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Particulate Emission from Agricultural Waste Fired Boiler

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ABSTRACT: In the current overview paper, particulate emissions from the combustion of agricultural residues are discussed. The influence of operating parameters and fuel quality was investigated. Studies on the mass concentration, number concentration and size distribution of particles emitted from agricultural waste fired boiler are presented. Mass concentrations of particles in the flue gas from small scale combustion appliances reported in the literature to be in the range of 8 - 2095 mg/Nm3, while particle number concentrations in the range of 7.0 x 10-2 to 1.8 x 108 particles/cm3. The dominating chemical compositions of the particle emissions were Ca followed by K, Mn and Mg. Organic Carbon (OC), Elemental carbon (EC), Elemental emission, Poly-cyclic Aromatic hydrocarbon (PAH) and emission of different size particles (PM<0.1 to PM10) were also reported. Combustion temperature is the most important factor in determining PAH composition.

KEYWORDS: Particulate Matter, Combustion technologies, Fly-ash, Agricultural wastes.

1 INTRODUCTION

Agricultural waste is a kind of agro-waste from agricultural or related industries like bagasse, rice husk, coffee husk, macadamia nuts, palm shell, groundnut shell, coconut shell, cotton waste, briquettes etc. Conversion of agricultural waste is a well established technique for generating heat and power. The impact of this conversion is of wide concern due to its adverse effects on air quality and human health, especially in the many developing countries where agricultural waste is often used in industrial boiler and other heating systems. The emission content more than 350 chemical species, including volatile and semi volatile organics from C_2 to C_{20}, particle-phase organics such as (PAHs), methoxylated phenols, organic and elemental carbon, inorganic species, elements, and carbon-14 [1]. Particulate matter (PM), one of many pollutants emitted from agricultural waste combustion contain organic and elemental carbon or black carbon. There are different characteristics between particles emitted from various sources according to their size, density and emission rate. For example, particulate emission rates of a boiler of a palm oil mill plant equipped with a multi-cyclones particulate arrestor varied from 8.51 g/s to 126 g/s with an average of 44.3±31.6 g/s [2]. Residential wood combustion boiler emits a range of 4-9 g/kg dry fuel of particulate matter (<2.5 μm) and 5-22 g/kg volatile organic compounds. Utilization of high quality wood fuel, such as wood pellets produced from natural, uncontaminated stem wood, would generate the least PM compared to other wood fuel types. The impact of particulate matter on atmosphere is also depends on the size of particulates. It is known that sub-micron-sized particle (e.g., 0.1–1 μm) whether in the form of solid or droplet plays a role to decrease visibility [3]. Exposure to ultra-fine particulates (PM0.01 – PM2.5) could increase the risk of severe respiratory diseases [4]. Control techniques of particle emission also vary according to the types of waste. For example, kaolin can be used for the reduction of the particle emission from residential combustion of oat grain. However, applying kaolin addition to combustion increases the emissions of acidic gases such as HCl and SO_2 as a side-effect [5].

Many review papers have been published that discussed biomass as a fuel for boiler or on the characteristics of PM emitted from different large scale biomasses combustions [6], [7], [8]. There is not enough report available that describes briefly about characteristics of PM specifically from agricultural wastes sources. The aim of this paper is to analyze the properties of particle emissions of different agricultural waste fired furnaces. In addition size segregated particulate matter emitted from agricultural waste fired boiler found in literature are summarized in this paper.

2 Particulate Matter

Solid particles and liquid droplets like dust, dirt, and smoke found in air and originate from a variety of anthropogenic and natural sources are called particulate matter (PM). PM is also referred as a pollution of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals, and soil or dust particles. These elements have adverse effect on human health and also have impacts on climate and precipitation. Size is an important property of particles. Atmospheric particulates can be categorized as suspended particulate matter (SPM), Respirable Suspended Particle (RSP, those found near roadways and dusty industries, are larger than 2.5 micrometers and smaller than 10 micrometers in diameter), fine particle (FP, those found in smoke and haze, diameter of 2.5 micrometer or less), ultrafine particles (UFPs, less than 100 nanometers in diameter) and Soot (impure carbon particles resulting from the incomplete combustion of hydrocarbons).

Particles diameter that are 10 micrometers or smaller are dangerous for human health, because those are the particles that generally pass through the throat and nose and enter directly the lungs. These particles are readily emitted from sources such as forest fires, or they can form when gases emitted from power plants, industries and automobiles react in the air [9]. PM is usually formed from chemical reactions in the atmosphere and through fuel combustion (e.g., motor vehicles, power generation, industrial facilities, residential fire places, wood stoves and agricultural burning). PM has a significant effect on human health. If these particles are inhaled, it may affect the heart and lungs and cause serious health effects. Exposure to PM has been associated with hospital admissions and several serious health effects, including premature death. People with asthma, cardiovascular or lung disease, as well as children and elderly people, are considered to be the most sensitive to the effects of fine particulate matter. Adverse health effects have been associated with exposure to PM over both short periods (such as a day) and longer periods (a year or more). Fine particulate matter is also responsible for environmental effects such as corrosion, soiling, and damage to vegetation and reduced visibility. The main constituents of airborne particulate matter are UPFs. These particulates are occurred both naturally and by artificially. Natural sources of UFPs are hot volcanic lava, ocean spray, and smoke. Manmade sources of UFPs are byproducts, like emissions, from specific processes, combustion reactions, or equipment such as printer toner and automobile exhaust [10], [11]. The main exposure to UFPs is through inhalation. UFPs can easily be inhaled due to its size. Comparing to the behavior of inhaled PM10 and PM2.5, ultrafine particles are deposited in the lungs [12], and also they have the ability to penetrate tissue or to be absorbed directly into the bloodstream. It's therefore not easy to remove from the body and may have serious effect [6]. Exposure to UFPs, even if components are not very toxic, may cause oxidative stress, inflammatory mediator release, and could induce lung disease and other systemic effects [13]. Soot is restricted to the product of the gas-phase combustion process but it is also extended to include the particles that become airborne during pyrolysis which are more properly identified as cokes or chars. Soot is also pyrolysed fuel particles of coal, cenospheres, charred wood, petroleum coke, and so on theorized to be the second largest cause of global warming [14], [15]. Sources of soot is coal burning, internal combustion engines, power plant boilers, hog-fuel boilers, ship boilers, central steam heat boilers, waste incineration, local field burning, house fires, forest fires, fireplaces, furnaces, etc. Soot has also some indoor environment sources such as smoking of plant matter, cooking, oil lamps, candles, quartz/halogen bulbs with settled dust, fireplaces, defective furnaces, etc. Soot those found from ventilation system is capable of darkening surfaces or making particle agglomerates. Long-term exposure to urban air pollution containing soot increases the risk of coronary heart disease, according to a major study published in New England Journal of Medicine in 2007 [12].

2.1 Ambient air limit of PM

World Health Organization (WHO) has an Air Quality Guideline (AQG) to achieve air quality that protects human health. WHO encourages every country to consider adopting an increasingly stringent set of standards, tracking progress through the monitoring of emission reductions and declining concentrations of particulate matter. The guideline and interim target (IT) values of the AQG shows the concentrations at which increased mortality responses due to particulate matter air pollution. Fig. 1 shows the current data on PM reported by WHO proposed for annual and daily mean concentrations. Three ITs were defined since countries may find these ITs particularly helpful to understand progress over time in the process of steadily reducing population exposures to PM [16].

Table 1. Standard particulate matter (Daily average, Yearly average and Allowed no. of exceedence/yr) of different countries according to the WHO guideline (2006)

Name of the country	Allowed no. of exceedence/yr		Daily average		Yearly Average	
	PM 10	PM 2.5(μg/m³)	PM 10 (μg/m³)	PM2.5 (μg/m³)	PM 10	PM 2.5 (μg/m³)
Australia	None	None	None	8	50	25
China	None	None	70	35	150	75
EU	35	None	40	25	50	None
Hong kong	9	9	50	35	100	75
Japan	None	None	None	15	100	35
South Korea	None	None	50	25	100	50
USA	1	None	None	15	150	35
Malaysia	None	None	50	-	150	-
Bangladesh	None	None	150	65	50	15

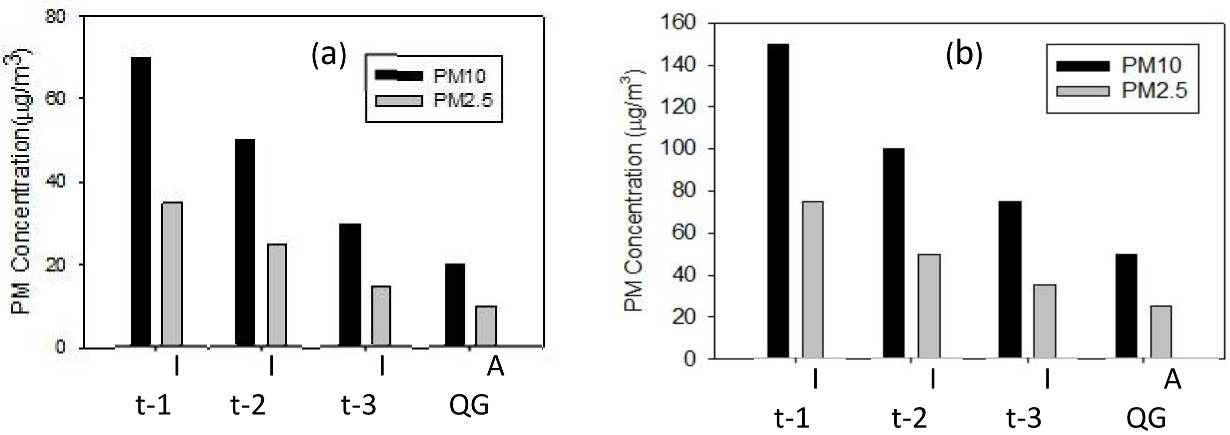

Fig.1. *Comparison of PM_{10} and $PM_{2.5}$concentration according to WHO air quality guidelines (2006), interim target (IT) and Air Quality Guidelines (AQG). (a) Annual mean concentration, (b) 24 hour concentration*

The European Commission and the United States Environmental Protection Agency have revised their air quality standards for particulate matter according to the WHO Air Quality Guideline. Table-1 presents the ambient air quality guidelines adopted by selected countries in the world where recent emphasize is given on PM emission [17].

