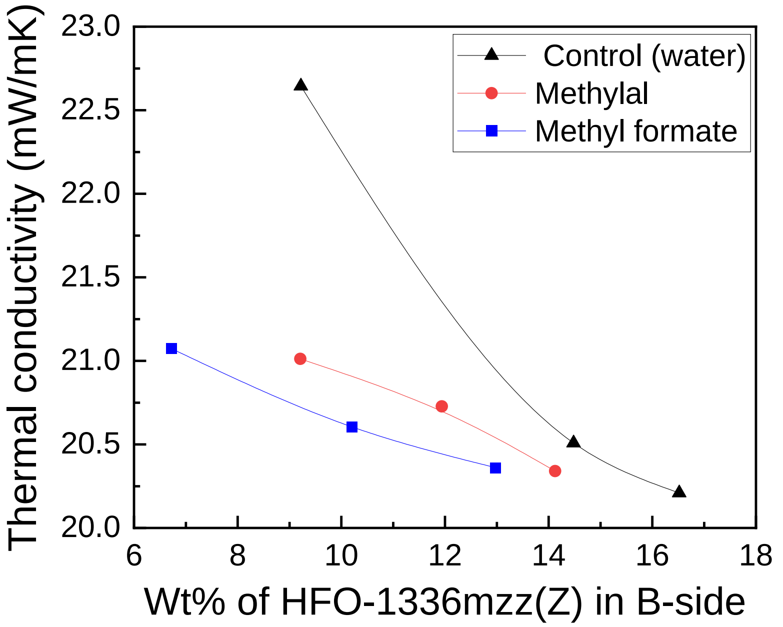


Figure 4. Impact of weight percent of HFO-1336mzz(Z) on the thermal performance in blends with methylal, methyl formate, and 2.55% water [15].

1.2.3 Methylal

Table 2 shows the effect of the ratio between methylal (also known as dimethoxymethane) and HFO-1336mzz(Z) in the formulations and its results. Increasing the amount of methylal in the formulation has a negative effect on the foam's thermal performance, closed-cell content, and dimensional stability. Also, Figure 4 shows the initial thermal performance data, recorded at 23°C, which reveals a significant effect, demonstrating the improvement in thermal performance with an increase of HFO-1336mzz(Z). Essentially, this result indicates the potential for an extended period of enhanced insulation performance by adding HFO-1336mzz(Z). However, the commercial adoption is difficult due to deficiencies in performance, specific formulation and flammability.

The incorporation of methyl formate and/or methylal in HFO blends was explored as shown in Table 2 but the development of commercially viable spray foams does not seem feasible. Undertaking a reformulation project will require careful consideration and resolution of several challenges, including the following:

1. Effect on flammability of polyol formulations (for shipping and application): The introduction of these substances can influence the flammability characteristics of polyol formulations during shipping and application stages.

2. Storage stability of polyol formulations: The stability of polyol formulations might be affected by the inclusion of methyl formate and/or methylal, necessitating measures to maintain adequate storage stability.

3. Formulation reactivity: The reactivity of the overall formulation might be altered owing to the introduction of these new components, requiring a thorough understanding of their interactions.

4. Dimensional stability: The inclusion of methyl formate and/or methylal could affect the dimensional stability of the resulting foam products, which needs to be carefully assessed and managed.

5. Insulation performance: The insulation performance of the foam, a critical attribute, may be influenced by the addition of these compounds, necessitating evaluations to ensure target performance levels are met.

6. Foam cellular structure and physical properties: The cellular structure and physical properties of the foam could be affected by the incorporation of methyl formate and/or methylal, demanding a comprehensive analysis of resulting changes.

Addressing these challenges through systematic testing, formulation adjustments, and a thorough understanding of the underlying chemistry is vital to achieving successful reformulation while maintaining the desired foam properties and performance.

1.2.4 CO_2 (Water)

Open-cell spray formulations incorporate a water content ranging from 15% to 25% by weight of the total formulation, which serves a crucial role in producing sufficient CO_2 to function as the blowing agent [16, 17]. This water concentration is notably higher compared with other applications of PU foam insulation, presenting distinctive challenges in terms of formulation. The rate at which CO_2 is generated plays a key role in the foaming and expansion process. Consequently, the reaction between water and isocyanate must occur rapidly to ensure optimal results. In cases where CO_2 is not produced quickly enough, the foam is susceptible to sagging or collapsing, preventing the achievement of the desired density or yield.

The accelerated CO_2 generation also plays a physical role in expanding some of the foam’s cells. This process is integral for maintaining the proper pressure equilibrium between the foam’s interior and exterior. If an excess number of cells remain closed, the foam contracts during the cooling phase after the exothermic reaction. This contraction leads to external pressure exceeding internal pressure, causing the foam’s surface to retract. This phenomenon is commonly referred to within the industry as *foam tightening*. This tightening becomes noticeable through a reduction in the foam’s size and the appearance of wrinkles or puckers on the surface.

Assessments of CO_2 as an FBA in HP machines were carried out using a Graco E-20 machine and a Graco Fusion Air Purge gun equipped with an AR4242 mix chamber [17]. Throughout the process, the hose for both the A and B sides was maintained at temperatures of 40.55°C (105°F), 48.89°C (120°F), and 57.22°C (135°F). Meanwhile, the dynamic pressure was consistently maintained within the range of 6.89 to 7.58 MPa (1,000 to 1,100 lbf/in^2). The foam’s final density and shrinkage were all varied by formulations and processing parameters. In this study, the foam composition consisted of approximately 16%–21% by weight of water (CO_2). As a result of this formulation, the foam’s density was approximately 8 kg/cm^3 (0.5 lb/ft^3) [17].

The addition of water in HFO blends was tested by Sowder, and the sample preparation was done by using a Graco Reactor E-30 proportioner and a Fusion AP gun [13]. The specific settings used are described in Table 3.

Table 3. Specific settings

A-side primary heater setpoint: 125°F	A-side dynamic pressure: 8.27 MPa (1,200 lbf/in^2)
B-side primary heater setpoint: 125°F	B-side dynamic pressure 8.27 MPa (1,200 lbf/in^2)
Hose heat setpoint: 125°F	Mix chamber: AR4242

To enhance the cost-effectiveness of the HFO formulation, the researchers opted to reduce the proportion of HFO-1336mzz(Z) while simultaneously raising the water content. This adjustment aimed to maintain the target core foam density. By increasing the water content to 2.45 wt % and reducing HFO-1336mzz(Z) to 9.5%, the resulting foam's thermal performance is decreased 10%. This alteration led to a notable rise in the concentration of CO_2 within the cell gas. However, when subjected to the hot humid dimensional stability test (ASTM D2126), the change in volume surpasses the permissible limit of 15%. In summary, raising water loadings can result in reduced dimensional stability or the impairment of other properties. Table 4 summarizes the blowing agents currently used in HP-SPF.

Table 4. Summary of FBA currently use in HP-SPF

Criteria	**HFOs**	**Methyl formate**	**Methylal**	**CO_2 (water)—open cell**	**CO_2 (water)—closed cell**	**CO_2**	**trans-1,2 dichloroet-hylene (TDCE)**
Blowing Agent Flammability	Non-flammable	Flammable	Flammable	Non-flammable	Non-flammable	Non-flammable	Flammable
Foam thermal insulation performance	Excellent	Dependent on primary blowing agent used	Dependent on primary blowing agent used	Poor	Poor	Dependent on primary blowing agent used	Dependent on primary blowing agent used
Foam physical properties	Excellent	Issues with long term dimensional stability	Dependent on primary blowing agent used	Low density/low compressive strength limits where product can be used	Good	Dependent on primary blowing agent used	Dependent on primary blowing agent used
Compatibility with Spray foam processing equipment	Yes	No	No	Yes	Yes	No	Yes
Environmental Considerations	None	None	VOC by EPA	None	None	None	VOC by EPA
Safety Considerations	None	Flammable	Flammable	None	Can result in high reaction exotherm - fire hazard	High pressure cylinders required	Flammable, toxicity issues

Table 4. Summary of FBA currently use in HP-SPF (continued)

Criteria	HFOs	Methyl formate	Methylal	CO_2 (water)—open cell	CO_2 (water)—closed cell	CO_2	trans-1,2 dichloroethylene (TDCE)
Overall suitability as a blowing agent in this application	Suitable for all high pressure spray foam	Suitable, but only as an additive, but blend must be non-flammable	Suitable, but only as an additive, but blend must be non-flammable	Suitable in applications where good mechanical properties are not required	Suitable where low lambda is not critical	Suitable where low lambda is not critical	Suitable, but only as an additive

EPA: US Environmental Protection Agency

1.3 SUMMARY

Hydrochlorofluoroolefins and hydrofluoroolefins are well established foam blowing agents (FBA) in High-Pressure Spray Foam (HP-SPF) applications due to the resulting excellent physical properties and thermal insulation performance. Additionally, they are non-flammable and compatible with spray foam processing equipment, making them suitable for these applications. Methyl formate and methylal can be used as additives. Still, mixtures containing these additives must be non-flammable to be acceptable. Carbon dioxide (CO_2) water based blowing agents for HP-SPF could be suitable where the thermal performance (i.e., thermal resistivity) of foams is not critical. Trans-1,2 dichloroethylene (TDCE) could also be used as additives and in limited quantities due to toxicity issues.

1.4 BLOWING AGENT NOT WIDELY USED IN HP-SPF

1.4.1 Hydrocarbons

HCs find widespread use in diverse applications such as foam boards, integral skin products, and more. However, their application in spray foam applications has been hindered by safety concerns related to their high flammability. Table 5 summarizes the characteristics of hydrocarbons that prevent their use in High-Pressure spray foam applications.

Table 5. Summary of FBAs not currently in use in HP-SPF

Characteristic	Hydrocarbons
Blowing agent flammability	Flammable
Foam thermal insulation performance	Unknown
Foam physical properties	Unknown
Compatibility with spray foam processing equipment	No
Environmental considerations	VOC by US Environmental Protection Agency
Safety considerations	Flammable
Overall suitability as a blowing agent in this application	Not suitable

In the process of SPF application, a fraction of the blowing agent is inevitably released into the atmosphere [4, 6, 18, 19]. Consequently, the flammability of the blowing agent itself emerges as a pivotal concern for SPF applications, and different strategies have been explored to mitigate potential ignition sources. Despite these efforts, no blends have emerged as definitive solutions to completely address this issue. The problem persists, resulting in the formation of flammable mixtures that necessitate safety precautions.

1.5 SUMMARY

Hydrocarbons (HCs) are not used as blowing agents for High-Pressure Spray Foam applications due to their high flammability. During a typical spray foam application, a fraction of the blowing agent is inevitably released into the atmosphere, which requires additional safety precautions because of the resultant flammability of mixtures containing hydrocarbons. Hence, due to flammability issues and incompatibility with equipment, hydrocarbons are not currently in use for HP-SPF applications.

1.6 LOW-PRESSURE SPRAY FOAM (LP-SPF)

Figure 5 depicts the application process for two-component (isocyanate and polyol side) low-pressure spray foam (LP-SPF). The applied pressure for LP-SPF is less than 1.72 MPa (250 lbf/in^2) and requires enough blowing agent and/or propellant to entirely dispense the contents of the isocyanate(A-side) and polyol resin (B-side) mixtures (e.g., polyol, catalysts, surfactants). Typically, the two components are combined in a static mixer, maintaining the foaming mixture's consistent texture and pattern during spraying. Once mixed, the foaming reaction begins. Thus, to maintain the correct stoichiometry, both parts must be kept at their predetermined ratio during the entire dispensing process. LP-SPF is typically employed in smaller areas and delivered in refillable systems or kits that are maintained at pressures less than 1.72 MPa (250 lbf/in^2).

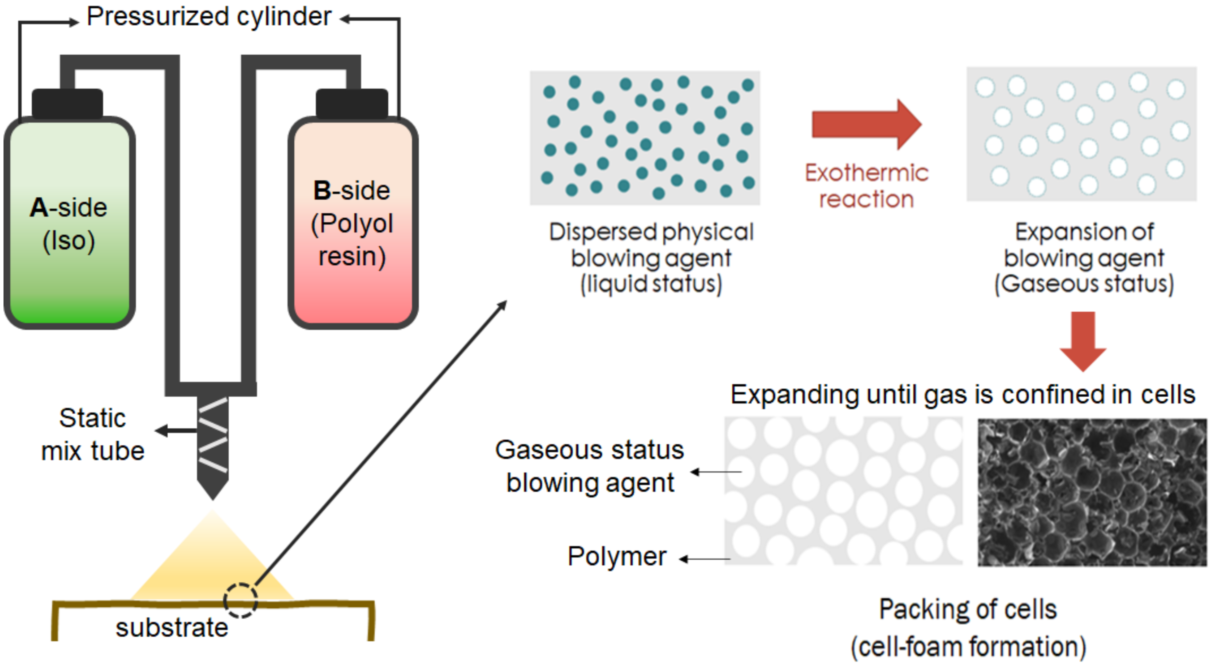


Figure 5. Schematic of LP-SPF and foaming process.

1.6.1 HFOs

Because of HFCs' high GWP, they are being phased out, and the FBA used in both Low-Pressure and High-Pressure SPF has been shifting to HFOs. Numerous studies have been conducted to explore the potential of HFOs as replacements for HFCs in the SPF market (see figure 6). Cline et al. conducted an assessment using HFO-1234ze(E) as an alternative to HFC-134a for LP-SPF [20]. They optimized the formulation by using HFO-1234ze(E) as the primary blowing agent, yielding an initial thermal conductivity at 24℃ ranging from 22 to 24 mW/mK when evaluated in accordance with ASTM C518. This performance is comparable with the typical products currently available in the market. Their comparison of various physical properties of the final foam, including closed-cell content, density, cell structure, and foam appearance, concluded that HFO-1234ze(E) can effectively replace HFC-134a.

Blemings et al. reported that HFO-1336mzz(E) offers a feasible alternative to HFC-134a for LP-SPF [11]. By adjusting the formulation, the thermal conductivity of SPF containing HFO-1336mzz(E) ranges between 20 and 24 mW/mK at 24℃, closely resembling the thermal conductivity of SPF formulated with HFC-134a (as shown in figure 6). They further elucidated that the final foam's density and closed-cell content align with prevailing values in the current SPF market.

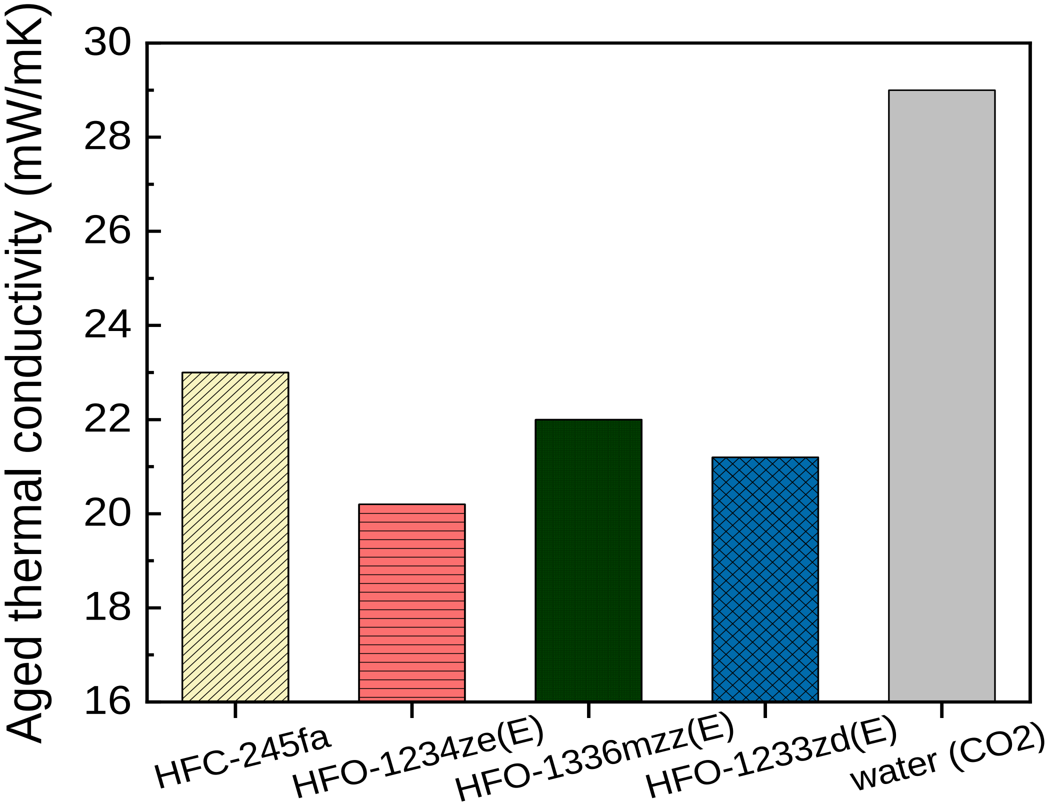


Figure 6. Effect of different blowing agents on the aged thermal performance of spray foam. All values were measured at 24℃ after 90 days in accordance with ASTM C518 [11, 19, 21].

HFO-1233zd(E) has been evaluated and compared with HFC-245fa and CO_2 (water). Foam was made using formulation commercially designated as FOAM-LOK II 4G [21]. Foams generated using HFO-1233zd(E) exhibit an 8% improvement in long-term thermal performance compared with the HFC-245fa system and a substantial 75% decrease in lambda when contrasted with foams produced using CO_2 (water) as the blowing agent. Furthermore, the thickness needed to attain an equivalent level of air leakage performance for the HFO-1233zd(E) system is notably less—more than 50% less than that necessary for HFC-245fa-blown foams and a remarkable 78% less than the requirement for CO_2 (water)–blown foams. Table 6 summarizes the effects of different FBAs on HP-SPF.

