



Review on Pollutants from the Solid Biomass Combustion

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ABSTRACT

This review considers the pollutants formed by the combustion of solid biomass fuels. The availability and potential use of solid biomass fuels is discussed. This is followed by the methods used for characterisation of biomass and their classification. The various steps in the combustion mechanisms are given together with a compilation of the kinetic data. The chemical mechanisms for the formation of the pollutants: NO_x , smoke and unburned hydrocarbons, SO_x , Cl compounds, and particulate metal aerosols are outlined. Examples are given of emission levels of NO_x and particulates from combustion in fixed bed combustion, fluidised bed combustion and pulverised biomass combustion and co-firing. Modelling methods for pollutants are outlined. The consequential issues arising from the wide scale use of biomass and future trends are then discussed.

Keyword: Triazole, triazene, Chemoselective reaction, phosphorous ylide

INTRODUCTION

This review is concerned with the combustion of solid biomass fuels, either directly, or with minimal pre-processing, as a primary energy source and the resultant environmental pollution. There is an expanding market in the use of biomass for supplying both transport fuels and electricity/heat. In the former case, the interest is in producing derived liquid biofuels for transportation purposes via first or second generation processing technologies [1] i.e. produced by physical, biological (fermentation), chemical or thermal processing. For electricity and heat generation, solid biomass fuels are the main contenders. Consequently, there are pressures on supply to different sectors from a resource point of view. Some of these pressures are discussed briefly here, although a number of reviews have considered the utilisation and environmental aspects of different generation technologies [2] and [3].

Solid biomass covers a wide range of materials: woods, straws, agricultural residues, processing wastes, algae and seaweeds. Strictly it does not include peat which is partially decayed plant matter, manures, meat by-products and other waste foods. The early use of biomass was based on easy accessibility and availability, but the use decreased in many countries due to shortages in the 19th Century and by the emergence of fossil fuels. Biomass is still widely used in Developing Countries because it is cheap and easily available. In addition, the application technology is simple and the feedstock needs little in the way of processing, hence its popularity especially in countries with considerable reserves of biomass [4-8], despite major efforts to make available other technologies such as solar cookers. As is the case with conventional fuels, extensive compilations or data bases on the properties have been developed [9-12].

Today, there is renewed interest in many industrialised countries in biomass combustion, especially bio-heat, and, in

Europe, co-firing. Older technologies for bio-heat [13-15] are still widely employed but are now moving to a more advanced stage in many industrialised countries [16-18]. This is a result of environmental and climate change concerns, and because of security of energy supplies in a world where fossil fuels are concentrated in a few countries, and resources finite. Of the alternative renewable supplies biomass has the advantages that it is geographically widely available and it is a storable energy. While biomass possesses the advantage of CO_2 neutrality, or nearly so, there are potential problems concerned with the environmental pollution that it causes and the influence on food production. In many of the small combustion appliances there is significant atmospheric pollution - indeed it is estimated that many millions of people are exposed to the effects of wood smoke and 1.6 million people/annum die as a result of pollution [19-22]. Biomass feedstock expansion can have adverse impacts on the environment; particularly where there has been a major change of land-use (such as deforestation) when there can be little or no saving in Greenhouse Gas emissions. In this respect, economic and life cycle analyses are helpful. These can identify the benefit, if at all, of various strategies, but they are sensitive to the weightings set to the pollutants and particularly to carbon dioxide and the other greenhouse gases such as CH_4 and N_2O [23-25].

Predictions on the future usage of biomass are usually to 2050, and indeed some as far as to 2100 [26-28]. It has been concluded that the contribution from biomass could be raised to 200 EJ/year (4.8 Gtoe) by 2050 [29-30], but some estimates make it five times greater (24 Gtoe) [31]. Because of the competition of land for bioenergy crops versus food, and because of the sustainability requirement, there are advantages in integrated processes, where the primary value products, foodstuffs and oils are produced, and the agricultural residues and biomass wastes are used for energy applications.

There have been many studies of biomass sustainability for various regions of the world [29], [30] and [31]. Scrutiny is required with respect to deforestation to make way for crops, as has been the case with palm oil; and with respect to the production of feedstocks (e.g. wheat and maize) for liquid biofuels, where there is direct competition with food production, and where large inputs are required in crop production. These types of problems have implications for solid biomass production also. For instance in Europe [25] and [29], managed forests dominate the landscape in the north, and arable land in other parts. Conservative estimates suggest a total bioenergy potential from agriculture, forestry and waste of almost 300 Mtoe in 2030. Of this 142 Mtoe will come from agriculture alone. This is equivalent to 12% of the utilised agricultural area in 2030. While the improvement of food production techniques could release a significant amount of land for fuel production, there is interplay between the provision of liquid biofuels, solid biomass and food although, at present, greater attention has been devoted to the former [31] and [32].

Finally, the fate of the nutrients in the biomass is an important factor in its sustainability and utilisation. In some applications the biomass nutrients, potassium or phosphorous, can be recycled by returning ash back to the soil. But the nitrogen compounds cannot easily be recycled in this way even though they are often a major input into fuel production. None of the nutrients can be recycled if biomass is co-fired with coal.

Solid Biomass Combustion

As will be shown during this review, the scale of a combustion unit, as well as the biomass type and properties, have important impacts in terms of the pollution produced. Therefore, this section will give an overview of combustion equipment, and biomass types and their combustion characterisation.

Methods of biomass utilisation

A variety of methods of utilisation are possible for biomass which evolved from the technologies developed for the combustion of the solid fuels, coal and coke. These are described in standard text books on fuel technology and combustion engineering [33] and [34]. In some cases, biomass is burned in equipment designed for coal firing, with only slight modification, and this influences the pollutants formed. The methods available are open fires (up to 3 kW_{th}), simple stoves, Patsari cookers and household heating (1-10 kW_{th}), fixed bed combustors (up to 5 MW_{th}), moving or travelling grate (up to 100 MW_{th}), fluid bed (up to 500 MW_{th}) and pf/suspension firing/and co-firing (up to 900 MW_{th}). All combustion applications have the potential to release airborne pollutants: methane and volatile organic compounds (VOC); nitrogen oxides; sulphur oxides; hydrogen chloride; polyaromatic hydrocarbons (PAH); furans and dioxins; as well as organic and inorganic aerosol particulate. This review will concentrate mainly on the formation of the airborne pollutants.

