



SUPERCRITICAL CO₂ TECHNOLOGY
FOR POLYURETHANE SPRAY FOAM

UNDP REPORT

MAY 2013

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ASSESSMENT OF THE USE IN COLOMBIA OF THE SUPERCRITICAL CO₂ TECHNOLOGY

UNDP REPORT

Executive Summary

This project was developed as response to the Decision 55/43 of the Multilateral Fund Executive Committee and is part of a limited group of projects with the objective to assess new technology options that use non-ODP low GWP blowing agents.

In the context of Decision XIX/6 there is a concern on the availability in Article 5 parties of validated cost effective and environmental sound technologies to phase-out HCFC-141b. This is particularly critical for the application of polyurethane (PU) spray rigid foam where most of the end users are small enterprises with a poor control of the operation and safety discipline. Several work orders are done in-doors with limited ventilation.

The proven technical options to replace HCFC-141b as blowing agent for PU spray foam are mainly limited to high GWP HFCs, HFC-245fa or HFC-365mfc/HFC-227ea blend, which have GWP values of 1030 and 964 respectively. Recent publications show promissory results with the new unsaturated HFC/HCFC blowing agents, commonly known as HFOs, that exhibit GWP values lower than 10, but the commercial availability is uncertain for the time of the conversion. The barrier for hydrocarbon technology in this application is safety during foaming because of their flammability.

The present project was designed to evaluate in an article 5 party such as Colombia the performance of super-critical CO₂, a proven technology applied in Japan for PU spray foam since 2004. A local commercialised HCFC-141b based formation was used as standard. Espumlatex, the largest Colombian 100% owned PU system house, served as local technical host to coordinate the demonstration, foam application and testing activities. The experimental protocol included two statistical full factorial designs, one 2x2x3 for polyurethane foam (PUR) and other 2x2 for polyisocyanurate (PIR). The qualitative factors (independent variables) were the technology (super-critical CO₂ versus HCFC-141b), the foaming location (Barranquilla at sea level versus Bogota at 2600 m over sea level) and foam density. To check processability field in-door applications were done in industrial warehouses in Barranquilla and Bogota and to determine the physical properties test foam sprayed samples were prepared and analysed following ASTM and JIS methods in Achilles and Espumlatex laboratories. In addition few samples (PIR and PUR) were made for E-84 fire performance testing at QAI laboratories in the United States.

The following conclusions can be pointed out:

- Supercritical CO₂ technology is a non-flammable, 0 ODP and low GWP technology. Compared to HCFC-141b based technology it does not create any incremental industrial hygiene and safety hazard.
- Supercritical CO₂ is a proven commercialised technology for spray foam that has been used in Japan since 2004.
- In Colombia, a developing country with tropical weather and various levels of altitude over sea level, Supercritical CO₂ showed a similar processability to the standard HCFC-141b based system currently used. Polyol and isocyanate components of both technologies were stable during the six months of project duration.
- In terms of physical properties of PUR foam, compared to HCFC-141b based formulations Supercritical CO₂ showed:
 - ✓ Higher thermal conductivity but better aging. The difference in lambda value between the two technologies decreased with time.
 - ✓ Similar aging behaviour in compressive strength. Values kept stable with time (initial versus six months)
 - ✓ Similar dimensional stability performance at -20 °C. All values for both technologies were below 0.6%.
 - ✓ Improved dimensional stability at 60 °C and 96% RH.
 - ✓ Similar adhesion strength to galvanised steel.
- In terms of physical properties of PIR foam, compared to HCFC-141b based formulations Supercritical CO₂ showed the same performance pattern than PUR:
 - ✓ Higher thermal conductivity but better aging. The difference in lambda value between the two technologies decreased with time.
 - ✓ Similar aging behaviour in compressive strength. Values kept stable with time (initial versus six months)
 - ✓ Similar dimensional stability performance at -20 °C. All values for both technologies were below 0.6%.
 - ✓ Similar dimensional stability at 60 °C and 96% RH in absolute values. However, the behaviour was totally different: meanwhile Supercritical CO₂ experienced a negative change in volume the HCFC-141b formulation had a positive one.
 - ✓ Lower adhesion strength to galvanised steel.
- According to fire performance test ASTM E84-12c, run on just one sample per formulation, the PIR and PUR foams based on Supercritical CO₂ would be classified as A and B respectively (NFPA).
- The cost of the required retrofit of a typical spray machine to apply the Supercritical CO₂ is in the range from 9,800 to 13,700 US dollars for PUR foam and from 11,800 to 15,700 US dollars for PIR foam.

- Supercritical CO₂ technology is based on proprietary polyol and isocyanate formulations developed by Achilles. The FOB price in Japan of the Supercritical CO₂ system by kg is 7 dollars.
- Supercritical CO₂ technology is a patented technology owned by Achilles Corporation. The interested parties should come to an agreement with Achilles on technology fees.

1. INTRODUCTION

In the context of Decision XIX/6 there is a concern on the availability in Article 5 parties of validated cost effective and environmental sound technologies to phase-out HCFC-141b in the different foam applications.

This project was developed as response to the Decision 55/43 of the Multilateral Fund Executive Committee and is part of a limited group of projects with the objective to assess new technology options that use non-ODP low GWP blowing agents. UNDP has prepared six demonstrations projects covering a wide spectrum of foam applications on methyl formate, methylal, pre-blended hydrocarbons and HFO-1234ze for XPS. They are already completed or are being implemented. The present project was designed to evaluate in developing countries the performance of supercritical CO₂, a relatively new technology currently used in Japan for polyurethane (PU) spray rigid foam.

PU spray rigid foams are closed-celled, air tight, resistant to mildew and fungal attack, provide no food value to rodents and have good vapour barrier properties (Randall & Lee, 2002). They find utility as an *in situ* applied insulation in applications where irregular shapes or the need for a monolithic layer of foam exists. These applications include building envelope, pipe insulation, tank insulation, rail cars, residential roofing and floors (Gum, 1992). Spray foam is now finding increasing use in retrofitting/refurbishing roofs, walls, floors and windows of existing buildings as well as in new constructions such as commercial offices, industrial factories and warehouses, agricultural pig and chicken farms (Randall & Lee, 2002). In the 2008 Progress Report the Foams Technical Options Committee (FTOC) states: “*PU Spray Foam is being increasingly recognized as an efficient means of retrofitting a number of building types*”.

For developing countries, the proven technical options to replace HCFC-141b as blowing agent for PU spray foam are mainly limited to high GWP HFCs, HFC-245fa or HFC-365mfc/HFC-227ea blend, which have GWP values of 1030 and 964 respectively (100yr ITH, IPCC 4th Assessment Report 2008). Recent publications show promissory results with the new unsaturated HFC/HCFC blowing agents, commonly known as HFOs, that exhibit GWP values lower than 10, but the commercial availability is uncertain for the time of the conversion (Bodgan, 2011; Costa, 2011). The barrier for hydrocarbon technology in this application is safety during foaming because of their flammability. This issue is particularly critical for this sector where most of the enterprises are small in size with a poor control of the operation and safety discipline. Several work orders are done indoors with limited ventilation.

One alternative that has been sporadically applied is the use as sole blowing agent of CO₂ generated from the water-isocyanate reaction (all water blown foam). It is a non-flammable and low GWP technology that does not require significant modifications in the machinery. However, despite of some success, three major drawbacks are generally associated with this approach: poor dimensional stability, caused by the high CO₂ permeability through the polyurethane matrix; poor adhesion to

the different substrates due to the significant polyurea content of the polymer and relatively high thermal conductivity.

In 2004, in an effort to overcome some of the weaknesses of water blown foam, Achilles Corporation, a Japanese company, patented a spray technology based on the direct injection of CO₂ to a PU all water blown system (Japanese Patent JP2004107376). It was reported that with a minor modification to a conventional spray machine (Gusmer FF type with a 1:1 mixing ratio by volume) and by adding 1.5% of liquid CO₂, isotropic cells were obtained which lead to dimensional stable foams at the density comparable to HCFC-141b blown foams (Ohnuma & Mori, 2003, figure 2). Figure 1 shows how the modified equipment looks like. Liquid CO₂ cooled to 0 °C with a heat exchanger is supplied to the Gusmer auxiliary pump which is remodelled so that brine might circulate internally and injected to the polyol component.

