Figures to accompany IACC14 paper

Note that pictures have been deleted due to file size

Low Temperature Regeneration of Spent Activated Carbon Theory and Applications

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TC	days/bed	yrs/bed
375	4.7	
350	14.3	
300	70.5	
250	501.7	1.4
200	5.07E+03	13.9
150	9.03E+04	2.5E+02
100	3.47E+06	9.5E+03
50	4.14E+08	1.1E+06
25	8.25E+09	2.3E+07
0	2.84E+11	7.8E+08

Figure 1

The Criterion for Gas Adsorption

For Spontaneous adsorption to occur at a specific site, ϵ, the potential energy of the adsorption site must satisfy:

$$\epsilon_{Ads.}(\text{at site}) >= RT \ln \{Psat/P\}$$

Therefore, every adsorption site within the carbon structure with an adsorption potential equal to or greater than the above criterion will be occupied by an adsorbate molecule, condensed from the gas phase.

Figure 2

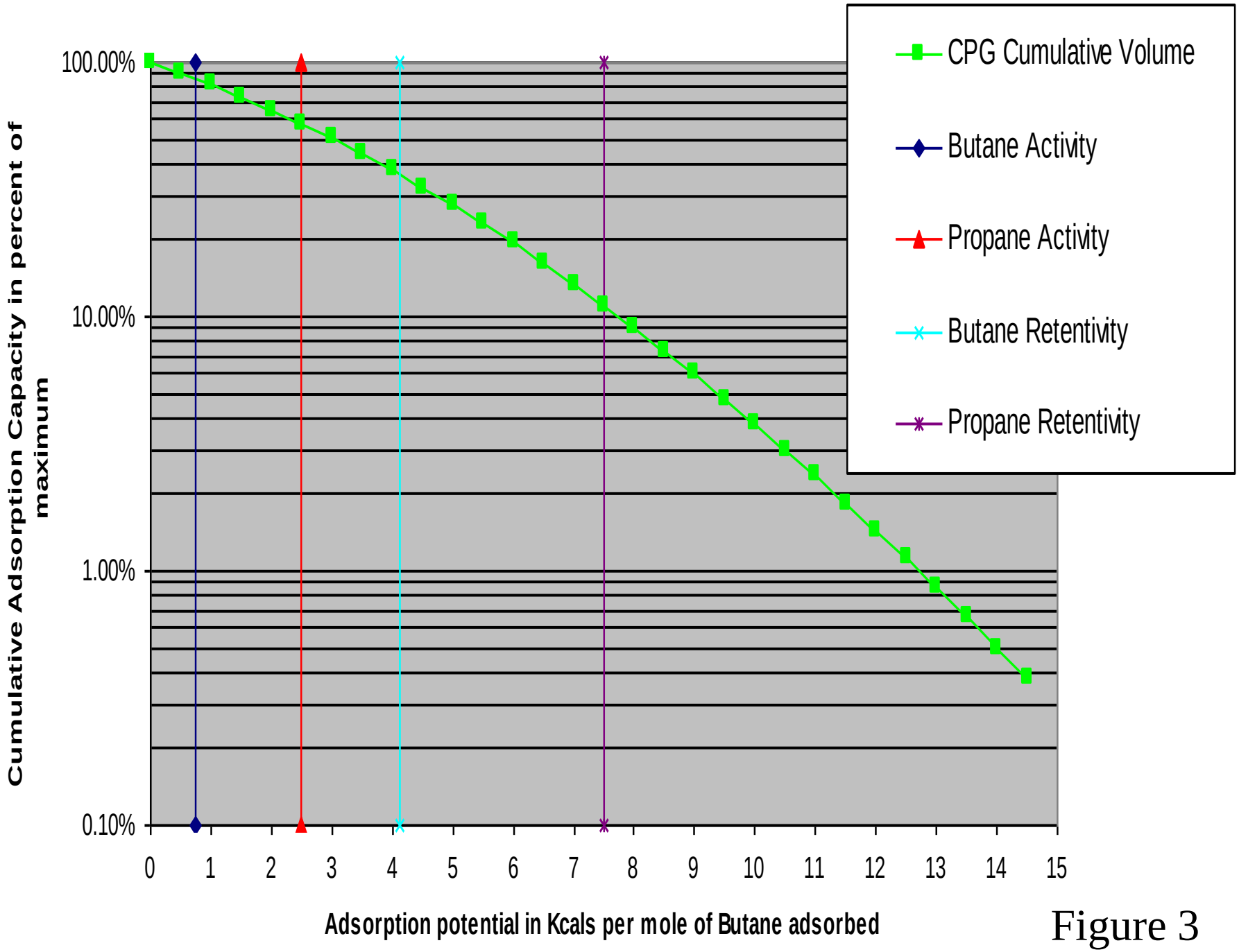
CPG Cumulative Volume
Butane Activity
Propane Activity
Butane Retentivity
Propane Retentivity
100.00%
10.00%
1.00%
0.10%
Cumulative Adsorption Capacity in percent of maximum
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Adsorption potential in Kcals per mole of Butane adsorbed

Figure 3

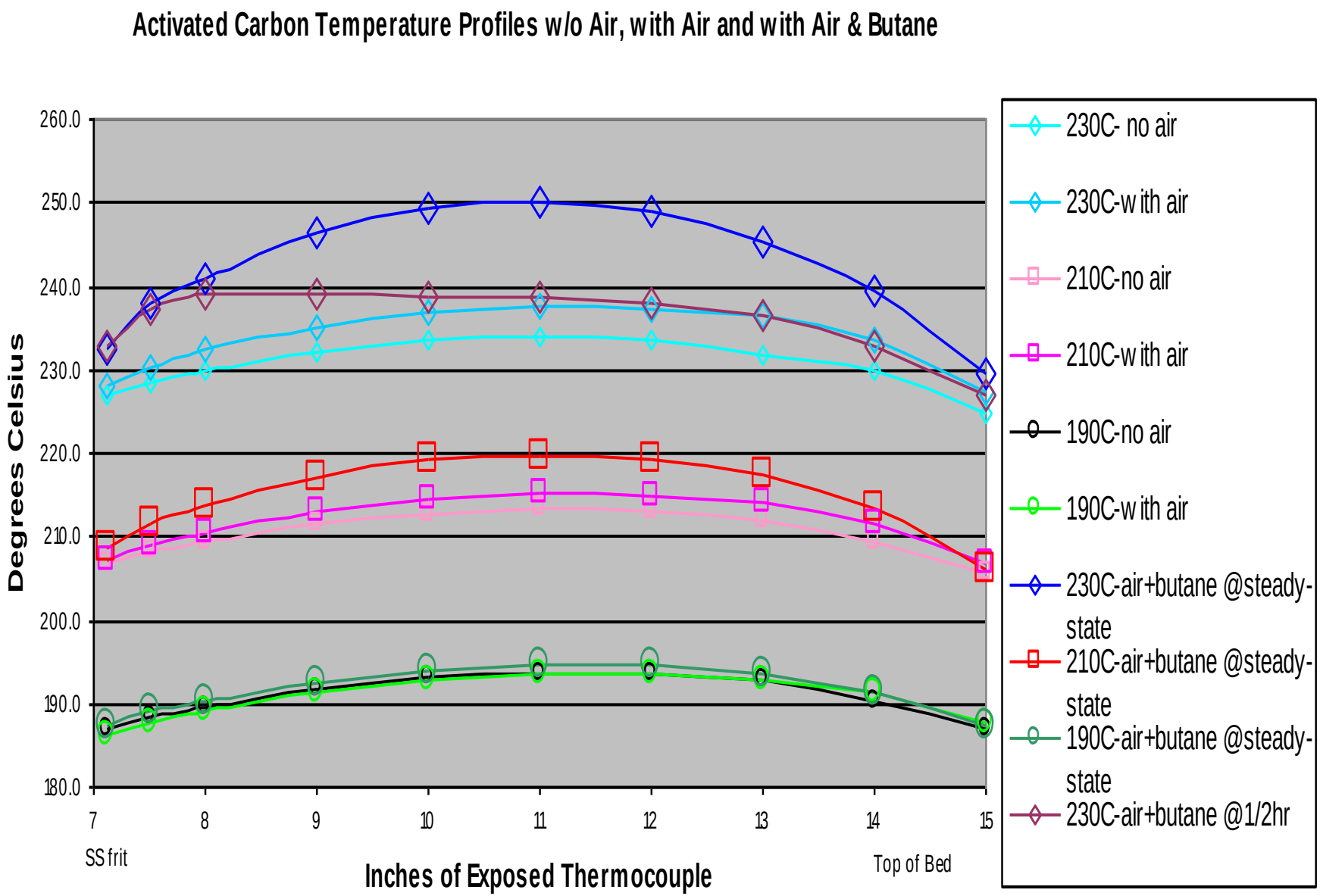
Activated Carbon Temperature Profiles w/o Air, with Air and with Air & Butane
Degrees Celsius
260.0
250.0
240.0
230.0
220.0
210.0
200.0
190.0
180.0
7
8
9
10
11
12
13
14
15
SS frit
Top of Bed
Inches of Exposed Thermocouple
230C- no air
230C-with air
210C-no air
210C-with air
190C-no air
190C-with air
230C-air+butane @steady-state
210C-air+butane @steady-state
190C-air+butane @steady-state
230C-air+butane @1/2hr

Figure 4

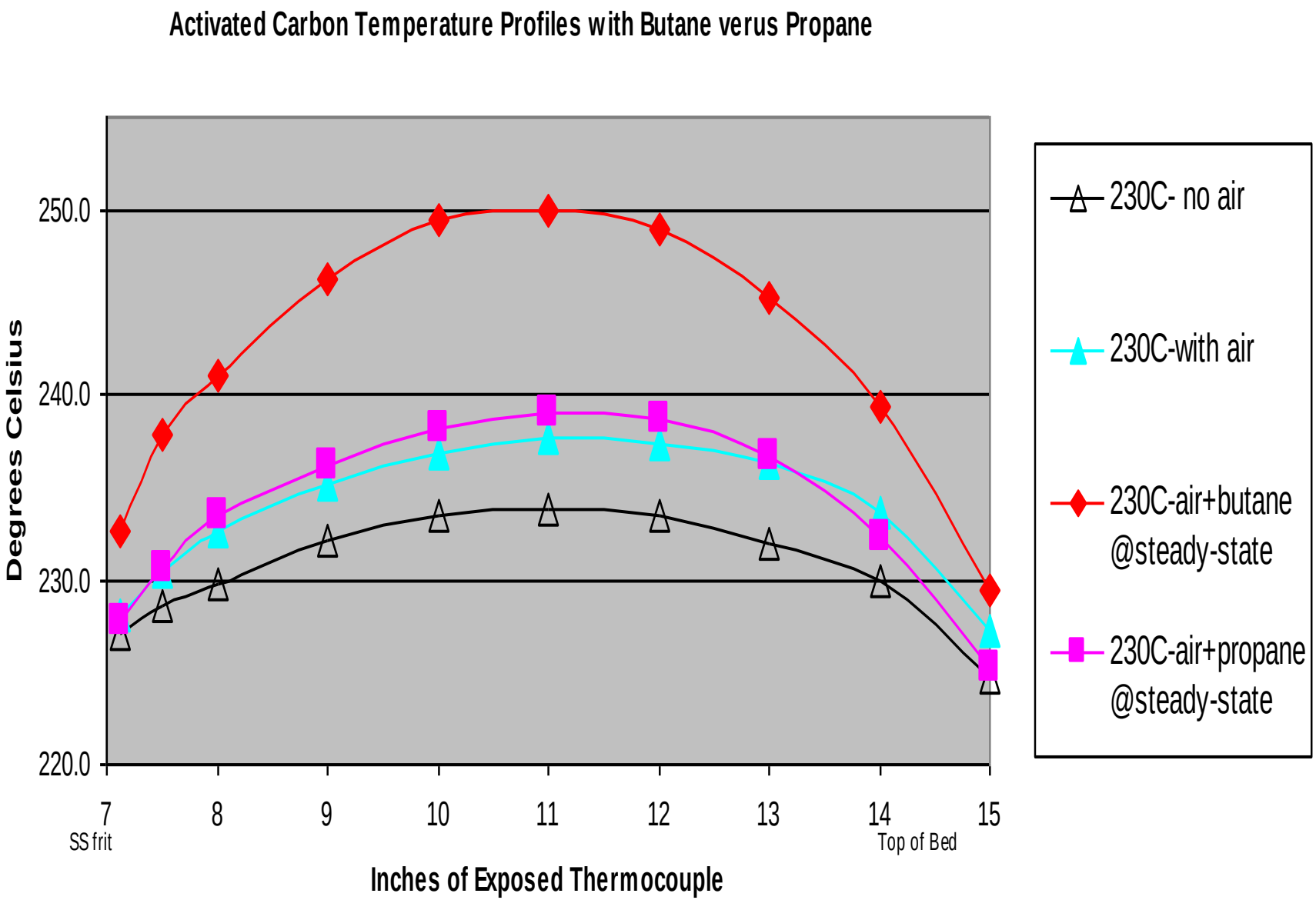
Activated Carbon Temperature Profiles with Butane verus Propane
Degrees Celsius
250.0
240.0
230.0
220.0
7
SS frit
8
9
10
11
12
13
14
Top of Bed
15
Inches of Exposed Thermocouple
230C- no air
230C-with air
230C-air+butane @steady-state
230C-air+propane @steady-state

Figure 5

Pyrolyzation of Spent Carbon ...