Solid biomass forms

Solid biomass fuels are available in a variety of forms. These include the traditionally available logs and straws, and also processed products such as chips, pellets and pulverised fuels mainly from wood, straw and a range of agricultural residues. Many of the traded biomass conform to standards with respect

to dimensions, moisture content, ash and nitrogen. In pellet making small particles (2-5 mm) of the biomass are compressed whilst steam heated and the lignin acts as a binding agent [35] and [36]. Alternatively a binder may be added. Pellets are now an accepted form of fuel for many smaller units and are becoming widely used and internationally traded [37] and [38]. This also means that there are a variety of, often bespoke, feeding and storing arrangements.

Fluidised bed and travelling bed equipment will take larger particles thus minimising the amount of energy required for processing. Power stations require a fuel pulverised to a size similar to that of pulverised coal in order to achieve a high combustion intensity required by their design. Direct firing of pulverised biomass or the co-firing [39] and [40] with coal requires particles that are ground to less than 1 mm in size which presents a problem with fibrous biomass, and is difficult and expensive (in terms of energy and money). Fibrous biomass requires about 5 times the energy of bituminous coal, however the process of torrefaction [41] and [42] can modify the nature of the products making it easier to mill [11] and [43]. Agricultural process residues including nut products, such as Palm Kernel Expeller (PKE), and olive waste are available in ground form and are less fibrous than woods and grasses.

Solid biomass types and classification

Conventional solid fossil fuels are classified by a range of standard tests, which are determined by a number of considerations. Commercially, the 'value' of a fuel as determined by calorific value, volatiles, ash content and similar parameters is important, as are safety considerations (flammability characteristics). Technically there are other criteria that determine the mode or ease of transportation or ease/efficiency of use in the end application (e.g. density, hardness, particle size). Finally, environmental factors (S, N contents) are also important.

Until recently solid biomass fuels were not traded on a large scale commercially and apart from specialist applications of industrial waste from sugar cane bagasse, palm olive and from paper manufacture. Most of the applications were for domestic heating and cooking. The development in the last decade of biomass on a large industrial scale has prompted the use of standard test methods and in the case of solid fuels the methods developed for coal coking and combustion were used in the first instance. Many of these were based on the existing methods for solid fuels, such as the international standards by ASME, BS, ISO etc [11].

Now the tremendous diversity of biomass feedstock is recognised, there is a need for a comprehensive classification system which covers both physical and chemical specifications and could allow the user to predict the behaviour of a biomass feedstock, via correlations with results from a few simple fuel characterisation tests. Some properties which might be useful to predict include: storage potential; self-heating potential; milling behaviour; pyrolysis behaviour; tar yield; volatile composition; yield and composition of the char and its reactivity towards oxygen; impact of inorganic composition (more variable for biomass compared to coal), on ash behaviour.

Biomass material can be broadly classified into groups based on the general assessment of their source. The resultant major groups are as follows:

- ❖ Woody: pine chips, an energy crop, willow.
- ❖ Herbaceous: two energy crops are listed-Miscanthus and Switch Grass.
- ❖ Agricultural residues: wheat straw, rice husks, palm kernel expeller, bagasse (a sugar cane residue), olive residue or olive cake (the waste from olive oil mills).

Animal wastes such as cow dung form another category although these are not strictly biomass.

Characterisation by chemical analysis

The simplest method of classification is based on chemical analysis [44] and [45]. A method has been suggested by Nowakowski et al. [44] which parallels the type of approach adopted for early coal classification systems, is based on a van Krevelen diagram (plot of H/C versus O/C atomic ratios (daf)). The premise in this classification is that biomass feedstocks that fall within clusters in the van Krevelen diagram will have similar properties, regardless of their category.

This type of approach has now been used by a number of research groups [35], [44] and [45] and there has been marked success in the prediction of other properties, such as calorific value, [46] and some success in predicting lignin, and other similar quantities [47] and [48] from such a plot for lignocellulosic biomass. It should be noted that while some properties, such as calorific value correlate extremely well by this approach, other fuel parameters such as volatile matter or fixed carbon correlate less well, because these parameters are strongly influenced by both heating rate and ash content/composition. There is added difficulty in that the analyses vary across different particle size fractions of the heterogeneous biomass samples [49]. Variation is seen between leaf and stem as well as bark [50] and the analyses are affected by time of harvest, geographic origin, fertilizer treatment and length of storage. [51] and [52].

Solid Biomass Combustion and the Formation of the Major Pollutants

. General mechanism

Biomass combustion consists of the steps: heating-up; drying; devolatilisation to produce char and volatiles, where the volatiles consist of tars and gases; combustion of the volatiles; combustion of the char.

Wet Biomass → heating up/drying → dry biomass

Biomass → volatiles (tars and gases) + char

Volatiles + air → CO + CO₂ (+PAH + unburned hydrocarbons + soot + inorganic aerosols)

Char + air → CO + CO₂

Volatiles (N, S, K, etc) → N, S, K based pollutants

Char (N, S, K, etc) → N, S, K based pollutants

Early predictions of biomass combustion used simplified rate expressions for each of these steps [34], [35], [36], [53] and [54], while recent models include more detailed, biomass-specific chemistry to better predict burn-out and pollution formation indicated in Fig. 1. Modelling of each of these steps is discussed in the following sections.

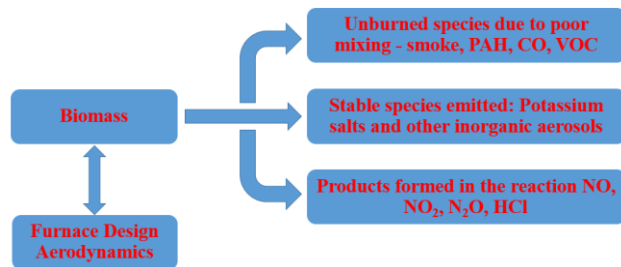


Fig. 1. Diagram of the pollutants formed during biomass combustion.

