Estimation of Combustion Stoichiometry for Complex Fuels

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Abstract

A framework for estimating simplified, mass-conserving combustion stoichiometry for complex fuels was developed. It was intended for process modelling applications in the context of industrial decarbonisation. Biomass and subbituminous coal are complex with variable ash content depending on the source. This complicates the formulation of variable reaction stoichiometries. This study proposes a method that uses literature-sourced compositional data and arbitrary molecular weights.

Keywords. Stoichiometry, Biofuel, Ash, GHG Emissions.

1. Introduction

A framework for estimating simplified combustion stoichiometry for otherwise complex fuels is desired. This would contribute to advancing the accessible process modelling for combustion of compositionally complex fuels like biomass, black liquor, and coal. These fuels are worth modelling because they represent the relevant heating solution options amidst the global energy transition towards renewable sources. The stoichiometry is important to model as it quantifies the CO2 emissions that are essential to model for the decarbonisation incentives of global climate change.

In process modelling the stoichiometry encodes for a given reaction the ratio between reactants converting to products. A material inventory analysis could be done before and after a reaction to evaluate what this ratio should be. For complex fuels there is a high chance for inconsistencies, for example the variety of different types of biomasses. There is a benefit in being able to specify differing ash contents or to assess how different ash contents can impact behaviour of processes with such reactions.

Reactions should conserve mass; this leads to difficulties when one would like to adjust the stoichiometry to account for a different fuel ash content. The standard for balancing chemical reactions is to do an elemental balance of atoms which are necessarily conserved outside of nuclear reactions. But ash and complex fuel types are made up of a variety of elements of different weights, so a rigorous elemental balance is unreasonable for these compounds. One solution to the stoichiometry is to simply add more ash to the products stoichiometry to simulate increased ash content being produced from the fuel, but the mass balance then becomes false. A more nuanced approach algebraic approach should be used to conserve mass balance. The equations used should be algebraically linear for efficiency in a computational modelling implementation.

Various literature measurement data for compositional analyses of the various fuels this current paper is interested in. However, they are limited by not being compiled into a usable combustion stoichiometry framework for process reaction modelling. For the accurate stoichiometry estimation of complex impure fuels, multiple points of corroborating literature measurement data that impacts the stoichiometry should be compiled to characterise accurate combustion stoichiometry.

The approach developed in this study was applied to subbituminous coal and wood biomass fuel types.

2. Experimental procedure

Provide sufficient details to allow the work to be reproduced by an independent researcher. Methods that are already published should be summarized and indicated by a reference. If quoting directly from a previously published method, use quotation marks and cite the source. Any modifications to existing methods should also be described.

This section can contain *Material and methods* and *Theory/calculation*. A Theory section should extend, not repeat, the background to the article already dealt with in the Introduction and lay the foundation for further work. In contrast, a Calculation section represents a practical development from a theoretical basis.

The literature data measurements gathered to deconvolve combustion stoichiometry were as follows:

- Compositional data
- Sub-element molar weight
- Emissions factor data

From these data measurements would be used to estimate stoichiometry parameters and decide molecular weights, largely for nominal mole to mass conversions. The molecular weight is arbitrary if it is used consistently as was done in this study.

Ash was considered as its own molecular component within coal and biomass. But it is not a molecule, so ash itself must be characterised by estimations based on literature. Compositional data compiled by AL-Kharabsheh et al. (2022b) was weighted then used to weight the molecular weight of constituents to determine a nominal molecular weight for ash. This was arbitrary but some molecular weight value should be decided for consistency throughout the methods of this study. The results are as shown in Table 1.

Table.1. Ash compositional estimation by literature measurements for molecular weight and heat capacity.

