Annex V

DEMONSTRATION PROJECT AT FOAM SYSTEM HOUSES IN THAILAND TO FORMULATE PRE-BLENDED POLYOL FOR SPRAY POLYURETHANE FOAM APPLICATIONS USING LOW-GWP BLOWING AGENTS

WORLD BANK REPORT
SUBMITTED ON BEHALF OF THE ROYAL GOVERNMENT OF THAILAND

April 22, 2019

Introduction

1. The demonstration project at two foam system houses to formulate pre-blended polyol for spray polyurethane (PU) foam applications using low-global warming potential (GWP) blowing agent was submitted by the World Bank on behalf of the Royal Thai Government to the 75th meeting of the Executive Committee (ExCom) and resubmitted for the ExCom's approval at the 76th meeting. At the 76th meeting, the ExCom approved the project at a total cost of US $355,905.

2. The project was prepared consistent with the decision of the Meeting of the Parties (Dec. XIX/6) whereby there was a concern of the availability of validated cost effective and environmentally sound technologies to phase out HCFC-141b in the different foam applications in Article 5 countries.

3. The PU foam sector in Thailand comprises of 215 enterprises using 1,723 metric tons (MT) of HCFC-141b, in the manufacturing of rigid PU foam, including spray foam applications. Stage I of the HCFC Phase-out Management Plan (HPMP) of Thailand addressed 1,517 MT of HCFC-141b using in all PU foam applications, excluding consumption in the spray foam sub-sector due to the absence of low-GWP alternatives for this sub-sector. According to Stage II HPMP, the current HCFC-141b consumption in the spray foam sub-sector reduces from 349.1 MT in 2010 to 286.65 MT in 2017. The total HCFC-141b consumption is distributed among 102 spray foam enterprises of which, 71 enterprises were established prior to September 2007. Existing spray foam companies and their consumption is shown in Table 1.

Table 1: Summary of Spray Foam Companies and their Average HCFC-141b Consumption

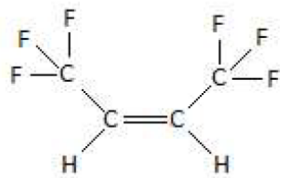
	No. of Companies	No. of Eligible Companies	Total HCFC-141b Consumption
Companies consume more than 10 MT	5	5	216.34
Companies consume more than 2 but less than 10 MT	10	8	52.41
Companies consume less than 2 MT	87	58	17.90
Total	**102**	**71**	**286.65**

4. The Stage II HPMP including funding for phasing out HCFC-141b in the spray foam was approved at the 82nd ExCom Meeting. The total funding provided for the spray foam sector, which is the only PU foam applications using HCFC-141b in Thailand, under the Stage II HPMP is US $1,732,597 to be released to Thailand from 2018 – 2022.

Background

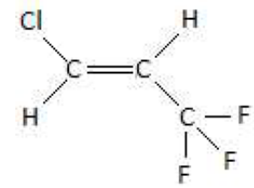
5. For developing countries, the proven technical options to replace HCFC-141b as a blowing agent for PU rigid foam are mainly limited to high GWP HFCs as HFC-245fa or HFC-365mfc/HFC-227ea blend, which have GWP values of 1030 and 965, respectively (100 years ITH, IPCC 4th Assessment Report 2008). Recent publications show promising results with the new unsaturated HFC/HCFC blowing agents, commonly known as HFOs, that exhibit GWP values lower than 10 (Bodgan, 2011; Costa, 2011). These options present themselves as viable alternatives not only their low GWP but also their better safety performance in comparison with hydrocarbon technology. Flammability is the critical barrier to the spray foam applications where most foam applicators are small and medium scale enterprise and the nature of the applications where significant leakage of blowing agents make hydrocarbon unacceptable.

6. The project was designed to evaluate two HFO molecules as co-blowing agents with CO_2 generated from the water-isocyanate reaction: HFO-1336mzz(Z) and HFO-1233zd(E) as per the project proposal that was approved by the ExCom. Figures 1 and 2 show the chemical formulas of the blowing agents evaluated in this project. The physical properties of the two HFO molecules are summarized in Table 2.



cis-1,1,1,4,4,4-hexafluoro-2-butene

Figure 1. HFO-1336mzz(Z)



(E) 1-chloro-3,3,3-trifluoropropene

Figure 2. HFO-1233zd(E)

Table 2: Physical Properties of HCFC-141b and HFOs

Property	**HCFC-141b**	**HFO-1336mzz(Z)**	**HFO-1233zd(E)**
Suppliers	-	Chemours	Arkema
Boiling Point (°C)	32	33	19
Thermal Conductivity of Gas (Mw/m.K) at 25oC	9.5	10.7	10
ODP	0.11	0	0
GWP	782	2	1

Project Objectives

(a) To strengthen the capacity of two local system houses to formulate, test and produce pre-blended polyol using HFOs (namely, HFO-1336mzz(Z) and HFO-1233zd(E)) for small and medium-sized enterprises (SMEs) in the PU spray foam sector;
(b) To validate and optimize the use of HFOs co-blown with CO_2 for spray foam applications to achieve a similar thermal performance to that of HCFC-141b with minimum incremental operating costs (to optimize the HFO ratio to 10 per cent);
(c) To prepare a cost analysis of the different HFO-reduced formulations versus HCFC-141b-based formulations; and
(d) To disseminate the results of the assessment to system houses in Thailand and other countries.

7. The approved demonstration project selected Bangkok Integrated Trading (BIT) and South City Petroleum, which are the two major suppliers of HCFC-141b pre-blended polyol to spray foam enterprises in Thailand. The two companies have different baseline technical capacities. BIT is a small-scaled system house with one chemist in its research team, while South City Petroleum is a much larger chemical company with a variety of products in addition to polyol systems. South City Petroleum has more than 4 chemists in their research and development team.

8. The project started on November 13, 2017 after the sub-grant agreements were signed by the enterprises and Government Savings Bank (GSB), the financial agent for the Multilateral Fund supported projects in Thailand. The implementation of the project was completed on December 15, 2018.

Project Implementation

Table 3. Project Implementation Timeframe

Activities	Actual Date
Planning for system development and verification testing	December 2017
Specification of foaming equipment and site preparation	July 2018
Procurement and installation of equipment at the system houses	July 2018
Raw materials acquisition	September 2018
Trials/testing/analysis	December 2018
Report and Review meeting.	December 2018
Technology dissemination workshop	December 2018
End of formula development	Mid of December 2018
Project completion (External testing completion)	Mid of January 2019
Submission of PCR	February 2019

Experimental

Experimental Design

9. At the beginning of the project, an international expert on foam formulations visited the two companies and provided them with technical training on the theory of the PU foam technology, and the basic concept for conducting the experiments. However, the actual design and implementation of the experiment was the responsibility of each system house. Therefore, the actual research and development process was varied from one company to another depending on the baseline technical capacity and the final formulations could be different as they were designed to meet the need of the different groups of clients.