Pollutants are formed alongside the main combustion reactions from the N, S, Cl, K as well as other trace elements contained in the volatiles and char. CO, PAH and soot, together with characteristic smoke markers of biomass combustion such as levoglucosan, guaiacols, phytosterols and substituted syringols [20] are released if the combustion is incomplete, due to factors such as local stoichiometry (mixing), temperature, residence time etc. Thus, the atmospheric emissions can contain tar aerosols and soot, which together with fine char particles and metal-based aerosols such as KCl, form smoke. The nitrogen compounds are partially released with the volatiles, whilst some forms a C-N matrix in the char and is then released during the char combustion stage forming NO_x and the NO_x precursors, HCN and HNCO. Sulphur is released as SO₂ during both volatile and char combustion. KCl, KOH and other metal containing compounds together the sulphur compounds form a range of gas phase species, which can be released as aerosols, but importantly also deposit in combustion chambers.

The development of models to predict the formation of these pollutants has been a continuing research effort for many decades. Models have been applied to a range of applications and particle sizes, ranging from small pulverised particles less than 1 mm in diameter, to chip, or larger still such as logs, and at the extreme to trees in forest fires. Because of the coupling between chemistry and heat and mass transfer during particle conversion, fuel size has a major effect on the emissions. Although the general features are well understood, there is still debate regarding the relative roles of the controlling mechanisms. Pyrolysis might be controlled by either the chemical kinetic rate or the internal heat transport rate, and char oxidation might be controlled by the chemical kinetic rate or internal or external diffusion rates. The actual rates in the regimes for drying, pyrolysis, char formation and char combustion depend on particle size and can be defined as thermally thin, or thermally thick with thermal wave regimes. In the first case, the temperature is constant across the particle and this is normally assumed in the heating up step for small (pf) particles in the drying and pyrolysis steps. For larger particles, in fluidised or fixed beds, a thermal wave is assumed to pass through the particle, causing sequential drying, pyrolysis, char formation and then combustion. In this situation all the regimes coexist. The thermally thick case is assumed when there is large sized material involved and considerable thermal gradients.

Particle heating and moisture evaporation

Biomass moisture content plays a significant role in the combustion process. Typically newly cut woods contain up to about 50 wt% moisture, present as bound and free water, and

even after considerable ambient drying the moisture content is still about 15-20%. For combustion of small particles (e.g. co-firing with pf coal) the particles are assumed to heat up virtually instantly, but there is an efficiency loss due to the latent energy of water evaporation from the biomass. Because of this, and because of the high content of moisture in some biomass, a drying process is usually carried out separately, which significantly affects the temperature and stability of the flame. However in the large-scale utilisation of biomass the drying process is energy intensive and there is industrial interest in using fuels with high moisture contents at one extreme, or pre-processed by using pelletisation or torrefaction at the other, where the use of energy is optimised [11].

Many drying models have been developed, and early models for biomass drying were those used for pulverised coal [55] and [56], but recently, more detailed models have been developed for larger particles [57] and [58].

Devolatilisation of biomass

Devolatilisation or thermal pyrolysis occurs in the early stages of combustion of solid biomass and plays an important role, since a large part of the original biomass is converted to volatile products [59]. Typically the temperature at which pyrolysis starts is about 160-250 °C for biomass fuels compared to about 350 °C for bituminous coal [60].

The amount and nature of the pyrolysis products depend on both the final temperature and the heating rate, and are influenced by the size of the biomass particles. Fast heating, under moderate to high temperature, yields more volatiles. High temperatures favour gas production over volatile organics and tars. Thus, in pf biomass combustion, volatiles that are produced during the heating up process crack to form mainly CO, CO₂, H₂O, together CH₄, VOC, H₂ and some trace inorganic products [61], [62], [63] and [64]. While in pf combustion the heavy hydrocarbon content in the biomass volatiles is relatively low, it is more significant in fixed bed and fluid bed combustion systems.

The volatile content of biomass usually contributes about 70% of the heat of biomass combustion which is compared with about 36% for coal volatile combustion. Therefore volatile combustion dominates the biomass combustion processes and char combustion is of less importance in terms of thermal efficiency than it is in the coal combustion. However, the char can still contain up to a third of the energy content of the biomass, and this together with the increasingly more stringent particle emission legislation, makes the prediction of unburned carbon in ash still important. This prediction is difficult for both coal and biomass firing due to the complex behaviour of the 'least easy to burn' fraction, such as the high lignin-containing elements, (e.g. knots in wood and nodes in straw). The additional complexities in the biomass char combustion lies in the high content of inorganic species, which may act as a catalyst or an inhibitor.

Further, factors such as low carbon content, low heating value, and high moisture content of biomass compared with bituminous coal, makes the former difficult to ignite and can lead to problems of flame stability, particularly when burning biomass fuel alone. However, once ignited, the overall burning rate of pulverized biomass fuels is usually considerably higher than that of coal due to the rapid release of volatiles, and high

porosity of the biomass char particles. Extensive measurements have been made of the devolatilisation rates and products [65] and the kinetics have been summarised in [66].

Combustion of the gases and tars

Combustion of volatiles and tars is a key step for the formation and potential emission of VOC, tars, PAH and soot. The composition, and hence calorific value, of the gases, tars and chars derived from biomass depend on the heating rate, final temperature, and mineral (especially potassium) content. The distribution of the trace species such as N, Cl, P and the metals between the gases, the tar and the char is important in relation to their subsequent reaction and formation of pollutants. Unlike coal char, the generated bio-char contains a significant amount of oxygen the amount of which is determined by the final temperature. The oxygen content decreases with an increase in temperature under pyrolysis conditions [67] and [68] but there is lack of information obtained directly from combustion situations.

A vast amount of experimental data is available on the composition of the major products produced at the laboratory scale and summarized recently [69]. Another source is the computed values obtained via the network pyrolysis programs, FG-Biomass, CPD and FlashChain [70]. These models can give information on the gas species, the tars and the composition of the char. Additionally information can be given on the nitrogen partition between the char, tar and gases, important for considering NO_x release during combustion.

