PHYSICAL BLOWING AGENTS

FOR PU / PIR FOAMS –
A SHORT HISTORY

PHYSICAL BLOWING AGENTS

More than you wanted to know!

Topics

- Jargon
- Types of Blowing Agents
- How they work
- Requirements
- Nomenclature
- History
- Blowing Agent choices
- Thermal Conductivity
- The Future - Blends

JARGON

- HC : Hydrocarbon
- CFC : Chloro Fluoro Carbon
- HCFC : Hydro Chloro Fluoro Carbon
- HFC : Hydro Fluoro Carbon

- ODP : Ozone Depletion Potential
- GWP : Global Warming Potential
- VOC : Volatile Organic Compound

Types of Blowing Agents

- **Chemical**
  - Give off Gas with Chemical Rxn or Decomposition $\longrightarrow$ CO_2 or N_2
- **Physical**
  - Boiling Point at or near RT
  - Expand with heat

How Physical BAs Work

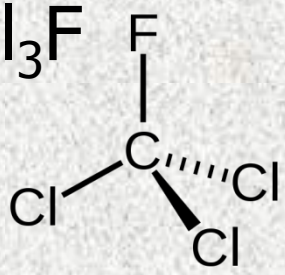
- Low Boiling Liquid
  - Soluble in Raws
  - Insoluble in Foam
- Heat ← Foam Exotherm
  - SURFACTANT & CATALYSTS
- POOF! FOAM

BA Requirements

- What makes a good BA?
  - Low Boiling Liquid [> RT]
  - Efficient Cost Structure
    - Molecular Weight - Low to Moderate
  - Solubility
    - in PU ingredients
    - None in PU polymer
  - Zero ODP, Zero GWP, non-VOC
  - Flammability – Low to None
  - Good Thermal Properties

Nomenclature – DuPont System

- $C_{n-1}\ H_{n+1}\ F_n$
- CFC-11 : TrichloroFluoroMethane - CCl_3F
  - C = 1 1-1 0
  - H = 0 0+1 1
  - F = 1 1 1



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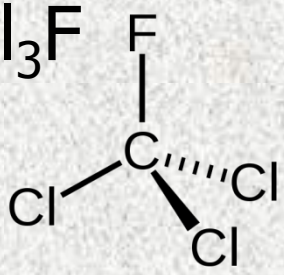
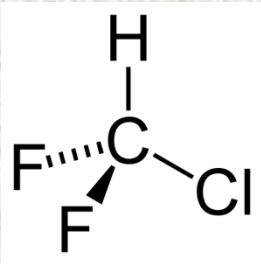
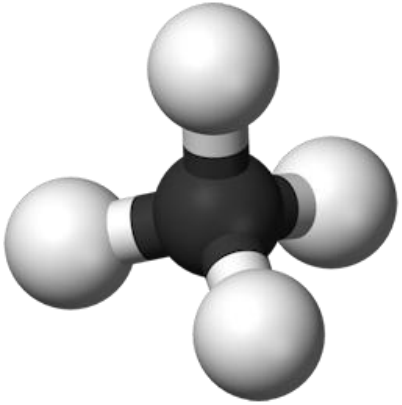


- HCFC-22 : ChloroDifluoroMethane - $CHClF_2$
  - C = 1 1-1 0
  - H = 1 1+1 2
  - F = 2 2 2