Table 6. Effect of different FBAs on the HP-SPF's characteristics [21]

	HFC-245fa	**HFO-1233zd(E)**	**CO_2 (water)**
Thermal conductivity after 90 days at 60℃ (mW/mK), ASTM C518	22.9	21.2	37.0
Compressive Strength (lbf/in^2) ASTM D1621	24.9–30.0	24.9	—
Closed-cell content (%)	>90	>90	<10
Dimensional stability, 28 days at 71℃/100% relative humidity Δ vol %, ASTM D2126	3	4	4

HFO-1233zd(E) has been actively used in various commercial low pressure SPF (e.g., HANDIFOAM CHANNEL FILL [HFO]), and the final foam's aged thermal conductivity value is approximately 24.0 mW/mK [10]. This result is 17% better than the foams blown with water. This improvement might be because of several reasons; first, in the case of water-blown spray foams, CO_2 gas is generated during the foaming reaction and works as a blowing agent. Because CO_2 has higher thermal conductivity than HFO-1233zd(E), this addition increases the foam's thermal conductivity. Secondly, as depicted in Figure 7, the diffusion coefficient of CO_2 is much larger than that of HFO, accelerating the foam insulation's aging.

Sowder has tested the long-term thermal performance of the SPF formulated with HFO-1336mzz(E), and the reduction in thermal performance was 2.7% after 3.5 years [22].

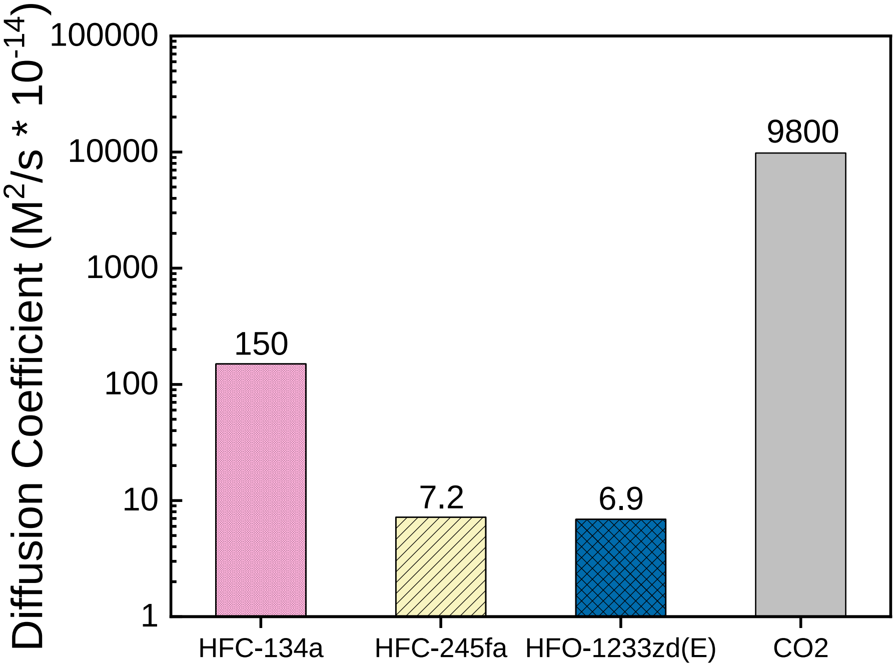


Figure 7. Diffusion coefficients of different blowing agents at 20℃ [2].

1.6.2 CO_2 (Carbon Dioxide)

Combinations of CO_2 gas and HFO-1233zd(E) blends have been employed as an FBA in the Dupont Froth-Pak Spray foam [23]. This product has been reported to satisfy all relevant code requirements. The foam's density measures at 28.03 kg/m^3 (1.75 lb/ft^3), and its compressive strength is 0.11 MPa (16 lbf/in^2). Its initial thermal conductivity, as determined by ASTM C518, is 21.5 mW/mK, and the thermal conductivity of the aged foam is approximately 37.7 mW/mK. Notably, this change in thermal performance is substantial, reaching approximately 75%, which surpasses the changes observed in SPF blown with HFOs [24]. The pronounced disparity arises because CO_2 diffuses out at a faster rate than HFOs, leading to more rapid air infiltration into the cells. As a result, the more CO_2 present in the foam, the quicker the cells release CO_2 into the surrounding environment. This unique property can also affect the foam's dimensional stability, implying that volume changes within the foam can be considerably greater when it contains higher levels of CO_2. Cline's research reveals that the dimensional stability of SPF blown with HFOs is below 7%, yet Froth-Park SPF exhibits a volume change of 14% [10, 23]. Both measurements of dimensional stability were conducted at 70°C and 100% relative humidity, adhering to ASTM D 2126 requirements. Interestingly, when CO_2 is combined with HFOs in LP-SPF, the long-term thermal performance and dimensional stability of the final foam tend to deteriorate compared with SPF without CO_2, as depicted in Figure 8

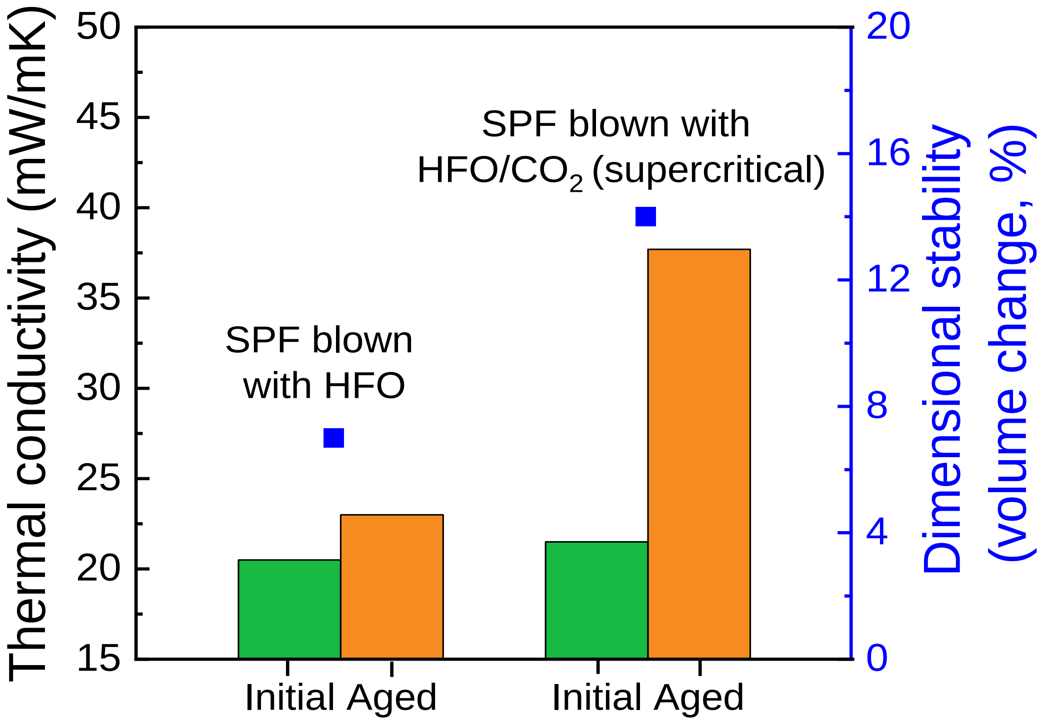


Figure 8. Effect of blowing agent on SPF's thermal performance and dimensional stability. The main blowing agent data on the left side of the graph are HFO-1233zd(E), and the data on the right side are the co-blowing agent of HFO-1233zd(E)/supercritical CO_2 [20, 23].

Furthermore, Blemings conducted experiments involving the addition of varying amounts of CO_2 to HFO-1336mzz(E)/water blends and conducted dispensing trials on the isocyanate and polyol resin side mixtures [11]. It was observed that a higher concentration of CO_2 in the polyol resin side caused the HFOs to liquefy in the cylinder. Consequently, this liquefaction lowered the overall vapor pressure, counteracting the dispensing process within the pressurized cylinder. To counter this effect, Blemings introduced 0.26% to 0.52% of CO_2 into different formulations and subsequently measured the foam's density, closed-cell content, thermal performance, and compressive strength (as shown in Table 7). When the foam was blown solely using HFO-1336mzz(E) and water, the foam exhibited properties such as a density of 30.43-32.03 kg/m^3 (1.9–2.0 lb/ft^3), closed-cell content ranging from 92% to 94%, thermal conductivity of 20.3 mW/mK, and compressive strength between 0.133 and 0.15 MPa (19.3 and 21.7 lbf/in^2). However, upon injecting CO_2 into the formulation, the foam's density increased to a range of 32.03-44.85 kg/m^3 (2.0–2.8 lb/ft^3). Additionally, the closed-cell content varied depending on the formulations, spanning a range from 10% to 90%. Foams with closed-cell content of approximately 90% were achieved through the addition of a foam stabilizer, which incurs an increase in the overall manufacturing cost. Regarding the thermal performance of the final foam, the thermal conductivity ranged from 21.8 to 35.2 mW/mK, and the compressive strength of foams containing CO_2 spanned from 0.08 to 0.227 MPa (12.9 to 33 lbf/in^2), indicating higher compressive strength values in certain formulations.

Table 7. Effect of the addition of CO_2 (water) on the final foam's properties [11]

	HFO-1336mzz(E)/water blends	**HFO-1336mzz(E)/water/CO_2 blends**
Thermal performance (mW/mK)	20.3	21.8-35.2
Closed-cell content (%)	92–94	10–90
Final foam density (lb/ft^3)	1.9–2.0	2.0–2.8
Compressive strength (lbf/in^2)	19.3–21.7	12.9–33

Overall, very little liquified CO_2 can be added to the SPF application to meet the current market standards. As illustrated in Figure 8 and outlined in Table 7, SPF formulated with HFOs surpasses HFO/CO_2 co-blown foam with respect to attributes such as density, closed-cell content, and thermal performance. Consequently, optimizing the use of liquified CO_2 within SPF requires further research and development efforts to achieve higher quantities and enhance overall performance.

1.6.3 CO_2 (Water)

During the foaming process, CO_2 gas is generated from the reaction between water and isocyanate groups. So, water acts as a chemical blowing agent in PU foam. The CO_2 that is generated also acts as a source of cell nucleation and allows the foam to expand and create a fine, uniform cell structure [25]. This process is why most rigid PU foam formulations contain small amounts of water. Because of the low cost of water, this method has increased in interest to maximize its amount in SPF formulations. Depending on the total amount of water in the SPF and their final formulations, water can produce open-cell or closed-cell structures.

To generate enough CO_2 as a blowing agent in the open-cell SPF, 15–25 wt % of the total formulation of water needs to be added to the blend if no other blowing agent is used [17]. Among the overall processes of PU foam formation, the water and isocyanate reactions are much quicker than other reactions; thus, the CO_2 formation rate is critical to the overall process of foaming and expansion. When the rate is too slow, the final foam's density and yield can be too high because of collapsing and sagging cells. Also, a high CO_2 generation rate bursts too many cells, which can physically damage foams and create high open-cell content (Figure 9). Therefore, maintaining the right pressure balance by adding adequate amounts of water is very important. Typically, open-cell foam has a density of approximately 8 kg/m^3 (0.5 lb/ft^3) and a thermal conductivity of approximately 40 mW/mK.

In closed cell foam, interconnected closed pockets are created, when the cells do not rupture during the process of expansion as shown in Figure 9. The typical final closed foam density and aged thermal conductivity are 35.24 kg/m^3 (2.2 lb/ft^3) and 29.4 mW/mK, respectively. The density of the final foam is similar to the foam blown with HFCs and HFOs. However, the long-term thermal performance is poorer than the SPF blown with HFCs or HFOs. This poorer performance is because the gas thermal conductivity of CO_2 is much higher than that of HFO, as described in Figure 6. The CO_2 diffuses out quickly during the aging process, and air diffuses into the cell until a CO_2–air equilibrium is reached [2]. Because air is a better thermal conductor than CO_2, the thermal performance is reduced once air gets into the foam. SPF blown with water, HFC, and HFO have also been compared to see the effect of the blowing agent on the final foam's performance. In the case of the thermal performance of the final foam, SPF that is blown with HFC-245fa and HFO-1233zd(E) has 25% lower thermal conductivity values compared with the SPF blown with water only [25]. This reduction is because of the water-only blowing foam containing only CO_2 in the foam, which has a higher thermal conductivity than HFC-245fa and HFO-1233zd(E). The dimensional stability of water-only blown SPF is much poorer than SPF blown with HFC-245fa and HFO-1233zd(E). This poor performance is owing to CO_2 having a much higher diffusion coefficient than HFOs or HFCs. In the case of the foam's density, the one blown with water is 13% higher than SPF blown with HFC-245fa and HFO-1233zd(E), meaning that more material will be needed to achieve equivalent insulation performance [26]. Thus, using water only as the foam-blowing agent for closed-cell SPF is not beneficial as an insulation material.

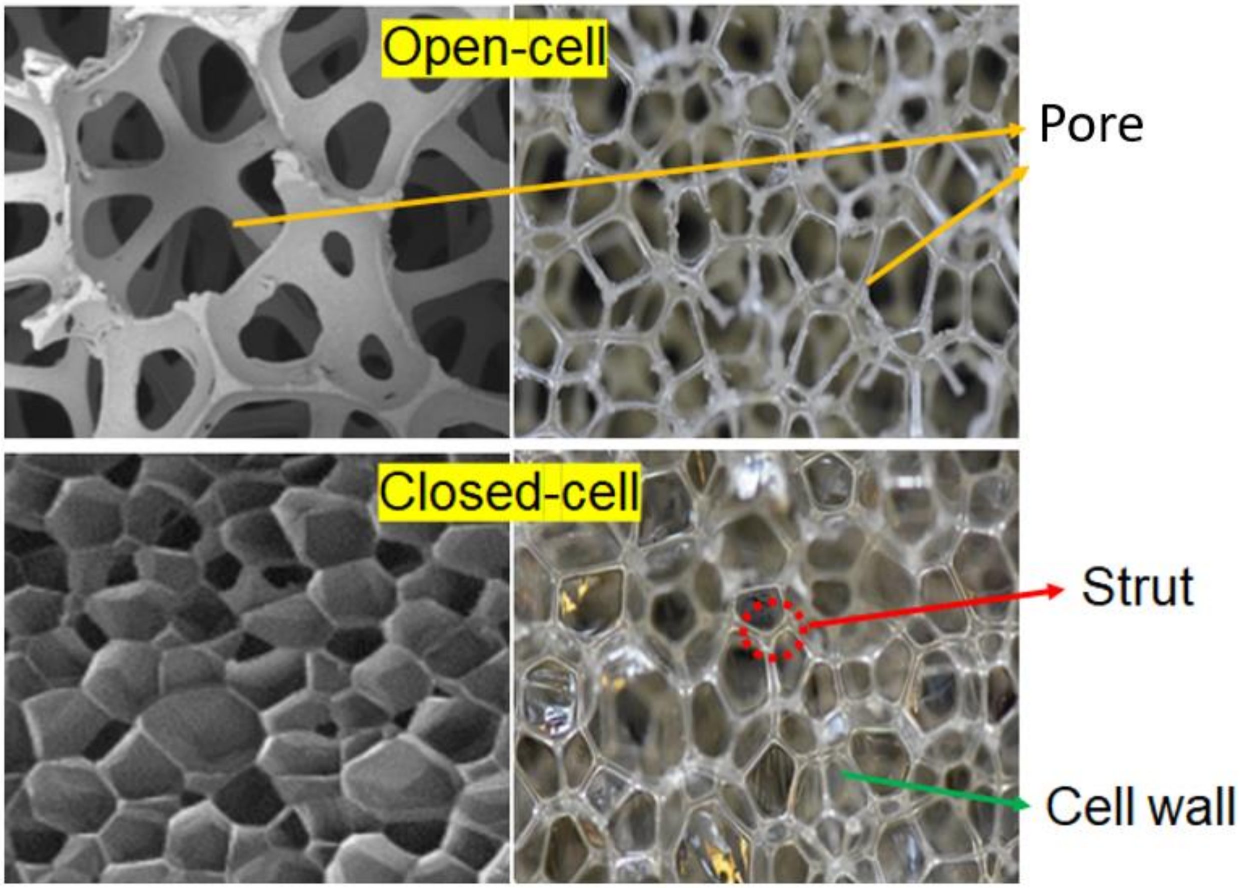


Figure 9. Structure of open- and closed-cell SPFs. Both left images are scanning electron micrographs (images are obtained from https://www.jm.com/en/blog/2020/june/spray-foam--open-cell-vs--closed-cell/), and the right images are microscopic images [27].

1.6.4 Trans-1,2-Dichloroethylene

Because of the very short atmospheric lifetime of trans-1,2-dichloroethylene (TDCE), the chemical has a very low GWP and no ODP. Various blends containing TDCE have been adopted as an FBA in the SPF market but are not used as a major blowing agent in SPF. US Environmental Protection Agency (EPA) limits the amount of TDCE used in spray foam to no more than 5% by weight of the total formulation [28]. It has been reported that when HFCs were predominantly employed as the physical blowing agent in SPF, TDCE played a role in enhancing the solubility of the polyol resin side mixture and augmenting the fire performance of the foam [29].

By elevating the concentration of TDCE in the HFC-134a/TDCE/water co-blowing agent mixture, the thermal performance of the resultant foam improved by approximately 15%, transitioning from 29.1 mW/mK to 24.7 mW/mK. Wu posited that this enhancement could be attributed to the high loading of HFC-134a, which tended to cause pinholes in the free-rise foam [29]. Additionally, TDCE led to a reduction in the foam's core density, moving from 2.5 to 2.0 lb/ft^3, underscoring TDCE's superior blowing capability compared with HFC's. However, once the TDCE's concentration in the co-blowing agent surpassed 30 mol %, it began to adversely affect the foam's dimensional stability. Under hot and humid conditions (70°C, 97% humidity), the foam experienced expansion of up to 19%. Notably, Wu noted that the volume expansion exhibited significant deviations within the same TDCE loading, indicative of an irregular foam structure. Despite TDCE's positive effects on thermal performance and foam density when used with HFCs, its incorporation is limited by the foam's dimensional stability considerations.

The use of TDCE in blends with HFO-1336mzz(E) as co-blowing agents has been explored within LP-SPF systems [9]. Blemings details that the inclusion of TDCE in its liquid state aids in the dispensing of SPF, thereby enhancing the physical attributes of the resulting foam. However, the study encompassed only a limited number of formulations involving TDCE, thereby restricting a comprehensive understanding of its effect on foam characteristics. According to their findings, foams produced through the incorporation of TDCE as a co-blowing agent exhibit attributes such as closed-cell content of approximately 75%, a density of approximately 32.03 kg/m^3 (2.0 lb/ft^3), and thermal performance ranging from 23.6 to 26.2 mW/mK. No matter how TDCE performs on the final foam, TDCE cannot be used as a major blowing agent in SPF because of its flammability [30]. Table 8 summarizes all of the FBAs currently used in LP-SPF.