10. In general, the experiments were conducted in three stages. The first stage was to determine blend stability of different formulations. The second stage was to determine the lowest percentages of the blowing agents in the blended polyol that provide desirable reactivity including cream time, gel time, and tact-free time. Once these percentages were determined, additional tests were done to determine physical properties of the foam products. These physical properties were density, K-factor, compressive strength, and dimension stability. The properties of new formulations were compared with the baseline HCFC-141b formulations.

Bangkok Integrated Trading

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11. To determine the optimum percentage of the new blowing agents, reactivity tests were carried out for 5 different percentages by weight of blowing agent to polyol (i.e., 5%, 10%, 15%, 20% and 25%). Compositions of raw materials are shown in Tables 4 and 5.

Table 4: Compositions of raw materials in HFO-1233zd(E) blended polyol formulation

Percentage of Blowing Agent	5%	10%	15%	20%	25%
Polyol (kg)	18	18	18	18	18
Water (kg)	0.558	0.486	0.414	0.342	0.27
Blowing Agent: 1233zd(E) (kg)	0.9	1.8	2.7	3.6	4.5

Table 5: Compositions of raw materials in HFO-1336mzz(Z) blended polyol formulation

Percentage of Blowing Agent	5%	10%	15%	20%	25%
Polyol (kg)	18	18	18	18	18
Water (kg)	0.63	0.54	0.45	0.36	0.27
Blowing Agent: 1336mzz(Z) (kg)	0.9	1.8	2.7	3.6	4.5

12. The detailed foam formulations for HFO-1233zd(E) and HFO-1336mzz(Z) developed by BIT for this demonstration project are summarized in Tables 6 and 7. Each formulation consisted of polyol, blowing agent, catalyst and additive, and isocyanate. For this demonstration project, BIT used a blend of sucrose-initiated polyol, Mannich-initiated polyol and polyester-initiated polyol. In addition, a combination of at least three catalysts were used to achieve desirable blowing, gelling and trimerization reactions. The test results provided initial indications on the optimal percentages of the blowing agents which did not severely affect the reactivity of the formulation. Once the optimal percentages were determined, further refinement of formulations were carried out to address other foam properties. The final percentage of the blowing agents may be slightly different from these initial tests.

Table 6: Foam system formulation for various percentage of HFO-1233zd(E) blowing agent and cost impact

Ingredients/HFO-1233zd(E)	5%	10%	15%	20%	25%	HCFC-141b
Blend of polyols, parts by weight	100	100	100	100	100	100
Catalyst package, parts by weight	5.30	5.30	5.30	5.30	5.30	5.44
HFO-1233zd(E), parts by weight	5.97	11.93	17.90	23.86	29.83	30.14
Iso/polyol index	1.15	1.15	1.15	1.15	1.15	1.15
HFO mole fraction in cell gas	0.18	0.34	0.47	0.59	0.70	0.85
HFO percent in foam, %	2.01	4.06	6.15	8.28	10.45	9.88
Cost of PU system, US$/kg*	2.18	2.39	2.61	2.83	3.06	2.15
Reduction percent, %	79.64	58.85	37.70	16.15	-5.80	

*Best estimates based on the initial formulations provided by the enterprise.

Table 7: Foam system formulation for various percentage of HFO-1336mzz(Z) blowing agent and cost impact

Ingredients/HFO-1336mzz(Z)	5%	10%	15%	20%	25%	HCFC-141b
Blend of polyols, parts by weight	100	100	100	100	100	100
Catalyst package, parts by weight	7.46	7.46	7.46	7.46	7.46	5.44

HFO-1336mzz(Z), parts by weight	6.33	12.65	18.98	25.30	31.63	30.14
Iso/polyol index	1.15	1.15	1.15	1.15	1.15	1.15
HFO mole fraction in cell gas	0.14	0.27	0.40	0.52	0.65	0.85
HFO percent in foam, %	2.01	4.09	6.24	8.46	10.76	9.88
Cost of PU system, US$/kg*	2.22	2.60	3.00	3.41	3.83	2.15
Reduction percent, %	79.64	58.60	36.85	14.34	-8.95	

*Best estimates based on the initial formulations provided by the enterprise.

13. Reactivities of all the formulations shown in Tables 6 and 7 were conducted by using cup tests. The following parameters were measured: (i) cream time; (ii) gel time; (iii) tact-free time; and (iv) free-rise density. The results of these tests are shown in Table 8.

Table 8: Results of Reactivity Tests for both blowing agents

Blowing Agent	**HFO-1233zd(E)**					**HFO-1336mzz(Z)**				
Percentage	5%	10%	15%	20%	25%	5%	10%	15%	20%	25%
Cream time (sec)	4	4	4	4	4	5	5	5	5	5
Gel time (sec)	9	9	10	10	10	9	9	9	9	9
Tact-free-time (sec)	15	16	16	16	16	15	16	15	16	15
Free-rise Density (Kg/m3)	35.5	35.5	35.5	35.6	35.6	36.7	36.7	36.75	36.7	36.7

14. Based on the results of the reactivity tests, all foam formulations exhibited similar and acceptable cream time, gel time, tact-free-time and free-rise density for both HFO-1233zd(E) and HFO-1336mzz(Z). Additional tests on adhesion and foam shrinkage were conducted. The 5% formulations for both HFO-1233zd(E) and HFO-1336mzz(Z) provided poor performance on the adhesion and shrinkage. At the 10% level and higher, the HFO-1336mzz(Z) blown foam rendered acceptable adhesion performance, and shrinkage was found to be limited. Through the evaluation of foam adhesion and shrinkage, the final percentages of blowing agent of 13% and 10% were selected for HFO-1233zd(E) and HFO-1336mzz(Z) formulations, respectively.

Table 9. Experimental Design

Factors (Independent Variables)	**Levels**
	Bangkok Integrated Trading
Type of HFO	HFO-1336mzz(Z)
	HFO-1233zd(E)
Mole fraction of HFO into the gas cells (reduction percent of HFO compared to HCFC-141b formulation)	0.85 (0%)
	0.35 (59%) HFO-1336mzz(Z)
	0.45 (47%) HFO-1233zd(E)

15. BIT's baseline HCFC-141b foam formulation having 0.85 mole fraction in the gas cells was used as a reference standard. Three specimens for each blowing agents were produced. The objective of BIT is to reduce HFO in the formulation in order to maintain price competitiveness to the extent possible when comparing with HCFC-141b formulation. The 10% HFO-1336mzz(Z) formulation results in the reduction of the mole fraction of the blowing agent in the gas cells to 0.35, which is equivalent to 59% reduction compared to HCFC-141b. Similarly, the 13% HFO-1233zd(E) formulation reduces the mole fraction of the blowing agent in the gas cells to 0.45, which is equivalent to 47% reduction compared to HCFC-141b formulation.

