I. Group Contribution Method to Predict the Flame Resistance of Polycarbonates

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II. Transparent OSU-Compliant Polycarbonate Copolymers

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Rich Lyon, Stas Stoliarov, Rich Walters

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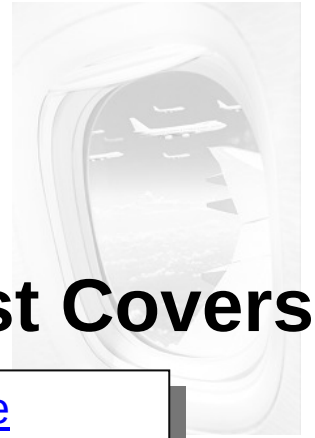
Scott van Wormer

Boeing Labs
Vasan Sundaram, Hank Lutz, Joel Peterson, Pete Guard, Jim Griffing, Kjersta Larson, Steve Moffitt

the challenge:



BOEING: Flame Resistant Transparent Dust Covers

Ignitability, Melting/Dripping	**Heat release**	Smoke release
60-sec vertical Bunsen burner	**OSU 65/65: Ohio State U calorimeter**	National Bureau of Standards smoke chamber
6” burn length	**65 kW • min/m² total (during first 2 min)**	specific optical density < 200 (during 4-min test)
15-s specimen extinguishing time	**65 kW/m² peak rate (during first 5 min)**	Toxicity (OEM): CO, HCN, HF, HCl, SO2, NOX
3-s drip extinguishing time		

expensive, kgs of material, not “screening” tool

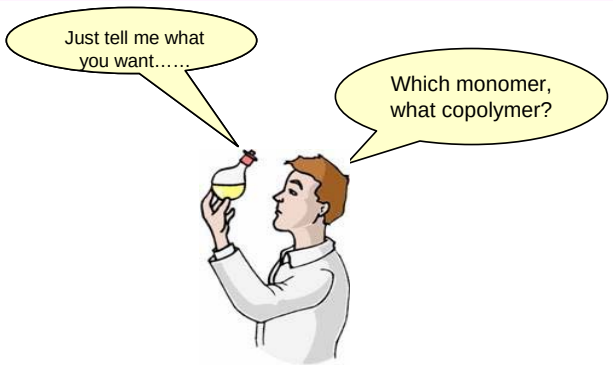
gms of material; many, many formulations to examine

the solution: convergence of 3 key "events"

1

GE Global Research
GE Plastics (Sabic Innovative Plastics)

POLYCARBONATES



2

"Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions"

by DW van Krevelen

3

"Calculating Polymer Flammability from Molar Group Contributions"
DOT/FAA/AR-01/31
by Richard Walters and Richard E Lyon

…… and a key testing methodology and database (PCFC)

Flammability Testing (Lyon-Walters)

4

Microscale Combustion Calorimetry

Flame tests

Bench-Scale

Component-Scale

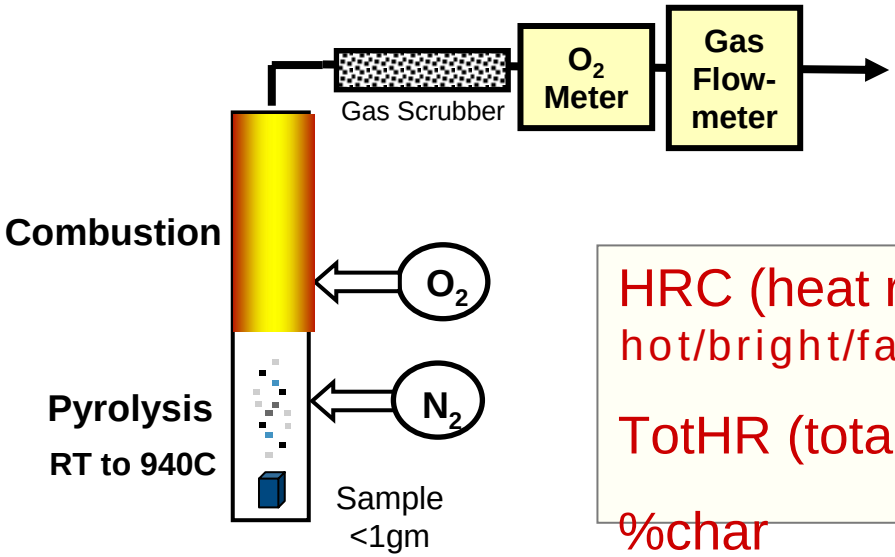
Milligram | Gram | Kilogram | Metric Ton

Model → PCFC → OSU → Large Scale Tests

Pre-screen *Screen*

Small amounts of material
No geometry, processing dependence
Complete combustion, thermodynamic and kinetic effects

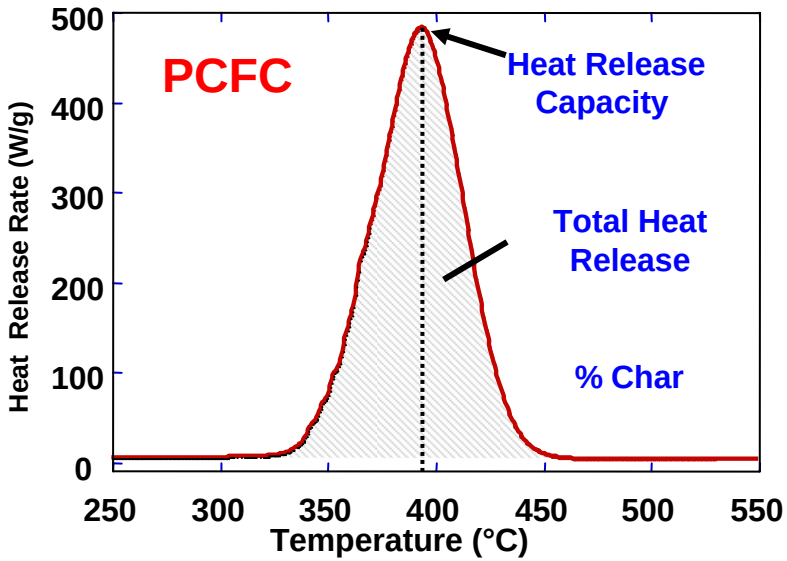
PCFC: Pyrolysis-Combustion Flow Calorimetry (Lyon, Walters)

