Decombustion Theory

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

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Understanding and Reducing Combustion Emissions

Solid fuels do not burn homogeneously in domestic appliances.

Quantification of emissions requires using calculated fuel parameters such as:

- HHV

- LHV

- CO_2MAX

- Siegert formula constants

- Fuel moisture

Understanding and Reducing Combustion Emissions

How do we know what is burning? Analysing the fuel before a test gives the fuel analysis, but that is not necessarily what burns at any given moment!

If we burned a *random* mix of fuels we would have "*random fueling*".

If we burn a single known solid fuel inhomogeneously we will have "*random burning*".

For the analyst, there is no difference between *random fueling* and *random burning*: the calculated result will be *incorrect*.

Understanding and Reducing Combustion Emissions

To make a valid comparison between stove tests, we must answer the questions,

What just burned?

and

When did it burn?

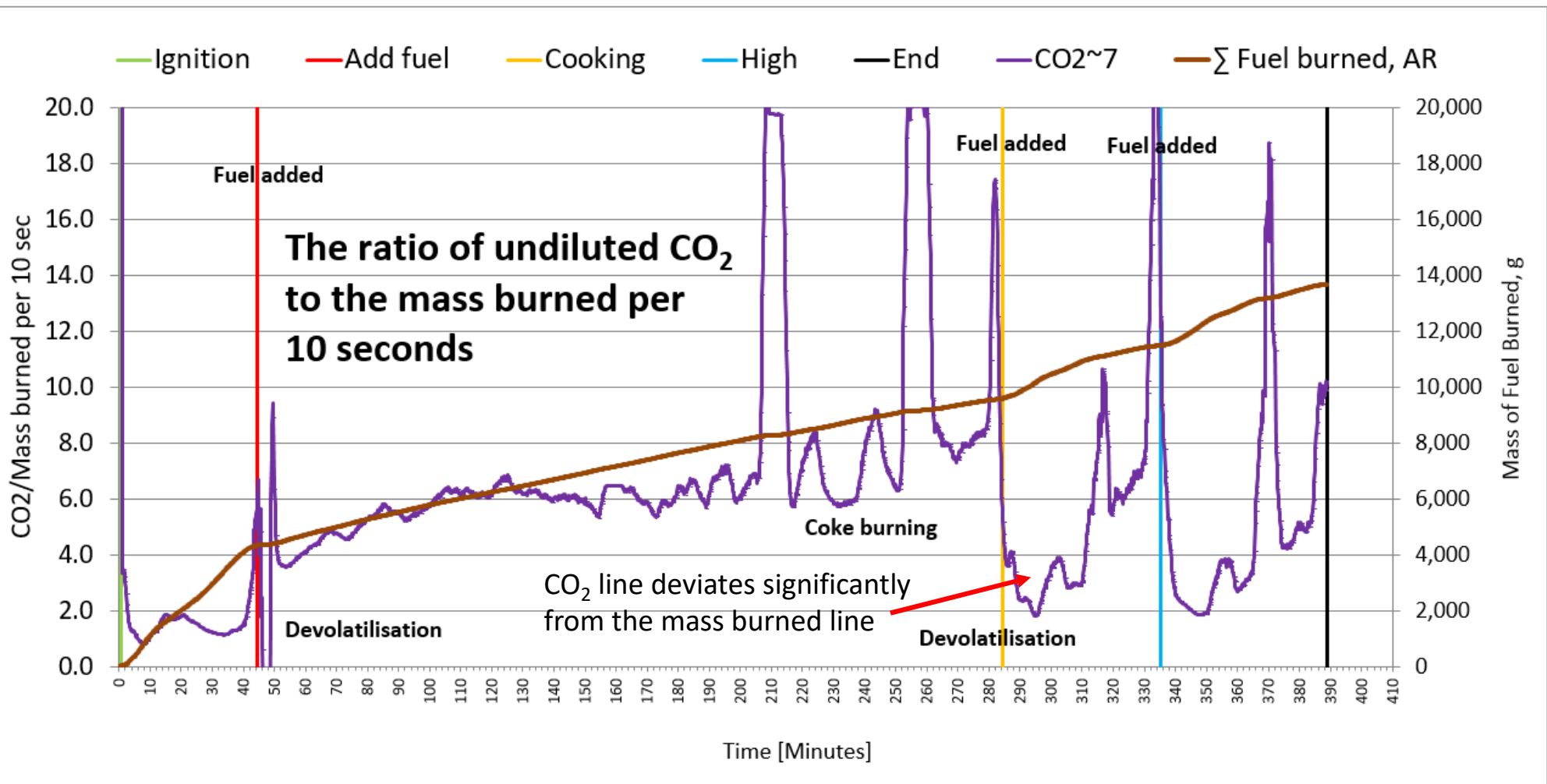Conventional analysis methods do not provide the answer.

