
Alternative Technologies for the Rigid Foam Sector

Miguel W. Quintero
UNDP Consultant
March, 2014

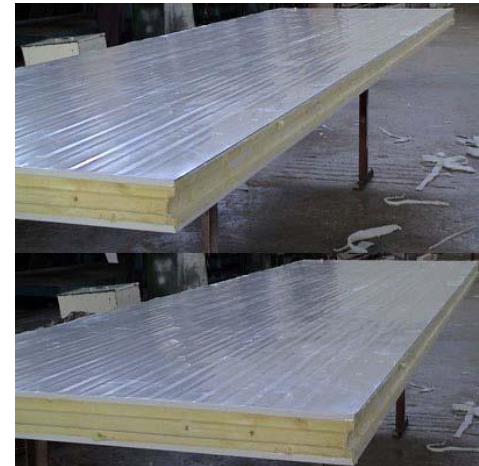
POLYURETHANE RIGID FOAM

Appliances

- Refrigerators, freezers
- Commercial refrigeration (Bottle containers, displays)
- Water/solar heaters, etc.

Construction/ Transportation/ Piping

- Panels (continuous, discontinuous)
- Blocks
- In situ applications (spray)
- Pipe insulation & PIP



Other uses (structural, wood imitation, floral, flotation, etc.)

ROLE OF THE BLOWING AGENT

Physical Expansion of the Foam

- *Generation of CO₂ by iso-water reaction*
- *Evaporation of the external blowing agent*

Contribution of thermal performance

- *Remains in the closed cells*
- *Low gas thermal conductivity*

REQUIRED FOAM PROPERTIES

- Insulation Capability
- Mechanical Strength
- Easy of Processing
 - ✓ *Ability to fill all the cavities*
- De-mould Time
 - ✓ *Productivity*



...at the lowest foam density!

BLOWING AGENT CHARACTERISTICS

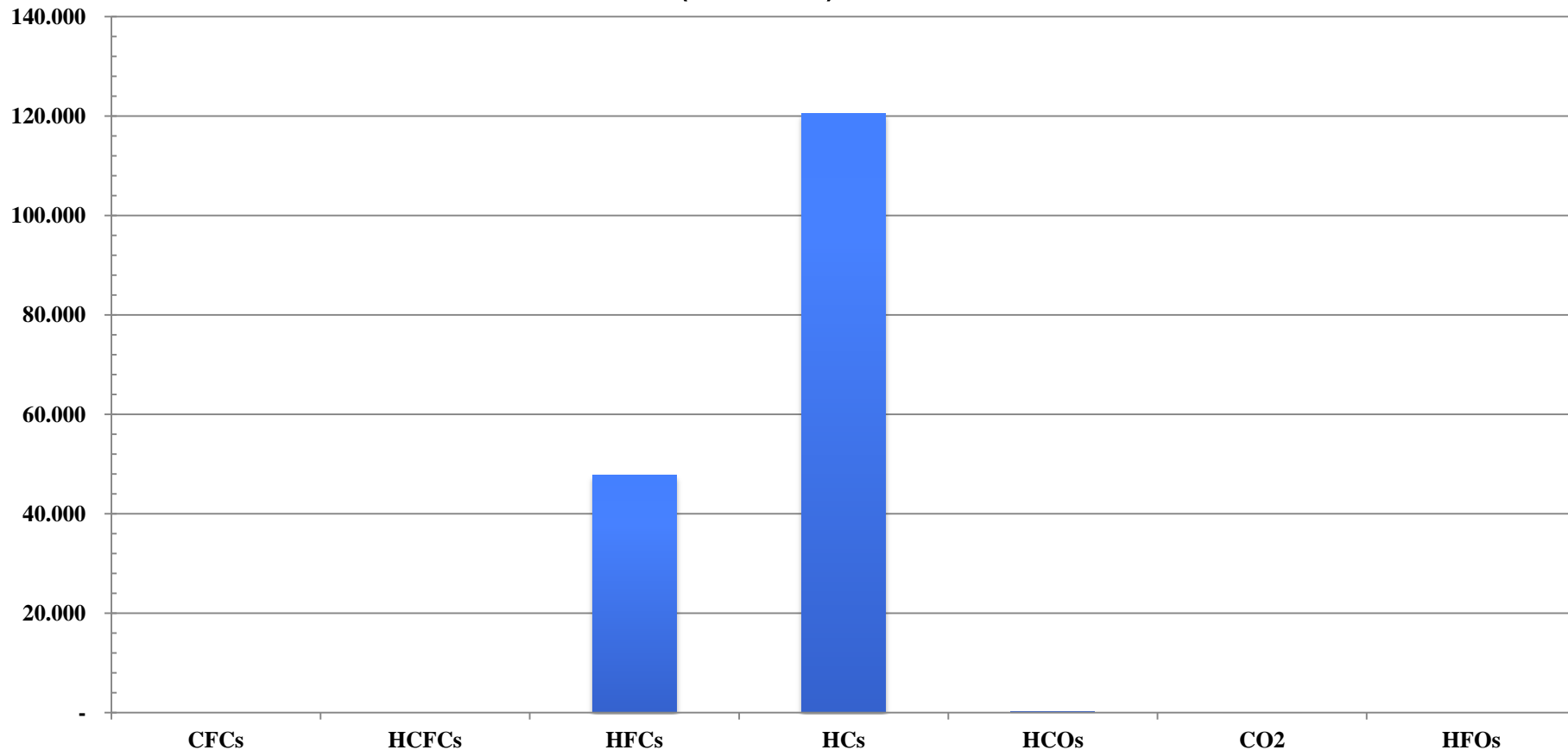
Foam requirement	Relevant Blowing Agent Characteristic
Ease of Processing	<i>Flammability</i> <i>Boiling Point</i> <i>Solubility in the polyols</i>
De-mould time	Broadly independent
Insulating Performance	<i>Gas thermal conductivity</i> <i>Permeability</i> through cell wall
Mechanical Strength	<i>Boiling Point</i> <i>Solubility in the PU matrix</i>