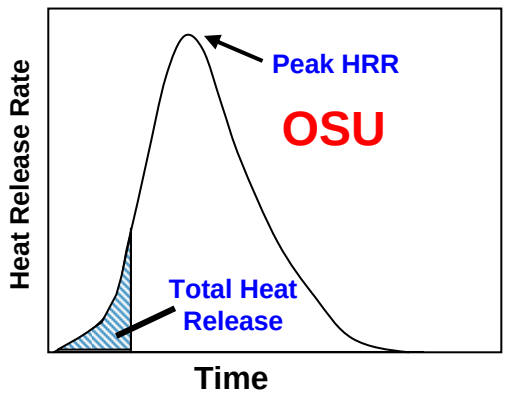


HRC (heat release capacity)….how hot/bright/fast

TotHR (total heat release) …..how much fuel

%char …..how much isn't fuel





Key Requirements to Successful Modeling

TEST/DATABASE: LARGE, CONSISTENT, VERIFIED

One operator

One machine

One test protocol

Reference materials

Literature verification

One class of materials

Polycarbonates

MODEL: SIMPLE, PHYSICALLY APPEALING, PARAMETERIZED

Additivity

Inverse Additivity

Maxwell Model

OPTIMIZATION: model to data

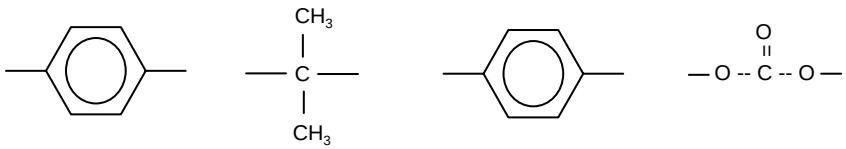
~90% consistent (~10% outliers)

User Beware: Don't look too hard, you're bound to find "inconsistencies"

Cannot predict special effects, transitions, geometric or processing artifacts (drip, buckle, melt, skin formation, bubbling….)

Example: additivity of group contributions

BPA-polycarbonate



Group Contribution to HRC	13.1	85.5	13.1	13.6	Σ=125.3	$(\frac{kJ}{mole-^oK})$
Molar Mass	76	42	76	60	M=254	$(\frac{gm}{mole})$

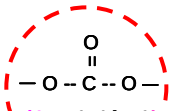
HRC = Σ/M = 492 J/g-^{o}K

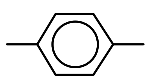
(some measured values: 528, 476, 504, 547)

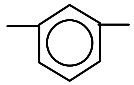
HRC: Optimization

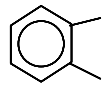
Ψ_i (kJ/mole/°C)
model/W&L

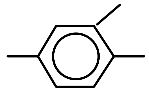
38 groups (W&L had 42)

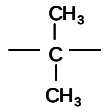

(3: **13.6/-49**)

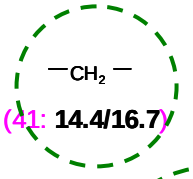

(4,5: **13.1/28.8**)


(6,7: **13.1/28.8**)


(8: **23.0/**)

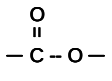

(12: **43.2/**)

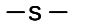

(25: **85.5/29.5**)

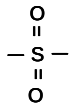

(41: **14.4/16.7**)


(42: **11.1/-11.6**)

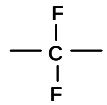

(43,44: **-12.6/-22**)

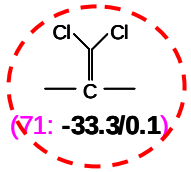

(45: **3.1/-13.7**)

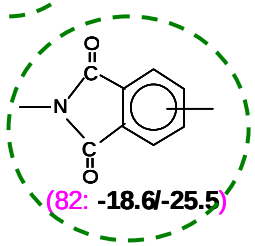

(52: **7.9/-10.9**)

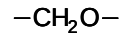

(53: **-10.9/-19.2**)

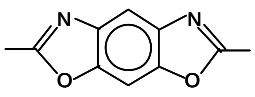

(59: **6.1/7.6**)

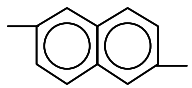

(67: **2.5/1.8**)

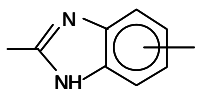

(71: **-33.3/0.1**)

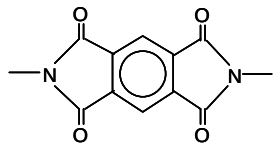

(82: **-18.6/-25.5**)


(135: **5.8/4.18**)

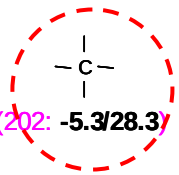

(136: **-3.3/-18.9**)

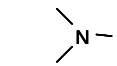

(137: **39.6/69.5**)

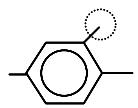

(139: **-1.0/-8.8**)

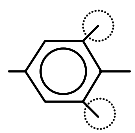

(141: **-27.7/-36.4**)

(201: **5.7/26.6**)

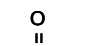

(202: **-5.3/28.3**)


(203: **-1.7/-43.0**)


(204: **24.7/30.6**)

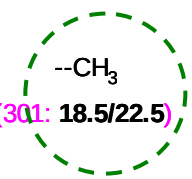

(205: **0.4/15.1**)

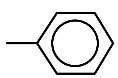

(209: **-98.5/-53.5**)