Table 8. Summary of FBA currently in use in LP-SPF

Criteria		**HFOs**	**CO_2 gas**	**CO_2 (water)—open cell**	**CO_2 (water)—closed cell**	**Trans-1,2-dichloroethylene (TDCE)**
Blowing agent flammability		Non-flammable	Non-flammable	Non-flammable	Non-flammable	Flammable
Blowing agent vapor thermal conductivity at 25°C (mW/mK)		10.6~11.5	16.6	16.6	16.6	—
Foam thermal insulation performance (mW/mK)	Initial	20–24	~22	37~40	Unknown	Dependent on the primary blowing agent used
	Aged	21–24	~38	37~40	~37	
The core density of the foam (lb/ft^3)		~2	~1.8	~0.5	~2.2	Dependent on the primary blowing agent used

Table 8. Summary of FBA currently in use in LP-SPF (continued)

Foam compressive strength (ASTM D1621)	Excellent	Good	Good	Poor	Dependent on the primary blowing agent used
Closed-cell content, ASTM D2856 (%)	>90	—	<10	—	Dependent on the primary blowing agent used
Dimensional stability, 70° C, 95% relative humidity (volume changes, %)	~2	~14	—	Unknown	Dependent on the primary blowing agent used
Compatibility with spray foam processing equipment	Yes	Yes	Yes	Yes	Yes
Environmental considerations	None	None	None	None	VOC by US Environmental Protection Agency
Safety considerations	None	HP cylinders required	None	Can result in high reaction exotherm—fire hazard	Flammable, toxicity issues
Overall suitability as a blowing agent in spray foam application	Suitable for all spray foam	Suitable where low lambda is not critical	Suitable in applications where good mechanical properties are not required	Suitable where low lambda is not critical	Suitable, but only as an additive, not the primary blowing agent

1.7 SUMMARY

Hydrochlorofluoroolefins and hydrofluoroolefins are widely used blowing agents for low-pressure spray foam (LP-SPF) applications. They are non-flammable, exhibit adequate compressive strength and are compatible with spray foam processing equipment. Liquified CO_2 based blowing agents are non-flammable and can produce adequate compressive strength for closed-cell foams. They could be suitable where thermal performance of foam is not critical. On the other hand, open-cell foams produced using CO_2 (water) based blowing agents do not have good compressive strength, making them not suitable for LP-SPF applications. CO_2 (water) open-cell based FBA are suitable for LP-SPF only when good mechanical properties are not required. In addition, CO_2 (water) blowing agents are only acceptable where closed-cell foams with low thermal conductivity are not critical. Finally, Trans-1,2 dichloroethylene (TDCE) is flammable restricting its use only as an additive for LP-SPF applications.

1.8 BLOWING AGENTS NOT WIDELY USED IN LP-SPF

Owing to global warming issues, interest has increased in developing alternative chemistries in the foam industry. Attempts to reduce the usage of or find alternatives to halogenated FBAs have been conducted. Hydrocarbons (primarily pentane isomers), methyl formate, methylal, or their blends have been considered as possible alternative FBAs for SPF systems [4, 6]. Still, their high flammability has hindered their use in all LP-SPF application.

1.8.1 Hydrocarbons (HC)

Hydrocarbon blowing agents such as *n*-pentane, isopentane, and cyclopentane are commonly used for other applications such as foam board, integral skin, appliances, panels, and others. In the case of SPF applications, some portion of the blowing agent is emitted into the atmosphere [4, 6, 18, 19]. In the case of hydrocarbons, these emissions can cause explosive atmospheres, especially in poorly ventilated spaces. Thus, the flammability of the blowing agent itself is critical for SPF applications. Different mitigation strategies have been considered to remove the potential ignition sources. However, no blends have been successful in resolving this issue.

Owing to HCs' flammability and explosivity properties, they are unsafe [6] to use in high–urban density areas, so the manufacturer's plant location can be limited. Also, converting plants to use flammables is costly for all enterprises. Dealing with hydrocarbon blowing agents is especially very restricted and not a financially viable option for small enterprises [4, 6].

1.8.2 Methyl Formate

Adopting methyl formate is also an alternative because of its very low GWP and zero ODP. However, owing to its flammability, methyl formate itself cannot be used as a blowing agent in the SPF system. Limitations in blend stability and poor long-term dimensional stability are also challenges that need to be overcome. Nonetheless, using methyl formate in blends with HFOs is being reevaluated because of methyl formate's low cost. A few studies have been undertaken to add methyl formate to HFOs for SPF applications [11]. Owing to flammability ratios, the amount that could be added was very limited, and none of the evaluated formulations have met the industry standards yet.

1.8.3 Methylal

Methylal has a negligible GWP, no ODP, low photochemical ozone-creating potential, and a good toxicological profile. It is in the Significant New Alternatives Policy (SNAP) as acceptable for PU application, including SPF, and commercialized under the Novicell name. Sendijarevic tested the performance of Novicell for blowing capacity, density, thermal performance, dimensional stability, and compressive strength [31]. The blowing capacity of physical blowing agents are estimated from their molecular weight; the lower the molecular weight, the better the blowing capacity. Methylal has 76 g/mol, and HFO's molecular weight is within the range of 134–165 g/mol. So, Sendijarevic claimed that half the amount of a current HFO's loading of methylal that makes the foam is comparable with current market standards. Also, they describe that methylal has good solubility with polyol resins, and no major change is needed in formulations to obtain a reasonable cellular structure. The foam's density and thermal conductivity are approximately 2.2–2.4 lb/ft^3 and 22.5–24.0 mW/mK, respectively. Also, the compressive strength of foam blown with the methylal and HFO-1336mzz(Z) co-blowing agent is over 30 lbf/in^2, which exceeds the requirements of SPF (>15 lbf/in^2) [32]. But when only methylal is used as a physical blowing agent, the produced foam's dimensional stability is over 25%, which is unacceptable in the SPF industry (<15%) [32]. To overcome this issue, the researchers added a cell regulator (CR-100B), which improved the dimensional stability to 1.5% (volume change). However, that approach can be costly, and all foams are made with the pouring method. Still, this method is not the same as the actual SPF system and needs to be tested in a pressurized system. Table 9 summarizes the characteristics of FBAs not currently used in LP-SPF.

Table 9. Summary of FBAs currently not in use in LP-SPF

	Hydrocarbons	**Methyl formate**	**Methylal**
Blowing agent flammability	Flammable	Flammable	Flammable
Blowing agent thermal conductivity at 25℃ (mW/mK)	11.4~14.5	Good	Good
Foam physical properties	Unknown	Issues with long-term dimensional stability	Fair
Compatibility with spray foam processing equipment	No	No	No
Environmental considerations	VOC by EPA	None	VOC by EPA
Safety considerations	Flammable	Flammable	Flammable
Overall suitability as a blowing agent in spray foam application	Not suitable	Not suitable	Not suitable

EPA: US Environmental Protection Agency

1.9 SUMMARY

Hydrocarbons are highly flammable, which prevents their use in some low-pressure spray foam applications. Methyl formate as FBA is flammable, which makes them also not suitable for LP-SPF applications. In the case of mixtures containing methyl formate, they show poor dimensional stability, which creates significant technical challenges. As for Methylal mixtures used as blowing agents, they show acceptable dimensional stability and thermal conductivity properties. However, problems of flammability make them not suitable for LP-SPF applications.

1.10 CRITICAL ISSUES NEED TO BE ADDRESSED

Blends of HFOs with other alternatives or finding alternative FBA options are minimal and still need to be developed. Owing to safety-related issues, FBA options will often require different testing methods to certify the product and check the qualification. This process will not only be for the blowing agent itself but also for the foam products in which it is used. Developing new formulations and qualifications and gaining code approvals, considering all processes, can take a minimum 18 months to a few years [6].

2. BOARDSTOCK

2.1 BLOWING AGENTS IN BOARDSTOCK

For purposes of this report, boardstock encompasses two different types of foam, phenolic and polyurethane/polyisocyanurate. Each are discussed separately below.

Figure 10 shows several FBA used in the foam boardstock with their relative environmental impact. Hydrocarbons and HFOs are prime candidates for FBA since they have zero ODP and very low GWP.

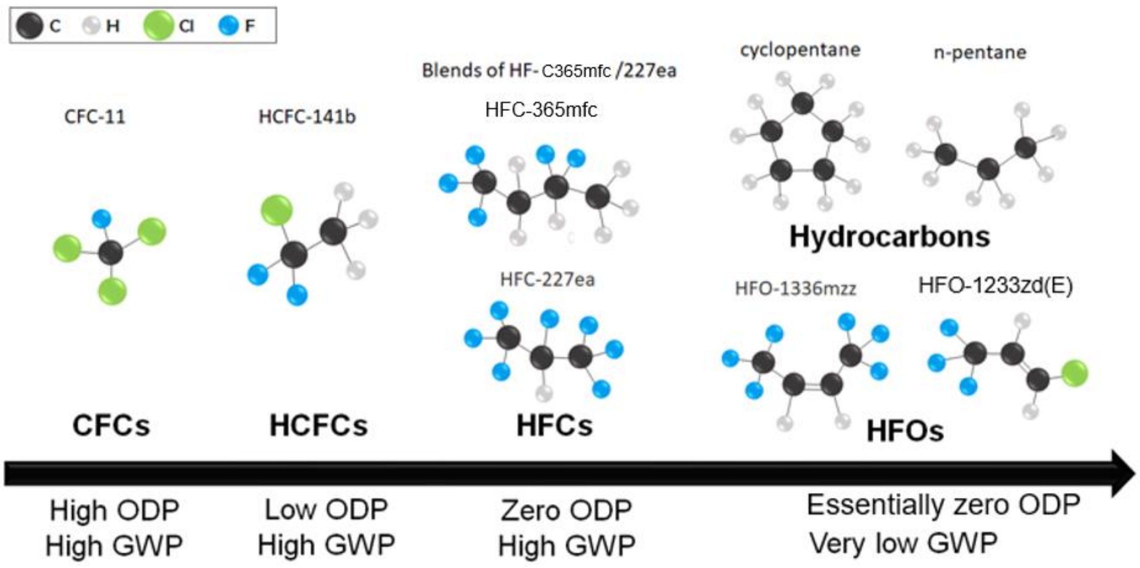


Figure 10. FBA generations in the foam boardstock and their environmental impact.

2.2 BLOWING AGENT CURRENTLY IN USE IN POLYURETHANE/ POLYISOCYANURATE FOAM BOARD

2.2.1 HFOs

HFO-1233zd(E) exhibits a low gas thermal conductivity, comparable to that of HCFC-141b which is a historical baseline blowing agent, although not current in use today. In addition to its low GWP, HFO-1233zd(E) does not exhibit either a flashpoint or flammability limit under ambient conditions. Rigid laminated boardstock foam blown with HFO-1233zd(E) only was evaluated by Costa's work [33] (table 10). The foam's thermal conductivity at 24°C was 18.3 mW/mK, with a foam density of 1.83 lb/ft^3. The closed-cell content was measured at 93.7%, and the dimensional stability at 70°C/97% relative humidity indicated a 4.4% volume change.

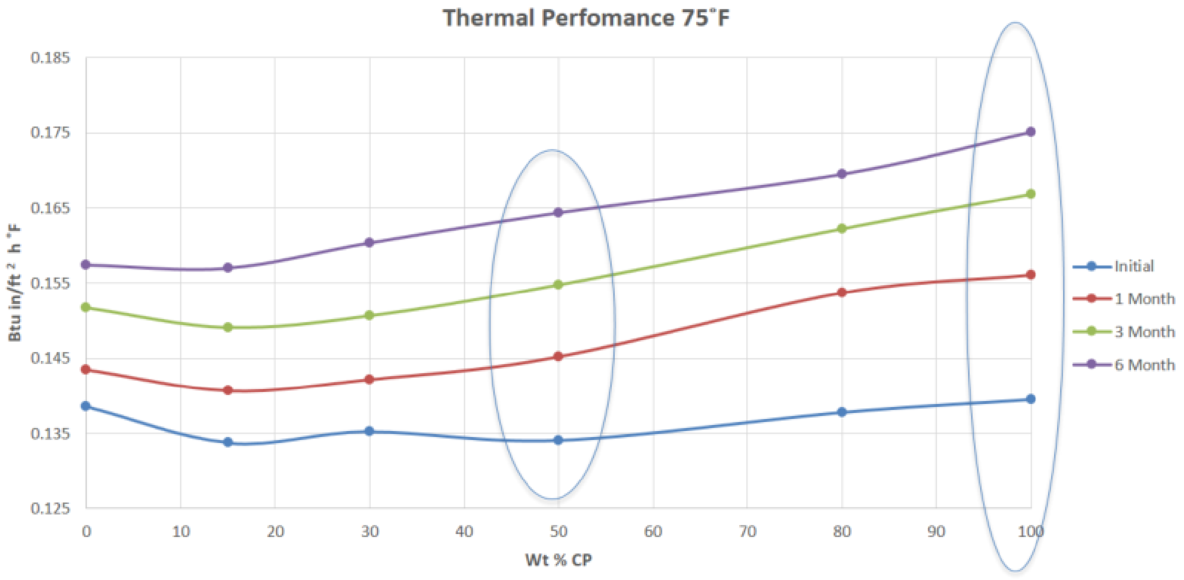
Table 10. Initial and aged thermal conductivity of foam samples [33]

	Thermal conductivity in mW/[K·m^3] ([Btu·in]/[h·ft^2·°F]						
Sample*	**Normal/ isopentane control**	**HCFO-1233zd (10%)**	**HCFO-1233zd (20%)**	**HCFO-1233zd (40%)**	**HCFO-1233zd (60%)**	**HCFO-1233zd (80%)**	**HCFO-1233zd (100%)**
Initial							
0°C (32°F) mean test temperature	**22.2 (0.1540)**	**21.2 (0.1473)**	**20.6 (0.1425)**	**19.3 (0.1338)**	**18.2 (0.1261)**	**17.2 (0.1193)**	**16.2 (0.1126)**
10°C (50°F) mean test temperature	**21.1 (0.1462)**	**20.6 (0.1426)**	**20.2 (0.1398)**	**19.5 (0.1351)**	**18.7 (0.1299)**	**18.0 (0.1245)**	**16.9 (0.1175)**

Table 10. Initial and aged thermal conductivity of foam samples [33] (continued)

24°C (75°F) mean test temperature	**21.6 (0.1500)**	**21.4 (0.1485)**	**21.2 (0.1471)**	**20.8 (0.1446)**	**20.2 (0.1404)**	**19.4 (0.1347)**	**18.3 (0.1271)**
1 month aged							
0°C (32°F) mean test temperature	**22.8 (0.1580)**	**21.9 (0.1519)**	**21.3 (0.1475)**	**20.2 (0.1398)**	**19.1 (0.1324)**	**18.1 (0.1254)**	**17.2 (0.1196)**
10°C (50°F) mean test temperature	**21.8 (0.1511)**	**21.3 (0.1477)**	**20.9 (0.1541)**	**20.3 (0.1411)**	**19.6 (0.1362)**	**18.8 (0.1306)**	**18.0 (0.1246)**
24°C (75°F) mean test temperature	**22.4 (0.1555)**	**22.2 (0.1539)**	**22.0 (0.1507)**	**21.7 (0.1507)**	**21.2 (0.1468)**	**20.3 (0.1408)**	**19.3 (0.1339)**
2 month aged							
0°C (32°F) mean test temperature	**23.7 (0.1645)**	**22.8 (0.1582)**	**22.1 (0.1534)**	**20.9 (0.1451)**	**19.8 (0.1373)**	**18.8 (0.1302)**	**18.2 (0.1260)**
10°C (50°F) mean test temperature	**22.6 (0.1564)**	**22.0 (0.1528)**	**21.6 (0.1499)**	**21.0 (0.1456)**	**20.3 (0.1406)**	**19.5 (0.1354)**	**18.9 (0.1311)**
24°C (75°F) mean test temperature	**23.2 (0.1607)**	**22.9 (0.1591)**	**22.7 (0.1573)**	**22.4 (0.1553)**	**21.9 (0.1516)**	**21.0 (0.1459)**	**20.3 (0.1408)**
4 month aged							
0°C (32°F) mean test temperature	**24.6 (0.1705)**	**23.7 (0.1640)**	**23.0 (0.1597)**	**21.8 (0.1514)**	**20.7 (0.1435)**	**19.7 (0.1368)**	**19.1 (0.1328)**
10°C (50°F) mean test temperature	**23.2 (0.1612)**	**22.7 (0.1575)**	**22.3 (0.1549)**	**21.7 (0.1508)**	**21.1 (0.1465)**	**20.6 (0.1425)**	**20.0 (0.1385)**
24°C (75°F) mean test temperature	**23.8 (0.1648)**	**23.6 (0.1633)**	**23.4 (0.1623)**	**23.2 (0.1606)**	**22.7 (0.1577)**	**22.1 (0.1535)**	**21.5 (0.1488)**
***Samples were 2.54 cm (1 in.) thick and aged at room temperature.**							

Foams blown with HFO-1336mzz(Z) and cyclopentane show better thermal insulation performance compared to 100% cyclopentane, suggesting slower diffusion rate of HFO-1336mzz(Z) [34]. However, the initial insulation value of foams prepared with HFO-1336mzz(Z) as the sole blowing agent have a relatively lower values when compared with HFO-1336mzz(Z)/cyclopentane blends. Although HFO-1336mzz(Z) offers significant benefits as a primary FBA, its higher boiling point and molecular weight can present challenges in optimization [34]. Therefore, the use of co-blowing agents is gaining interest for enhancing overall performance and resource efficiency. HFO-1336mzz(Z) can form minimum boiling azeotropes with various FBAs, including cyclopentane, isopentane, *n*-pentane, methyl formate, and methylal [34, 35]. This formation results in a reduction of the net boiling point and heats of vaporization, mitigating the effect of condensation and minimizing the loading of HFO-1336mzz(Z). The addition of water as a third component for CO_2 generation can provide further benefits through heat generation, polymer modification, and balancing of cell gas pressure [34, 35]. The aged thermal performances of HFO-1336mzz and cyclopentane are shown in Figure 11.



