HFC 245fa Blown Polyurethane Foams with Lower Thermal Conductivity

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ABSTRACT

Since the phase out of HCFC 141b as a blowing agent in the United States over two years ago, HFC 245fa has been the blowing agent of choice for making polyurethane rigid foams with the lowest thermal conductivities. Even though HFC 245fa has a significantly higher vapor thermal conductivity than HCFC 141b, it has been possible to formulate HFC 245fa-blown foams that matched the insulating performance of the HCFC 141b-blown foams they replaced.

It is well known that the thermal conductivity of polyurethane foam insulation is comprised of three components: conduction through the solid polymer, conduction through the cell gas and radiation. Conduction through the polymer is related to the polymer's structure and the foam density. Conduction through the cell gas is related to the composition of the gas which can vary as a function of temperature. The radiation component of thermal conductivity is related to the cell size of the foam. All of these factors – polymer structure, foam density, cell gas composition, and cell size – can be controlled to some extent through adjustments to the foam formulation.

This work shows that skillful formulation makes it possible to achieve further k-factor improvements using HFC 245fa as the blowing agent. In at least one instance, an improvement of up to 9% compared to today's good HFC 245fa-blown polyurethane foams was demonstrated.

INTRODUCTION

In the United States, HFC 245fa was the blowing agent selected by most appliance manufacturers to replace HCFC 141b when it was phased out after being used for several years. To make the transition as easy as possible, these manufacturers initially wanted to match the properties of their current HCFC 141b system when they converted. Despite the higher thermal conductivity of HFC 245fa, we were able to accomplish this. Next, because HFC 245fa was both more costly and less efficient than HCFC 141b as a blowing agent, the manufacturers wanted to improve their foam ecomonics by minimizing the amount of HFC 245fa it contained.

Since long before the conversion, we have continuously worked to improve polyurethane insulating foams prepared using HFC 245fa as the blowing agent and have presented these results at past API Conferences. However, these efforts have primarily been directed toward either optimization of processing parameters to get the most out of the HFC 245fa formulations [1,2] or reducing the HFC 245fa content of a foam system to improve its economics while maintaining excellent foam properties [3,4,5].

While we continue to make improvements to conventional foam systems blown with HFC 245fa, this paper will explore another direction. In this paper, we will look only at how much we can improve the k-factor or insulating ability of HFC 245fa-blown rigid foam using conventional polyurethane raw materials.

THEORETICAL CONSIDERATIONS

It is well documented that the overall thermal conductivity of rigid polyurethane foam can be viewed as consisting of three separate components; thermal conductivity of the cell gas, thermal conductivity of the solid polymer and radiation which is related to the cell size [6,7]. A forth component, that of convection, is normally ignored because of the insignificant effect it has on the thermal conductivity of rigid foam. This model can be represented by the following equation:

$$k_{foam} = k_{gas} + k_{polymer} + k_{radiation} \qquad (1)$$

According to this model, one only needs to minimize the thermal conductivity of the cell gas, reduce the cell size, and decrease the thermal conductivity and amount of the solid polymer present to optimize the thermal conductivity of the foam.

Effect of Cell Gas Composition

The composition of the cell gas has the biggest overall contribution to the overall thermal conductivity of polyurethane rigid foam. In this paper, we will only be considering foams blown with a combination of HFC 245fa and carbon dioxide generated from the reaction of water with isocyanate. No additional physical blowing agents will be considered.

HFC 245fa has a vapor thermal conductivity of 0.083 BTU-in/hr-ft^2-°F at 20°C [8] and it is generally accepted that CO_2 has a significantly higher thermal conductivity of about 0.115 BTU-in/hr-ft^2-F. The thermal conductivity of the cell gas consisting of HFC 245fa and CO_2 will be a weighted average of these two values. The picture is somewhat clouded by the facts that the vapor thermal conductivity of both HFC 245fa and carbon dioxide change as a function of temperature, and that at sufficiently low temperatures, HFC 245fa will begin to condense, reducing the amount present in the vapor phase. However, despite these complications, it is still clear that to reduce the thermal conductivity of the cell gas, one should increase the amount of HFC 245fa while reducing the amount of water used in the formulation, and that the lowest possible vapor thermal conductivity is achieved when there is no CO_2 present in the foam.