16. The isocyanate/polyol index is 115/100 for HFO-1336mzz(Z) and 115/100 for HFO-1233zd(E). The gel time and the free rise density are kept constant for all the experiments.

Responses and Test Methods

17. Table 10 summarizes the responses and associated test methods employed for determining the respective responses.

Table 10. Responses and Test Methods Employed by Bangkok Integrated Trading

Table 8 Responses and Test Methods: Bangkok Integrated Trading			
Property		**Test**	**Testing Laboratory**
Reactivity at machine		Visual	In-house
Density		ASTM D-1622	In-house
K-Factor		ASTM C-518	In-house
Compressive strength		ASTM D-1621	In-house
Adhesion strength		Metal Sheet and Roof Tile	In-house
Dimensional stability		ASTM D-2126	In-house
Aging (*)	K-Factor	ASTM C-518	In-house
	Compressive Strength	ASTM D-1621	In-house
Fire Performance		ASTM D-568-77, ASTM D-635-03	KMUTT

(*) K-Factor and Compressive Strength: 2 weeks, 3 weeks, 1 month

Preparation of Foam Samples

18. After blending the fully formulated polyol, the fully formulated polyol and isocyanate were applied by using a high-pressure machine GRACO Reactor H-VR sprayer (financed by the Project) at the conditions shown in Table 11. The final spray foam sheet was made by spraying the mixture of formulated polyol and isocyanate horizontally back-and-fort on a large cardboard paper at a rate of 3 – 4 passes per one inch of thickness. The final foam sheet has a thickness of 4 – 5 inches. Three foam sheets were made (one for each blowing agent: standard HCFC-141b; 13% HFO-1233zd(E) formulation; and 10% HFO-1336mzz(Z) formulation). All foam samples/specimens for different blowing agents were made from the respective foam sheets by cutting the sheets into a number of pieces with specific dimensions conforming with testing standards summarized in Table 10.

Table 11. Spray Foam Conditions

Spray machine	GRACO Reactor H-VR Sprayer
Spray gun	Air Purge Spray Gun
Percentage by weight of CO_2, %	Not applicable
Ambient Temperature, ºC	28º – 32ºC
Relative Humidity, %	52% - 62%
Substrate Temperature, ºC	40ºC
Iso Temperature, ºC	50ºC
Polyol Temperature, ºC	50ºC
Primary Heater	Off

Hose length, m	15
Hose Temperature, ºC	50ºC
Static Pressure, psi	1,700
Dynamic Pressure, psi	1,700

Stability of Polyol Blend

19. Polyol blended with HFO-1336mzz(Z) using regular catalysts demonstrates excellent stability. To achieve the same results with HFO-1233zd(E), special catalysts are required. Polyol with catalysts and additives were mixed and retained in test tubes from 1 – 3 weeks. All formulations showed good stability. There was no precipitation observed after three weeks. Table 12 summarizes the reaction times of the three different foam formulations.

Table 12. Reactivities of Baseline Foam Formulations and those with New Blowing Agents

Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
Mole fraction in the gas cells	0.85	0.45	0.35
Weight of blowing agent in formulation (%)	9.88	4.32	5.43
Reduction by weight (%)	0	56.25	44.99
Cream time (sec)	4	4	5
Tack free time (sec)	14	16	16
Cream time (sec) after 1 week	4	4	5
Tack free time (sec) after 1 week	14	16	16

20. The stability tests on foam reactivity and physical properties such as dimensional stability, K-factor, and compressive strength were conducted and the results of three different blowing agent formulations are shown in Tables 13 - 15. It was found that reactivity times of new foam formulations (with 13% of HFO-1233zd(E) are similar to reactivity times of HCFC-141b blown foam.

Table 13. Dimensional Stability

Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
Foam density (kg/m^3)	38.04	38.77	39.07
Dimension stability 70ºC (%ΔV), 24 hrs	0.30	0.59	0.47
1st week	0.40	0.68	0.58
2nd week	0.46	0.73	0.63
Dimension stability -30ºC (%ΔV), 24 hrs	-0.64	-0.57	-0.70
1st week	-0.87	-0.77	-0.83
2nd week	-0.90	-0.82	-0.92
Dimension stability 70ºC+95% RH (%ΔV), 24 hrs	0.47	2.03	1.82
1st week	0.71	2.06	1.86

2nd week	0.94	2.13	2.02

21. The density of the foam blown with HFO-1233zd(E) an HFO-1336mzz(Z) was slightly higher than the density of the HCFC-141b blown foam. The density increase was less than 3% in comparison with the HCFC-141b blown foam. Dimension stability of foam produced with new HFO formulation was comparable to HCFC-141b blown foam. After two weeks, the foam dimension changes were within 1 - 2% for the three testing conditions (-30°C, 70°C, and 70°C with high humidity level).

Table 14. Comparison of K-Value of HFCF-141b with K-Factor of HFOs Blown Foam

Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
Initial K-Factor (mW/m.K)	21.40	24.20	26.10
2nd week	22.00	24.90	27.00
3rd week	22.40	25.40	27.30
4th week	22.70	26.00	27.80

Note: The variance in densities of foam samples from unevenly spraying makes comparison a challenge.

22. The initial K-values of 13% HFO-1233zd(E) and 10% HFO-1336mzz(Z) blown foam were higher than the K-value of HCFC-141b blown foam. The increase is about 10% for the HFO-1233zd(E) formulation and about 20% for the HFO-1336mzz(Z) formulation). The insulation property gradually deteriorated over time. While the K-value of the HFO-1336mzz(Z) formulation was the highest; however, it showed a slower rate of increase after four weeks in comparison with the HFO-1233zd(E) formulation.

23. The 10% increase in the K-value was acceptable to BIT's spray foam customers. Hence, the HFO-1233zd(E) formulation was more desirable. To make the insulation performance of the HFO-1336mzz(Z) formulation comparable to the HFO-1233zd(E) formulation, BIT could have increased the amount of the blowing agent; however, such increase would result in a higher cost which was not desirable.

Table 15. Compressive Strength

Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
Initial Compressive Strength (kPa)	184.80	188.20	190.59
2nd week	185.97	187.38	189.34
3rd week	183.94	188.75	191.49

Note: Compressive strength of test samples vary depending on quality of the foam cells which affects the compressive strength of the test samples.

24. The experiment showed that the compressive strength of spray foams produced by three different formulations were comparable and stable over the experiment period of three weeks.

Fire Performance

Table 16. Results of Fire Performance Tests Based on ASTM Standards

Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
ASTM D568-77	-	Extinguished	Extinguished
ASTM D635-03	-	Extinguished	Extinguished

Note: Tests were conducted at KMUTT

25. The foam specimens based on the two HFO formulations were subject to fire safety tests which were conducted by King Mongkut University of Technology Thonburi's (KMUTT) laboratory. The testing procedures of ASTM D568-77 and ASTM D635-03 were employed. The test results confirmed that HFO-1233zd(E) blown foam and HFO-1336mzz(Z) foam met the fire safety standards.