Desorption/charring : As a function of the adsorbate

Simple Desorption - No char formed

Alkanes(<C10), Aromatics(<C4 side chain), Acids and Alcohols(<C6),

Ethers, Polynuclear aromatics (<4 fused rings)

Adsorbate bonds break - pieces desorb below 1000F

Alkanes(>C10),Aromatics(>C4 side chain), Aliphatic Alcohols,

Alkenes and Alkynes(<C10), Esters,Organic Halides, Aldehydes, Ketones

Adsorbate destroyed low level of (2-5%) char formed

Aliphatic Alcohols(>C10), Alkenes and Alkynes(>C10), Aromatic acids,

any large molecule (>C20)

Figure 6

Adsorbate destroyed high levels of (>5%) char formed

Amines, Aromatic alcohols,Aliphatic acids, Conjugated Alkenes and Alkynes

Figures 7, 8 & 9 deleted due to file size (jpg's)

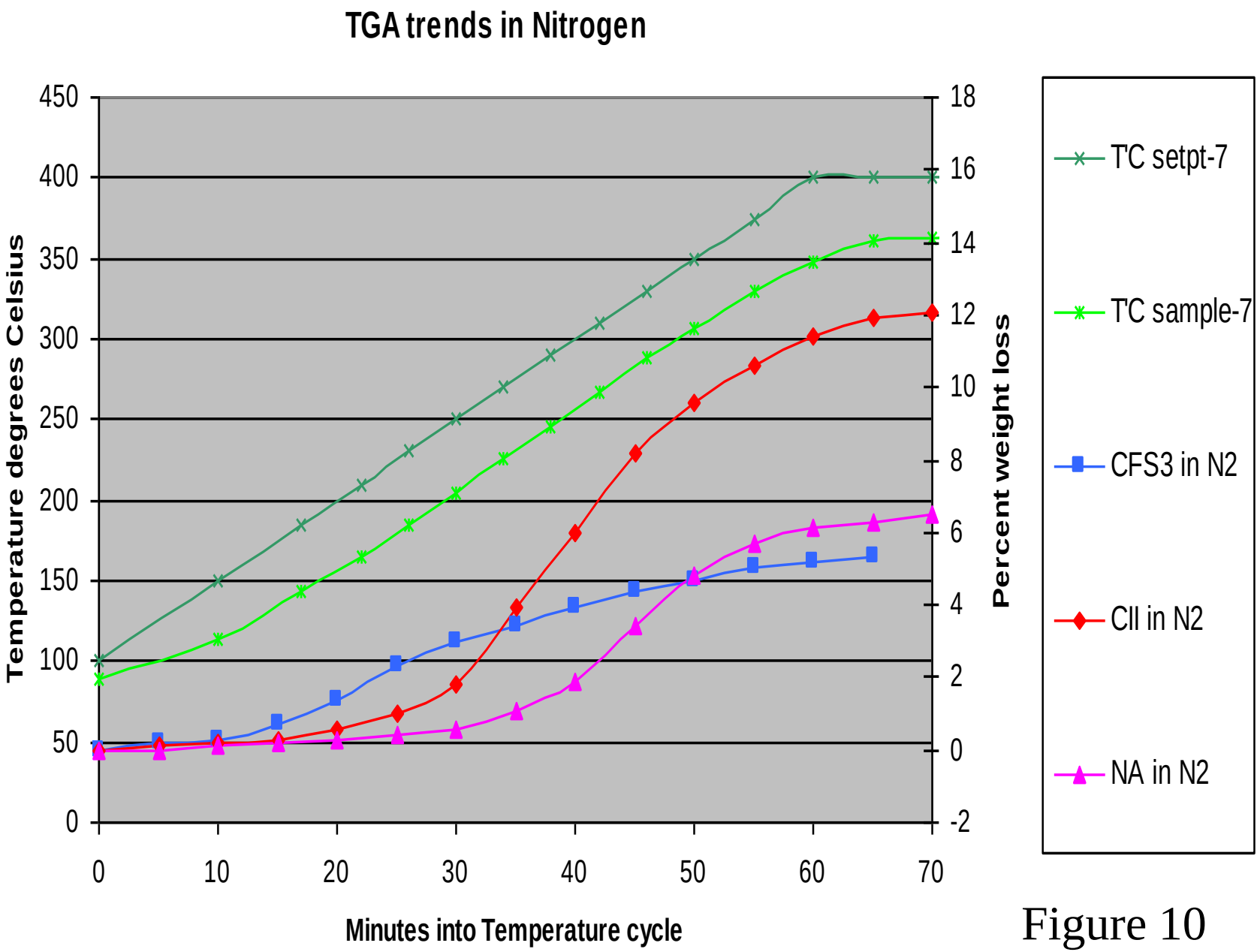
TGA trends in Nitrogen
Temperature degrees Celsius
Percent weight loss
Minutes into Temperature cycle
450
400
350
300
250
200
150
100
50
0
18
16
14
12
10
8
6
4
2
0
-2
0
10
20
30
40
50
60
70
TC setpt-7
TC sample-7
CFS3 in N2
CII in N2
NA in N2

Figure 10

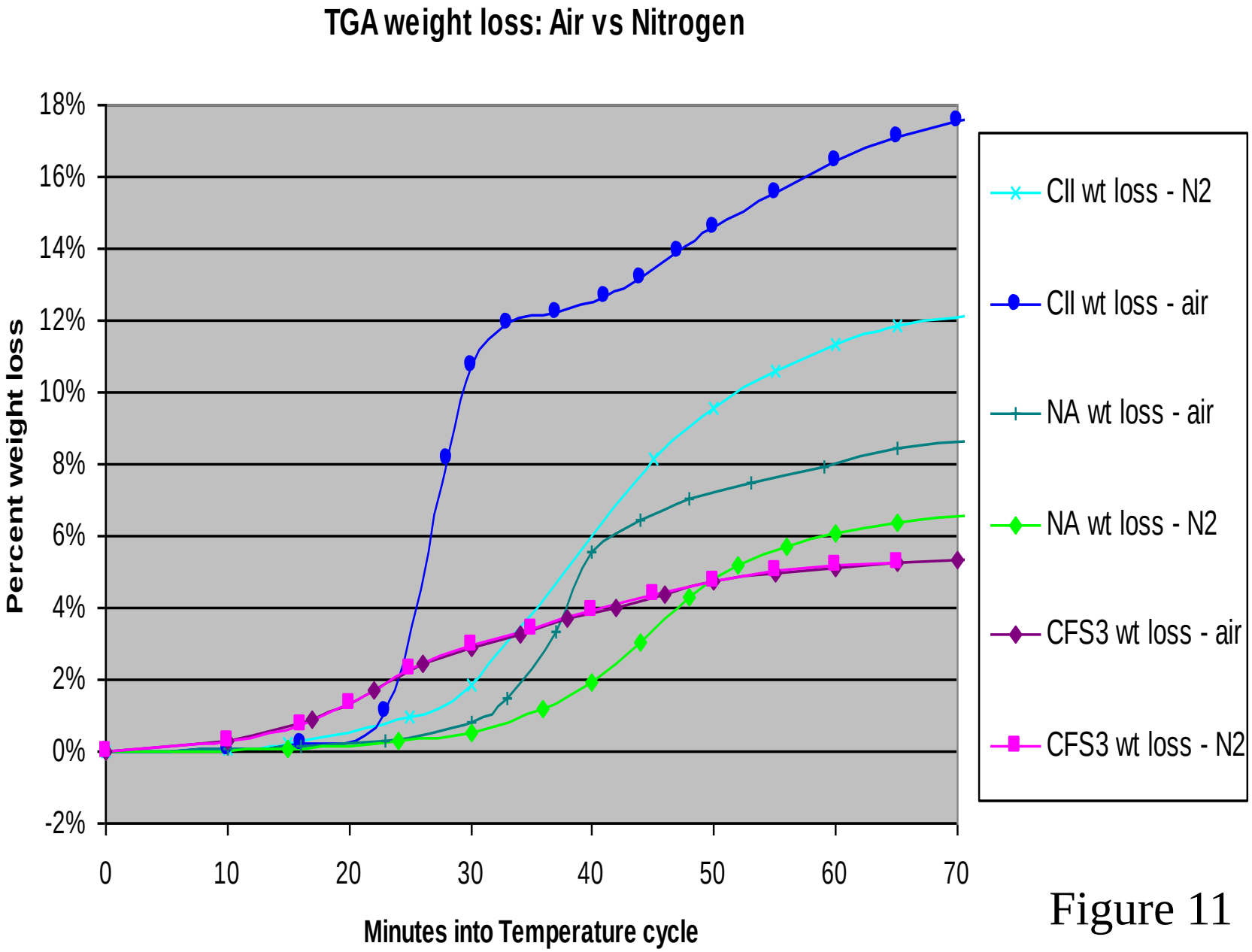
TGA weight loss: Air vs Nitrogen
Percent weight loss
18%
16%
14%
12%
10%
8%
6%
4%
2%
0%
-2%
0
10
20
30
40
50
60
70
Minutes into Temperature cycle
CII wt loss - N2
CII wt loss - air
NA wt loss - air
NA wt loss - N2
CFS3 wt loss - air
CFS3 wt loss - N2

Figure 11

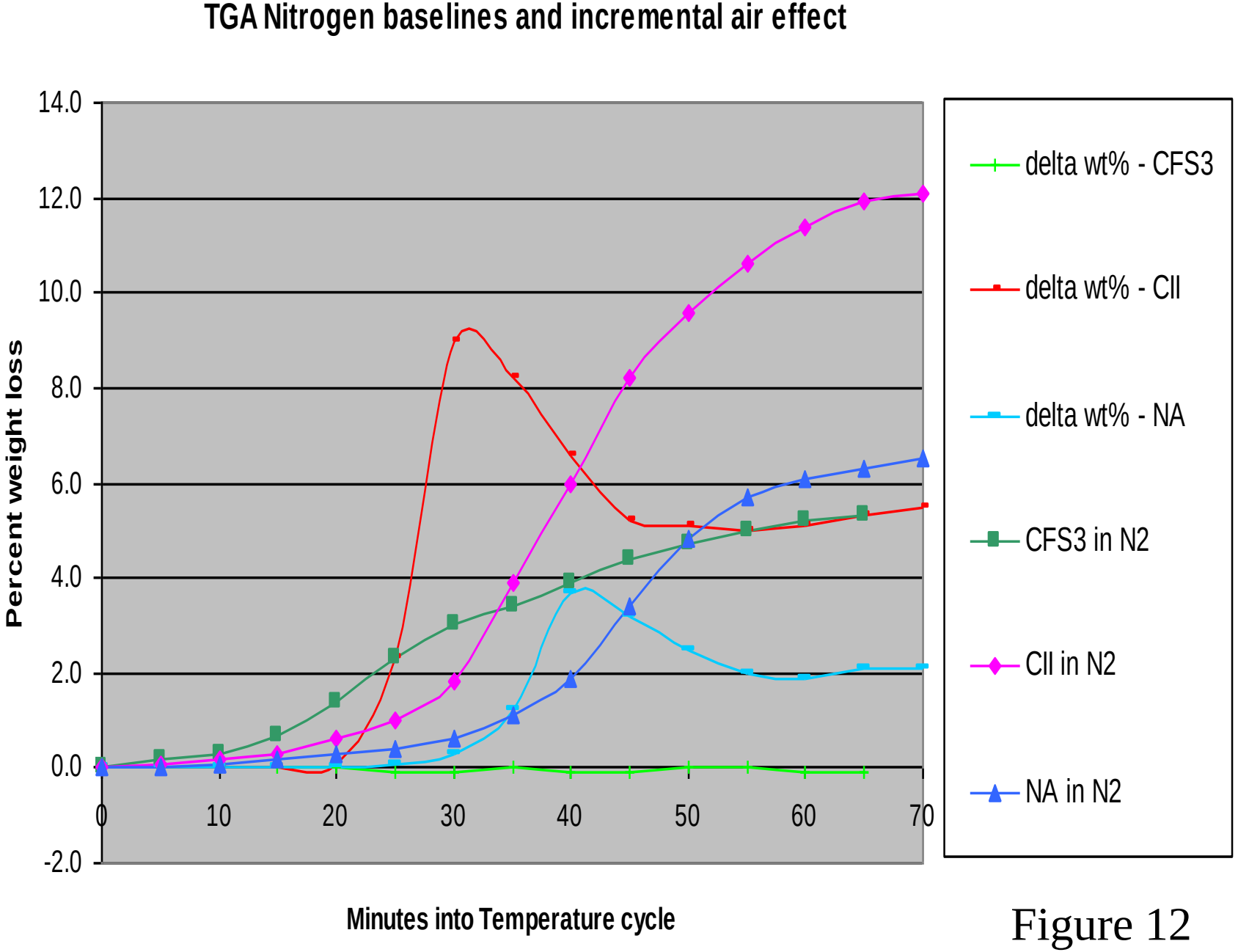
TGA Nitrogen baselines and incremental air effect
Percent weight loss
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
0
10
20
30
40
50
60
70
Minutes into Temperature cycle
delta wt% - CFS3
delta wt% - CII
delta wt% - NA
CFS3 in N2
CII in N2
NA in N2