METHANE SERIES



H

CH4
50

CH3CL
40

CH3F
41

CH2CL2
30

CH2CLF2
31

CH2F2
32

CHCL3
20

CHCL2F
21

CHCLF2
22

CHF3
23

Cl

F

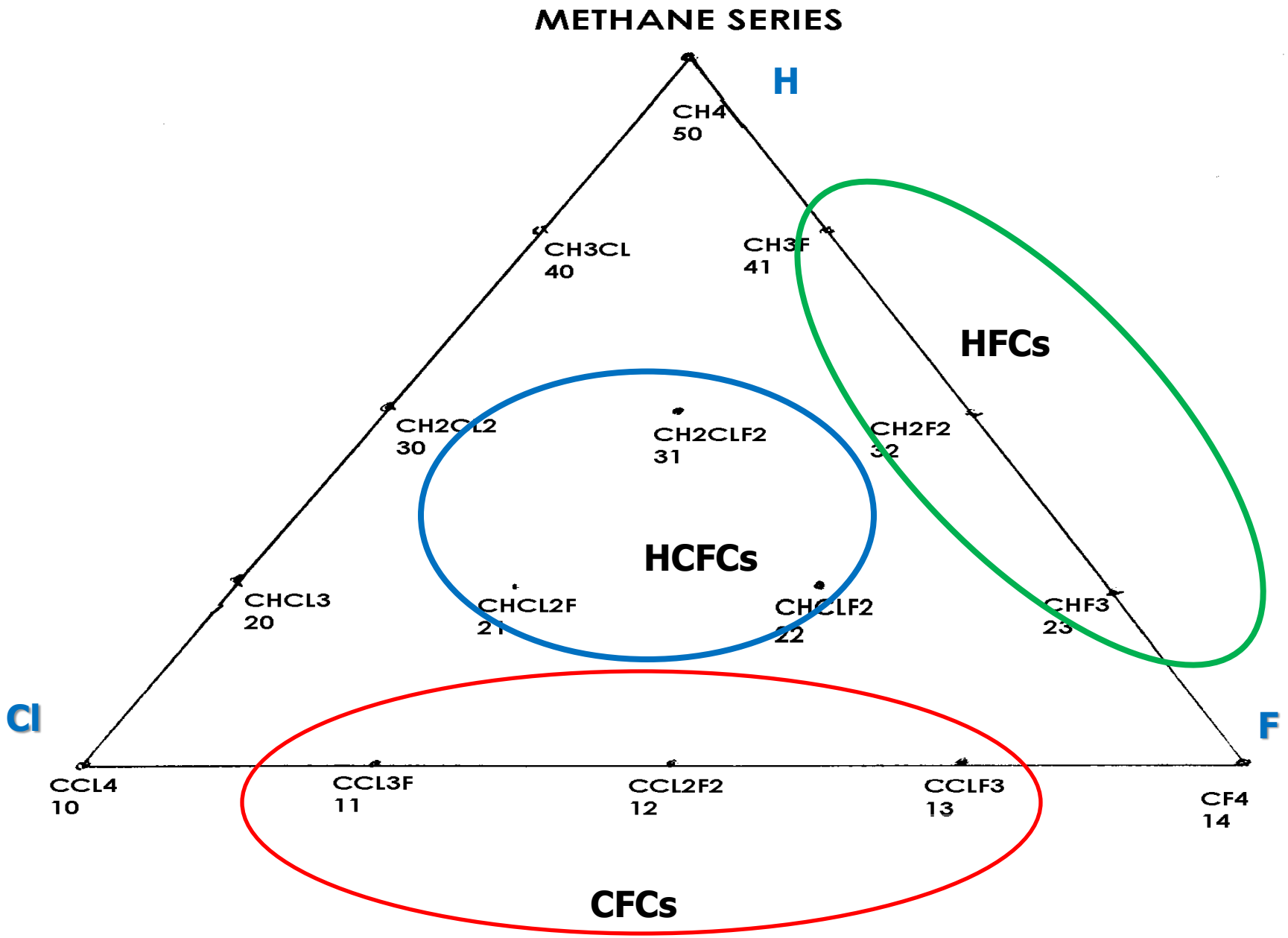
CCL4
10

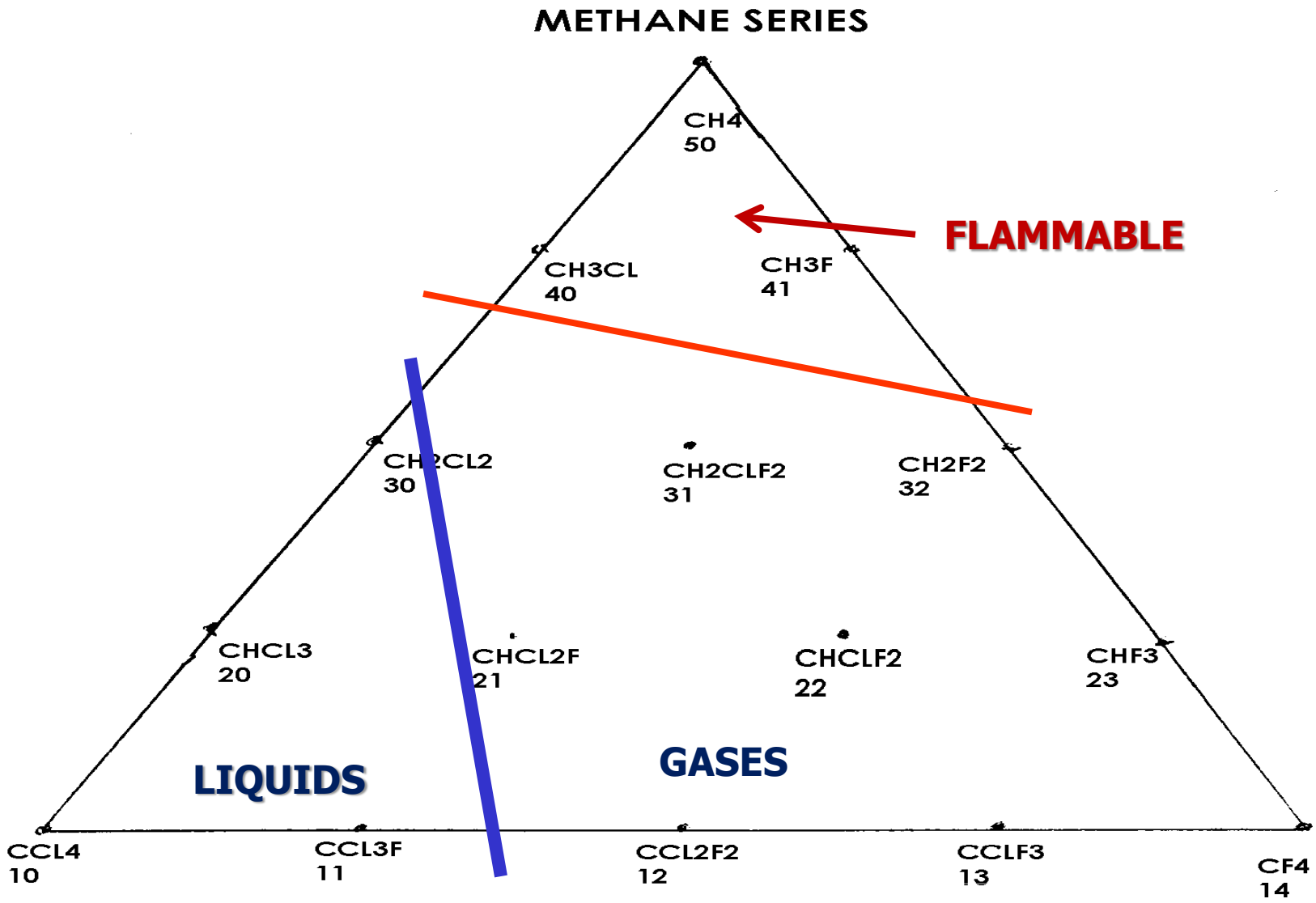
CCL3F
11

CCL2F2
12

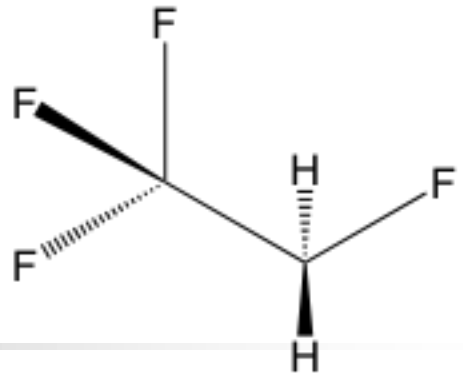
CCLF3
13

CF4
14

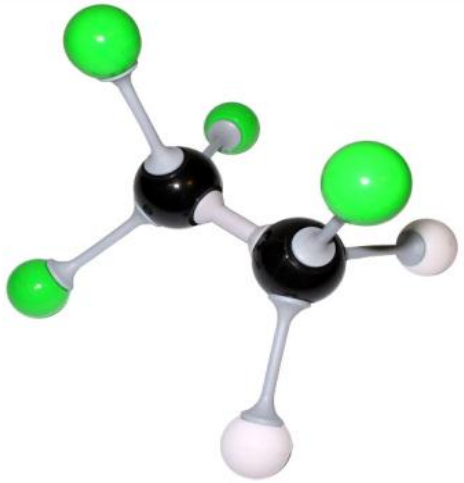

METHANE SERIES
H
CH4
50
CH3CL
40
CH3F
41
HFCs
CH2CL2
30
CH2CLF2
31
CH2F2
32
HCFCs
CHCL3
20
CHCL2F
21
CHCLF2
22
CHF3
23
Cl
F
CCL4
10
CCL3F
11
CCL2F2
12
CCLF3
13
CF4
14
CFCs


METHANE SERIES
CH4
50
CH3CL
40
CH3F
41
FLAMMABLE