BLOWING AGENTS IN DEVELOPED COUNTRIES

- Hydrocarbons – Dominant Technology
 - ✓ Not adequate for spray foam
 - ✓ Blend with HFCs/ HFOs to improve thermal conductivity
- Saturated HFCs
 - ✓ Used in North America in **domestic refrigeration** (HFC-245fa)
 - ✓ Preferred option for **spray**
 - ✓ Used for panels (**Flame Retardancy**)
 - ✓ **Small and medium enterprises**
- All water-blown foams (CO₂)
 - ✓ **Small and medium enterprises**
 - ✓ **Spray** foam (**CO₂ Supercrítico** en Japón)
- Minimum used of Oxygenated Hydrocarbons (**Methyl Formate, Methylal**)

STATUS IN DEVELOPED COUNTRIES

Blowing Agent Consumption – Developed Countries – 2010
(tonnes)



HYDROCARBONS

	<i>HCFC-141b</i>	<i>Cyclo-Pentane</i>	<i>n-Pentane</i>	<i>Iso-Pentane</i>	<i>Iso-Butane</i>
Chemical Formula	CCl_2FCH_3	$(\text{CH}_2)_5$	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$
Molecular Weight	117.0	70.1	72.1	72.1	58.1
Boiling Point (°C)	31.9	49.3	36	28	-11.7
Gas Conductivity (mW/m.K @ 10°C)	8.8	11.0	14.0	13.0	15.9
Flammable Limits in Air (vol.%)	5.6 – 17.7	1.4 - 8.0	1.4 - 8.0	1.4 - 7.6	1.8 - 8.4
GWP (100 yr time horizon)	725	<25*	<25*	<25*	<25*
Price (USD/kg)	2.0 – 4.0	2.0 – 4.0	2.0 – 4.0	2.0 – 4.0	2.0 – 4.0

^ Measured at 0° C * Precise figure varies according to local atmospheric conditions

SATURATED HFCs

	<i>HCFC-141b</i>	<i>HFC-134a</i>	<i>HFC-245fa</i>	<i>HFC-365mfc</i>	<i>HFC-227ea</i>
Chemical Formula	CCl ₂ FCH ₃	CH ₂ FCF ₃	CF ₃ CH ₂ CHF ₂	CF ₃ CH ₂ CF ₂ CH ₃	CF ₃ CHF CF ₃
Molecular Weight	117.0	102	134	148	170
Boiling Point (°C)	31.9	-26.2	15.3	40.2	-16.5
Gas Conductivity (mW/m.K @ 10°C)	8.8	12.4	12.5 (20 °C)	10.6 (25 °C)	11.6
Flammable Limits in Air (vol.%)	5.6 – 17.7	None	None	3.8-13.3	None
GWP (100 yr time horizon)	725	1430	1030	794	3220
Price (USD/kg)	2 – 4	6 – 13	9 - 13	8 - 12	8 - 12

CO₂ FROM WATER

CONVENTIONAL FORMULATIONS

- **Adhesion** issues due to foam friability
- Reduced **energy efficiency**/ High K value
- High CO₂ permeability/ **High molded density**