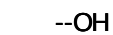

(214: **-13.5/-39.5**)

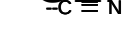
W&L: wide variety of polymers (86)

GE: mostly polycarbonates (73)


(301: **18.5/22.5**)

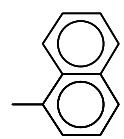

(305: **12.5/19.0**)

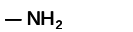

(308: **4.8/-19.8**)

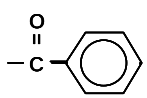

(309: **-36.6/-17.6**)

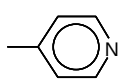

(310: **-11.8/-34.7**)


(313: **-4.0/-14.8**)


(326: **108.6/**)


(334: **-1.4/-13.9**)

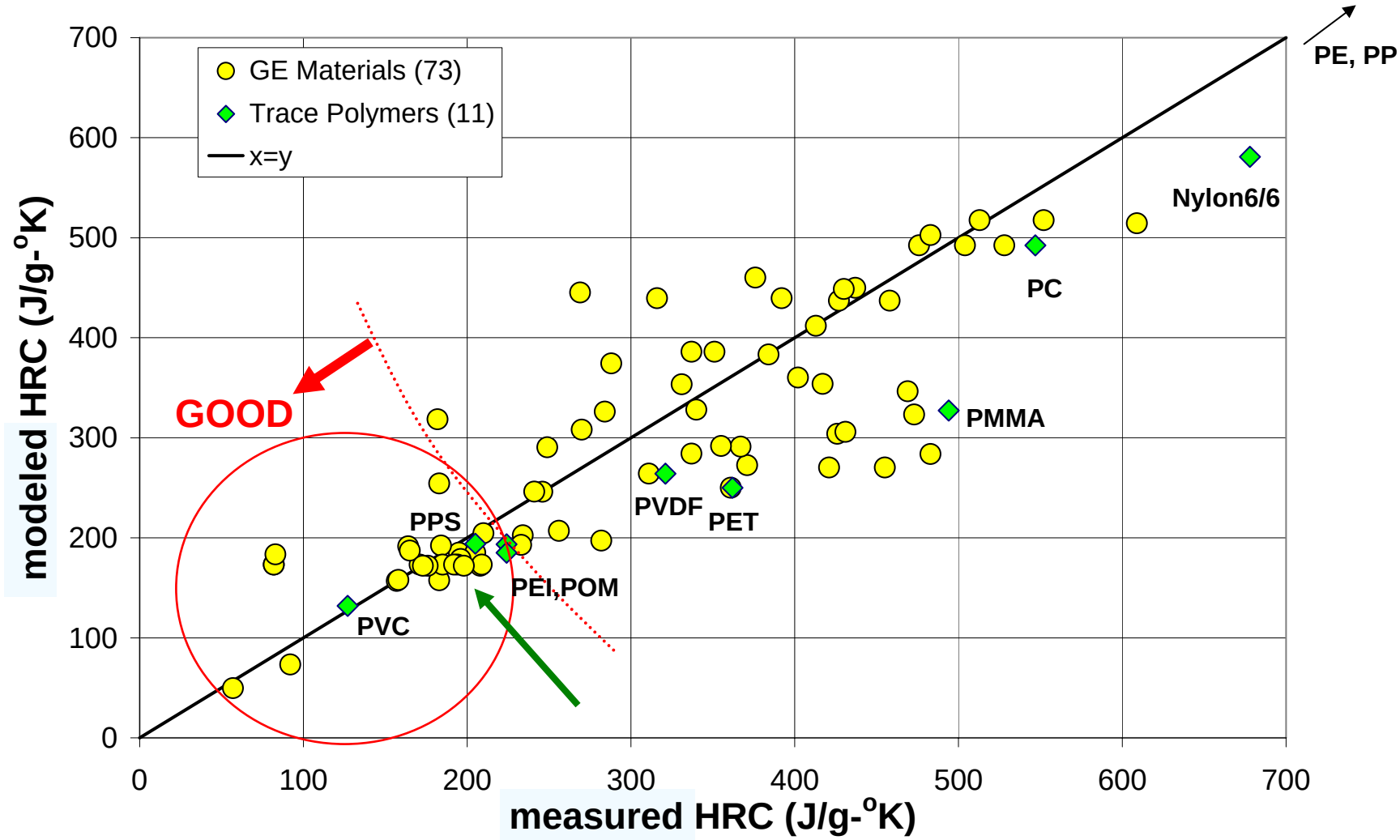

(335: **-17.3/-23.2**)


(336: **39.6/18.7**)

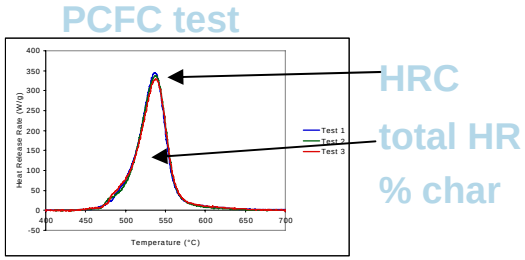
User Beware: Don't look too hard, you're bound to find "inconsistencies"

