Analysis of Biomass Ash Fusion Behaviour and Characterization for Industrial Applications

By

Muhammad Assad Munawar

Reg # 00000274577

Session 2018-20

Supervised by

Dr. Asif Hussain Khoja

A Thesis Submitted to US-Pakistan Center for Advanced Studies in Energy in partial fulfilment of the requirements for the degree of
MASTERS of SCIENCE in
THERMAL ENERGY ENGINEERING

US-Pakistan Center for Advanced Studies in Energy (USPCAS-E)
National University of Sciences and Technology (NUST)
H-12, Islamabad 44000, Pakistan
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THESIS ACCEPTANCE CERTIFICATE

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ABSTRACT

To reduce the greenhouse emissions, the utilization of biomass is proficient path for producing power and its impact on accumulative carbon footprint. Generation of power from these sources (biomass) produces residue majorly in the form of ash. However, as demand of power production rises, the utilization of the biomass as feedstock increases resultantly the quantity of residue (ash) rise in power plants. Formation of the ash in biomass power plants nurtures number of problems exclusively low fusion temperature, agglomeration, fouling, handling of ash and its utilization for energy applications. In this study, the biomass ash was investigated for ash fusion analysis, characterization and its utilization as a catalyst in methane decomposition. In mainstream, biomass bottom ash (BBA) and biomass fly ash (BFA) fusion temperatures were systematically determined. The BBA and BFA were modified using laboratory synthesized CeO_2 nanoparticles to enhance the fusion temperature. Moreover, the BBA, BFA and modified CeO_2-BBA/BFA samples were characterized by (Carbon, Hydrogen, Nitrogen-Sulphur) CHN-S, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and X-ray fluorescence (XRF) analysis to investigate the physicochemical properties and its suitability for the catalysis applications. The detailed characterization inferred that BFA has significant potential in improving the ash fusion temperature and catalysis due to the presence of metal oxides such as Fe_2O_3, SiO_2 and CaO. Furthermore, the BFA is employed as catalyst support for cobalt (Co) impregnation. Co loaded BFA was employed for methane (CH_4) decomposition for hydrogen production in a fixed bed reactor. The Co/BFA proved with stable catalytic activity of more than 330 min on stream with optimum H_2 yield of 29%. The direct employment of biomass ash as a catalyst shows a potential in further catalytic applications.

*Keywords***:** Biomass fly ash, Biomass bottom ash, Coal fly ash, Ash fusion temperature

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List of Abbreviations

BFA: Biomass fly ash

BBA: Biomass bottom ash

CFA: Coal fly ash

GHG: Greenhouse gases

EJ/yr: Exajoule per year

TWh: Terawatt-hour

AFT: Ash fusion temperature

OT: Original temperature

DT: Deformation temperature

ST: Spherical temperature

HT: Hemispherical temperature

FT: Flow temperature

List of Publications

1. **Muhammad Assad Munawar,** Asif Hussain Khoja*, Muhammad Hassan, Rabia Liaquat, Salman Raza Naqvi, Muhammad Taqi Mehran, Ali Abdullah, Faisal Saleem. "Biomass Ash Characterization, Fusion analysis and its applications in catalytic decomposition of methane". **Fuel** Volume 285 (IF=5.57, W Cat, Q1) by Elsevier. (**Published**)
2. **Muhammad Assad Munawar**, Asif Hussain Khoja*, Salman Raza Naqvi, Muhammad Taqi Mehran, Muhammad Hassan, Rabia Liaquat, Usama Fida Dawood. "Challenges and opportunities in biomass ash management and utilization in novel applications". Submitted in **Renewable and Sustainable Energy Reviews.** (**Under review**)

Chapter 1

Introduction

1.1 Background of the Study

Owing to swift population growth, demand of energy is amassed day by day. An obvious upshot has increased the demand of fuel particularly the fossil fuels for example coal, gas and oil used as main sources of energy after industrial revolution [1]. To meet energy demand, the conventional power plants were installed based on the fossil fuels. Globally 80% of electricity is being produced using fossil fuel [2]. However, there are major concerns regarding plentiful usage of fossil fuels likewise depletion and their effects on the climate and environment concerns. Global warming and air pollution, especially CO_2 emissions have been considered as significant issues of climate change [3].

In green-house gases (GHG), CO_2 emissions is major contributing factor for high emissions [4]. From developing countries, green-house gases mainly comprise of 76.7% CO_2 [5]. Alongside the diminution of fossil fuels and their outcomes on environment, usage of renewable sources such as biomass, wind and solar, are seeking huge attention. Hence, it is necessary to rely on renewable energy sources or more reliable sustainable path that provide least environmental collision and are accessible in abundant bulk in order to overcome energy demand and shelter the assured future for energy supplies [6, 7]. Many countries are shifting towards renewable energy sources to reduce energy risk. There are several renewable energy resources which can be used for energy making from which biomass is strong contender found almost every part of the world [8]. Biomass is attaining more and more attentiveness as upstanding, free and non-depleting source [9].

