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GLOBAL KINETICS OF THE RATE OF VOLATILE RELEASE FROM BIOMASSES IN COMPARISON TO COAL

M.A. Saeed, G.E. Andrews, H.N. Phylaktou and B.M. Gibbs

Energy Research Institute, School of Chemical and Process Engineering, University of Leeds, LS2 9JT,
Leeds, UK

Corresponding authors: pmmas@leeds.ac.uk/azamsaeed86@hotmail.com , profgeandrews@hotmail.com,
h.n.phylaktou@leeds.ac.uk

Abstract

The chemistry involved in the propagation of pulverised biomass flames is not well understood. All biomass fuels release volatiles at a much lower temperature than coal and the proportion of volatiles is much greater than for coal, typically 80% compared to 30%. Thus, the rate of release of volatiles from biomass fuels is much more important in the pulverised fuel flame propagation than it is for coal, where the rate of char oxidation is more important. The rate of release of volatiles from dry biomass follows three stages: the first stage for typically 10% of the volatiles occurs over 200 – 300°C, the second stage of about 70% of the total volatile mass occurs over the temperature range 300 – 400°C. Finally, there is a slow loss of volatiles, accounting for remaining 20% of volatiles, over the temperature range 400 – 900°C. Stagg's quick approximation method was used to determine the kinetics for the rate of volatile yield. Biomass samples were found to have lower activation energies and higher rate of release of volatiles in comparison with coal samples, up to 300 – 400°C. Similar release rates were found for the 3rd stage of volatile release. The release of volatiles at low temperatures potentially makes the biomass pulverised fuel more reactive and one consequence is shown in the measurement of minimum explosion concentration, MEC. A good correlation was found between activation energies and the MEC, determined on the Hartmann equipment. There is currently little understanding of the composition of the volatiles released at low temperatures from biomass, as most publications are for pyrolysis conditions at high temperature. It is possible that the volatiles are a mixture of mainly H₂, CO and CH₄ and the likely proportions of these were calculated from

the elemental and thermo-gravimetric analysis. This was done for a range of biomasses and this showed that the most important volatile gas is likely to be CO and that CH₄ yield is very low. This means that the conventional model used in coal combustion of char plus methane combustion is not applicable to biomass combustion.

Nomenclature

A	Pre-exponential factor	LFL	Lean flammability limit
A/F	Area to fuel ratio	m	Normalised volatile yield
CV	Calorific value (MJ/Kg)	MEC	Minimum explosible concentration
daf	Dry ash free basis	Mtoe	Million tonnes of Oil Equivalent
dm/dt	Rate of normalised volatile loss	T _A	Activation temperature
dP/dt	Rate of pressure rise (bar/s)	T _c	Characteristic temperature
E	Activation energy (KJ/mol)	ΔT _c	Characteristic temperature range
FC	Fixed carbon (%)	T _S	Solid material temperature
GHG	Greenhouse gas	VF	Volatile fraction
HC	Hydrocarbon	VM	Volatile matter (%)
k	Rate constant		
Special characters			
φ	Equivalence ratio		

1 Introduction

Pulverised biomass combustion in existing pulverised coal power stations is one of the most cost effective routes to greenhouse gas (GHG) reductions in electric power supply. In 2014 5.8% of the UK's supplied electricity was generated from pulverised biomass mainly used in existing coal fired power stations [1]. This was a 25.7% increase on 2013 and in 2014 was 19.69 Mtoe [1]. It was the fastest growing renewable electricity source between 2013 and 2014. In spite of its growing use, the mechanism of combustion of pulverised biomass has received relatively little study. The properties of biomass are quite different from those of coal and these will result in different burning mechanism. Perhaps the greatest difference between the two fuels is the much higher proportion of

volatile matter in biomass. The rate at which volatiles are released from biomass and the global kinetics of this volatile release are studied in the present work, with the aim that the global kinetics can be incorporated into CFD modelling of biomass combustion.

Biomass fuels have a lower bulk density, higher volatile content, lower calorific value and higher moisture content than coal and a greater fire and explosion risk[2, 3]. Woody biomass fuels have a more variable composition than coal [4-10] and they are also more difficult to mill due to their fibrous structure.

A wide range of biomass sources from wood to agricultural wastes are studied in the present work, some of which were supplied in pellet form but were crushed to extract the original pulverised biomass. The agricultural biomass was milled and sieved in the laboratory. A characteristic of biomass is its fibrous structure, which makes biomass difficult to mill in equipment designed for the milling of brittle coal.

Thermally treating the biomass by heating at around 260–320°C, is a process known as torrefaction. This causes (among other changes) the biomass to become brittle and easier to mill. An alternative thermal treatment process that also destroys the fibrous structure is “steam-explosion” treatment which involves heating to similar temperatures with hot steam at high pressure and then releasing this pressure so that the water absorbed in the biomass ‘explodes’ out shattering the biomass. Steam exploded biomass is often referred to as ‘black pellets’ as the final fuel pellets are black. Both types of thermally treated biomass were included in the present study for comparison. The parent wood was yellow pine and this is also included in the study [11].

The high volatile content of biomass and thermally treated biomass and its ease of release make biomass more reactive than coal. One measure of this increased reactivity is the lean flammability limit or minimum explosion concentration (MEC) [4] and this was the method used in the present work using the Hartmann dust explosion equipment. This equipment was modified to enable the flame propagation speed (another reactivity parameter) to be determined.

The high reactivity of biomass is also shown in the large number of explosion and fire incidents in pulverised biomass production, storage and utilisation in power plants. Many biomass fire/explosion incidents have occurred in the past and are still happening [4, 12]. The detailed investigations of these biofuels need to be assessed properly before their adoption and retrofitting of the plants [5, 6]. The present work gives both reactivity information in the form of the rate of volatile release and the MEC.

Biomasses are more reactive and have different chemical characterisation than coal [7, 8]. They have higher volatile yield and lower fixed carbon content compared to coals [9, 10]. The adoption of biomass as a partial or complete replacement for coal requires the measurement of the chemical and physical properties and the chemistry involved in their conversion. Particle size and the heating rates greatly affect the rate of release of volatiles due to the thermal inertia of the particles. The rate of release of volatiles is a critical parameter for the stability of the pulverised fuel flames on burners. It has been observed that decreasing the particle size and increasing the heating rate results in an increase in the rate of release of volatiles up to a critical point [9, 10]. It was observed that biofuels of coarse particle size range of 300-500 μm were still explosible in contrast to coals of similar particle size [13-16]. Woody biomasses showed a decrease in the MEC with a decrease in particles size. However, the ash derived crop residues when milled enriched the finer fraction with more ash contents. The enhanced yield of ash in the finer fraction acts as an inert and counterbalances the effect of particle size on the lean flammability limit [13].

The minimum explosive concentrations of the biomasses are found to be much leaner than for coal and even hydrocarbon gases in terms of equivalence ratio [3, 13, 15, 17-20]. Most of the data on the MEC in the literature are expressed in terms of g/m^3 , which when converted to equivalence ratio helps to compare the results with equivalent LEL data for other fuels [21]. Most hydrocarbon fuels have their lean flammability limits at half of their stoichiometric concentration. Oxygenated fuels such as biomass were found to have their MEC much leaner than the LEL for gaseous hydrocarbons

[3, 13, 15, 17-21]. It was also observed that coal and biomass fuels have no upper flammability limit. Deguingand & Galant [22] employed weak spark ignition for the determination of the upper flammable limit and found apparent upper flammable limit of coal dust to be $\sim 4 \text{ kg/m}^3$, which is more an ignitability limit rather than a flammability limit because of the weak ignition source. Wolanski [23] found that increasing the concentration reduces the flame temperature below its limit value and also observed that the dusts do not have upper flammability limit.