Figure 12

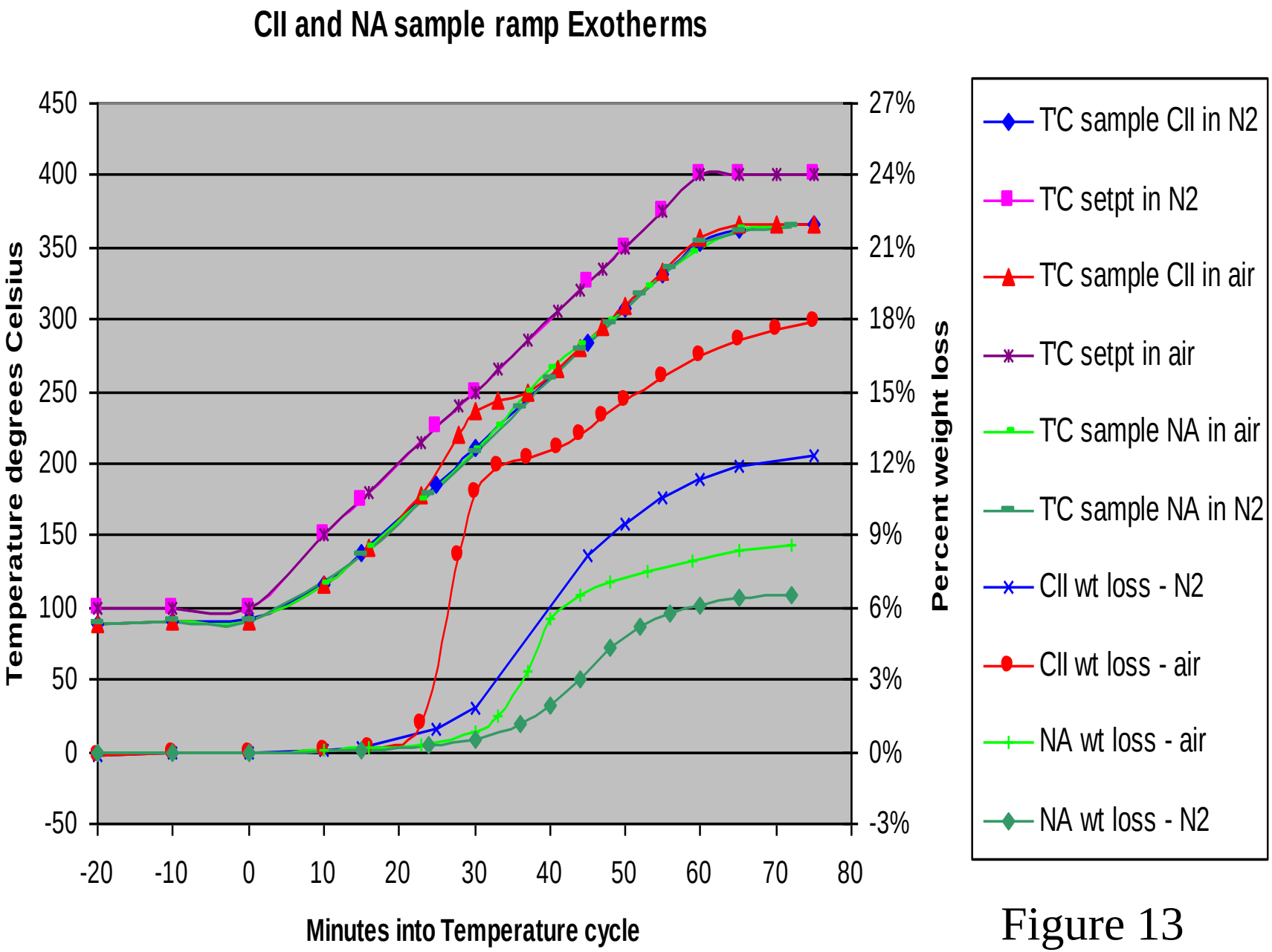
CII and NA sample ramp Exotherms
Temperature degrees Celsius
Percent weight loss
Minutes into Temperature cycle
450
400
350
300
250
200
150
100
50
0
-50
27%
24%
21%
18%
15%
12%
9%
6%
3%
0%
-3%
-20
-10
0
10
20
30
40
50
60
70
80
T'C sample CII in N2
T'C setpt in N2
T'C sample CII in air
T'C setpt in air
T'C sample NA in air
T'C sample NA in N2
CII wt loss - N2
CII wt loss - air
NA wt loss - air
NA wt loss - N2

Figure 13

Thermodynamics of Adsorption

Adsorption in the particle

Tug of War

Freedom of Solution or

Freedom of the gas phase

Figure 14

Adsorption	Solution/Vaporization
VS	
Highly desirable position	Ordinary position
but very little freedom.	but lots of freedom. of movement
High potential energy (depends on site)	Relatively low potential energy
Little entropy (like condensed phase)	High entropy (depends on pressure/conc.)
Finer the pore-the greater the energy	Lower the pressure/conc.-higher the entropy

Criterion for Adsorption from Solution

For Spontaneous adsorption to occur at a specific site

ε, the potential energy of the adsorption site, must satisfy:

$$\varepsilon_{Ads.}(\text{at site}) >= RT \ln \{Csat/C\}$$

Therefore, every adsorption site within the carbon structure with an adsorption potential equal to or greater than the above criterion will be occupied by a solute molecule., precipitated from solution.

Figure 15

Adsorption Sites on Activated Carbon
Distribution of Adsorption Forces for Butane