The energy obtain from biomass is carbon free as compare to fossil fuel because when biomass is combusted the total content of CO_2 produced will be equal to the total content of CO_2 taken from environment during growth of the biomass [10]. Energy obtain from biomass provides 59.2 EJ/yr or 10.3 % to global energy supply according to World Bioenergy Association [11]. Hence biomass is favorable basis of energy which can be used in various ways to generate the power. Major division of renewable energy technologies were installed from which volume of bioenergy was 5.3% and from power generation was 8.6%, in 2015 [12]. Electricity generated by biomass was 493 TWh which was approximately 2% of world electricity production [13]. However, utilization in the combustors of the power plant for steam generation is common and developed technique practiced in masses.

Different kind of biomasses are available for use as feedstock in power plants (boiler industry) are available for bioenergy power generation such as wood residue, wood chips, agriculture residue, rice husk, wheat straw, unusually crops for example miscanthus, panic grass and waste material [14]. Various types of biomass used such as forestry, municipal solid waste (MSW), agriculture waste ad industrial waste for power generation. Apart from the pros of utilizing the biomass as feedstock for the power plant, there are certain cons to be discussed. Utilization of biomass in power plants produces residues such as ash after combustion of alkali content. The biomass fired power plants produces two types of ashes such as fly ash and bottom ash. The oxides with light weight flue with exhaust gases is known as Fly ash and the unburnt particles heavier in weight is Bottom ash [15]. The ash consist of notable mass of contaminated metals which may include SiO_2, Al_2O_3, CaO, MgO, Ni, Pb, K_2O, Zn, Sr etc [16].

The ash handling and utilization is major challenge in the biomass fired power plants. The biomass fired power plants have higher bottom ash content due to the low fusion temperature and moisture in the feedstock [17, 18]. Hence ash handling, utilization and management in the biomass fired power plant is acute challenge to encounter [19]. The extensive concerns regarding biomass power plants are ash disposal, ash storage, ash usage, transportation, presence of unburnt carbon in bottom ash and to minimize the overall environmental impact [20]. In general, biomass ash content is observe from two different angles, with respect to environmental effects and disposal issues [21]. Currently the ash is usually stored in dumping grounds causes serious harm to environment as utmost origin of inert pollution as well as the aesthetic of the region [22-24].

The frequent rise in ash capacity will result in reducing ash storage amenities and spreading cost. Distribution regarding utilization of ash can be categorize in three major steps derived from biomass (1) agricultural usage (2) as a fuel and (3) in construction [20, 25, 26]. Furthermore, fly ash shows good characteristics to be used in the material science and engineering applications such as energy storage materials and nanomaterials for industrial catalysis.

1.2 Problem Statement and Hypothesis

Due to alkaline nature biomass, it results in low ash fusion temperature. Ash formation and Ash handling are major issues in biomass feed power plants. Low ash fusion temperature give rise to higher fouling in boilers, higher scaling, agglomeration, lower efficiency. Moreover, huge amount of unburnt particles in bottom ash. It is well known fact that biomass based boilers face problems like production of ash in huge quantity, low ash fusion temperature and huge moisture content in ash. Due to alkalinity nature of biomass, unburnt amount of particles, low fusion temperature and on other hand production of bottom ash in huge quantity is major problem in biomass boiler. As a result, a significant method was adopted to get rid of this major problem by using nano particles. Cerium oxide increased the thermal stability of ash via increasing fusion temperature. The cobalt further when used as direct support with biomass ash also help in increasing selectivity and conversion of CH_4.