The kinetics for volatile yield and their chemical characterisation will help to understand the mechanism of flame propagation in pulverised biomass. A range of biomass samples including woody and agricultural biomass were investigated for the release of volatiles using thermal gravimetric analysis (TGA) and their devolatilisation kinetics were derived using Staggs's [24-26] quick approximation method. Two different models, as developed by Staggs [24-26], were applied for the kinetic study of these biomasses: Series Reaction Model and Competitive Reaction Model.

2 Experimental Techniques

The elemental analysis of biomass and coal used a Flash 2000 Thermo Scientific Analyser. It consists of a single reactor with temperature of 1800°C for the detection of Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) with O found by subtracting the mass of CHNS from the original mass. At this extreme temperature, the material is converted into carbon dioxide, water, nitric oxides and sulphur oxides. These combustion products are separated by a chromatographic column and detected using a Thermal Conductivity Detector (TCD).

Proximate analysis (water content, volatile matter, fixed carbon and ash) was carried out using a Shimadzu TGA-50 thermo-gravimetric analyzer. It consists of a mass balance attached to a ceramic sample pan in a furnace. It records the weight loss with time and temperature and from this the moisture, volatile, fixed carbon and ash content can be determined. The operating procedure was:

1. The sample was heated in nitrogen from ambient temperature to 110°C at a rate of 10°C/min and maintained at 110°C for 10 minutes so as to completely dry the sample. This determined the water content.
2. The temperature was increased to 910°C at a rate of 25°C/min and held for 10 min to stabilise the weight after the volatile loss. This determined the volatile content.
3. Air was introduced at 910°C to react with any fixed carbon. The mass loss was the fixed carbon content. The remaining material left after this was inert ash.

Calorific values were determined in the Parr 6200 bomb calorimeter and are thus on an as received basis and include the CV reduction due to the water and ash content. They can be converted into a CV on a daf basis by dividing by the proportion of the total mass that is not water or ash.

The combustion reactivity of the pulverized biomass mixtures was determined using the Hartmann explosion tube equipment [13, 15, 19]. The apparatus used was originally a Group A/B flammability screening apparatus comprising a 1L vertical perspex tube with 322 mm length and 61 mm internal diameter mounted on a base that contained the compressed air dispersion control system. A remote control handset operates the ignition arc and air dispersion. The continuous arc was achieved from a high voltage power supply and the spark was on before the dispersion of dust in the tube.



Fig. 1 Modified Hartmann tube

Known masses of powder were loaded into the dispersion cup. The top of the tube was always covered with a bursting vent (20 μm thickness aluminium foil secured with a locking ring). When the tube was securely positioned vertically onto the base; 7 bar (g) compressed air was supplied to an internal 50 mL reservoir of air. The dust was dispersed by opening a solenoid valve that started the flow of compressed air. The released air impinges on the dust at the bottom of the vessel raising into a cloud that is ignited by the spark. The dust concentration is the mass of dust used divided by the total volume of air in the vessel at the start of the test plus the injected air expanded to the same atmospheric conditions – a total volume of 1.35 litres.

The modifications introduced to the apparatus included the fitting of a piezoelectric Keller PAA-11 pressure transducer to record the pressure histories during each test; three bare bead type-K thermocouples were mounted at 50 mm, 100 mm and 150 mm above the igniter in order to record the time at which the flame arrived to each of the thermocouples; the air dispersion pressure was adjusted to 7 bar (g) to achieve better repeatability of tests, by forcing a more even distribution of the powder within the tube. The modifications introduced, facilitated the determination of ignition of the powder in near limit mixtures so that reliable minimum explosion concentrations (MEC) could be determined. The MEC is a measure of the mixture reactivity, but other measures of the mixture reactivity could also be determined as a function of the concentration. The measurement of the rate of pressure rise just before the vent burst is proportional to the mass burning rate and the determination of flame speeds between thermocouples is related to the fundamental mixture burning velocity. These additional data, in turn, allowed the charting of reactivity with concentration and determination of most reactive mixtures.

An explosion was deemed to have taken place if the overpressure due to reaction was ≥ 100 mbar, or if the flame travelled to the thermocouple fitted at 100 mm distance from the ignition source. This made the equipment similar to the EU gas Lean Flammability Limit determination standard method [27]. This has an 80mm diameter tube that is 300mm long with ignition 60mm from the bottom and a limit flame propagation criteria of the flame moving 100mm from the spark.

3 Determination of the Stoichiometric A/F

A consequence of the variable composition of biomass is that the stoichiometric A/F by mass for biomass is variable. This has important consequences for burner control of excess air. In the literature on biomass combustion, particularly that relating to the explosion hazards, pulverized biomass concentrations are always expressed in units of g/m^3 and until the work of Andrews and Phylaktou [21] there was no conversion of concentration into equivalence ratio or the mixture concentration relative to the stoichiometric concentration. In contrast all publications on combustion for gas/air mixtures express the mixture concentration in terms of equivalence ratio. The stoichiometric A/F can be computed by carbon and oxygen balance from the element composition of the biomass. The stoichiometric A/F can be converted to g/m^3 at ambient volumetric conditions using the density of air as $1200 \text{ g}/\text{m}^3$ and the conversion from the stoichiometric A/F is given in Eq. 1.

$$\text{Concentration } \text{g}_{\text{fuel}}/\text{m}^3_{\text{air}} = 1200 / \text{A/F}_{\text{stoichiometric}} \quad [1]$$

For example for a typical wood with a stoichiometric A/F of 6 the concentration is $200 \text{ g}/\text{m}^3$. In contrast, a pure hydrocarbon (gas, liquid or solid) has a stoichiometric A/F of about 15 and a concentration of $80 \text{ g}/\text{m}^3$. The stoichiometric A/F of the selected samples were calculated by carbon and oxygen balance utilizing the elemental H/C (y) O/C (z), N/C (w) and S/C (k). The stoichiometric F/A is given by Eq. 2.

$$CH_yO_zN_wS_k + aO_2 \rightarrow bCO_2 + cH_2O + dNO_2 + eSO_2$$
$$\text{Stoichiometric } \left(\frac{F}{A}\right) = \frac{(12 + y + 16z + 14w + 32k)}{\left[\left(1 + \frac{y}{4}\right) - \frac{z}{2} + w + k\right] \cdot 137.9} \quad [2]$$

The stoichiometric actual A/F can be calculated from the stoichiometric A/F on a daf basis using Eq. 3.

$$\text{Actual}(A/F) = \text{Stoichiometric}(A/F)[1 - (x_w + x_a)] \quad [3]$$

Where x_w and x_a are the mass fractions of the moisture and ash contents in the sample respectively.

4 Chemical Characterisation

The chemical characterisations of selected biomass samples are shown in Table 1. This includes the elemental analysis, the proximate analysis, the calorific value and the stoichiometric A/F on a daf and actual basis.

Figure 2 shows the H/C ratio against O/C for different bioamasses and coals. Proportions of these components of biomass vary from one biomass to another and as they have quite different H/C and O/C ratio the variability of biomass is mainly due to the variability of the constituent components of biomass. Also included in Fig. 2 is the composition of the main constituents of biomass: cellulose, hemicellulose and lignin (based on chemical formulae of $C_6H_{10}O_5$, $C_5H_{10}O_5$ and a mixture of $C_9H_{10}O_2$, $C_{10}H_{12}O_3$, $C_{11}H_{14}O_4$ for lignin respectively [28, 29]).