Component	Wood Ash Compositions from Literature[A]					Average	Cp@ 1000[K][B]	Weighted Cp	mw	Weighted mw
							[J/mol/K]	[J/mol/K]	[g/mol]	[g/mol]
SiO_2	48.96	25	55.52	2.7	29.1	32.3	69	2225.7	60.1	1938.1
Al_2O_3	11.24	0.76	3.11	1.3	10.3	5.3	125	667.8	144.9	774.3
CaO	11.59	35.6	9.92	61	35.6	30.7	54	1660.1	56.1	1723.9
Fe_2O_3	0.6	2.76	0.41	1.3	6.55	2.3	150	348.6	159.7	371.1
MgO	5.05	1.76	2.32	8.7	4.7	4.5	51	229.8	40.3	181.6
Sum:	77.44	65.88	71.28	75	86.25	75.2		5131.9		4989.0
Weighted:	1.03	0.88	0.95	1.00	1.15	1		68.27		66.370

Note.
[A] (AL-Kharabsheh et al., 2022)
[B] (Chase, 1998)

An ultimate analysis of subbituminous coal was estimated by data provided by Mares (2009) and is summarised in Table 2. This was used to estimate its arbitrary molecular weight. This data was also used as a reference point for conserving the elemental balance across the reaction.

Table.2. Ultimate analysis of subbituminous coal used to estimate molecular weight.

Component	mol%	mw [g/mol]	mw weighted
C	0.73	12.01	8.77
H	0.05	1.01	0.05
O	0.17	16.00	2.72
N	0.01	14.01	0.14
ash	0.03	66.37	1.99

Sum	0.99		11.86

Wood biomass was assumed to be pure cellulose with some percentage of ash. Wood is up to 50% cellulose on a dry basis with other dry content including lignin and hemicellulose (Dongre et al., 2024). All three have a similar elemental composition of Carbon, Hydrogen, and Oxygen, with an average standard deviation of these elemental compositions between the three molecules of 0.0556 as calculated by Table 3. Thus, the assumption that all dry matter in wood biomass was reasonable. This also fixed the arbitrary molecular weight to that of cellulose, 162.14 [g/mol].

Table 3. Comparing elemental composition of the common molecular wood constituents Lignin, Cellulose, and Hemicellulose.

		Elemental Composition			Elemental % Composition			Standard Deviation
Element	mw [g/mol]	Lignin	Cellulose	Hemi-cellulose	Lignin	Cellulose	Hemi-cellulose	
Carbon	12.01	31	6	1	40.79%	28.57%	25.00%	0.0828
Hydrogen	1.01	34	10	2	44.74%	47.62%	50.00%	0.0264
Oxygen	16.00	11	5	1	14.47%	23.81%	25.00%	0.0576
Sum		76	21	4			Avg. std. dev.:	0.0556

A literature emissions factor of 26.2 [ton-Carbon/TJ] for subbituminous coal was used as corroborating data to its combustion stoichiometry (Simmons, 2001). A literature emissions factor of 1.7 [kg-CO_2-e/kg] was not used as corroborating data, but instead as a validation reference point for the results of this study (Ministry for the Environment, New Zealand, 2024).

The combustion stoichiometry for biomass wood was nontrivial as it was assumed to cellulose with a known elemental composition that could easily fixed by an element balance. Coal instead used the ultimate compositional analysis in corroboration with the assumed emissions factor to fix CO_2 stoichiometry. All Hydrogen in coal was assumed to convert into H_2O, and all Nitrogen into N_2. The subsequent Oxygen reactant needed to fulfil the fixed CO_2 and H_2O products could then be fixed. These elemental balance relations are expressed in the following equations:

$$v_{N_2} = y_N/2 \quad (1)$$
$$v_{H_2O} = y_H/2 \quad (2)$$
$$v_{O_2} = -\left(y_H/4 + v_{CO_2}\right) + y_{O_2}/2 \quad (3)$$

Where:

v = reaction stoichiometry

y = ultimate analysis coal composition [mol%]

As the ultimate analysis included ash content, ash missing from the stoichiometry products would indicate a net mass imbalance. By converting the stoichiometry to a mass basis, the mass balance could resolve the required products ash stoichiometry. It is also retroactively resolved the nominal coal molecular weight. By this mixed-elemental balance approach, the nominal stoichiometry for coal were summarised in Table 4.