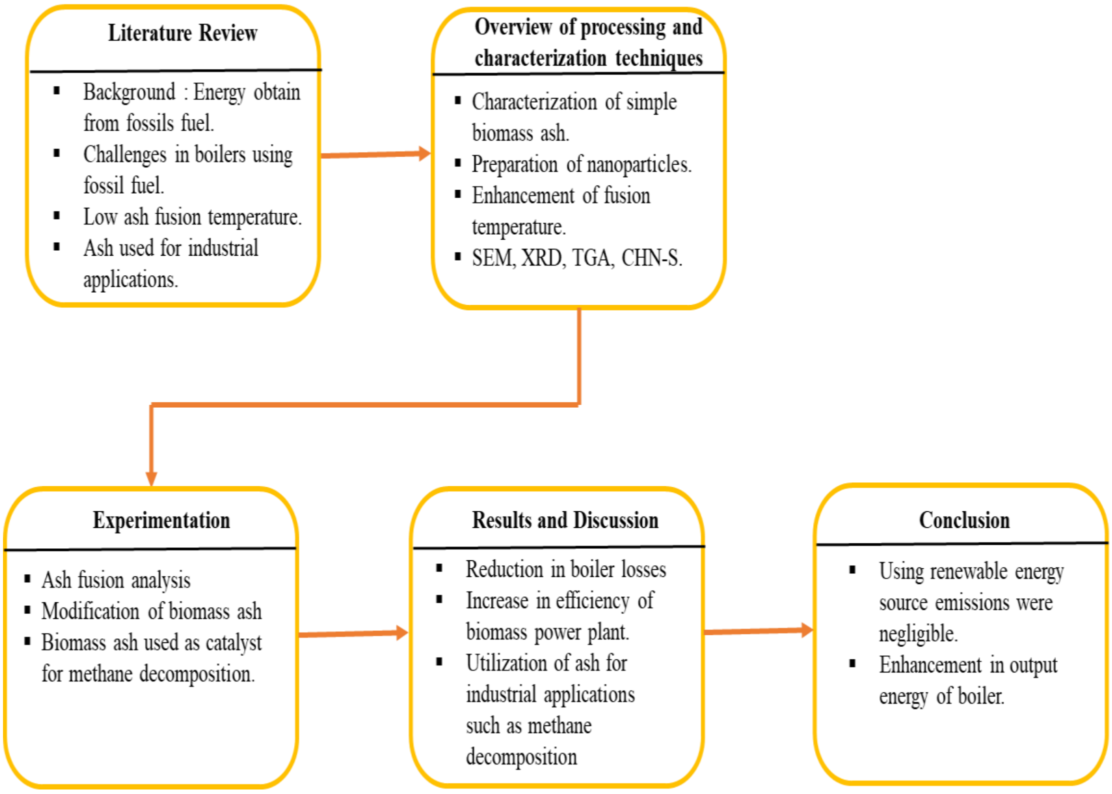
1.3 Research Objectives

- To determine the ash fusion temperature of biomass ash and compare with standard coal ash.
- To characterize the biomass-based ash using various techniques.
- To modify the biomass ash using metal oxide nanoparticles to increase fusion temperature.
- Extensive utilization of biomass fly ash as direct support for industrial catalysis and reforming applications.

1.4 Scope of the Study

In past few years, different techniques were being adopted to enhance the fusion temperature of biomass fly ash and biomass bottom ash while introducing more extensive ways and methods for increasing biomass ash fusion temperature to reduce boiler losses while increasing boiler and power plant efficiency. Making variation in base to acid ratio, making different blends have made great success in enhancing fusion temperature of biomass ash in biomass based boilers. Somehow the fusion temperature has been increased by these methods but another technique which is attaining more significance is using of different nano particles. In this, different type of oxides is used based upon their chemical and physical properties to increase the low ash fusion temperature for example calcium oxide, Cerium oxide, aluminium oxide etc. However, after enhancing the fusion temperature by using cerium oxide, the biomass ash shows good properties in various industrial applications. In this study Cobalt based biomass ash was used as direct support for catalyst for methane decomposition.

Flow chart of Thesis



We commence with a literary review of utilization of fossil fuels for energy production. In this problems/challenges rising in power plants due to fossil fuel were studied. It is followed by an overview of the processing and characterization tools and techniques. Next comes the experimentation section. The experimentation section is a combination of two basic subsections; In first section, ash fusion analysis and different characterization techniques such as SEM, XRD, TGA, FTIR, XRF, CHN-S were performed to analyzed the simple biomass ash. In second part, modification of biomass ash using nanoparticles, characterization and utilization of simple and modified biomass ash for methane decomposition were done. Following the experimentation section is the results and discussion section. In end the ash fusion temperature was enhanced through by which the losses were reduced in boiler and using renewable energy sources are also favourable for environment.

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Chapter 2

Literature Review

2.1 Biomass as an Energy Originator

Considering biomass as an energy source, generates less air pollutants than conventional energy sources (fossil fuels) and decreases the waste (footprint) discarded to the landfills [2]. Biomass is converted into energy typically by direct combustion, this process is still used for producing energy globally [3]. Biomass feedstock, which is combusted to produce energy, originates from different sources such as agricultural residue, forest Woodstock and energy crops such as Miscanthus etc. Figure 2.1 displays the types of power generation systems that can be used to generate power from biomass.

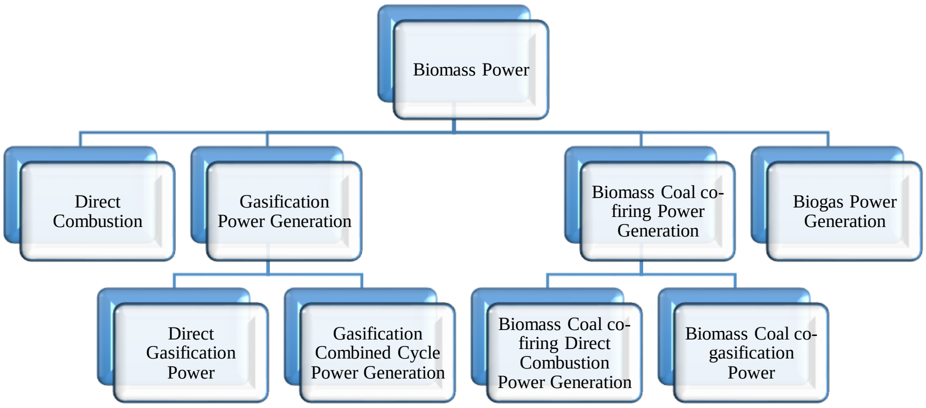

Figure 2.1 Different types of biomass-based power generation

In the direct combustion process, biomass based fired power houses employ the use of technology which is very analogous to fossil fuel based power plants [3, 4]. Firstly, biomass is burnt to produce steam which in turn rotates a turbine driving a generator resulting in the production of electricity [3, 5]. Due to the hazards of ash build up, merely certain kinds of biomass are utilized for combustion directly [6]. In the process of gasification, combustible gas is produced by conversion of biomass (also known synthesis or syn gas) which is used to rotate highly efficient gas turbine producing electricity [7]. In the process of pyrolysis, biomass is thermo-chemically converted into oil which is burnt like fossil fuels to produce energy [8]. To produce energy biomass can also be used as primary and secondary fuel source [3]. In direct combustion, biomass is considered as a primary fuel source to produce energy, whereas in gasification and pyrolysis, biomass is considered as a secondary fuel source to produce energy. Biomass can likewise use in conjunction with coal in biomass-coal co-fired power generation to produce energy. These power plants are regarded as the most promising short term options for energy production as they reduce net CO_2 release from traditional fossil fuel power plants [8].