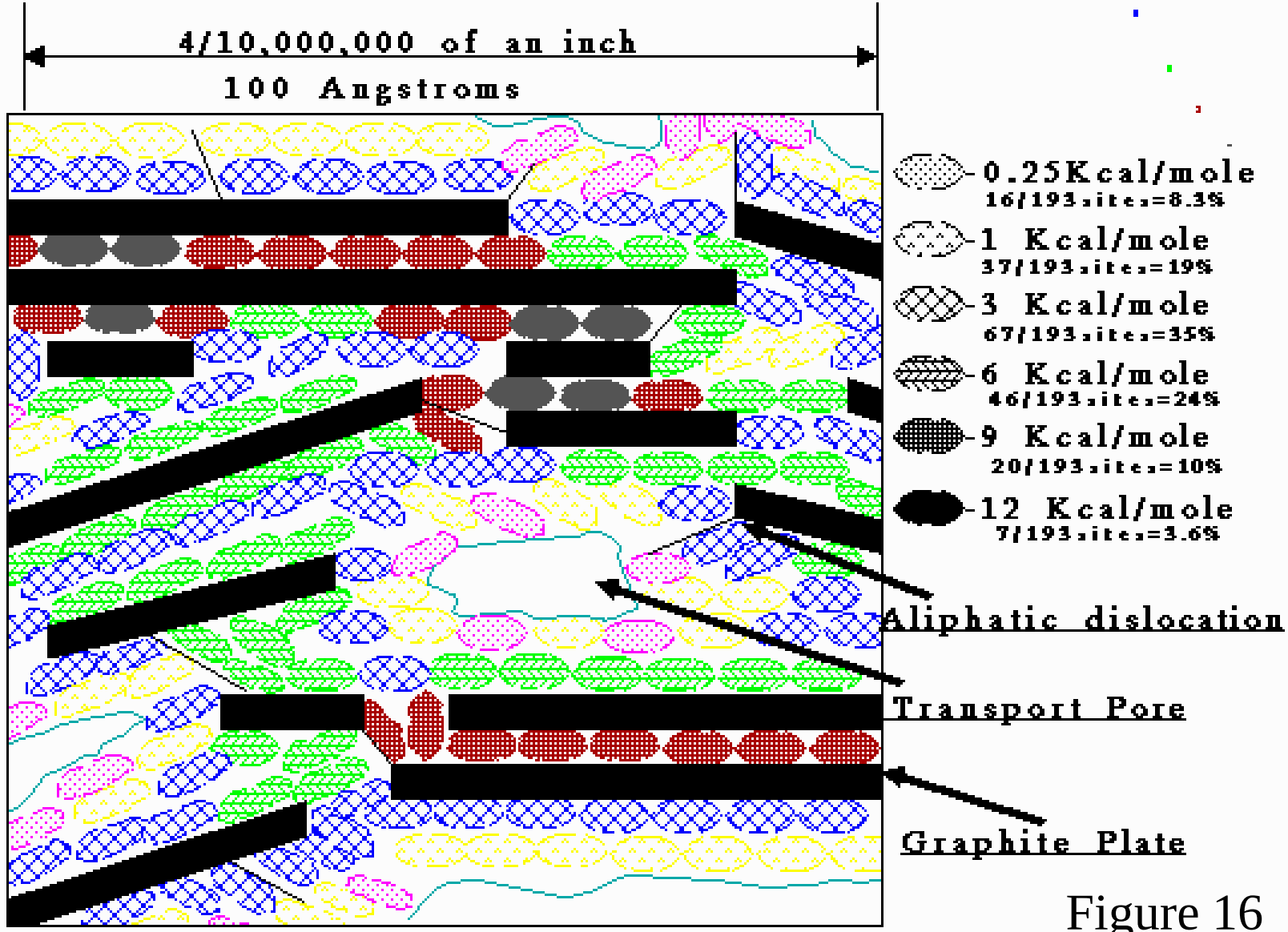

Figure 16

TF5AD

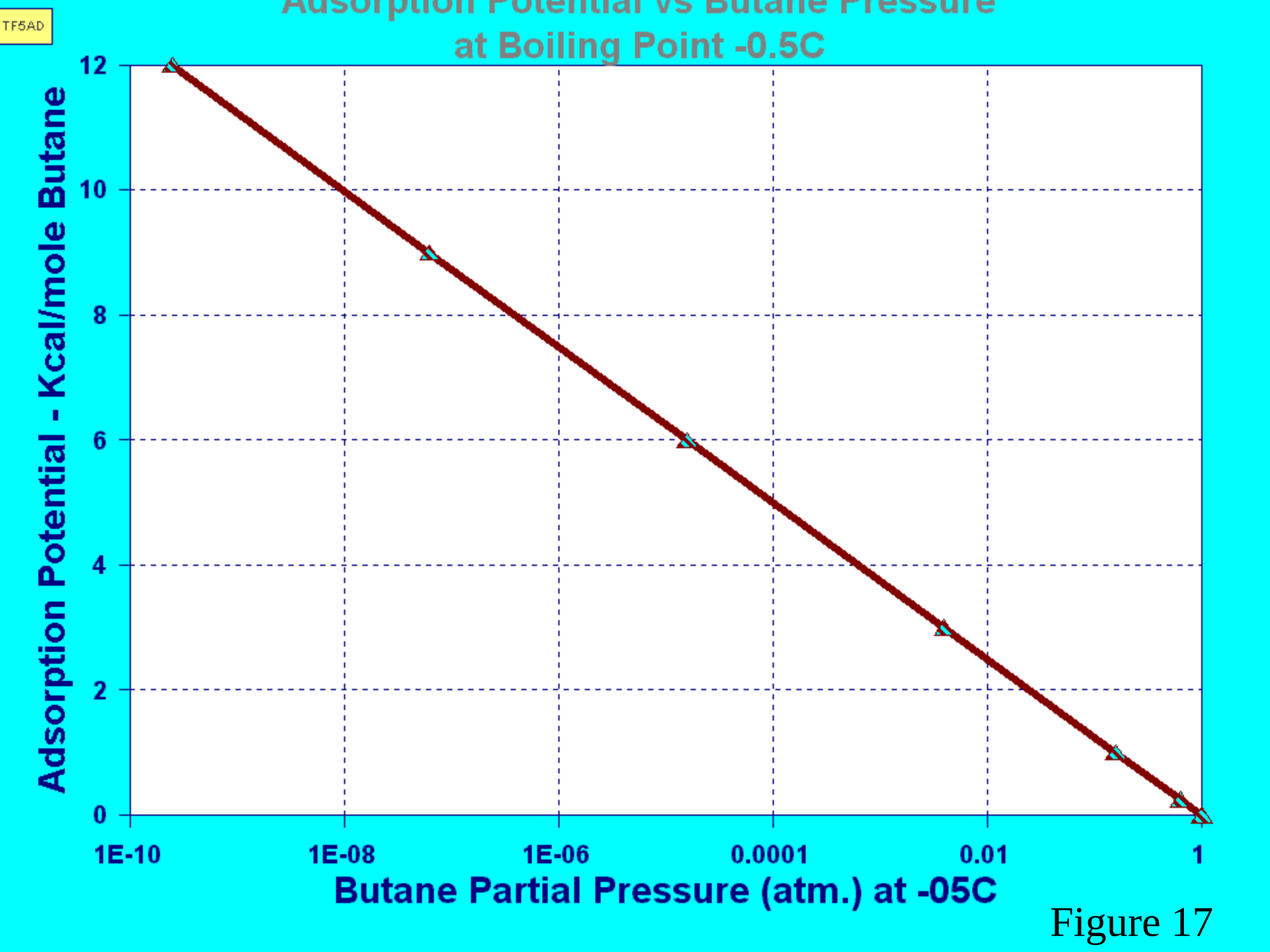

Figure 17

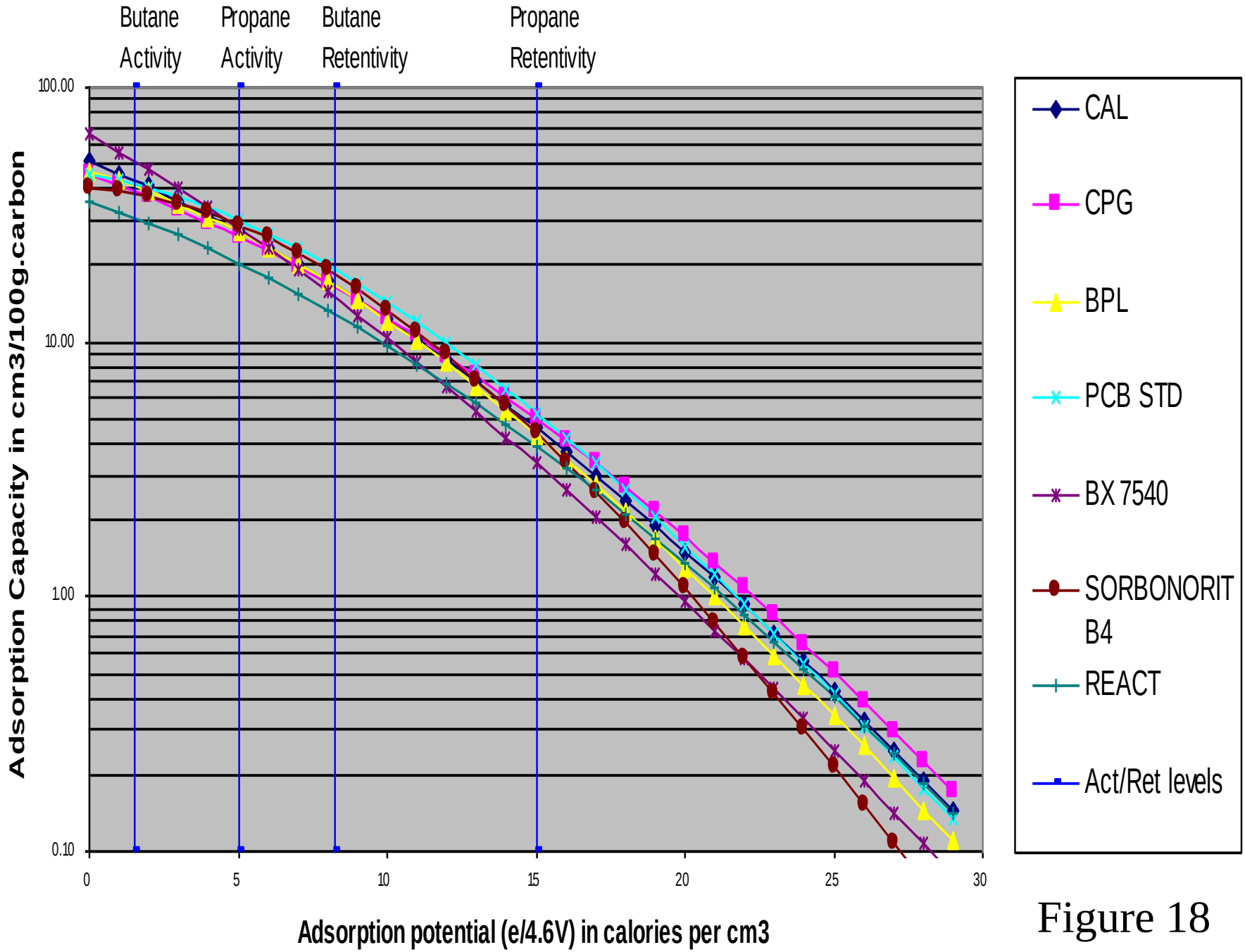
Butane Activity
Propane Activity
Butane Retentivity
Propane Retentivity
100.00
10.00
1.00
0.10
Adsorption Capacity in cm3/100g.carbon
0
5
10
15
20
25
30
Adsorption potential (e/4.6V) in calories per cm3
CAL
CPG
BPL
PCB STD
BX 7540
SORBONORIT B4
REACT
Act/Ret levels

Figure 18

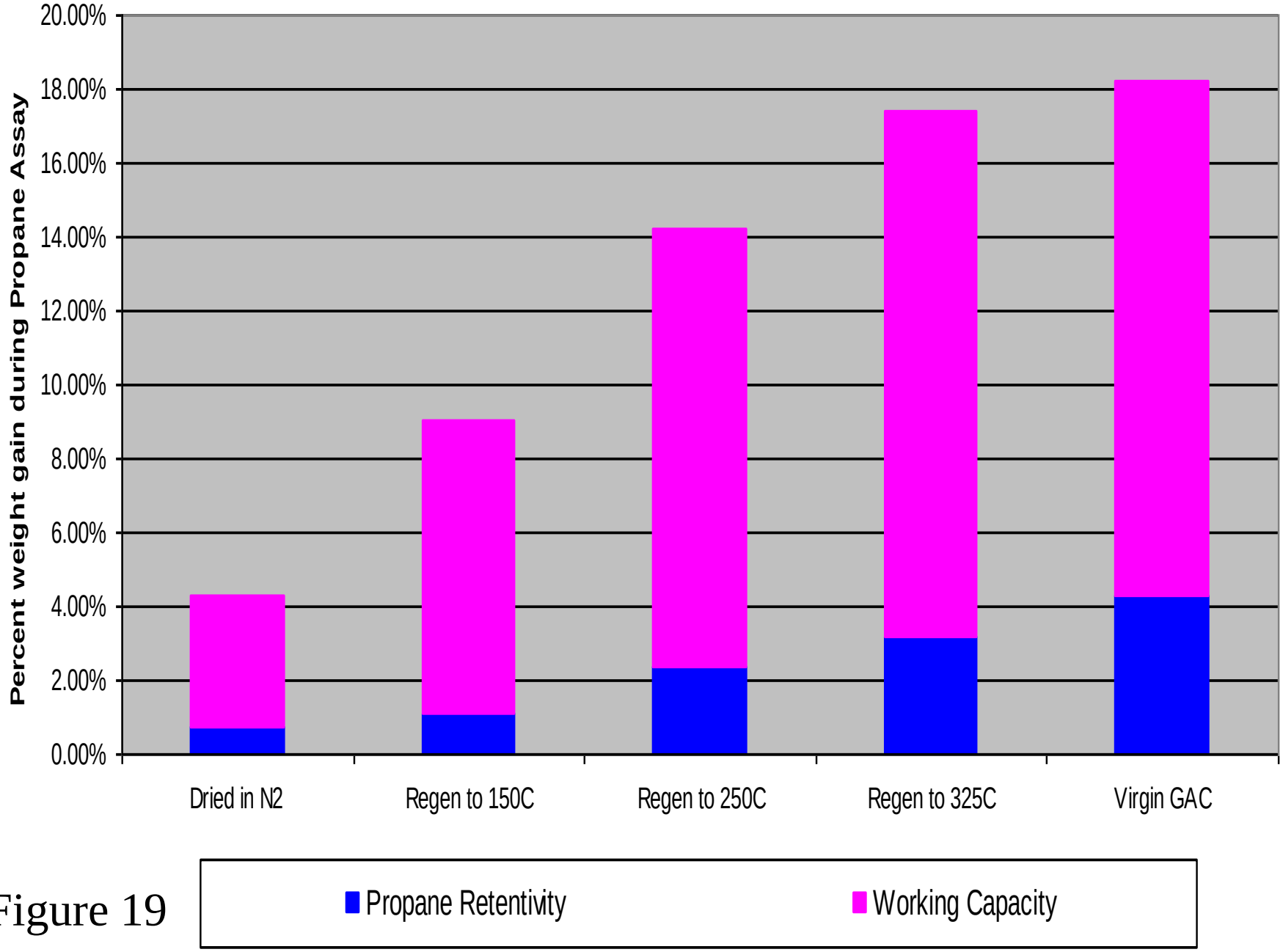
Percent weight gain during Propane Assay
20.00%
18.00%
16.00%
14.00%
12.00%
10.00%
8.00%
6.00%
4.00%
2.00%
0.00%
Dried in N2
Regen to 150C
Regen to 250C
Regen to 325C
Virgin GAC
Propane Retentivity
Working Capacity