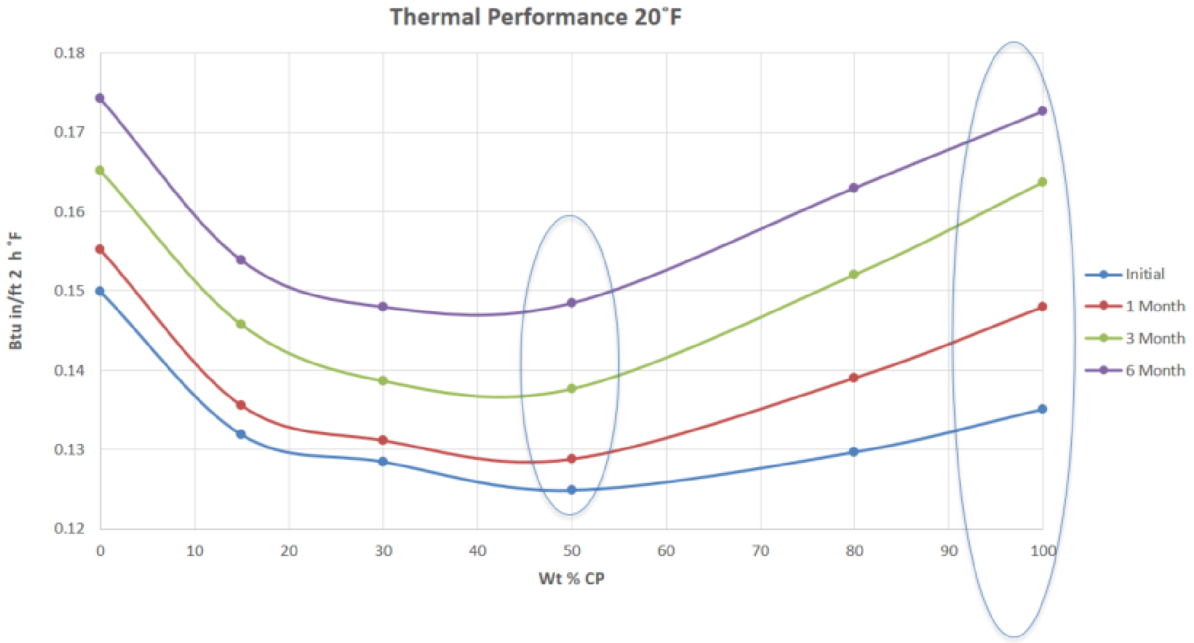


Figure 11. Aged thermal performance of HFO-1336mzz (Z)/Cyclopentane (Cp) blend polyisocyanurate foam samples at (top) 75°F (23°C) and (bottom) 20°F (−6.6°C) [34].

2.2.2 Hydrocarbons

Hydrocarbons are the primary blowing agent used in boardstock. As non-ozone-depleting substances with a low GWP, they offer a sustainable alternative for foam production. Importantly, their use is not subject to regulations imposed by the Montreal Protocol, which targets ozone-depleting substances [4]. As a result, this industry is using hydrocarbon technology.

As shown in Figure 11, foams produced using HCs exhibited a greater loss in thermal conductivity (*k*-values) over time compared with foams made with a blend of HFO-1336mzz(Z) and cyclopentane. This observation aligns with fundamental studies that suggest HFO-1336mzz(Z) has a lower effective diffusion coefficient than cyclopentane, resulting in HFO-1336mzz(Z) staying in the foam for a longer duration [36]. The prolonged retention of HFO-1336mzz(Z) in the foam may have a positive effect on insulation value and subsequent energy consumption, assuming that blowing agent concentration directly influences these factors.

Table 10 summarizes the test results for thermal performance, encompassing initial and aged assessments [33]. The thermal conductivity exhibited a notable enhancement as the concentration of HFO-1233zd(E) increased. This trend was also reported in different studies. The thermal conductivity of foam samples was measured at three different temperatures 0°C, 10°C, and 24°C (32°F, 50°F, 75°F)—to provide a comprehensive evaluation of the blowing agent.

The addition of HFO-1233zd(E) to the blowing agent formulation delivered twofold improvements to the foam’s thermal performance. The overall insulation capacity exhibited improvement across the entire temperature range of assessment in contrast to the solely pentane-blown control. Particularly at the colder temperatures of 0°C (32°F) and 10°C (50°F), samples containing HFO-1233zd(E) show much better insulation capacity than the control. This behavior can be attributed to pentane’s higher boiling point; when exposed to lower temperatures, pentane condenses within the cells, reducing its effectiveness as an insulating gas [33, 37]. The observations in dimensional stability, the percentage of closed cells within all formulations, demonstrated negligible differences for all samples. Each composition fell within the acceptable range, maintaining values between 94% and 98%. Additionally, the free rise density of all samples consistently averaged at 1.81 ± 0.02 lb/ft^3 (29.0 ± 0.3 kg/m^3) for all the foams.

Furthermore, Bogdan conducted a comparison between polyisocyanurate (PIR) boards blown with HFO-1233zd(E) and pentanes [21]. The foam densities for those blown with HFO-1233zd(E) and pentanes were 1.88 and 1.85 lb/ft^3, respectively. Given the comparable core densities, it is reasonable to make valid property comparisons between PIR boards using HFO-1233zd(E) and those employing pentanes as blowing agents (see Table 11).

Table 11 shows the comparison of their thermal, physical, and fire properties. It highlights that PIR blown with HFO-1233zd(E) yields comparable physical properties and closed-cell content to the pentanes. HFO-1233zd(E) significantly enhances the fire resistance properties of the formulation. In essence, the formulation containing HFO-1233zd(E) requires a lower amount of flame retardant to achieve the same level of fire retardancy as the formulation with pentanes. Most notably, the foam’s thermal insulation value at 10℃ with HFO-1233zd(E) is approximately 12% better than the control foam using pentanes, as depicted in Figure 12. This result demonstrates that HFO-1233zd(E) not only offers improved fire performance but also enhances the thermal efficiency of the foam.

Table 11. Thermal, physical, and fire properties of PIR boards blown with HFO-1233zd(E) and pentanes [21]

	HFO-1233zd(E)	Pentanes
Thermal properties		
Lambda at 10°C	17.1	19.0
Physical properties		
Compressive strength (kPa)		
Parallel	>120	>120
Perpendicular	>100	>100
Closed-cell content (%)	>95	>95
Fire properties		
B2 burn test, DIN 4102 (cm)	8	13

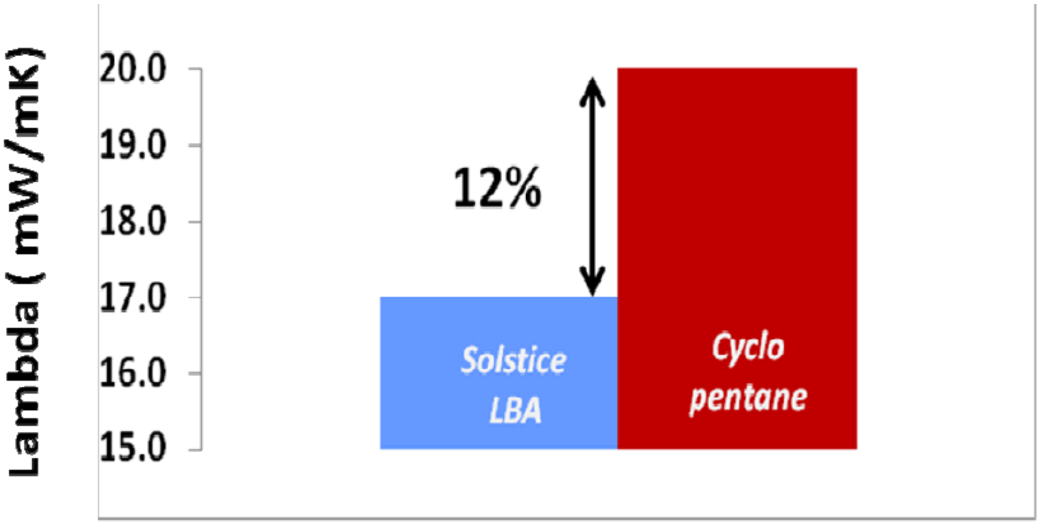


Figure 12. Comparison of thermal performance of PIR foam at 10°C [21].

Hydrocarbons are commonly used as FBAs in the production of PIR boardstock. The use of HCs in larger manufacturing facilities offers advantages related to the economy of scale, which results in lower operating costs and optimized efficiency [4, 38]. Hydrocarbons, like pentanes, are widely used in these applications because of their favorable properties, cost-effectiveness, and suitability for large-scale manufacturing processes. These blowing agents contribute to the foam’s insulation properties and overall performance, making them a preferred choice in the industry.

However, the trend toward energy-efficient building construction and the emphasis on reducing heating and cooling loads have been driving the exploration of more advanced insulation materials and technologies. Blending HFOs or HCFOs with HCs is one potential avenue to enhance the thermal performance of insulation materials such as PIR boardstock. HFOs and HCFOs are known for their low GWP and compatibility with environmental regulations.

By incorporating HFO/HCFO blends with HCs, manufacturers can potentially achieve higher thermal efficiency in their insulation products without compromising on safety, sustainability, or compliance with regulations. As advancements continue in insulation technology and building codes become more stringent, the industry may indeed explore and adopt such blends to meet the evolving demands of energy-efficient construction.

The classification of HCs as VOCs is an important aspect to consider because they can contribute to ground-level smog formation, especially in populated areas [4, 38]. The potential benefits of combining HCs with fluorocarbons to enhance thermal efficiency in foam systems are noteworthy. However, it is important to acknowledge that even with such blends, flammability remains a concern, necessitating stringent safety measures and precautions during production, handling, and use. This requirement highlights the need to address potential environmental impacts and ensure that the benefits of using these blowing agents are balanced with appropriate abatement measures to mitigate any negative effects. Overall, the choice of FBAs clearly involves a careful consideration of multiple factors, including environmental impact, safety, energy efficiency, and regulatory. Table 12 summarizes the comparison of HCs and HFOs.

Table 12. Comparison of HFOs and HCs under different criteria

Criteria	HFOs	HCs
Blowing agent flammability	Non-flammable	Flammable
Foam thermal insulation performance	Excellent	Good
Foam physical properties	Excellent	Excellent
Compatibility with foam processing equipment	Yes	Yes
Environmental considerations	None	VOC by US Environmental Protection Agency
Safety considerations	None	Flammable
Overall suitability as a blowing agent in this application	Suitable	Suitable

2.3 SUMMARY

Hydrofluoroolefin blowing agents are adequate alternatives for PU/PIR foam board applications as they are non-flammable and possess excellent insulation and physical properties. Hydrocarbons (HCs) are also acceptable for PU/PIR foam board applications due to their good thermal insulation and physical properties. However, hydrocarbons are highly flammable, which will require general safety precautions to be considered as FBAs for PU/PIR foam applications.

2.4 BLOWING AGENTS NOT WIDELY USED IN PU/PIR FOAM BOARD

2.4.1 Methyl Formate

The use of methyl formate as an alternative blowing agent in PU foam applications can be considered for various rigid foam applications. However, it appears that the use of methyl formate as a primary or sole blowing agent for rigid foams has faced challenges and limitations, particularly in terms of dimensional stability. Previous attempts to produce foams using methyl formate as the primary blowing agent have reportedly resulted in unsatisfactory outcomes, including foam shrinkage of more than 10% and poor dimensional stability. For instance, US Patent No. 5,283,003 by Chen highlights the need for additional blowing agents, such as organic or hydrocarbon agents, to achieve dimensionally stable foam when using methyl formate [39]. Their work indicated that a combination of methyl formate and other blowing agents such five-carbon hydrocarbons (*n*-pentane, isopentane, and cyclopentane) should make up at least approximately 20% by weight of the total blowing agent combination for better results. Additionally, US Patent No. 5,883,146 by Tucker discusses the use of formic acid (or a salt thereof) as a blowing agent but in combination with a C_1 to C_4 [40]. These examples illustrate that using methyl formate as a single blowing agent for foams may not have been successful because of issues related to foam stability and dimensional changes. Instead, a combination of methyl formate with other blowing agents has been suggested to achieve more satisfactory foam properties, including better dimensional stability.

Also, it is crucial to note that although the technology holds potential, certain factors need careful consideration and evaluation [41].

1. **Application suitability:** The suitability of using methyl formate as a blowing agent varies across different rigid foam applications. Some applications might be well-suited, and others might require a case-by-case analysis and further optimization.

2. **Safety concerns:** To minimize safety risks for downstream users, projects involving methyl formate are advised to be implemented through fully formulated systems provided by system suppliers. This approach helps ensure that safety measures and guidelines are properly incorporated.

3. **Chemical compatibility:** Before adopting methyl formate, it is essential to verify its compatibility with the existing chemical formulations and materials in the system.

4. **Packed density:** Minimum packed density requirements should be observed to ensure the desired performance of the foam.

5. **Health, safety, and environmental factors:** Incorporating health, safety, and environmental recommendations is crucial in adopting methyl formate technology to mitigate potential risks.

6. **Acidity implications:** The implications related to acidity resulting from the use of methyl formate should also be taken into account.

7. **Distribution and handling:** In small- and medium-sized enterprises, methyl formate is recommended to be used in preblended form through systems houses. This approach helps minimize health and safety risks associated with handling such substances.

8. **Market penetration:** The necessary infrastructure and adoption might take 1–2 years in many regions, especially in countries where methyl formate is not yet in use.

9. **Regional context:** The application of methyl formate technology should be carefully evaluated based on the local situation prevailing in each country. Local regulations, infrastructure, and market conditions play a significant role in determining its viability.

In summary, although methyl formate technology offers promise as an alternative blowing agent for rigid foam applications, its adoption should be approached with careful consideration of foam physical property, safety, compatibility, and regional factors. Collaboration with system suppliers and adherence to health, safety, and environmental guidelines are key to successful implementation.

2.4.2 Methylal

Methylal is an environmentally acceptable blowing agent with a low GWP and no ODP [42]. It has a favorable toxicological profile and has received approval from the US Environmental Protection Agency's (EPA's) SNAP program for use in many PU foam applications. Methylal belongs to the acetals family and demonstrates excellent solubility with conventional polyols [42]. This solubility and stability in PU foam systems make methylal a viable choice for various foam applications, aligning with both environmental and performance considerations.

The PU foams were produced according to the procedure outlined in Figure 13, involving the gradual replacement of HFO-1233zd(E) with methylal while maintaining a consistent water level [43]. The substitution of HFO-1233zd(E) with methylal led to a decrease in the thermal performance and dimensional stability of the PU foams, as shown in Figure 13. Specifically, the foam produced solely with HFO-1233zd(E) exhibited a thermal conductivity of 21.5 mW/mK, and the foam produced solely with methylal had a thermal conductivity of 23.5 mW/mK. Moreover, the dimensional stability (volume changes) of the foam at 70°C/95% relative humidity increased significantly, reaching 37%, which is not suitable for commercial applications (Figure 14).

Despite the substitution of HFO-1233zd(E) with methylal, the foam density remained essentially the same at various substitution rates. In contrast, the control foam produced using only water without any foam blowing agents resulted in higher density foams. These findings suggest that the constant blowing capacity can be maintained by replacing 12 parts of HFO-1233zd(E) with 6 parts of HFO-1233zd(E) and 3 parts of methylal, or by fully replacing 12 parts of HFO-1233zd(E) with 6 parts of methylal, without significantly affecting the free-rise foam density. However, the complete replacement of HFO-1233zd(E) with methylal led to a 24% decrease in compressive strength. These findings suggest that although methylal can substitute for a certain proportion of HFO-1233zd(E) in the formulation to achieve comparable foam performance, the primary component of the FBA in the mixture must be HFO-1233zd(E). Table 13 summarizes the characteristics of FBAs not currently used in foam boardstock.