2.1.1 Biomass Based Fire Power Houses

As discussed earlier, these power plants function like coal based fired power plant except for moisture content which is very high in biomass. For this purpose, the biomass has to be subjected to drying before combustion [9]. The following Figure 2.2 displays the schematic of typical biomass based fired power plant.

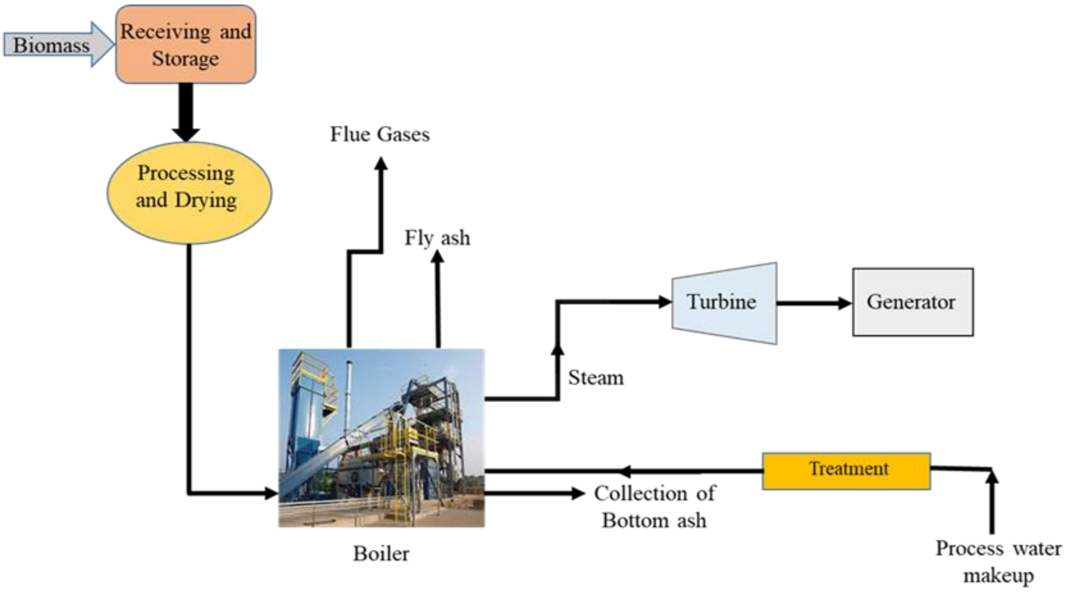

Figure 2.2 Direct combustion of biomass fired power plant [10]

Biomass based fired power plant produces energy built on the (Organic) Rankine cycle [9]. There may be a slight variation in the designing of power plant owing to the types of biomass burnt, the pre-treatment required and co-generation (if any). For example the following Figure 2.3 illustrates the process flow diagram of Rankine cycle co-generation power plant which uses date palm wastages as biomass feedstock [9].

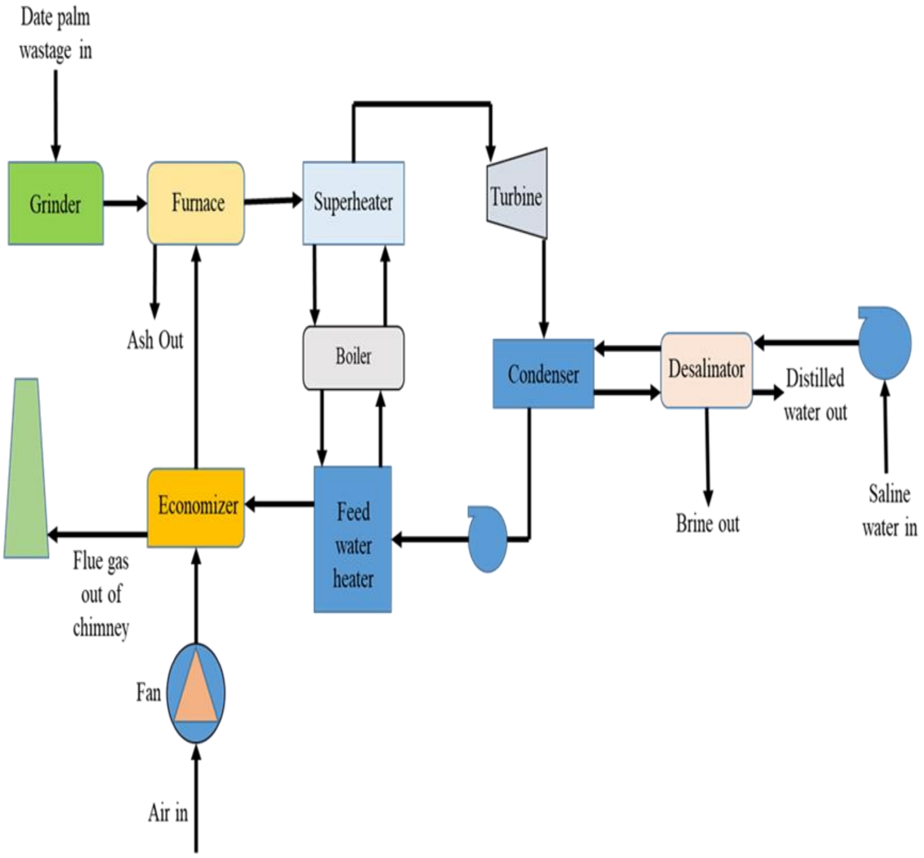

Figure 2.3 Schematic flow diagram of cogeneration power plant [9]