Char combustion

The chars formed represents about 10-30% of the total biomass by weight but their combustion form important pathways for the release of many pollutants especially nitrogen and many inorganic species. Of course char, or charcoal, can be formed as a separate carbonisation process, and their combustion has been studied for many years [71] and [72]. In most combustion furnaces the biomass is directly injected, so all the processes occur in situ. In thermally-thin particles char combustion occurs after the end of the devolatilization, although in practice a small fraction of char oxidation begins earlier and co-exists with the devolatilisation process. In thermally-thick particles, where a reaction front passes from the external surface to the centre of the particle, the char combustion can be inhibited by the diffusion of escaping volatile products from inside the particle. However, co-existence of devolatilisation and char combustion is observed in practice. Biomass char may contain a significant fraction of the original oxygen and catalytic potassium in the biomass, depending upon the temperature it experiences, thus char combustion behaviour can be significantly different at the temperatures found in fluidised or fixed bed combustion compared to that in pf combustion. Consequently these two cases of char combustion are being considered separately here.

Chemical Mechanisms for the Formation of Trace Pollutants

The previous section has outlined the current knowledge regarding biomass and introduced routes to the formation of the major pollutants CO and the incompletely combusted hydrocarbon based pollutants. The nature of the pollutants produced depends on the form of combustion. Generally large combustion units, with carefully monitored combustion control

form low levels of pollutants whereas small units with poor mixing, poor instrumentation and no control tends to result in high levels of pollutants. The pathways leading to the formation of pollutants have already been shown. Smoke is a consequence of secondary reactions arising from unburned volatiles. The trace species, S, Cl, K and Na can influence the course of combustion as already described but can have an impact on soot and PAH formation, and can influence the emissions of SO₂, HCl and aerosols [73].

Extensive studies have been made of pollutants emitted from small stoves, large domestic and commercial rigs, power plant involving fluidised beds or pf combustion, and co-firing of biomass and coal and these are outlined in the following sections.

Smoke and unburned hydrocarbons

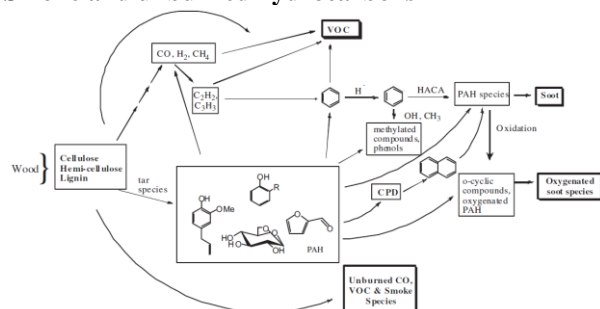
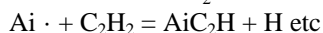
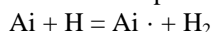


Fig. 2. Pathways leading to smoke and unburned volatiles.

A general mechanism for the organic components in smoke formation is set out in Fig. 2. Smoke consists of a number of components: carbonaceous soot; inorganic, organic, and aqueous aerosols; CO, VOC and PAH; and also small particles of char (unburned fuel/carbon) from the disintegrating fuel particles and entrained in the hot gases and vapours. There are approaches for modelling the formation of carbonaceous soot, aerosols, CO, VOC, and PAH, but modelling the entrainment of unburned fuel/char, which can be a significant component, is extremely difficult. Fortunately because the particle sizes of the latter are larger than those nucleated from the gas phase it is more readily controlled. The inorganic aerosols are discussed later. Fig. 2 summarises the routes to organic emissions and soot emission from biomass combustion. Soot can be produced during the combustion of biomass and the extent of the soot and its nature is a function of the combustion conditions and the post-flame temperature-time history. During the combustion of the biomass both pyrolysis and oxidative pyrolysis of the biomass components occurs with the release of tars and vapours. In most applications, the particles are large and all the combustion processes take place as a thermal wave through the particle either as a self-sustaining flame front, as smouldering or as pyrolysis. The initial products obtained are a function of the composition of the biomass, the water content and the stoichiometry.

The species given in Fig. 2 are caused by incomplete combustion and hence the level of the emissions can be controlled by the design features ensuring mixing of the fuel and air [74]. If the temperature is low (below ~ 700 °C) as might be the case in small cook stoves and units based on smouldering combustion, and there is poor mixing, then compounds in the bottom half of Fig. 2 dominate in the smoke. At higher temperature (above ~ 900 °C) which would be the

case in larger domestic combustors and industrial furnaces, emissions of pyrolysis products decrease and compounds in the top half of Fig. 2 become more dominant. In the combustion of hydrocarbons the HACA mechanism would dominate where acetylene formed in the early part of the combustion zone would first form benzene, then polycyclic aromatic compounds which would go on to form soot. References to HACA and related mechanisms leading to the formation of soot in hot flames are given in [75]). In this mechanism, which stands for ‘H-Abstraction-C₂H₂-Addition’ the key growth species is acetylene and the flame temperature has to be hot enough to form acetylene. The acetylene forms benzene in the first instance which goes on to successively produce increasingly large PAH species ultimately leading to soot particles. Overall the reaction can be represented by



In the case of biomass combustion additional routes involving aromatic species and reactive intermediates such as cyclopentadiene derived from the lignin come into play, but this depends on the amount of lignin in the biomass and the reaction conditions [76]. Emissions of soot and the precursor aromatic and PAH compounds are compounded by poor mixing where pockets of unburned vapours may exit the combustion system. A considerable number of studies have been made on emission of smoke and other pollutants, particularly of fixed bed grate combustors with small or medium thermal capacity, and also from moving bed combustors and suspension or pf combustion. General guides are available via compilations of emission factors. Similarly, extensive studies have been made of the PAH and dioxin emissions [77].

A considerable body of information exists on the related process of smoke from the combustion of hydrocarbon fuels, but whilst there are some similarities there are fundamental differences. The particulate from biomass consists of large polyaromatic hydrocarbons, oxygenated aromatic compounds and pyrolytic PAH material derived from these compounds, residual unburned char particles and products that are condensed on the particulates [19], [20] and [78]. The nature of the resultant aerosols depends on the way in which they are formed and on their time-temperature history as they emerge from the combustion zone through the flue and are emitted into the atmosphere [22] and [32].

