

Decombustion Theory

Determining real-time emissions during the inhomogeneous combustion of solid fuels

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A report on the development of the Decombustion Theory and work conducted at

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Understanding and Reducing Wood Combustion Emissions

Prior to reducing emissions, we must be able to quantify them.

Prior to quantifying them, we must understand how to measure them.

Prior to measuring them, we must understand what is happening in the fire.



Understanding and Reducing Wood Combustion Emissions

The first thing we learned about what happens in a wood fire is that the wood does not burn homogeneously.

Emissions are quantified by calculation. The mass of smoke is given in terms of time or mass of fuel burned, i.e.

- milligrams per minute
- grams per kilogram burned



Understanding and Reducing Wood Combustion Emissions

Regulation requires setting performance targets. With both approaches, we are required to quantify the mass emitted, the mass burned and the time interval.

The mass burned [kg][lbs] is really a proxy for a quantum of energy [kJ][MJ][BTU].

The metric “emissions per unit time” does not require knowing anything about the fuel or the process of combustion.



Understanding and Reducing Wood Combustion Emissions

If what is burning is changed, the energy available and the emissions also change.

How do we know what we are burning? We choose a standard fuel and use it in all tests.

Burning with a random mix of fuels would be “inhomogeneous fuelling”.



Understanding and Reducing Wood Combustion Emissions

But if our selected standardized fuel does not burn homogeneously we no longer know what just burned.

In a wood stove most of the volatiles burn away first and the char remains to be burned at the end (or not, depending).

This inhomogeneous combustion describes a typical wood fire. Unfortunately for the tester It is exactly the same as burning “random fuel”.



Understanding and Reducing Wood Combustion Emissions

Comparisons of test results may no longer be valid because three stoves will burn the standard fuel in three different ways.

Emissions might be reduced, they might not.

A number of strategies have been used to constrain the error, but error it gives, and the error is large.

To rate performance we must answer the questions, *What just burned?* and *When did it burn?*



Decombustion Theory – Long Method

In 2010 we at the SeTAR Centre began applying the idea that we could get a better estimation of the CO mass if we could calculate how many moles of combustion products were emitted in given time period.

With five variables and only four formulas, it turned out to be quite difficult to calculate. It required making certain assumptions which forced me to ignore my No. 1 rule,