The most commonly used types of direct combustion biomass fired power plants are (i) grate based firing system (ii) fluidized bed combustor (iii) suspension burners [11, 12]. Grate firing and fluidized combustion systems allow flexibility in terms of fuel composition where either entirely biomass can be combusted or co-fired up along using coal, although biomass pellets, raw biomass are used to co-fired using pulverized coal or gas by suspension flames. Air-dehydrated biomass is then added to it in a lesser share [11, 12].

2.1.2 Ash Production in Power Plants

Ash or solid residue is produced in power plant furnaces due to thermal degradation or breakdown of the feedstock when it is subjected to combustion, pyrolysis and incineration [13]. It is inorganic fire-retardant constituent of fuel which is left after combustion, which consist most part of minerals of unique biomass feedstock [14]. Figure 2.4 shows ash production in various countries. Due to diverse compositions of different feedstock of biomass available, the produced ash varies [15]. Usually, high ash matter significantly lessens energy output obtained from particular biomass feedstock [13].

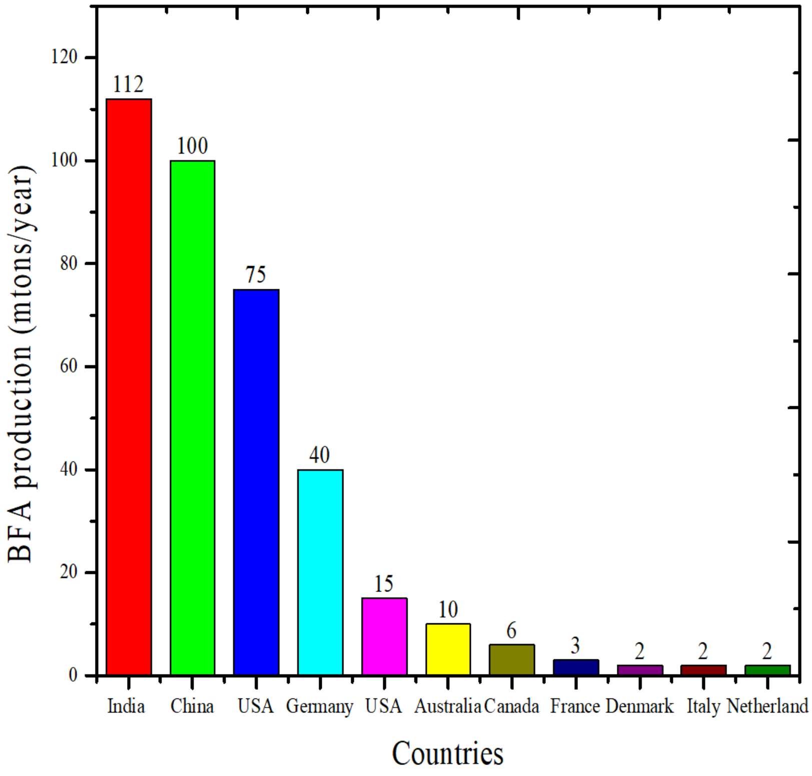

Figure 2.4 Production of ash (million tonnes/year) in various countries (Adopted from IEA-2020)

The following Table 2.1 show the ash content (proximate analysis or percentage by weight) of different biomass feedstock.

Table 2.1 Composition of ash of various biomass feedstock (Turare 2002)

Biomass feedstock	**Ash content (% by wt.)**
Wood chips	0.1
Cotton Gin thrash	17.2
Alfalfa seed straw	6
Barley straw	10.3
Charcoal	2-5
Wheat stalks	7.4
Walnut shell	1.1
Rice hulls	16-23
Coal	5-17

2.1.3 Types of Biomass Ash and Composition/Constituents of Ash

Burning of biomass results in ash formation. Two kind of ash namely Bottom ash and Fly ash which is produced in the biomass fired/coal fired /co-fired power plant [15]. They might differ in properties due to fuel to fuel, fuel type, altered origin of biomass, biomass feedstock used, functional conditions and type of process employed [16]. Usually, the composition ratio of ash depends upon the inorganic elements present in the biomass feedstock burnt [17]. The major ash making constituents in biomass comprises of CaO, Ti, Al, Fe, P, Na, S, Si and Mg [14, 18, 19].

These elements are particularly important because of their presence in the fly ash causes health problems but nevertheless, there is some silver lining to them as well as they can be beneficial for use in other industries such as construction etc which shall be discussed in detail at a later stage. The configuration of ash upsets, its performance under high temperature of burning and in gasification reactors [20]. Furthermore, the feedstock plant species and its growth conditions also dictates the constituents of ash [21]. Usually, it has been found out that fly ash is concentrated with heavy metals while bottom ash contains them in a lower concentration [14]. As Table 2.2 displays phase configuration of biomass ash.