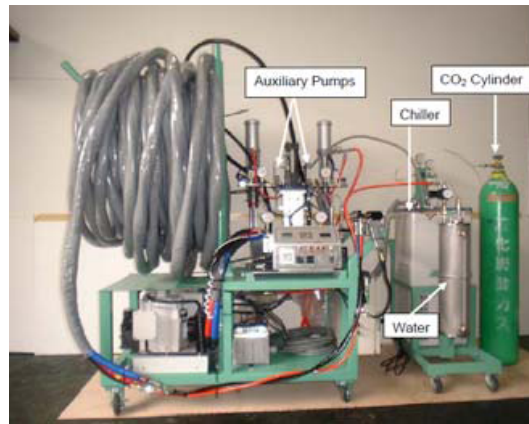


Figure 1. Modified spray machine for Supercritical CO₂

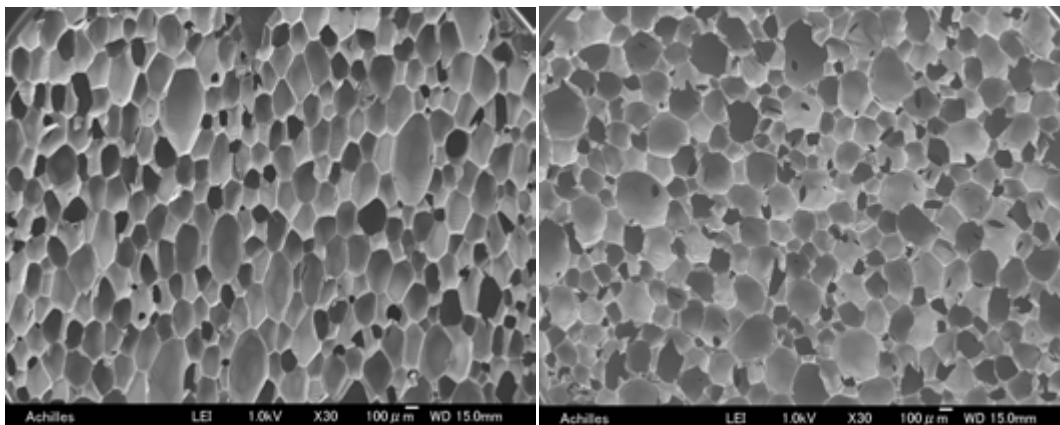


Figure 2. Spray foam with 0% liquid CO₂ versus spray foam with 1.5% liquid CO₂

The FTOC registered this development and in its 2008 progress report wrote: “*Super-critical CO₂ spray foam technologies have become established in Japan but market penetration is no more than 10%. The technology is yet to make any significant market penetration beyond Japan*”.

2. PROJECT OBJECTIVES AND IMPLEMENTATION

According to the document submitted and approved in the 60th meeting of the Executive Committee of the Multilateral Fund held in Montreal in April 2010, the project objectives are:

1. Make a technical and economic assessment of the use in an Article 5 party (Colombia) of the super-critical CO₂ technology for the application of PU spray rigid foam. **Local commercial formulation based on HCFC-141b served as standard.**
2. Disseminate the technology to interested system houses in Colombia and other Latin American countries.

Espumlatex, the largest Colombian 100% owned PU system house, served as local technical host to coordinate the demonstration, foam application and testing activities.

The start-up of the project took place the week of July 25, 2012. The implementation was done in a team effort among Achilles Corp., Espumlatex, the National Ozone Unit (UTO) and UNDP. The following activities were carried out:

| Activity | Date |
|--|-----------------------------------|
| Project Kick-off. Definition of evaluation plan and experimental protocol. | June 25 - 29, 2012 |
| Shipment of injection equipment modified to use the Supercritical CO ₂ technology. Shipment of Achilles PU materials, nationalization and in-land transportation. | July 13 - September 30 |
| Application of Supercritical CO ₂ and HCFC-141b based systems. Preparation of foam samples to test physical properties | October 1 - 7 |
| Evaluation of foam physical properties (Espumlatex, Achilles, QAI laboratories) | October 15, 2013 - March 31, 2013 |
| Preparation of Final Report | May, 2013 |
| Presentation of the final results and conclusions in an international seminar | June, 2013 |

3. EXPERIMENTAL

3.1 Experimental Design

When a specific process or experiment is repeated under what are, as nearly as possible, the same conditions, the observed results are never identical (Box & Hunter & Hunter, 1978). This statement is particularly true in the field of PU foam. This fluctuation that occurs from one repetition to another is called *experimental error* and refers to variations that are unavoidable such as human errors of measurement, analysis and sampling. The no consideration of experimental error can lead to false conclusions about the *real* effect of a specific independent variable. In the line of these

thoughts and having in mind that usually is most efficient to estimate the effects of several variables simultaneously, it was decided to apply for this project the technique of statistical design of experiments, commonly known as DOE.

Two full factorial designs were conducted, one 2x2x3 for polyurethane foam (PUR) and other 2x2 for polyisocyanurate (PIR). The qualitative factors (independent variables) and levels are described in tables 1 and 2. *Genuine* replicates were made in all points of the design to have the best estimate of the error variance across the experimental region.

| Table 1. Experimental Design for PUR | |
|---|---|
| Factors (independent variables) | Levels |
| Technology | Supercritical CO ₂ |
| | HCFC-141b, High Water |
| | HCFC-141b, Low Water |
| Location | Barranquilla: sea level, high ambient temperature (30 °C), high relative humidity (80%) |
| | Bogotá: 2,600 m over sea level, low ambient temperature (20 °C), moderate relative humidity (60%) |
| Foam Density | High |
| | Low |

| Table 2. Experimental Design for PIR | |
|---|---|
| Factors (independent variables) | Levels |
| Technology | Supercritical CO ₂ |
| | HCFC-141b |
| Location | Barranquilla: sea level, high ambient temperature (30 °C), high relative humidity (80%) |
| | Bogotá: 2,600 m over sea level, low ambient temperature (20 °C), moderate relative humidity (60%) |

3.2. Formulations

For **Supercritical CO₂ technology** three Achilles proprietary water blown formulations were used:

- PUR formulation, 30 kg/m₃ density, designed for walls in Japan. It was applied in Bogota and Barranquilla. For the experimental design it was denominated as “Supercritical CO₂, PUR, Low Density (LD)”.
- PUR formulation, 40 kg/m₃ density, designed for roofing. It was applied in Bogota and Barranquilla. For the experimental design it was denominated as “Supercritical CO₂, PUR, High Density (HD)”.
- PIR formulation, 30 kg/m₃ density, designed for walls in Japan. It was applied in Bogota and Barranquilla. Because of the high altitude over sea level for the application in Bogotá a reduced amount of water was added in the machine, directly to the polyol component. For the experimental design it was denominated as “Supercritical CO₂, PIR”.

For **141b based technology** five Espumlatex proprietary formulations, four for PUR and one for PIR, were used:

- PUR formulation, high water content, low density. It was applied in Bogota and Barranquilla. For the experimental design it was denominated as “HCFC-141b, PUR, High Water (HW), Low Density (LD)”.
- PUR formulation, high water content, high density. It was applied in Bogota and Barranquilla. For the experimental design it was denominated as “HCFC-141b, PUR, High Water (HW), High Density (HD)”.
- PUR formulation, low water content, low density. It was applied in Bogota and Barranquilla. For the experimental design it was denominated as “HCFC-141b, PUR, Low Water (LW), Low Density (LD)”. **This is the commercial formulation sold by Espumlatex in the local market.**
- PUR formulation, low water content, high density. It was applied in Bogota and Barranquilla. For the experimental design it was denominated as “HCFC-141b, PUR, High Water (HW), High Density (HD)”. **This is the commercial formulation sold by Espumlatex in the local market.**
- PIR formulation. It was applied in Bogota and Barranquilla. For the experimental design it was denominated as “HCFC-141b, PIR”.