Field Test

26. Two field tests were conducted at Bangkok Integrated Trading's facility. Two of its major customers were invited to witness the field test. The test simulates applying spray foam on the wall by spraying two new foam formulations against a metal sheet and roof tiles. Visual inspection and simple tests were conducted at the sites. Based on this set-up, the customers are satisfied with the basic properties of the spray foam made from both HFO-1233zd(E) and HFO-1336mzz(Z) formulations. These properties include cell size appearance, reaction time, adhesion and foam strength. The costs of the two formulations are similar. The customers preferred the spray foam made from HFO-1233zd(E) blowing agent due to its foam appearance.

Fig. 3 Field Demonstration of HFO blown foam (HFO-1233zd(E)) at BIT

Fig. 4 Field Demonstration of HFO blown foam (HFO-1336mzz(Z)) at BIT

Incremental Capital Cost

27. The demonstration project as approved by the ExCom also provided financial supports to BIT to acquire one spray foam machine and thermal conductivity testing machine. These pieces of equipment were critical to the development of new foam formulations and for demonstration of the final products. As described in the project proposal, the enterprise anticipated that reduction of the blowing agent in the formulation would require additional water content in the polyol system and that consequently led to the increasing ratio of isocyanate and polyol (different foam index). Therefore, the spray foam machine with adjustable ratios of isocyanate and polyol was acquired by the project. To facilitate development and testing of new formulation, the thermal conductivity testing machine was provided.

28. The spray foam machine purchased by BIT was made by a Graco machine (Model: Reactor H-VR). The injection rates of isocyanate and polyol could be varied within the range from 1:1 to 2.5:1. The thermal conductivity tester purchased by BIT are Thermtest Model HFM-100. The approved funding levels for the spray foam machine and thermal conductivity tester were US $40,000 and US $5,000, respectively. The actual costs paid by BIT were US $43,675 and US $29,821, respectively. Detailed financial information will be provided in the Project Completion Report.

Cost Effectiveness of BIT's HFO Based Formulations

29. Cost comparison and cost effectiveness of the two new foam formulations were calculate based on the chemical costs purchased by BIT. Table 17 was developed based on the following costs of the following chemicals: US $3.20/kg of HCFC-141b; US $16/kg of HFO-1233zd(E); and US $22/kg of HFO-1336mzz(Z).

Table 17. Cost of Foam Production and Incremental Operating Cost of HFO Formulations

BIT	141b system			1233zd(E) system			1336mzz(Z) system		
	Parts	Unit Cost (US$/kg)	Price	Parts	Unit Cost (US$/kg)	Price	Parts	Unit Cost (US$/kg)	Price
Polyol Blend	100.00	1.86	186.00	100.00	1.71	171.00	100.00	1.69	169.00
Additives & Catalysts	5.44	10.50	57.12	5.30	12.50	66.27	13.26	3.98	52.74
Other Additives	15.13	2.50	37.83	16.00	2.26	36.20	16.57	1.90	31.48
Blowing Agent	30.14	3.20	96.45	12.00	16.00	192.00	16.57	22.00	364.54
Sub-total	150.71		377.39	133.30		465.47	146.40		617.76
Isocyanate	154.48	1.80	278.06	144.41	1.80	259.94	158.60	1.80	285.48
Sub-total	154.48		278.06	144.41		259.94	158.60		285.48
Total	305.19		655.46	277.71		725.41	305.00		903.24
Price of foam (US$/kg)			2.15			2.61			2.96
IOC (US$/kg 141b)						4.72			8.24

30. While the cost of producing on kg of foam increased by 20% - 40% in comparison with the cost of the baseline foam produced with HCFC-141b. The incremental operating costs of the new HFOs formulations were about US $4.72 – US $8.24/kg of HCFC-141b.

South City Petroleum

31. Almost all spray foams in Thailand prefer to purchase polyol systems pre-mixed with a blowing agent. The objective is to replace HCFC-141b with HFO-1233zd(E) and HFO-1336mzz(Z) without significantly increasing the price of the pre-blended polyol since the spray foam market is extremely price sensitive. Because of this constraint, the company aims to develop new HFO formulations with the HFO content not exceeding 10% of the weight of the polyol without significantly compromising the foam performance. Reactivity tests were conducted for two different percentages of the blowing agents (both HFO-1233zd(E) and HFO-1336mzz(Z)) at 5% and 10% of the weight of the polyol. At the five percent of both blowing agents, the amount of the water content to compensate the lower amount of blowing agents exceeded 4.5% in the formulations. The higher water content demonstrates adverse effects on the foam stability. Hence, only the 10 percent blowing agent formulation was further developed. The isocyanate/polyol index of at least 120 was employed to reduce friability problems and increase the catalyst to enhance trimerization in order to improve flam retardant property and foam strength.

Table 18. Experimental Design

Factors	**Levels**		
Blowing Agent	**% Usage in Blended Polyol**	**Mole Fraction in Gas Cell**	**% Reduction**
HCFC-141b	30	0.84	
HFO-1336mzz(Z)	10	0.34	59.52
HFO-1233zd(E)	10	0.37	55.95
HFO-1336mzz(Z)	5	0.17	79.76
HFO-1233zd(E)	5	0.16	80.95

Type	HCFC-141b	HFO-1233zd(E)	HFO-1336mzz(Z)	HFO-1233zd(E)	HFO-1336mzz(Z)
	30%	10%		5%	
Initial mole fraction, CO_2	0.16	0.63	0.66	0.64	0.83
Initial mole fraction, blowing agent	0.84	0.37	0.34	0.16	0.17

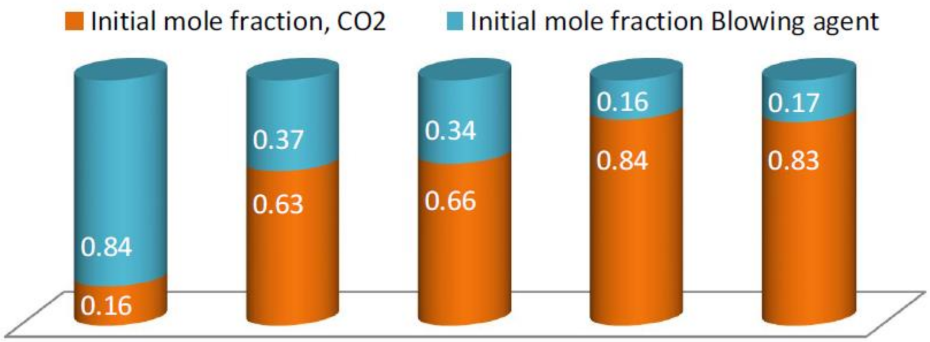


Fig. 5 Initial mole fractions of two co-blowing agents

Fig. 6 Cup tests for the two new HFO formulations

32. As mentioned above, the 5% HFO formulations contained more than 4.5% of water in the formulations. The high-water content could adversely affect chemical stability of polyester initiated polyols and some water-sensitive catalysts, which could result in formation of more opened cells, higher K factors and friability of the final foam products.