CH2CL2
30
CH2CLF2
31
CH2F2
32
CHCL3
20
CHCL2F
21
CHCLF2
22
CHF3
23
LIQUIDS
GASES
CCL4
10
CCL3F
11
CCL2F2
12
CCLF3
13
CF4
14

134 eh?



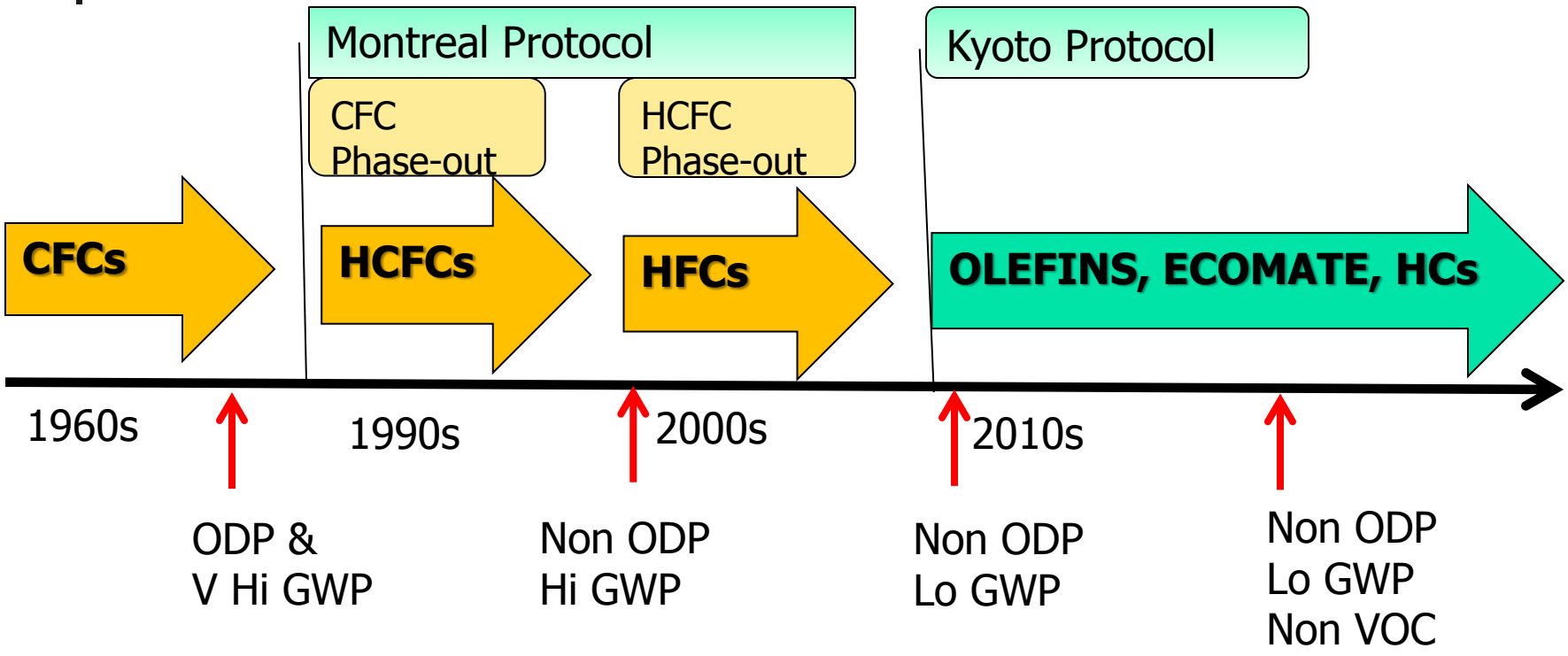
- HFC-134a
  - $C_{n-1}\ H_{n+1}\ F_n$
  - C=2, H=2, F=4
  - Therefore $C_2H_2F_4$
    - $CHF_2 - CHF_2$ **134**
    - $CH_2F - CF_3$ **134a**
    - **The highest symmetry gets the lowest name!**



HISTORY

- First Blowing Agent – Water
- Organic solvents – Flammability
- Chlorinated Solvents – Hi BPts, Solvency
- Dupont Refrigerants
  - R11 BPt>RT POUR
  - R12, R22 BPt<RT FROTH