The table 3 summarizes the blowing agent characteristics of the HCFC-141b based formulations for PUR:

| Table 3. Blowing agent characteristics of HCFC-141b formulations for PUR | | | | |
|---|-------|-------|-------|-------|
| | LW-LD | LW-HD | HW-LD | HW-HD |
| CO ₂ moles /kg of polymer | 0.23 | 0.21 | 0.66 | 0.58 |
| HCFC-141b moles /kg of polymer | 0.94 | 0.84 | 0.38 | 0.38 |
| Total gas moles/kg of polymer | 1.17 | 1.05 | 1.04 | 0.96 |
| Initial mole fraction, CO ₂ | 0.19 | 0.20 | 0.64 | 0.61 |
| Initial mole fraction HCFC-141b | 0.81 | 0.8 | 0.36 | 0.39 |

3.3. Spray application conditions

Field in-door applications of both systems, Supercritical CO₂ and HCFC-141b, were done in industrial warehouses in Barranquilla and Bogota. *Both materials were easy to process and no particular issues were observed.*

For physical test samples the foam was sprayed to a thickness of 5 mm in one primer and three passes applied in crossed directions (dead time between passes: 1 minute) on 1.50 m x 0.80 m pieces of plywood. Additional samples were sprayed on 2.50 m long pieces for E-84 testing. The Table 4 shows the spray conditions.

| Table 4. Spray conditions | | | | |
|---|-------------------------------|--------------------------|--------------------------------|---------------------------------|
| | Supercritical CO ₂ | | HCFC-141b | |
| | Barranquilla | Bogota | Barranquilla | Bogota |
| Spray machine | NF-12J Proportioning unit | | Graco E-10 | |
| Spray gun | GAP Pro (round pattern) | | Fusion AP | |
| Percentage by weight of CO ₂ , % | 1.0 for PUR, 1.75 for PIR | | Non applicable | |
| Ambient Temperature, °C | 31 | 19 - 20 | 31 | 19 - 20 |
| Relative Humidity, % | 62 - 89 | 62 - 69 | 62 - 67 | 52 - 62 |
| Substrate Temperature, °C | 31 | 19 - 20 | 32 | 20 - 22 |
| Iso Temperature, °C | 45 | 45 | 50 | 50 |
| Polyol Temperature, °C | 45 | 45 | 49 | 49 |
| Primary Heater | Off | 45 | Off | Off |
| Hose length, m | 45 | 45 | 15 | 15 |
| Hose Temperature, °C | 40 (PUR) 45 (PIR) | 40 (PUR) 45 (PIR) | 40 | 40 |
| Static Pressure, psi | 1,000 | | 1,600 | |
| Dynamic Pressure, psi | 750 | | 1,400 | |
| Tack Free Time, /Rise Time, (s/s) | 6/10 (PUR) 2/5 (PIR) | 10/15 (PUR) 3/7 (PIR) | 2/7 sec (PUR) 2/5 sec (PIR) | 4/12 sec (PUR) 2/7 sec (PIR) |

3.4. Test Methods

Table 5 lists the different test methods to determine the foam physical properties

| Table 5. Test Methods | | |
|------------------------------|----------------|----------------------------|
| Property | Test | Testing Laboratory |
| Reactivity | Visual | In-situ during application |
| Foam core density | ASTM D-1622 | Espumlatex |
| Thermal Conductivity | ASTM C-518 | Espumlatex |
| Compression strength | ASTM D-1621 | Espumlatex |
| Adhesion strength | ASTM D-1623 | Espumlatex |
| Water vapour permeability | JIS A-9526 | Achilles |
| Water absorption | JIS A-9511 | Achilles |
| Closed cell content | ASTM D-2856 | Achilles |
| Dimensional stability | ASTM D-2126 | Espumlatex |
| Aging | | |
| Thermal Conductivity | ASTM C-518 | Espumlatex |
| Compressive strength | ASTM D-1621 | Espumlatex |
| Fire Performance | ASTM E-84, 12c | QAI Laboratories |

4. RESULTS

During the six months of the duration of the project the polyol side formulations of both technologies, Supercritical CO₂ and HCFC-141b based, were stable and no component separation was observed. The table 6 and 7 show the physical properties of the PUR and PIR foams. They correspond to the experimental designs described in tables 1 and 2.

| Table 6. Physical Properties of PUR foam | | | | | | | | | | | | |
|--|-------------------------------|--------|--------|--------|----------------------|--------|--------|--------|-----------------------|--------|--------|--------|
| Property | Supercritical CO ₂ | | | | HCFC-141b, Low Water | | | | HCFC-141b, High Water | | | |
| | Barranquilla | | Bogota | | Barranquilla | | Bogota | | Barranquilla | | Bogota | |
| | HD | LD | HD | LD | HD | LD | HD | LD | HD | LD | HD | LD |
| Core Density, kg/m ³ | 46.5 | 35.3 | 38.0 | 28.5 | 43.6 | 37.8 | 36.0 | 31.0 | 45.0 | 48.3 | 41.2 | 34.6 |
| | 44.1 | 41.1 | 33.9 | 33.6 | 44.2 | 40.5 | 39.3 | 31.1 | 45.1 | 47.3 | 43.9 | 36.5 |
| Thermal Conductivity, 24°C, 24 hours, mw/mK | 34.23 | 33.95 | 34.09 | 34.02 | 23.97 | 24.84 | 24.47 | 23.79 | 25.99 | 28.84 | 28.47 | 28.37 |
| | 34.11 | 33.94 | 34.07 | 33.99 | 24.23 | 24.24 | 24.11 | 24.34 | 27.32 | 29.01 | 29.78 | 28.56 |
| Thermal Conductivity, 24°C, 2 weeks at 20 °C and 50% RH, mw/mK | 34.19 | 34.04 | 34.30 | 34.05 | 24.68 | 25.82 | 25.40 | 24.88 | 29.81 | 29.84 | 29.89 | 29.58 |
| | 34.06 | 33.88 | 34.19 | 34.01 | 24.83 | 25.18 | 25.11 | 24.92 | 29.05 | 30.04 | 30.36 | 29.57 |
| Thermal Conductivity, 24°C, 4 weeks at 20 °C and 50% RH, mw/mK | 34.22 | 34.28 | 34.19 | 34.19 | 25.35 | 26.05 | 25.80 | 25.37 | 30.19 | 30.16 | 30.15 | 29.33 |
| | 34.07 | 34.04 | 34.03 | 34.03 | 25.42 | 25.61 | 25.76 | 25.56 | 29.68 | 30.35 | 30.70 | 30.36 |
| Compressive Strength, parallel to rise, kPa | 179.98 | 191.00 | 158.20 | 134.78 | 313.37 | 254.48 | 248.76 | 206.24 | 350.60 | 302.43 | 265.25 | 174.29 |
| | 206.32 | 211.05 | 160.27 | 153.08 | 330.79 | 268.94 | 275.35 | 189.37 | 343.67 | 306.85 | 249.03 | 202.20 |
| Compressive Strength, parallel to rise, 6 months, kPa | 213.41 | 189.79 | 151.61 | 123.83 | 326.28 | 251.45 | 248.95 | 204.36 | 325.64 | 289.19 | 289.50 | 195.61 |
| | 233.68 | 245.68 | 154.51 | 136.54 | 339.74 | 299.32 | 269.66 | 171.86 | 339.34 | 305.15 | 264.46 | 235.16 |
| Dimensional Stability, -20 °C, 24 hours, Vol. % | 0.026 | -0.414 | -0.126 | -0.304 | 0.021 | -0.003 | -0.141 | -0.269 | 0.032 | -0.056 | -0.010 | -0.071 |
| | -0.150 | 0.094 | -0.115 | -0.121 | 0.082 | 0.045 | -0.242 | 0.055 | -0.139 | -0.067 | -0.023 | -0.677 |
| One week, % | -0.145 | -0.568 | -0.023 | -0.389 | -0.045 | -0.003 | -0.221 | -0.378 | 0.092 | -0.189 | 0.065 | 0.108 |
| | -0.531 | -0.198 | 0.014 | -0.329 | -0.224 | -0.069 | -0.040 | -0.243 | -0.004 | -0.173 | 0.075 | -0.146 |
| Two weeks, % | -0.139 | -0.262 | -0.132 | -0.563 | 0.045 | -0.138 | -0.332 | -0.024 | 0.105 | 0.074 | -0.113 | -0.126 |
| | -0.433 | 0.069 | -0.039 | -0.056 | 0.165 | 0.032 | -0.242 | -0.433 | 0.022 | 0.036 | 0.010 | -0.267 |
| Dimensional Stability, 60 °C, 95% RH, 24 hours, Vol. % | 3.114 | 1.056 | 10.449 | 3.231 | 1.903 | 2.933 | 2.939 | 2.882 | 0.284 | 1.679 | 0.979 | 1.813 |
| | 1.731 | 2.030 | 8.103 | 3.132 | 1.542 | 2.514 | 2.501 | 2.817 | 0.445 | 1.795 | 2.112 | 1.796 |
| One week, % | 0.572 | 0.584 | 6.066 | 1.009 | 2.456 | 3.534 | 3.153 | 3.201 | 0.510 | 1.660 | 0.791 | 1.867 |
| | -0.809 | 0.783 | 4.803 | 0.745 | 1.987 | 3.302 | 2.922 | 3.178 | 0.482 | 2.100 | 1.594 | 1.496 |
| Two weeks, % | 0.069 | 0.430 | 5.271 | 0.412 | 2.521 | 3.789 | 3.347 | 3.382 | 0.743 | 1.821 | 0.814 | 1.727 |
| | -1.314 | 0.545 | 4.261 | 0.515 | 2.156 | 3.585 | 3.094 | 3.302 | 0.878 | 2.037 | 1.720 | 1.328 |
| Dimensional Stability, 70 °C, Ambient RH, 24 hours, Vol. % | -2.670 | 0.315 | 3.724 | 0.189 | -0.114 | 0.780 | -0.664 | 0.453 | -0.962 | -0.822 | -1.551 | -1.101 |
| | -0.768 | -0.080 | 1.116 | 0.595 | -0.103 | -0.233 | 0.407 | 0.139 | -0.883 | -0.399 | -0.544 | -1.147 |
| One week, % | -3.084 | -0.240 | 2.972 | -0.438 | -0.043 | 0.886 | -0.672 | 0.961 | -0.709 | -0.510 | -1.400 | -0.842 |
| | -1.387 | -0.831 | 0.639 | -0.058 | 0.044 | -0.090 | 0.485 | 0.036 | -0.684 | -0.638 | -0.274 | -0.931 |
| Two weeks, % | -3.893 | -0.473 | 2.883 | -0.451 | 0.098 | 1.073 | -0.432 | 1.293 | -0.627 | -0.808 | -1.002 | -0.381 |
| | -1.726 | -0.399 | 0.630 | -0.244 | 0.212 | -0.043 | 0.641 | 0.662 | -0.591 | -0.023 | 0.058 | -0.470 |
| Closed Cell Content, % | 64.30 | 64.00 | 83.50 | 71.10 | 75.80 | 81.50 | 92.30 | 91.60 | 78.40 | 81.80 | 89.10 | 90.10 |
| | 72.30 | 73.90 | 80.10 | 82.00 | 69.90 | 78.10 | 91.80 | 90.50 | 74.10 | 86.60 | 90.40 | 90.30 |
| Water absorption, g/100 cm ² | 0.80 | 1.12 | 1.17 | 1.53 | 0.77 | 1.01 | 0.58 | 0.42 | 0.76 | 0.84 | 0.56 | 0.81 |
| | 0.75 | 0.93 | 1.02 | 1.31 | 0.84 | 0.88 | 0.56 | 0.50 | 0.73 | 0.92 | 0.57 | 0.63 |
| Water Vapour Permeability, ng/Pa.s.m | 3.44 | 6.06 | 4.57 | 5.89 | 3.88 | 4.61 | 3.72 | 4.14 | 4.43 | 4.46 | 4.41 | 4.97 |
| | 3.92 | 3.82 | 5.62 | 4.00 | 3.59 | 4.01 | 3.65 | 3.57 | 4.33 | 4.62 | 4.14 | 4.74 |
| Adhesion Strength to metal (galvanized steel), N/cm ² | 14.33 | 20.56 | 7.83 | 14.99 | 11.14 | 4.31 | 11.36 | 8.46 | 12.34 | 20.59 | 6.63 | 15.47 |
| | 13.96 | 15.33 | 7.94 | 15.24 | 4.70 | 1.66 | 31.35 | 8.02 | 15.91 | 6.66 | 27.99 | 15.59 |