The stoichiometric A/F_{daf} are shown as a function of H/C in Fig. 3 and this shows the wide variation with biomass composition. Also shown is that the stoichiometric A/F of hemicellulose is 3.15 and 9.56 for Lignin and these cover the entire spectrum of biomass compositions. This again shows that biomass composition variability is controlled by the varying cellulose, hemicellulose and lignin proportions. The calorific values by bomb calorimetry in Table 1 are reduced for biomass with a high water and ash content such as agricultural waste material. If the water is removed and a process to remove the ash is used, such as acid water washing, then the higher calorific value on a daf results, which is also shown in Table 1. The increase in CV for agricultural waste biomass on a daf basis is considerable and for these high ash fuels, acid washing to remove ash components such as potassium will be essential; as the reduction in flame temperature from the low CV will make good heat transfer in boilers difficult. It is known that the CV_{daf} of biomass is correlated to the elemental analysis and Eq. 4 [30] is a common relationship used for this.

$$CV_{higher} = 1.87\%C^2 - 144\%C - 2820\%H + 63.8\%C\%H + 129\%N + 20147 \text{ kJ/kg} \quad [4]$$

Table 1: Chemical Characterisation of the selected biomass and coal samples

Biomass	C	H	N	O	H ₂ O	VM	VM	FC	Ash	CV		Stoich A/F daf.	Stoich A/F
	%	%	%	%	%	%	%	%	%	MJ/kg		g/g	actual
	daf	daf	daf	daf			daf			actual	daf		g/g
Rice Husk	49.8	6.4	1.1	42.7	7.7	62.3	83.7	12.2	17.9	15.2	20.4	6.15	4.58
Bagasse	55.6	7.3	1.3	35.7	7.2	67.1	92.3	5.6	20.1	15.6	21.5	7.46	5.42
Wheat Straw	50.6	6.4	1.4	41.5	6.8	60.7	86.2	9.7	22.8	14.5	20.6	6.35	4.47
Corn Cobs	45.9	6.0	1.2	46.8	7.1	69.4	82.5	14.8	8.8	14.8	17.6	5.4	4.54
Peanut Shell	53.7	6.6	1.5	38.2	7.0	66.4	78.1	18.6	8.0	18.2	21.4	6.9	5.87
Black pellet	52.8	5.8	0.4	41.0	4.4	73.0	78.6	19.9	2.7	19.5	21.0	6.28	5.83
Yellow pine	51.0	6.1	0	42.9	5.4	77.5	83.4	15.3	1.7	19.9	21.4	6.12	5.69
Pine	52.7	6.1	0.5	40.7	6.7	75.3	84.6	13.7	4.3	19.2	21.6	6.42	5.71
HW Sawdust	50.8	5.9	0.4	42.9	6.0	78.4	85.6	13.2	2.4	19.4	21.2	6.04	5.53
CWW1	56.5	6.0	0.6	36.8	4.9	73.8	89.9	8.3	13	18.3	22.3	6.98	5.73
CWW2	50.8	4.7	0.4	43.9	6.7	85.5	94.1	5.4	2.4	19.1	21.0	5.58	5.07
Kellingley Coal	82.1	5.2	3.0	6.96	1.7	29.2	36.9	50.0	19.1	25.0	31.6	11.6	9.19
Colombian Coal	81.7	5.3	2.6	9.6	3.2	33.7	41.3	47.8	15.3	26.4	32.4	11.2	9.13

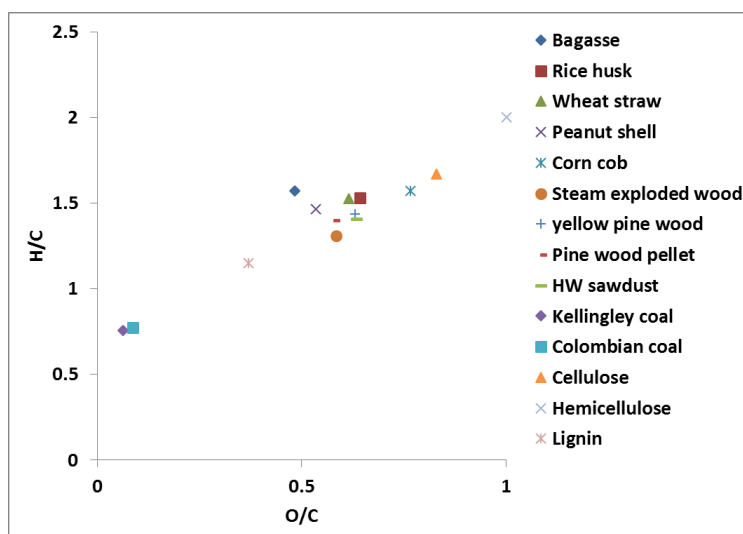


Fig. 2 H/C vs O/C plot for selected biomass samples

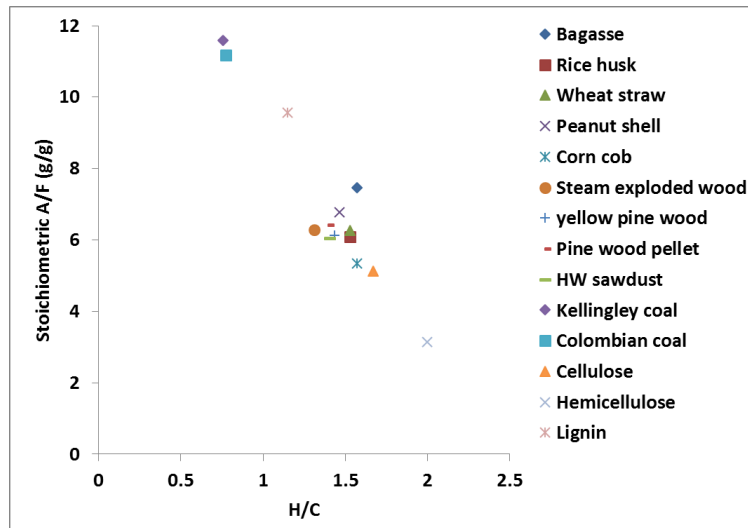


Fig. 3 H/C vs stoichiometric A/F by mass

A consequence of Eq. 4 is that a high oxygen content of biomass, which reduces the % of all the other components, reduces the CV. Lignin has the lowest oxygen content at 21.3% with hemicellulose the highest at 55.0% and cellulose at 49.8%. A high CV_{daf} thus occurs for biomass with high lignin content and a low CV occurs for biomass with high hemicellulose content.

4.1 Volatile Matter Determination

Figure 4 shows that the normalised TGA release of volatiles was similar for all biomass and yet had significant differences, which are shown more clearly in the rate of mass loss plots in Fig. 5. The release of volatiles for the coal samples was found to occur at a much higher temperature compared to biomass samples, as shown in Figs. 4 and 5. Biomass samples release 80-90% of their volatiles in the temperature range of 350-450°C, whereas for coal samples the release of volatiles was only about 30%. Fig. 5 shows that the peak rate of release of volatiles from biomass is higher than for coal and occurs at lower temperatures. Also for some biomass samples, there were two sharp peaks observed showing the decomposition of hollo-cellulose at lower temperature with subsequent lignin decomposition at higher temperature. Decomposition of these components depends on their overlapping structure and level of ash contents in the sample [31, 32].