Time Line of Change



Blowing Agent - Environmental Characteristics

- ecomate is an attractive long term environmental option

	ODP	GWP	VOC
CFC 11	1	4000	0
HCFC 141b	0.1	630	0
HCFC 22	0.05	1700	0
HCFC 124	0.02	480	0
HCFC 142b	0.06	2000	0
HFC 134a	0	1300	0
HFC 245fa	0	790	0
Cyclopentane	0	11	YES
ecomate	0	0	0

HISTORY

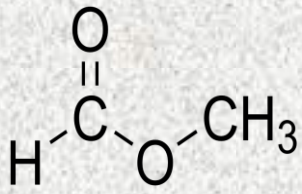
- CFCs – ChloroFluoroCarbons
  - R11 : CCl_3F R12 : CCl_2F_2
  - **BANNED FROM SALE IN US 1998**
- HCFCs – HydroChloroFluoroCarbons
  - R141b : CH_3CCl_2F
  - **BANNED FROM SALE IN US 2004, USE 2005**
- HFCs - HydroFluoroCarbons
  - R134a, R245fa
- HFOs – HydroFluoroOlefins - pending
  - 1336mzz-Z 1233zd-E

HISTORY

- HCs – HydroCarbons
  - Back on scene
  - PENTANES – nC5, iC5, cC5
- WATER
  - Used in Packaging, & Foams > 4 pcf
  - Co-Blow w Others for Cost
- Ecomate
  - New kid on Block

ECOMATE®

- **Ecomate** [METHYL FORMATE]



$C_2H_4O_2$

- BP 32 ºC
- LAMBDA = 10.7 @25ºC
- GWP = 0 ODP = 0
- MW = **60**

Cost Efficiency

Blowing Agent	$/lb *	Mol Wt	Factor	$/mole
HCFC-141b	**	117	1.00	Ref
HCFC-22	**	86.5	0.74	-25%
HFC-245fa	****	134	1.15	+350%
HFC-134a	***	102	0.87	+70%
cC5	**	70	0.60	-45%
nC5	*	72	0.62	-70%
ecomate®	*	**60**	**0.51**	**-65%**

Understanding Insulation

- **Thermal Conductivity** – the ability to resist heat/cold transfer or flow.

- Expressed as:
  - K-factor [BTU-in/ft^{2}hrF], or
  - Lambda [mW/m^{o}K]
  - It is **independent of thickness**

- The lower the K-Factor, the better the insulation.

INSULATION

- THERMAL PROPERTIES
- Each Generation was poorer than the last

Physical Blowing Agent	Thermal Conductivity	
	Gas Lambda	Avg Foam K-Factor
CFC-11	**8**	**0.11**
HCFC- 141b	**10**	**0.14**
HFC-245fa	**12**	**0.145**

- Each Generation was more Costly !

Current & Past BAs

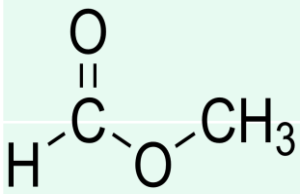
BLOWING AGT	GAS LAMBDA
CFC-11	8
HCFC-141b	10
HFC-134a	13
HFC-365mfc	10.6
HFC-245fa	12
ECOMATE	10.7
WATER [CO_2]	16
HC-nC5	15
HC-iC5	14
HC-cC5	12

Properties of PURE Physical BLOWING AGENTS

structures

Ecomate®

MF

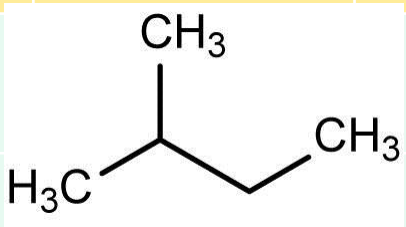


C2H4O2

ML

C3H8O2

iC5

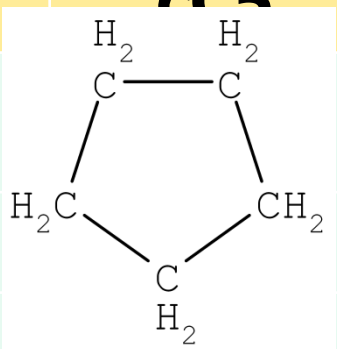


C5H12

nC5

C5H12

cC5



C5H10

Properties of PURE Physical BLOWING AGENTS

physical							
BA	**MF**	**ML**	**iC5**	**nC5**	**cC5**	UNITS	
MW	**60**	76.1	72	72	70	g/mol	**Lowest MW – less needed**

Ecomate – Low cost, less needed, more efficient !

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MW	**60**	76.1	72	72	70	g/mol	**Lowest MW – less needed**
BP	32	42.3	28	36	49	^{0}C	**BP – same as 141b**

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BP	32	42.3	28	36	49	^{0}C	**BP – same as 141b**
λ_{gas}, at 20 ^{0}C	**10.7**	11-14	14	14	11	mW/m^{0}K	**Lowest Lambda – more efficient**

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λ_{gas}, at 20 ^{0}C	**10.7**	11-14	14	14	11	mW/m^{0}K	**Lowest Lambda – more efficient**
SpGr	0.98	0.86	0.62	0.63	0.75	g/l	**Higher – Like water**

Ecomate – Low cost, less needed, more efficient !

Properties of PURE Physical BLOWING AGENTS

environmental							
BA	**Ecomate (MF)**	**ML**	**iC5**	**nC5**	**cC5**	UNITS	
ODP	0	0	0	0	0		
GWP	<1.5	<1.5	11	11	11	CO_2=1	**Negligible GWP**
MIR [Smog]	**0.06**	0.94	1.45	1.31	2.39	ETHANE= 0.28	**No SMOG**

Ecomate – more Environmentally Friendly !

Properties of SOME neat Physical BLOWING AGENTS

flammability							
BA	**MF**	**ML**	**iC5**	**nC5**	**cC5**	UNITS	
FLASH Pt	**-19**	-18	-51	-49	-37	^{0}C	**LESS HAZARD**

Ecomate – Less Hazardous !