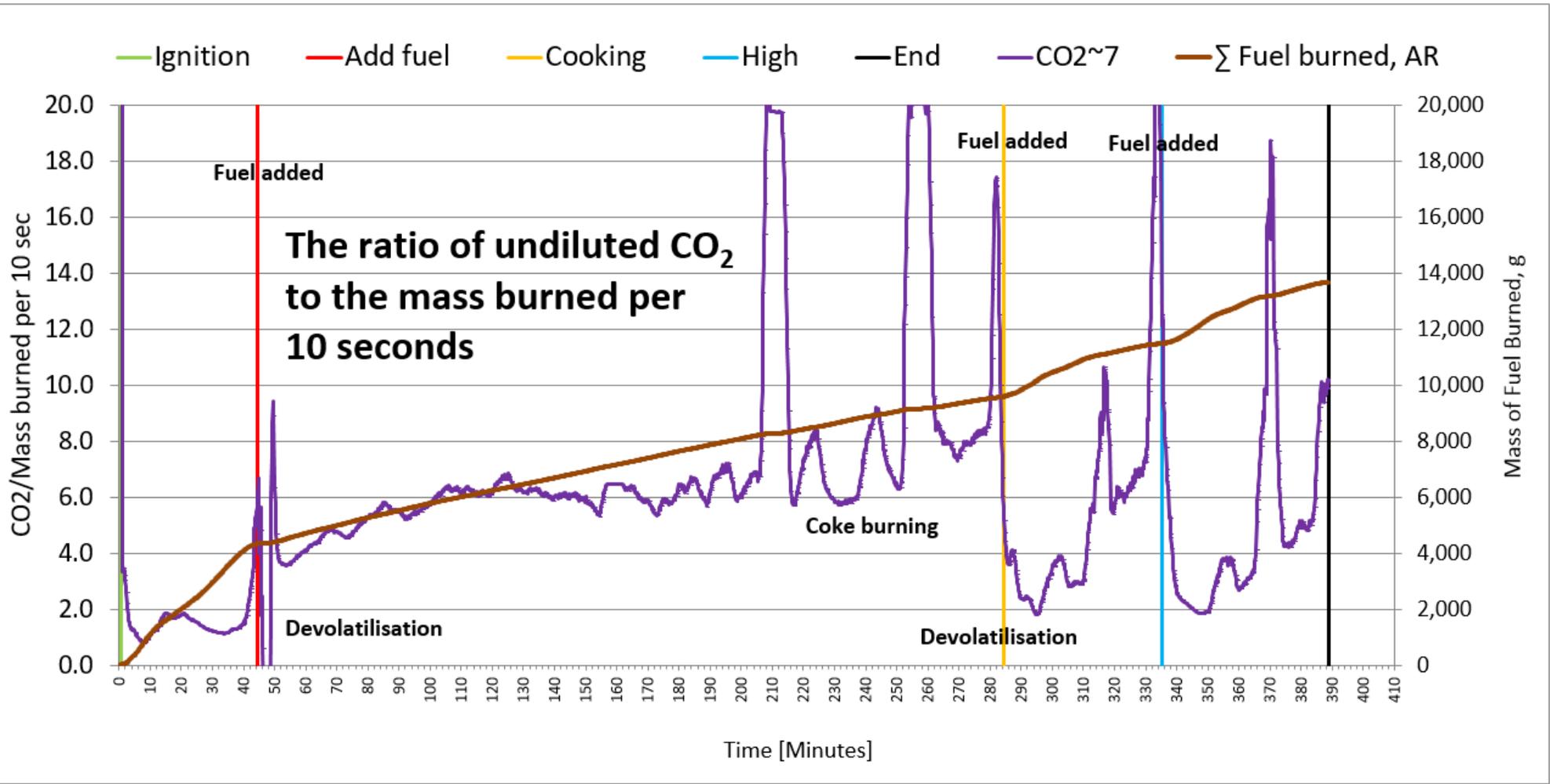
“Never assume *anything!*”

Decombustion Theory – Long Method

Making certain assumptions, I started in 2010 using a 'longhand' method of calculating the mass of CO in any volume of gas.

Important:

Knowing the fuel composition and using a carbon balance method doesn't work well for efficiency because the ratio of the mass of carbon burned to the mass of fuel burned varies considerably during, implying the HHV also changes considerably.



Decombustion Theory – Long Method

The longhand method involves estimating the total number of moles of all gases in the exhaust stream and relating the measured CO [ppm] concentration to the total.

Orange Section	Emission Factors									
Gas, ppmv	CO2(EF)	SO2(EF)	NO(EF)	NO2(EF)	CO(EF)	H2(EF)	H2S(EF)	Combustion H2O	H2O	Oxygen
Burnable oxidised element mole mass	44	64	30	46	26	1	34	18	18	18
Burnable element mole mass	12	32	14	14	12	1	1	1	18	18
Σ Burnable element mole mass	628	628	628	628	628	628	628			
Σ EF values, All Sections	65,451,754	63,773	31,821	31,823	509,940	-	-			
Mass units, burned elements detected in each gas	785,421,051	2,040,738	445,493	445,516	6,119,281	-	-	19,257,814	56,803,422	303,741,126
Fuel moisture, Oxygen and Hydrogen in raw fuel	32.34%									
Mass of fuel burned, g missing from the scale	1,566.89									
All C+S+N in mass units	794,472,079									
Estimated total emissions in mass units incl H + O	1,174,274,441									
Total Carbon mass units	791,540,331									
Percent of carbon mass that is CO	0.77%									
Percent of carbon mass that is CO2	99.23%									
CO/CO2 ratio	0.78%									
Mass of original elements, g	1,048	2.7	0.6	0.6	8	-	-	26	76	405
% of original element mass in the detected gases	66.89%	0.17%	0.04%	0.04%	0.52%	0.00%	0.00%	1.64%	4.8%	25.87%
Combustion products emitted, g	3,843	5.4	1.3	2.0	18	-	-	231	76	405.3
					0.40	CO g/MJ firepower				
Mass to be emitted					4,119.18	grams if perfectly burned				
Actual mass					3,770.88	combustion was inhomogeneous				

Decombustion Theory – Long Method

This enabled the creation of 4 separate sections of a burn sequence, each typical of the discrete tasks we were characterising.