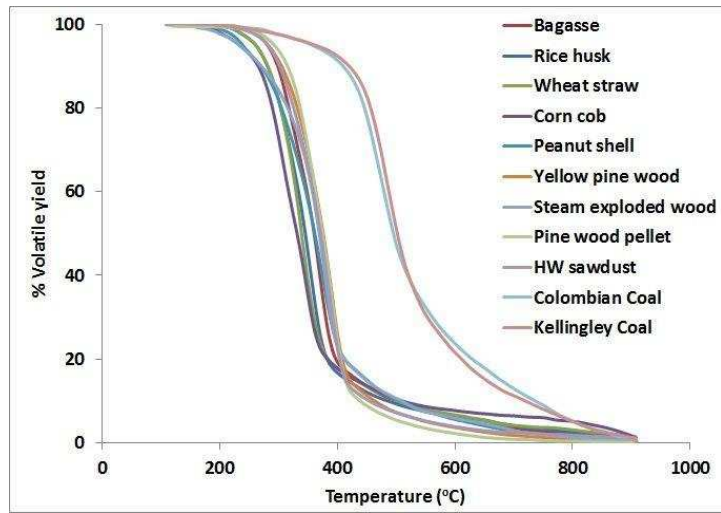


Fig. 4: Percentage yield of volatiles vs temperature for biomass samples in comparison to coals

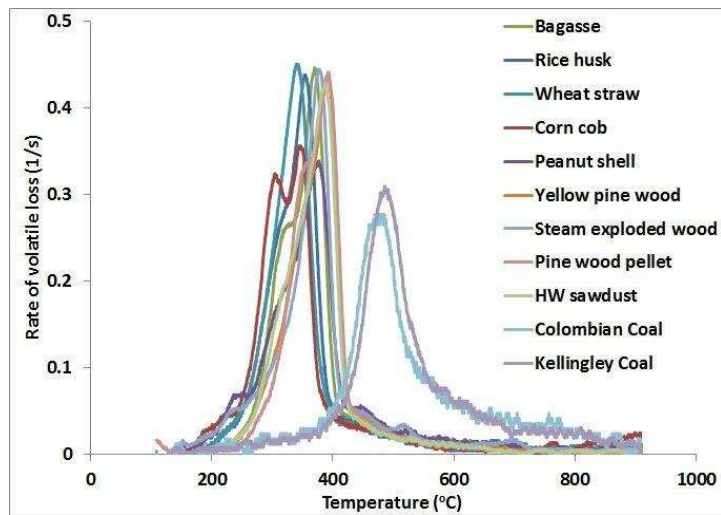


Fig. 5: Rate of volatile loss vs temperature for biomass samples in comparison to coals

4.2 Correlations of Biomass Volatile Fraction

Table 1 shows that on a raw particulate basis the volatile fraction (VF) of all the biomass studied varied from 60.7 – 85.5% on an as received basis and on a dry ash free (daf) basis it varied from 78.1 – 94.1%. Although all biomass have a high VF there is significant difference in the VF for different biomass. The use of the daf VF was because the water and ash content were variable and considered to have little influence on the volatile release.

Figure 6 shows the data of the volatile fraction against H/C molar ratio of the biomass and coal samples. It shows that biomass samples with higher H/C ratio produce higher volatile fraction in contrast to coal

samples. The data scatter for biomass is large and could not be correlated. Fig. 7 shows the volatile fraction plotted as a function of the O/C molar ratio. This again shows that biomass samples have higher volatile fraction and O/C compared to coal samples. For biomass samples, the O/C is the dominant factor in the volatile fraction this would imply that CO was the main component of the volatile gases. Pyrolysis of biomass samples also showed the major proportions of CO that increase further for fast/flash pyrolysis employing higher heating rate and higher temperature [33, 34]. The measured CV and the volatile fraction are reasonably well correlated, as shown in Fig. 8. As the volatile fraction of biomass increases Fig. 7 shows that the oxygen content also increases. A limiting condition of 100% volatiles that are all CO is shown in Fig. 8 to be not far below the extrapolated line. There would be some hydrocarbons as well, but CO is likely to dominate the volatile gas composition.

4.3 Computation of Volatile Composition by Elemental Balance

If the composition of the volatiles is assumed to be exclusively CO, CH₄ and H₂ then the relative amounts can be computed from the elemental and TGA proximate analysis. The results of this computation are shown in Table 2 for two different assumptions. The first computation assumes that under very rapid heating in flames all the biomass becomes volatile and the mean composition of the released gases is the same as the biomass elemental composition.

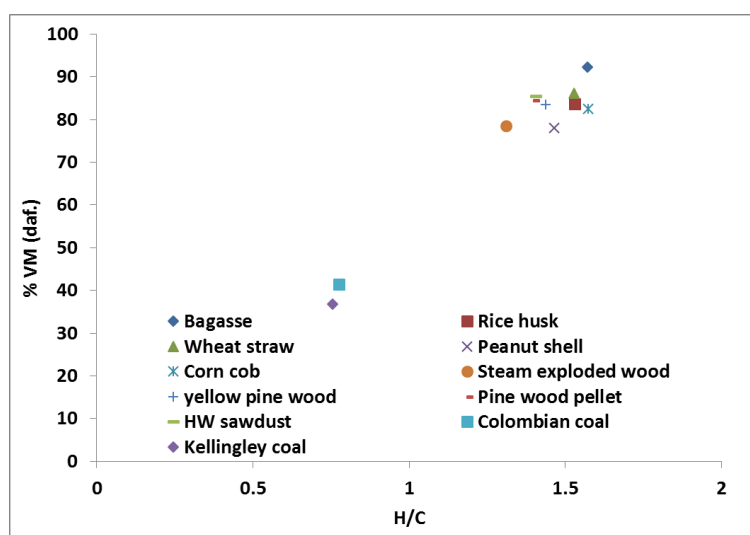


Fig. 6 Correlation of % VM (daf) with H/C

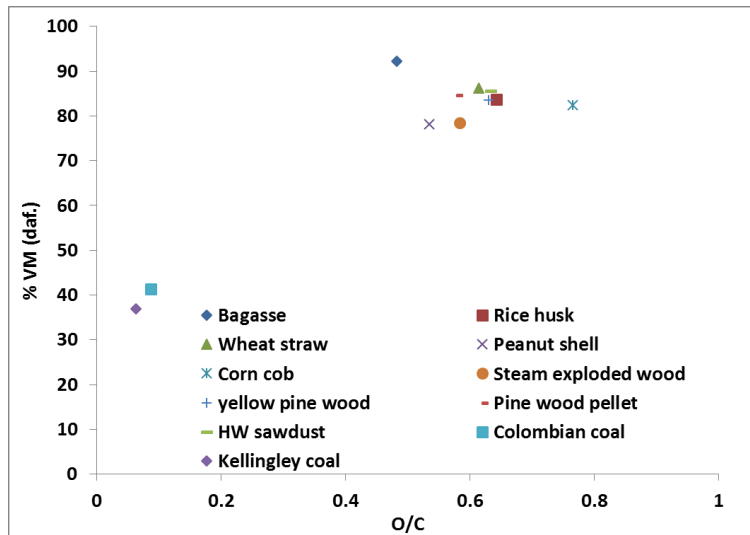


Fig. 7 Correlation of % VM (daf) with O/C

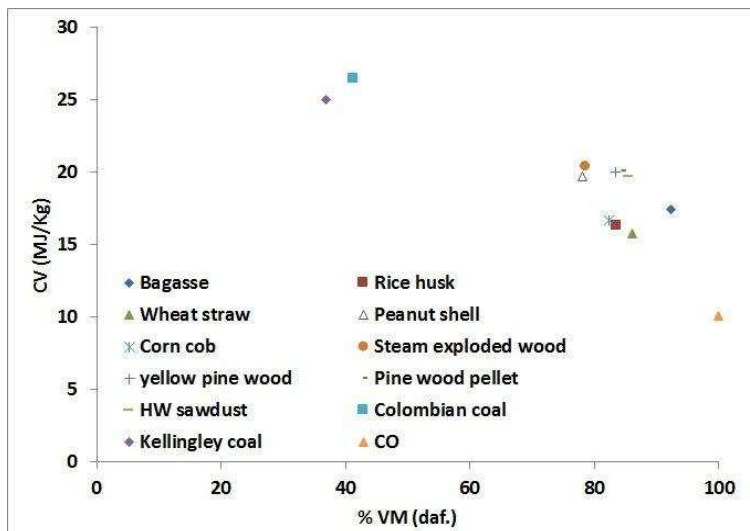


Fig. 8 Correlation of CV with the % volatile matter

The second computation assumes that the fixed carbon determined by TGA does not appear in the gas phase and hence the mean carbon content of the volatiles is reduced from that in the biomass.