Optimization of HRC data

Fit to 84 tests



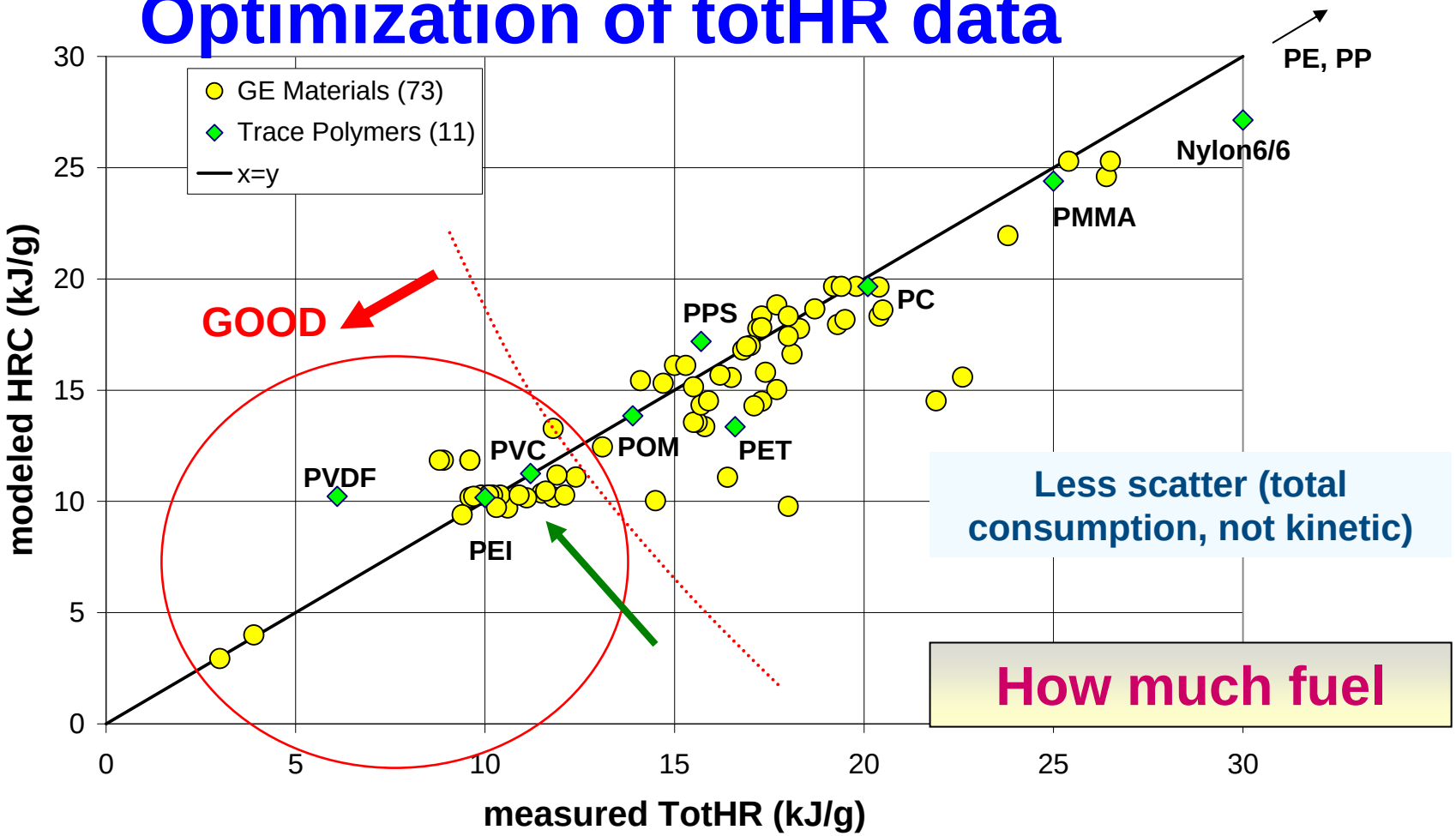
"how brightly does it burn" HRC < 200 J/g/°K



Expanded PCFC modeling

3 Variables, 3 Models, 3 Criteria

Optimization of totHR data



Less scatter (total consumption, not kinetic)

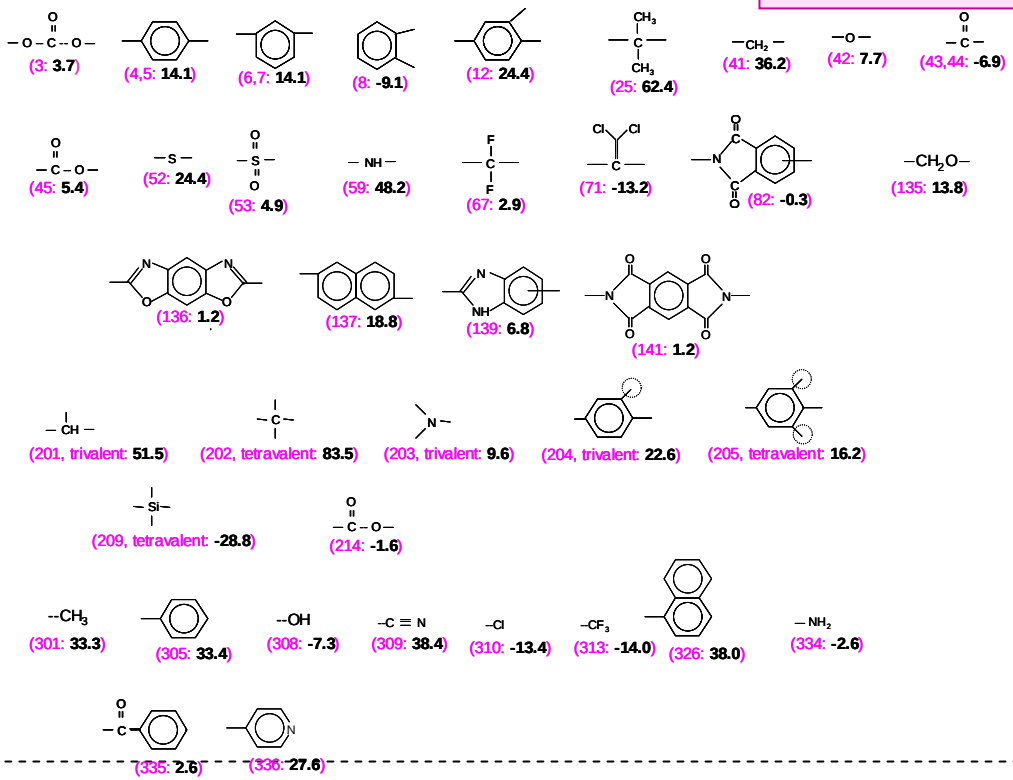
How much fuel

FR Criterion: Total Heat Release < 12kJ/g

Model for Total Heat Release

Tot HR: Optimization

kJ/gm

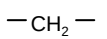


We have normalized (divided) each group's contribution by their respective molar mass, to illustrate their "total fuel content"