	Event Occurs on Line Number:	Stove Power per section Kilowatts	Water Pot Standard Pot 1 Eff %	CO emitted during this portion, g
Add fuel	8	8.5	0.0%	45.9
Banking	275	Minutes of burn 44		
Low	275	5.6	0.0%	56.6
Add fuel	1,733	Minutes of burn 243		
Cooking	1,733	4.1	3.7%	16.2
High	2,014	Minutes of burn 47		
High	2,014	4.6	0.0%	10.3
End	2,350	Minutes of burn 56		

Decombustion Theory – Short Method

In April 2016 the development of the **Short Method of the Decombustion Theory** was announced at the pellet stove competition hosted by the Brookhaven National Laboratory.

It showed that the water vapour can be separated into its two sources by simultaneously assuming that:

- the ratio of hydrogen to oxygen in water is constant
- the ratio of oxygen to hydrogen released from the fuel is constant, even if that fuel combusts inhomogeneously

By assuming the O and H are proportionally co-emitted during the decomposition of the fuel, it is possible to calculate what fraction of the oxygen water vapour in the exhaust gases originated from the dry fuel. Given any one O or H value allows the others to be calculated.

Decombustion Theory – Short Method

Variables:

a = the elemental oxygen in the wet gas sample originating from dry fuel [ppm]

b = the elemental hydrogen in the wet gas sample originating from dry fuel [ppm]

c = the elemental oxygen in the wet gas sample originating from fuel moisture [ppm]

d = the elemental hydrogen in the wet gas sample originating from fuel moisture [ppm]

Decombustion Theory – Short Method

Constants

$C1 = a+c =$ Total oxygen from the dry fuel + oxygen from the fuel moisture
(from measurements and decombustion calculation)

$C2 = b+d =$ Total hydrogen from the dry fuel and the fuel moisture
(from measurements and decombustion calculation)

$C3 = a/b =$ Ratio of oxygen in the dry fuel to the hydrogen in the dry fuel
(from fuel analysis and calculation)

Decombustion Theory – Short Method

The oxygen a that originated from the dry fuel is determined using the formula

$$a = (C1 - C2/2)/(1 - 1/(2 \cdot C3))$$

Expanded it is

$$a = ((a+c) - (b+d)/2)/(1 - 1/(2 \cdot (a/b)))$$

Assumptions

1. Hydrogen and Oxygen are present in the Fuel and Water in known ratios
2. Fuel O and Fuel H are released homogeneously from biomass even if the fuel burns inhomogeneously.

Example of the number of moles and the ratios created:

Fuel O = a	8.22
Fuel H = b	47.34
H ₂ O O = c	2.98
H ₂ O H = d	5.96
Fixed ratio a/b	0.17
Fixed ratio c/d	0.50
ΣO a+c	11.20
ΣH b+d	53.30

Step 1: Combust the Fuel

Combust some fuel and measure the resulting gas composition.

Burn in air, no EA Undiluted				
Undiluted moles of gases after burning	Added combustion air containing O ₂ , N ₂ , Ar and CO ₂	Total Moles of Combustion Gases	Total % of Wet Combustion Gases	
60.77	0.1311	60.90	17.49	Carbon
			-	Oxygen
22.87			-	Hydrogen
4.75		27.62	7.93	Moisture from fuel
0.06		0.06	0.02	Sulfur
0.67		0.67	0.19	Nitrogen in Fuel
	3.0604	3.0604	0.88	Argon from Air
	255.84	255.84	73.48	N ₂ from Air
89.12 moles of gas	259.04 moles gas+air	348.16	100 %	

Step 2: Decombustion

De-Combustion					
	Delete Air				
	Split H2				
Moles of elements Entrained with air	Remove air: CO ₂ , NAr+O, Mol Elements	Split Fuel H from H ₂ O, Mol Elements	g	Estimated ARAF Ultimate Analysis % mass	
0.1357	62.901	62.901	75.548	75.55	Carbon
71.3027	11.19897	8.2205	13.152	13.15	Oxygen
	53.29593	47.339	4.772	4.77	Hydrogen
	Water O >>	2.979	5.366	5.37	Moisture from Fuel
	Water H >>	5.957			
	0.060	0.060	0.194	0.19	Sulfur
	0.692	0.692	0.969	0.97	Nitrogen in Fuel
3.1675	-				Argon from Air
264.80	-				N ₂ from Air
71.44 moles	128.15 moles	128.15 moles	100.00	100.00	
			Mass	%	