3 AGRICULTURAL WASTE AS BOILER FUEL

There are large quantities of residues available, associated with agricultural production and processing industries that can be used as a fuel of many industrial boilers. The combustion of these residues in boiler seems to be a promising technique for the future to contribute both the reduction of greenhouse gases and the solution of the waste disposal problems. The use of these renewable wastes becomes popular as sources of energy or an alternative fossil-based feedstock.

Rice husk and straw are the most important agricultural residues in quantity (657,680 million tones per year), amounting to 43% of the total residues. Rice is cultivated in more than 75 countries in the world. Over 97% of the rice husk are generated in the developing countries. The worldwide annual husk output is about 80 million tones. China alone generated some 54 million tones of rice husks every year. Spain generates about 618,000 tones of rice husk per year [18]. Some 4.7 million tones of this agricultural residue are produced in Thailand, which corresponded to 70.5×109 MJ of energy potential (as estimated based on the fuel calorific value of 15 MJ/kg). Significant amount of energy, equivalent to about one million tones of crude oil, has been annually recovered from rice husk and used for heat and power generation in Thailand [19].

Coffee is one of the most important agricultural commodities in the world and is the second largest traded commodity after petroleum. After harvesting, coffee cherries are dried to separate the coffee bean from outer skin, pulp, parchment and silver skin. After processing (wet and dry process), the resulting solid waste is collectively termed parchment husks. For every one ton of clean coffee produced, 0.28 tons of parchment husks, 2 tons of pulp would be generated [20]. Spent coffee ground is also a solid residue with fine particle size, high humidity (in the range of 80–85%), organic load, and acidity, obtained during the treatment of raw coffee powder with hot water or steam for instant coffee preparation. Coffee husks have been used as a main feed stock for biomass briquettes in East African region.

The husk and shell of coconut is a good source of charcoal and can be used as fuel in industrial boiler. Activated carbon manufactured from coconut shell is considered extremely effective for the removal of impurities. In Thailand, the coconut husk is used as a potting medium to produce healthy forest tree saplings. The process of husk extraction from the coir bypasses the retting process, using a custom-built coconut husk extractor. In parts of South India, the shell and husk are burned for smoke to repel mosquitoes that seriously pollute the environment.

Peanuts and tamarind are popular food products in many of the Asian countries. Annually, about 25 million tons of peanuts (or about 70% of the world crop) are produced in Asia, whereas some 400 thousand tones of tamarind fruits are produced. As with many other shell-type biomasses exhibiting excellent combustion properties (high reactivity and substantial calorific value), both peanut and tamarind shells can be considered as potential fuels for small-scale heat and power plants.

Palm oil is one of the main agricultural products in some ASEAN countries such as Malaysia and Indonesia. Palm fiber and shell are generated abundantly as waste materials during palm oil extraction process. In Malaysia, for example, 31 million tones of fresh fruit bunch is produced annually and 7 million tones of oil palm empty brunch, 4.5 million tones of fiber and 1.9 million tones of fruit shell are generated as solid wastes. These materials are burned in the mill boiler as fuel to supply energy to the mill on a day to day operation. Some parts of fiber and fruit shell wastes are utilized as boiler fuels for steam generation in some palm oil mills. Palm fruit shell wastes are also utilized as a feedstock of activated carbon. However, these resources have a low calorific value (about half that of petroleum oil) because of a large amount of oxygen functional groups such as -COOH, -OH, etc [21].

Sugarcane has an important potential for the human sustainable development and modernization on a larger scale in developing countries. It also has rich typologies of high energetic content by-products like leaves and tops, bagasse and molasses. Among that bagasse is abundantly generated in the sugar mill process, is used as fuel of combustion boiler. Combustion of bagasse generates heat and power that meet at least the great part of the electricity for the mill. However the potential of bagasse base cogeneration, considering high-efficiency energy production.

3.1 Limitation of Agricultural Waste as Fuels

Large amount of crop residues are produced in the world every year. The amount of crop residues produced in 2001 was estimated at ~0.5 x10^9 Mg/yr in the USA (Table 2) and ~4x10^9 Mg/yr in the world (Table 3). About 75% of the residues produced, both in the USA and world and elsewhere, is that from cereals (e.g., corn, rice, wheat, sorghum, millet, barley, rye). For example, the data in Table 4 show that rice and rice-based cropping systems produce ~ 0.6 x 10^9 Mg/yr of crop residues in the tropics [22], [23]. Despite the large generation of agricultural residues, there utilization as fuel is still low. For example, in Finland, some 4 million tones of different types of agricultural waste are produced annually and about 2.2 million tones could be potentially collected and used as a source of energy. However, only 15– 20% is utilized mainly as cattle and the rest is either ploughed back into the soil or burnt on the field [24]. In Kenya, only 35% of total agricultural residue is used for energy production, mainly bagasse in the sugar processing industries [25]. The uses of agricultural residues also depend on some physical and chemical properties of the residue like Moisture content, Bulk density, Ash content, volatile matter, Pollutant emission etc.

In many cases, the moisture contents of the residues are determined by the process of separating the residues from the crop product. The lower the content of moisture in residue is better as a fuel of boiler. High moisture content is the cause of poor ignition, reduce the combustion temperature, which in turn hinders the combustion of the reaction products and finally affects the quality of combustion. Densities of agricultural residues have impacts on their processing, transportation, storage and firing. Most agricultural residues have low bulk density that complicates their use as fuel. Ash content of agricultural residues is an important parameter. For the combustion of agricultural residues with high ash contents required efficient ash removal equipment which increase the operation cost. Some agricultural residues content low melting properties of ash due to the presence of potassium oxide that cause of scaling, fouling and corrosion of the heat transfer surface of boiler. Content of high volatile matter in agricultural waste indicates that the residues are easier to ignite and to burn that affect the overall combustion process. It's very important to ensure complete combustion of volatile matter to decrease low emission of CO, hydrocarbon and other hydrocarbons. The other important criteria related to the combustion of agricultural residues are the contents of sulphur, nitrogen, chlorine etc, which are expected to lead the formation of gaseous pollutants.

Table 2. Estimates amount of residues produced in the U.S. in 1991 and 2001

	Estimates of Residues (10^6) Mg/yr	
Crop	1991	2001
Cereals	325	367
Legume	58	82
Oil crops	17	20
Sugar crops	25	14
Tubers	5	5
Tota	430	488

Table 3. Estimates the amount of residues produced in the World in 1951 and 2001

	Estimates of Residues (10^6) Mg/yr	
Crop	1991	2001
Cereals	2563	2802
Legumes	238	305
Oil crops	162	108
Sugar crops	340	373
Tubers	148	170
Total	3448	3758

Table 4. Estimates of crop residues reduction in the rice and rice based cropping system in the tropics and the world

Region	Estimates of Residues (10^6) Mg/yr
Asia	166
Africa	39
South America	55
Sub-Total Tropic	250
World Total	604

4 THERMAL EMISSION PROCESS OF PM

4.1 THERMOCHEMICAL CONVERSION OF AGRICULTURAL FUELS

Inorganic species from agricultural waste exhibit large variations in compositions and amounts, depending on the source of the waste. Using different thermal conversion processes (combustion, pyrolysis, gasification or other) and various technologies (grate furnace, fixed or fluidized bed, entrained flow reactor) give biomass a wide variety of operating conditions with differences in atmosphere, pressure and temperature [26].

4.1.1 COMBUSTION

Combustion is the simplest method in which agricultural waste can be used for energy and has been used for millennia to provide heat include space heating, water heating, steam rising for electricity generation or motive force etc. Combustion has a great variety of phenomena with wide application in industry, the sciences, professions, and home, and the application is based on knowledge of physics, chemistry and mechanics. Major amounts of particulate matter are released to the atmosphere by the combustion of solid wastes. Agricultural waste fuels content atoms in different quantities and some of these too can be oxidized, with the oxide released as gas in the flue gasses, or as solid ash or slag. Other atoms potentially found in biomass include Nitrogen (N), Phosphorous (P), Potassium (K), Silicon (Si) and Sulphur (S). Some other trace elements such as some heavy and alkali metals may also be present in some agricultural wastes. The features of various combustion methods are shown in Table 5 [27]. Combustion heat is usually used for power generation and heat production by recovering heat through heat transfer devices such as steam and hot water using boilers and heat exchangers.

Table 5. Combustion type and feature of agricultural fuels

Combustion method	Combustion type	Features
Fixed bed combustion	Horigental grate water cooling grate Dumping grate	Grate is level or sloping. Used in small scale batch furnace for biomass containing little ash.
Moving bed combustion	Forward moving grate, Reserve moving grate	Grate moves gradually and is divided into combustion zone and after combustion zone. Can be applied to wide range of fuels from chip type to block type.
Fludized bed combustion	Bubbling fludized bed combustion, Circulation fludized bed combustion	Used sand for bed mineral, keep fuel and sand in furnace in boiling state with high pressure combustion air. Suitable for high moisture fuel
Rotary hearth furnace combustion	Klin furnace	Used for combustion of high moisture fuel. Restricted to fuel size on its fluidity.
Burner combustion	Burner	Burns wood powder and fine powder

4.1.2 GASIFICATION

Gasification is a form of pyrolysis carried out at high temperatures in order to optimize the gas production. It is also a partial oxidation or partial combustion process whereby a carbon source is broken down resulting in the production of a hot, dirty, low calorific value gas like CO and CO_2+H_2 and possibly methane (CH_4). The resulting gas known as producer gas, consists huge number of particulates including carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. Gasification technology can be used for:

- Heating water in central heating, district
- Heating or process heating application
- Steam for electricity generation
- Internal combustion engine

If the gasification takes place at a relatively low temperature, such as 700 ^{o}C to 1000 ^{o}C, the product will have a relatively high level of hydrocarbon. This type of gasification is called low temperature gasification. On the contrary, high temperature gasification is (1200 ^{o}C to 1600 ^{o}C) leads to few hydrocarbons in the product gas, and a higher proportion of CO and H_2. Gasification methods are classified according to combinations of conditional factors shown in Table 6 [27].

Table 6. Classification of Gasification Method

Classification	Conditional fact
Gassification pressure	Normal pressure (0.1-.012 MPa), High pressure (0.5-2.5 Mpa)
Gassificaton temperature	Low temp (700ºC and below), High temp (700ºC and above)
Gassification agent	Air, oxygen, steam and combination of them. Carbon dioxide.
Heating	Direct gasification, Indirect gasification.
Gasifier type	Fixed bed, flow bed, circulating flow bed, entrained bed, mixing bed.