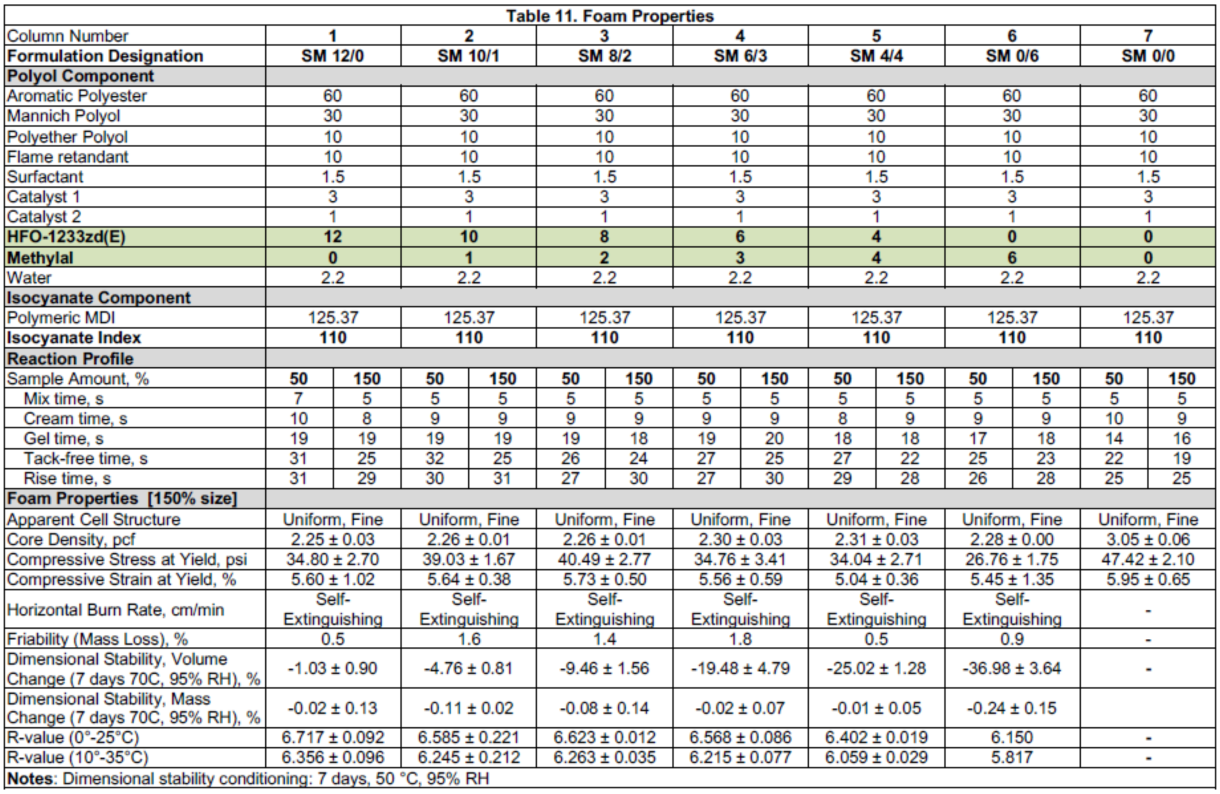


Table 11. Foam Properties

Column Number	1		2		3		4		5		6		7	
Formulation Designation	**SM 12/0**		**SM 10/1**		**SM 8/2**		**SM 6/3**		**SM 4/4**		**SM 0/6**		**SM 0/0**	
Polyol Component														
Aromatic Polyester	60		60		60		60		60		60		60	
Mannich Polyol	30		30		30		30		30		30		30	
Polyether Polyol	10		10		10		10		10		10		10	
Flame retandant	10		10		10		10		10		10		10	
Surfactant	1.5		1.5		1.5		1.5		1.5		1.5		1.5	
Catalyst 1	3		3		3		3		3		3		3	
Catalyst 2	1		1		1		1		1		1		1	
HFO-1233zd(E)	**12**		**10**		**8**		**6**		**4**		**0**		**0**	
Methylal	**0**		**1**		**2**		**3**		**4**		**6**		**0**	
Water	2.2		2.2		2.2		2.2		2.2		2.2		2.2	
Isocyanate Component														
Polymeric MDI	125.37		125.37		125.37		125.37		125.37		125.37		125.37	
Isocyanate Index	**110**		**110**		**110**		**110**		**110**		**110**		**110**	
Reaction Profile														
Sample Amount, %	**50**	**150**	**50**	**150**	**50**	**150**	**50**	**150**	**50**	**150**	**50**	**150**	**50**	**150**
Mix time, s	7	5	5	5	5	5	5	5	5	5	5	5	5	5
Cream time, s	10	8	9	9	9	9	9	9	8	9	9	9	10	9
Gel time, s	19	19	19	19	19	18	19	20	18	18	17	18	14	16
Tack-free time, s	31	25	32	25	26	24	27	25	27	22	25	23	22	19
Rise time, s	31	29	30	31	27	30	27	30	29	28	26	28	25	25
Foam Properties [150% size]														
Apparent Cell Structure	Uniform, Fine		Uniform, Fine		Uniform, Fine		Uniform, Fine		Uniform, Fine		Uniform, Fine		Uniform, Fine	
Core Density, pcf	2.25 ± 0.03		2.26 ± 0.01		2.26 ± 0.01		2.30 ± 0.03		2.31 ± 0.03		2.28 ± 0.00		3.05 ± 0.06	
Compressive Stress at Yield, psi	34.80 ± 2.70		39.03 ± 1.67		40.49 ± 2.77		34.76 ± 3.41		34.04 ± 2.71		26.76 ± 1.75		47.42 ± 2.10	
Compressive Strain at Yield, %	5.60 ± 1.02		5.64 ± 0.38		5.73 ± 0.50		5.56 ± 0.59		5.04 ± 0.36		5.45 ± 1.35		5.95 ± 0.65	
Horizontal Burn Rate, cm/min	Self-Extinguishing		Self-Extinguishing		Self-Extinguishing		Self-Extinguishing		Self-Extinguishing		Self-Extinguishing		-	
Friability (Mass Loss), %	0.5		1.6		1.4		1.8		0.5		0.9		-	
Dimensional Stability, Volume Change (7 days 70C, 95% RH), %	-1.03 ± 0.90		-4.76 ± 0.81		-9.46 ± 1.56		-19.48 ± 4.79		-25.02 ± 1.28		-36.98 ± 3.64		-	
Dimensional Stability, Mass Change (7 days 70C, 95% RH), %	-0.02 ± 0.13		-0.11 ± 0.02		-0.08 ± 0.14		-0.02 ± 0.07		-0.01 ± 0.05		-0.24 ± 0.15			
R-value (0°-25°C)	6.717 ± 0.092		6.585 ± 0.221		6.623 ± 0.012		6.568 ± 0.086		6.402 ± 0.019		6.150		-	
R-value (10°-35°C)	6.356 ± 0.096		6.245 ± 0.212		6.263 ± 0.035		6.215 ± 0.077		6.059 ± 0.029		5.817		-	

Notes: Dimensional stability conditioning: 7 days, 50 °C, 95% RH

Figure 13. Formulation of foams blown with different ratios of HFO-1233zd(E)/methylal and final foam's properties [43]

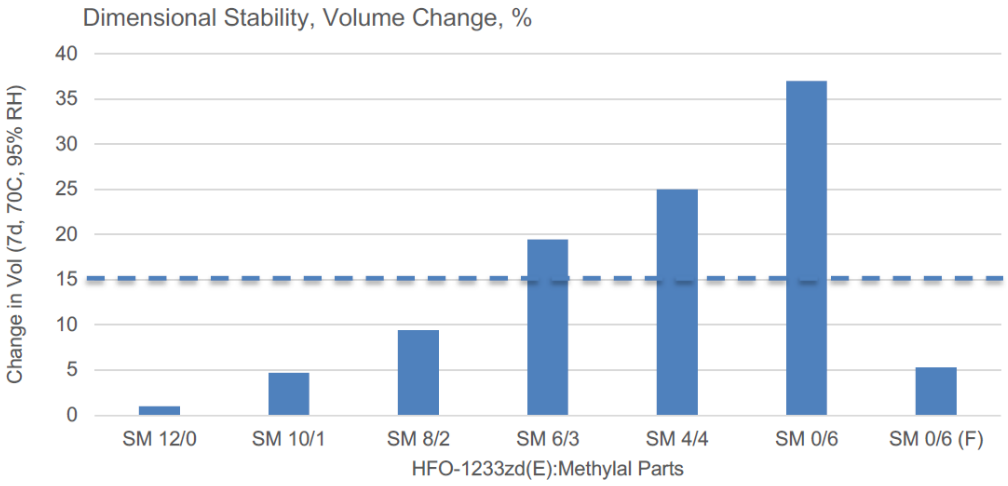


Figure 14. Dimensional stability of free-rise foam with indicated ratios of HCFO-1233zd(E) (S) and methylal (M). Measured foam's density is 2 lb/ft^3 [43].

Table 13. Summary of FBAs currently not in use in foam boardstock

	Methyl formate	**Methylal**	**CO_2 (water)**	**Supercritical CO_2**	**TDCE**
Blowing agent flammability	Flammable	Flammable	Nonflammable	Nonflammable	Flammable
Foam thermal insulation performance	Unknown	Unknown	Poor	Poor	Dependent on primary blowing agent used
Foam physical properties	Unknown	Unknown	Unknown	Unknown	Dependent on primary blowing agent used
Compatibility with foam processing equipment	Yes	Yes	Yes	No	Yes
Environmental considerations	None	VOC by EPA	None	None	VOC by EPA
Safety considerations	Flammable	Flammable	None	HP cylinders required	Flammable, toxicity issues
Overall suitability as a blowing agent in this application	Not suitable	Not suitable	Suitable where low lambda is not critical	Suitable where low lambda is not critical	Suitable, but only as an additive

2.5 SUMMARY

Methyl formate and methylal are not suitable as foam blowing agents for boardstock applications. This is due to poor foam thermal insulation and physical properties. They could be used as additives only. Additionally, CO_2 based FBA for boardstock could potentially be used when thermal performance of foam is not critical. These are compatible with foam processing equipment. Finally, Trans-1,2 dichloroethylene (TDCE) based FBA for boardstock applications could only be used as additive with considerations for toxicity issues.

2.6 PHENOLIC FOAM

Phenolic foam is a rigid, polymeric foam made using phenolic resin and other additives. Phenolic foams were first introduced commercially in early 1940s in German industry as a substitute for balsa [44]. Currently, the largest market for phenolic foams is phenolic boardstock and block foams, which are primarily used for pipe insulation. Phenolic foams exhibit excellent fire-resistant properties, good thermal insulation, and superior mechanical properties; however, problems of high cost and incompatibility when exposed to moisture pose competitive barriers in their widespread adoption [45]. Phenolic foams are more widely used in Europe and are growing in Japan, as well as more recently gaining traction in China because of its fire-resistant properties with good thermal insulation performance [46]. In the United States, phenolic foams became popular in the 1980s as a thin board insulation that fit within the confined spaces of buildings. However, phenolic foams used in 1980s created sulfonic acid when exposed to humidity or air moisture, which led to corrosion problems, making them less popular as an insulation foam for building applications [47].

The choice of blowing agent used is a key factor in determining the thermal insulation properties of the foam. HCs such as pentane, cyclopentane, and hexane are used as blowing agents in phenolic foam production [48-50]. Most medium- and large-scale manufacturers use HCs because they can offset high initial capital costs with the lower operating costs of pentanes. Other types of blowing agents are also used, such as HFOs and chloropropane.

HFOs provide an alternative to HCs that can eliminate flammability issues and the capital investment cost. Additionally, foams blown with HFOs exhibit improved thermal insulation performance compared with HCs. Table 14 shows the list of alternative blowing agents evaluated for phenolic foam, which can be used to understand the trade-offs of phenolic foams for various applications.

Table 14. Alternative blowing agents for phenolic foams

Criteria	HFOs	HCs	Methyl formate	Methylal	CO_2 (water)	Supercritical CO_2	2-chloropropane	TDCE
Commercially adopted	Yes	Yes	Yes	No	No	No	Yes	No
Blowing agent flammability	Non-flammable	Flammable	Flammable	Flammable	Non-flammable	Non-flammable	Flammable	Flammable
Foam thermal insulation performance	Excellent	Good	Unknown	Unknown	NA	NA	Good	Unknown
Foam physical properties	Excellent	Excellent	Unknown	Unknown	Unknown	Unknown	Excellent	Dependent on primary blowing agent used
Compatibility with foam processing equipment	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes
Economically viable	No	Yes	Yes	Yes	Yes	Unknown	Yes	Yes
Environmental considerations	None	VOC by EPA	None	VOC by EPA	None	None	VOC by EPA	VOC by EPA
Safety considerations	None	Flammable	Flammable	Flammable	None	HP cylinders required	Flammable; possible mutagen	Flammable, toxicity issues
Overall suitability as a blowing agent in this application	Suitable	Suitable	Not suitable	Not suitable	Suitable where low lambda is not critical	Suitable where low lambda is not critical	Suitable, but only when blended with other blowing agents	Suitable, but only as an additive

EPA: US Environmental Protection Agency

3. POLYURETHANE AND POLYISOCYANURATE RIGID PANEL

Metal insulated panels consisting of a PU or PIR foam core with two metal, or other rigid facers are frequently used in roof and wall insulation for cold storage, such as walk-in coolers and freezers, public refrigerated warehouse storage, and big-box retailers. One of the key components in determining the thermal insulation value of panels is the choice of blowing agent used in synthesizing PU and PIR rigid foams. Numerous types of blowing agents are currently in use around the world, such as HFC 245fa and HCs in developed countries (e.g., US, European Union, and Japan) and HCFC-141b in China and the Middle East. With the transition to blowing agents with less environmental impact, need and interest is growing to identify alternative blowing agents to replace HCFCs and CFCs around the world.

3.1 HFO-1233zd(E)

HFO-1233zd(E) is a commercially proven blowing agent for polyurethane foams used in rigid panels. A recent study evaluated the performance of insulated panels produced using HFO-1233zd(E) and cyclopentane using a reefer container, which consisted of discontinuous and continuous panels [21]. Figure 15 shows the comparison of the initial thermal conductivity values of foam produced using HFO-1233zd(E) and cyclopentane, which reveals that foams with HFO-1233zd(E) provide 7% lower thermal conductivity at 10°C, which is important for cold storage applications.

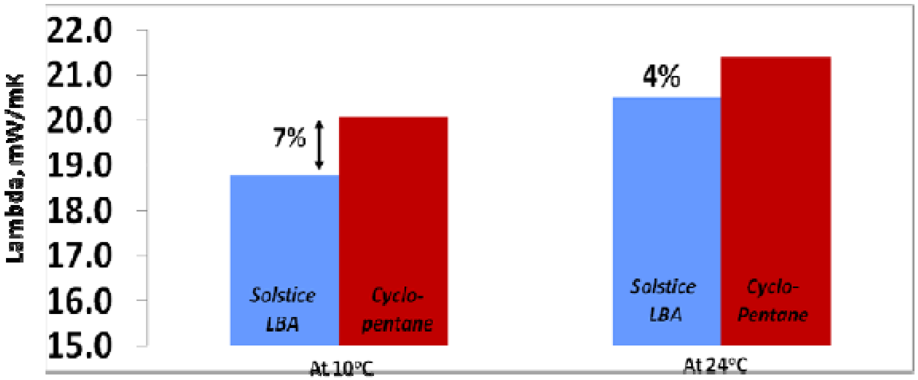


Figure 15. Thermal conductivity of foams with different blowing agents at different temperatures [21].

Table 15 shows the physical properties of PU-insulated panels used in the reefer container made using blowing agents HFO-1233zd(E) (indicated as “Solstice LBA”) and cyclopentane. All the foams were evaluated after 24 h of aging at −29°C, 70°C and 70°C/95% relative humidity. This analysis suggests that HFO-1233zd(E) shows comparable compressive strengths to cyclopentane in both the parallel and perpendicular directions. Furthermore, no significant difference exists in dimensional stability at different temperatures and relative humidity values when compared with cyclopentane.

Table 15. Reefer container trial: Physical properties of foams made with HCFO-1233zd(E) and cyclopentane [21]

Physical properties	HCFO-1233zd(E)	Cyclopentane
Tensile strength (kPa)	350	333
Compressive strength (kPa)		
Parallel	231	266
Perpendicular	222	253
Dimensional stability (vol %)		
24 h at −30°C	0.08	0.02
24 h at 70°C/95% relative humidity	2.28	2.47
Closed-cell content (%)	>90	>90

Another study evaluates the performance of discontinuous panels using HCFO-1233zd(E) (indicated as “Solstice LBA” in the charts), cyclopentane (indicated as C-C5 in the charts), and blends of HCFO-1233zd(E). Figure 16 shows the initial thermal conductivity of foams with various blends of HCFO-1233zd(E). In general, foams made using HCFO-1233zd(E) show a better insulation performance when compared with all other blends and cyclopentane and blending with cyclopentane at 75/25 mol % shows a comparable *k*-factor with that of HCFO-1233zd(E), which is a promising solution for freezers and cooler applications. Additionally, a cyclopentane blend of 50/50 mol % shows similar *k*-factor values at temperatures above 55°F, suggesting potential applications for coolers, which are appropriate for slightly elevated temperatures compared with freezers.

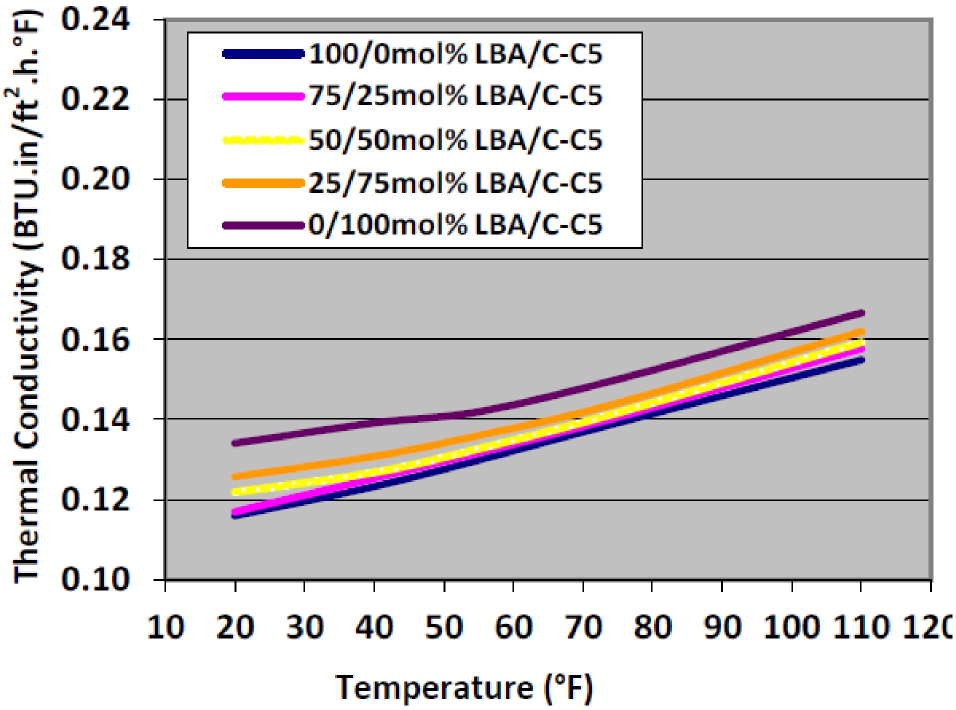


Figure 16. Initial thermal conductivity of foams with various HCFO-1233zd(E) ("LBA")/cyclopentane blends [51].

Figure 17 shows the *k*-factor values after 28 days of aging for HCFO-1233zd(E) and cyclopentane blends. The results show that the insulation performance increases as the temperatures decrease, suggesting promising long-term performance for cold storage applications. HCFO-1233zd(E) consistently outperforms cyclopentane and blends of cyclopentane, demonstrating better thermal insulation performance at all evaluated temperatures [51].

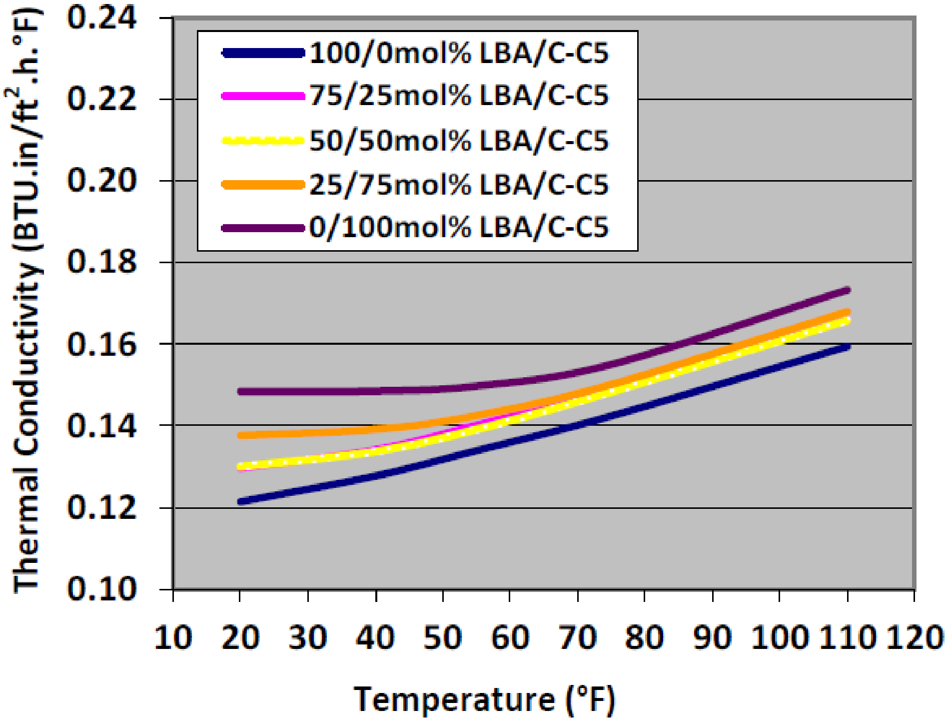


Figure 17. The 28-day thermal conductivity of foams with various HFO-1233zd(E) ("LBA")/cyclopentane blends [51].