HD: High Density. LD: Low Density

| Table 7. Physical Properties of PIR foam | | | | |
|--|-------------------------------|--------|--------------|--------|
| Property | Supercritical CO ₂ | | HCFC-141b | |
| | Barranquilla | Bogota | Barranquilla | Bogota |
| Core Density, kg/m ³ | 40.8 | 37.0 | 43.0 | 32.3 |
| | 35.7 | 37.8 | 44.4 | 32.4 |
| Thermal Conductivity, 24°C, 24 hours, mw/mK | 34.42 | 34.02 | 28.39 | 20.70 |
| | 34.27 | 34.11 | 27.92 | 20.82 |
| Thermal Conductivity, 24°C, two weeks at 20 °C and 50% RH, mw/mK | 34.66 | 34.33 | 30.05 | 22.48 |
| | 33.76 | 34.27 | 28.23 | 22.22 |
| Compressive Strength, parallel to rise, kPa | 141.18 | 126.32 | 225.37 | 132.89 |
| | 119.38 | 144.49 | 235.59 | 134.43 |
| Compressive Strength, parallel to rise, 6 months, kPa | 119.15 | 139.77 | 221.62 | 140.29 |
| | 129.40 | 130.58 | 209.99 | 142.68 |
| Dimensional Stability, -20 °C, 24 hours, Vol. % | 0.258 | 0.598 | 0.117 | -0.041 |
| | 0.148 | 0.013 | 0.156 | -0.229 |
| One week, % | 0.018 | -0.228 | -0.023 | -0.120 |
| | -0.194 | -0.044 | 0.072 | -0.178 |
| Two weeks, % | 0.299 | -0.449 | -0.018 | 0.030 |
| | 0.572 | -0.023 | 0.067 | -0.006 |
| Dimensional Stability, 60 °C, 95% RH, 24 hours, Vol. % | -1.695 | -2.121 | 4.355 | 3.347 |
| | -1.920 | -2.768 | 5.904 | 2.565 |
| One week, % | -3.197 | -3.798 | 3.721 | 4.865 |
| | -3.851 | -4.904 | 4.986 | 4.211 |
| Two weeks, % | -3.731 | -4.180 | 3.107 | 5.944 |
| | -4.371 | -5.502 | 4.406 | 5.537 |
| Dimensional Stability, 70 °C, Ambient RH, 24 hours, Vol. % | -0.877 | -0.292 | -0.484 | -0.371 |
| | -1.515 | 0.033 | -0.387 | -0.316 |
| One week, % | -2.929 | -1.618 | 0.212 | -0.086 |
| | -4.108 | -1.042 | -0.767 | -0.226 |
| Two weeks, % | -3.768 | -2.168 | -0.053 | -0.030 |
| | -3.793 | -1.554 | -1.073 | -0.067 |
| Closed Cell Content, % | 19.60 | 39.60 | 88.50 | 86.50 |
| | 42.20 | 53.10 | 89.30 | 84.50 |
| Water absorption, g/100 cm ² | 1.67 | 1.70 | 1.94 | 3.13 |
| | 1.59 | 1.54 | 1.89 | 3.26 |
| Water Vapour Permeability, ng/Pa.s.m | 8.63 | 5.88 | 8.58 | 6.34 |
| | 8.38 | 6.27 | 8.62 | 6.59 |
| Adhesion Strength to metal (galvanized steel), N/cm ² | 7.58 | 6.57 | 16.97 | 11.23 |
| | 8.71 | 9.34 | 16.30 | 6.89 |

The table 8 shows the results of the fire performance test, ASTM E-84, run on four foam samples: Supercritical CO₂, PUR and PIR, and HCFC-141b, PUR -low water content- and PIR.

| Table 8. Fire Performance Test, ASTM E84-12c | | | | |
|---|----------------|--------------|-----------------|------------|
| Technology | | Flame Spread | Smoke Developed | NFPA Class |
| Supercritical CO ₂ | PUR | 70 | 331 | B |
| | PIR | 20 | 286 | A |
| HCFC-141b | PUR, low water | 390 | 100* | C |
| | PIR | 25 | 200 | A |

* Due to heat production and lack of air flow through the chamber, the test was terminated at 1 minute, 42 seconds. Had the test continued for the normal 10 minute period, the flame spread value would have remained unchanged. The smoke number is the smoke value at time of termination.

5. ANALYSIS OF RESULTS

To assess the statistical significance of the effect of the different factors on the foam properties an analysis of variance (ANOVA) was developed for each property. In this section the ANOVA of few selected foam properties, critical for the thermal insulation performance, such as initial thermal conductivity (lambda value) and aging of lambda value, will be shown for PUR and PIR. The analysis of core density, dimensional stability, compressive strength, aging of compressive strength and adhesion to galvanised steel are described in the annex 1.

5.1. PUR foam

Analysis of initial thermal conductivity for PUR

The tables 9 and 10 show a summary of the results of the initial thermal conductivity (Lambda value) and the corresponding ANOVA.

| Table 9. Lambda Value, 24 °C, 24 hours, mW/mK | | | | | | | |
|--|-------------------------------|-------|----------------------|-------|-----------------------|-------|---------|
| | Supercritical CO ₂ | | HCFC-141b, low water | | HCFC-141b, high water | | AVERAGE |
| | HD | LD | HD | LD | HD | LD | |
| Barranquilla | 34.17* | 33.95 | 24.10 | 24.54 | 26.66 | 28.93 | 28.72 |
| Bogotá | 34.08 | 34.01 | 24.29 | 24.07 | 29.13 | 28.47 | 29.01 |
| AVERAGE | 34.05 | | 24.25 | | 28.29 | | |
| | AVERAGE | | | | | | |
| HD | 28.74 | | | | | | |
| LD | 28.99 | | | | | | |

* All the values are the average of two genuine replicates (table 6).

| Table 10. ANOVA of Lambda value, 24 °C, 24 hours | | | | | | |
|--|--------------------|----------------|-------------|----------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P* | |
| Technology | 2 | 388.174 | 194.087 | 1052.437 | 0.000 | Significant |
| Density | 1 | 0.388 | 0.388 | 2.1039 | 0.173 | |
| Location | 1 | 0.479 | 0.479 | 2.5974 | 0.133 | |
| Tec*Dens | 2 | 0.977 | 0.489 | 2.6489 | 0.112 | |
| Dens*Loc | 1 | 1.978 | 1.978 | 10.7257 | 0.007 | Significant |
| Tec*Loc | 2 | 1.582 | 0.791 | 4.2892 | 0.039 | Significant |
| Pure Error | 12 | 2.213 | 0.184 | | | |

* Probability of Type I error (rejecting the null hypothesis when it is in fact true). If $P < 0.05$ it is considered that the effect of the factor is significant.