Properties of SOME neat Physical BLOWING AGENTS

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FLASH Pt	**-19**	-18	-51	-49	-37	^{0}C	**LESS HAZARD**
LFL	**5**	1.6	1.4	1.5	1.1	vol%	**LESS HAZARD**

Ecomate – Less Hazardous !

Properties of SOME neat Physical BLOWING AGENTS

flammability							
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LFL	**5**	1.6	1.4	1.5	1.1	vol%	**LESS HAZARD**
% Oxygen	**53.3**	42.1	0	0	0	Wt%	**LESS HAZARD**

Ecomate – Less Hazardous !

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% Oxygen	**53.3**	42.1	0	0	0	Wt%	**LESS HAZARD**
Electrical Conductivity	**1.92 x 10^{9}**	?	<1	<1	<1	pS/m	**Water = 4.3 x 10^{6} LESS HAZARD**

Ecomate – Less Hazardous !

Properties of SOME neat Physical BLOWING AGENTS

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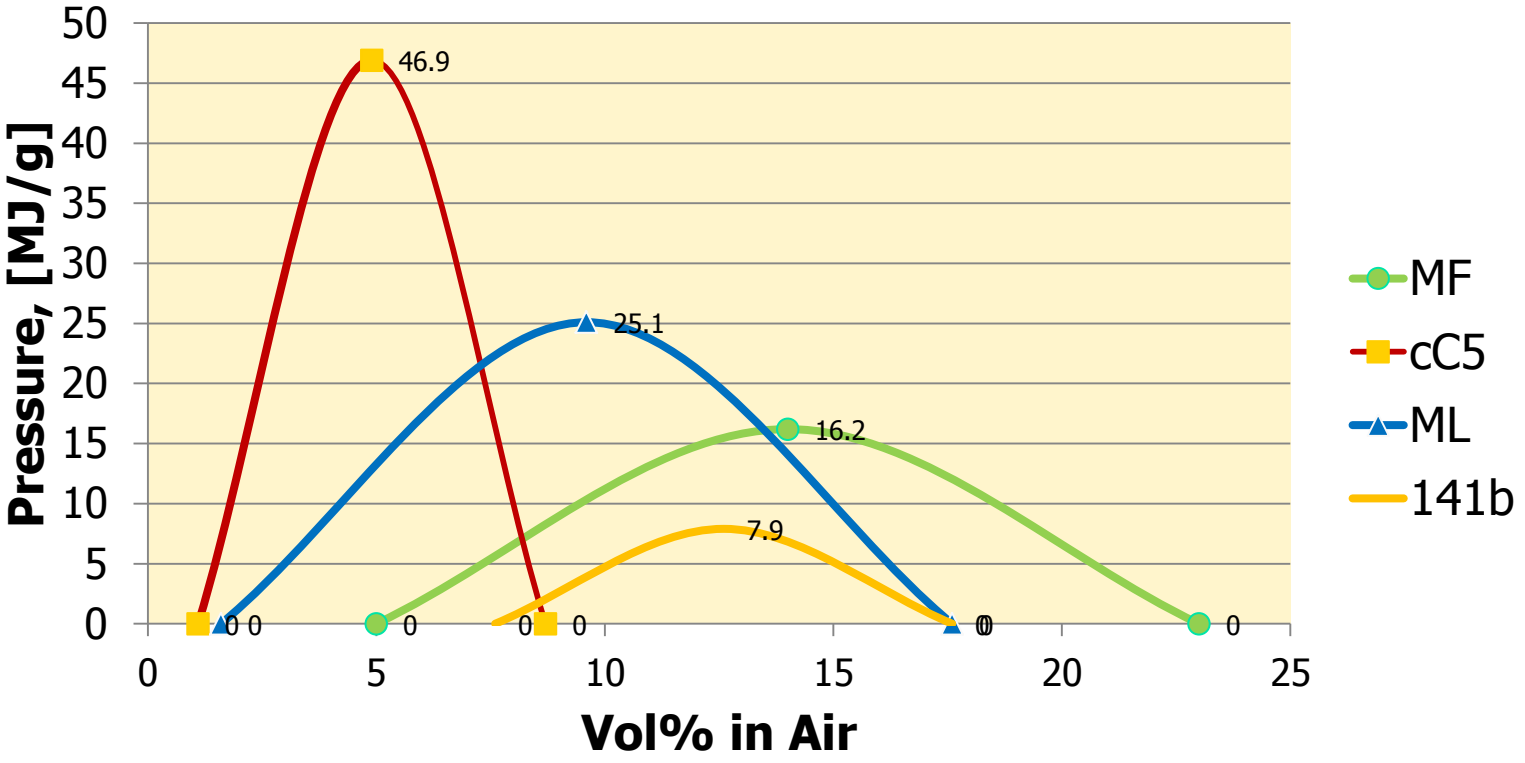
% Oxygen	**53.3**	42.1	0	0	0	Wt%	**LESS HAZARD**
Electrical Conductivity	**1.92 x 10^9**	?	<1	<1	<1	pS/m	**Water = 4.3 x 10^6** **LESS HAZARD**
Heat of COMBUSTION	**16.2**	25.1	46.7	49.7	46.9	MJ/g	**LESS HAZARD**

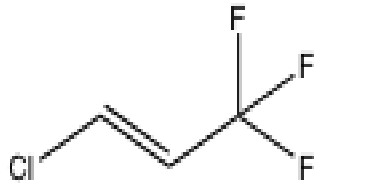
Ecomate – Less Hazardous !

Relative Pressures on Burning



HFOs - Future Stars ?