Figure 18 and Figure 19 show the compressive strength and dimensional stability, respectively, for foams with various blowing agent blends. Foams were evaluated after 28 days aging at −29°C, 90°C, and 70°C/95% relative humidity as per the ASTM D-2126-09 standard. Compressive strengths were tested at parallel and perpendicular directions per ASTM D-1621-10. Foams with HC blends show similar parallel and perpendicular compressive strengths, with slightly higher values for cyclopentane blends, as shown in Figure 17. Furthermore, Figure 18 reveals that the stability of foams improved gradually with the addition of the HFO-1233zd(E) blowing agent, and foams with HFO-1233zd(E) show at least 50% better dimensional stability at elevated temperatures compared with HCs [43].

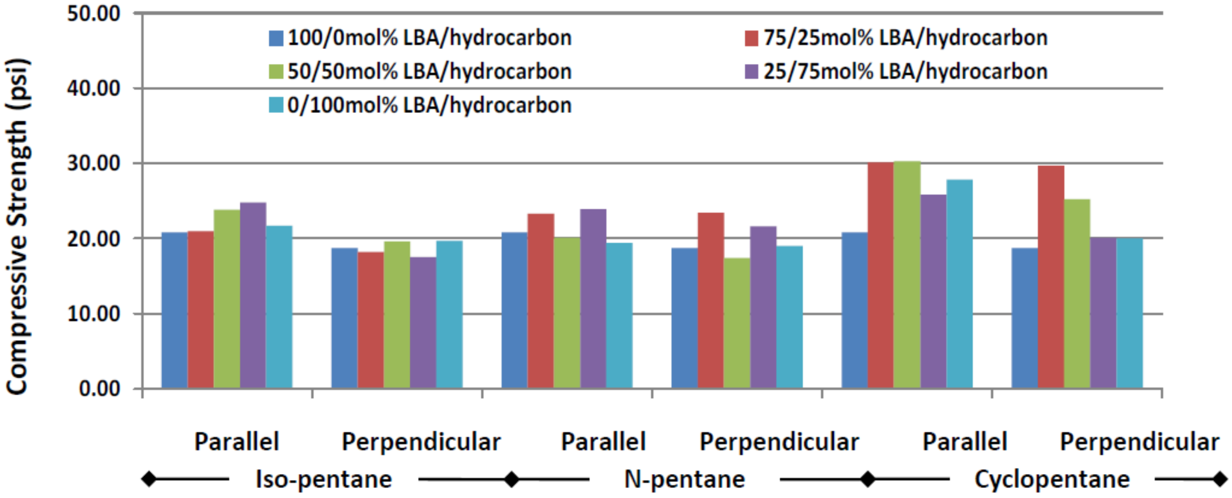


Figure 18. Compressive strength of foams with various HFO-1233zd(E) ("LBA")/HC blends [51].

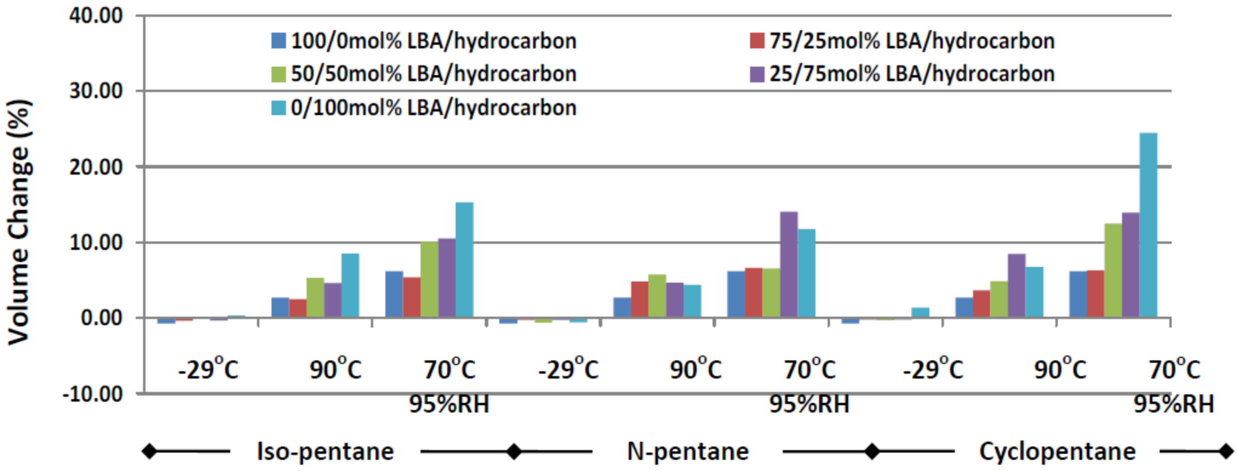


Figure 19. The 28-day dimensional stability of foams with various HFO-1233zd(E) ("LBA")/HC blends [51].

Figure 20 shows the thermal conductivity of foams with various HFO-1233zd(E) and methyl formate bends. The results reveal that HFO-1233zd(E) provides the best insulation performance by providing the lowest initial *k*-values at all elevated temperatures, and the 75/25 mol % methyl formate blends show slightly higher *k*-values compared with the HFO-1233zd(E) blowing agent. Figure 21 shows thermal conductivity values after 28 days of aging. HFO-1233zd(E) consistently outperforms all other blends by showing the lowest *k*-values, which is promising for cold storage applications. Furthermore, blends above 50% of methyl formate do not show any additional benefit in thermal performance, as shown in Figure 21 [51].

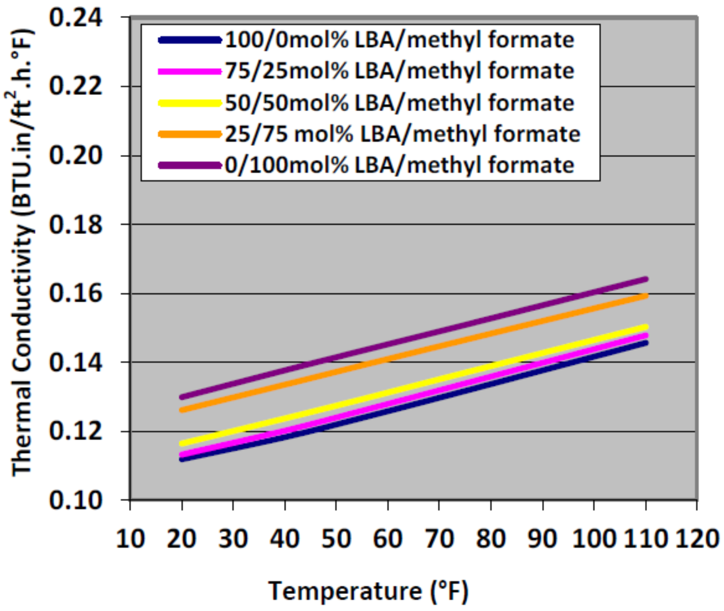


Figure 20. Initial thermal conductivity of foams with various HFO-1233zd(E) ("LBA")/methyl formate blends [51].

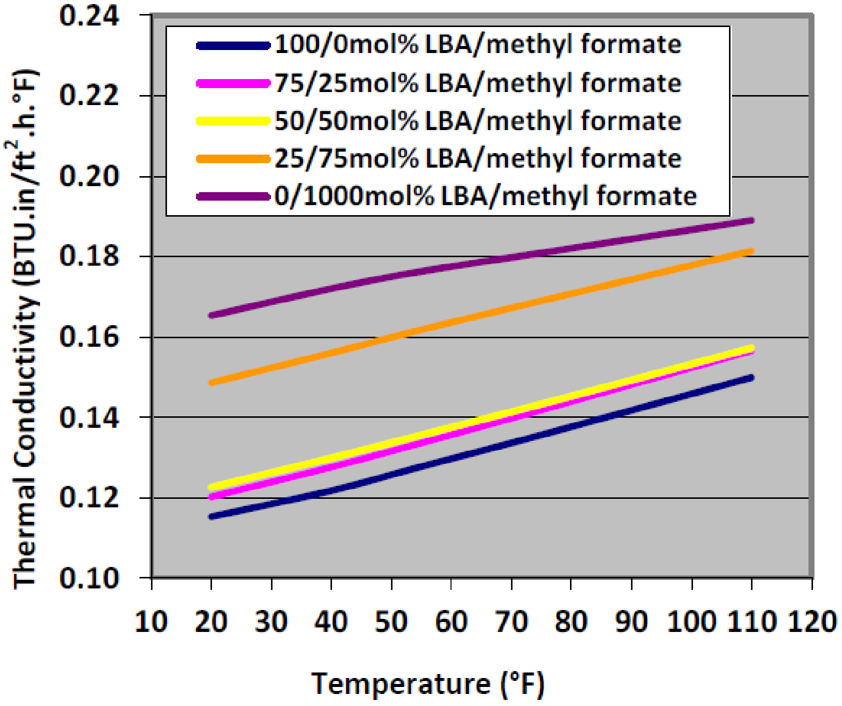


Figure 21. The 28-day thermal conductivity of foams with various HFO-1233zd(E) ("LBA")/methyl formate blends [51].

Figure 22 shows the compressive strength of foams made with HFO-1233zd(E) and methyl formate blends. No significant difference is seen in compressive strength for different blends for perpendicular (15 to 20 psi) and parallel (20 to 25 psi) directions. However, methyl formate shows poor performance in terms of dimensional stability, as shown in Figure 23. With the addition of HFO-1233zd(E), the dimensional stability of foams improves significantly at elevated temperatures, as shown in Figure 23.

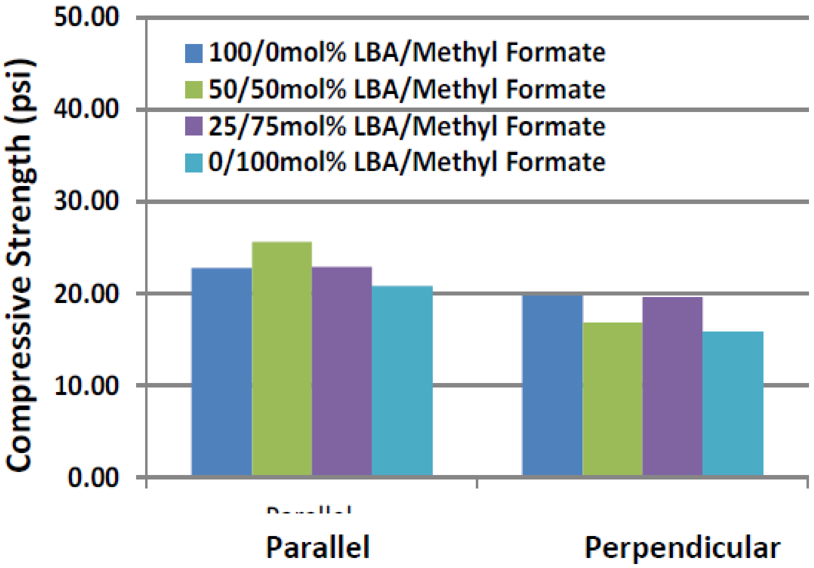


Figure 22. Compressive strength of foams with various HFO-1233zd(E) ("LBA")/methyl formate blends [51].

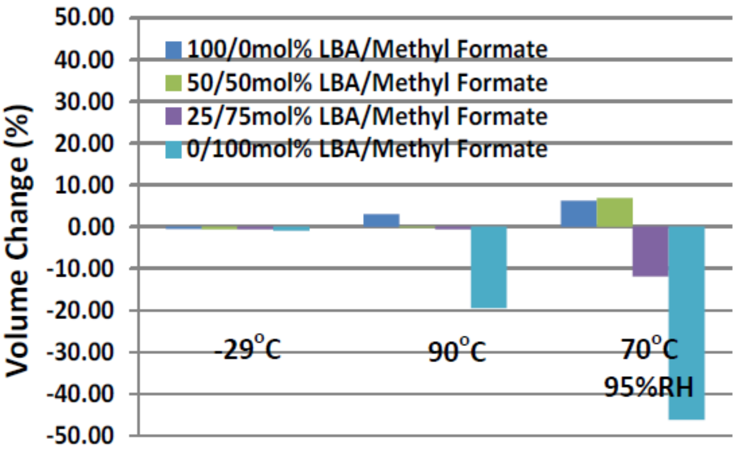


Figure 23. The 28-day dimensional stability of foams with various HFO-1233zd(E) ("LBA")/methyl formate blends [51].

Table 16 shows the flammability performance of foams with various blends performed using the DIN 4102 B2 test method. All samples should have values below the 15 cm gauge height to pass the DIN 4102 B2 test. As shown in Table 16, HCFO-1233zd(E) has the best flame retardancy compared with all other blends. In contrast, foams made with HCs show poor flammability, and the flame retardancy improves with the addition of HCFO-1233zd(E). Additionally, foams made using methyl formate pass the flammability test; however, the flammability remains unchanged even after the addition of HFO-1233zd(E).

Table 16. Measured flame height of foam samples during the flammability test [51]

Test evaluation	**Solstice LBA/Isopentane mol% Ratio**				
B2 Test Evaluation	100/0	75/25	50/50	25/75	0/100
Flame Height, cm	10	11	12	12	17
Test evaluation	**Solstice LBA/N-pentane mol% Ratio**				
B2 Test Evaluation	100/0	75/25	50/50	25/75	0/100
Flame Height, cm	10	12	12	14	19
Test evaluation	**Solstice LBA/Cyclopentane mol% Ratio**				
B2 Test Evaluation	100/0	75/25	50/50	25/75	0/100
Flame Height, cm	10	11	12	13	15
Test evaluation	**Solstice LBA/Methyl Formate mol% Ratio**				
B2 Test Evaluation	100/0	75/25	50/50	25/75	0/100
Flame Height, cm	11	13	14	14	14

Flammability of foams was evaluated as per DIN 4102-1: Class B2 Materials

HFO-1233zd(E) and cyclopentane were used as an FBA for a panel application. The preparation of all foams was conducted using an HP foam machine [21]. The formulation was tailored to achieve a free rise density of approximately 1.89 lb/ft^3. The process involved blending a polyol premix and isocyanate through an impingement mechanism at the head of the machine. The mixture was then poured into a preassembled mold in a continuous, one-shot process until a specified quantity was attained.

Subsequently, a comprehensive analysis of physical and thermal properties was conducted, enabling a direct comparison between the two blowing agents. This illustrates a comparison of the initial thermal conductivity of foams using HCFO-1233zd(E) and cyclopentane at two distinct temperatures: 10℃ and 24℃. Specifically, foams produced with HCFO-1233zd(E) exhibit approximately 7% better thermal performance compared with those employing cyclopentane at 10℃. Furthermore, HFO-1233zd(E) outperforms cyclopentane by demonstrating a decrease of up to 4% in thermal conductivity at 24℃.

Also, as depicted in Figure 24, HFO-1233zd(E) shows similar compressive strength in both the parallel and perpendicular to rise directions. Additionally, no notable distinctions in dimensional stability are observed across varying temperatures and conditions when comparing foams using HFO-1233zd(E) and cyclopentane. Table 17 summarizes the results of the comparison.

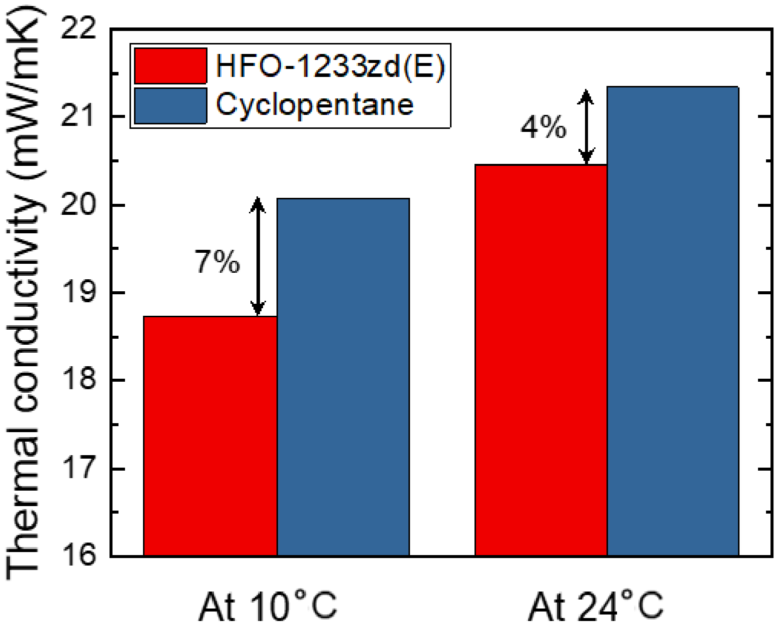


Figure 24. Thermal and physical properties of foams blown with HFO-1233zd(E) and cyclopentane [21].

Table 17. Summary of HFO-1233zd(E) and cyclopentane results

	HFO-1233zd(E)	Cyclopentane
Thermal conductivity at 10℃ (mW/mK)	18.74	20.08
Thermal conductivity at 24℃ (mW/mK)	20.45	21.34
Compressive strength, parallel (lbf/in^2, psi)	33.5	38.6
Compressive strength, perpendicular (lbf/in^2, psi)	32.2	36.7
Dimensional stability, 24 h at 70℃, 95% relative humidity (vol %)	2.28	2.47
Closed-cell content (%)	>90	>90

3.2 HFO-1336mzz(E)

Another promising blowing agent is the HFO-1336mzz(E) or HFO-1336mzz(E)/cyclopentane-based PIR panel formation. Figure 25 shows the plot of variation of the *k*-values for panel foam made with HFO-1336mzz-E/cyclopentane blends compared with a cyclopentane-blown PIR foam. The results reveal that with the addition of HFO-1336mzz(E) to a cyclopentane based formulation, the foams show a 16% improvement in overall insulation performance at 20°F and an 8% improvement at 75°F [52]. These results suggest that HFO FBAs can deliver excellent insulation performance, and the blends with HCs also perform better for cold chain applications.

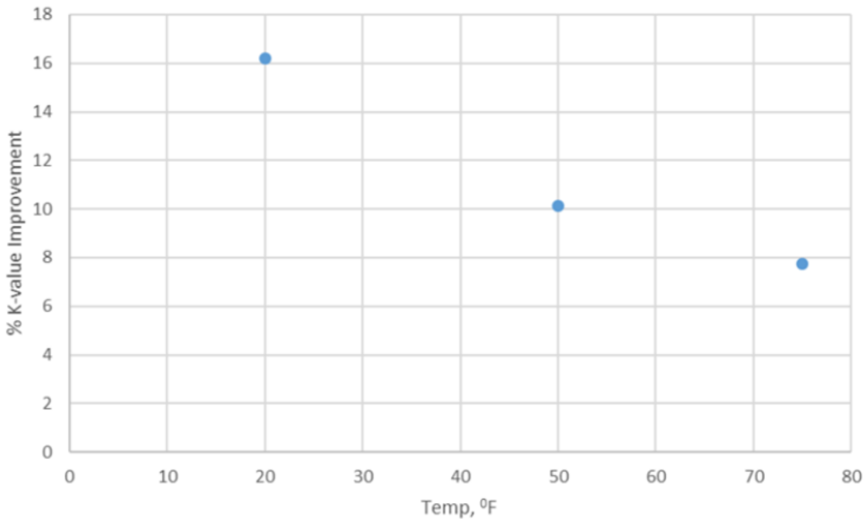


Figure 25. Comparisons of *k*-values for panel foam made with HFO-1336mzz-E/cyclopentane blend vs. cyclopentane [52]. The cyclopentane mixture containing 10% moles of HFO-1336mzz-E.