Each identified "group" has a particular "contribution" that is "added" into the sum Σ

examples

PE

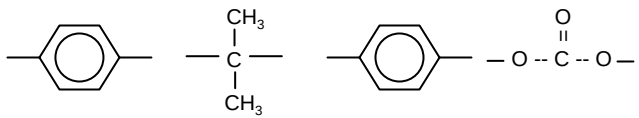


36.2

$\Sigma/M = 36.2$ kJ/g

high "fuel content"

BPA-PC

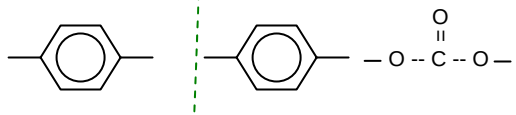


14.1 62.4 14.1 3.7

$\Sigma/M = 19.7$ kJ/g

medium "fuel content"

BP



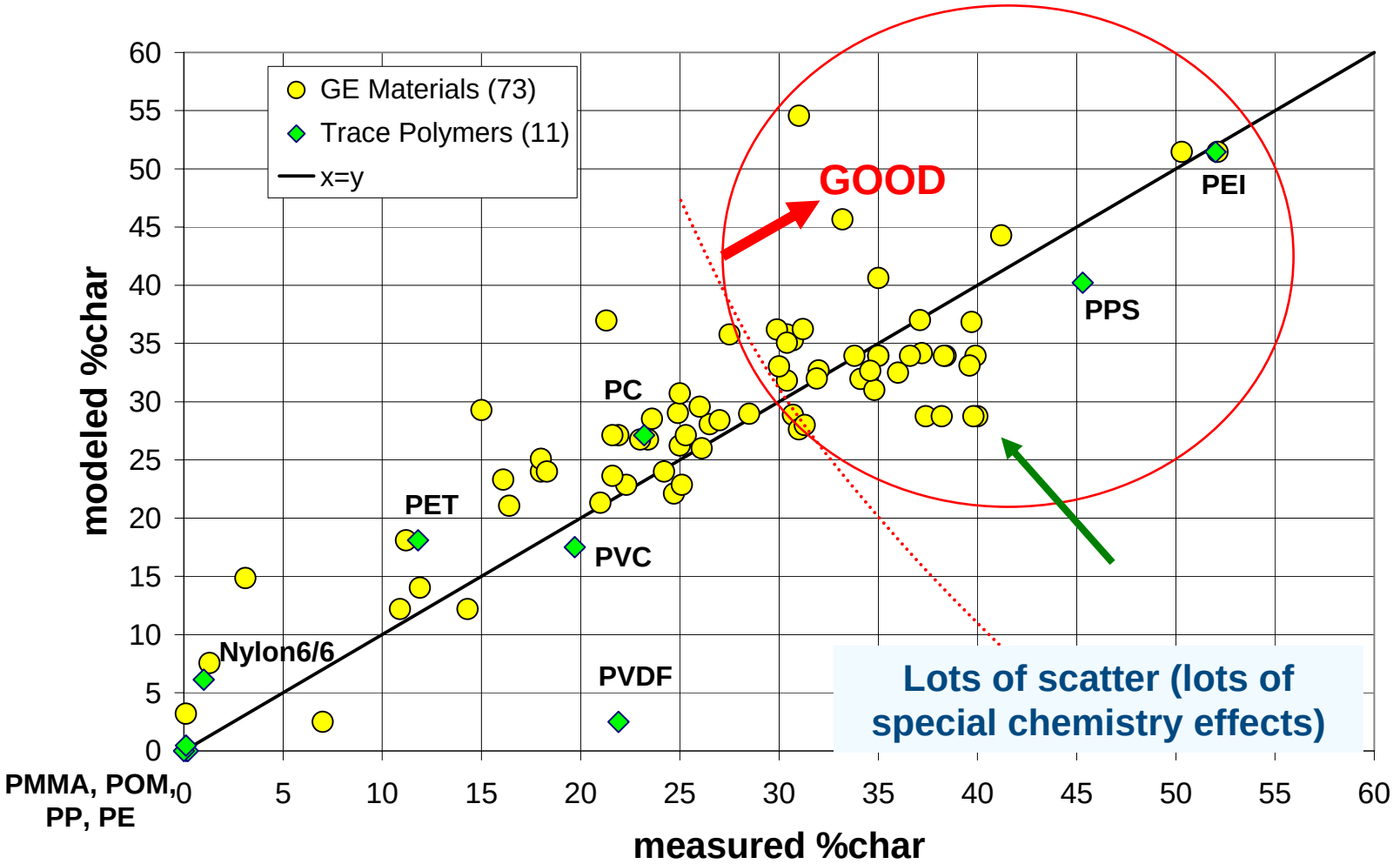
14.1 14.1 3.7

$\Sigma/M = 11.2$ kJ/g

low "fuel content"

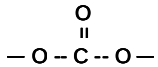
Similar Modeling for % char

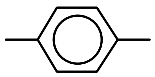
How much isn't fuel?