In order to convert solid biomass into inflammable gas, a substance to accelerate the chemical reaction is necessary. This substance is called the gasification agent. Gasification agents mainly include air (N_2, O_2), oxygen (O_2), water H_2O, or CO_2 are applied as an appropriate mixture.

4.1.3 Pyrolysis

Agricultural waste fuels are consisted mainly of carbon, hydrogen and oxygen. Pyrolysis is the precursor to gasification, and takes place as part of both gasification and combustion. It is a thermal destruction of organic materials in the absence of oxygen. The products of pyrolysis include liquid (bio-oil or bio-crude), charcoal and non-condensable gasses, acetic acid, acetone and methanol by heating to about 750 K. There are two types of pyrolysis, such as lower temperature pyrolysis (around 400 ^{o}C), which produce more solid char (slow pyrolysis) and higher temperature pyrolysis (around 500 ^{o}C) that produce much higher proportion of bio-oil. Pyrolysis of wood has been studied as a zonal process. [28]. The main chemical components of agricultural fuels are cellulose, hemicellulose and lignin. The cellulose, hemicellulose and lignin are decomposed by increasing the temperature. Solid residue is char in the yield of 10 to 25%. Thermal degradation properties of hemicelluloses, celluloses and lignin can be summarized as follows, thermal degradation of hemicelluloses > of cellulose > of lignin [29]. Thermal degradation of cellulose occurred through two types of reaction: a gradual degradation, decomposition and charring on heating at lower temperatures: and a rapid volatilization at higher temperatures [30]. The pyrolysis gas contains CO_2, and CO, H_2, C_{1-5} hydrocarbon as combustible gas. The char has the higher heating value of 32 MJ/kg, and it is useful as a feedstock for activated carbon.

4.1.4 Carbonization

Carbonization (or carbonisation) is a term for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis or destructive distillation. It is often used in organic chemistry with reference to the generation of coal gas and coal tar from raw coal. By carbonization process, charcoal can be obtained as main product by heating such solid fuels as wood, bark, bamboo, rice husks, etc. at 400-600 °C in the almost or complete absence of air or oxygen. In case of discrimination from 'dry distillation' aiming at the recovery and utilization of liquid products, 'charcoal making' is used as the terminology. Carbonization customarily means charcoal making, although it is the general term including dry distillation. The overall scheme of carbonization reaction is represented in Fig 2.

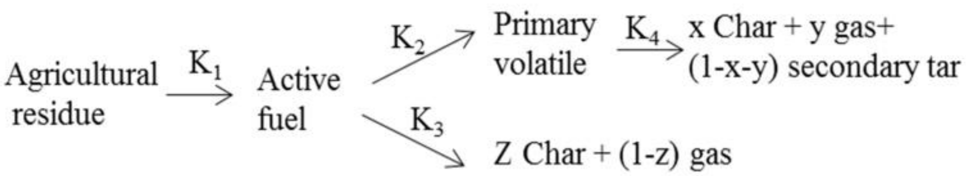

Fig. 2. Overall carbonization scheme, K_1-K_4: rate constant; x,y,z: fraction

4.1.5 HYDROTHERMAL GASIFICATION

Hydrothermal designates an aqueous system at elevated temperatures and pressures. It is a treatment of agricultural residue in hot compressed water, usually above 350 ^{o}C and above 20 MPa to obtain combustible gas. Fig 3 shows a phase diagram of water, at which gas-liquid equilibrium line starts from the triple point and ends at the critical point. Hydrothermal condition is found around the critical point. When both temperature and pressure is higher than critical temperature and critical pressure is also high, the state is called supercritical water, gasification in supercritical water is called "supercritical water gasification". This hot compressed water enjoys high reactivity, and when agricultural fuel is placed in this water, it is gasified by hydrolysis and pyrolysis reactions. This process has multiple stages. In the first stage solid waste converts into gases, then gases are condensed into oils. In the final stage the oil are conditioned and synthesized to produce syngas. Chemical composition and properties of syngas are of different samples are summarized in Table 7 [31].

Table 7. Chemical composition and properties of syngas of different agricultural waste samples

Chemical composition and properties of syngas from different samples.

	Syngas yield (g)	Hydrogen yield (g)	Energy yield (kJ)	Apparent thermal efficiency (–)
Oil palm	52.4	2.86	685	1.11
Mangrove	47.6	2.48	668	0.91
Paper	38	1.64	411	0.85
Food waste	29.3	1.56	477	0.9
Polystyrene	36.8	3.03	677	0.47

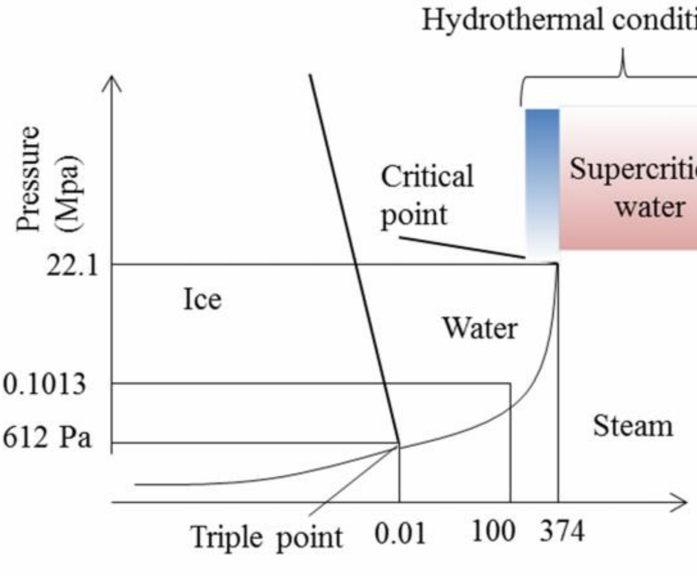

Fig.3. Phase diagram of water

4.1.6 HYDROTHERMAL LIQUEFACTION

Hydrothermal liquefaction, which is also referred to as hydropyrolysis, is a thermochemical conversion process in which high temperatures and pressures are used to decompose complex organic material, including biomass. It is a kind of pyrolysis in hot compressed water of around 300 °C and 10 MPa. Since hydrothermal liquefaction proceeds in water, many kinds of reaction can be taken place at different reaction temperatures. Fig. 4 shows the reactions which are occurred in the hot compressed water.

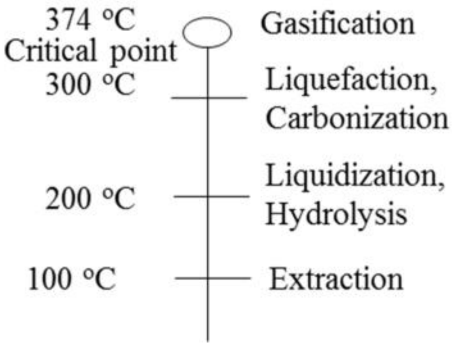

Fig.4. Reaction which occur in the hot-compressed water

4.2 MEASUREMENT TECHNIQUES OF PM

An in-depth epidemiological and toxicological analysis of PM should involve a wide and complete characterization focused on several aspects: (i) physical parameters (dimension, shape, surface area, concentration, etc.), (ii) chemical parameters (chemical composition, surface reactivity, etc.), and (iii) epidemiological parameters (organs or tissues involved, personal subjectivity, assumption rate) [32]. PM can be classified as a function of the aerodynamic equivalent diameter (da), which is defined as the diameter of a unit density sphere having the same terminal settling velocity as the particle in question [33]. Airborne PM presents a diameter da ranging from few nanometers to tens of micrometers. Particles size less than few hundreds of nanometers are better characterized in terms of number concentration rather than mass (or volume) concentration, which is more significant for large particles. The basic method to measure mass concentrations of PM off-line in flue gases is discontinuous gravimetric sampling on quartz or glass fiber filters, which have been in a desiccator or a room with controlled humidity prior to sampling. In the case of continuous measurements of PM_{10} and $PM_{2.5}$, Tapered element oscillating micro-balance is a well established instrument. Various analytic methods are used to measure particle number and particle mass distribution. For measurements of mass size distribution, low pressure cascade impactors are frequently used. There are several instruments available for on-line measurements of particle number. Some of these instruments are Scanning mobility particle sizer (size range from few nanometer to 1 µm), Electric low pressure impactor (size range 7 nm to 10 µm), Aerodynamic particle sizer (size range~ 0.5 µm to~ 10 µm), Fast mobility particle sizer (size range 5.6nm to 0.56 µm). Fig. 5 shows the most common methods for continuous and discontinuous measurement of particulate emission. In air pollution studies UFPs, PM and PM_{10} are used to indicate particles with a da smaller than 0.1, 1, 2.5 and 10 µm respectively, whereas the total mass of particulate matter is defined total suspended particulate (TSP).