Table 2.2 Phase composition of biomass ash

Matter	**State and Type of constituents**	**Phase and mineral components**
Fluid matter	Gas, Solid and Liquid	Moisture or gas, gas- liquid inclusions associated with both organic and inorganic matter.
Organic matter	Crystalline/ Solid Solid/ Non-crystalline	Structural ingredients mainly cellulose, lignin and hemicellulose extractives.
Inorganic matter	Amorphous/Solid Crystalline/ Solid Semi-crystalline/ Solid	Amorphous phases like glasses and silicates. Mineral species from phosphates, silicates, carbonates, sulphates, oxyhydroxides and nitrates. Poorly crystallized mineraloids of some phosphates, silicates and hydroxides.

2.2 Ash Related Problems

Biomass is deliberated to be renewable energy source and best substitute of fossil fuels having high energy potentials [22, 23]. According to chemical compositions of biomass ash, it consists of many kinds of biomass residual but mostly contains straws, grasses and canes type's biomass ash. These types of ashes cause the problem in boiler during flowing through heat transfer equipment. The fuel used in the boiler has high concentration of alkaline metals. Alkaline metals include phosphorus, potassium, chlorine and sodium [14]. These types of fuels cause to reduce the melting point of ash due to formation of complex structured eutectic salts. Because of these salts, fouling and slagging problems happens in super-heater tubes of boiler [24, 25].

The main reasons behind the boiler's problems are deposit formation, corrosion, fouling and slagging. These problems come from alkaline metals' fuels. Alkaline metals' fuels contain high concentration of phosphorus, potassium, chlorine and sodium. These problems cause to reduce the boiler's life and efficiency as well as increase the operating cost and carbon dioxide emissions [26]. These problem also effects on the combustion temperatures, causes corrosion, reduces heat transfer rate and furthermore causes erosion in boiler tubes as shown in Figure 2.5.

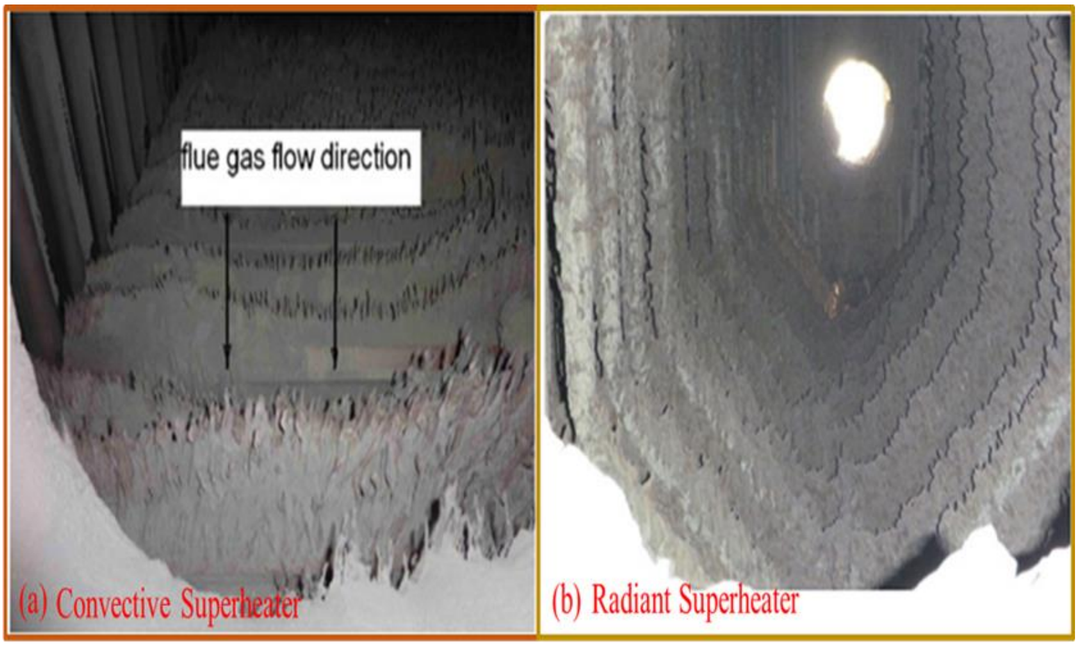

Figure 2.5 Slagging and Fouling in Boiler's heating Surface [26]

2.3 Characteristics of Biomass Ash

2.3.1 Chemical Characteristics of Biomass Ashes

Now a days one the major resource of renewable energy is the biomass [39]. One of the significant feature of the ash obtained from biomass is its chemical composition. This feature helps us to study the uses and behaviour of elements in combustion material. In addition, it also important to note that there is a significant variation while we use biomass's chemical composition as fuel. The reason is that the chemical composition is not only linked with the vegetation type. It is also related to the conditions of the soil which can influence the growth of vegetation and detrital component's composition [40]. Most of researchers studied on the chemical compositions of biomass ashes.

Grzegorz Zajac et al. [16] conducted a research study on chemical composition of biomass ash and studied its main components. Objective of the researcher was to gain the information about major constituents of biomass ash and their uses. The reference data was obtained by the 35 species of biomasses which were used in combustion processes. These species were divided further into groups and classes depending upon the origin. This data was used to study the possible uses of such ashes. The team was keen to use these biomasses in the field of agriculture. The range of the ash content of biomass was from 0.37% to 10.44%. It was observed from the chemical composition of biomass ash microelements like K, Ca, S and P that are dominated. The dominance of these elements make sense that these biomass ashes can be used for agricultural development. It is also interesting to note that these biomass ashes also contain some amount of other microelements like Cu. Zn, and Mn [41]. Presence of these elements also increases the possibility that these biomass ashes can make the use in fertilizers.