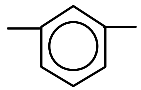


FR Criterion: % char > 30%

Char: Optimization


(3: **-1%**)

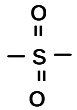

(4,5: **46%**)

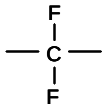

(6,7: **46%**)

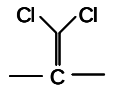

(42: **1%**)

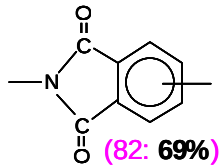

(43,44: **25%**)

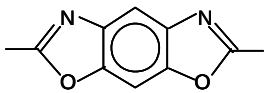

(52: **27%**)

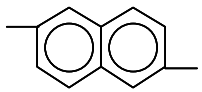

(53: **-1%**)

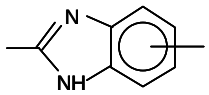

(67: **3%**)

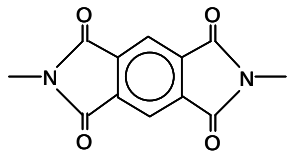

(71: **83%**)


(82: **69%**)

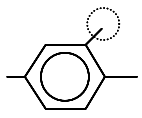

(136: **81%**)

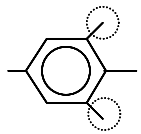

(137: **43%**)

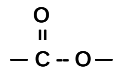

(139: **75%**)

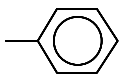

(141: **60%**)

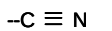

(202, tetravalent:: **-18%**)


(204, trivalent: **28%**)


(205, tetravalent: **65%**)

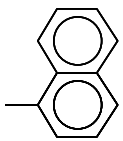

(214: **6%**)

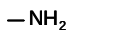

(305: **8%**)

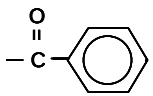

(309: **4%**)

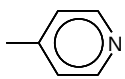

(310: **31%**)


(313: **58%**)

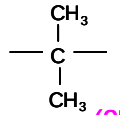

(326: **0%**)

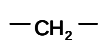

(334: **4%**)

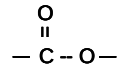

(335: **92%**)


(336: **0%**)

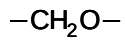
fix 0%


(25)


(41)


(45)


(59)


(135)

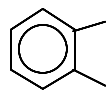

(201, trivalent)


(203, trivalent)

--CH_3 (301)

--OH (308)

fix 100%


(8)


(209, tetravalent)

Summary

- Lyon-Walters HRC model specialized for polycarbonates using PCFC data

- New additive group contribution model for total heat release and % char developed

- Established 3 FR Criteria: HRC<200J/g/oK; totHR<12kJ/g; %char>30%

- Successful prediction of several FR transparent formulations

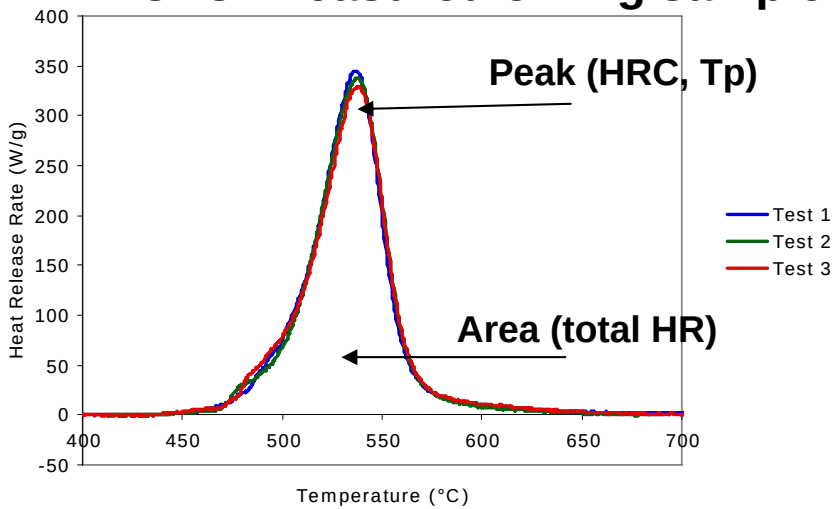
2 More Things

- PCFC testing vs OSU testing

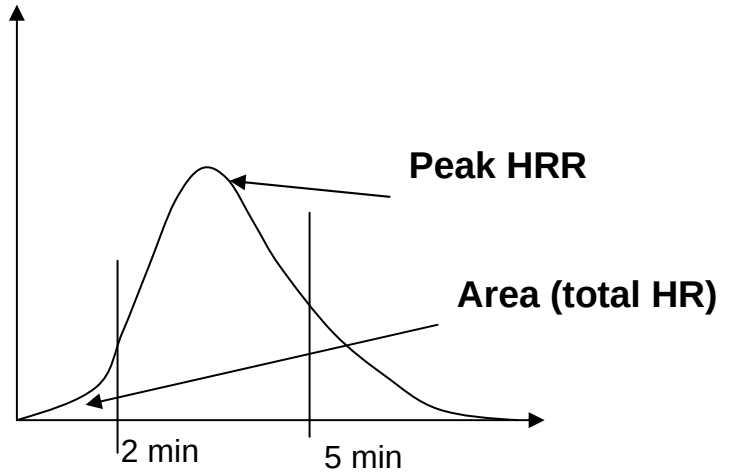
- An even simpler “atomic contribution” model??

PCFC vs. OSU Tests: Correlations?