The results are shown in Table 2 where there are negative amounts for a gas, this indicates that an elemental balance could not be achieved and hence there must be other gases present than the three assumed. However, there are only a few cases of negative values and so in most cases the simple three gas assumption may be valid.

Table 2 shows that if the mean composition of the biomass volatiles is the same as the solid biomass (daf) then CO varies between 63 – 83% by mass and CH₄ varies between 15 and 39% with little hydrogen.

However, for coal the assumption results in impossible amounts of methane, high hydrogen and low CO. Thus, as is well known, this model is not realistic for coal but it could be for biomass. If the fixed carbon is not turned into volatile with rapid flame heating, then the predictions are much more sensible for coal with 56% CO and 49% CH₄. In modelling of coal combustion the volatiles are often assumed to be methane. For biomass the predicted CO is increased from the previous case to 70 – 100% roughly and lower CH₄ is predicted in the range 0-30%. Some hydrogen is also predicted for some biomass. Both cases could be reasonable for biomass. The low level of char in biomass combustion in explosions and furnaces indicates that assuming the mean composition of the volatiles is the same as that of the biomass, may be reasonable and some CFD models of biomass combustion make this assumption.

Table 2 Computation of the volatile composition based on elemental balance and the assumption of CO, CH₄ and H₂ as the only gases in the volatiles

Biomass	Including FC with the Volatiles					Volatile excluding FC				
	Formula	Stoich. A/F	CO	CH ₄	H ₂	Formula	Stoich. A/F	CO	CH ₄	H ₂
Rice Husk (RH)	CH _{1.53} O _{0.64}	6.15	76%	24%	0%	CH _{2.10} O _{0.97}	4.85	92%	2%	7%
Bagasse (B)	CH _{1.57} O _{0.48}	7.46	63%	39%	-2%	CH _{1.73} O _{0.57}	6.96	70%	30%	0%
Wheat Straw (WS)	CH _{1.53} O _{0.61}	6.35	74%	26%	0%	CH _{1.95} O _{0.85}	5.29	87%	8%	5%
Corn Cobs (CC)	CH _{1.57} O _{0.77}	5.40	83%	15%	2%	CH _{2.35} O _{1.25}	3.87	101%	-12%	10%
Peanut Shell (PS)	CH _{1.46} O _{0.53}	6.88	68%	34%	-2%	CH _{2.56} O _{1.15}	4.46	98%	-7%	10%
Steam exploded wood (BP)	CH _{1.31} O _{0.58}	6.31	72%	29%	-2%	CH _{1.46} O _{0.66}	5.91	77%	22%	0%
Yellow pine wood	CH _{1.44} O _{0.63}	6.12	75%	25%	0%	CH _{1.86} O _{0.86}	5.18	87%	8%	5%
Pinewood pellet (BLZ)	CH _{1.40} O _{0.58}	6.45	72%	30%	-1%	CH _{2.03} O _{0.95}	4.84	91%	2%	6%
Hardwood sawdust (DFL)	CH _{1.41} O _{0.63}	6.06	75%	25%	0%	CH _{1.97} O _{0.93}	4.90	90%	4%	6%
Kellingley Coal (K Coal)	CH _{0.75} O _{0.06}	11.59	13%	109%	-22%	CH _{1.39} O _{0.39}	8.07	56%	49%	-5%
Colombian Coal (C Coal)	CH _{0.77} O _{0.09}	11.18	17%	103%	-20%	CH _{1.37} O _{0.40}	8.01	56%	49%	-5%

5 Stagg's Quick Approximation Method for Kinetic Data from TGA

Stagg's [24-26] quick approximation method was used to determine the kinetic data for the rate of volatile's yield from a solid that is applicable for low temperature TGA analysis. Two different models were developed: the Series Reaction Model and the Competitive Reaction Model. The model assumption, for both the series and competitive reaction models, were a first order reaction, as in Eq. 5, and $T_c/\Delta T_c \gg 1$, where T_c is the characteristic temperature (temperature for 50% of the mass fraction i.e. $c=0.5$) and ΔT_c = Characteristic temperature range.

$$\text{Rate Constant 'k'} = Ae^{\left(\frac{-T_A}{T_s}\right)} \quad [5]$$

Where T_A is the activation temperature, A is pre-exponential factor and T_s is the solid material temperature

$$T_A = -\frac{T_c^2}{c \cdot \Delta T_c \cdot \log(c)} \quad [6]$$

$$A = \frac{\left(H \times \text{Exp}\left(\frac{T_A}{T_c}\right)\right)}{c \times \Delta T_c} \quad [7]$$

Here 'H' is heating rate.

T_c and ΔT_c are adjusted until the integral of the residual error approaches zero using GRG non-linear solving method in the 'Solver' option in Microsoft Excel.

5.1 Series Reaction Model

Figure 4 shows that the rate of release of volatiles from dry biomass follows three stages: the first stage occurs over 200– 300°C and accounts for typically 10% of the volatile loss. The second stage is the rapid mass loss of about 70% of the total volatile mass over the temperature range 300 – 400°C. Finally, there is a slow loss of volatiles accounting for about 20% of the volatile loss over the temperature range 400 – 900°C. These three stages were present in the coal samples but at much higher temperatures. In this proposed simple model, the rate of release of volatiles was split into two stages and the first stage combines the initial first and second stages. Cellulose and hemicellulose in the biomass break down in the lower temperature range release the primary

volatiles. In the later stage, some remaining contents of cellulose and hemicellulose decompose, possibly to tar, but it is mainly hard lignin that partially decomposes, depending on the heating rate and temperature. This later volatile loss is due to the higher decomposition temperature of lignin. The variability of cellulose, hemicellulose and lignin in biomass gives the variability in the rate of volatile loss in Figs. 4 and 5. With slow heating rate and low temperatures, there is some char residue left. It is possible that in propagating flames in pulverised biomass, where heating rates are much higher than in a TGA, that the fixed carbon will be less and the yield of CO will be higher.

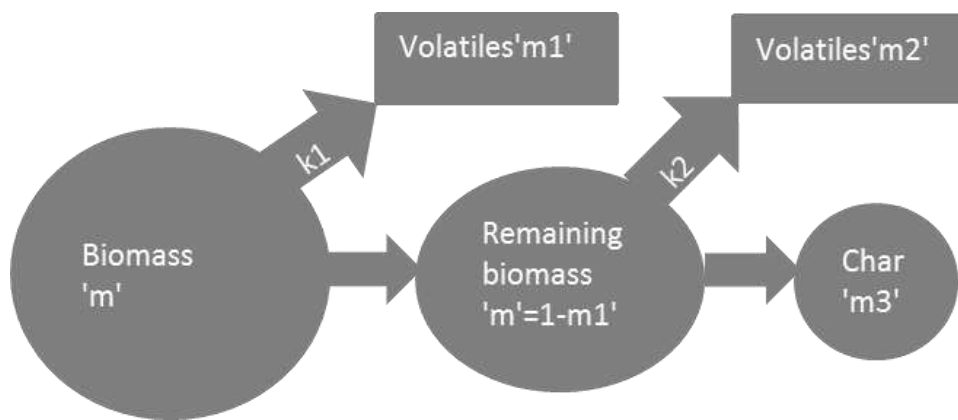


Fig. 9: Series Model for Rate of Volatile release

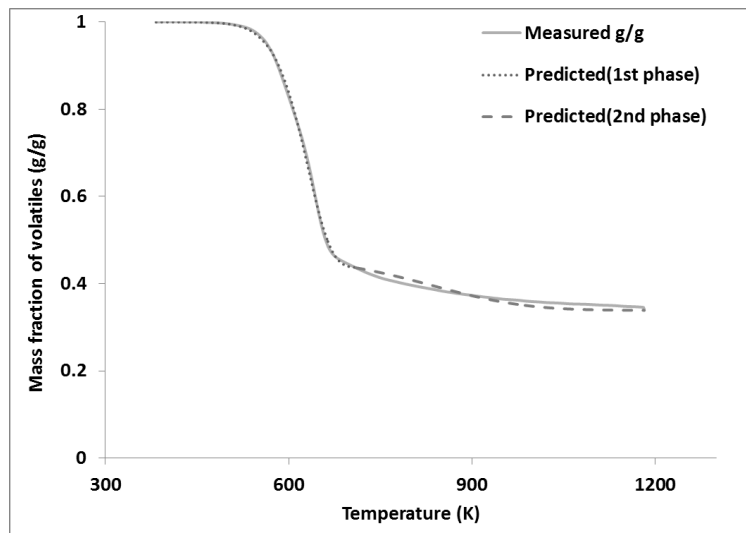


Fig. 10: Predicted % yield of volatiles vs. temperature for two phases in comparison to experimental TGA result