Zającet al. [1] obtained results of their study of biomass ashes also reveals that their chemical composition has significant diversity. Behind this diversity, there can be many possible factors. In general, these factors are linked to Raw Material of biomasses from which the ashes are obtained. Combustion processes, preparation of fuel, storage and transportation of material and harvest techniques can also be some key factors causing the diverse chemical composition of biomass ashes. Still, lot of work is required in this field. Especially, using the ash obtained from biomass as fertilizer and monitoring its effect on soil for a long time can give use useful information.

2.3.2 Thermal Characteristics of Biomass Ashes

In small industries, slagging is big problem during the process of biomass combustion. It is believed that the co-combustion technology can be used as a solution to this slagging problem. However, when the mixture of coal and biomass is subjected to combustion and its ash is studied, the fact reveals that it has unique thermal characteristics as compared to the individual source's ash [42]. Tjokorde W. Samadhi et al. [1] conducted a research to study to check whether the co-combustion or blending of biomass and coal is even feasible or not in small scale industries by identification of thermal properties of ash obtained after the combustion of mixture of the both. Generally, the small industries have fixed bed boilers which do not have some proper control system for temperature.

In this scenario, selecting the fuel for combustion for safe operation becomes more critical and needs more attention. The fuel sources used for this study were bamboo, palm oil empty fruit bunch and coal. Two-degree centroid simplex design model [43] was used to construct this research study. Two furnaces i.e. High temperature ashing furnace [44] and fixed bed furnace [45] were used in this study. Sequentially, every single sample was subjected to combustion in both furnaces in small scale. The carrying out temperature for this process was ranging from 550^0C to 750^0C. The thermal characteristics of AFT (Ash Fusion Temperature) and mineral composition of the samples were studied visually. It was detected in results that the ash fusion temperature of resulted ash is less than the temperature of coal but higher than the original source of biomass. It was also observed by the researchers that the initial deformation temperature of resulted ash by co-combustion is greater than the ash obtained by coal or biomass in their pure form. The ash obtained from coal has lesser alkali content as compare to the ash obtained from a biomass, this implies to the overall lesser temperature of ash fusion.

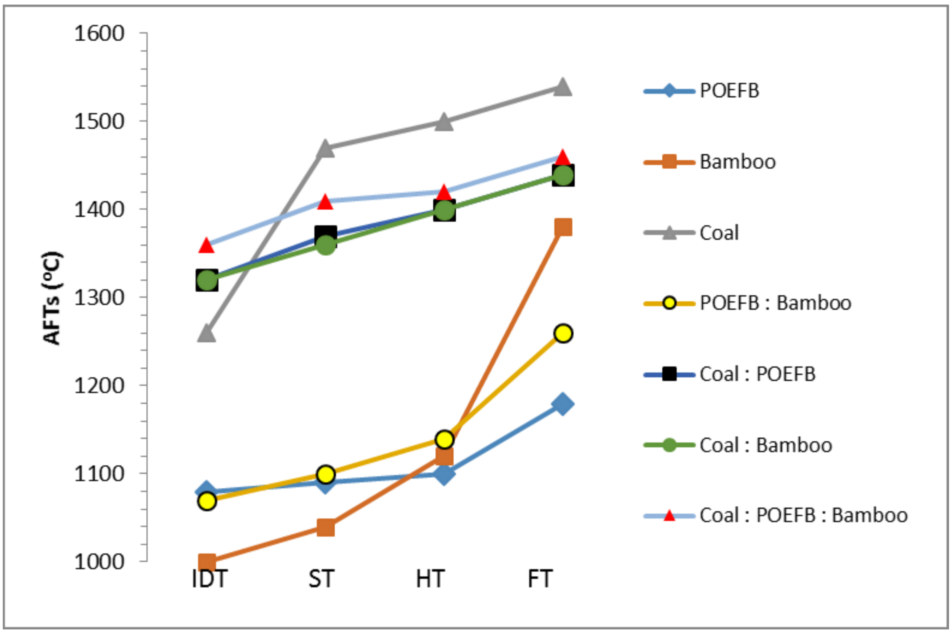

Figure 2.6 Fuel material effecting the ash fusion index [1]

2.4 Characterization of Biomass Ash

In present era, there is a significant increase in demand for the alternate renewable energy sources. One main reason for this increase in demand is because of strictness in environmental laws following the pollution problems. Woody biomass is considered one of the famous alternate non fossil renewable energy source which is used in co-combustion now days. In Europe, it has greatest growing renewable energy source. By the year 2030, its contribution in Europe is expected to be 200% [46, 47].

Many researches have been conducted for the characterization of the woody biomass so far and many more are on the way. V. Sklivaniti et al [48] conducted a research to study the suitability of woody biomass as the alternate material for the composite cement production. This research was carried out by characterization of the ash which was obtained by the combustion of the olive plants. The researchers prepared 6 distinct mixtures for this purpose. These mixtures were prepared by alternating Portland cement for 10, 7, 5, 3 and 2w%. Following techniques were used by researchers to carry out the characterization of woody bottom biomass ash i.e. particle size distribution [49] X-Ray diffraction [50] and chemical analysis [51]. The mechanical and physiochemical properties of the cement produces by the mixture was studied by their final and initial setting time, soundness and standard consistency. Compressive strength on 1,7 and 27 days were also studies.