NO_x and nitroso compounds

NO_x production during the combustion of fossil fuels has been studied extensively, and in the case of coal combustion arises from three main mechanisms: thermal- NO_x from high temperature oxidation of atmospheric N₂, prompt-NO_x from the reaction of fuel-derived radicals with atmospheric N₂, and fuel-NO_x from oxidation of nitrogen which is chemically bound in the fuel. The mechanisms of the first two routes are well known [79], the former being dependent on the reaction of oxygen atoms with molecular nitrogen and the latter the reaction of CHi species with molecular nitrogen. Their contribution usually only a small percentage (<30%) to the total amount of NO_x produced in most biomass combustion systems, even with those with long residence times (>1 s). The majority of the NO_x is produced from the fuel-bound nitrogen which in

biomass is present as inorganic nitrate and ammonium ion, amino compounds (includes proteinaceous fraction), heterocyclic purines, pyrimidines and pyrroles.

Fuel-nitrogen containing species will be released in combustion both during the devolatilisation and in the char combustion stage. In many boilers, NO_x formation during the volatile combustion can be controlled by stoichiometry control, whereas NO_x formation from char combustion is more difficult to control. Thus, an important factor is the nitrogen partitioning between the volatiles and char [38]. It can be determined experimentally, for example in [38], or by devolatilisation codes, although this method is not very accurate at present for biomass compounds.

The release of SO_x and Cl compounds

Sulphur is a major plant nutrient and is necessary for the metabolism of plants. Normally it is taken up from the soil in the sulphate form although it can be assimilated from sulphur dioxide in the air, and the leaves have the highest content. Biomass tends to contain only small amounts of sulphur (0.1-0.5% dry plant matter, which is small compared with most coals) and the substitution of coal by biomass in co-firing is usually advantageous in this respect, although it can play a role in aerosol formation.

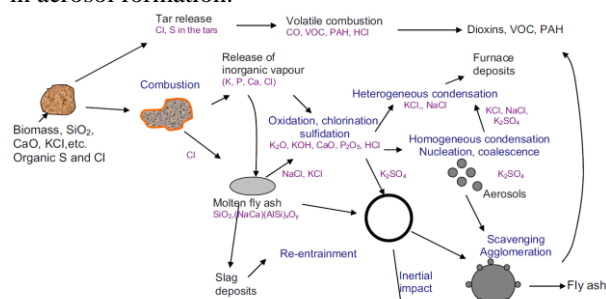


Fig. 3. Aerosol, deposits and pollutant formation pathways for K, Cl and S compounds.

The concentration of chlorine in biomass ranges from 0.2 to 2% and the high concentrations found in some straws is a major combustion problem. F is also present at low concentrations (typically > 0.001 wt%). Both Cl and S are present both as organo-compounds, but mainly as inorganic salts (particularly potassium salts) in solution in the xylem and phloem. Both chlorine and sulphur are released partly during devolatilisation, and the more refractory salts are retained and released during char combustion [80]. Chlorine can react with metals such as K and Na, forming vapours and then aerosols during the cooling processes. This also leads to deposits on the furnace walls. Chlorine (as HCl) can also react with organic constituents producing dioxins. The various reaction steps are given in Fig. 3.

The release of metals from the char is by sublimation or evaporation of the oxides, hydroxides or chlorides. Thus the emission of KCl has an apparent activation energy close to that of the sublimation energy of KCl of 211 kJ/mol [81].

Apart from the aerosols dioxins can be formed. The formation of dioxins is complex, and in the early days of co-firing there was concern that the addition of the Cl-containing biomass would cause environmental problems. Essentially any hydrocarbons present in the hotter regions of flue gases can

rearrange to give initially benzene and then phenols under oxidising circumstances. These readily form phenoxy radicals and these can combine to give dioxin precursors. Chlorination catalysed by metals in the fly ash can give polychlorinated dioxins. Since biomass flue gases, especially straw, contains HCl, this is a potential problem [82]. However as long as combustion is complete, so decreasing the amount of C/H species in the flue gases then the atmospheric environmental problem is minimised.

Metals and particulate metal aerosols

Biomass contains metals of which the most important is potassium, which varies from several thousand ppm in energy crops to a few wt% (dry basis) in certain agricultural residues. On combustion these are released, forming inorganic species which can condense and are deposited in the furnace causing slagging, fouling and corrosion, but a small quantity can be released into the atmosphere as aerosols, as illustrated in Fig. 3. This former aspect is a major topic considered in many reviews and will only be considered in outline here where it impacts on the environmental issues.

As far as emissions are concerned the various metal components are released [83] and interact in the gas phase with sufficient reaction time available to come to equilibrium, the products thus depend on the temperature. The most important species present would be K, Na and Ca compounds, the volatile metals Pb and Zn and S and P as indicated in Fig. 3, together with other trace metals such as Cr, Mn, Fe, Co, Ni, Cu, Ga and As. Their composition would depend on the nature of the biomass and mainly on the resultant amounts of K, Cl, HCl, SO_2 and SO_3 and their interaction, and on the temperature, as shown in Fig. 4. These products on reaching cooler parts of the combustion chamber, condense and some are emitted as aerosols of alkali sulphate or alkali chloride in particles with sizes less than $1 \mu\text{m}$. These fine particles are enriched in most of these elements with respect to the bulk fly ash due to vaporization and subsequent condensation.

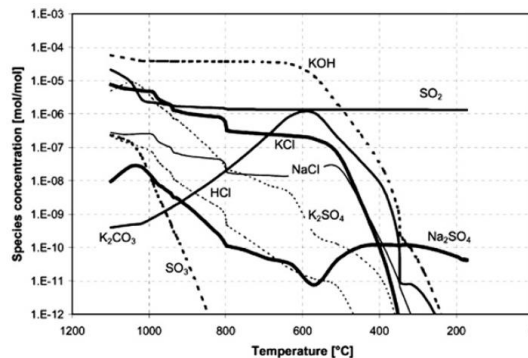


Fig. 4. Equilibrium gas phase species relevant for aerosol formation during beech combustion.