NEW GENERATION

Improved Adhesion & Foam Structure

Formic Acid for flow-ability (**corrosiveness**)

Note: Used in all formulations for **co-blowing**

Used for **Spray Foam** in U.S. & Europe & Japan (Supercritical CO₂)

DEVELOPING COUNTRIES AND DECISION XIX/6

- In polyurethane (PU) foam HCFCs are used in:
 - ✓ Rigid foam and Integral Skin
- Most of the countries in the implementation of first stage
 - ✓ Initial focus in large enterprises (domestic refrigeration, continuous panels)
 - ✓ Hydrocarbons...widely dominant technology (> 25 MT of HCFC-141b)
 - ✓ Saturated HFCs...transition to HFOs
 - ✓ Oxygenated hydrocarbons (methyl formate, methylal)
 - ✓ Concern on Small and Medium Enterprises
- Preparation of second phase of the HPMP

OPTIONS FOR SMALL/MEDIUM ENTERPRISES

- **Hydrocarbons (HC)** (> 15-20 tons of HCFC-141b per year)
 - ✓ **Pre-blended** hydrocarbons
 - ✓ **Direct addition** of HC in the mixhead
- **HFOs (unsaturated HFCs)**
 - ✓ Price and availability
- New generation of **all water-blown formulations**
 - ✓ Optimisation of foam density & adhesion & thermal conductivity
- **Methyl Formate**
- **Methylal**

EMERGING OPTIONS – UNSATURATED HFCs/HCFCs (HFOs)

Name	Formacel® 1100	Solstice™ Liquid BA	Forane™ 1233zd
Common name	1336mzzm(Z)	1233zd(E)	1233zd(E)
Chemical Formula	Cis-CF ₃ -CH=CH-CF ₃	Trans-ClCH=CH-CF ₃	Trans-ClCH=CH-CF ₃
Molecular weight	164	130.5	130.5
Boiling Point (°C)	33	19	19
Gas conductivity(mW/m K @ 10°C)	10.7	10.6 (25 °C)*	9
Flammable Limits in Air (vol.%)	No	No	No
GWP (100 years)	8.9	<7***	<7***
Price (US\$/kg)	11.0 – 17.0	11.0 – 17.0	11.0 – 17.0

Substance	HCFC-141b	Methylal	Methyl Formate
Chemical Formula	CCl_2FCH_3	$\text{CH}_3\text{OCH}_2\text{OCH}_3$	$\text{CH}_3(\text{HCOO})$
Molecular Weight	117.0	76.1	60
Boiling Point (°C)	31.9	42	31.5
Thermal Conductivity (gaseous) (mW/m*K @ 15°C)	8.8	N. A.	10.7 (@ 25°C)
Flammability limits (% vol.)	5.6 – 17.7	2.2 – 19,9	5,0 – 2.0
GWP (100 years horizon)	725	"Negligible"	"Negligible"
Price (USD/kg)	2 – 4	1.4 -1.7	2 – 4

ALL WATER-BLOWN FOAMS

- **Old** formulations:
 - ✓ High thermal conductivity/ High foam density
- **New generation**: Better flow & Similar density to HCFC-141b
 - ✓ Commercial refrigeration, discontinuous panels, spray
- **Non flammable**
- **Not necessary to modify** injection equipment

Physical foam tests (GIZ & BASF)

For all the systems the results **show compliance** with required performance of the foam.

		BAU - HCFC 141b			Water-blown		
Test Parameter	Unit	Average			Average		
Core density	g/l	42.4	±	2.0	39.1	±	2.3
Compressive strength	N/mm ²	0.172	±	0.02	0.145	±	0.014
Closed cell content	%	92	±	0	91	±	1
Thermal conductivity at 23° C	mW/mK	21.9	±	0.7	23.6	±	0.7
Foam weight	kg	15.36			13.07		
Foaming ratio	Pol : Iso	100.00	:	130	100.00	:	156
141b content	grams	801.39			0.00		

The density for the water-blown is sufficient and the **adhesion of all the samples were good**, no further density required!

NOT A SINGLE TECHNOLOGY

- **Hydrocarbons**
 - ✓ *Pre-blended Hydrocarbons*
 - ✓ *Third stream to mixhead*
- New generation of **water blown systems**
- **Oxygenated hydrocarbons** (methylal, methyl formate)
- Unsaturated HFC & HCFCs (**HFOS**)
 - ✓ *Reduced formulations ?*
 - ✓ *Saturated HFCs...transitional stage*