Figure 19

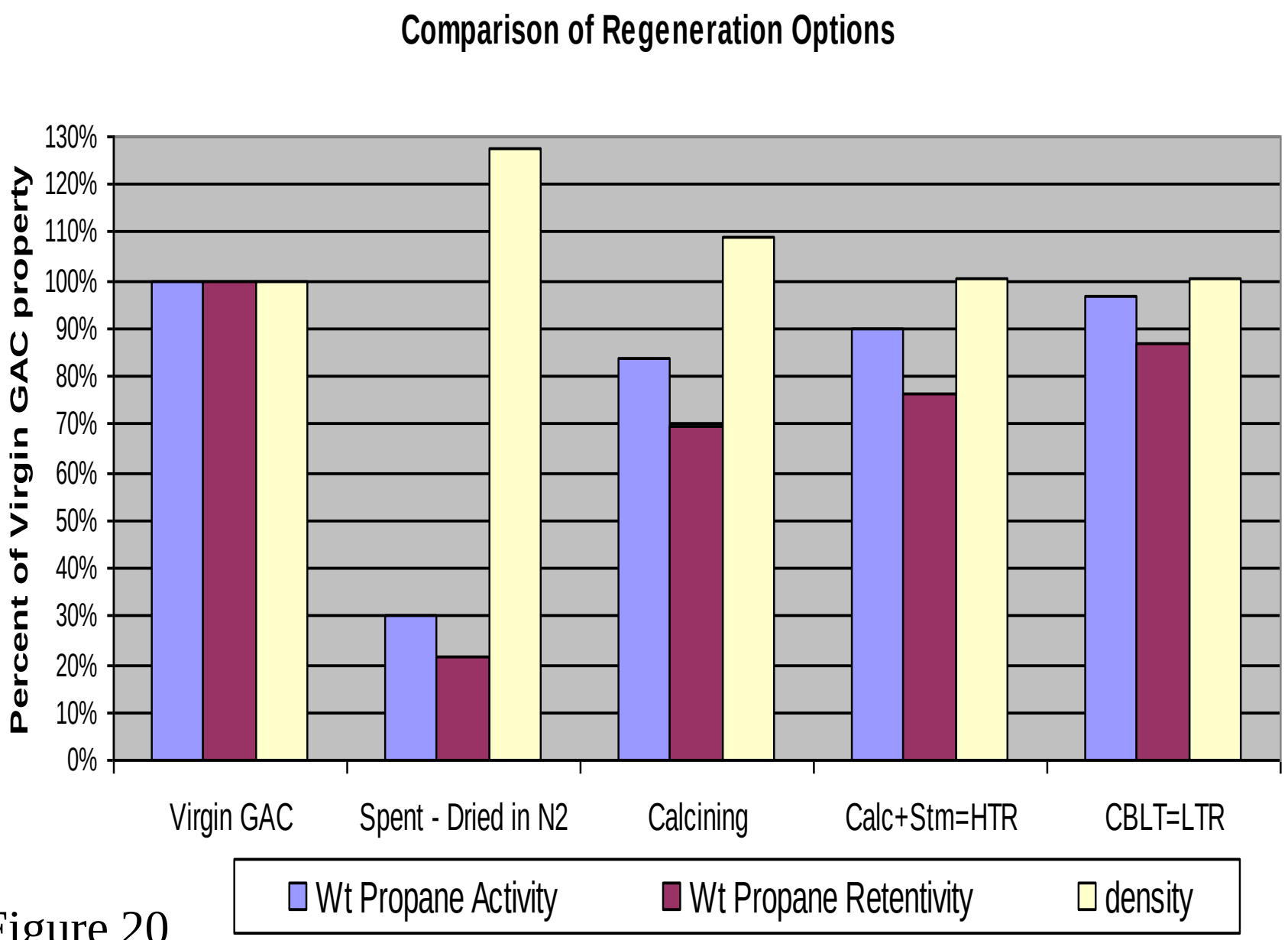
Comparison of Regeneration Options
Percent of Virgin GAC property
130%
120%
110%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Virgin GAC
Spent - Dried in N2
Calcining
Calc+Stm=HTR
CBLT=LTR
Wt Propane Activity
Wt Propane Retentivity
density

Figure 20

TF5AC

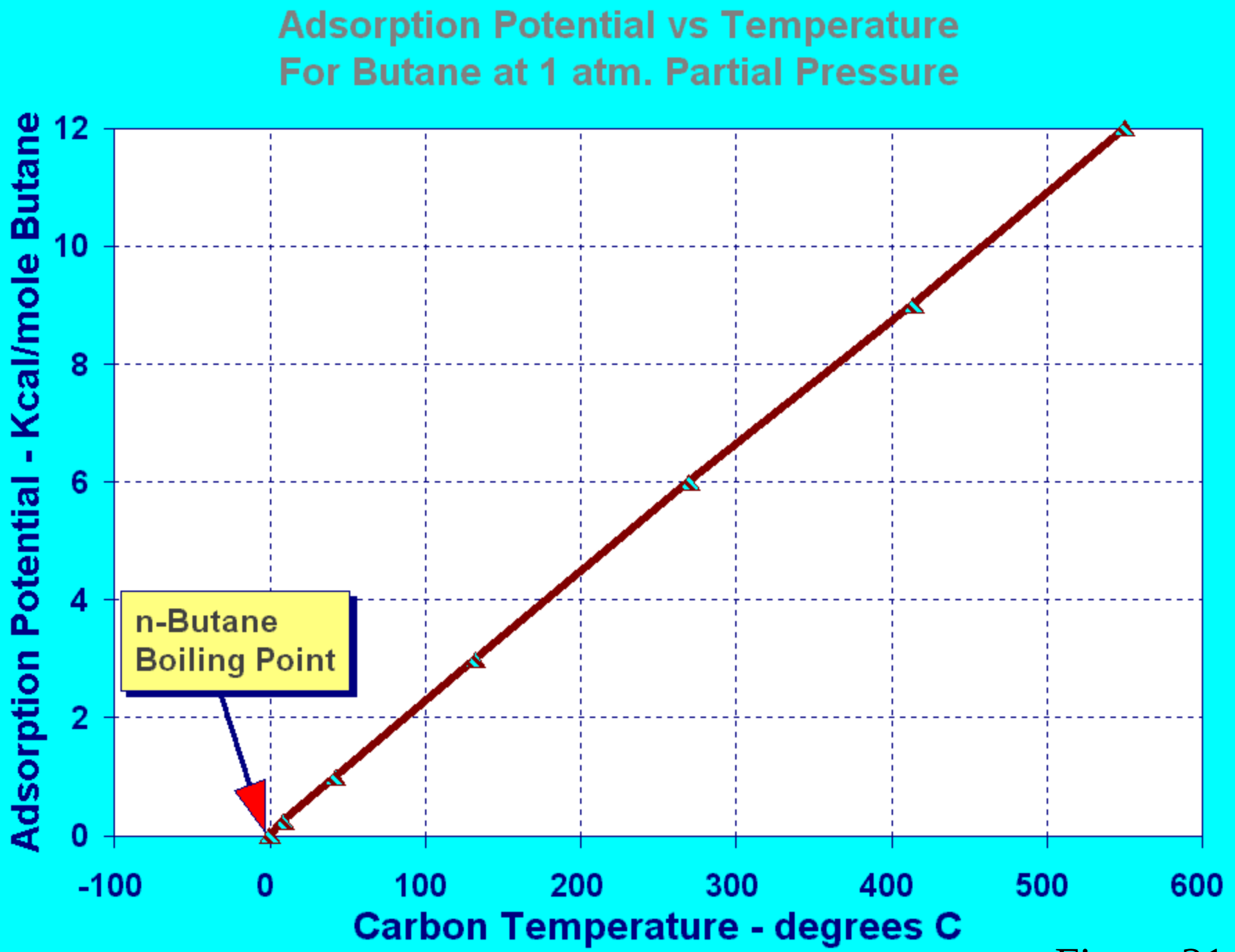

Figure 21

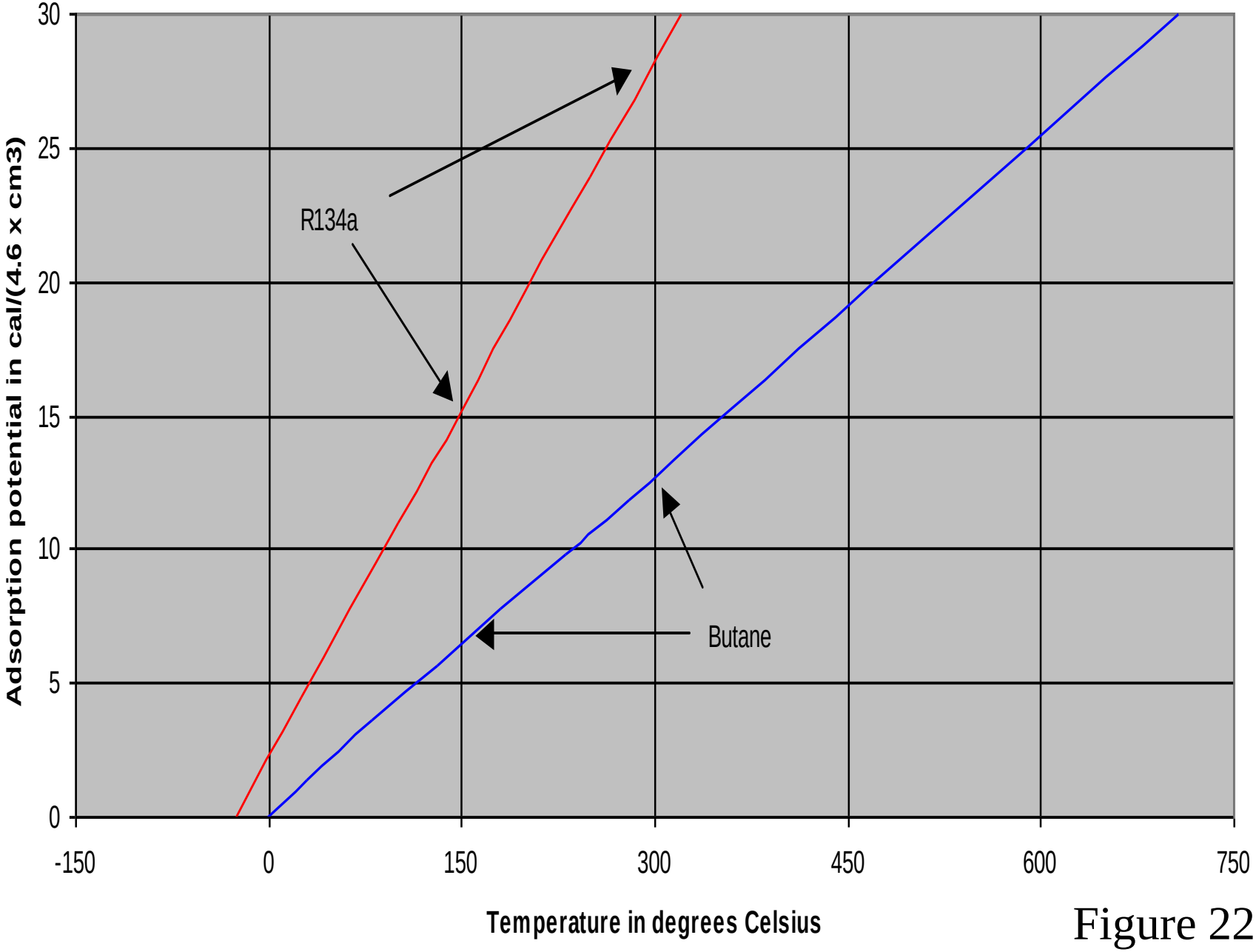
Adsorption potential in cal/(4.6 x cm3)
30
25
20
15
10
5
0
-150
0
150
300
450
600
750
Temperature in degrees Celsius
R134a
Butane