PCFC: Measured on mg sample



OSU: Measured on a large part



Total HR= **how much will burn**
%Char = how much will not burn
HRC = **how brightly will it burn**

totHR<12kJ/g
HRC<200J/g/°K

How much will burn in 2 mins
How brightly will it burn in 5 mins

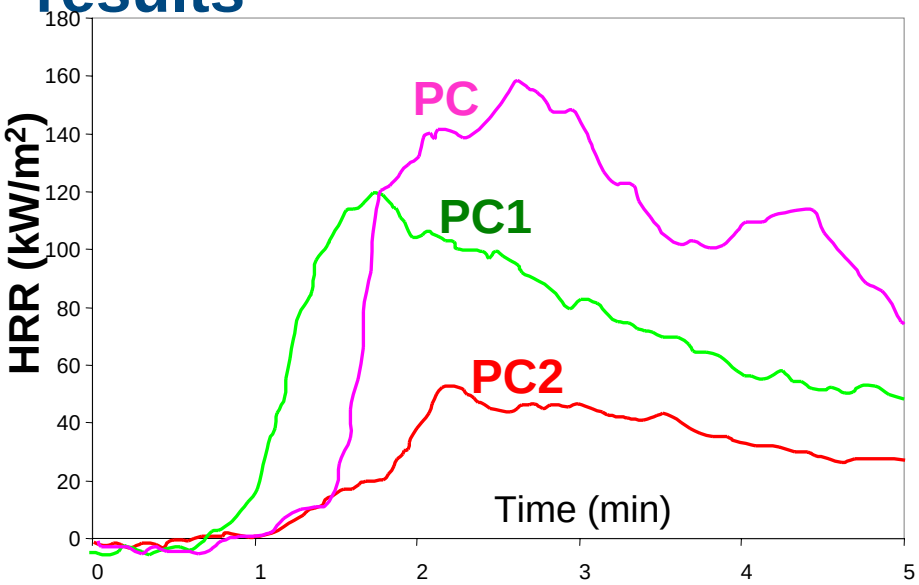
totHR (2min) < 65kW-min/m2
Peak HRR (5min) < 65kW/m2

OSU= f (kinetics, thermodynamics, rheology, geometry, drip, bubbles….)

PCFC – total combustion/flammability
OSU – additional factors important

FR agents in PC: OSU results differ from PCFC results

OSU



PC1>PC (2min totHR~same; peak low
PC2>PC

PCFC

Composition	HRC	Total HR	Tp	% Char
PC	476	19.4	557	25.3
PC2	134	9.3	491	24.1
PC1	453	19.3	541	23.8

PC1~PC
PC2>PC

PCFC test captures the reduction of heat release for PC2; Does not capture the time-dependence behavior of PC & PC1

Tot HR: Optimization

kJ/gm

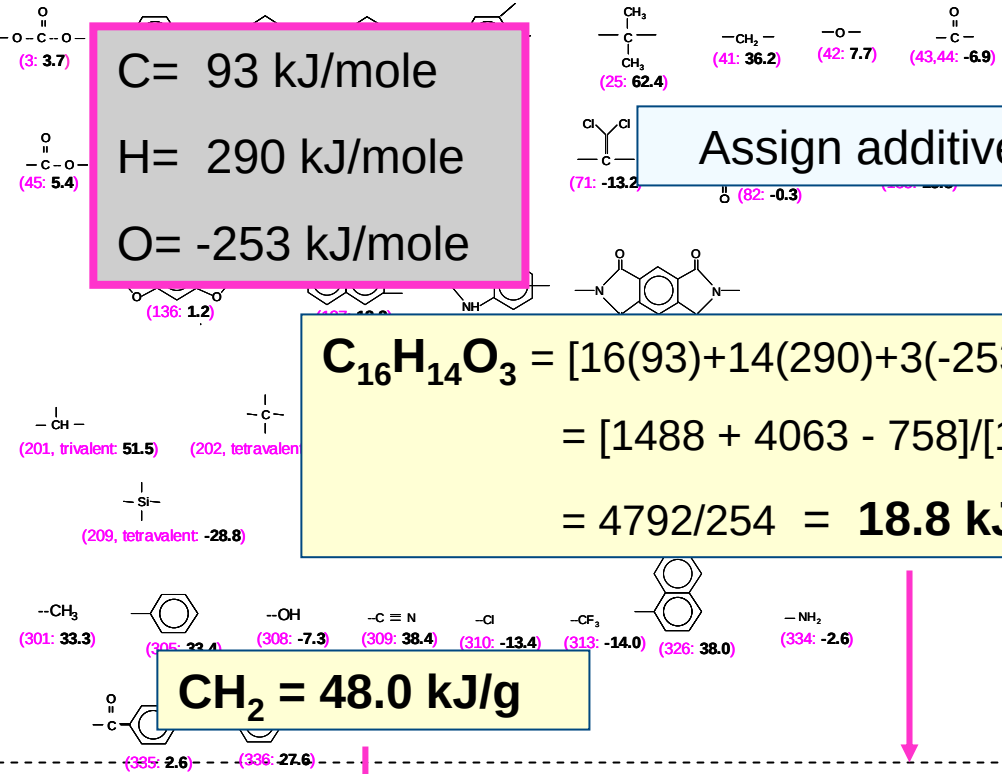
Atomic Model for Total Heat Release

C= 93 kJ/mole

H= 290 kJ/mole

O= -253 kJ/mole

Assign additive group contribution value to atoms



$C_{16}H_{14}O_3$ = [16(93)+14(290)+3(-253)]/[16(12)+14(1)+3(16)]

= [1488 + 4063 - 758]/[192 + 14 + 48]

= 4792/254 = **18.8 kJ/g**

has a

that is

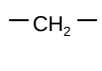
"added" into the sum Σ

CH_2 = 48.0 kJ/g

$C_{13}H_8O_3$ = 13.1 kJ/g

examples

PE



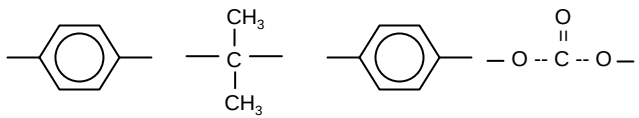
36.2

Σ/M = 36.2 kJ/g

high "fuel content"

45.3 meas

BPA-PC



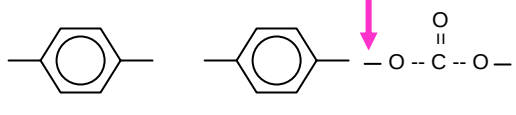
14.1 62.4 14.1 3.7

Σ/M = 19.7 kJ/g

medium "fuel content"