Most of the alkali metal compounds are deposited in the combustion chamber, in which case it is necessary to have an understanding of the transformations that take place in the formation of the ash. This is particularly complex if silica is one of the products. Condensed alkali metal compounds form sticky surfaces onto which ash particles adhere producing deposits, and their effect is dependent on the furnace type. In large furnaces using pulverised fuel or travelling grate combustion stations with a high furnace temperature much of

the deposition occurs on the superheaters. In fluidised beds, bed agglomeration can take place. In grate units, both corrosion and deposits are observed depending on the conditions. These deposits can break off giving larger particulates in the flue gases which can readily be captured by pollution control equipment.

Additives can be used to control boiler deposit problems arising from the deposition of alkali metals. But the way this is undertaken differs from that with coal. For example, if calcium compounds are added to remove sulphur, this would influence the interplay between the S and Cl compounds and would result in the formation of increased KCl, which is not the desired outcome. However, whatever action is taken impinges on the emissions of both gases and particulates.

Emissions from different combustion types

The emissions from all combustion devices consist of gases, particulates and the residual ash. The control of gaseous pollutants involves the interplay between achieving complete combustion to minimise unburned CO, hydrocarbons and associated products such as carbonaceous smoke (soot) and PAH, and on the other hand minimising NO_x by reducing the temperature and residence time [84]. The disposal or utilisation of ash from the bottom of the furnace or from particulate collection devices presents another pollution issue but this aspect is not considered here.

The emissions are largely determined by the size of the combustion unit, and the legislation which is applicable reflects the effect of size, although this varies from country to country. In the EU new combustion plant larger than 300MW_{th} are limited to an emission of 200 mg/Nm³ at 6% O₂ for NO_x, 20 mg/Nm³ for particles, and 200 mg/Nm³ for SO₂. These emission limits have become increasingly stringent over time. Similar limits apply in the USA, Japan and other major countries. Proposed limits in the EU will be lower for NO_x. For smaller combustion plant the emission limits are higher at present, and in the case of plant below 500 kW the solids emission may be five times as high or not legislated at all. A considerable amount of information is available on emission factors [44] and [48] and whilst the NO_x may be similar to that for oil fired burners it is much higher than gas fired units. Smoke emissions are high and consequently there is a need to reduce these levels.

Pollutant Formation Modelling

The modelling of biomass has followed that used for coal combustion. In the latter case, considerable attention has been directed to the combustion of pulverised coal, which is the major industrial use of coal, and much less attention directed to fluidised bed combustion and fixed bed combustion. This is the same order of difficulty in modelling pollutant formation. In the past much more attention has been directed to modelling the gases, NO and CO than to the particulates.

Biomass combustion can be modelled by the following five main tasks:

- ❖ Gas phase flow and volatile combustion predictions, including pollutant predictions;
- ❖ Particle fluid dynamics and inter-phase heat/mass transfer;
- ❖ Devolatilisation modelling and combustion of the gases released;

- ❖ Char combustion and fragmentation modelling;
- ❖ Pollutant release including gases, coarse and fine particles.
- ❖ In addition there are three interconnected aspects of CFD modelling that have to be considered:
- ❖ Conservation equations - which track the reactants, the products and heat release rates;
- ❖ Heat transfer in the furnace enclosure which determines the temperature field;
- ❖ Aerodynamics that determine the flow and residence times.

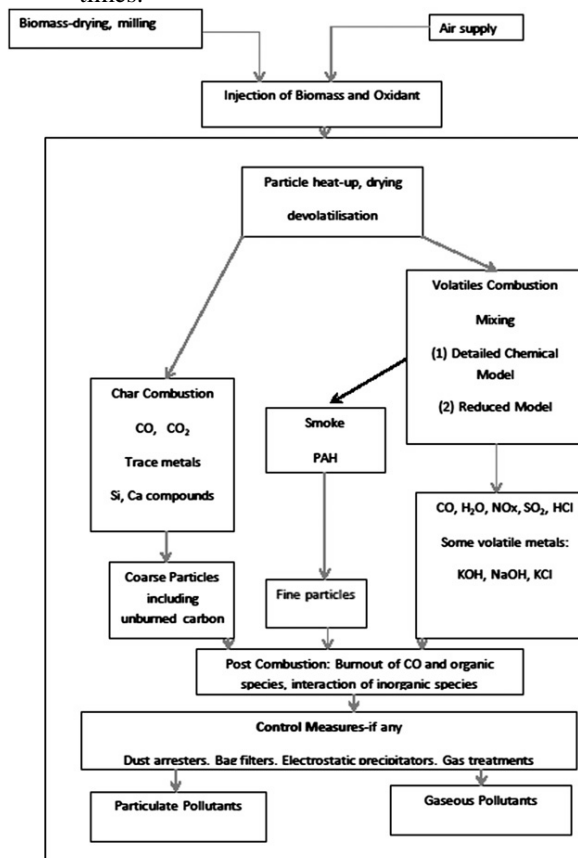


Fig. 5. Diagrammatic outline of the reactions involved in the modelling of pollutants from the combustion of biomass.

Correct prediction of the flow and temperature fields is important especially for NO_x estimation. The choice of the turbulent models influences the prediction of the emission of the unburned gaseous species since much of this material results from turbulent eddies containing incompletely reacted products. The use of the LES (large eddy simulation) turbulence model as opposed to RANS (Reynolds-Averaged Navier Stokes) may be important in these types of predictions. The key equations are those for conservation, mass, energy and species which have been set out in many text books. The main features of the chemical mechanisms have been set out and the way they are interconnected is set out in Fig. 5. Again it is possible to use large reaction mechanisms with hundreds of reactions but for CFD applications these are usually reduced. Some aspects of modelling biomass combustion are relatively easily undertaken but those dealing with fixed or fluid beds are extremely complex because of the difficulty of including the fragmentation or attrition of the solid phase material. In the

next section the outcomes of some major examples of modelling of pollutant formation will be considered.

Modelling fixed or moving bed combustion

Much of the early work on modelling pollutant formation from grate (fixed bed) has been summarized by Saastamoinen and Taipale [85]. The models present a number of problems because, whilst the gaseous combustion occurring in the furnace chamber above the surface of the bed is relatively easy to simulate, this is not true of the bed combustion itself. The bed consists of irregular shaped particles where the initial fuel size may be tens or hundreds of millimetres or more, and whilst the term ‘fixed’ is used, combustion is not uniformly continuous and the particles are constantly moving. The fuel is often fed on a batch basis and in addition the bed is not fixed in space and holes can appear through the bed in a random manner, known as ‘channeling’. Moving or travelling grate furnace arrangements are simpler in many respects in that input and movement of the fuel particles in the bed can be treated in a statistical manner, although channeling still occurs. Many of the modelling studies undertaken relate to the heat and mass transfer in the furnace and these are not considered here, but only those relating to pollution formation.