Decombustion Theory – Long Method

In 2010 we at the SeTAR Centre began by estimating the CO_2 mass by calculating how many moles of combustion products were emitted in a given time period.

Making certain assumptions, I started by using a 'longhand' method of calculating the mass of CO_2 and CO in any volume of gas based on the gas composition as measured, not as assumed from the original fuel composition.

I compared the CO_2 emitted to the mass of fuel burned when fuel was added periodically. The actual mass of CO_2 emitted deviates significantly from the theoretical mass based on carbon balance or missing-mass calculations.

The ratio of undiluted CO_2 to the mass burned per 10 seconds

Legend: —Ignition —Add fuel —Cooking —High —End —CO2~7 —∑ Fuel burned, AR

Y-axis (left): CO2/Mass burned per 10 sec
Y-axis (right): Mass of Fuel Burned, g
X-axis: Time [Minutes]

Fuel added

Fuel added   Fuel added

Devolatilisation

Coke burning

CO_2 line deviates significantly from the mass burned line

Devolatilisation

Decombustion Theory – Long Method

The longhand method estimates the total number of moles of all gases in the exhaust stream and relating the measured CO or CO_2 (etc) 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	16
Burnable element mole mass	12	32	14	14	12	1	1	1	18	16
∑ Burnable element mole mass	628	628	628	628	628	628	628			
∑ 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

Fuel was combusted inhomogeneously

Decombustion Theory – Short Method

Later I developed the **Short Method of the Decombustion Theory** and announced it at the Alliance for Green Heat competition hosted by the Brookhaven National Laboratory in New York State, 2016-04-07.

The Short Method separates water vapour from (a) fuel moisture and (b) burning fuel hydrogen into its two sources by assuming that:

- the ratio of oxygen to hydrogen 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 thermal decomposition of solid fuels, it is possible to estimate what fraction of the oxygen water vapour in the exhaust gases originated from the dry fuel.

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
(calculated from the ultimate analysis of the fuel)

Decombustion Theory – Short Method

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

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

Expanded, it is

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

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.

Measured values from a test:

Moles of oxygen and hydrogen

In the exhaust ➜

Fuel O = a	8.22
Fuel H = b	47.34
H_2O O = c	2.98
H_2O H = d	5.96
Fixed ratio a/b	0.17
Fixed ratio c/d	0.50
$\sum$O a+c	11.20
$\sum$H b+d	53.30

Use the decombustion formula to determine a

De-Combustion					
Moles of elements Entrained with air	Delete Air Split H2 Remove air: CO_2, NAr+O, Mol Elements	Split Fuel H from H_2O, Mol Elements	g	Estimated ARAF Ultimate Analysis % mass	
0.1357	62.901	62.901	75.548	75.55	Carbon
71.3027	$a+c$ 11.19897	a 8.2205	13.152	13.15	Oxygen
	$b+d$ 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	%	

Convert molar fractions to mass fractions

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

From the result of the decombustion, the HHV can be calculated in real time even though the fuel changes continuously. Also the LHV, the CO_2MAX and thermal efficiency.

Impact on other metrics

Calculating the total mass of smoke emitted requires knowing the volume of gases emitted. This presents 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 unburned residual fuel.

The more oxygen a fuel contains, the less air needed to burn it. Standard combustion formulas for *air demand* do not consider this in real time.

Significance of Real-Time Fuel Analysis

Using the decombustion theory allows one to estimate how much oxygen must be supplied by air to supplement the fuel-oxygen in order to burn the fuel completely.

The oxygen provided by air, expressed as a fraction of the total oxygen demand, is here termed the *stoichiometric oxygen demand ratio* (StOxR)

StOxR = (air oxygen) / (total oxygen demand for stoichiometric combustion)

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

Significance of Real-Time Fuel Analysis

By using Decombustion Theory to estimate the fuel chemistry, measure the dilution by air and the change in mass during some time interval, one can calculate the total volume of emitted gases.

Calculating the correct value of Lambda (λ) (total air demand). For a fuel containing no oxygen this is given by:

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

Normalised to 0% excess O_2 the undiluted concentration of any trace gas is

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

Significance of Real-Time Fuel Analysis

However the "1" in "EA+1" assumes that the StOxR is 1:1 which is never the case for a fuel containing oxygen even if it is burned homogeneously.

In the early fire, the oxygen and hydrogen leave the fuel more easily than the carbon, resulting in a low StOxR value, with most combustion oxygen originating from within the fuel.