- **HFCO 1233zd-E** [*Honeywell Solstice LBA*]



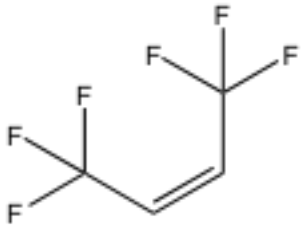
1-chloro-3,3,3,-trifluoropropene

$C_3H_2ClF_3$

- BP 19 ºC
- LAMBDA = ? @25ºC
- GWP = <7
- MW **130**

HFOs - Future Stars ?

- **HFO 1336mzz-Z** [*DuPont's FEA1100*]

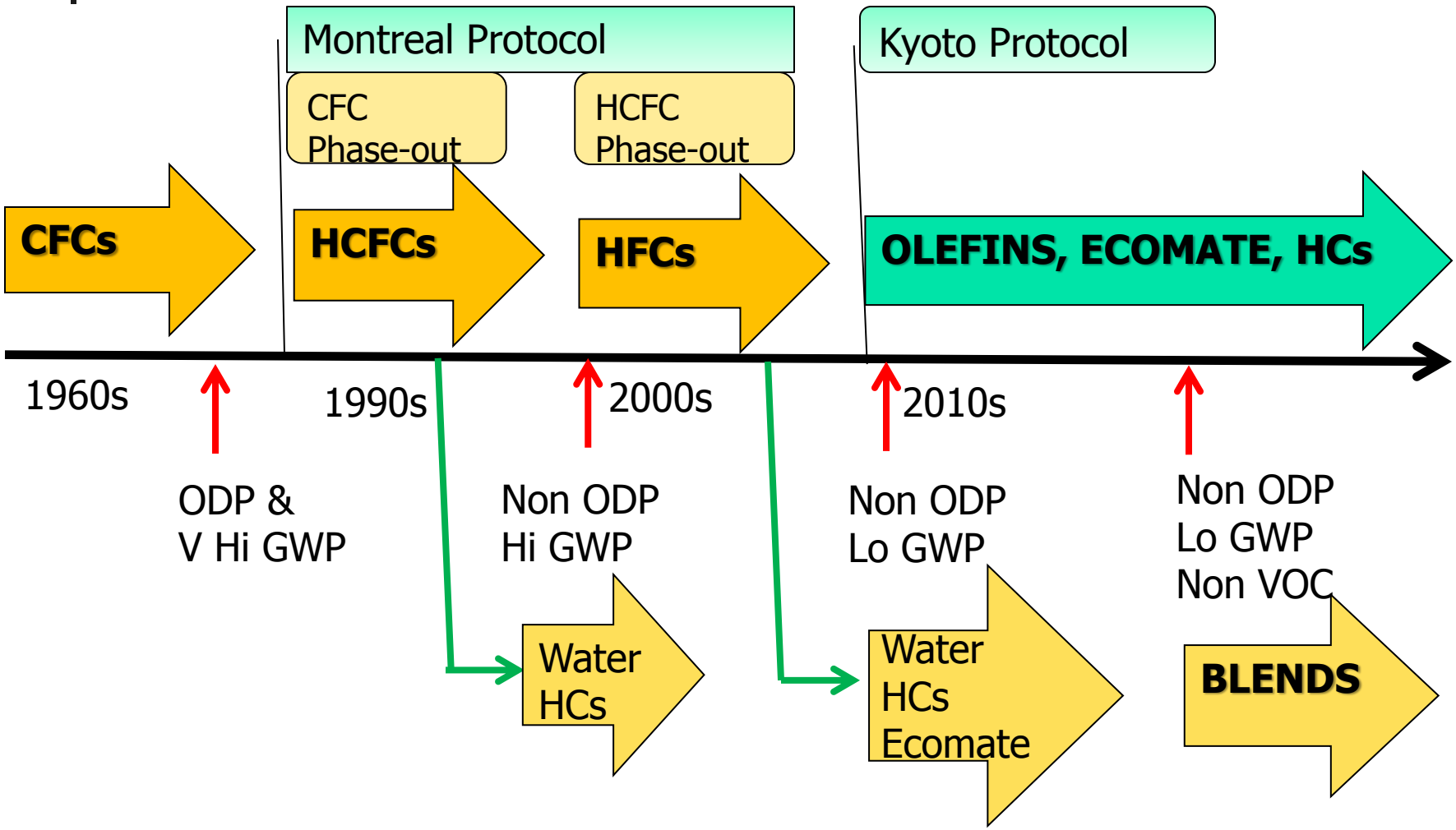


cis-1,1,1,4,4,4-hexafluoro-2-butene

$C_4H_2F_6$

- BP 33 ºC
- LAMBDA = 9.7 @25ºC
- GWP = 9.4
- MW = **164**

The Future - BLENDS



Why Blend ?

- To Reduce Costs
- To Improve Properties
  - Physical
  - Thermal
  - Performance
- To Find Synergies

Past Blends

- Blends have always been "the norm"
- CFCs
  - Liquid CFC-11
    - Blends –w Froth CFC-12 allowed low temp applications
    - Lower thermals - With H_2O
- HCFCs
  - 141b – used more water to reduce solubility, shrinkage