The amount of k-factor improvement possible depends both on the initial and final cell gas compositions. If one increases the molar ratio of HFC 245fa to CO_2 from 70:30 to 100% HFC 245fa, the thermal conductivity of the gas decreases from 0.093 to 0.083 or by 0.010 BTU-in/hr-ft^2-°F.

However, the presence of water in a polyurethane foam formulation does more than generate CO_2. It also generates significant heat, which helps to vaporize the HFC 245fa and expand the gases formed.

Effect of Solid Polymer

Another way foam can transmit heat is through the solid polymer itself. Heat transmission through the polymer is dependent on both the thermal conductivity of the polymer and the volume fraction of polymer present in the foam. It may be possible to develop a solid polymer with a significantly lower thermal conductivity than those of conventional polyurethanes, but that is beyond the scope of this study. Instead, we will primarily concern ourselves with the effect foam density has on k-factor.

The thermal conductivity of solid polyurethane has been measured at around 1.3 BTU-in/hr-ft^2-°F (9) and it has a typical density of about 1.2 g/ml or 75 lb/ft^3. As a result, in a 2.0 lb/ft^3 density foam, the polymer accounts for only about 2.7% of the foam by volume and contributes about 0.035 BTU-in/hr-ft^2-°F to the thermal conductivity.

Based on equation 1, the obvious way to optimize the foam's k-factor is to reduce the foam density. Reducing the density by 10%, from 2.0 to 1.8 lb/ft^3, would be expected to reduce the thermal conductivity due to the polymer proportionally, or by only about 0.0035 BTU-in/hr-ft^2-°F.

Effect of Cell Size

It is well known that reducing cell size improves the thermal conductivity of rigid polyurethane foam by decreasing the radiation component of thermal conductivity. Figure 1 shows the contribution of cell size on thermal conductivity for typical rigid foam.

This figure shows that the thermal conductivity due to radiation increases linearly with cell diameter and that the contribution is larger at the higher temperature. The amount of improvement possible by reducing cell size depends on both the initial cell size and the cell size that can be achieved. For rigid foam with a cell diameter of 150 microns the radiation contributes about 0.014 BTU-in/hr-ft^2-°F at 75°F. Reducing the cell size by 50%, to 75 microns would give an improvement of 0.007 BTU-in/hr-ft^2-°F if all other factors affecting k-factor remained the same.

However, decreasing the cell size increases the area of the cell windows and total length of struts present. If we think of the cells as cubes as illustrated in Figure 2, we can easily see the effect. If we have a cube with an edge length of 1 cm, then the total surface of the cube is 6 cm^2. It would take 8 cubes with an edge length of ½ cm to occupy the same volume as the 1-cm cube, and these would have a total surface area of 9 cm^2. The length of struts framing the windows will also increase. The 1-cm cube is framed by 12 cm of struts while the 8 small cubes described above will be framed by 28 cm of struts.