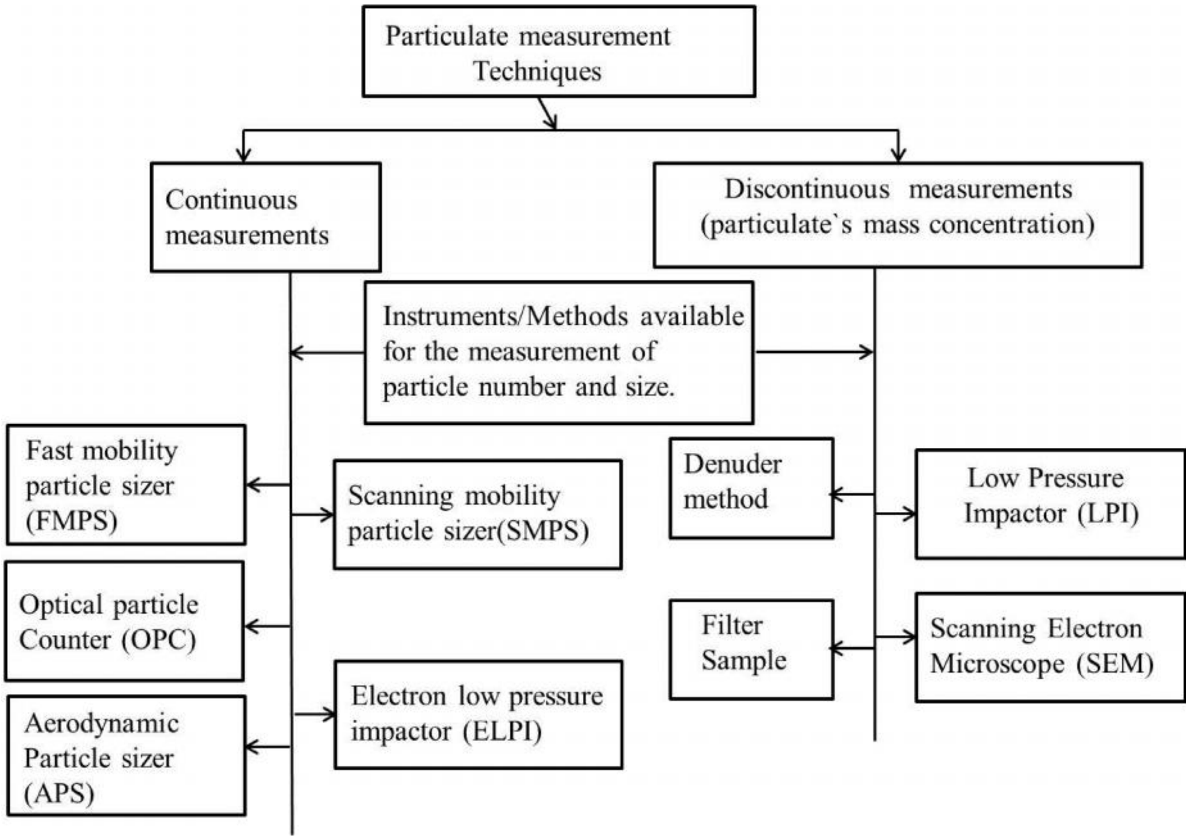

Fig. 5. Flow diagram of the different measurement techniques for particle number size distributions, particle concentration

5 PARTICULATE EMISSION FROM AGRICULTURAL WASTE FIRING BOILER

This Section reviews the findings or results published in the research article available related to the particle emission for agricultural waste fired boiler.

Kaivosoja, et al. [34] had a comparative study on emission and toxicological of fine particles from wood and oil boilers in small (20-25KW) and medium (5-10MW) scale. Aim of their study was to compare four alternatives for providing decentralized energy production in small communities in terms of their flue gas emissions and toxicological properties of the emissions. This experiment showed that the lowest PM emission was 0.1 mg M/J from small-scale light fuel oil combustion. In the case of medium-scale wood combustion, PM emission values from a grate fired wood combustion boiler (10 MW) without particulate filtration were the highest (264 mg M/J). But the value substantially reduced down to 0.6 mg M/J after using an electrostatic precipitator (ESP). From their point of view the heavy fuel combustion was found to be the worst energy production option, because it produced large amount of SO and PAH emissions and its PM12emission contained harmful metals such as vanadium and nickel. They have a proposal to the environmental license or the legislation authority that in the long term, in addition to the emission amounts, also the toxicity of the emissions should be taken into account when regulating the emission limits for the plants.

Guofeng, et al. [7] studied about the Emission factors of parent PAHs, nitrated PAHs and oxygenated PAHs for indoor corn straw burned in a brick cooking stove under different burning conditions. According to their observation, fuel charge size had not much influence on the pollutant emissions, gas-particle partitioning of freshly emitted organics was mainly controlled by the absorption and fuel burning rate, air supply amount, and modified combustion efficiency were the three most significant influencing factors for emission.

Wang, et al. [35] analyzes the behavior of pollutant gas emissions during the firing of wheat straw and coal blends by using thermogravimetric analysis. The emission characteristics of gas pollutants such as HCl, SO_2, CO_2 and NO_x were determined by coupled Fourier transform infrared (FTIR) measurements. Their experimental result revealed that the emissions of HCl, SO_2, CO_2 and NO were closely related to the volatile combustion and char reacting stages. HCl emission was mainly released during the volatile combustion at the temperature between 220 and 450 °C. The analysis showed that the blended sample with 40% coal and 60% straw by mass produced the lowest levels of HCl, NO_x, and SO_2 gas emission. So they come to an end with a decision that combining the straw and coal can produce better emission control.

Oanh, et al. [36] characterize the properties of PM emission from open burning of rice straw. PM size distribution was measured across 8 size ranges (from <0.4 mm to >9.0 mm). The largest fractions of PM were associated with $PM_{2.5}$. The most significant components they found were $PM_{2.5}$ and PM_{10} include water soluble ions and levoglucosan. Relative abundance of some methoxyphenols (e.g., acetylsyringone), PAHs (e.g., fluoranthene and pyrene), organochlorine pesticides also served as additional signatures for the PM emission at their experiment. This study also gives a lesson that the presence of these toxic compounds in PM of burning smoke increases the potential toxic effects of the emission. The emission factor obtained in this study can be used to estimate the emission from rice straw burning in other countries in Asia where comparable conditions exist.

Guofeng, et al. [37] had a field study in rural china to find actual Emission factors (EFs) after combustion of residential wood. In their experiment, they combusted 17 wood fuels and one bamboo in a typical residential stove in rural China to measure the EFs of PM, organic carbon (OC) and elemental carbon (EC), as well as to investigate the influence of fuel properties and combustion conditions on the EFs. Their study explained that Shrubby biomass combustion produced higher EFs than tree woods, and both species had lower EFs than those of indoor crop residue burning. By using a nine-stage cascade impactor, they found that size distributions of PM emitted from tree biomass combustions were unimodal with peaks at a diameter less than 0.4 µm (PM0.4), much finer than the PM from indoor crop residue burning. Approximately 79.4% of the total PM from tree wood combustion was PM with a diameter less than 2.1 µm ($PM_{2.1}$). PM size distributions for shrubby biomasses were slightly different from those for tree fuels. On the basis of the measured EFs, total emissions of PM, OC, and EC from residential wood combustion in rural China in 2007 were estimated at about 303, 75.7, and 92.0 Gg.

Saidur, et al. [38] reported about the development of a fluidized bed combustor (FBC) for the combustion of Rice husk in a lab scale and observed the PM emission. They used river sand as the bed material. The Fluidized bed was operated at 15–25 kg/h of rice husk feed for various excess air factors (20-100%) and for the different fuel particle sizes. They investigate the effect of fuel feed rate , excess air factor and fuel particle size on the concentration profiles of the major gaseous emissions (CO and CO_2), combustion efficiency , as well as the temperature profiles along the combustor height. By increasing the excess air, the combustion efficiency is decrease due to unburnt carbon and incomplete combustion. The concentration of CO have a maximum value at active combustion zone. Based on CO emission and unburned carbon content in fly ash, the maximum combustion efficiency of the rice husk FBC was found to be 95%.

Johansson, et al. [39] studied particle emissions from an old type wood log boiler, a modern wood boiler and a pellet boiler. Number concentrations and size distributions were measured by ELPI, while mass size distribution done by DLPI. There result revealed that the mass concentration of particles was 180 times higher in old type wood boiler compared to the pellet boiler. They also observed that old type wood log boiler emitted larger number of particles than from wood pellet boiler. So it is important to pay attention to the old type combustion appliances. It was seen from experimental data that the variation in number size distribution was small with maximum around 130 nm (nanometer) from the flue gas of pellet combustion.

Obernberger, et al. [40] investigated particle emissions from a moving grate boiler (440 kW) fired with various agricultural waste such as spruce and bark. Characterization of particle emissions was done on the basis of Berner low pressure impactor. Elemental analysis was done with the combination of SEM/EDX. The mass concentrations of fine particles for spruce were 20 mg/Nm^3, while and 60 mg/Nm^3 for bark fuel. Particle mass concentrations were dominated by fine mode ($PM_{1>}$ 90% of PM10) with an aerodynamic diameter between 0.1 µm and 0.5 µm for all cases and was highly correlated with the K, S and Cl content of the fuel.

6 Particulate Characteristics

Many studies have been focusing on direct measurement and characterization of particulate emissions from agricultural waste burning district energy systems in order to quantify and explain the levels and parameters affecting the formation of air pollutants. Characterization of particulate matter emitted from firing of agricultural residues has been investigated in this chapter. Parameters concerned in this study are comprised of total number concentration, total mass concentration, chemical composition and particle morphology.

6.1 Mass Concentration

Table 8 presents the summary of the particle mass concentrations and from various combustion appliances in different agricultural wastes fuels available in the literature [8], [37], [38], [39], [40], [41], [42], [43], [44], [45]. The value of mass concentrations of particles from combustion of different agricultural wastes (rice husk, bagasse, pine pellets, rice straw, willow, forest residues, straw etc.) were found between 8 and 2095 mg/Nm^3. The lowest mass concentration was obtained from the bagasse based fuel burner. The highest mass concentrations were reported during the combustion of 12 different types of straw at 18-25MW boiler output. From the mass concentration data, it's been found that particle mass concentrations are affected by both combustion appliances and fuel parameters. The mass concentration increases under unsatisfactory combustion conditions due to particles originating from incomplete combustion. For example, unsatisfactory combustion conditions can be a result of low combustion rate due to high moisture content in the fuel or low excess air ratio. Fig. 6 shows a graphical comparison of the particle mass concentrations against various combustion appliances, it showed that mixer of 12 different types of straw and wood log boilers give higher emissions of particle mass concentrations compared to pellet boilers.