33. The characteristics of foam blown with 10% of HFO-1233zd(E) and HFO-1336mzz(Z) are summarized in Table 19. With 10% of the blowing agents, both formulations require an additional amount of water in order to maintain the free rise density at the same level as the HCFC-141b formulations.

Table 19. Characteristics of Foam with Alternative Glowing Agents

Type	**HCFC-141b**	**HFO1233zd(E)**	**HFO-1336mzz(Z)**
CO_2 moles/kg of polymer	0.23	0.63	0.68
Blowing agent moles/kg of polymer	1.24	0.36	0.34
Total gas moles/kg of polymer	1.47	0.99	1.02
Initial mole fraction, CO_2	0.16	0.63	0.66
Initial mole fraction, Blowing agent	0.84	0.37	0.34
Blowing agent in foam (%)	12.66	4.49	5.28
Reduction percent (%)	-	64.56	58.29

Preparation of Foam Samples

34. After blending the fully formulated polyol, the fully formulated polyol and isocyanate were applied by using a high-pressure machine GRACO Reactor H-VR sprayer (financed by the Project) at the conditions shown in Table 20.

Table 20. Spray Conditions

Spray Gun	Fusion AP
Injection pressure, psi	1200
Isocyanate temperature, ^{o}C	Room temperature
Polyol temperature, ^{o}C	40 - 45
Substrate (metal sheet and roof tile) temperature* ^{o}C	Room temperature (28^{o}C)

*Samples for adhesion tests

35. The final spray foam sheet was made by spraying the mixture of formulated polyol and isocyanate horizontally back-and-fort on a large cardboard paper at a rate of 3 – 4 passes per one inch of thickness. The final foam sheet has a thickness of 4 – 5 inches. Three foam sheets were made (one for each blowing agent: standard HCFC-141b; 10% HFO-1233zd(E) formulation; and 10% HFO-1336mzz(Z) formulation). All foam samples/specimens for different blowing agents were made from the respective foam sheets by cutting the sheets into several pieces with specific dimensions conforming with testing standards summarized in Table 21.

Table 21. Test Methods Employed by South City Petroleum

<table>
<tr><th colspan="5">Table X. Test Methods: South City Petroleum</th></tr>
<tr><th colspan="2">Property</th><th>Test</th><th>Testing Laboratory</th><th>Specimen Dimension</th></tr>
<tr><td colspan="2">Reactivity at machine</td><td>Visual</td><td></td><td></td></tr>
<tr><td colspan="2">Density</td><td>ASTM D-1622</td><td>In-house</td><td>10 cm * 10 cm * 10 cm</td></tr>
<tr><td colspan="2">K Factor</td><td>ASTM C-518</td><td>HFM-100 Heat flow meter from Thermtest, Canada and Eko Japan</td><td>30 cm * 30 cm * 2.54 cm</td></tr>
<tr><td colspan="2">Compressive Strength</td><td>ASTM D-1621</td><td>In-house</td><td>3 cm * 3 cm * 3 cm</td></tr>
<tr><td colspan="2">Adhesion Strength</td><td>Hand Peeling</td><td>In-house</td><td>Roof tile and netal sheet</td></tr>
<tr><td colspan="2">Dimension Stability</td><td>ASTM D-2126</td><td>In-house</td><td>10 cm * 10 cm * 10 cm</td></tr>
<tr><td colspan="2">Water Absorbent*</td><td>Volume (%)</td><td>In-house</td><td>10 cm * 10 cm * 2.54 cm</td></tr>
<tr><td rowspan="2">Aging*</td><td>K Factor</td><td>ASTM C-518</td><td>HFM-100 Heat flow meter from Thermtest, Canada and Eko Japan</td><td>30 cm * 30 cm * 2.54 cm</td></tr>
<tr><td>Compressive Strength</td><td>ASTM D-1621</td><td>In-house</td><td>3 cm * 3 cm * 3 cm</td></tr>
<tr><td colspan="2" rowspan="2">Fire Performance</td><td>UL94</td><td>National Metal and Materials Technology Center (MTEC)</td><td>1.3 cm * 12.5 cm * 1.3 cm</td></tr>
<tr><td>ASTM D-568 and ASTM D-635</td><td>Institute for Scientific and Technological Research and Services (ISTRS), King Mongkut University of Technology Thonburi (KMUTT)</td><td>50 cm * 10 cm * 3 cm</td></tr>
</table>

*K factor: 1 week and 1 month; compressive strength: initial and 1 month; and water absorbent: 2 hours and 24 hours.

Stability of Polyol Blend

36. The stability of fully formulated polyol was evaluated by monitoring the hand-mixed reactivity in the laboratory. The results are summarized in Table 22.

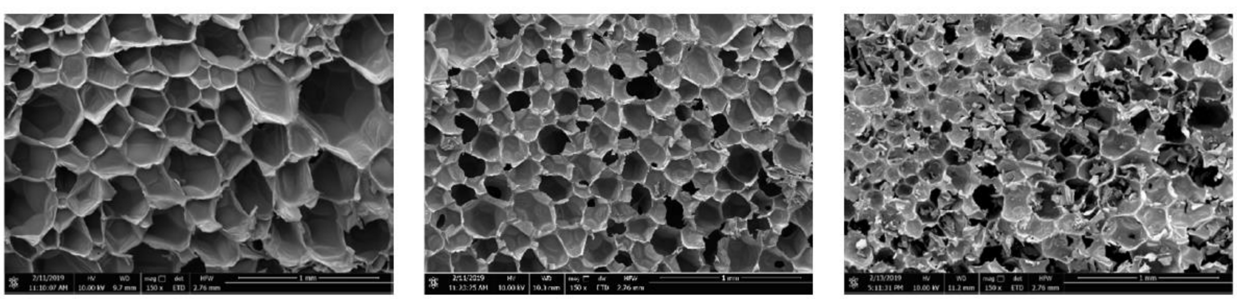
Table 22. Stability of Polyol Blends

Blowing Agent	HCFC-141b	HFO-1233zd(E)			HFO-1336mzz(Z)		
Mole fraction in gas cells	0.84	0.37			0.34		
Weight percent of blowing agent in formulation (%)	30.00	10.00			10.00		
Mole fraction different percent (%)	-	55.95			59.52		
Chemical characteristics	initial	initial	2nd Week	4th Week	initial	2nd Week	4th Week
Cream time (sec)	3	4	4	4	4	4	4
Gel time (sec)	5	6	6	6	6	7	6
Track free time (sec)	8	7	7	7	7	8	7
End of rise (sec)	12	13	13	14	14	14	15
Cup density (kg/m^3)	30.63	32.98	34.45	34.96	35.14	35.68	36.55
Upper cup density (kg/m^3)	26.09	26.29	25.59	26.86	27.23	28.13	26.26

37. All samples were kept at the normal room temperature which is the industry practice for storing the raw materials. The results confirmed that reaction activities of both HFO formulations are quite stable. However, it was still advisable that the HFO-1233zd(E) pre-blended polyol be stored in air-conditioned room as the temperature of the storage rooms could become much higher in summer.