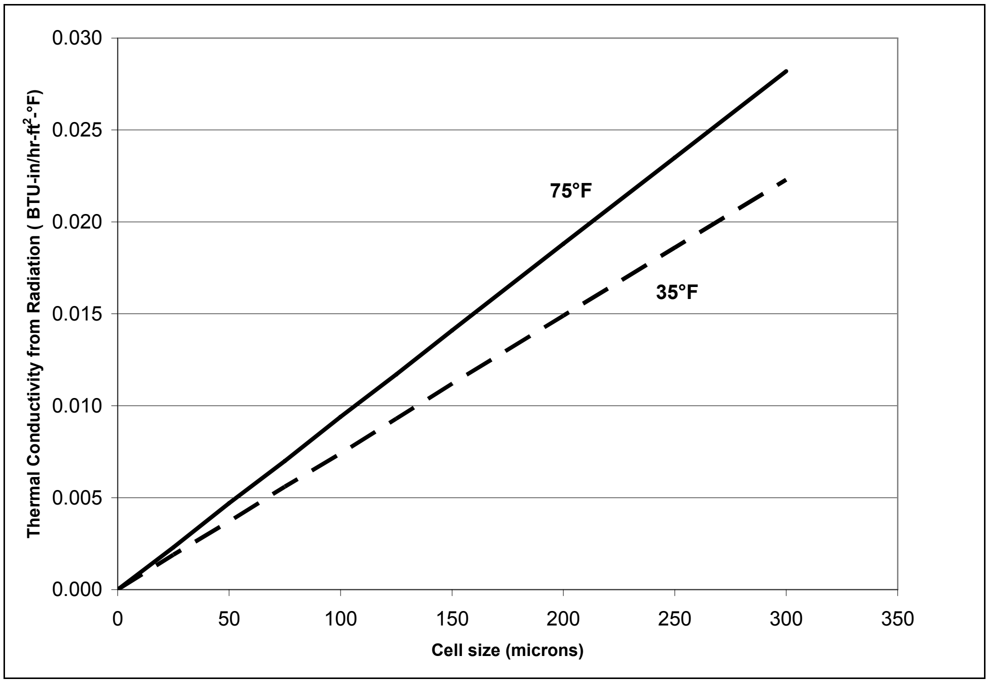

***Figure 1**. Radiation Contribution to Rigid Foam Thermal Conductivity as a Function of Cell Size at 35 and 75°F*

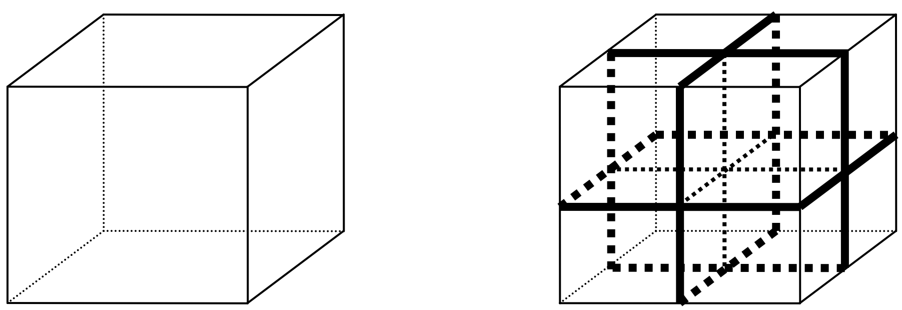

***Figure 2.** Diagram Showing the Additional Windows and Struts Formed as Cell Size Decreases.*

Because the windows and struts of the original 1-cm cell are shared with neighboring cells, this representation overestimates the effect of reducing cell size. Nevertheless, the ultimate effect of decreasing the cell size is that more windows and struts are formed. If one succeeds in reducing cell size while maintaining foam density the windows and struts must become thinner, which can negatively impact the closed cell content and strength of the foam.

Because of the complex interrelations between cell size, blowing agent composition and foam density, it may not be possible to optimize all three factors simultaneously to minimize the k-factor.

Effect of Foam Quality

Although it is not specifically addressed in equation 1, foam quality can also have a large effect on the k-factor of polyurethane foams. Foam quality is sometimes difficult to define, but in general, the best insulating foams have uniformly small cell sizes, high closed cell contents, and little or no skin or densification at the foam/substrate interface. In addition, they should be free of voids or worm holes.

HAND-MIXED EVALUATION OF FOAMS

All hand-mixed foam evaluations were performed using the following the general procedures: The masterbatch (consisting of polyol, surfactant, catalyst, water, and HFC 245fa) was prepared ahead of time and both it and the isocyanate were cooled to 10°C prior to use. The desired amount of masterbatch was first weighed into an appropriate mix container. The isocyanate was then added to the masterbatch and vigorously mixed with a high speed stirrer for 5 seconds before being poured into the desired foam container or mold.