Significance of Real-Time Fuel Analysis

Estimated ARAF Ultimate Analysis % mass	
72.99	Carbon
12.71	Oxygen
4.61	Hydrogen
8.57	Moisture from Fuel
0.19	Sulfur
0.94	Nitrogen in Fuel
	Moisture from Air

The HHV can be calculated in real time as the fuel evolves, as can the LHV, the CO_{2MAX} and the efficiency.

Significance of Real-Time Fuel Analysis

Calculating the total mass of smoke emitted requires knowing the volume of gases emitted. This throws up an interesting challenge.

To know accurately the emissions rate per kg burned requires knowing whether or not the missing mass is fuel or fuel moisture, and the nature of the residual fuel.

Significance of Real-Time Fuel Analysis

Using the decombustion theory allows an estimation to be made of how much oxygen must be supplied by air to supplement the fuel-oxygen to completely burn the fuel. The oxygen which must be provided by air, expressed as a fraction of the total oxygen demand, is here termed the *stoichiometric oxygen demand ratio*

$$StOxR = (\text{air oxygen}) / (\text{total oxygen demand for stoichiometric combustion})$$

Example: If $StOxR = 0.85$ then 85% of the total oxygen will come from the air and the other 15% from oxygen in the fuel molecules.

Significance of Real-Time Fuel Analysis

Knowing the decombusted fuel chemistry and the level of dilution by air and the change in mass during any time interval permits the calculation of the total volume of emitted gases.

It also permits the calculation of Lambda (λ), the total air demand. Normalised to 0% excess O₂ the undiluted concentration of PM or CO is

$$\text{Excess Air factor} + 1 = \lambda$$

The CO emission factor is

$$\text{CO [ppm]} * \lambda = \text{CO}_{\text{EF}} \text{ [ppm]}$$

Significance of Real-Time Fuel Analysis

However that “1” in “EA+1” assumes that the StOxR is 1:1. It is never the case for a fuel containing oxygen.

As shown in the previous chart, in the early fire the oxygen and hydrogen leave the fuel more easily than the carbon, resulting in a low StOxR value.