Cell Structure Appearance

38. Cell structures of foams produced by different blowing agents are showed in Fig. X. The test results confirmed that foams produced by the three formulations (30% HCFC-141b; 10% HFO-1233zd(E); and 10% HFO-1336mzz(Z) contained mostly spherical shapes resulting in higher compressive strength and good dimension stability. However, the test results also showed that due to a higher water level in the formulations, the foam structures contained more opened cells.



(a) 30% HCFC-141b (b) 10% HFO-1233zd(E) (c) 10% HFO-1336mmz(Z)

Fig. 7 Cell Structures of Foam Produced from Three Different Blowing Agents

Compressive Strength

39. Comprehensive strength of foam produced with three different blowing agents: (i) 30% HCFC-141b formulation; (ii) 10% HFO-1233zd(E) formulation; and (iii) 10% HFO-1336mzz(Z) formulations was measured immediately after the production and one month later. For each formulation, separate sets of samples were tested for the initial compressive strength and the compressive strength after 1 month. Since the foam samples were made from larger foam sheets that were sprayed manually, the property of the foams may not be consistent, and it may affect the accuracy of the results.

Table 23. Compressive Strength (kPa)

Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
Initial	194.00	256.00	206.00
1 month later	189.73	204.77	244.37

40. In spite of the above imperfection, the test results suggested that the new HFO formulations provided the final foam products with higher compressive strength than the foam products made with the HCFC-141b formulation. This improvement may be attributed to the use of different combinations of polyol types to compensate with the counter effect from the higher level of water in the formulations.

Dimension Stability

41. The dimension stability tests were conducted at two different temperature levels at two different occasions. The first tests were undertaken one week after the foam samples were made, and the second tests were done another week later. At both temperature levels, the foam products made by the new formulations exhibited acceptable dimension stability. That is, the volumes of the samples changed less than 2% during the first two weeks after the samples were made. The results are shown in Table 24.

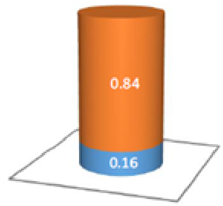
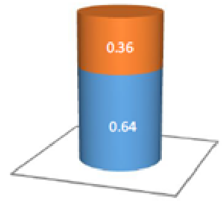
Table 24. Results of Dimension Stability Tests

Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
Foam Density (kg/m^3)	38.18	39.51	34.64
Dimension Stability at 70 ºC (%ΔV)			
1st Week	1.96	0.43	-0.56
2nd Week	1.90	0.37	-0.71
Dimension Stability at -30 ºC (%ΔV)			
1st Week	-0.34	-0.46	-0.48
2nd Week	-1.39	-0.46	-0.31

K-Factor

42. The test results confirmed that the new HFO formulations had higher thermal conductivity than the HCFC-141b formulation. This was anticipated since the HFO formulations resulted in foam products with a higher mole fraction of CO_2 in the foam cells.

Table 25. K-Factors (mW/mK)*

Blowing Agent	HCFC-141b		HFO-1233zd(E)		HFO-1336mzz(Z)	
Mole Fraction in Gas Cell Blowing Agent CO_2						
Foam Density (kg/m^3)	38.57	40.67	47.82	44.38	43.86	47.24
1st Week	20.00	21.94	24.74	22.19	26.88	21.58
4th Week	23.40	23.70	28.56	29.50	31.16	30.70

*Upper temperature: 35ºC; Lower temperature: 15ºC; Mean temperature: 25ºC

43. Because of the expected ununiform foam structure due to the manual spray operations, two samples were used for each test condition. The variance densities of the foam samples were the outcome of the unevenly spraying process.

44. In general, it was still reasonable to draw a conclusion that the foam products manufactured from the two HFO formulations had higher thermal conductivity that those produced with the HCFC-141b formulations. This was the direct implication of having a higher mole fraction of CO2 in the gas cells. However, the increase was slightly higher, which was around 21.58 – 26.88 mW/mK, when the foam products were kept at the room conditions for one week. This range was acceptable to the industry. The thermal conductivity continued to change over the course of one month.

Hand Peeling Adhesion Tests

45. Since most spray foam applications in Thailand were done on metal sheet roof and roof tile or concrete, the adhesion tests were made to demonstrate the adhesion strength of the spray foams against these two substrates. The samples were prepared by spraying three different fully blended polyols and isocyanate on the two substrates at 28ºC. The adhesion tests were done by peeling the foam out from the substrates. Three different failure types including the foam adhesive failure, thin layer cohesive failure, and cohesive failure, were observed. It was considered an adhesive failure if the foam could be removed completely from the surface. The thin layer cohesive failure was considered if it left a thin layer of foam on the surface of the substrates. Foams with a good adhesion property were those foams that could not be peeled off from the surface of the substrates. The peeling force applied to the samples would result in foam cracks. The test results are summarized in Table 26.

Table 26. Hand-Peeling Adhesion Test Results

Materials	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
Metal sheet roof	**100% Thin layer Failure**	**100% Thin Layer Failure**	**100% Thin Layer Failure**
Adhesion Performance	Good	Good	Good
Roof tile	**100% Cohesive Failure**	**100% Cohesive Failure**	**100% Cohesive Failure**
Adhesion Performance	Excellent	Excellent	Excellent

46. All foams adhered excellently on the roof tile. High peeling force was required and resulted in breaking the foam. This failure mode is shown in Fig. 8.