To determine gel times, a total of 250 g material was mixed and poured into a cardboard cup having a volume of about 2.5 liters. The rising foam was repeatedly touched with a thin stick until the foam adhered to the stick and a string formed as the stick was pulled away. The time elapsed from start of mixing until the first string was observed was recorded as the gel time. The free rise cup density was determined by cutting off the foam even with the top of the cup. The weight of foam remaining was then divided by the volume of the cup to obtain the foam density.

To prepare panels for testing, a 25” high x 13” wide x 2” thick metal mold with a detachable lid was used. The mold was heated to 120°F (50°C) before the desired amount of material was poured into the mold and allowed to rise. The minimum fill weight was first determined by allowing the foam to rise above the top of the open mold. After curing, the excess material was trimmed off and the resulting foam weighed. The minimum fill density was then calculated by dividing this foam weight by the volume of the mold. Test panels are prepared in a similar manner, except that the mold’s lid was attached before the rising foam reached the top. The foam was left in the mold for 3.5 minutes before being removed. Core foam samples from panel were cut for testing. The formulations and results we obtained are shown in the following table.

Table 1. Formulations and Results of Handmix Evaluations on Lower k-Factor Foam.

System/Polyol	Conventional Foam	A	B	C	D
Polyol	70 - 76	78	78	78	79
Added Water	0.8 - 1.6	0.00	0.00	0.00	0.00
HFC-245fa	23 - 28	22	22	22	21
Total Masterbatch	100.00	100.0	100.0	100.0	100.00
Isocyanate	90 - 130	108	88	86	83
Gel Time (seconds)	45 - 70	30	30	31	30
Free Rise Cup Density (lb/ft^3)	1.4 - 1.7	2.1	2.1	2.1	2.1
Minimum Fill Density (lb/ft^3)	1.7 - 1.9	2.4	2.6	2.5	2.5
Packed Density (lb/ft^3)	1.9 - 2.1	2.6	2.7	2.6	2.6
Over pack (%)	8 - 12	8	5	4	5
Core Density (lb/ft^3)	1.6 - 1.8	2.4	2.4	2.2	2.2
Closed Cells (%)	85 - 90	90	90	90	91
75°F k-Factor (BTU-in/hr-ft^2-°F)	0.132 - 0.137	0.129	0.128	0.126	0.125
Ave. Cell Diameter (microns)	125 - 150	106	88	85	90

The first column presents values we consider typical of foam for appliance applications in which k-factor is of high importance. In general, the key properties of these foams are similar to the HCFC 141b foam that they replaced.

The foams listed in the following columns are systems designed to minimize the k-factor of the foam. Because we wanted to minimize the k-factor of the foam, we did not add any water to the formulation – only the residual water from the polyol (typically less than 0.1%) was present. We also adjusted the catalyst level to generate relatively fast gel times to minimize the amount of time cells had to coalesce. The gel times listed in this table may not appear unusually fast, but one must keep in mind that chemical temperatures of 10°C were used, and that under these conditions, gel times are usually in the range of 45 – 70 seconds. In these low k-factor foams, the HFC 245fa levels were not drastically different from a typical HFC 245fa-blown appliance foam system, but because no added water was used, all of the densities were significantly higher.

As the table shows, for typical appliance formulations in hand-mixed foam we normally obtain k-factors of 0.132 - 0.137 BTU-in/hr-ft^2-°F. Using this range as a baseline, the k-factors obtained for the foams above represent improvements ranging