The ‘Series Reaction Model’ mechanism is shown in Fig. 9 and involves two routes to the release of volatiles: directly from the original biomass and via low temperature pyrolysis that produce material, such as tar, that subsequently decomposes to release volatiles. Kinetic equations for the release of volatile from these two phases are given by Eqs. 8 and 9. The production of char is given by Eq. 10.

$$\frac{dm}{dt} = -k_1 m \quad [8]$$

$$\frac{dm'}{dt} = -k_2 m' \quad [9]$$

$$m_3 = (m' - m_2) \quad [10]$$

The rate of release of volatiles for the two phases was predicted using this model and compared with the experimental TGA results for slow heating rate of 25°C/min as shown in Fig. 10, for one of the biomass in Fig. 4. The fit to the data by the model was very good for the first two phases of the volatile release, showing that modelling them as one first order volatile release reaction was valid. The fit to the last stage of volatile release was not as good, but was reasonable. It is the good fit to the rapid volatile release phase that is important as this is most important in flame propagation.

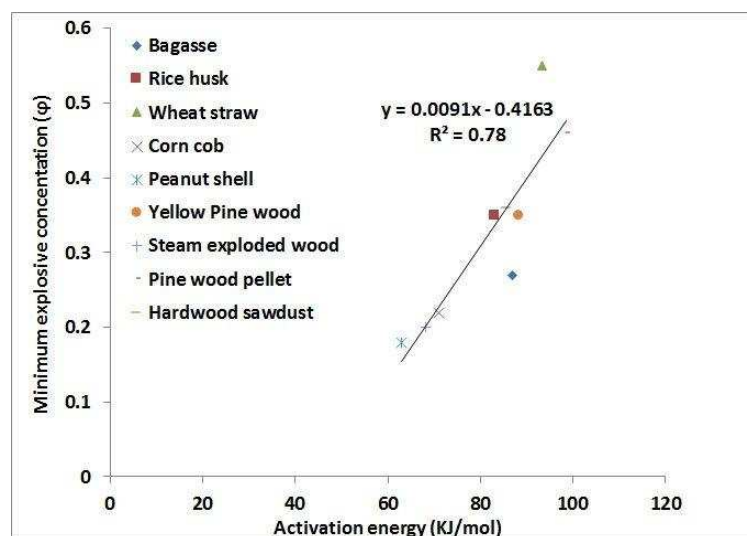


Fig. 11: Correlation of MEC with activation energies based on the series reaction model for *volatile's loss of biomass samples*

Table 3: Predicted Kinetics for two phases in TGA volatile's loss in series reaction model

Materials	Activation energy (KJ/mol)		Activation energy 'E' (MJ/kg)		Rate Constant 'k' (1/s)		MEC
	1st phase	2nd phase	1st phase	2nd phase	1st phase	2nd phase	Eq. ratio
Bagasse	87.0	38.2	4.09	1.79	$1.7E+5e^{10468.8/T}$	$0.67e^{4593.4/T}$	0.27
Rice husk	83.1	38.9	3.45	1.62	$1.2E+5e^{9999.1/T}$	$0.66e^{4682.1/T}$	0.35
Wheat straw	93.3	36.8	3.94	1.55	$1.2E+6e^{11218/T}$	$0.7e^{4425.8/T}$	0.55
Corn cob	71.0	40.7	2.72	1.56	$1.5E+4e^{8545.6/T}$	$0.63e^{4902/T}$	0.22
Peanut shell	63.0	35.5	2.82	1.59	$1.5E+3e^{7578.4/T}$	$0.72e^{4269.7/T}$	0.18
Yellow pine wood (YPW)	88.4	32.4	3.76	1.38	$1.6E+5e^{10631.1/T}$	$0.83e^{3716.2/T}$	0.35
Steam exploded wood (BP)	68.2	35.3	3.00	1.55	$3.7E+3e^{8208.4/T}$	$0.73e^{4251.1/T}$	0.2
Pinewood pellet (BLZ)	98.5	31.9	4.32	1.40	$1.0E+6e^{11854.4/T}$	$0.8e^{3841.3/T}$	0.46
Hardwood sawdust (DFL)	85.7	34.2	3.63	1.45	$1.0E+5e^{10310.3/T}$	$0.75e^{4114.3/T}$	0.36
Colombian Coal	105.6	39.8	7.45	2.81	$2.6E+5e^{12703.6/T}$	$0.64e^{4790.9/T}$	0.39
Kellingley Coal	111.0	38.1	8.06	2.77	$5.6E+5e^{13352.3/T}$	$0.67e^{4586.4/T}$	-

Table 4 Particle size distribution in the MEC tests

Samples	d(0.1)	d(0.5)	d(0.9)
Bagasse (B)	24.3	125.6	356.0
Rice husk (RH)	13.6	191.6	563.8
Wheat Straw (WS)	18.8	126.1	441.5
Corn cob (CC)	45.0	147.8	453.8
Peanut shell (PS)	25.4	147.8	453.8
Steam exploded wood (BP)	13.3	51.9	151.8
Yellow pine wood (YPW)	30.7	198.3	629.6
Pine wood pellet (BLZ)	33.0	180.4	569.2
HW sawdust (DFL)	28.0	184.2	576.3
Colombian Coal (C Coal)	6.8	28.1	85.2
Kellingley Coal (K Coal)	5.0	25.5	65.3

Activation energies and rate constants obtained from this Series Reaction model are given in Table 3 for all the biomass and the coal samples. The activation energies in Table 3 showed lower activation energy for biomass fuels than coal. Higher activation energies reflect higher energy requirements for the release of volatiles.

The lean limit MEC of the selected biomass samples as determined using the modified Hartmann explosion tube are compared with these activation energies in the Table 3. Activation energies for the first phase showed a good correlation with the MEC as shown in Fig. 11. Table 3 shows that activation energies for the second phase were almost similar and hence the late release of volatiles is not contributing to the difference in the rate of volatile release and the MEC differences for different biomasses. This is to be expected as it is the initial volatile release that is going to control the flame propagation rate and hence the MEC.

Figure 11 shows poor agreement with the trend for wheat straw (high MEC) and Bagasse (low MEC) for similar activation energy. One explanation for this could be differences in the ash content, but Table 1 shows that there is little difference in ash. Bagasse has more volatiles and a lower MEC than would be expected. It is possible that there are particle size differences with the pulverised bagasse being coarser than that for wheat straw in the Hartmann tests. All the biomasses were milled and sieved below 63 μm and the size distributions for the particles used in the MEC tests are shown in Table 4. Previous works by the authors [3, 11, 13, 15, 17-19, 35] have shown that particle size does affect the MEC. However, Table 4 shows that the size difference between bagasse and wheat straw were small. Hence, the reason for these two biomasses not following the trend of the other biomass in Fig. 11 is not known and further work is required over a wider range of biomass samples. In addition to the rate of volatile release activation energy on MEC as a reactivity parameter, its impact on flame propagation parameters was investigated. In the Hartmann equipment the concentration of biomass dust was varied to determine the peak reactivity concentration in terms of the rate of pressure rise prior to the bursting of the vent at the top of the vessel.