From table 9 it is concluded there is a statistical significant difference in the initial lambda value among the three systems: Supercritical CO₂ developed a thermal conductivity 20.3% higher than high water-HCFC-141b and 40.4% higher than low water-HCFC-141b. As expected the low water-HCFC-141b provided a better (lower) value than high water-HCFC-141b because of the greater initial mole fraction of HCFC-141b in the gas cell. No significant differences in Lambda between the two locations and the high and low density formulations were observed.

Lambda value, aged 4 weeks at 20 °C and 50% RH, 24 °C

The tables 11 and 12 describe the results of Lambda value, aged four weeks at 20 °C and 50% RH, and the corresponding ANOVA.

| Table 11. Lambda Value, 24 °C, 4 weeks, mW/mK | | | | | | | |
|---|-------------------------------|-------|----------------------|-------|-----------------------|-------|---------|
| | Supercritical CO ₂ | | HCFC-141b, low water | | HCFC-141b, high water | | AVERAGE |
| | HD | LD | HD | LD | HD | LD | |
| Barranquilla | 34.14 | 34.16 | 25.38 | 25.83 | 29.93 | 30.25 | 29.95 |
| Bogotá | 34.11 | 34.11 | 25.78 | 25.47 | 30.43 | 29.85 | 29.96 |
| AVERAGE | 34.13 | | 25.61 | | 30.11 | | |
| | AVERAGE | | | | | | |
| HD | 29.96 | | | | | | |
| LD | 29.94 | | | | | | |

| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
|------------|--------------------|----------------|-------------|---------|-------|-------------|
| Technology | 2 | 290.529 | 145.265 | 1725.91 | 0.000 | Significant |
| Density | 1 | 0.002 | 0.002 | 0.02 | 0.885 | |
| Location | 1 | 0.000 | 0.000 | 0.00 | 0.962 | |
| Tec*Dens | 2 | 0.041 | 0.021 | 0.24 | 0.787 | |
| Dens*Loc | 1 | 0.469 | 0.469 | 5.57 | 0.036 | Significant |
| Tec*Loc | 2 | 0.007 | 0.004 | 0.04 | 0.958 | |
| Pure Error | 12 | 1.010 | 0.084 | | | |

Results are similar to those of the initial lambda value (24 hours) but the difference among the three PU systems became shorter: Supercritical CO₂ provided a thermal conductivity 33.2% higher than high water-HCFC-141b and 13.3% higher than low water-HCFC-141b.

Aging of Lambda, 4 weeks versus 24 hours

The variation percentage of the lambda value, four weeks versus 24 hours, was calculated and analysed in a similar way than the other properties.

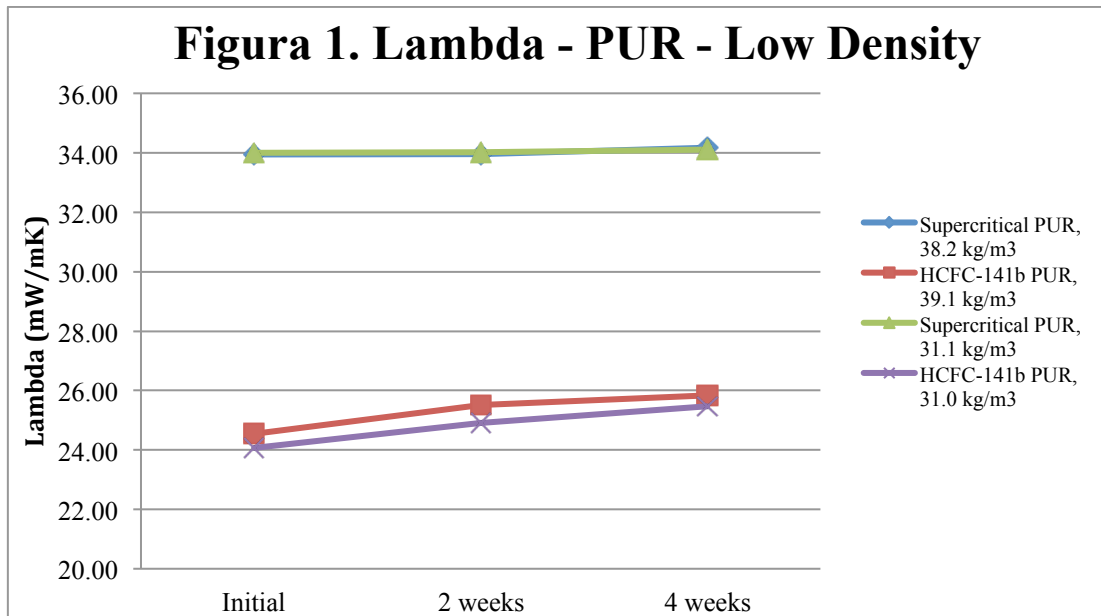
The tables 13 and 14 show a summary of the results and the corresponding ANOVA.

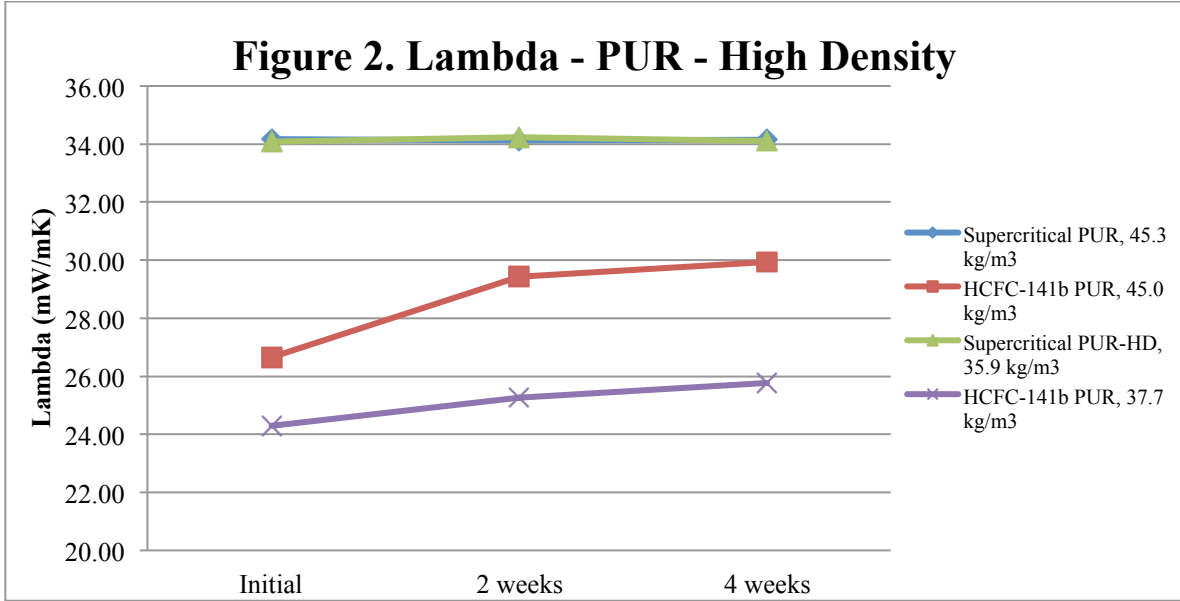
| | Supercritical CO ₂ | | HCFC-141b, low water | | HCFC-141b, high water | | AVERAGE |
|---------|-------------------------------|-------|----------------------|------|-----------------------|-------|---------|
| | HD | LD | HD | LD | HD | LD | |
| | Barranquilla | -0.08 | 0.64 | 5.33 | 5.26 | 12.39 | |
| Bogotá | 0.09 | 0.32 | 6.13 | 5.83 | 4.50 | 4.84 | 3.62 |
| AVERAGE | 0.24 | | 5.64 | | 6.58 | | |
| | AVERAGE | | | | | | |
| HD | 4.73 | | | | | | |
| LD | 3.58 | | | | | | |

| Table 14. ANOVA of variation percentage in lambda value | | | | | | |
|---|--------------------|----------------|-------------|-------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 2 | 187.161 | 93.581 | 28.17 | 0.000 | Significant |
| Density | 1 | 7.880 | 7.880 | 2.37 | 0.149 | |
| Location | 1 | 6.865 | 6.865 | 2.07 | 0.176 | |
| Tec*Dens | 2 | 20.403 | 10.202 | 3.07 | 0.084 | |
| Dens*Loc | 1 | 9.154 | 9.154 | 2.76 | 0.123 | |
| Tec*Loc | 2 | 23.233 | 11.617 | 3.50 | 0.064 | |
| Pure Error | 12 | 39.870 | 3.323 | | | |

The Supercritical CO₂ technology exhibited a statistically significant better performance than the 141b based systems: its variation percentage was in average 0.24% compared to 5.64% of low water-HCFC-141b and 6.58% of high water-HCFC-141b.