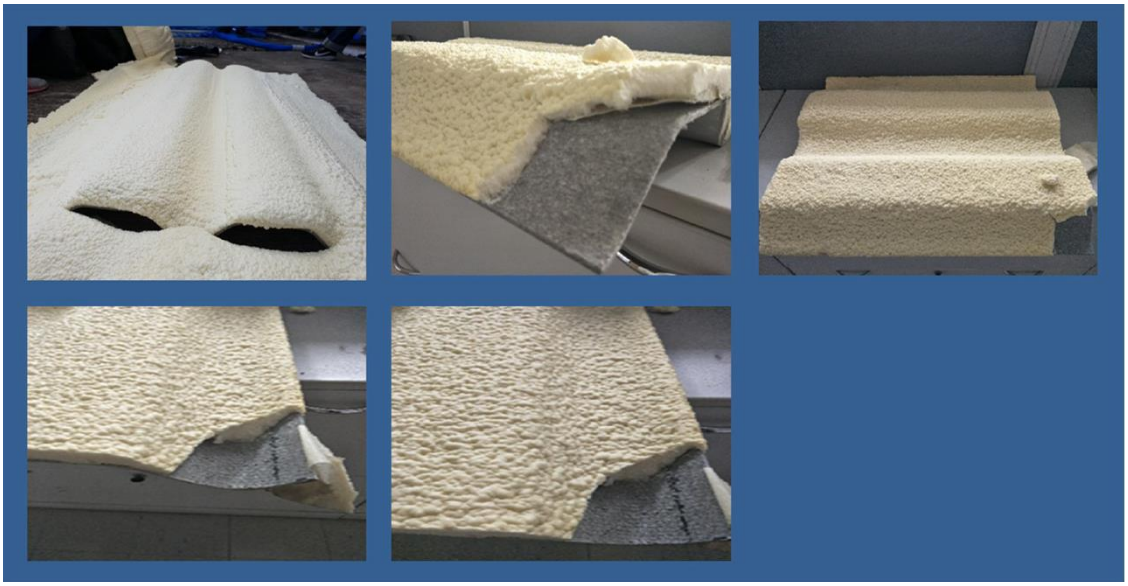


Fig. 8 Hand-peeling tests for spray foam with a roof tile as substrate

47. For the metal roof surface, all foams were peeled out of the surface of the substrate by high peeling force; however, there was thin skin of foam remaining on the metal surface as shown in Fig. 9.

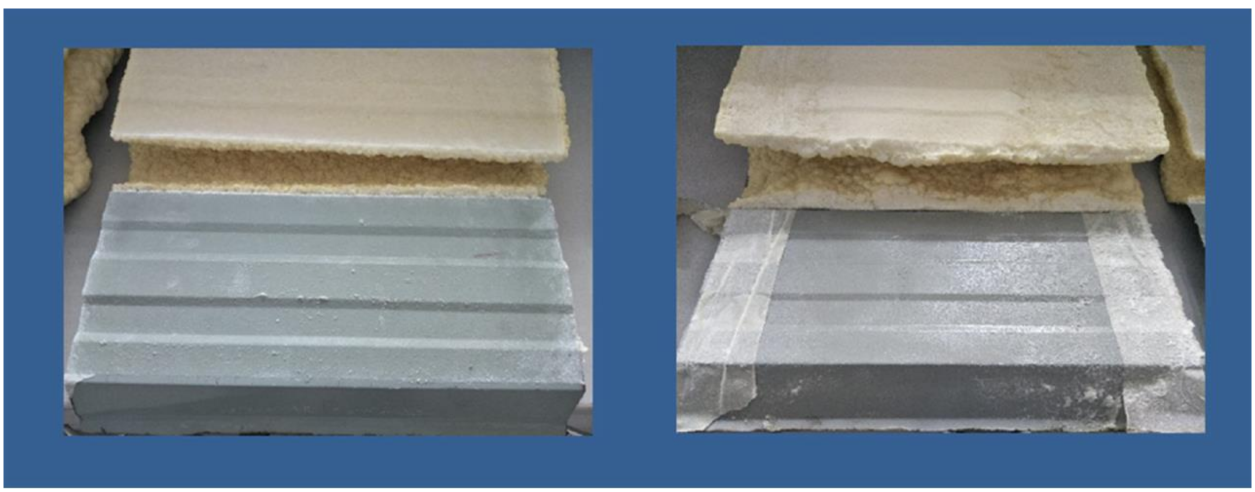


Fig. 9. Hand-Peeling Tests for spray foam with metal roof sheet as a substrate.

Water Absorbent

48. South City Petroleum also conducted water absorbent tests of their baseline and new HFO formulations because this property was considered as one of the key parameters in its product specifications. Four samples from each formulation were prepared. The four samples were divided into two groups. The first two were immerged into water for two hours. Another set of two samples for each formulation were immerged into water for four hours before the tests were taken.

49. The results of the water absorbent tests for a total of 12 samples produced with three different formulations were summarized in Table 27.

Table 27. Water Absorbent Test Results (%Volume)

Blowing Agent	**HCFC-141b**		**HFO-1233zd(E)**		**HFO-1336mzz(Z)**	
Dipping period	2 hrs.	24 hrs.	2 hrs.	24 hrs.	2 hrs.	24 hrs.
Sample 1	0.83	2.61	1.01	3.11	1.06	3.11
Sample 2	1	2.34	1.51	4.27	1.55	3.81

50. Foam samples made from the two new HFO formulations demonstrated higher percentage of water absorbent that the HCFC-141b formulated foam samples. The higher water absorbent in the HFO formulations was the results of more opened cells in the foam structure due to the increasing water content in the HFO formulations which was required to compensate for the lower quantity of the blowing agents.

Fire Performance

51. Flame retardant property of foams blown with different blowing agents was conducted by employing two different international standards: (i) UL 94; and (ii) ASTM -568 and ASTM D-635. Foam samples made from the two HFO formulations passed the UL 94 standard V-0 level tests. The foam samples that were subject to a vertical flame stopped within 10 seconds and the foam drips were not inflamed.

52. The ASTM D-568 standard tests confirmed that the foam samples made with the HFO formulations were self-extinguished within 1 – 2 seconds when they were subject to a vertical flame. Moreover, the burn propagated less than 3 mm. Similarly, the ASTM D-635 standard tests for a horizontal flame position also yielded the same results for the samples made from the two HFO formulations. Therefore, these foam samples were considered to meet ASTM D-568 and D-635 standards. The test results based on both standards are summarized in Table 28.

Table 28. Fire Performance Test Results

Table XX. Fire Performance Test Results			
Blowing Agent	**HCFC-141b**	**HFO-1233zd(E)**	**HFO-1336mzz(Z)**
UL 94	V-0	V-0	V-0
ASTM D-568 and ASTM D-635	Self-Extinguished	Self-Extinguished	Self-Extinguished

Field Tests

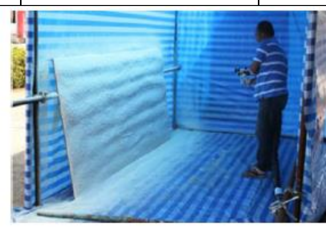
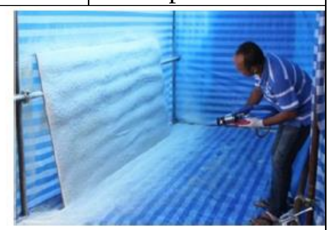
53. Because of a lower quantity of an HFO blowing agent in order to keep the product cost competitive, the rising of foam had to be compensated by generating CO2 as a co-blowing gas from the additional water content to enhance the water-isocyanate reaction. Therefore, the new HFO formulations, which had a higher water content, consumed more isocyanate. The ratio between the HFO blended polyol and isocyanate was adjusted to about 0.78:1 or 0.82:1 by volume. However, most Thai spray foamers only had spray machines with a fixed ratio at 1:1 by volume. As a result, the field tests were then operated at South City Petroleum’s facility.