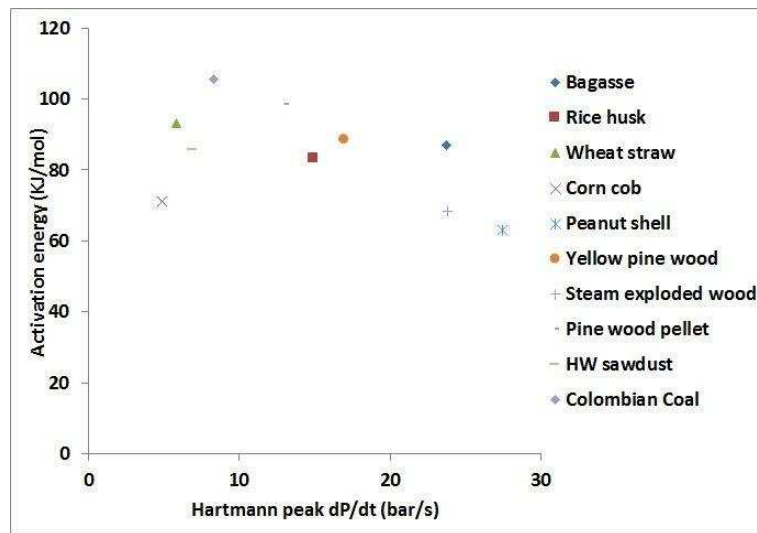


Fig. 12: Correlation of the activation energy for volatile release with the initial rate of pressure rise in the Hartmann.

The correlation of this with the volatile release activation energy is shown in Fig. 12. This shows no correlation between the rate of pressure rise and the activation energy. This was unexpected as the rate of flame propagation is often modelled as the release of volatiles followed by combustion. It is likely that flame propagation is controlled by the rate of heating of the particles by conduction and radiation from the flame front. The release of volatiles is a consequence of this heating and not the cause of the heating.

5.2 Competitive Reaction Model

In this reaction model, the slow heating rate in the TGA is assumed to result in the competitive reactions shown in Fig. 13. The model assumes that heating results in the release of tars with some primary volatiles that form secondary volatiles with the build-up of some char. This model has no direct production of volatiles from the original biomass, which is a key feature of the Series Reaction model. This model may be more applicable for crop residues with higher ash contents that retard the release of volatiles [31]. Even at higher heating rate, the release of volatiles slows down under the influence of ash. The net effect is the release of volatile matter with some residual char contents mainly composed of ash.

The kinetic equations for the release of volatile for these phases are given below;

$$\frac{dm_1}{dt} = -k_1 m_1 \quad [11]$$

$$\frac{dm_2}{dt} = -(k_2 + k_3) m_2 \quad [12]$$

$$\frac{dm_3}{dt} = k_3 m_2 \quad [13]$$

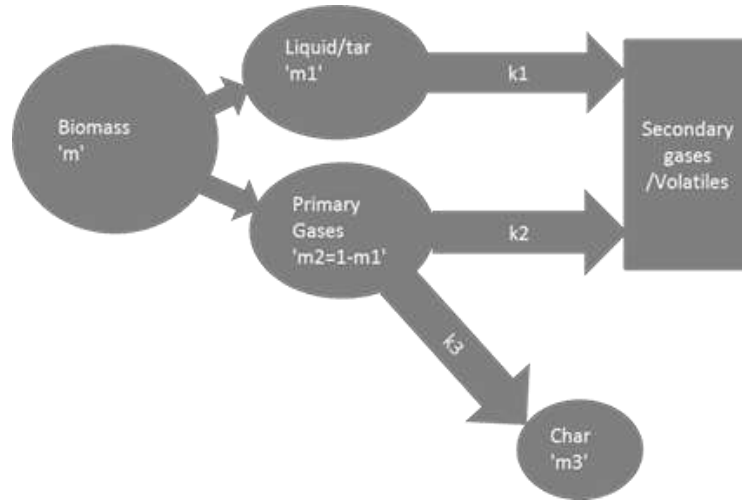


Fig. 13: Competitive Reaction Model for Rate of Volatile release with the build-up of char

Table 5: Predicted kinetics for TGA volatile's loss in competitive reaction model

Materials	Activation energy 'E' 'KJ/mol' (MJ/kg)			Rate Constant 'k' (s ⁻¹)		
	m ₁	m ₂	m ₃	k ₁	k ₂	k ₃
Bagasse	40 (1.9)	89 (4.2)	65.6 (3.1)	1.0e ^{4.0E+4/T}	1.7E+5e ^{8.9E+4/T}	1.0E+3e ^{6.5E+4/T}
Rice husk	41.1 (1.7)	84.3 (3.5)	34 (1.4)	1.0e ^{4.1E+4/T}	1.2E+5e ^{8.4E+4/T}	1.8e ^{3.4E+4/T}
Wheat straw	39.2 (1.7)	94.5 (4.0)	32.6 (1.4)	1.0e ^{3.9E+4/T}	1.1E+6e ^{9.4E+4/T}	1.9e ^{3.2E+4/T}
Corn cob	39.8 (1.5)	72.4 (2.8)	32.6 (1.3)	1.0e ^{3.9E+4/T}	1.4E+5e ^{7.2E+4/T}	1.8e ^{3.2E+4/T}
Peanut shell	40.3 (1.8)	60.9 (2.7)	35 (1.6)	1.0e ^{4.0E+4/T}	6.2E+2e ^{6.0E+4/T}	1.7e ^{3.5E+4/T}
Yellow pine wood (YPW)	38.4 (1.6)	86.4 (3.7)	38.5 (1.6)	1.0e ^{3.8E+4/T}	7.9E+4e ^{8.6E+4/T}	1.8e ^{3.8E+4/T}
Steam exploded wood (BP)	41.8 (1.8)	65.6 (2.9)	36.7 (1.6)	1.0e ^{4.2E+4/T}	1.5E+3e ^{6.6E+4/T}	1.8e ^{3.7E+4/T}
Pinewood pellet (BLZ)	36 (1.6)	100.6 (4.4)	38.4 (1.7)	1.0e ^{3.6E+4/T}	1.2E+6e ^{1.0E+5/T}	1.8e ^{3.8E+4/T}
Hardwood sawdust (DFL)	39.2 (1.7)	84.4 (3.6)	38.4 (1.6)	1.0e ^{3.9E+4/T}	6.0E+4e ^{8.4E+4/T}	1.8e ^{3.8E+4/T}
Colombian Coal	62.4 (4.4)	332.6 (23.5)	80.2 (5.7)	80.8e ^{6.2E+4/T}	148.4e ^{3.3E+5/T}	1.0e ^{8.0E+4/T}
Kellingley Coal	30.9 (2.2)	182 (13.2)	83.4 (6.1)	0.16e ^{3E+4/T}	1.0E+10e ^{1.8E+5/T}	5.1E+3e ^{8.3E+4/T}

An example of the data fit for the competitive reaction model to the TGA results is shown for pine wood in Figs. 14 and 15. The fit to the volatile release is better for the competitive reaction model. The kinetic data derived from the competitive reaction model fits to the TGA data for all the biomass and coal samples is shown in Table 5. However, the final stage of the volatile loss is not the critical contribution to the flame propagation and Table 5 shows that the kinetics of this stage are similar for biomass for K_1 and K_3 but are significantly different for K_2 . This implies that the dominant route in first two stages of the volatile loss is as good as for the series reaction model in Fig. 10. However, the fit to the final stage of this model to volatiles is the same as for the series model, direct evolution of gases from the biomass with subsequent pyrolysis of these gases. The route via tar and char was not a major difference between the biomass. The dominance of the direct release of volatiles from the biomass in the three stage process is shown for pine wood in Fig.16. This shows that the added complexity of the competitive reaction model is not justified and the series reaction model is adequate for modelling the volatile release and for correlation of the MEC. The correlation of the MEC data with the volatile release kinetic fit to the TGA data for the competitive reaction model is shown in Fig. 17.