These results are graphically shown in figures 1 and 2.





5.2. PIR foam

Initial thermal conductivity for PIR

The tables 15 and 16 show the results of initial thermal conductivity (lambda) and the corresponding ANOVA.

| Table 15. Lambda Value, 24 °C, 24 hours, mW/mK | | | |
|--|-------------------------------|-----------|---------|
| | Supercritical CO ₂ | HCFC-141b | AVERAGE |
| Barranquilla | 34.35* | 28.16 | 31.25 |
| Bogotá | 34.07 | 20.76 | 27.41 |
| AVERAGE | 34.21 | 24.46 | |

* All the values are the average of two genuine replicates (table 7).

| Table 16. ANOVA of lambda value, 24 °C, 24 hours | | | | | | |
|--|--------------------|----------------|-------------|--------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 1 | 190.060 | 190.060 | 5590.0 | 0.000 | Significant |
| Location | 1 | 29.440 | 29.440 | 865.8 | 0.000 | Significant |
| Tec*Loc | 1 | 25.323 | 25.323 | 744.8 | 0.000 | Significant |
| Pure Error | 4 | 0.136 | 0.034 | | | |

From table 16 there is a statistical significant different in the initial lambda value between the two systems: on average Supercritical CO₂ developed a thermal conductivity 39.9% higher than HCFC-141b although the difference greatly varied with the location (significant interaction between technology and location).

Thermal Conductivity (lambda), aged 4 weeks at 20 °C and 50% RH, 24 °C

The tables 17 and 18 describe the results of the thermal conductivity (lambda), aged four weeks at 20 °C and 50% RH, and the corresponding ANOVA.

| Table 17. Lambda Value, 24 °C, 4 weeks, mW/mK | | | |
|--|-------------------------------|-----------|---------|
| | Supercritical CO ₂ | HCFC-141b | AVERAGE |
| Barranquilla | 34.06 | 29.51 | 31.78 |
| Bogotá | 33.59 | 23.41 | 28.50 |
| AVERAGE | 33.82 | 26.46 | |

| Table 18. ANOVA of lambda value, 24 °C, 4 weeks | | | | | | |
|--|--------------------|----------------|-------------|--------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 1 | 108.511 | 108.511 | 580.27 | 0.000 | Significant |
| Location | 1 | 21.550 | 21.550 | 115.24 | 0.000 | Significant |
| Tec*Loc | 1 | 15.839 | 15.839 | 84.70 | 0.001 | Significant |
| Pure Error | 4 | 0.748 | 0.187 | | | |

Results were similar to those of the initial lambda value (24 hours) but the difference between the two PU systems became shorter: Supercritical CO₂ provided a thermal conductivity 27.8% higher than HCFC-141b. It is important to note the significant interaction between the technology and location, especially in the case of HCFC-141b that provided when sprayed in Barranquilla a lambda 26% higher than the formulation applied in Bogotá. Supercritical CO₂ gave similar values for both locations.

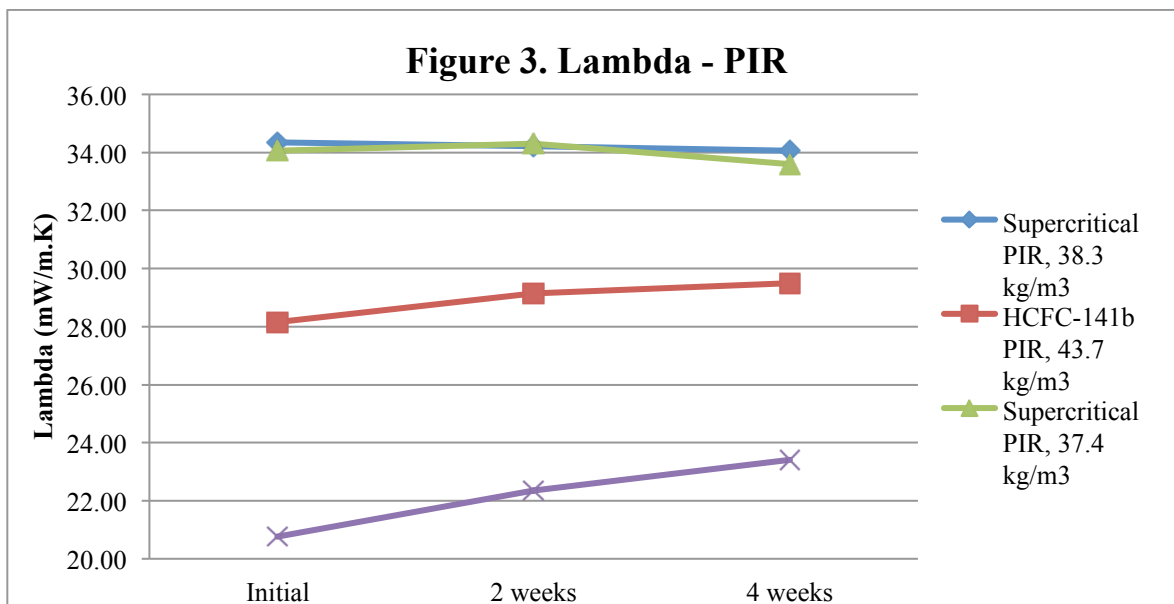
Aging of Lambda value, 4 weeks versus 24 hours

The variation percentage of the lambda value, 4 weeks versus 24 hours, was calculated and analysed in a similar way than the other properties. The tables 19 and 20 show a summary of the results and the corresponding ANOVA.

| Table 19. Variation Percentage in Lambda Value, 4 weeks versus 24 hours | | | |
|--|-------------------------------|-----------|---------|
| | Supercritical CO ₂ | HCFC-141b | AVERAGE |
| Barranquilla | -0.85% | 4.56% | 1.85% |
| Bogotá | -1.42% | 11.31% | 4.94% |
| AVERAGE | -1.14% | 7.93% | |

| Table 20. ANOVA of variation percentage in lambda value | | | | | | |
|--|--------------------|----------------|-------------|--------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 1 | 0.0164463 | 0.0164463 | 176.32 | 0.000 | Significant |
| Location | 1 | 0.0019077 | 0.0019077 | 20.45 | 0.011 | Significant |
| Tec*Loc | 1 | 0.0026864 | 0.0026864 | 28.80 | 0.006 | Significant |
| Pure Error | 4 | 0.0003731 | 0.0000933 | | | |

The Supercritical CO₂ technology exhibited a statistically significant better performance than the 141b based system: the lambda values measured in 4 weeks were in average 1.14% lower that the initials (24 hours) meanwhile the thermal conductivity of HCFC-14b based formulation increased by 7.93%. This result is graphically observed in figure 3.



6. SAFETY & INDUSTRIAL HYGIENE

The Supercritical CO₂ technology is based on PU all water blown systems. Compared to conventional HCFC-141b based formulations they do not exhibit any incremental issue on safety and industrial hygiene. Nevertheless, when not properly handled the PU chemicals can severely affect the human health. Handling procedures and precautions stipulated by suppliers should be followed. The Material Safety Data Sheets (MSDS) of the Achilles products for Supercritical CO₂ are provided in the Appendix.

7. INCREMENTAL COSTS OF THE SUPERCRITICAL CO₂ TECHNOLOGY

7.1. Incremental Capital Costs

Several conventional spray machines can be retrofitted to work with Supercritical CO₂ technology.

The critical features that they should have are:

Proportioning Pump: working pressure of 2,000 psi, piston stroke equal or higher than 3 inches.

Heated hose: longer than 45 meters (40 °C for PUR, 45 °C for PIR).