Table 8. Mass concentration of particle emissions from different agricultural waste combustion appliance

Heating appliance	Sample	Thermal Output	Measuring techniques	Fuel/Moisture (m,%)	Mass Concentration(mg/Nm^3)	Ref
Fixed bed combustor (FBC)	Rice husk	-	ELPI	8.5	8	[37]
Fixed bed combustor	Baggase	-	ELPI	14.2	6.5	[37]
Pellet boiler (PB)	Pine Pellet	16KW	LPI, TCI	7.3	160	[40]
Pellet boiler	Pine Pellet	11KW	LPI, TCI	7.3	490	[40]
Straw fired boiler (SFB)	Rice straw	13MW	Cascade impactor	13.2	502-902	[38]
Fluidized bed combustor (FBC)	Willow	3-5MW	BLPI	55±5	600	[39]
Pellet boiler	Wood pellets	2MW	-		57.8-99.1	[43]
Pellet boiler	Wood briquettes	2.5MW	-	25	85	[8]
Pellet boiler	Wood Chips	70KW	-	60	92-107	[45]
-	Wood logs (hard wood)	-	-	-	2000	[45]
Grate fired boiler (GFB)	Swedish forest residues	35MW	DLPI	-	230-320	[44]
Grate fired boiler	Swedish willow	35MW	ELPI	-	530-620	[41]
Lab. Scale boiler	Straw (12 types)	18-25 MW	ELPI	-	75-2095	[42]

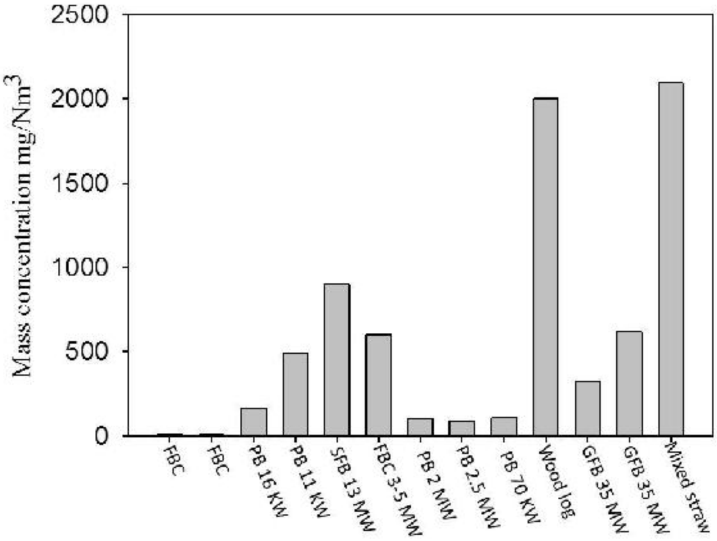

Fig. 6. Comparison of particle mass concentrations against combustion appliances

6.2 NUMBER CONCENTRATION

Combustion of agricultural wastes typically leads to particle emissions dominated by submicron particles, and with uni-modal size distributions for number concentrations. Particle number concentrations are related to the particle size. Incomplete combustion produces lower number emissions but larger particle sizes than complete combustion. Particle number concentrations in the flue gas from agricultural wastes combustion appliances reported in the literature are in the range of 7.0×10^{-2} to 1.8×10^{8} particles/cm^3 (Table 9) [41], [42], [46], [47], [48], [49], [50]. Particle number distributions were mainly dominated by fine particles but dependent on combustion conditions. As shown in Table 9 the particle number concentration and their size distribution depend on combustion appliances and fuel properties. There were also significant differences in the particle number concentration emissions from different combustion appliances. The number concentration and size distribution mode strongly depend on the phase of combustion.

Table 9. Number concentration of particle emissions from different agricultural waste combustion appliance

Heating appliance	Sample	Thermal Output	Measuring techniques	Fuel,Moisture (m,%)	Number Concentration (particles/cm^3)	Ref.
Fixed bed boiler	Rice husk	-	ELPI	8.5	1.6×10^4	[41]
Fixed bed boiler	Baggase	-	ELPI	14.2	1.5×10^5	[41]
Straw fired boiler	Rice straw	13KW	SMPS	13.2	1.1×10^7	[42]
Wood boiler	Wood logs	35KW	-	-	7.0×10^2	[46]
Wood boiler	Wood chips	-	-	60	0.085 (7.9% O2), 0.060 (11.6% O2)	[50]
Wood boiler	Wood chips	-	-	60	0.087 (2.7% O2), 0.080 (6.2% O2)	[50]
Lab scale boiler	Straw (12 types)	18/25MW	-	-	1.2×10^7	[47]
Grate fired boiler	Dry wood pellets	0.8-1.5MW	-	-	~ 0.9	[49]
Grate fired Boile	Wet forest Residues	0.8-1.5MW	-	-	~ 0.10	[49]
Lab. Scale Reactor	Wood logs	20 KW	-	-	1.8×10^8	[48]

6.3 CHEMICAL COMPOSITION

The fuel composition and content of inorganic ash-forming matter varies from fuel sources, conversion techniques etc. For example, forest residue, hay and straw normally contain larger amounts of ash, and larger concentration of chlorine and sulphur, than wood pellets and wood briquettes. These fuels also contain larger amounts of water than the refined fuels, pellets and briquettes. Woody fuel has relatively low alkali content as well as a low chlorine concentration. Dayton, et al. [47] proposed that during combustion of fuel with a high concentration of alkali as well as chlorine, alkali compounds are released primarily through vaporization and decomposition. Arnsfeld, et al. investigated that agricultural wastes fuels have low concentrations of alkali, chlorine and sulphur, and the main alkali compound was found in the fly-ash was potassium sulphate [46]. Paulino, et al. developed an unique method for the quantitative measurement of the elemental composition of particulate matter (PM) by wavelength dispersive X-ray fluorescence (WDXRF) analyzing. [51] Chemical compositions of fine particle emissions from agricultural wastes combustion chamber reported in the literature are presented in Table 10. [45], [48], [49], [52], [53], [54] The dominating chemical compositions of the particle emissions were Ca followed by K, Mn and Mg. Fine particle formation and chemical compositions are influenced by fuel properties.

Table 10. Elemental composition of fine particle emission from agricultural waste combustion appliances

Parameter	Unit	Wood Pellet	Saw dust	Wood fired boiler with fuel oil (plant E)	Wood fired boiler with fuel oil (plant F)	Willow	Wood pellets	Wood fur-nace (Exce-ss air 1.4)	Wood fur-nace(Exce-ss air 1.8)	Palm Oil mill boiler
Moisture	Wt%	7	50	-	-	-	-	-	-	-
Ash	Wt%	<0.50	0.3	0.03	-	-	-	-	-	-
Bulh density	Kg/M3	591	240	0.9875 gcm-3	0.9969	-	-	-	-	-
Cl	Wt%	0.005	0.01	0.04	0.006	-	-	-	0.49	-
S	Wt%	0.027	0.02	0.91	0.89	-	-	9.2	4.8	-
K	mg/KG	493	400	-	-	13.2	6.8	53	32.5	9.52
Cd	mg/KG	0.14	0.1	-	-	104	16	-	-	-
Zn	mg/KG	13.2	10	-	<0.1	-		0.12	0.061	1.22
Pb	mg/KG	0.43	2	2.9	<0.1	29	38	-	-	-
Cr	mg/KG	0.6	1	0.9	14	-	-	-	-	0.342
Cu	mg/KG	1.1	2	-	<0.1	-	-	-	-	-
Ca	mg/KG	900	900	-	-	25.6	29.9	3	6	-
Mg	mg/KG	150	150	0.008	-	2.2	2.8	0.23	0.72	-
Mn	mg/KG	147	147	0.54	2.1	0.3	2	0.048	0.058	0.079
Hg	mg/KG	0.02	0.02	<0.2	<0.01	-	-	-	-	-
As	mg/KG	<0.1	<0.1	<0.1	<0.1	-	-	-	-	0.0179
P	mg/KG	60	60	-	-	-	-	0.1	0.18	-
Na	mg/KG	20	20	-	-	-	-	-	-	-
Ref.		[49]	[48]	[54]	[54]	[45]	[45]	[52]	[52]	[53]

6.4 ULTIMATE COMPOSITION

Table 11 summarizes the ultimate analysis data of different types of agricultural wastes reported in literature. By evaluating the value of C,H,O we can estimate the heating value of these fuels. The percentage of N, S and Cl data helps to study of the environmental impact of these fuels [3], [37], [38], [44], [55], [56], [57], [58], [59].

Table 11. Ultimate analysis of different types of agricultural waste (wt %, dry basis)

Sample	C	H	N	O	S	Ref.
Wheat straw	39.9	5.74	0.22	46.59	0.11	[56]
Corn Straw	42.11	5.58	0.55	47.12	0.03	[52]
Pine wood	50.4	6.28	0.13	42.8	-	
Palm Kernel Shell	53.9	6.24	0.37	37.3	-	
Palm Kernel Shell	61.3	5.46	0.56	37.3	-	
Palm Kernel Shell	62.9	5.21	0.54	28.9	-	
Almond shell	60.9	5.14	0.2	32.4	-	
Charcoal	84	2.93	0.58	10.1	-	
Palm empty fruit bunch	40.7	5.4	0.3	47.8	1.2	
Pine Pellets	46	6.2	0.5	47.3	<0.01	[53]
Chinese Pine	49.1	6.32	0.18	44.41	-	[34]
Bamboo	48.75	5.98	0.26	45.02	-	
Oats	46.8	5.82	0.31	-	0.09	[41]
Barley	44.9	5.51	0.54	-	0.19	
Coffee husk	45.4	4.9	1.1	48.3	0.35	[55]
Cotton husk	50.4	4.9	1.1	39.8	0.01	
Tea waste	48	5.5	0.5	44	0.06	
Rice husk	38.1	4.7	1.5	29.3	0.1	[2]
Pine Pellets	46.2	6.2	0.5	<0.01	-	[54]
Industrial wood wastes	45.5	5.9	3.5	45.1	-	
Peach stone	47.7	5.9	1.3	45.1	-	
Peanut shell	48.1	5.48	1.3	30.04	0.08	[2]
Rice husk	36.4	4.84	0.44	25.11	0.17	[35]

6.5 PROXIMATE COMPOSITION

Table 12 shows proximate analysis data of different types of agricultural waste from literatures [3], [55], [57], [58], [60], [61], [62], [63] which presents the percentage of volatile matter, fixed carbon and ash contents. To study the combustion phenomenon of agricultural waste fuel, this analysis is very important. For example, ash contents in biomass fuels can cause ignition and combustion problems. If melting point of the dissolved ash is low, this causes fouling and slagging problems. High volatility of the fuel offers many advantages as a combustion feedstock. Moreover, high fixed carbon and volatile matter increase the heating value of any agricultural waste fuels.