54. Two major spray foam companies in Thailand (Narongrit, and Lohr Trade and Consulting) were invited to participate in the field test on December 11, 2018. Both spray foam companies had opportunities to use South City Petroleum’s spray machine funded by the MLF to spray the two new HFO formulations

and to inspect the final foam products. At the end of the field test, both enterprises were asked for their opinions on the following: chemical reaction, foam appearance, foam strength, adhesion performance, and the overall view of the two new HFO formulations. The results of the interviews were included in Table 29.

Table 29. Field Test Interview Results

Filed Test	**HFO-1233zd(E)**		**HFO-1336mzz(Z)**	
	Narongrit	**Lohr Trade and Consulting**	**Narongrit**	**Lohr Trade and Consulting**
Chemical reaction	Little slow	Appropriate	Appropriate	Little fast
Foam cell appearance	Appropriate	Appropriate	Appropriate	Appropriate
Foam strength	Appropriate	Appropriate	Appropriate	Appropriate
Adhesion on substrate	Fair	Good	Fair	Fair
Satisfaction	Reaction time to be improved	Appropriate	Appropriate	Reaction time to be improved

55. Both invited enterprises were confident that the HFO formulations could be used in the Thai industry as a replacement for the HCFC-141b formulation. They were satisfied with the cell size appearance, reaction time, adhesion and foam strength. The only area of improvement suggested by the enterprises was the reaction time. One suggested that the HFO-1233zd(E) formulation should be improved to have faster reaction, while another suggested to slow down the reaction time of the HFO-1336mzz(Z) formulation.

Incremental Capital Cost

56. The demonstration project as approved by the ExCom also provided financial supports to South City Petroleum to acquire one spray foam machine and thermal conductivity testing machine. These pieces of equipment were critical to the development of new foam formulations and for demonstration of the final products. As described in the project proposal, the enterprise anticipated that reduction of the blowing agent in the formulation would require additional water content in the polyol system and that consequently led to the increasing ratio of isocyanate and polyol (different foam index). Therefore, the spray foam machine with adjustable ratios of isocyanate and polyol was acquired by the project. To facilitate development and testing of new formulation, the thermal conductivity testing machine was provided.

57. The spray foam machine purchased by South City Petroleum was made by a Graco machine (Model: Reactor H-VR). The injection rates of isocyanate and polyol could be varied within the range from 1:1 to 2.5:1. The thermal conductivity tester purchased by South City Petroleum are Thermtest Model HFM-100. The approved funding levels for the spray foam machine and thermal conductivity tester were US $40,000 and US $5,000, respectively. The actual costs paid by South City Petroleum were US $41,692 and US $22,253, respectively. Detailed financial information will be provided in the Project Completion Report.

Cost Effectiveness of South City Petroleum's HFO Based Formulations

58. Cost is the major issues in this industry. The new HFO formulations must be price competitive in comparison with the current HCFC-141b formulations. Table 30 provides cost comparison between the HCFC-141b formulations and the two HFO formulations. The following costs of the blowing agents were use in the calculation: US $2.86/kg of HCFC-141b; US $14/kg of HFO-1233zd(E); and US $20/kg of HFO-1336mzz(Z).

Table 30. Cost of Foam Production and Incremental Operating Cost of HFO Formulations

South City Petroleum	141b system			1233zd(E) system			1336mzz(Z) system		
	Parts	Unit Cost (US$/kg)	Price	Parts	Unit Cost (US$/kg)	Price	Parts	Unit Cost (US$/kg)	Price
Polyol Blend	100.00	1.76	175.70	100.00	1.58	158.03	100.00	1.58	158.03
Additives & Catalysts	5.27	9.36	49.32	12.90	12.68	163.54	16.13	6.75	108.88
Other Additives	24.03	1.84	44.16	18.68	1.84	34.42	15.19	2.27	34.42
Blowing Agent	40.27	2.86	115.07	13.16	14.00	184.24	13.13	20.00	262.60
Sub-total	169.57		384.25	144.74		540.23	144.45		563.93
Isocyanate	231.80	1.68	390.44	135.40	1.68	228.07	137.72	1.68	231.97
Sub-total	231.80		390.44	135.40		228.07	137.72		231.97
Total	401.37		774.70	280.14		768.30	282.17		795.91
Price of foam (US$/kg)			1.93			2.74			2.82
IOC (US$/kg 141b)						8.10			8.88

59. For the HFO-1233zd(E) formulation, a new catalyst package was required to overcome the formulation stability. While the cost of HFO-1233zd(E) was significantly lower than the cost of HFO-1336mzz(Z), the cost of the new innovative catalyst package for HFO-1233zd(E) made the overall incremental operating cost of the HFO-1233zd(E) formulation only slightly less expensive than the HFO-1336mzz(Z) formulation.

Summary

60. The results of the demonstration project to develop reduced HFO polyol formulation systems at BIT and South City Petroleum confirmed that the spray foam formulations with HFO blowing agents of about 10% of the polyol weight and proper adjustments on the choice of polyol and the catalyst package could yield the foam properties that were still acceptable to the Thai spray foam market. While the HFO-1233zd(E) formulation demonstrated instability in the formulation, the issue could be solved by introducing a new catalyst package. Spray foams blown with HFOs exhibited adhesion performance that was acceptable to the market.

61. Reactivity time of the new reduced HFO formulations is similar to the HCFC-141b formulation. This was acceptable to the Thai market. Density of spray foam made from the reduced HFO formulations was slightly higher than the baseline HCFC-141b formulation. The slight increase in the compressive strength was also observed. Similarly, the initial K-factors of the reduced HFO formulations were 20 – 30% higher than the HCFC-141b formulation. All properties of HFO blown foams were quite stable over time. Both HFO formulations passed the fire performance tests.

Table 31. Summary of Key Performance of HFO Formulations of BIT and South City Petroleum

	BIT		South City Petroleum	
	-1233zd(E)	-1336mzz(Z)	-1233zd(E)	-1336mzz(Z)
Reactivity				
Cream time (sec)	4	5	4	4

Gel time (sec)	9	9	6	6
Tack-free time	16	16	7	7
Foam Properties				
Foam Density (kg/m^3)	38.77	39.07	39.51	34.64
K-Factor (mW/m.K)	24.20	26.10	24.74	26.88
Compressive Strength (kPa)	188.20	190.59	256.00	206.00
Cost				
Cost of PU System ($/kg foam)	2.61	2.96	2.74	2.82
Incremental Operating Cost ($/kg HCFC-141b)	4.72	8.24	8.10	8.88

62. Reduction of the blowing agents required an additional amount of water to generate CO2 from the water-isocyanate reaction. Consequently, an additional amount of isocyanate which made the polyol and isocyanate ratio by volume deviated from 1:1 was required. Most spray foam enterprises in Thailand would have to either retrofit or replace their existing spray machine to be able to apply these new formulations.