A number of studies have been made of larger fixed bed combustors for residential and commercial applications combustion using a variety of fuels [86] and [87]. The earlier published modelling studies were related to the use of fuels such as wood with an irregular size or briquettes made of sawdust or straw. Later studies were much more general and looked at the influence of the many factors involved such as bed size, level of moisture, particle size etc. Cylindrical pot furnace studies are useful because of the consistency of the combustion process, and this has been used to investigate NO_x formation from several woods and wood pellets [48]. Because of intermittent combustion in practical systems, the complex gas flow, heat transfer and reaction within the bed, many models have concerned efficiency studies or partial modelling of pollutant formation in the combusting gases above the bed [88] and [89].

The introduction of pellet burners in the last decade has simplified these calculations since the fuel is more uniform and combustion much more consistent. Many researchers have carried out simulation studies of biomass combustion for large particles and pellets, for example references [84] and [88].

Modelling the emission of pollutants from larger thermal capacity (about tens of MW_{th}) grate units follows the same modelling methods, although the gas flows, especially in the injection of secondary air and in the heat exchanger section, are more complex. CFD modelling in these furnaces has been extensively reviewed by Yin et al. [80]. This review shows how little work has been devoted to modelling pollutant formation in biomass combustion, rather attention has been directed to the problems of ash deposition. There are however a number of examples related to both fixed bed and travelling grate combustion. Khor et al. [88] and [89] simulated packed-bed combustion of biomass particles with size ranging from 5 to 35 mm using the FLIC program which enables a study to be made of combustion in a moving bed. This however would only permit prediction of the release of species (volatiles, CO, NH₃, HCN, KOH and HCl etc.) from the bed and subsequent reaction

of these products in the combustion chamber above the bed would have to followed using CFD modelling coupled with an appropriate chemical mechanism. The amounts emitted would be dependent to a large extent on the design of this part of the equipment. A typical computation for a moving grate burning wood is given in Fig. 6 showing the temperature in the bed and the concentration of CO produced.

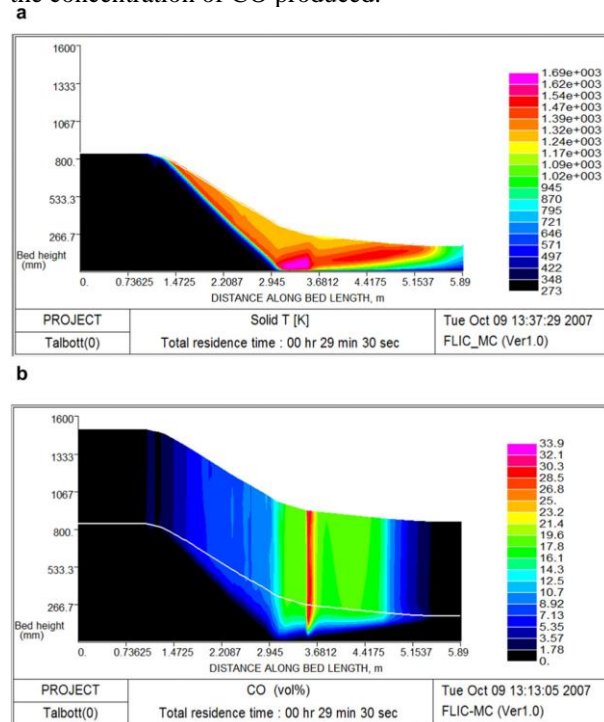


Fig. 6. Modelling moving grate combustion showing (a) the reaction zone and bed combustion, the temperature of the solid bed is in K. (b) The CO concentration (vol%) immediately above the bed, the position of which is shown by the white line.

Modelling fluid bed combustion

Fluid bed combustion is one of the major methods of utilizing biomass for power generation [90]. A considerable number of plants are installed using a variety of different types of biomass, being particularly suitable for wet agricultural residues. The designs are largely based on those for coal combustion and two types of designs are used, namely bubbling fluidized bed (BFB) and circulating fluidized bed combustors (CFBC), both of which operate with bed temperatures of about 800 °C. The main difference between coal combustion and biomass combustion are the large amount of volatiles produced in the latter case, the greater reactivity, and lower SO_x and NO_x (and N₂O) emissions. Thus the BFB system is suitable for many applications where neither staged combustion nor is in-bed sulphur removal necessary. It also has the advantage that large particle sizes are possible. Typical plant sizes are 50-100 MW_{th} and, as such, are capable of using major pollution control equipment. Large plant of this type usually has to conform to National Emission Directives and so the level of emission has to be achieved by a combination of the combustion chamber design and the flue gas clean-up plant, which will involve particulate and possibly NO_x units. If the K, Cl, Si contents are high, this can lead to submicron emissions. As with most large-scale combustors the amount of NO_x and the metals can

be determined by modelling or equilibrium modelling [91] and [92].

Pulverised biomass combustion and co-firing

The modelling of the combustion of small pulverised biomass particles is readily undertaken using CFD methods, although the modelling of the release of the pollutants is much harder. Many studies have been made of pf coal combustion and in a similar way studies have been made of co-firing using a two-component fuel. Since the amount of biomass is often less than 20% thermal the main flame properties such as temperature or velocity are largely determined by the coal combustion processes. The key to the correct prediction of NO_x is the correct prediction of the temperature distribution in the furnace especially if staged burners are used.

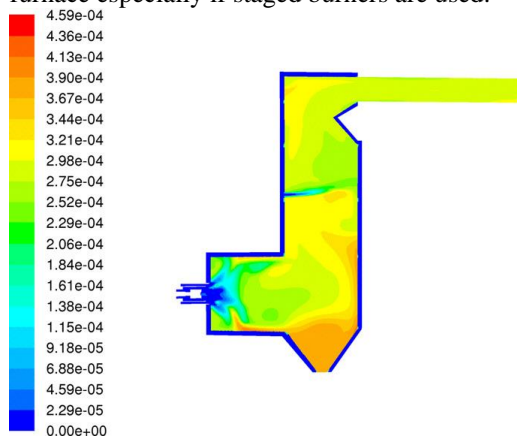


Fig. 7. Modelling NO_x formation during the combustion of pulverised wood in a 1 MW_{th} , Combustion Test Facility. The NO concentration is given in mol/mol.