Table 12. Proximate analysis of different types of agricultural waste (wt %, dry basis)

Sample	Temp/Level	Moisture	Ash	Volatile matter, %	Fixed Carbon
Wheat straw	-	4.81	7.1	79.52	8.57
Corn Straw	-	4.38	4.39	81.94	9.31
Pine wood	Low	-	0.41	-	-
Palm Kernel Shell	Raw	-	2.17	-	-
Palm Kernel Shell	Medium	-	2.27	-	-
Palm Kernel Shell	High	-	2.5	-	-
Almond shell	High	-	1.36	-	-
Charcoal	500-600oC	-	2.38	-	-
Pine Pellets	150	7.3	1.3	-	-
Chinese Pine	-	9.1	0.25	84.77	14.98
Bamboo	-	8.18	0.51	84.94	14.55
Oats	150	9.2	4.67	80.7	-
Barley	150	8.1	9.39	74.3	-
Palm empty fruit bunch	-	-	4.6	67.5	27.9
Coffee husk	-	-	2.8	76.5	20.7
Cotton husk	-	-	17.3	62.9	19.9
Tea waste	-	-	1.5	85.5	13
Rice husk	-	-	19.5	606	19.9
Pine Pellets	-	7.3	1.3	80.5	10.9
Industrial wood wastes	-	6.3	1.8	76.9	15
Peach stone	-	7.1	1.4	75.6	15.9
Peanut shell	-	-	5.7	65.4	19.6
Rice husk	-	6.1	20.6	58.4	14.9

6.6 ASH ANALYSIS

The composition of agricultural waste ash is strongly dependent on the species of the plant. The content of potassium, sodium, chlorine and phosphorous in fuel depend on the available nutrients, soil quality, fertilizers and weather condition. Table 13 shows the composition of fly ashes of different types of agricultural waste fuels. [3], [57], [58], [60], [63] Agricultural waste fuels can be divided into three different types according to the content of the calcium, potassium and silicon.

Table 13. Ash analysis of some biofuels (mass basis % ash)

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	P_2O_5	K_2O	Na_2O	Cl	others
Pine Pellets	20.9	6.2	21.6	26.2	0.3	4.3	4.2	11.5	2.5	0	2.3
Palm empty fruit bunch	11.04	0.29	6.93	12.67	2.35	2.16	4.02	53.07	-	5.8	1.93
Wood pellets	4.3	1.3	1.5	55.9	1.3	8.5	3.9		0.6	-	0.1
Ricestraw	77.2	0.55	0.5	2.46	0.83	2.71	0.98	12.59	1.79	-	0.04
Industrial wood waste	15.6	7.4	3.7	40.6	3.7	11.5	2.2	2.4	2.1	-	1.3
Peach stone	5.5	2.3	6	12.1	2.4	12.3	25.7	30.4	1.9	-	1.1
Peanut shell (feed rate=60kg/h)	50.49	11.14	5.27	8.52	-	3.21	-	9.85	0.02	-	-
Peanut shell (feed rate=45kg/h)	51.46	10.67	4.96	8.37	-	3.11	-	10.66	0.02	-	-
Peanut shell (operating time 10h)	14.11	80.33	0.38	0.87	-	0.51	0.19	1.54	-	-	0.24
Peanut shell (operating time 20h)	28.26	62.78	0.89	1.54	-	0.74	0.34	3.77	-	-	0.16
Peanut shell (operating time 30h)	33.64	56.15	1.19	1.72	-	0.76	0.39	4.62	-	-	0.13

6.6.1 CA, K RICH AND SI LEAN ASH FUEL

Table 14 is the examples of this type of agricultural waste fuel. These types of fuel are rich in calcium, potassium and low content of nitrogen (0.3–0.7 w-% in dry solids), sulphur (0.03–0.05 w-% in dry solids) and ash (0.1–6 wt% in dry solids). Moisture contents of these fuels are often high, up to 50–80 %, reducing net calorific value of fuel.

Table 14. Calcium and Potassium rich and silicon lean ash agricultural wastes

Elements	Forest residue	Peat
SiO_2	11.6	32.1
Al_2O_3	2.0	17.3
Fe_2O_3	1.8	18.8
CaO	40	15.1
MgO	4.8	2.5
K_2O	9.2	1.4
Na_2O	0.6	0.5

6.6.2 SI AND CA RICH AND K LEAN ASH FUEL

Most of the fuels in this type belong to herbaceous or agricultural biofuels. Some of the fuels, like straws of cereals have also relatively high potassium (K) and chlorine (Cl) contents. Rice straw and peanut shells have very high SiO_2 contents in ash as shown in Table 15.

Table 15. Silicon rich and Calcium and Potassium lean ash agricultural wastes

Elements	Peanut shell	Rice straw
SiO_2	50.49	77.2
Al_2O_3	11.14	0.55
Fe_2O_3	5.27	0.5
CaO	8.52	2.46
MgO	3.21	0.83
K_2O	9.85	1.79
Na_2O	0.02	0.04

6.6.3 Ca, K, and P rich ash fuel

Sunflower stalk ash and rapeseed expeller ash from food production are examples of the third type of agro-waste fuel ash (Table 16), having K_2O, CaO and P_2O_5 as the major ash components [64]. These agro-waste fuels contain some chlorine that increase the risk of chlorine induced high temperature corrosion of super heaters. Composition of fly ashes in for the same fuel also varies on the feed rate as well as different periods of combustor operation. For example, Table 17 shows the composition of fly ashes (as the weight percentage of representative oxides) generate when firing peanut shells at 60 kg/h and 45 kg/h for similar excess air, about 40% [8]. For these two ash analyses, the total sum of oxide percentages was below 100%, which indicated the presence of some amount of carbonates in the ashes. A comparison of the ash compositions revealed quite weak effects of operating conditions (via the bed temperature and residence time) on the percentage of individual constituents in the analysis. Table 18 shows the composition of alumina sand (prior to testing) and that of the reused bed material after different time periods of combustor operation [8]. Here we see that the content of SiO_2 and K_2O in the alumina-based bed material were found to be significantly increased with time, whereas other components presented in the fly ash at noticeable levels (such as CaO, MgO, Fe_2O_3 and P_2O_5) exhibited a moderate/weak time increment of their contents in the grains.

Table 16. Examples of ash composition of sunflower stalk and rapeseed expeller

Elements	Sunflower stalk	Rapeseed expeller
SiO_2	3.1	0.0
Al_2O_3	0.1	0.0
Fe_2O_3	0.2	0.3
CaO	6.6	15.0
MgO	4.3	9.0
K_2O	27.5	22.8
Na_2O	0.0	0.0
P_2O_5	18.5	41.1
other	39.7	11.8

Table 17. Examples of ash composition of peanut shell firing boiler in excess of air at different feed rate

Elements	Peanut shell(feed rate=60kg/h)	Peanut shell(feed rate=45kg/h)
SiO_2	50.49	51.46
Al_2O_3	11.14	10.67
Fe_2O_3	5.27	4.96
CaO	8.52	8.37
MgO	3.21	3.11
K_2O	9.85	10.66
Na_2O	0.02	0.02

Table 18. Examples of ash composition of peanut shell firing boiler in excess of air at different time instants

Elements	Peanut shell (operating time 10h)	Peanut shell (operating time 20h)	Peanut shell (operating time 30h)
SiO_2	14.11	28.26	33.64
Al_2O_3	80.33	62.78	56.15
Fe_2O_3	0.38	0.89	1.19
CaO	0.87	1.54	1.72
MgO	0.51	0.74	0.76
K_2O	0.19	0.34	0.39
Na_2O	1.54	3.77	4.62

6.7 Size Segregated Particle Emission

The particle size distribution is important, since this physical parameter determines the mass and number density, lifetime and atmospheric transport, or optical scattering behavior of the particles in the atmosphere. Epidemiological studies shown that particulate matter can pose adverse health effects such as respiratory, cardiovascular, allergic and lung cancer diseases. These health issues associated with airborne particulate matter depend on the concentration, size, and chemical composition of particles. Particle size determines where particles are deposited in the respiratory tract. Agricultural wastes emissions constitute a highly variable fraction of the atmospheric aerosol. This fraction is predominantly found in the fine size mode in concentrations ranging from 20 to 50% of the total fine particle mass [65]. The total carbonaceous aerosol comprises is classified in two main fractions: organic carbon (OC) and elemental carbon (EC). The OC fraction is composed of a huge variety of organic compounds, ranging from low molecular-weight compounds [66]. On the other hand, the EC fraction can be pictured as more or less disordered stacks of graphene layers or large polycyclic aromatics with a surface coverage by oxygen-containing functional groups and nitrogen species [67]. While EC is essentially a primary pollutant, emitted directly during the incomplete combustion of biomass and, principally, fossil carbonaceous fuels. Primary OC is directly emitted into the atmosphere as liquid phase, solid particle phase or as semi-volatile vapours, which condense under the atmospheric conditions [68]. Secondary OC is developed in-situ by chemical reactions of gas-phase compounds, or by condensation of gaseous species on existing particles [69]. Tables-19 [36], [60], [70], Table-20 [36], [60], Table-21 [36], [70], [71] and Table-22 [36] shows size segregated emission factors for PM, OC, EC, elemental emission, PAH from different emissions sources. Combustion temperature is the most important factor in determining PAH composition. Burn temperature depends primarily on the combustion air supply, but is also influenced by the amount of fuel burning, fuel moisture content and type of burn. Hot flames generally produce a lower amount of particulate matter as well as lower organic pollutants such as polycyclic aromatic hydrocarbons. However, flames with higher temperatures tend to produce relatively more particles in the ultrafine range.