The table 39 lists the models of typical spray machines that are suitable for retrofit and the associated cost.

| Table 21. Suitable spray machines suitable to retrofit and associated retrofitting cost | | |
|--|-----------------------------|-----------------------------|
| Model | PUR (US dollars) | PIR (US dollars) |
| Gusmer models: FF 1600(converted hydraulically-driven), HF-1600 | 9,800 | 11,800 |
| Gusmer models: H-2000, H20/35 | 13,700 | 15,700 |
| Graco models: A-20, A25 | 9,800 | 11,800 |
| Graco models: H-25 | 13,700 | 15,700 |

The Supercritical CO₂ technology is a patented technology owned by Achilles Corporation. The interested parties should come to an agreement with Achilles on technology fees.

7.2. Incremental Operating Costs

The Supercritical CO₂ technology is based on proprietary polyol and isocyanate formulations developed by Achilles. The FOB price in Japan for the PUR and PIR systems is 7.00 US dollars per kg. The CIF price of a HCFC-141b based spray system for PUR in Colombia is in the range from 3.80 to 4.20 US dollars.

8. CONCLUSIONS

- Supercritical CO₂ technology is a non-flammable, 0 ODP and low GWP technology. Compared to HCFC-141b based technology it does not create any incremental industrial hygiene and safety hazard.
- Supercritical CO₂ is a proven commercialised technology for spray foam that has been used in Japan since 2004.
- In Colombia, a developing country with tropical weather and various levels of altitude over sea level, Supercritical CO₂ showed a similar processability to the standard HCFC-141b spray system currently used. Polyol and isocyanate components of both technologies were stable during the six months of project duration.
- In terms of physical properties of PUR foam, compared to HCFC-141b based formulations Supercritical CO₂ showed:
 - ✓ Higher thermal conductivity but better aging. The difference in lambda value between the two technologies decreased with time.
 - ✓ Similar aging behaviour in compressive strength. Values kept stable with time (initial versus six months)
 - ✓ Similar dimensional stability performance at -20 °C. All values for both technologies were below 0.6%.
 - ✓ Improved dimensional stability at 60 °C and 96% RH.
 - ✓ Similar adhesion strength to galvanised steel.
- In terms of physical properties of PIR foam, compared to HCFC-141b based formulations Supercritical CO₂ showed the same performance pattern than PUR:
 - ✓ Higher thermal conductivity but better aging. The difference in lambda value between the two technologies decreased with time.
 - ✓ Similar aging behaviour in compressive strength. Values kept stable with time (initial versus six months)
 - ✓ Similar dimensional stability performance at -20 °C. All values for both technologies were below 0.6%.
 - ✓ Similar dimensional stability at 60 °C and 96% RH in absolute values. However, the behaviour was totally different: meanwhile Supercritical CO₂ experienced a negative change in volume the HCFC-141b formulation had a positive one.
 - ✓ Lower adhesion strength to galvanised steel.
- According to fire performance test ASTM E84-12c, run on just one sample per formulation, the PIR and PUR foams based on Supercritical CO₂ would be classified as A and B respectively (NFPA).
- The cost of the required retrofit of a typical spray machine to apply the Supercritical CO₂ is in the range from 9,800 to 13,700 US dollars for PUR foam and from 11,800 to 15,700 US dollars for PIR foam.

- Supercritical CO₂ technology is based on proprietary polyol and isocyanate formulations developed by Achilles. The FOB price in Japan of the Supercritical CO₂ system by kg is 7 dollars.
- Supercritical CO₂ technology is a patented technology owned by Achilles Corporation. The interested parties should come to an agreement with Achilles on technology fees.

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ANNEX 1. ANALYSIS OF VARIANCE OF THE FOAM PROPERTIES

In the section 5 of the report the ANOVA corresponding to the foam thermal conductivity and its aging was presented. In this annex the ANOVA of the rest of the foam properties are shown for PUR and PIR.

1. PUR

Foam Core Density

The tables A-1 and A-2 show a summary of the results of the foam core density (values taken from table 6) and the corresponding ANOVA. As expected there are statistically significant differences in density between the high and low density formulations (HD > LD), explained by the different recipes, and between the two locations (Barranquilla > Bogota), explained by the different altitudes over sea level. It is also observed that Supercritical CO₂ and low water-HCFC-141b exhibit similar core densities, but lower than high water-HCFC-141b.

| Table A-1. Foam core density, kg/m³ | | | | | | | |
|---|-------------------------------|------|----------------------|------|-----------------------|------|---------|
| | Supercritical CO ₂ | | HCFC-141b, low water | | HCFC-141b, high water | | AVERAGE |
| | HD | LD | HD | LD | HD | LD | |
| Barranquilla | 45.3* | 38.2 | 43.9 | 39.2 | 45.1 | 47.8 | 43.23 |
| Bogotá | 36.0 | 31.1 | 37.7 | 31.1 | 42.6 | 35.6 | 35.63 |
| AVERAGE | 37.63 | | 37.94 | | 42.74 | | |
| | AVERAGE | | | | | | |
| HD | 41.73 | | | | | | |
| LD | 37.13 | | | | | | |

* All the values are the average of two genuine replicates

| Table A-2. ANOVA of foam core density, PUR | | | | | | |
|---|--------------------|----------------|-------------|-------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P* | |
| Technology | 2 | 131.401 | 65.701 | 13.99 | 0.001 | Significant |
| Density | 1 | 126.96 | 126.960 | 27.04 | 0.000 | Significant |
| Location | 1 | 346.56 | 346.560 | 73.81 | 0.000 | Significant |
| Tec*Dens | 2 | 18.483 | 9.242 | 1.97 | 0.182 | |
| Dens*Loc | 1 | 14.727 | 14.727 | 3.14 | 0.102 | |
| Tec*Loc | 2 | 1.308 | 0.654 | 0.14 | 0.871 | |
| Pure Error | 12 | 56.34 | 4.695 | | | |

The tables A-3 and A-4 show a similar summary and ANOVA than the tables A-1 and A-2 but only comparing Supercritical CO₂ and low water-HCFC-141b in an effort to check if there is a significant difference in density between these two formulations.

| Table A-3. Foam core density, kg/m ³ | | | | | |
|---|-------------------------------|------|----------------------|------|---------|
| | Supercritical CO ₂ | | HCFC-141b, low water | | AVERAGE |
| | HD | LD | HD | LD | |
| Barranquilla | 45.3 | 38.2 | 43.9 | 39.2 | 41.64 |
| Bogotá | 36.0 | 31.1 | 37.7 | 31.1 | 33.93 |
| AVERAGE | 37.63 | | 37.94 | | |
| | AVERAGE | | | | |
| HD | 40.70 | | | | |
| LD | 34.86 | | | | |

| Table A-4. ANOVA of foam core density, PUR | | | | | | |
|--|--------------------|----------------|-------------|-------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 1 | 0.391 | 0.4 | 0.06 | 0.810 | |
| Density | 1 | 136.306 | 136.3 | 21.64 | 0.002 | Significant |
| Location | 1 | 237.931 | 237.9 | 37.78 | 0.000 | Significant |
| Tec*Dens | 1 | 0.106 | 0.1 | 0.02 | 0.900 | |
| Dens*Loc | 1 | 0.131 | 0.1 | 0.02 | 0.946 | |
| Tec*Loc | 1 | 1.156 | 1.2 | 0.18 | 0.680 | |
| Pure Error | 8 | 50.385 | 6.3 | | | |

From table A-4 it is concluded that there is no evidence that there is a density difference between the two PU systems: Supercritical CO₂ and low water - HCFC-141b. Having in mind that some foam properties depend on the density, particularly compressive strength and dimensional stability, *this result is important for a fair comparison.*

Aging of Compressive Strength, 6 months versus 24 hours

Similar to the case of lambda (table 13), from the table 6 the variation percentage of compressive strength, 6 months versus 24 hours, was calculated and analysed (Tables A-5 and A-6). From the ANOVA there is no evidence of any difference in aging among the three PU systems.

| Table A-5. Variation Percentage in Compressive Strength, 6 months versus 24 hours | | | | | | | |
|--|-------------------------------|--------|----------------------|-------|-----------------------|-------|---------|
| | Supercritical CO ₂ | | HCFC-141b, low water | | HCFC-141b, high water | | AVERAGE |
| | HD | LD | HD | LD | HD | LD | |
| Barranquilla | 13.69 | 6.73 | 3.30 | 4.47 | -4.47 | -2.57 | 3.52 |
| Bogotá | -4.03 | -10.48 | -1.02 | -5.56 | 7.10 | 12.46 | -0.25 |
| AVERAGE | 1.48 | | 0.30 | | 3.13 | | |
| | AVERAGE | | | | | | |
| HD | 2.43 | | | | | | |
| LD | 0.84 | | | | | | |

| Table A-6. ANOVA of variation percentage in compressive strength | | | | | | |
|---|--------------------|----------------|-------------|-------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 2 | 0.324 | 0.162 | 0.72 | 0.506 | |
| Density | 1 | 0.151 | 0.151 | 0.67 | 0.428 | |
| Location | 1 | 0.857 | 0.857 | 3.82 | 0.074 | |
| Tec*Dens | 2 | 1.068 | 0.534 | 2.38 | 0.135 | |
| Dens*Loc | 1 | 0.005 | 0.005 | 0.02 | 0.883 | |
| Tec*Loc | 2 | 9.810 | 4.905 | 21.86 | 0.000 | Significant |
| Pure Error | 12 | 2.692 | 0.224 | | | |