In large pf-fired, multi-burner furnaces, which use 20% or more biomass overall, the pulverised biomass is injected via individual biomass burners using 100% biomass. There have been only a few such studies. Ma et al. [57] have studied the combustion of pulverised wood and determined NO_x and unburned carbon in ash in a 1 MW_{th} Combustion Test Facility. A typical computed profile is shown in Fig. 7. The amount of NO computed on the basis that the fuel-N converts to HCN and then reacts to NO using the ANSYS FLUENT kinetics is 89 ppm, whereas if the NH_3 mechanism is used it is 266 ppm, the former being closer to the experimental results. In the case of most other fuels it is postulated that the latter is the main route, although it has been observed in industry that the injection of biomass in co-firing does not produce the expected reduction in NO associated with ammonia injection.

A number of researchers have made CFD studies of the effects of large aspect biomass particles, such as wood and straws since this has an impact on the burn-out rates of the particles [42], [44], [58] and [84]. Such particles have a significant effect on the application of CFD models since the particle flow field may be influenced and the particles may burnout more slowly. Often such particles are represented by spherical particles with the equivalent volume [88] so the burning rates are not quite right. But whether this assumption has much effect on the prediction of pollutant emission remains to be investigated.

POLLUTION CONTROL

Pollution arising from biomass combustion

The utilisation of biomass by means of direct combustion processes result in the release of gaseous and particulate pollutants to the atmosphere which can have significant effects if the pollutants emitted are not controlled [93] and [94]. Because of the move towards the use of solid biomass as a renewable energy source in many countries the future environmental impact has to be considered with care. This is made more difficult because of the diverse pattern of usage. This is on a scale of billions of economically disadvantaged users who use small units for heating and cooking - There are perhaps a billion users of units of about $10 \text{ kW}_{\text{th}}$ for heating, millions of users of units of about $10\text{-}100 \text{ MW}_{\text{th}}$ for industrial and commercial application, and thousands of large plant of about $1\text{-}4 \text{ GW}$, users who use co-firing or single fuel applications. It is clear that the most efficient use of biomass is by means of the large combustion units incorporating emission control equipment. Sustainability issues are also better handled with large plant, both from supply and recycling of ash aspects. In the case of large combustion units, say greater than 100 kW , the size of the unit enables opportunity for the burnout of soot particles either in the combustion chamber or in a secondary combustor. Likewise cyclones and electrostatic precipitators can be used. The major remaining problem are the inorganic aerosols which could be removed by scrubbing or by pre-treatment of the fuel, such as washing or using carefully selected low potassium fuel. Electrostatic precipitators however do not remove all of the submicron or ultra-fine material, nor does washing and research into this area is of major importance.

Many attempts have been made to improve designs of small heaters largely used in the Developing Countries. This involves improving the insulation, thus increasing the combustion temperature, which reduces the smoke and associated hydrocarbons but increases the NO_x . These units are so small it is not possible to incorporate staging or particulate removal. The interplay between the C/H/O/N species results in the reformation of methane which is a major problem. A possible reduction in smoke and aerosols can arise by the choice of fuel. In the case of the larger units, the combustor size permits a longer residence time and more complete burnout of the soot, but the fine particles still remain a problem. At the present time, the levels of NO_x and smoke are too high to permit any significant increase in biomass combustion (bio-heat) in any large town in any part of the world. Better combustion arrangements are required. Catalytic emission control units are helpful, as is the use of particle reduction equipment. The choice of pretreated fuels is also useful, in that the reduction of potassium and nitrogen reduces emission, and the use of wood chips results in a fuel that burns more uniformly with a reduced formation of char fragments compared with lump wood.

Large plant has the opportunity of reducing all forms of the pollutants and must be the preferred method of biomass combustion, but control of ultra-fine particles still remain a problem.

Atmospheric environment and health effects

The presence of biomass pollutants in the air significantly affects atmospheric processes. The effects range from acidification of clouds, rain, and fog, altering cloud microphysical processes in a small scale and mesoscale; and

altering the radiation balance of the earth, both directly, by absorbing and scattering incoming solar radiation, and indirectly, by acting as cloud condensation nuclei.

There are large scale effects, resulting from forest and grass fires, especially from particulate and ozone, and these compound problems in regions already having particulate pollution [95].

Numerous studies have investigated the characteristics of the particles produced from the influence on climate change. Measurements have been made of smoke (organic carbon, OC and elemental carbon, EC) and of the biological markers and show the considerable effects of these fires. EC relates to elementary, carbonaceous soot whilst OC relates to containing adsorbed incompletely combusted oxygenated products [96]. The extent of condensation of the oxygenated products on the solid carbon particles varies with the completeness of combustion and the time temperature history of the source and hence differs if emitted say via a hot chimney stack or an open source. There is thus some latitude in the definition of OC and EC.

CONCLUSIONS

The combustion of solid biomass already makes a significant contribution to world energy provision. It can play a much greater role than that at present, but ultimately the sustainable biomass resource is limited.

If the increased biomass use is by means of combustion in small units (e.g. for heat or cooking) is increased there could be serious environmental problems arising from particulates, particularly carbonaceous smoke, and from NO_x. In larger combustion units where good mixing reduces the carbonaceous element, or it is burned out in the combustion chamber or removed from the flue gases, there remains a potential health problem from submicron inorganic particles. In both cases fuel pre-treatment offers possible advantages. Large combustion units offer the best route to clean combustion because of the advantages of large scale efficient flue gas treatment plant.

The basic features of biomass combustion and resultant pollutant formation are understood but much of the detail is lacking. It seems that if biomass is to be more widely used as a major energy source then a greater understanding of the detailed processes is necessary. This needs to be across all aspects of the combustion and pollution processes. The analogy with the processes occurring in coal combustion is not adequate.

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