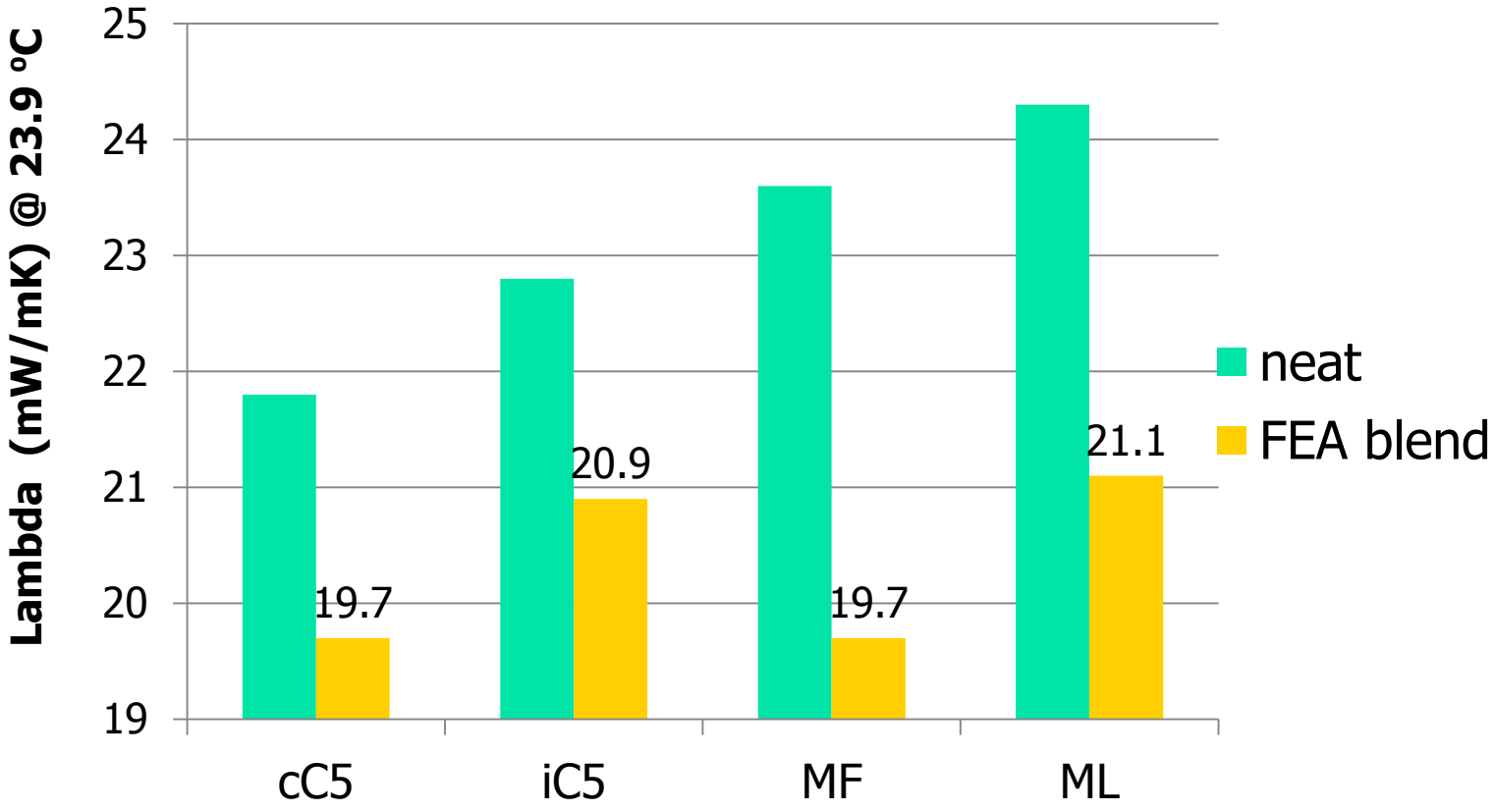
Past Blends

- HFCs
  - Use still more water to mitigate higher costs
  - 365mfc – used HFC-227ea blends to reduce flammability
- HCs
  - Only in controlled environments
  - nC5
    - With iC5 – to improve reaction profile, reduce catalysts
    - With cC5 – to improve thermals