3.3 SUMMARY

Fluorinated materials (HFOs, HCFOs) and hydrocarbons are commercially used as blowing agents for PU and PIR panels. Non-flammable HCFOs are practical when setting up manufacturing plants as they do not require safety mitigation. On the other hand, many large-scale manufacturers can afford to use of hydrocarbons (pentanes), which will require high initial capital investment but lower operating costs. Table 18 provides a summary of alternative blowing agents that can be used for PU and PIR panel applications.

Table 18. Summary of alternative blowing agents for PU and PIR panel.

Criteria	HFOs	HCs	Methyl formate	Methylal	CO$_2$ (water)	l CO$_2$	TDCE
Commercially adopted	Yes	Yes	Yes, as a blend	Yes, as a blend	Yes	No	No
Blowing agent flammability	Non-flammable	Flammable	Flammable	Flammable	Non-flammable	Non-flammable	Flammable
Foam thermal insulation performance	Excellent	Good	Fair	Fair	Poor	Unknown	Unknown
Foam physical properties	Excellent	Excellent	Fair	Fair	Good	Unknown	Unknown

Table 18. Summary of alternative blowing agents for PU and PIR panel. (continued)

Compatibility with foam processing equipment	Yes	Yes	Yes	Yes	Yes	No	Yes
Economically viable	Yes	Yes	Yes	Yes	Yes	Unknown	Yes
Environmental considerations	None	VOC by EPA	None	VOC by EPA	None	None	VOC by EPA
Safety considerations	None	Flammable	Flammable	Flammable	None	HP cylinders required	Flammable, toxicity issues
Overall suitability as a blowing agent in this application	Suitable	Suitable	Suitable	Suitable	Suitable where low lambda is not critical	Suitable where low lambda is not critical	Suitable, but only as an additive

4. APPLIANCES

The first use of rigid PU foam for insulating refrigerators and freezers can be traced back to 1963, and since then, rigid PU foam has become an important material to insulate appliance systems for commercial and domestic applications [3]. The rigid PU foam systems used by appliance manufacturers require raw materials, which include polymeric methylene diphenyl diisocyanate, polyol bends, and blowing agents.

The choice of blowing agents for producing rigid PU foams has been controlled by the Montreal Protocol, which replaced CFCs and HCFCs with blowing agents with less environmental impacts, such as HFCs and HCs. With the ever-rising global standards for energy efficiency in appliances, the selection of an optimum blowing agent is complex because it depends on several factors, such as end application, physical properties, thermal insulation performance, compatibility of foam system, legislation, cost, and environmental factors.

4.1 DOMESTIC APPLIANCES

For domestic refrigerators and freezers, blowing agents CFC-11 and HCFC-141b were once predominantly used before being replaced by zero-ODP agents HFC-245fa and cyclopentane. However, HFC-245a has a high GWP when compared with cyclopentane. Additionally, the insulation performance of foams produced using cyclopentane did not meet energy efficiency standards, but HFC-245fa have relatively good insulation properties, thus requiring additional improvements in thermal performance when using cyclopentane. Recent blowing agent alternatives include HFOs or HCFOs, or blends of HFOs with HCs.

4.1.1 HFO 1233zd(E)

One such low-GWP blowing agent alternative for rigid PU systems in appliances is the HFO-1233zd(E) that has good thermal insulation performance. Co-blowing agents with HFO-1233zd(E) such as water, methylal, TDCE, and methyl formate have been used and evaluated to reduce the loading concentrations of the HFO blowing agent. Figure 26 shows the initial insulation performance of foams produced using a 20% co-blowing agent and compared with HFC-245fa, HFO-1233(E), and cyclopentane controls. All the data shown represent thermal conductivity (*k*-factor or lambda) from 1 in. thick foam samples measured according to ASTM C518. Initial thermal conductivity (*k*-factor or lambda) at mean temperatures of 32°F, 50°F, and 75°F reveal that all co-blown foams showed better insulation performance when compared with cyclopentane control, and all the co-blown foams at 20% exhibit similar insulation performance with the exception of methylal. A similar trend in thermal insulation performance is shown by foams when prepared with a 40% co-blowing agent, as revealed in a previous study [53].

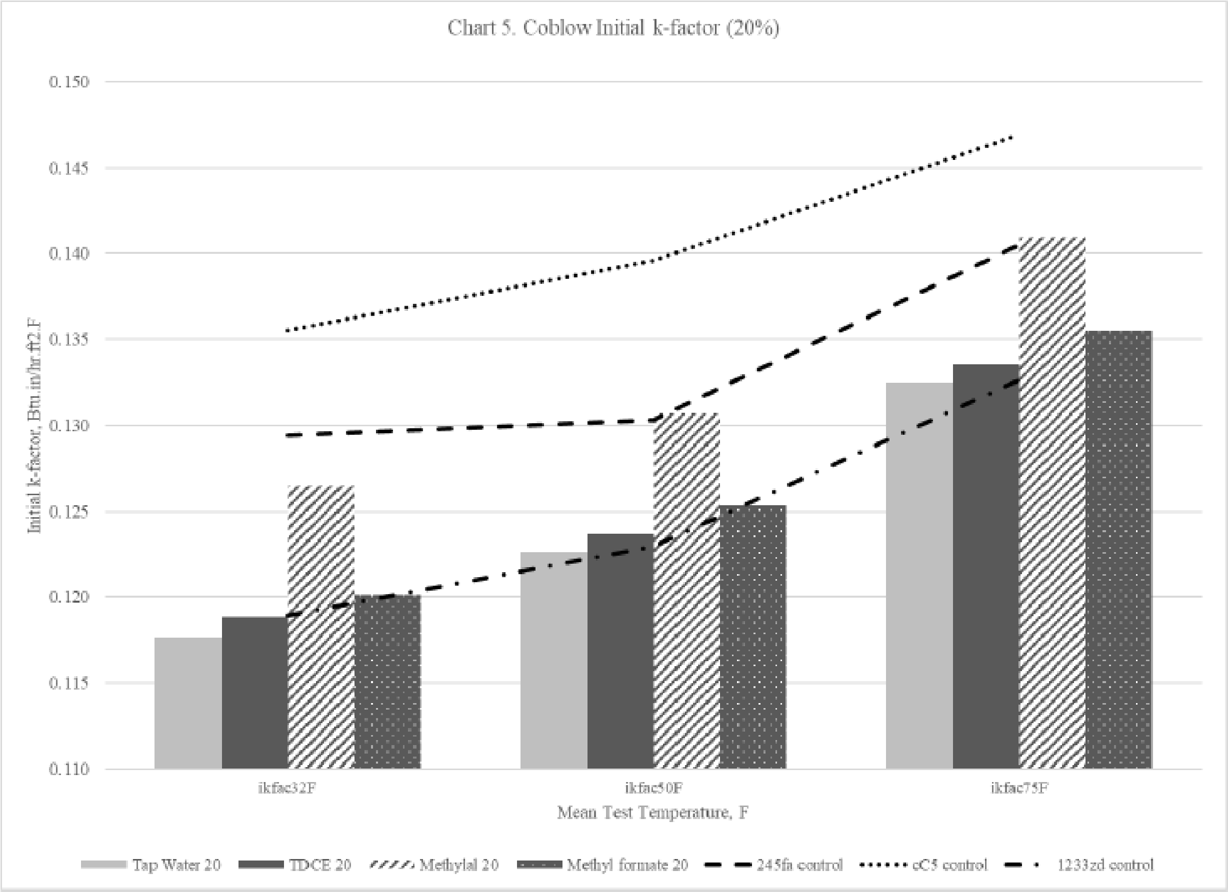


Figure 26. Plot of initial *k*-factor of co-blowing agent compared with HFC-245fa and HFO-1233zd(E) [53].

Figure 27 shows the plot of aged *k*-values of foams with 20% co-blowing agents compared with HFO-1233zd(E), cyclopentane, and HFC 245fa blowing agents. All the data shown represent *k*-values from 1 in. thick foam samples aged at room temperature for 6 months and measured according to ASTM C518. The results reveal two things. First, all rigid PU foams show an increase in thermal conductivity over time owing to a change in gas content and composition in the foams. The increase in thermal conductivity in foams is because of the ingress of air replacing the low–thermal conductivity and high-diffusivity CO_2, followed by slow diffusion of the physical blowing agent [3]. Second, HFO-245fa and HFO-1233zd(E) produced a similar performance in *k*-values, but cyclopentane foams have the highest *k*-values. Additionally, all the other foams closely follow the HFOs in insulation performance, although methylal has significant differences at higher temperatures, suggesting lower insulation properties after aging.

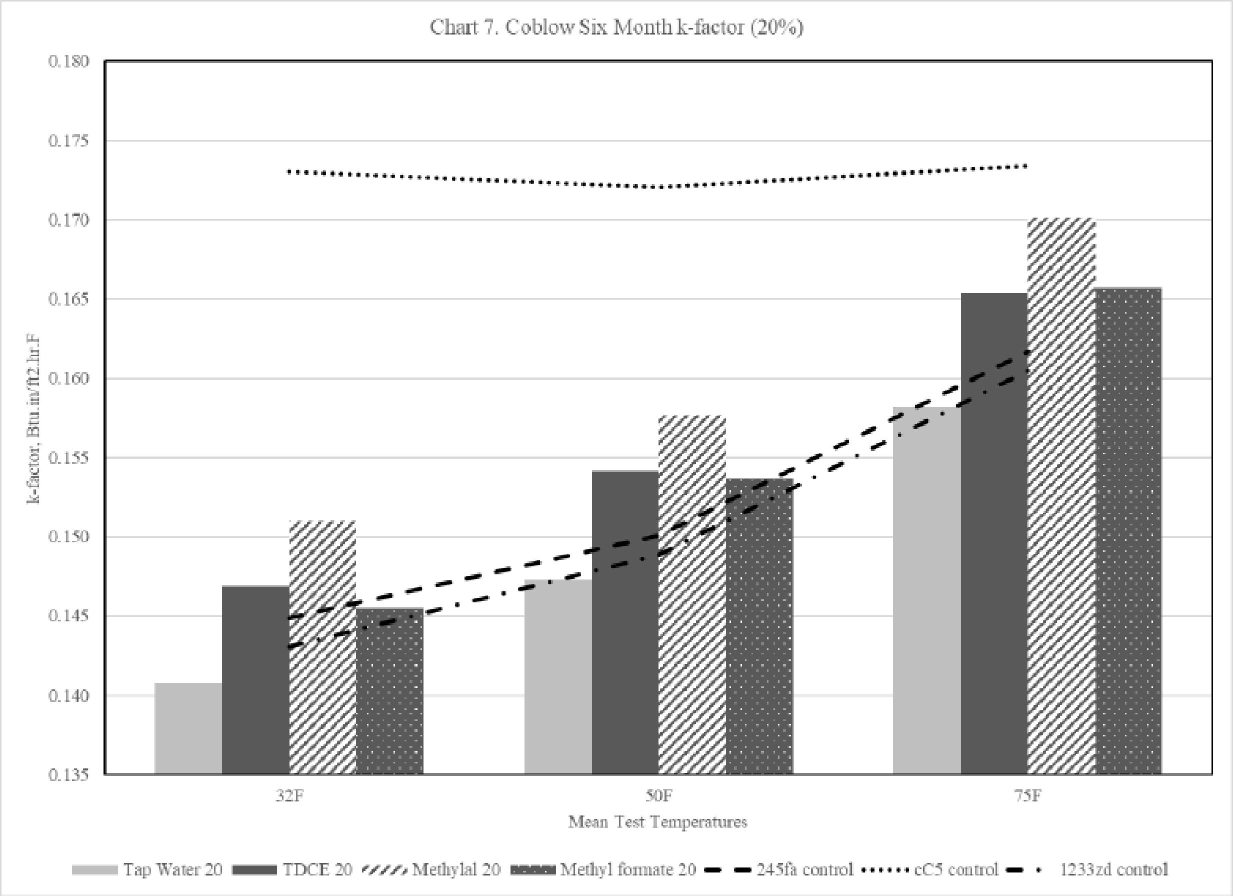


Figure 27. The 6-month aged insulation performance of 20% co-blown agents compared with HFC-45fa and HFO-1233zd(E) [53].

At a 40% level of co-blowing, Figure 28 shows that all the foams perform worse than HFOs but far better than cyclopentane foams. However, at 75°F, co-blown foams showed a similar-to-worse insulation performance than that of cyclopentane.

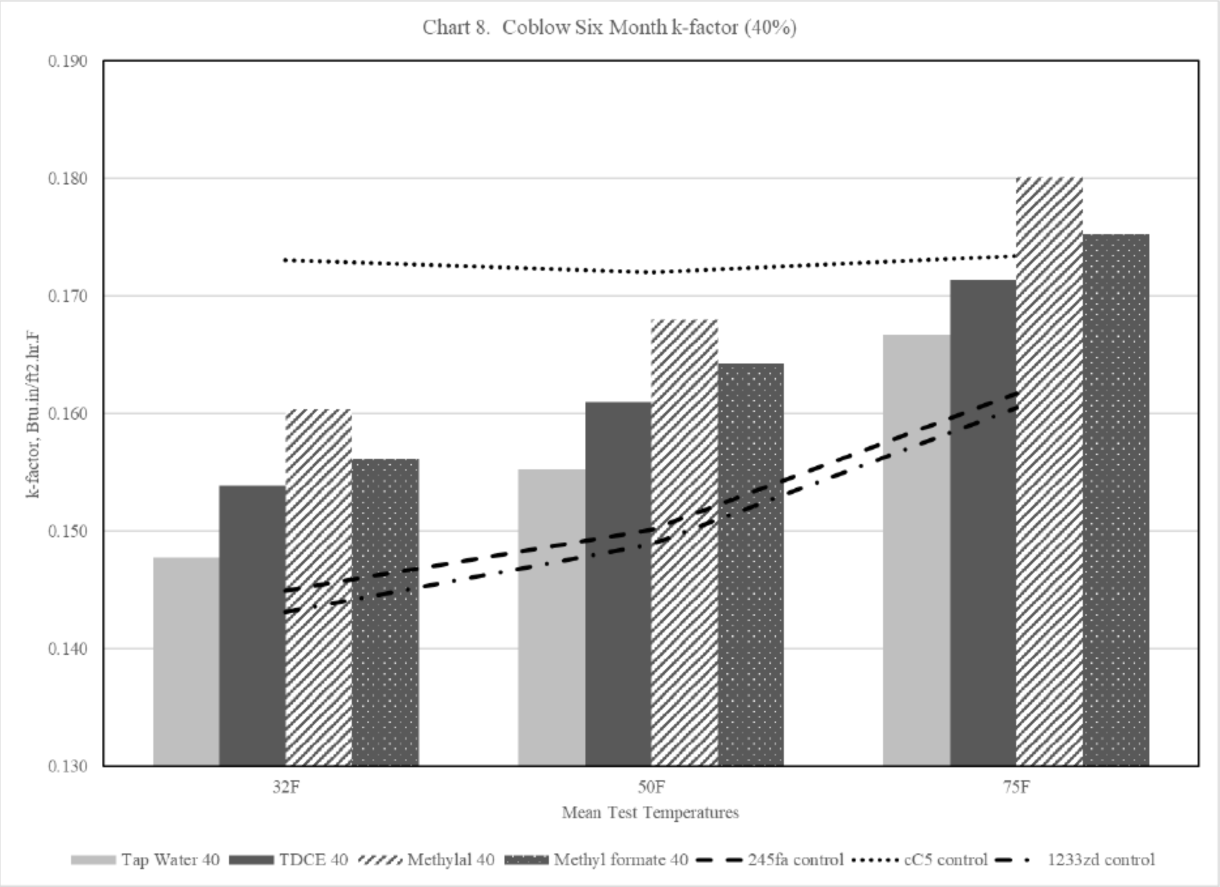


Figure 28. The 6-month aged insulation performance of 40% co-blown agents compared with HFC-245fa and HFO-1233zd(E) [53].

In another study, foams made from HFO-1233zd(E) were compared with HFC-245fa used in a domestic refrigerator/freezer. Because the foam thermal conductivity varies throughout the refrigerator because of variations in foam flow characteristics and densities, it is important to assess the thermal insulation performance of foams at various locations of the equipment. Figure 29 shows the average *k*-factors of blowing agents measured in various locations in refrigerators. Across multiple locations, HFO-1233zd(E) consistently performs better with significant performance improvements compared with HFC-245fa [54].

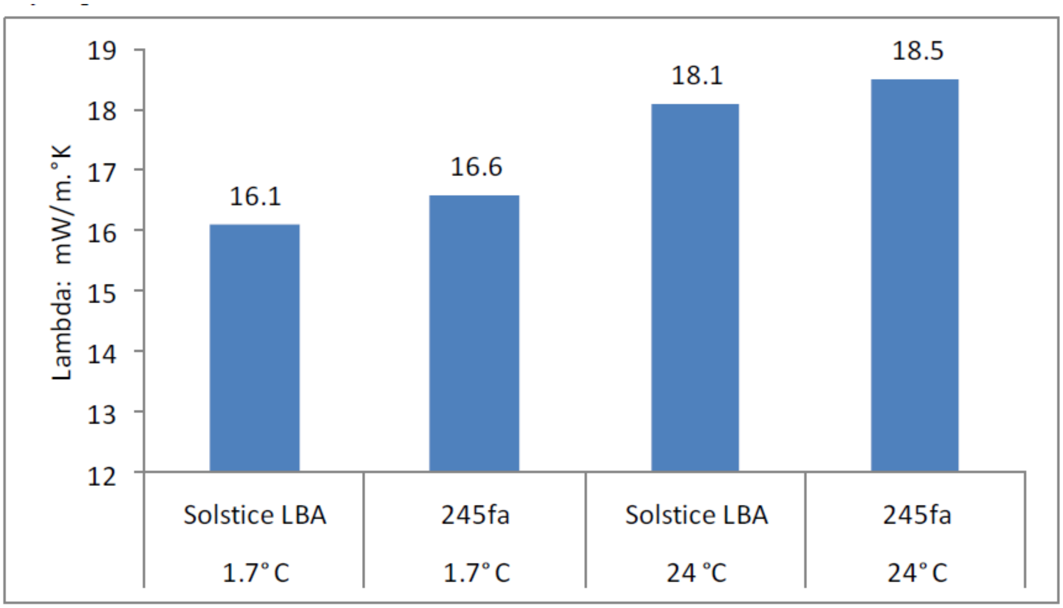


Figure 29. Comparison of *k*-factors measured across typical locations in refrigerators/freezers [54].