Dimensional Stability

As observed in the table 6, the values of dimensional stability at low temperature (-20 °C) were all below 0.6%. For this reason it was decided to analyse the dimensional stability at 60 °C and 95% RH (tables A-7 and A-8).

| Table A-7. Dimensional Stability at 60 °C and 95% RH, two weeks, Vol. % | | | | | | | |
|--|-------------------------------|-------|----------------------|-------|-----------------------|-------|---------|
| | Supercritical CO ₂ | | HCFC-141b, low water | | HCFC-141b, high water | | AVERAGE |
| | HD | LD | HD | LD | HD | LD | |
| Barranquilla | -0.622 | 0.488 | 2.338 | 3.687 | 0.811 | 1.929 | 1.438 |
| Bogotá | 4.766 | 0.463 | 3.220 | 3.342 | 1.267 | 1.527 | 2.431 |
| AVERAGE | 1.274 | | 3.147 | | 1.383 | | |
| | AVERAGE | | | | | | |
| HD | 1.963 | | | | | | |
| LD | 1.906 | | | | | | |

| Table A-8. ANOVA of Dimensional Stability at 60 °C and 95% RH, two weeks | | | | | | |
|--|--------------------|----------------|-------------|-------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 2 | 17.6668 | 8.833 | 50.38 | 0.000 | Significant |
| Density | 1 | 0.0204 | 0.020 | 0.12 | 0.739 | |
| Location | 1 | 5.8979 | 5.898 | 33.64 | 0.000 | Significant |
| Tec*Dens | 2 | 7.1311 | 3.566 | 20.34 | 0.000 | Significant |
| Dens*Loc | 1 | 9.3507 | 9.351 | 53.33 | 0.000 | Significant |
| Tec*Loc | 2 | 8.5984 | 4.299 | 24.52 | 0.000 | Significant |
| Pure Error | 12 | 2.1039 | 0.175 | | | |

There is a statistically significant difference in dimensional stability among the three PU systems: Supercritical CO₂ provided the best performance (average 1.274 % in volume change) followed by high water-HCFC-141b (3.147 %) and low water-HCFC-141b (1.383 %). The fact that the location when the foam was raised gave a significant difference could be explained by the variation in atmospheric pressure that is in equilibrium with the cell pressure during the foaming process (Bogota: 560 mm Hg; Barranquilla: 760 mm Hg).

Adhesion to metal (galvanized steel)

The tables A-9 and A-10 show a summary of the results and the ANOVA for the adhesion strength to galvanized steel. From the statistical analysis it is concluded that none of the factors has a significant effect on adhesion. There is no evidence that there exists a difference among the performance of the three PU systems in relation to adhesion.

| Table A-9. Adhesion strength to metal, N/cm ² | | | | | | | |
|--|-------------------------------|--------|----------------------|-------|-----------------------|--------|---------|
| | Supercritical CO ₂ | | HCFC-141b, low water | | HCFC-141b, high water | | AVERAGE |
| | HD | LD | HD | LD | HD | LD | |
| Barranquilla | 14.144 | 17.946 | 7.922 | 2.983 | 14.124 | 13.627 | 11.791 |
| Bogotá | 7.887 | 15.117 | 21.355 | 8.241 | 17.310 | 15.530 | 14.240 |
| AVERAGE | 13.773 | | 10.125 | | 15.148 | | |
| | AVERAGE | | | | | | |
| HD | 13.790 | | | | | | |
| LD | 12.241 | | | | | | |

| Table A-10. ANOVA of Adhesion Strength to metal | | | | | | |
|---|--------------------|----------------|-------------|------|-------|--|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 2 | 107.79 | 53.90 | 1.14 | 0.353 | |
| Density | 1 | 14.41 | 14.41 | 0.30 | 0.592 | |
| Location | 1 | 35.98 | 35.98 | 0.76 | 0.401 | |
| Tec*Dens | 2 | 212.00 | 106.00 | 2.23 | 0.150 | |
| Dens*Loc | 1 | 6.06 | 6.06 | 0.13 | 0.727 | |
| Tec*Loc | 2 | 192.93 | 96.47 | 2.03 | 0.174 | |
| Pure Error | 12 | 569.58 | 47.47 | | | |

2. PIR

Foam Core Density

The tables A-11 and A-12 show a summary of the results of the foam core density (values taken from table 7) and the corresponding ANOVA.

| Table A-11. Foam core density, kg/m ³ | | | |
|--|-------------------------------|-----------|---------|
| | Supercritical CO ₂ | HCFC-141b | AVERAGE |
| Barranquilla | 38.25 | 43.69 | 40.97 |
| Bogotá | 37.40 | 32.33 | 34.87 |
| AVERAGE | 37.83 | 38.01 | |

| Table A-12. ANOVA of foam core density | | | | | | |
|--|--------------------|----------------|-------------|--------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 1 | 0.067 | 0.06700 | 0.018 | 0.899 | |
| Location | 1 | 74.517 | 74.51700 | 20.302 | 0.011 | Significant |
| Tec*Loc | 1 | 55.166 | 55.16600 | 15.030 | 0.018 | Significant |
| Error | 4 | 14.682 | 3.67050 | | | |

From the table A-12 there is no statistical evidence of a difference in density between the foam samples of the two PU systems, Supercritical CO₂ and HCFC-141b. The average values are quite close, 37.83 versus 38.01 kg/m³.

Dimensional Stability

Similar to what happened with PUR foam, the values of dimensional stability (Vol. %) at low temperature (-20 °C) were all below 0.6%. For this reason it was decided to analyse the most critical case: dimensional stability at 60 °C and 95% RH (tables A-13 and A-14).

| Table A-13. Dimensional Stability at 60 °C and 95% RH, two weeks, Vol. % | | | |
|---|-------------------------------|-----------|---------|
| | Supercritical CO ₂ | HCFC-141b | AVERAGE |
| Barranquilla | -4.051% | 3.756% | -0.147% |
| Bogotá | -4.841% | 5.740% | 0.450% |
| AVERAGE | -4.446% | 4.748% | |

| Table A-14. ANOVA of Dimensional Stability at 60 °C and 95% RH, two weeks | | | | | | |
|--|--------------------|----------------|-------------|--------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 1 | 0.0169067 | 0.0169067 | 337.12 | 0.000 | Significant |
| Location | 1 | 0.0000713 | 0.0000713 | 1.42 | 0.299 | |
| Tec*Loc | 1 | 0.0003848 | 0.0003848 | 7.67 | 0.050 | Significant |
| Pure Error | 4 | 0.0002006 | 0.0000502 | | | |

From the table A-14 there is a statistically significant difference in dimensional stability between the two PU systems. The behaviour was totally different: meanwhile Supercritical CO₂ experienced a negative change in volume the HCFC-141b formulation had a positive one. Similar to PUR the foams raised in Bogota experienced a greater volume change in absolute values that those developed in Barranquilla.

Adhesion to metal (galvanized steel)

The tables A-15 and A-16 show a summary of the results and the ANOVA for the adhesion strength to galvanized steel.

| Table A-15. Adhesion strength to metal, N/cm² | | | |
|---|-------------------------------|-----------|---------|
| | Supercritical CO ₂ | HCFC-141b | AVERAGE |
| Barranquilla | 8.146 | 16.637 | 12.392 |
| Bogotá | 7.958 | 9.061 | 8.509 |
| AVERAGE | 8.052 | 12.849 | |

| Table A-16. ANOVA of Adhesion Strength to metal | | | | | | |
|--|--------------------|----------------|-------------|-------|-------|-------------|
| Factor | Degrees of Freedom | Sum of Squares | Mean Square | F | P | |
| Technology | 1 | 46.032 | 46.032 | 13.07 | 0.022 | Significant |
| Location | 1 | 30.143 | 30.143 | 8.56 | 0.043 | Significant |
| Tec*Loc | 1 | 27.293 | 27.293 | 7.75 | 0.050 | Significant |
| Pure Error | 4 | 14.084 | 3.521 | | | |

The table A-16 shows that there is a significant difference in adhesion to galvanised steel between the two PU systems: in average the HCFC-141b based formulation gave an adhesion strength 59.6% higher than Supercritical CO₂.

ANNEX 2. Material Safety Data Sheets of Supercritical CO₂ components

See PDF attachment.