Correct   Big error

If the measured excess are level is 50% (O_2=7%) and the StOxR is 0.25 then

$$\lambda = 0.50 + 0.25 = 0.75 \text{ (not } 0.5 + 1 = 1.5)$$

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

At the same dilution level (50% EA) 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 ppm (not 750).

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} or the total mass of CO emitted.

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

Using both the Decombustion Theory and applying the StOxR correction one can determine the true performance during any arbitrary period.

Using the combination helps develop stoves that have nearly perfect combustion, once they are ignited.
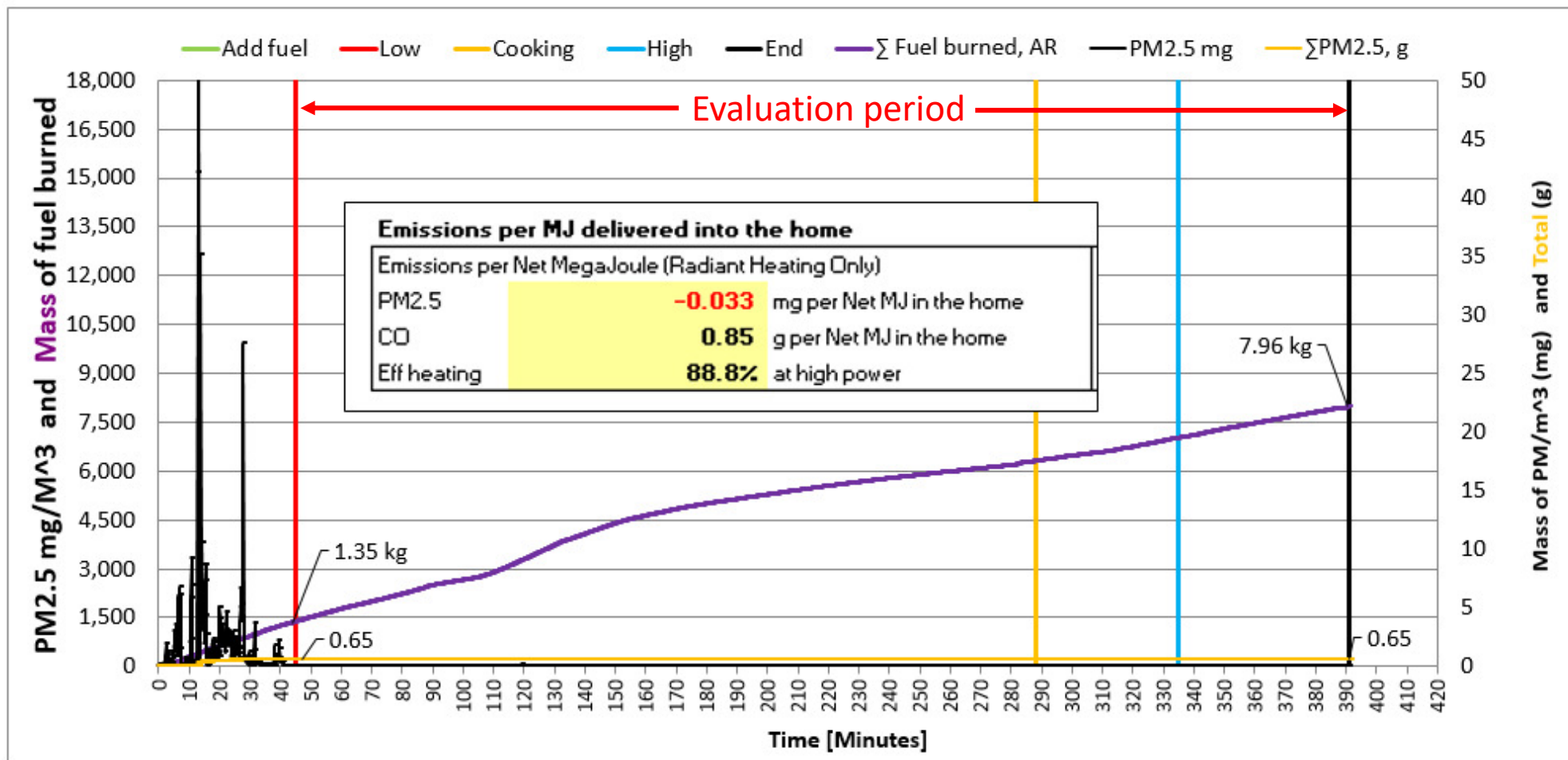
The PM$_{2.5}$ emission rate is -0.5 milligrams per kg burned during the test period of 345 minutes.

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Thank you!

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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.

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