Plastic liner compatibility of high-impact polystyrene (HIPS) was studied with an HCFO-1233zd(E) blowing agent. Using a thermal cycle testing, four refrigerators/freezers with doors were placed in an environmental chamber and were exposed to 54°C for 10 h, followed by an exposure to 34°C for 10 h. After repeating this cycle for 5 consecutive days, the HIPS liners did not show any blisters, cracks, or any visual degradation, suggesting good compatibility with HIPS liners [54].

Another important metric in refrigeration foam systems is the compressive strength of foams, which allow manufacturers to use less metal in their finished products. Figure 30 shows the plot of normalized compressive strength values of co-blown foams with 20%, 40%, and 80% loading concentrations compared with HCFO-1233zd(E) and HFC-245fa. All the 20% co-blown foams show a similar compressive strength when compared with HCFO-1233zd(E), and 40% co-blown foams show a lower compressive strength, except for water. None of the 80% level loading foams show an acceptable compressive strength performance. Additionally, cyclopentane foams showed the lowest level of normalized compressive strength values, and HFC-245fa exhibited the highest values of compressive strength [53].

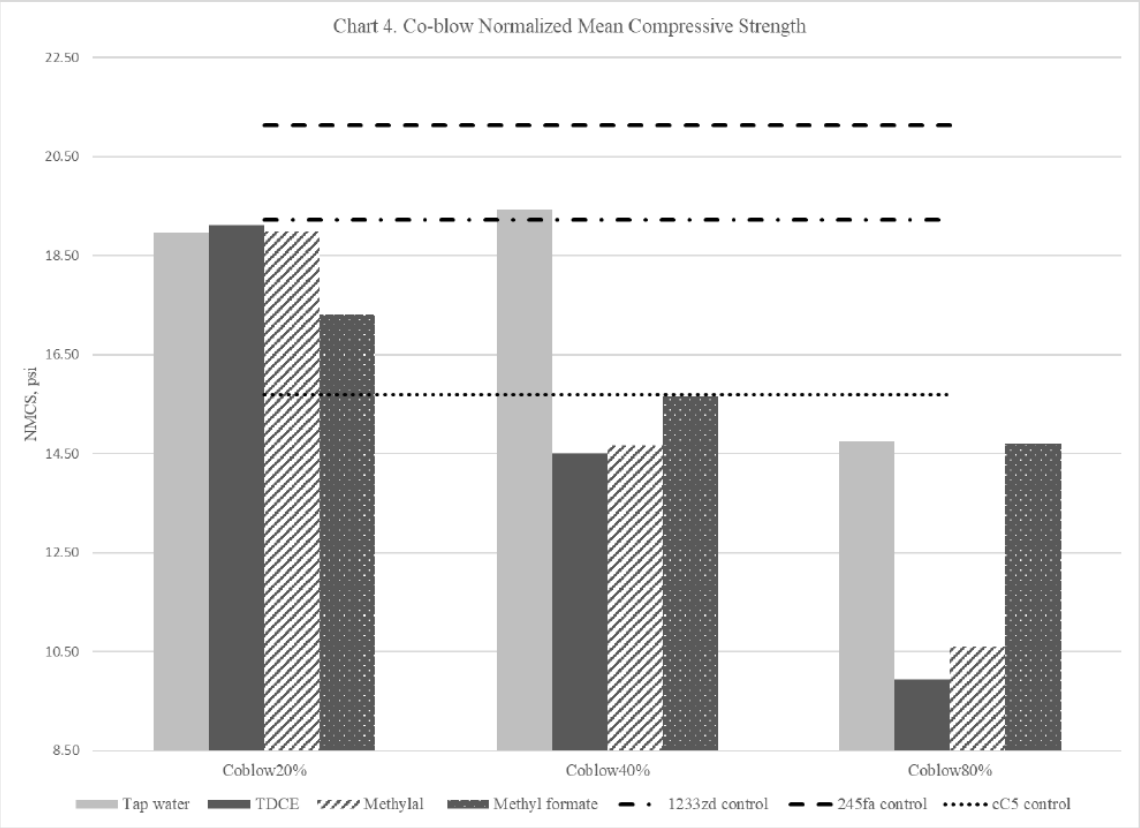


Figure 30. Plot of normalized mean compressive strengths for HCFO-1233zd(E) co-blowing agents compared with cyclopentane and HFC-245fa controls [53].

Another study reports the values of the compressive strength of PU foams prepared using HCFO-1233zd(E) in refrigerators/freezers. The typical compressive strength values of samples taken from various locations in the refrigerators/freezers are shown in Table 19 [55]. The values show an acceptable compressive strength with greater than 100 kPa at 10% deflection.

Table 19. Refrigerator PU foam compressive strength [55]

Cabinet Location	**Parallel (kPa/ *psi*)**	**Perpendicular (kPa/ *psi*)**
Fresh Food #1	118.3/ *17.15*	113.5/ *16.45*
Fresh Food #2	124.5/ *18.05*	123.2/ *17.85*
Freezer #1	138.7/ *20.10*	117.6/ *17.05*
Freezer #2	180.4/ *26.15*	161.5/ *23.40*
Mean	140.5/ *20.36*	129.0/ *18.69*
1) Compressive strength	@ 10% deflection	
2) PUR Foam Density	34.9 kg/m^3 / *2.18 lb/ft^3 (10% over pack*	
3) Typical acceptable value	> 103.5 kPa/ *15 psi*	

Furthermore, dimensional stability of PU foams provides an important metric in assessing the changes in foam dimensions when subjected to temperature variations. The volume changes or dimensional stability is reported in Table 20 from various locations in refrigerator/freezer compartments, which show that the average volume change is less than 1% at temperature extremes studied over 1-day and 7-day intervals [55].

Table 20. Refrigerator PU foam dimensional stability [55]

Cabinet Location	**Dimensional Stability (% volume change)**			
	1 day (-30°C)	1 day (70°C)	7 day (-30°C)	7 day (70°C)
Fresh Food #1	+0.70	-0.55	+0.25	-0.35
Fresh Food #2	+0.10	-0.30	-0.55	-0.60
Freezer #1	+0.05	-0.90	-0.55	+0.05
Freezer #2	-2.40	-0.75	-1.40	+0.00
Mean	-0.39	-0.63	-0.56	-0.23
1) PUR Foam Density	34.9 kg/m^3 (10% over pack)			
2) Typical Allowable Foam Volume Change	3.0 %			

In addition to excellent insulation performance, good dimensional stability, and acceptable compressive strength values, HFO-1233zd(E) shipment, storage, handling, and processing do not require flammability risk mitigation because it is nonflammable according to the ASTM E-681 test method [54]. Furthermore, the foaming process conditions of HCFO-1233zd(E), which include machine temperatures and pressures, are very similar to HFC-240fa, thus requiring no additional requirements to conventional existing PU equipment [55].

4.1.2 HFO-1336mzz(Z)

Another alternative blowing agent that was recently developed is HFO-1336mzz(Z), which has a low vapor thermal conductivity (10.7 mW/mK at 25°C) and is nonflammable in accordance with the ASTM E 681-09 test method performed at 60°C and 100°C [56]. Further development continues of a low-GWP foam expansion agent with improved insulating performance vs. current commercially available options. The thermal performance of foams produced using HFO-1336mzz-(Z) were studied and compared with HCs, as shown in Figure 31, where foams that were intact in the original cabinets from refrigerators made in a customer trial were aged at room temperature. The results reveal that the diffusion coefficient of HFO-1336mzz(Z) is lower than foams produced using HCs. Although longer retention of the blowing agent in the foams may contribute to energy savings, problems of higher boiling point and molecular weight limit widespread implementation in appliances [34]. Alternatives such as using co-blowing agents like cyclopentane, isopentane, and *n*-pentane reduce the boiling point and loading concentration of HFO-1336mzz(Z); however, problems of flammability and potential costs associated with equipment upgrades to accommodate HFO-1336mzz(Z)/HC blends pose additional challenges.

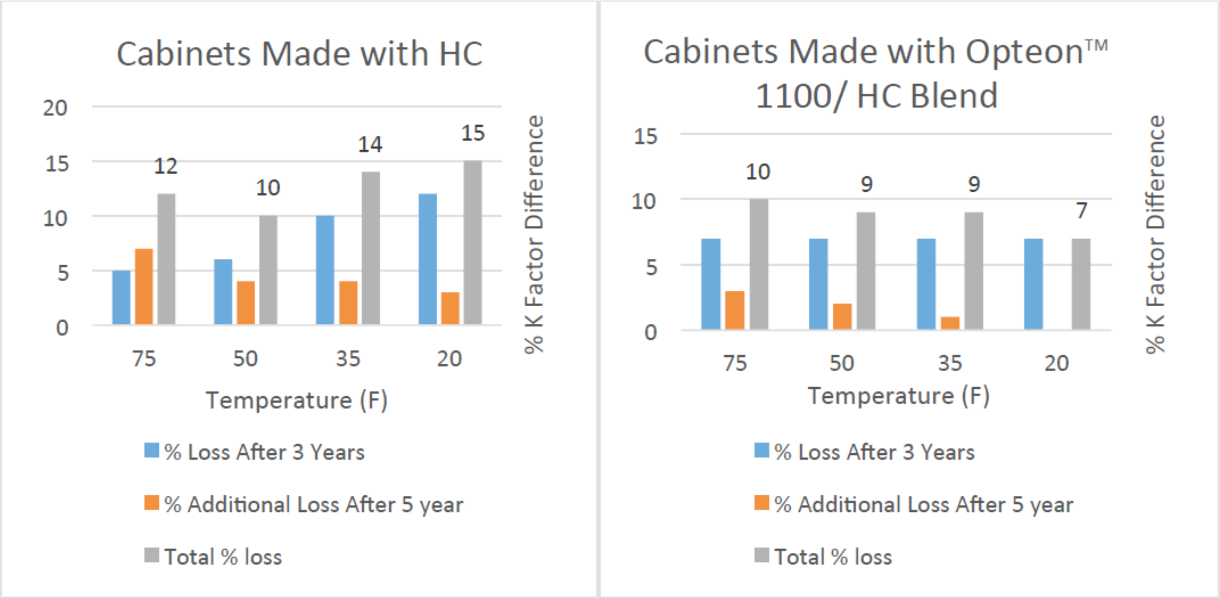


Figure 31. Comparison of *k*-factors in refrigerator foams with HCs and HFO- 1336mzz /HC blends [34].

A study published in 2013 on the compatibility of HFO-1336mzz(Z) in domestic refrigerators showed that HFO-1336mzz(Z)and HFO-1336mzz(Z)/HC blend system with a HIPS liner showed good compatibility without any signs of blistering or cracking [57]. The compatibility of blowing agents with an acrylonitrile butadiene styrene (ABS) liner showed ambiguous results; one study with an HFO-1336mzz(Z)/cyclopentane blend showed good blowing agent retention with 7% *k*-factor loss after 640 days of aging, and another study revealed that customers observed cracks on ABS refrigerators produced using HFO-1336mzz(Z)/cyclopentane, HCFO/cyclopentane, and HFC-245fa/cyclopentane and hydrochlorofluorocarbons (HCFCs) [57]. Another alternative is an HFO-1336mzz(Z)with water blend, which is a promising nonflammable option and shows good compatibility with HIPS and ABS liners, but a detailed validation study is required to assess the thermal insulation performance in refrigeration systems [58].

In a typical domestic refrigerator, the physical properties of HFO-1336mzz(Z)-based appliance foam is shown in Table 21 [52]. The values shown for the HFO-1336mzz(Z) blend meet the typical standards for the compressive strength for domestic refrigerators. Furthermore, dimensional stability analysis was conducted for foams produced using HFO-1336mzz(Z). Figure 32 shows the test for percent dimensional change of HFO-1336mzz-(Z) foams, which reveals that the HFO-1336mzz(Z) foam system is stable with acceptable dimensional change at the freezer (−5°F) and ambient (64°F) temperature conditions [34].

Table 21. Reactivity and physical properties of HFO-1336mzz-(Z)-based appliance foam [52].

Property	**Result (1100/1150)**	**Result (1100)**
Cream time (s)	3	3
Gel time (s)	28	41.7
Tack free time (s)	38	84.7
Free rise density (pcf)	1.5	1.7
Core density (pcf), ASTM D1622	1.90	1.95
75°F Initial K-factor (Btu in/ft^{2}h°F), ASTM C518	0.127	0.134

Table 21. Reactivity and physical properties of HFO-1336mzz-(Z)-based appliance foam [52]. (continued)

35°F Initial K-factor (Btu in/ft^{2}h°F), ASTM C518	0.119	0.128
Close cell content (% uncorrected), ASTM D6226	82	88
Compressive strength (psi), ASTM D1621	20	19
Compressive modulus (psi), ASTM D790	442	500

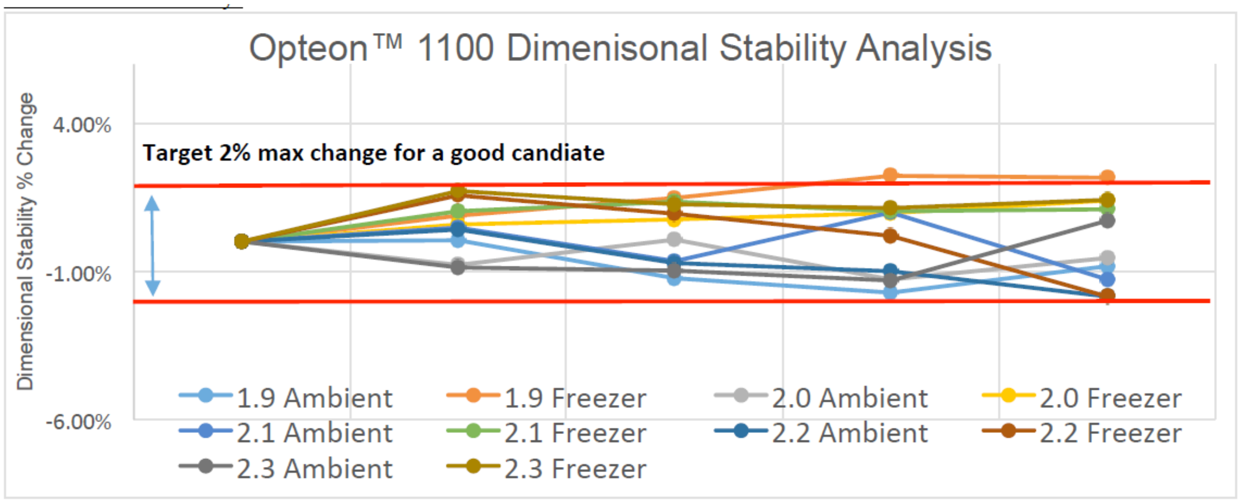


Figure 32. Dimensional stability analysis of PU foams produced using HFO-1336mzz(Z) for domestic refrigerators [34].

4.1.3 Vacuum Insulation Panels

Another alternative technology is the use of vacuum panels in domestic appliance. In Japan, appliance manufacturers have adopted hydrocarbon FBAs in combination with vacuum panels. Although the thermal conductivity of hydrocarbon FBA is higher compared to other types, blends of HCs with vacuum panels are used in combination to provide better energy efficiency. However, the use of vacuum insulated technology is limited and cannot completely replace foam due to cost, installation, design considerations, and maintenance challenges.

Table 22. Summary of alternative blowing agents used in domestic appliances.

Criteria	HFOs	HCs	Methyl formate	Methylal	CO_2 (water)	CO_2	TDCE
Commercially adopted	Yes	Yes	No	No	No	No	No
Blowing agent flammability	Non-flammable	Flammable	Flammable	Flammable	Non-flammable	Non-flammable	Flammable
Thermal insulation performance	Excellent	Good	Fair	Fair	Poor	Unknown	Unknown
Foam physical properties	Excellent	Excellent	Fair	Fair	Good	Unknown	Unknown
Compatibility with foam processing equipment	Yes	Yes	Yes	Yes	Yes	No	Yes
Economically viable	Yes	Yes	Yes	Yes	Yes	Unknown	Yes
Environmental considerations	None	VOC by EPA	None	VOC by EPA	None	None	VOC by EPA
Safety considerations	None	Flammable	Flammable	Flammable	None	High pressure cylinders required	Flammable, toxicity issues
Overall suitability as a blowing agent in this application	Suitable	Suitable	Not suitable	Not suitable	Not suitable	Not suitable	Not suitable

4.2 COMMERCIAL REFRIGERATION SYSTEMS (COMMERCIAL APPLIANCES)

Major emerging alternative technologies in the commercial appliance sector are based around HFO blowing agents. Typically, sandwich panels are used in commercial refrigeration applications, where the foam is sandwiched between steel or aluminum layers [45]. The size of foams used in the commercial sector is sometimes not a constraining factor, allowing the use of less-efficient insulation foams and making the choice of blowing agent less critical. This fact has encouraged PU foams based on CO_2 with poor insulating performance to be used for commercial refrigeration such as displays and vending machines. There is also a report of a methyl formate blowing agent use in the United States and Australia for commercial refrigeration [59]. Several commercial refrigeration systems manufactured by medium and large enterprises use HCs as the FBA. However, FBAs containing HCs create flammable mixtures, which require additional capital investments in meeting safety measures during manufacturing of foam systems [6].Table 22 and 23 provide a summary of alternative blowing agents used in domestic and commercial appliances, which can be used by enterprises of all scales to compare and evaluate the energy efficiency performance and costs associated with adopting a blowing agent.

Table 23. Summary of alternative blowing agents used in commercial appliances.

Criteria	HFOs	HCs	Methyl formate	Methylal	CO_2 (water)	CO_2	TDCE
Commercially adopted	Yes	Yes	Yes	Yes	Yes	No	No
Blowing agent flammability	Non-flammable	Flammable	Flammable	Flammable	Non-flammable	Non-flammable	Flammable
Foam thermal insulation performance	Excellent	Good	Fair	Fair	Poor	Unknown	Unknown
Foam physical properties	Excellent	Excellent	Fair	Fair	Good	Unknown	Unknown
Compatibility with foam processing equipment	Yes	Yes	Yes	Yes	Yes	No	Yes
Economically viable	Yes	Yes	Yes	Yes	Yes	Unknown	Yes
Environmental considerations	None	VOC by EPA	None	VOC by EPA	None	None	VOC by EPA
Safety considerations	None	Flammable	Flammable	Flammable	None	HP cylinders required	Flammable, toxicity issues
Overall suitability as a blowing agent in this application	Suitable	Suitable	Suitable	Suitable	Suitable where low lambda is not critical	Suitable where low lambda is not critical	Suitable, but only as an additive

4.3 SUMMARY

Most of the foam blowing agents used in domestic appliances and small refrigeration systems are either fluorinated (HCFO, HFO) and hydrocarbons materials. Foams produced with these blowing agents have good thermal insulation and physical properties, which are quite important to comply with the energy efficiency standards mandated for these applications. Manufacturers of domestic refrigerators currently use as blowing agents materials such as HCFO-1233zd(E) and HFO-1336mzz(Z), and hydrocarbons such as cyclopentane.

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