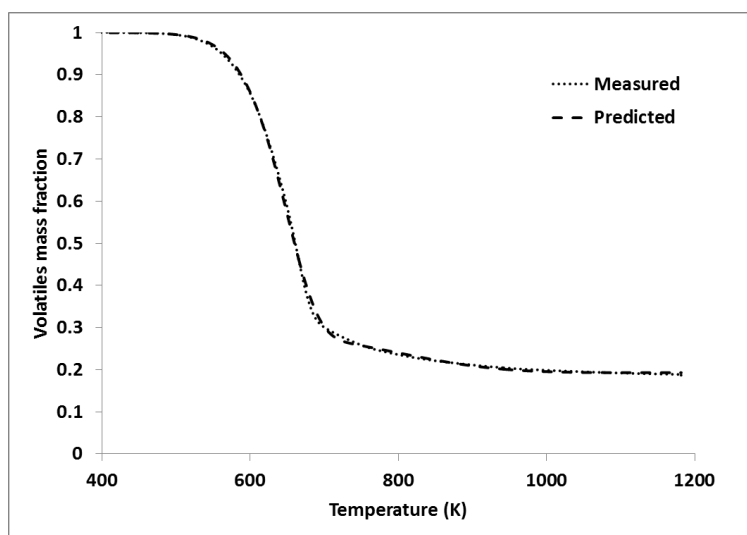


Fig. 14: Fit of the competitive reaction model for the % yield of volatiles from pine wood as a function of temperature in comparison to TGA experimental result

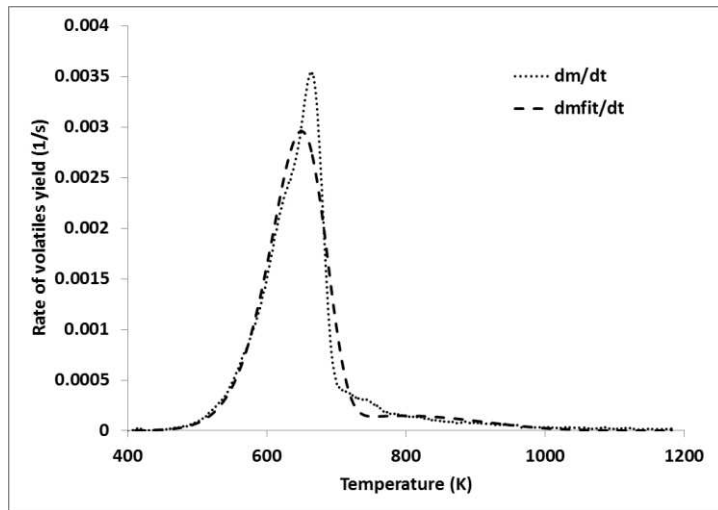


Fig. 15: Comparison of the data fit by the competitive reaction model with the experimental results for rate of volatile yield

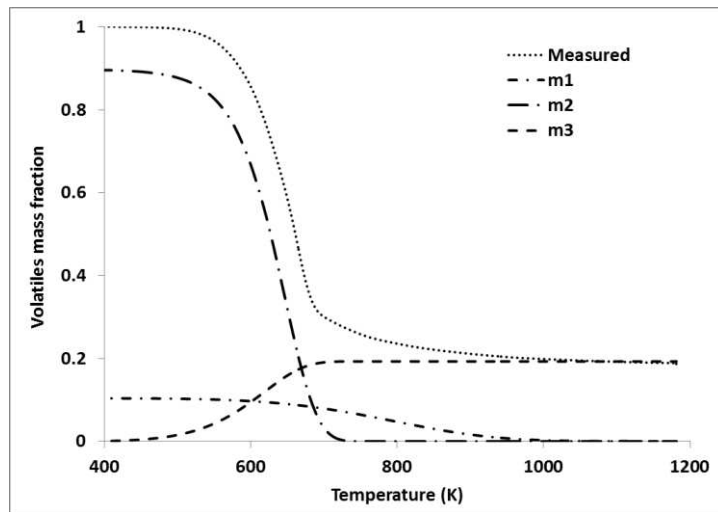


Fig. 16 Competitive reaction model showing the three routes to volatile release and char and tar formation

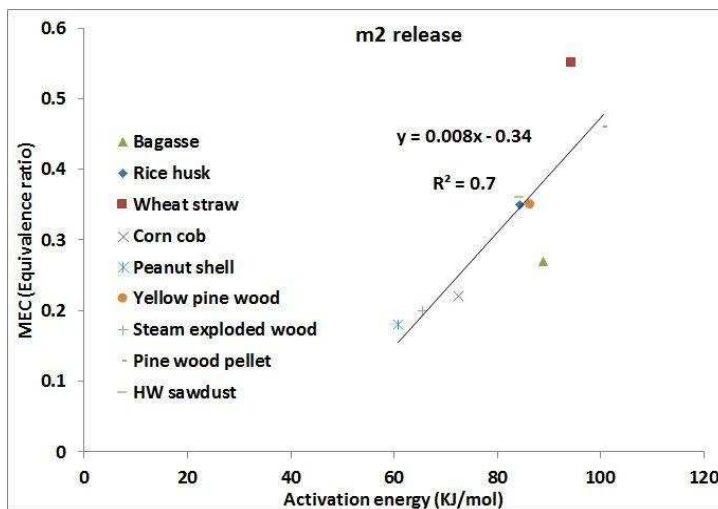


Fig. 17 Correlation of MEC with the direct biomass volatile release from the competitive reaction model.

This is very similar to the results in Fig.11 and the results for wheat straw and bagasse being well of the correlating line are also present.

Thermally-treated biomass, known as steam exploded biomass or a black pellet, that has more fines with regular shaped particles like coal, was found to have lower activation energy for volatile release as compared to most of the biomass samples. This was because the prime action of the thermal treatment is to break up the fibres in biomass to yield finer particles which facilitate the easier evolution of volatiles.

6 Conclusions

1. Biomass composition by elemental and proximate analysis is extremely variable and this leads to significant variability in the stoichiometric A/F by mass.
2. If CO, CH₄ and H₂ were assumed to be the only gases released during low temperature heating of biomass then it could be shown through CHO balance that CO was the most important gas. It is possible that for biomass with rapid heating, a greater proportion of volatiles will be released and the limiting condition of no fixed carbon in flame combustion was used to show that this would decrease the CO and increase the CH₄ yields, but this model would not be appropriate for coal.
3. Correlations for the volatile proportion of biomass were investigated and the H/C and CV were the best correlators, although there was significant data scatter.
4. Two kinetic models based on TGA analysis showed that biomass fuels were more reactive than coal due to the lower energy required to release the volatiles.
5. For the series reaction model, the activation energies of the biomass samples were lower than the coal samples due to fast release of volatiles.
6. The competitive reaction model also predicted low activation energies for biomass samples.
7. The low energy required to release volatile in biomass fuels was considered to be due to the soft and porous structure of the agricultural biomass.

8. MEC data showed that biomasses that released volatiles more easily had leaner MEC and hence were more reactive. However, there were some anomalous results for bagasse and wheat straw that did not fit this trend with no obvious reason for the difference.
9. There was no correlation between the initial rate of pressure rise in the Hartmann explosions and the volatile release activation energy. This indicates that it is the heating of the particles by conduction and radiation that controls the rate of propagation. The release of volatiles is a consequence of this heating and not the cause.

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