Table 19. EC, OC and TC values of size segregated particulate matter emitted from various sources

Element	Rice Straw (g/Kg)		Almond Pruning ($mgKg^{-1}$)			Rice straw ($mgKg^{-1}$)			Air of Yukohama city ($\mu g/m^3$)		
	$PM_{2.5}$	PM_{10}	$PM_{<0.1}$	$PM_{0.1-1.8}$	$PM_{>1.8}$	$PM_{<0.1}$	$PM_{0.1-1.8}$	$PM_{>1.8}$	$PM_{2.5}$	$PM_{2.5-10}$	PM_{10}
EC	57.7±27.9	56.9±25.3	0.04	0.13	-	0.07	0.42	-	1.94±1.2	0.25±0.10	0.22±0.20
OC	335.4±88	328±84.7	0.98	1.39	-	0.16	0.67	-	3.75±1.5	1.27±0.60	0.72±0.40
TC	393±64	385.5±63.3	-	-	-	-	-	-	-	-	-

Table 20. Mean concentrations of particulates of different sizes and their chemical compositions from rice straw burning boiler and air of an industry densely city of Japan

	Rice Straw (g/Kg)		Air of Yukohama city (μg/m³)		
Ion	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	$PM_{2.5-10}$	PM_{10}
Na+	2.56±2.77	3.53±3.84	0.25±0.20	0.68±0.50	0.22±0.30
K+	50±34	47.3±33.6	0.13±0.10	0.05±0.10	0.06±0.20
NH4+	23.8±11.7	22.8±9.2	2.27±2.0	0.28±0.30	0.22±0.30
Mg2+	0.11±0.22	0.18±0.28	0.05±0.02	0.06±0.10	0.02±0.0
Ca2+	0.15±0.41	1.08±1.06	0.02±1.0	0.17±0.40	0.05±0.01
F-	2.45±3.28	2.48±3.17	-	-	-
Cl-	69.3±31.6	68.6±30.7	0.21±0.40	0.44±0.40	0.23±0.20
NO3-	2.93±3.72	15.53±13.06	0.96±1.5	1.01±0.80	0.17±0.20
SO42-	9.82±7.21	15.53±13.06	3.80±2.6	0.22±0.40	0.04±0.10

Table 21. PAH emission factors from different sources of emissions

	Rice Straw (g/Kg)		Almond Pruning (mg/Kg)			Rice straw (mg/Kg)			Diesel Dominating free ways in Los Angeles (ng/m^3)	
PAH	$PM_{2.5}$	PM_{10}	$PM_{<0.1}$	$PM_{0.1-1.8}$	$PM_{>1.8}$	$PM_{<0.1}$	$PM_{0.1-1.8}$	$PM_{>1.8}$	(Ultra fine mode)	(Accumulation mode)
Fluoranthene	-	-	0.19	0.46	0.35	0.47	0.33	0.2	-	-
Phenanthrene	0.03±0.07	0.02±0.05	0.25	0.47	0.28	0.33	0.55	0.12		
Anthracene	0.02±0.01	0.01±0.01	-	-	-	-	-	-		
Fth	0.5±0.75	0.49±0.75	-	-	-	-	-	-	-	-
Pyrene	0.29±0.33	0.26±0.27	0.18	0.44	0.38	0.5	0.34	0.16		
Benzene(a) anthracene	0.12±0.18	0.11±0.14	-	- -		-	-	-	0.108	0.029
Chrysene	0.17±0.21	0.15±0.17	0.52	0.48	0	0.4	0.47	0.13	0.22	0.047
Benzo(b) fluoranthene	0.13±0.12	0.12±0.11	0.52	0.48	0	0.48	0.37	0.15	0.211	0.044
Benzo(k) fluoranthene	0.05±0.04	0.05±0.04	0.55	0.45	0	0.44	0.48	0.07	0.149	0.035
Benzo(a) pyrene	0.13±0.15	0.11±0.13	0.58	0.42	0	0.23	0.54	0.22	0.172	0.043
Dibenzo(ah) anthracene	0.08±0.1	0.08±0.1	0.54	0.46	0	0.55	0.47	0	0.013	0.004
Benzo(ghi) perylene	0.02±0.03	0.02±0.03	0.44	0.56	0	0.37	0.63	0	0.454	0.084
Indeno[1,2, 3-cd]pyrene	-	-	0.33	0.67	0	0.38	0.62	0	0.046	0.011

Table 22. Elemental emission (g/Kg) of particle matter from a rice straw firing boiler

	Rice Straw	
Element	$PM_{2.5}$	PM_{10}
Fe	0.038±0.108	0.105±0.306
Ni	0.036±0.068	0.047±0.070
Pb	0.045±0.094	0.115±0.197
Sr	0.013±0.029	0.016±0.028
Ti	0.015±0.046	0.016±0.043
V	0.091±0.130	0.140±0.191
Zn	0.036±0.099	0.066±0.155
Si	0.14±0.34	0.185±0.364
Al	0.18±0.33	2.53±2.47
Ca	0.85±1.33	2.65±3.40
Cd	0.009±0.023	0.009±0.022
Cr	0.080±0.169	0.163±0.292
Cu	0.171±0.409	1.24±0.24
Mg	0906±1.710	1.739±1.783
Mn	0.005±0.015	0.010±0.028
S	1.174±0.404	1.24±0.24
As	0.003±0.003	0.003±0.004
Se	0.0001±0.0002	0.0005±0.0004
Br	0.047±0.011	0.044±0.013
Rb	0.036±0.013	0.035±0.013
Zr	4E-05±7E-05	0.0002±0.0003
Ag	0.004±0.005	0.005±0.005
Sn	-	0.002±0.003
Sb	-	0.001±0.001
Ba	0.016±0.022	0.015±0.016
Bi	-	0.001±0.001

7 RELATIONSHIP BETWEEN FUEL TYPE AND PM EMISSION

7.1 FUEL TYPES ON PARTICLE EMISSION

The main agricultural fuels used in combustion systems are wood derived fuels, palm mill residues, rice husk etc. The growing demand of these fuels may lead to an unbearable pressure on the forest, since an increasing demand can drive to unsustainable levels of harvesting, with negative consequences for biodiversity, soil, and water conservation. Low-quality fuel can cause undesired effects in the equipment such as slagging, fouling or corrosion, and may originate substantial amounts of gaseous and PM emissions. On the other hand, the type of pellet has a significant impact on the emissions of CO, hydrocarbons (HC) and NO in the gaseous emissions side and generates high amounts of fine PM in the PM emissions side. Many studies showed that inorganic PM emissions were correlated with both the fuel ash content and the composition [72], [73]. According to their studies, PM emissions are significantly affected with the types of biomass fuel. Fig 7 showed a significant dependency of the fuel type on the emissions of dust for different agricultural waste fuels. The order of dust emission rate has changed slightly with increasing the temperature.

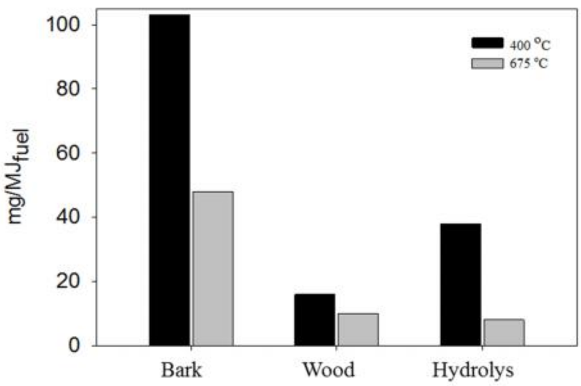

Fig. 7. Influence of fuel types on particle emission

7.2 INFLUENCE OF FUEL TYPES ON BOILER PERFORMANCE

Fig. 8 shows the CO, HC and NO emissions of the different agricultural fuel combustion boiler at thermal input 15-17 kW. The data repeatability for the gaseous and PM emissions was, on average, within 10-13% of the mean value. As shown in the Fig 8, wood pellet and bagasse present lower emissions of CO and NOx and Pine and olive wood has lower emission of HC compared to the other fuels [55], [62], [74]. The HC and CO emissions follow the same trend, since the emissions of both species are related with incomplete combustion. The higher emissions of CO and HC yield by the olive pruning and cork indicate poor combustion conditions since these emissions are also related with incomplete combustion. However, the HC emissions are always rather small for all samples tested. Fig 8 also reveals that the NO_x emission are comparatively lower which is due to the nitrogen content of fuels. NO_x emissions mostly result from the fuel content of N, while their formation from the combustion air plays only a little role. Once more, there is no solid indication for the influence of the operating conditions on NO_x.

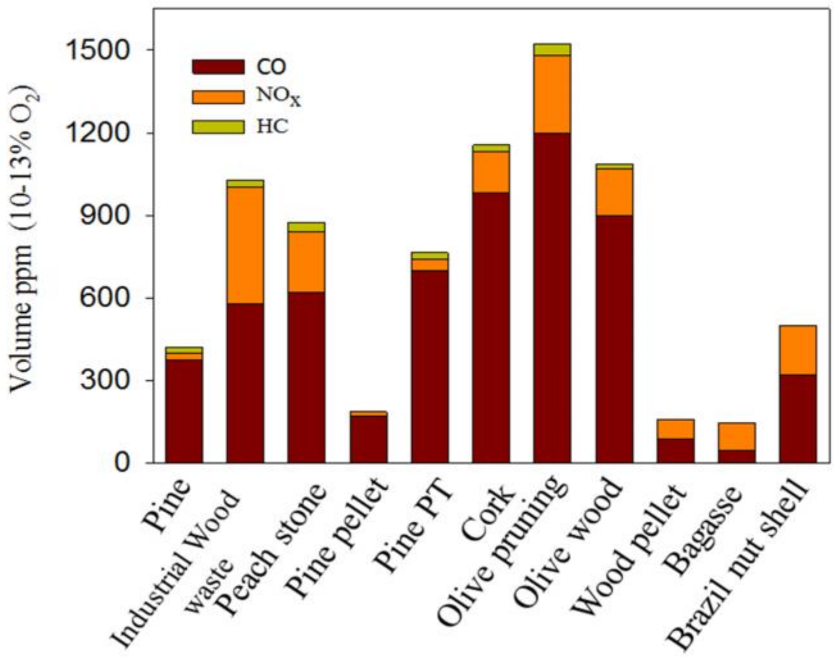

Fig. 8. CO, NO_x and HC emissions for different agricultural fuels at thermal input 15-17 (kW)

7.3 ASH CHARACTERISTICS OF AGRICULTURAL FUELS

Solid fuels always contain inorganic components that form ash during combustion process. Some of these components have volatile properties which form fine fly-ash fraction while the nonvolatile species typically form large ash particles that remain in the bottom of the furnace. The main ash forming species in agricultural waste fuels are K, Ca, S, Mg, Cl, P, Mn, Si, Fe, Al etc. Table 23 shows composition of the ash forming species in agricultural wastes fuels found in literature [34], [54], [72]. The clean fuel usually contains higher amount of elements forming positive ions like K, Na than anions like S. Cl etc. Generally the amount of ash present in organic molecules in woody fuels is higher than in other agricultural wastes. Drying of agricultural fuels leads to precipitation of ions in aqueous solution, affecting ash behavior during combustion.

Figure 9 illustrates SEM micrographs of the particle morphology collected on quartz filters for combustion of different agricultural fuels. A large majority in the number of fine particles were seen as round uniform shape in Fig 9(a), approximately in sizes 20–50 nm, of which the surface evaporated easily under the beam of the SEM. Perhaps these particles were composed of solid seeds with a layer of liquid sulphuric acid. In Fig 9(b), the samples contained smaller amount of fine particles bigger than 100 nm, of which some were irregular shaped spheres and some compact shaped agglomerates [54]. Fig 9(c-f) shows typical submicron PM collected from Portuguese pine, Spanish pine cork, olive wool and olive pruning. A large number of soot aggregates was observed in all Figures [74]. Size of the particle was observed from the SEM images shown in Fig 9(g-i) [55], [73].