Figure 22

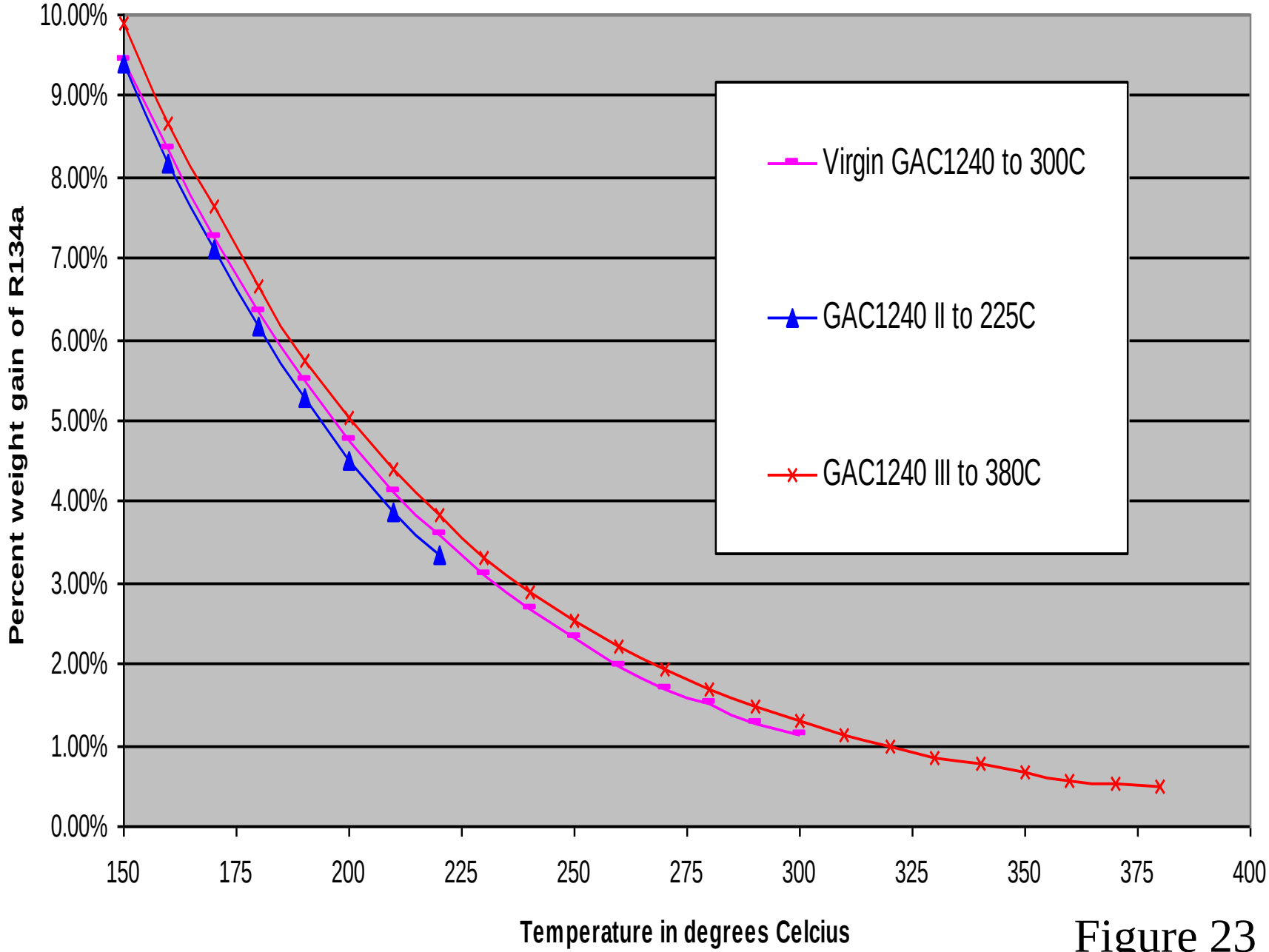
10.00%
9.00%
8.00%
7.00%
6.00%
5.00%
4.00%
3.00%
2.00%
1.00%
0.00%
Percent weight gain of R134a
150
175
200
225
250
275
300
325
350
375
400
Temperature in degrees Celcius
Virgin GAC1240 to 300C
GAC1240 II to 225C
GAC1240 III to 380C

Figure 23

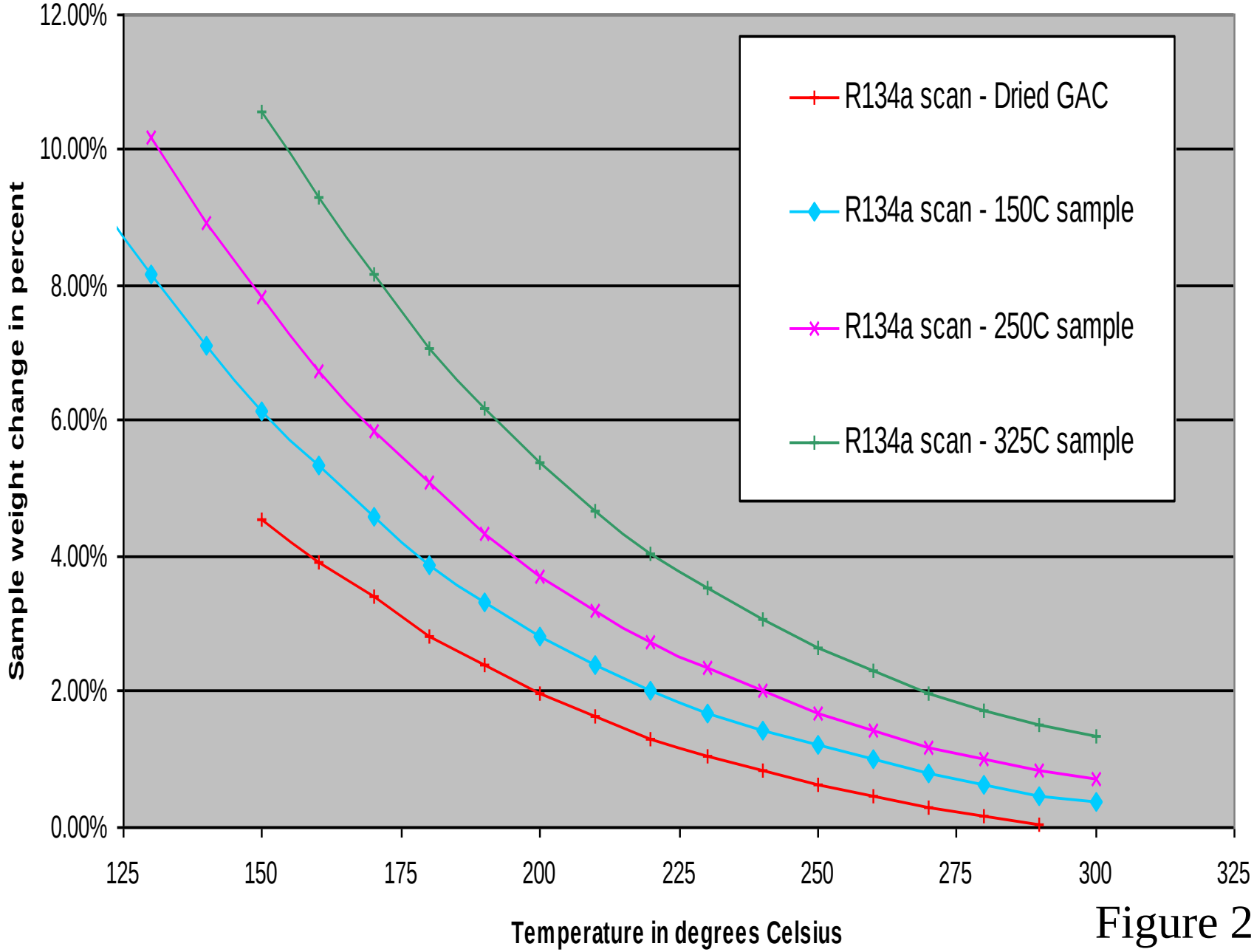
12.00%
10.00%
8.00%
6.00%
4.00%
2.00%
0.00%
Sample weight change in percent
125
150
175
200
225
250
275
300
325
Temperature in degrees Celsius
R134a scan - Dried GAC
R134a scan - 150C sample
R134a scan - 250C sample
R134a scan - 325C sample

Figure 24

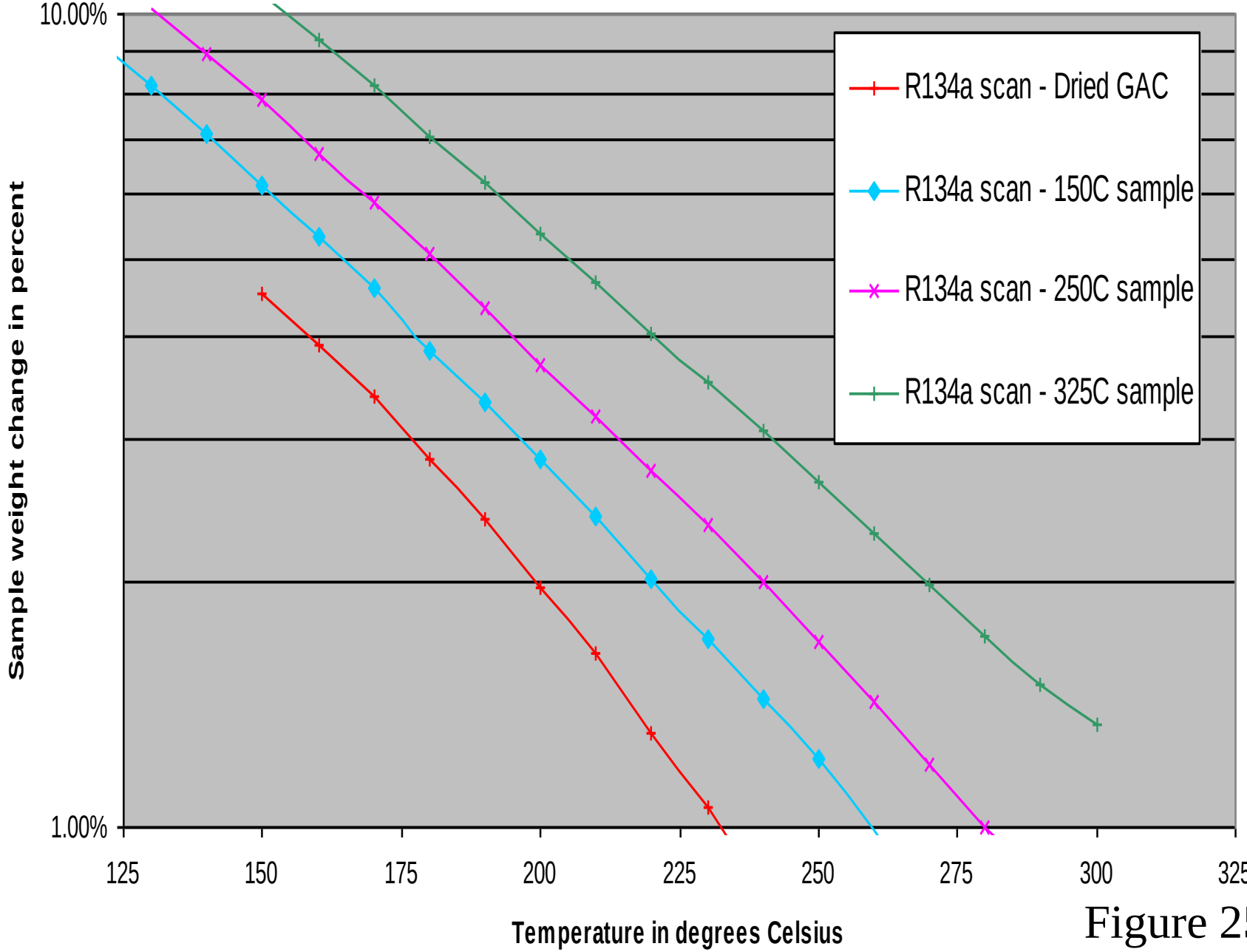
10.00%
1.00%
Sample weight change in percent
125
150
175
200
225
250
275
300
325
Temperature in degrees Celsius
R134a scan - Dried GAC
R134a scan - 150C sample
R134a scan - 250C sample
R134a scan - 325C sample

Figure 25

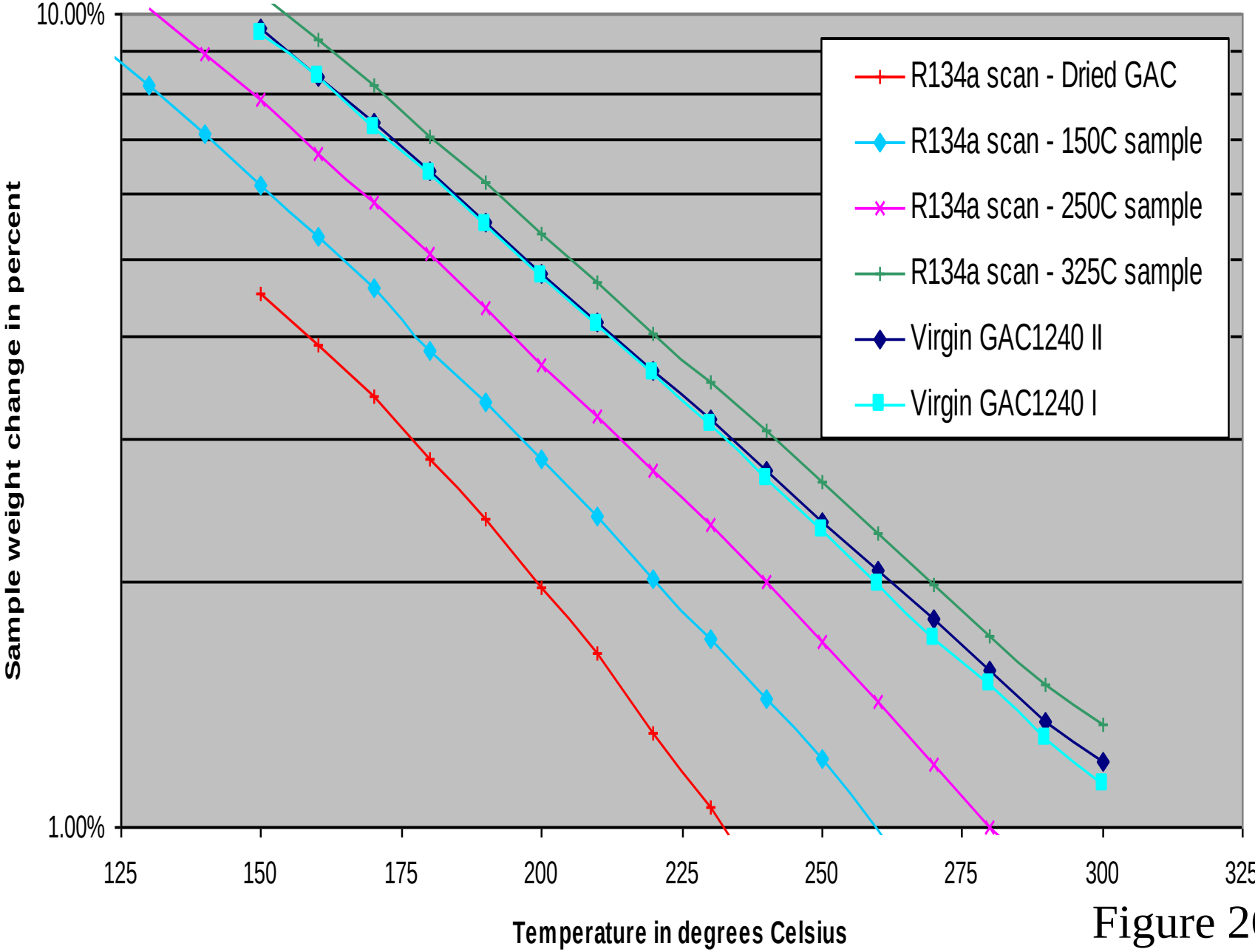
10.00%
1.00%
Sample weight change in percent
125
150
175
200
225
250
275
300
325
Temperature in degrees Celsius
R134a scan - Dried GAC
R134a scan - 150C sample
R134a scan - 250C sample
R134a scan - 325C sample
Virgin GAC1240 II
Virgin GAC1240 I