19.6 meas

BP

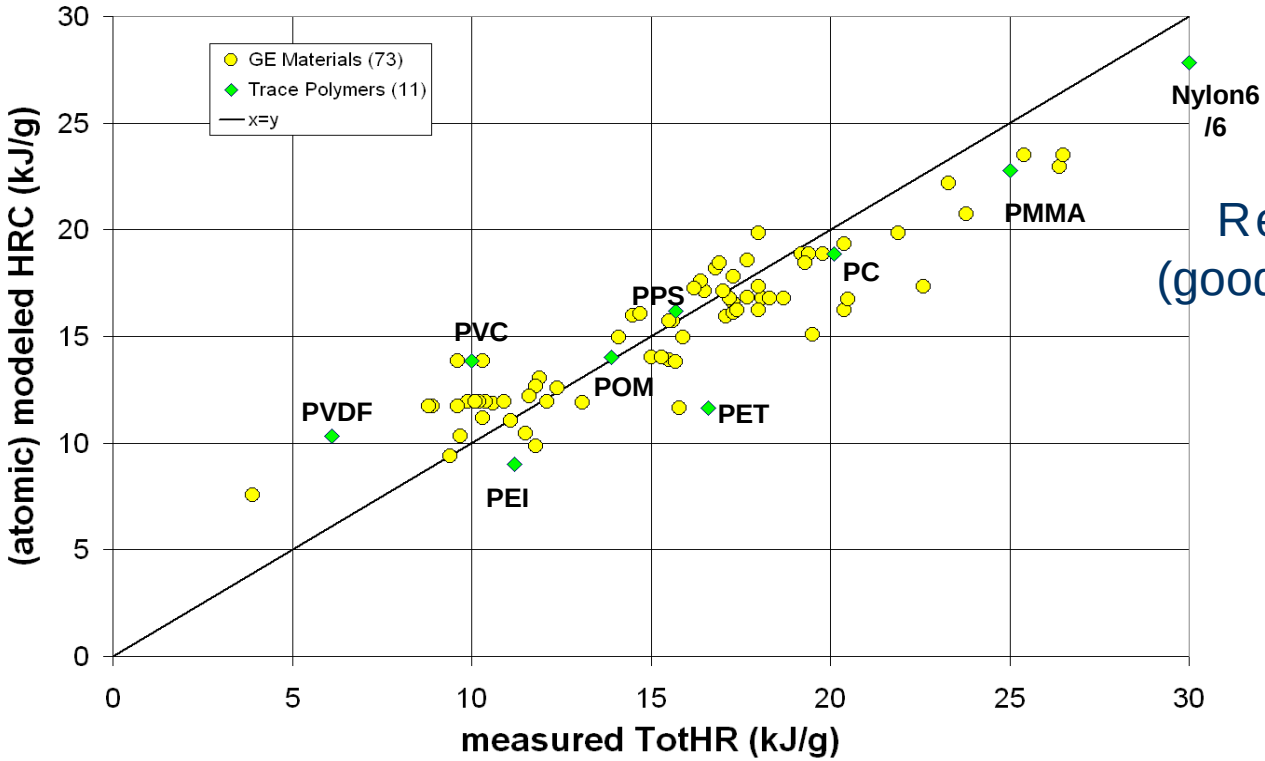


14.1 14.1 3.7

Σ/M = 11.2 kJ/g

low "fuel content"

Atomic model for totHR



Result of optimization
(good fit to simple atomic model)

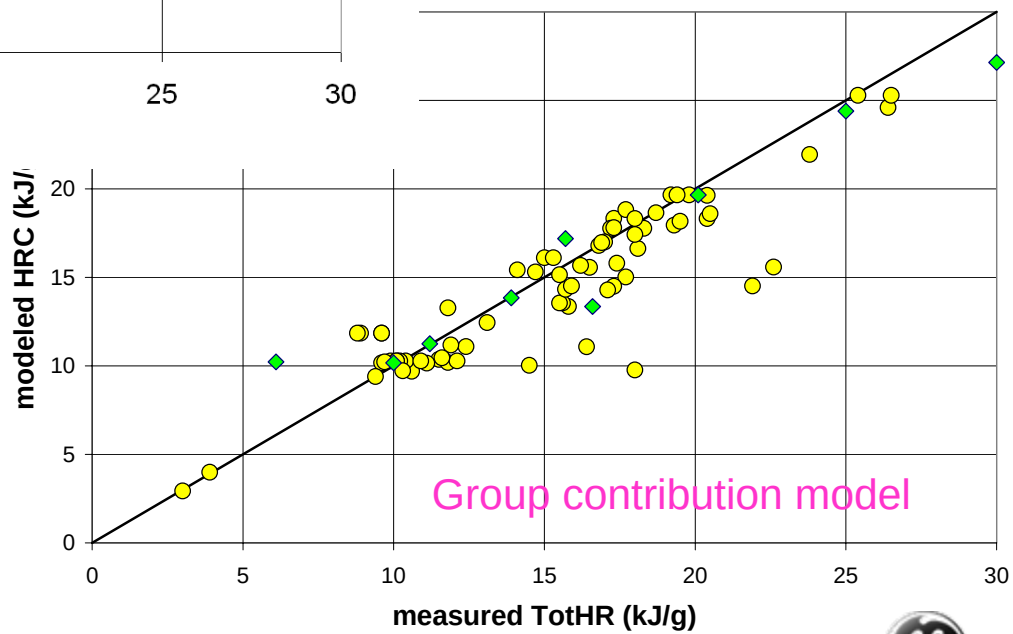
C= 93 kJ/mole

H= 290 kJ/mole

O= -253 kJ/mole

N= -345 kJ/mole

User Beware: Don't look too hard, you're bound to find "inconsistencies"



Group contribution model