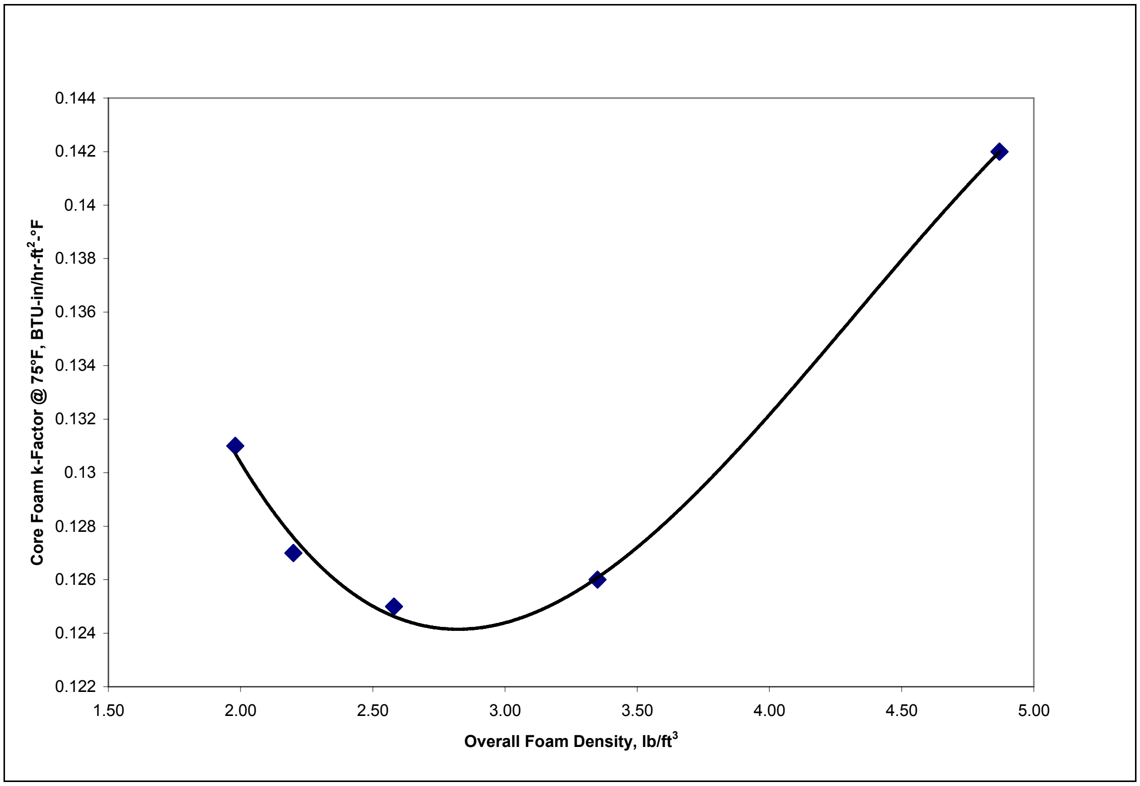

Figure 3. *Foam core k-factor as a function of density.*

from 2% to 9%. These k-factor improvements, however, do not come without some consequences. The most apparent drawback with these foams is their densities, which are 20 - 40% higher than conventional HFC 245fa-blown appliance foam.

To see if the density could be reduced without impacting the thermal conductivity, we increased the amount of HFC 245fa in System D by 5 and 10 parts in the masterbatch, still without the addition of water. We also decreased the HFC 245fa level in a few evaluations to see if further improvements could be achieved by increasing the density even more. As Figure 3 shows, by increasing the amount of HFC 245fa in the formulation we succeeded in reducing the foam density, but this was accompanied by an increase in thermal conductivity. The minimum k-factor appears to be at a foam density between 2.5 and 3.0 lb./ft^3.

MACHINE EVALUATIONS OF FOAM

For System D above, we foamed Bosch panels for evaluation and typical top mount cabinets using Hennecke high-pressure foam machines

Panel Evaluation

Panels were prepared using a Bosch mold with a liquid output of approximately 60 lb/minute at a pour pressure of 1500 psig. This mold measures 20 cm wide by 5 cm thick by 200 cm long and was held at 120°F and filled while in the vertical position. These results are shown in Table 2.