Figure 26

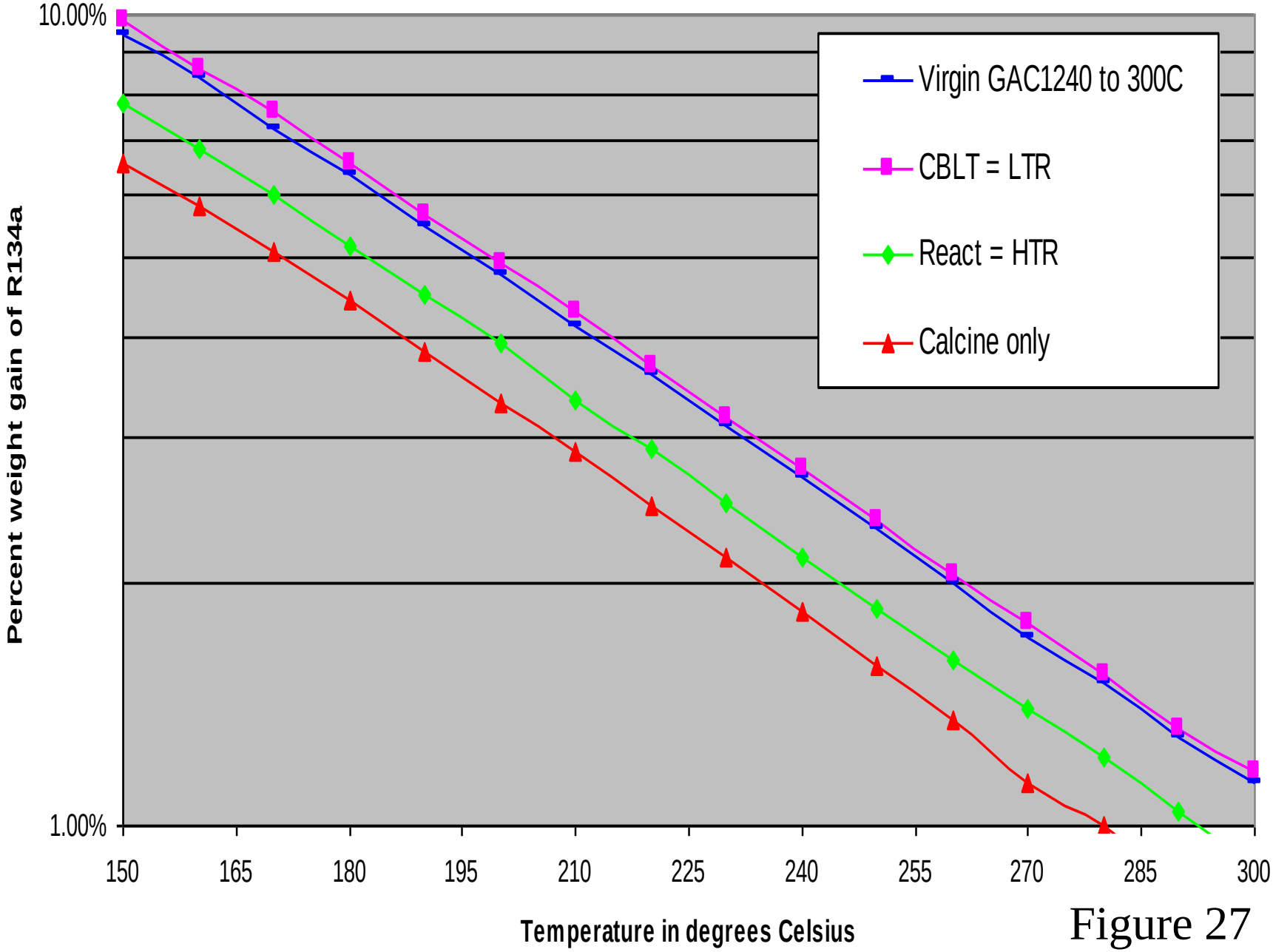
10.00%
1.00%
Percent weight gain of R134a
150
165
180
195
210
225
240
255
270
285
300
Temperature in degrees Celsius
Virgin GAC1240 to 300C
CBLT = LTR
React = HTR
Calcine only

Figure 27

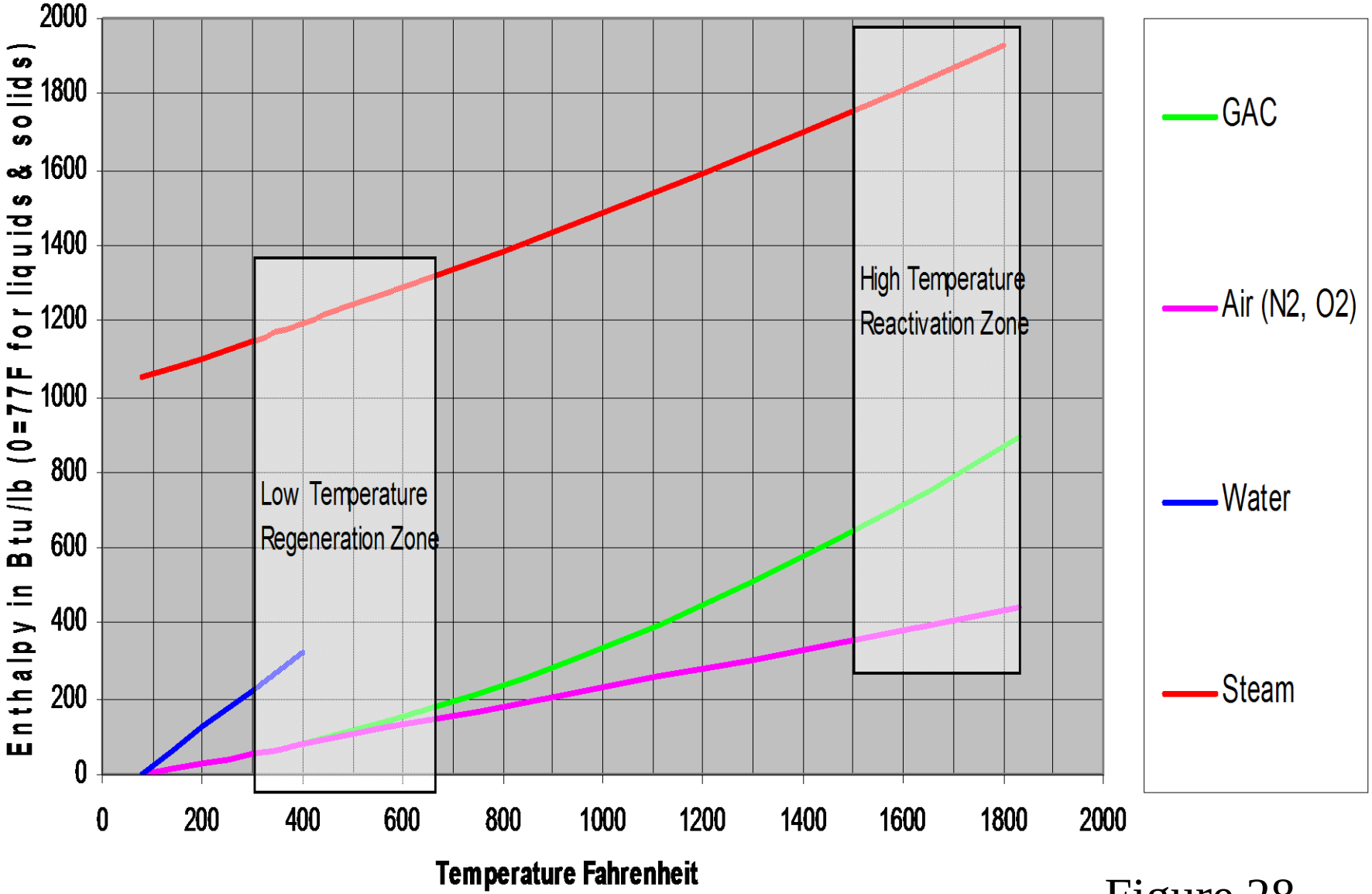
Enthalpy in Btu/lb (0=77F for liquids & solids)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Temperature Fahrenheit
Low Temperature
Regeneration Zone
High Temperature
Reactivation Zone
GAC
Air (N2, O2)
Water
Steam

Figure 28

TABLE 2: Table of Reaction Stoichiometries and Heats of Combustion

Key:

	oxygen	+	fuel		--->	products				dHcomb			
	O2(g)	C(s)	CO(g)	CH(l)*	CH2(l)**	C(s)	CO(g)	CO2(g)	H2O(g)				
mw	32	12	28	13	14	12	28	44	18	kcal	Btu	Btu	Btu
dHform	0.000	0.000	-26.416	1.953	-6.223	0.000	-26.416	-94.052	-57.798	gmole	#mole	#fuel	#O2
	0.5	1					1			-26.42	-47,549	-3,962	-2,972
	0.5		1					1		-67.64	-121,745	-10,145	-7,609
	1	1						1		-94.05	-169,294	-14,108	-5,290
reaction	1.5				1			1	1	-145.63	-262,129	-18,723	-5,461
	1				1		1		1	-77.99	-140,384	-10,027	-4,387
stiochiometry	0.5				1	1			1	-51.58	-92,835	-6,631	-5,802
	1.5			1				1	0.5	-124.90	-224,827	-17,294	-4,684
	1			1			1		0.5	-57.27	-103,082	-7,929	-3,221
	0.5			1		1			0.5	-30.85	-55,534	-4,272	-3,471

dHform in units of Kcal/gmole

CH(l)* based on 1/6th of the dHform of Benzene

CH2(l)** based on 1/6th of the dHform of Cyclohexane

Note: 1 kW*hr = 3412.1 Btu

1 watt = 14.34 cal per min

1 Btu = 252 calories

Figures 29, 30 & 31 deleted due to file size (jpg's)