Table 4. Subbituminous coal stoichiometry by the methods of this study

Component	Stoichiometry	Mw [g/mol]
Coal	-1	11.86
O_2	-0.548	32.00
H_2O	0.025	18.01

CO_2	0.621	44.01
N_2	0.005	28.01
Ash	0.005362	66.37

Now there is the issue of adjusting ash content relative to the nominal stoichiometry into a new ash content. Taking into consideration the desired mol% ash content and initial relative stoichiometries of fuel and ash, the new ash and fuel stoichiometries can be correctly evaluated to the correct new ash content. This was achieved by the new equations developed in this study shown in Equations 4 and 5.

$$v_{ash,n} = (\left((x_{ash} - v_{ash,i} mw_{ash})(-v_{fuel,i} mw_{fuel}) \frac{1}{1-(x_{ash}-v_{as\ ,i} mw_{ash})} \right) + v_{ash,i} mw_{ash})/mw_{ash} \quad (4)$$

$$v_{fuel,n} = -(\left((x_{ash} - v_{ash,i} mw_{ash})(-v_{fuel,i} mw_{fuel}) \frac{1}{1-(x_{ash}-v_{as\ ,i} mw_{ash})} \right) + v_{fuel,i} mw_{\text{fuel}})/mw_{\text{fuel}} \quad (5)$$

where:

$v_{ash,n}$ = new stoichiometry for ash [mol]
$v_{fuel,n}$ = new stoichiometry for fuel [mol]
$v_{ash,i}$ = initial stoichiometry for ash [mol]
$v_{fuel,i}$ = initial stoichiometry for fuel [mol]
x_{ash} = fuel ash content [mol%]
mw_{ash} = molecular weight of ash [g/mol]
mw_{fuel} = molecular weight of fuel [g/mol]

As biomass wood was nominally composed of only cellulose in its stoichiometry, these equations were applied to account for an ash content of 3 wt% to yield the summarised biomass stoichiometry in Table 5.

Table 5. Biomass wood combustion stoichiometry with ash.

Component	Stoichiometry	mw [g/mol]
Biomass	-1.0309	162.139
O2	-6	31.998
CO2	6	44.009
H2O	5	18.015
Ash	0.07556	66.37

3. Results

The ash-adjustment equations had to be robust to a variety of initial stoichiometries, molecular weights, and either increasing or decreasing from nominal ash content. This was tested for biomass wood combustion stoichiometry, and the results were illustrated in Figure 1. Notice that the added fuel and ash stoichiometries in ash basis (bottom) remain equivalent.

	initial	final (overwritten)		initial	final (overwritten)		initial	final (overwritten)	
mw_fuel (g/mol)	162.1394			162.1394			162.1394		
mw_ash (g/mol)	66.37		new mols:	66.37		new mols:	66.37		new mols:
-fuel (N_stoich)	1	167.154021	1.030928	1.1	181.387223	1.118712	1.1	177.787088	1.096508
ash (N_stoich)	0	5.014620619	0.075556	0.0002	3.047156687	0.045912	0.0005	-0.533066876	-0.00803
mass_ash%(of 1m BM)	0.03	0.03		0.03	0.01679918		0.03	-0.002998344	
mol_ash%(of 1N BM)	0.073288865	0.073288865		0.073288865	0.041039763		0.073288865	-0.007324841	
added mass_BM	5.014620619			3.033882687			-0.56625188		
equiv mass stoich ash	0	12.25052853		0.013274	7.443888547		0.033185	-1.302762218	
-fuel(m_stoich)	162.1394	27102.25261		178.35334	29410.01545		178.35334	28826.2918	
ash (m_stoich)	0	332.8203705		0.013274	202.2397893		0.033185	-35.37964854	
mass_ash%	0	0.012280174		7.44253E-05	0.006876562		0.000186063	-0.00122734	
	162.1394	167.154021		178.35334	181.387223		178.35334	177.787088	
added mass fuel	0	5.014621		0.013274	3.047157		0.033185	-0.533067	
added mass ash		5.014621			3.033883			-0.566252	

Figure 1. Demonstrating results of mass-conserving ash stoichiometry balancer.

4. Discussion

This technique is significant because it can generally be applicable to many complex fuels that have uncertain, but desire to be fixed, ash contents for the purpose of reaction modelling. The algebra can also be re used in a more computationally optimised code implementation.

Moisture content was not included, but fixing water content would be as trivial as re-specifying for water on either side of the stoichiometry so it was not a focus of this study.

The purpose of this study was not for chemical rigour, but for a practical approach to combustion stoichiometry for lean computational reactions.

5. Conclusions

This study developed an ash combustion stoichiometry framework for complex fuels. It estimated reaction stoichiometry properties by using corroborating literature data on subbituminous coal and wood biomass. Then a correlation was developed to make ash content flexible whilst conserving mass balance.

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