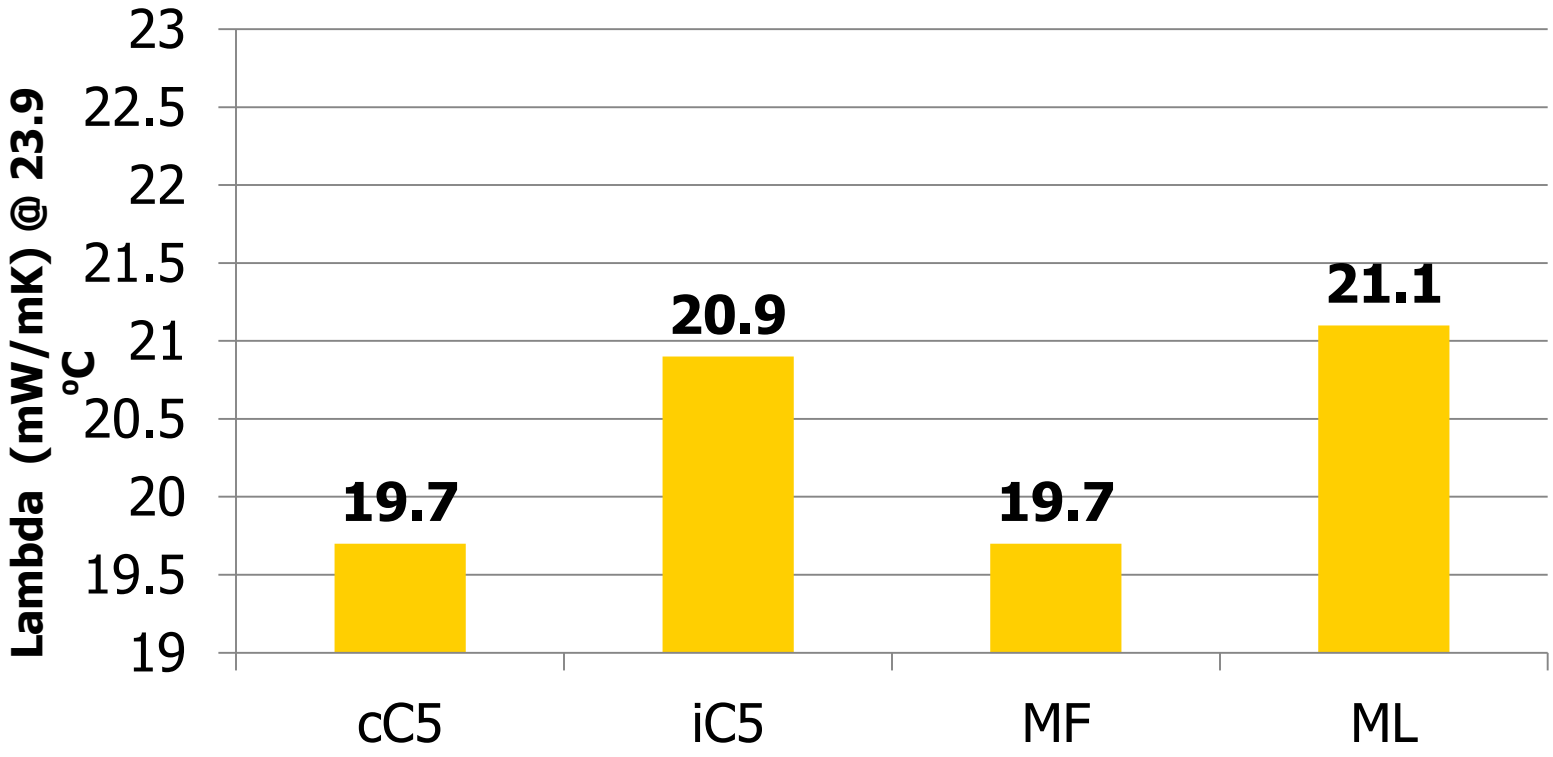
Future Blends

- HFOs
  - ✓ HFO 1336mzz-Z [*DuPont's FEA1100*] → blends
    - Optimize Properties
    - Improve Economics
      - Working with
        - HCs
        - Ecomate
        - Methylal
        - Water

Effect of FEA-1100 Blends
DuPont Data

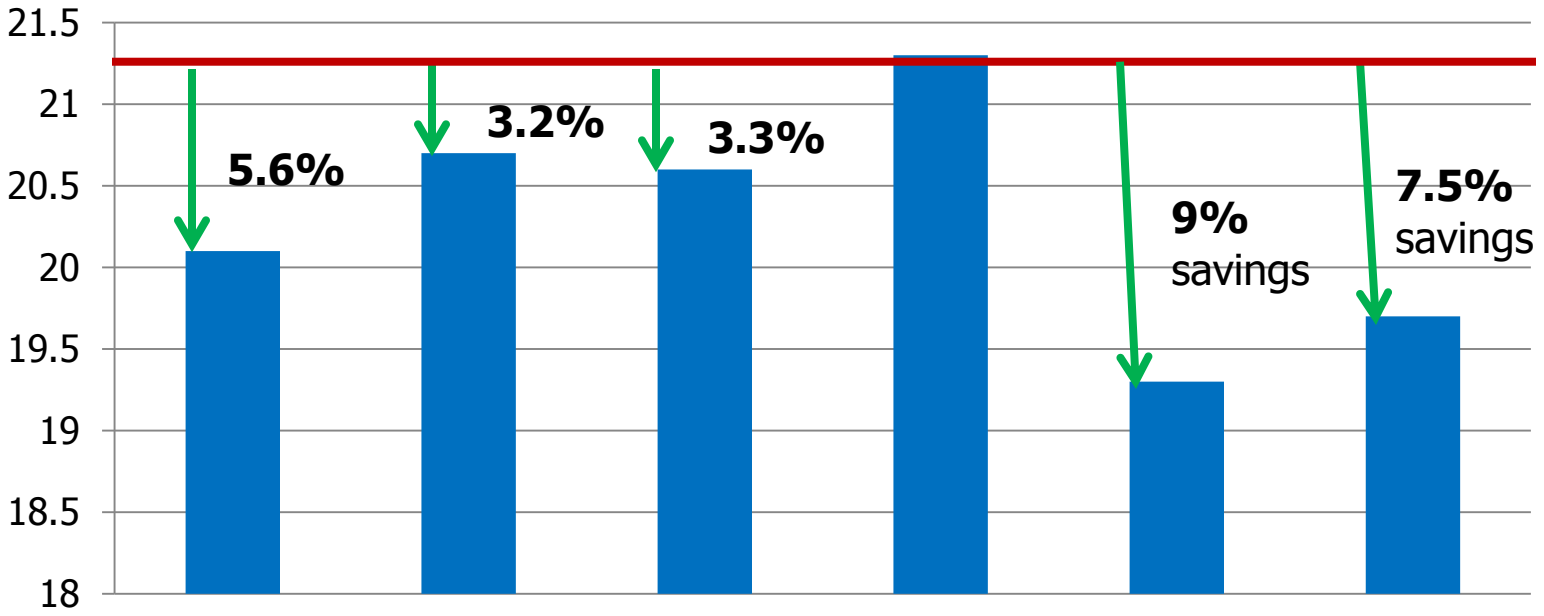


Effect of FEA-1100 Blends
DuPont data



Benefit of Blends - Refrigeration Foams

25°C	PURE ECOMATE 08B65	PURE ECOMATE 08M12	PURE ECOMATE 08M12-2	HC BLEND	ECOMATE HC Blend	FEA-1100 ECO Blend
Lambda	**20.1**	**20.7**	**20.6**	**21.3**	**19.3**	**19.7**



Ecomate Blends show Synergy !

Conclusions

- BA BLENDS have long been with us
  - To improve physical properties:
    - ✓ Flow
    - ✓ Adhesion
    - ✓ Thermal Conductivity
    - ✓ Solubility
    - ✓ Flammability
  - To improve economics

BLENDS – the new Paradigm

Because there is no "perfect" product

- ✓ HFOs will be blended also
- ✓ Blends w Ecomate will be BEST Choice!

Ecomate BLENDS can be:

- More Thermally Efficient
- More Environmentally Benign
- Less Flammable
- More Economical

- Because neat ecomate already has these properties!

- Thank You for your time!