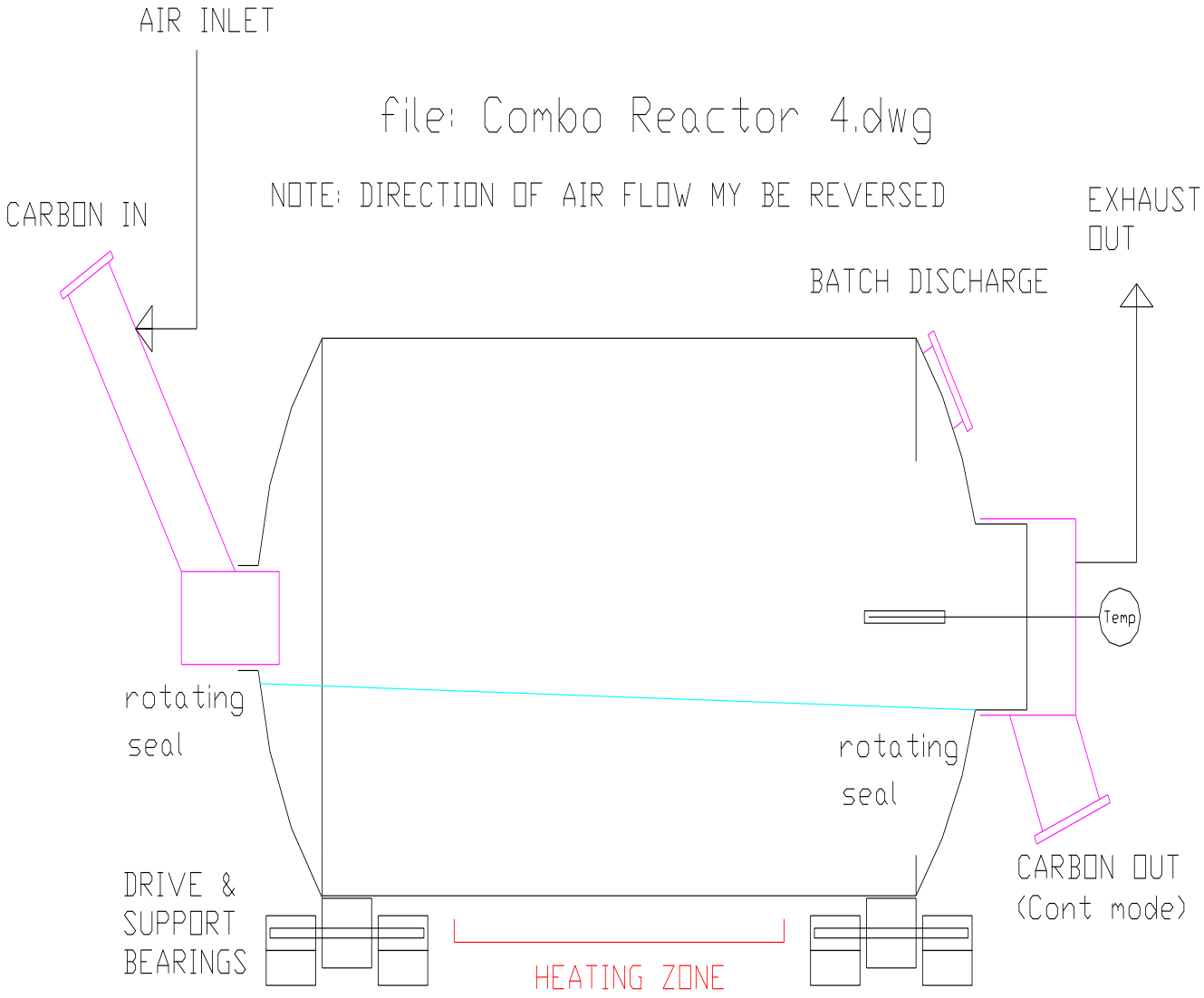
AIR INLET
file: Combo Reactor 4.dwg
NOTE: DIRECTION OF AIR FLOW MY BE REVERSED
CARBON IN
EXHAUST OUT
BATCH DISCHARGE
Temp
rotating seal
rotating seal
DRIVE & SUPPORT BEARINGS
HEATING ZONE
CARBON OUT (Cont mode)

Figure 32

CarbOxLT (LTR) vs Reactivation (HTR)

- Different Reaction Pathway & Conditions
  - HTR: Calcining adsorbates & Addn. Steam Activation
  - LTR: Surface Oxidation in air of Adsorbates
  - HTR: 850-1000 Celsius, LTR: 150-350 Celsius
  - HTR: Endothermic (add heat), LTR: Exothermic
  - HTR: raked bed <3” deep, LTR: stirred dense bed
- Different Economics of Operation
  - Capital: HTR: Refractory lined, LTR: CS/SS
  - Energy: HTR: 4,000+ Btu/#, LTR: <1,000 Btu/#
  - Losses/cycle: HTR: 3-5%, LTR: 1.5-3% (estimated)
  - Regeneration Efficiency: LTR > HTR

Figure 33

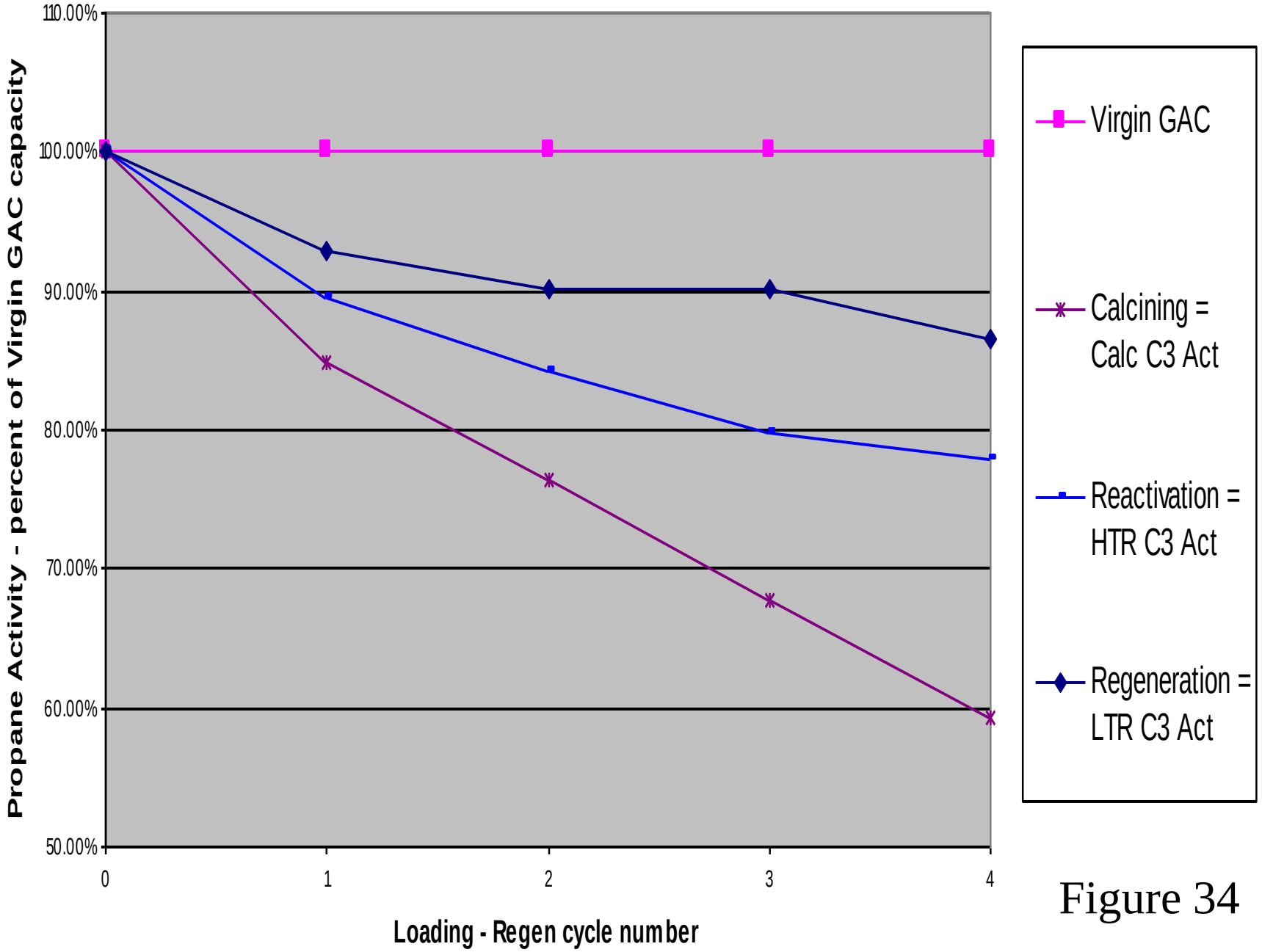
Propane Activity - percent of Virgin GAC capacity
110.00%
100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
0
1
2
3
4
Loading - Regen cycle number
Virgin GAC
Calcining = Calc C3 Act
Reactivation = HTR C3 Act
Regeneration = LTR C3 Act

Figure 34

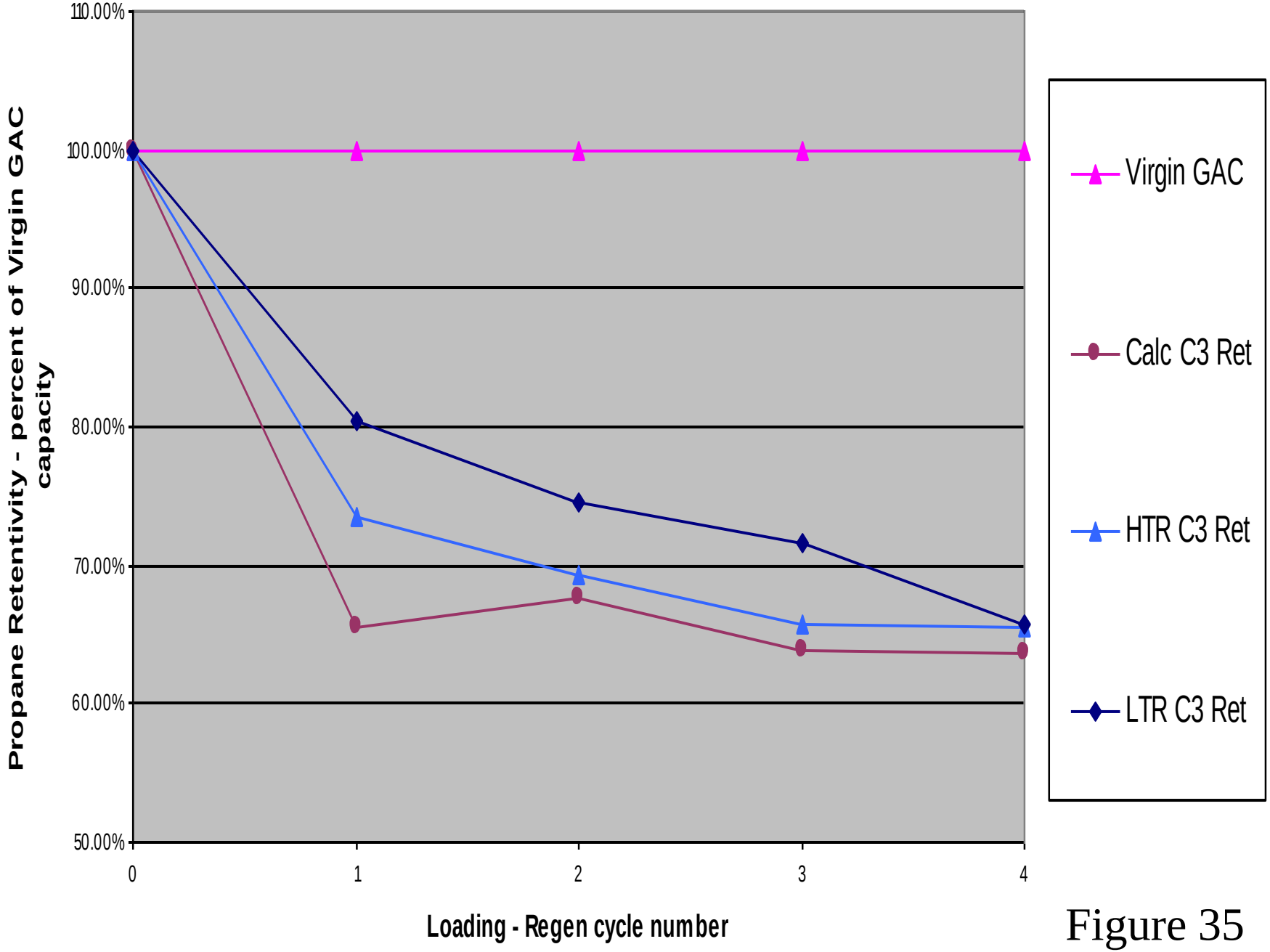
Propane Retentivity - percent of Virgin GAC capacity
110.00%
100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
0
1
2
3
4
Loading - Regen cycle number
Virgin GAC
Calc C3 Ret
HTR C3 Ret
LTR C3 Ret

Figure 35