If the excess air level is 50% and the StOxR is 0.25 then

$$\lambda = 0.75 \text{ not } 1.5$$

If CO concentration is 500 ppm, the CO_{EF} is $500 * 0.75 = 375$ (not 750) ppm

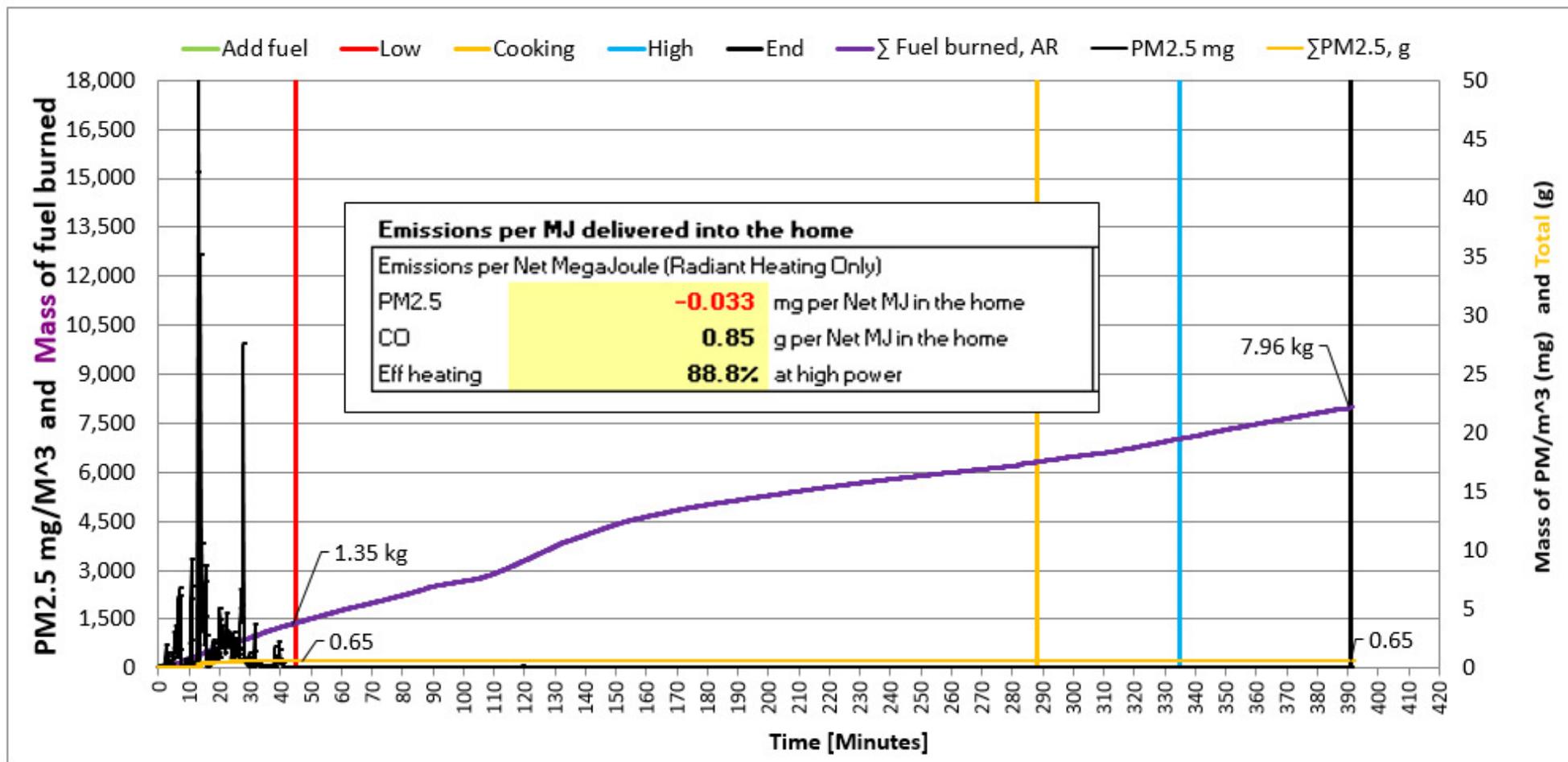
Late in the fire when the StOxR is 0.98, that same 500 ppm reading translates into a CO_{EF} of $500 * 1.48 = 740$ (not 375) ppm.

Significance of Real-Time Fuel Analysis

Without first decombusting the fuel and obtaining the fuel moisture level, it is not possible to know the actual CO_{EF} and thereby the total mass of CO emitted.

The same applies to the mass of $\text{PM}_{2.5}$ if the fuel is not completely burned at the end of the test.

Rather than restricting the assessment period to that time during which all the fuel is completely burned, Decombustion Theory permits one to start and end the test arbitrarily during any period of convenience and still obtain an accurate performance rating.



BJ4.0

The PM_{2.5} emission rate is -0.5 milligrams per kg burned during the test period of 345 minutes.

Thank you!

Appreciations:

Staff and graduate students at:

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Cape Peninsula University of Technology, Cape Town, South Africa

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Part 1, presented at Brookhaven National Laboratory, 7 April 2016

<http://www.forgreenheat.org/upload/upload/Crispin%20Chemical%20Mass%20Balance%20-%20Brookhaven%202016%20CPP.pptx>

Abstract:

Determining the efficiency of a stove or fireplace requires that the performance be calculated periodically and the results summed in some manner. Because solid fuels rarely burn homogeneously, it is difficult to know exactly what just burned, what was just dried and how much heat was lost up the chimney as a percentage of what heat was available at the time. To date, test methods have assumed that the fuel burned and dried homogeneously – something that usually just isn't so. Following the announcement at Brookhaven National Lab earlier this year of a new theoretical breakthrough in test analysis, this presentation takes a second brief look at the Decombustion Theory. It provides additional details on how this method works and the benefits it brings to product developers and regulators. It contains new information relevant to the rating of product efficiency and proposes a change to the calculations embedded in combustion analysers.