These results are consistent with those obtained in the hand-mix evaluations. The gel time was much faster and the densities much higher than those obtained with conventional HFC 245fa-blown foams. The 75°F k-factors also showed a sizable improvement compared to conventional foams. Significantly higher compressive strengths and closed cell contents were also obtained, and can be attributed to the higher densities.

Table 3. Machine Bosch Panel Results for Foam made using Formulation D		
Property	Conventional Foam	Formulation D
Gel Time (seconds)	27 - 39	18
Minimum Fill Density (lb./ft^3)	1.8 - 2.0	2.5
Packed Density (lb./ft^3)	2.0 - 2.2	2.6
Core Density (lb./ft^3)	1.8 - 2.0	2.4
75°F k-Factor (BTU-in/hr-ft^2-°F)	0.130 - 0.134	0.126
Perp. Comp Strength (lb./in^2)	20 - 25	29
Parallel Comp. Strength (lb./in^2)	30 - 35	47
Closed Cells (%)	88 - 92	94

Refrigerator Foaming

A typical top mount refrigerator cabinet was foamed using a Hennecke HK-550 high-pressure foam machine with a Hennecke MQ-18-2 mix head in a stationary fixture. The minimum fill density was first determined by under filling the cabinet such that a small void existed and extrapolating to determine the minimum amount of foam that would be required to fill the cabinet. A cabinet was then foamed at a density slightly above minimum fill for testing.

The cabinet was first tested for reverse heat leak using doors foamed with a conventional foam system. In the reverse heat leak test, the refrigerator with doors installed is placed in a cold room set at 0°F. The freezer and fresh food compartments are equipped with thermostats and heaters to control their temperatures at 80°F and 40°F respectively. While this is opposite of the way a refrigerator normally operates, it gives a good relative measure of how well the foam is insulating the refrigerator free from any confounding due to the mechanical components. It also allows one to measure the performance of the foam without the need to build up the refrigerator. The cabinet processing and reverse heat leak results are presented in Table 3.

Table 4. Processing and Reverse Heat Leak Results of Cabinet Foamed with Formulation D		
Property	Conventional Foam	Formulation D
Minimum Fill Density (lb/ft^3)	1.8 - 2.0	2.6
Packed Density (lb/ft^3)	2.0 - 2.2	2.8
Packing (%)	8 - 12	7.0
Demold Time (Minutes)	3 - 4	4.0
Freezer Heat Leak (BTU/hr)	125 - 135	119
Fresh Food Heat Leak (BTU/hr)	90 - 95	91
Total Heat Leak (BTU/hr)	220 - 230	210

Table 5. Results of Foam Samples from Cabinet Foamed with Formulation D		
Property	Conventional Foam	Formulation D
Core Density (lb./ft^3)	1.7 – 1.9	2.2
k-Factor @ 35°F (BTU-in/hr-ft2-°F)	0.119 - 0.122	0.117
k-Factor @ 75°F (BTU-in/hr-ft2-°F	0.135 - 0.138	0.130
Perp. Comp. Strength (lb./in^2)	15 - 25	30.7
Parallel Comp. Strength (lb./in^2)	20 - 30	35.5
Closed Cells (%)	85 - 90	91

After testing for reverse heat leak, the cabinet was cut up and foam samples from various locations tested for physical properties. The average results from these samples are shown in Table 5.

These results are consistent with those obtained in the handmix and machine panel evaluations. The densities were all significantly higher than those obtained with conventional HFC 245fa-blown foam systems while the k-factor was lower. This lower k-factor was also reflected in the reverse heat leak values, which were 4 – 9% lower than lower than typical values obtained even though conventional foam was present in the doors.

CONCLUSIONS

These results clearly show that if one is willing to increase foam density, it is possible to improve the k-factor of a foam system substantially compared to HFC 245fa-blown systems currently being used.

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BIOGRAPHY

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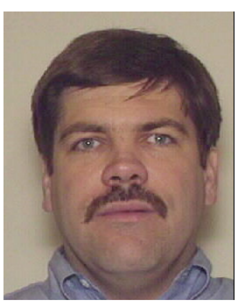

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