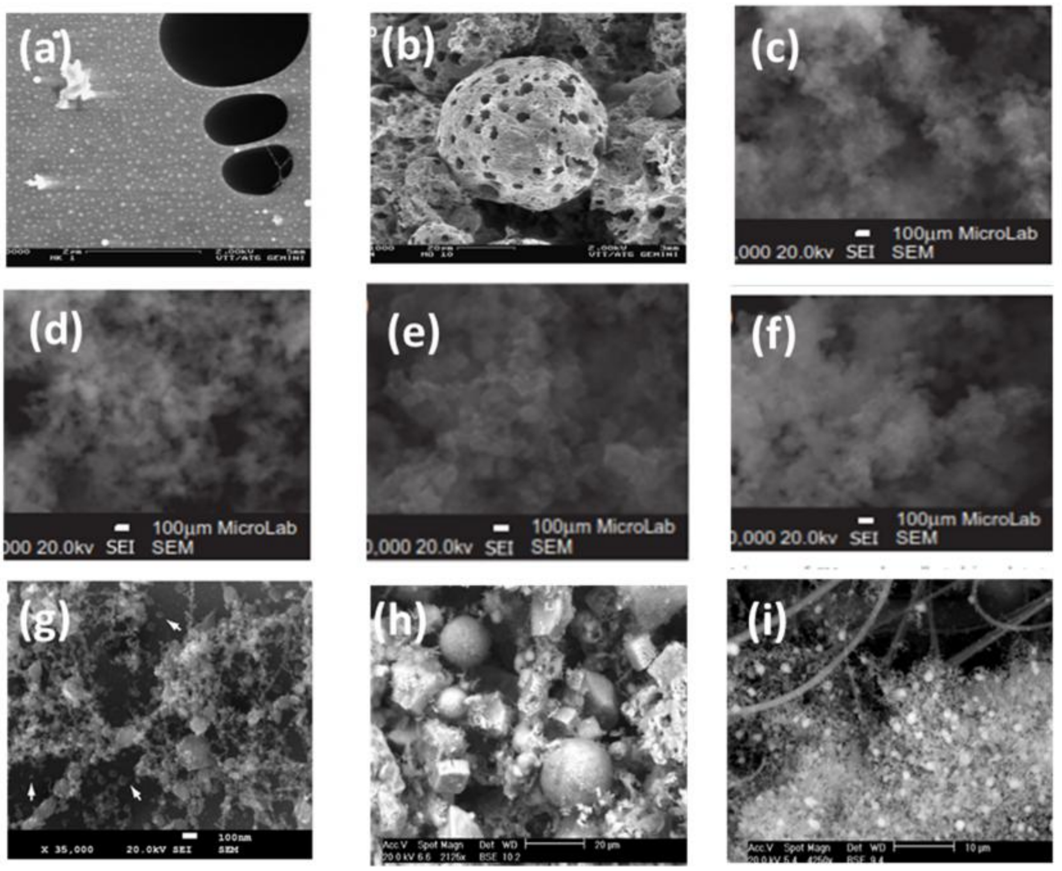

Fig. 9. SEM morphology of PM sample. (a) coarse particle: (b) collected from flue gases of wood combustion: (c) Portuguese pine: (d) Spanish pine :(e) cork: (f) olive wood: (g) pine pellet: (h) woody biomass: (i) bark pellet

Table 23. Properties and ash forming elements in the agricultural waste fuel (concentrations of elements given as mg/kg dry fuel)

Fuel	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl
Oat	24	640	80	5290	1330	40	43	4020	1640	-	28	578
Wood-pellet	10	940	10	670	200	70	10	40	70	-	7	42
Rape seed	-	5410	60	7910	3380	20	25	8880	4350	-	34	117
Rape seed residue	9	5980	90	10170	5410	50	36	12640	4910	-	58	92
Oat-peat	176	836	422	4270	1190	40	50	3278	1544	-	25	518
Pellet (Commercial)	-	752	-	409	164	-	-	49	53	-	9	41
Pellet (Birch bark)	-	3900	-	1250	426	-	20	459	342	-	127	300
Pellet (Alder bark)	-	7590	-	2695	582	-	-	577	567	-	103	98
Pellet (Pine seam)	-	792	-	661	267	-	-	232	135	-	10	51
Pellet (willow)	-	11700	-	3875	727	-	77	1200	891	-	211	82
Saw dust & bark	89	2900	67	1070	400	170	24	2451	90	78	42	80
Forest residue	170	1740	454	1470	357	141	26	169	128	158	23	1520
Pellet mix	1325	4146	4100	1200	527	120	610	500	900	5000	17	290
Wood dust	9	1280	25	475	228	73	214	90	73	-	29	99
Wood pellet	-	5	-	40	-	-	5	-	-	-	3	5
Wood	0.12	-	0.13	0.027	0.0025	0.13	-	-	-	0.0072	-	-

8 Particle Emissions Control

The combustion of any fuel will emit pollutants, and emissions from agricultural wastes will differ from that of other fuel sources. It is important to understand the types of emissions and to consider what measures can be taken to reduce impacts to ambient and on-the-ground air quality. This is especially important in the case of PM, which is a concern for public health. There are steps that can be taken to reduce these impacts on air quality and public health.

8.1 Emissions-Reduction Measures

To reduce PM emissions, special attention should be given to sourcing quality wood fuel, installing high-efficiency boilers, implementing best management practices, installing emissions-reduction equipment, ensuring proper sizing and stack height, and proper plant siting.

8.1.1 Fuel Selection

The quality of the fuel is an important factor in controlling the amount of PM emissions released. For agricultural wastes fuel based systems, the moisture and mineral content of the chips can affect the emissions coming out of the stack. Using clean and dried agricultural wastes will typically yield less PM emissions. Fuels that content more ash-forming minerals produce more particulates in the form of fly ash which is present in the exhaust gases at combustion. The Pellet Fuels Institute (PFI) has developed voluntary standards that gauge pellet fuel quality and these grades, from highest to lowest quality, include: Super Premium, Premium, Standard and Utility (Table 24) [75].

Table 24. Maximum allowable ash content for PFI-Grade pellet fuels

Maximum Allowable Ash Content for PFI-Grade Pellet Fuels	
Super Premium	0.5%
Premium	1.0%
Standard	2.0%
Utility	5.0%

8.1.2 BOILER SELECTION

A high-efficiency boiler with an automated feeding system should select to get maximum yield with fewer emissions. The size of the system should be based on the facility`s heat energy requirements. A fuel-heated boiler must provide air to oxidize its fuel. The system should additionally be equipped with an induced fan for better combustion control.

8.2 PM EMISSIONS-CONTROL EQUIPMENT

8.2.1 CYCLONES AND MULTI-CYCLONES

Cyclone is an air pollution control unit which removes particulates from an air, gas or liquid stream through vortex separation. Rotational effects and gravity are used to separate mixtures of solids and fluids. The method can also be used to separate fine droplets of liquid from a gaseous stream. The performance of a cyclone usually evaluated via its collection efficiency and pressure drop. The collection efficiency referred to the ability of the cyclone to separate the dust from the gas stream according to the dust size fraction. Many Studies have been carried out to improve the cyclone performance. Madhumita, et al. installed a unit called `Post Cyclone` to improve cyclone efficiency [76]. Wang et al. introduced a new type of cyclone known as circumfluent cyclone and was able to improve the collection efficiency 8% than the conventional one.[77]

Multi-cyclones is a type of cyclone which the miniature axial entry cyclones is preferred compare to the other type of cyclone due to its ability to achieve higher collection efficiency. A multi-cyclone uses numerous smaller diameter cyclones to improve efficiency. However, its ability in capturing particulate matter (PM) especially the fine particulate size fraction is limited. Norelyza, et al. developed a multi-cyclones unit known as MR-deDuster as particulate emission control device in palm oil mill plant to enhance the performance of multi-cyclone [78]. The newly developed MR-deDuster is capable to capture dust sized 2.4µm at 50% collection efficiency with a reasonable low pressure drop. The unit is also capable of achieving more than 95% total dust collection efficiency for all dust tested [79].

8.2.2 FABRIC FILTER

In the case of mechanical separators such as cyclones and multi-cyclones have a broad range and relatively lower collection efficiency, while the collection efficiency can be higher for that of fabric filters or baghouses. Fabric filter has ability to separate particles from a gas stream of any conditions with relatively high efficiency. But their applications in these facilities are short lived due to wear and tear of the fabric media. To overcome this problem, "Pre-Coat" material is used to coat a layer of inert material onto the surface of the fabric as a barrier of for protection as well as to allow a uniform air flow passing through the filter media [80]. A newly formulated filter aids material known as `PrekotAC`, an efficient dust separation agent in a fabric filter system was developed by Hajar and their groups [81], [82]. A considerable decrease in pressure drop was observed due to the effect of deviation in different particle size distributions of non-uniform particle size fractions for the PrekotAC mixture. Substantial savings could be achieved in the terms of maintenance costs with the application of PrekotAC in the industry.

9 CONCLUSION

In this paper, various factors leading to Sources of agricultural wastes, formation of particulate matter emissions from combustion of agricultural wastes fuel used in district heating applications as well as their impacts on human health were explained based on the literature survey. Especially particle emission level, conversion technology, emission factors, size segregated particulate emission factors have been characterized briefly and the following conclusions can be made.

- Large amount of crop residues (4×10^9 Mg/yr) are produced in the world every year. The combustion of these residues in boiler seems to be a promising technique to contribute both the reduction of greenhouse gases and the solution of the waste disposal problems.
- Performances of agricultural wastes as a boiler depend on some properties of residues like, Moisture content, bulk density, ash content, volatile matter, pollutant emission etc.
- Particles size less than few hundreds of nanometers are better to characterized in terms of number concentration rather than mass (or volume) concentration, which is more significant for large particles.
- The mass concentration increases under unsatisfactory combustion conditions due to particles originating from incomplete combustion.
- There is a slight tendency to a decreased number concentration of emitted particles for increasing moisture content in the fuel.
- The data regarding size segregated particulate emission from different sources are very few and quite scattered. More work is therefore needed to characterize the PM according to their size.

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