The outcomes of study reveals that woody bottom ash can work as the alternate for composite cement production. Is was further observed that this is more suitable for the class 32.5 and 42.5 of EN 197-1. Now days, biomass is considered to be major cause of renewable energy due to increasing environmental problems. Gasification, pyrolysis, liquefaction, solidification, combustion and some other thermochemical processes are being used to convert biomass into fuel with high heating value [52, 53]. Xueli Chen et al [54] conducted a study physicochemical properties of biomass ashes. Study was conducted on three different types of biomasses which includes Chinese Parasol leaf, pine sawdust and rice straw. These biomass materials were burnt at 500^0C, 600^0C and 815^0C respectively as shown in Figure 2.7.

The composition and ash content of the biomass material were analyzed. During the thermochemical conversion of biomass, many problems like slagging/fouling or biomass ash volatilization are occurred. These problems were investigated on basis of outcomes obtained by this research. As we increase the ashing temperature, it was observed that volatility of alkali metal increases. Surface morphology [55] and crystalline phase characteristics [54] were investigated of ash particles by SEM [56] and XRD analysis [57]. It was observed in results that for metal salts, the increment in ashing temperature results in decrement in diffraction intensities and for silicon compound the increment in ashing temperature also increases diffraction intensities. By these results it was concluded that ashing temperature has a close relation with ash [57] content crystalline phases [58] composition and surface morphology.

The researchers found that 600^0C ashing temperature is suitable temperature for optimal properties of ash. composition and surface morphology. The researchers found that 600^0C ashing temperature is suitable temperature for optimal properties of ash. The agro-industrial waste is inviting a lot of researchers to work on it and a plenty of work is done far. The main focus of researcher is how to reuse it. For instance, developing new material from agro-industrial waste can be great success. It can also be used in energy production by using any treatment like pyrolysis, gasification and combustion. Fermentative process on these waste may also generate valuable products.

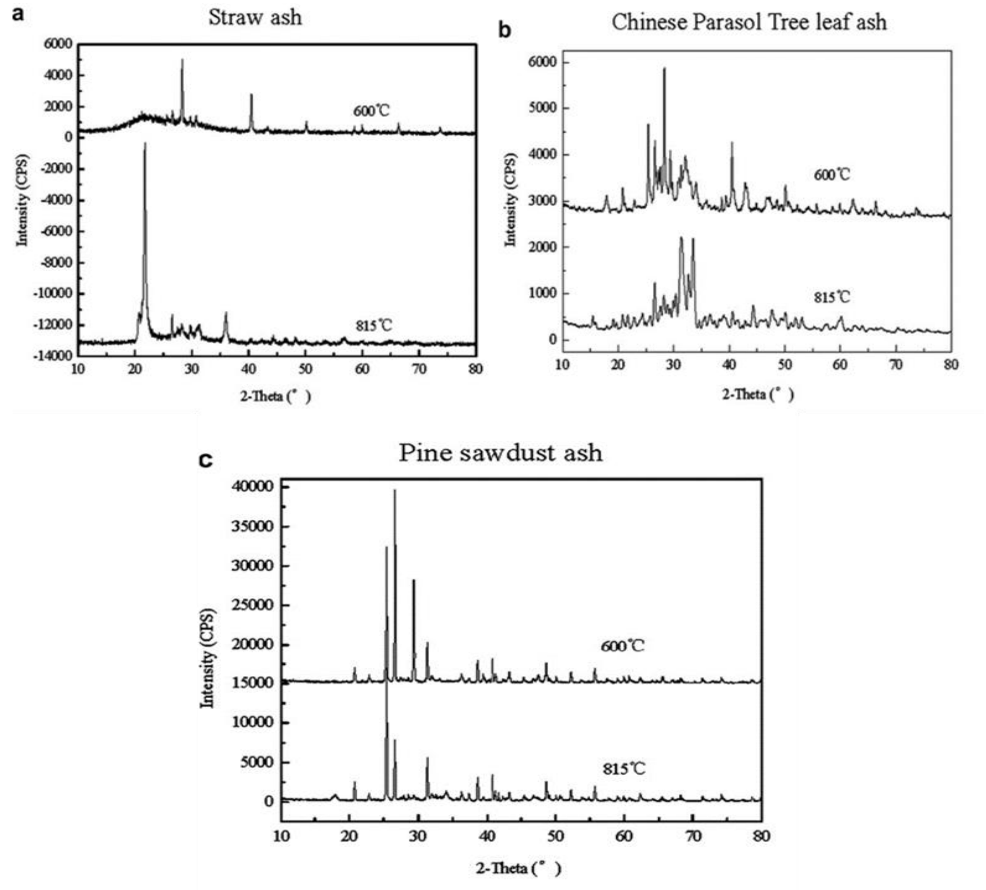

Figure 2.7 Relation between ashing temperature and diffraction intensities [53]

All these assumptions need more and more research. Alejandra Saffe et al [59] conducted a research to study thermo gravimetric analysis. The main purpose of study was to obtain bioenergy by using thermal processes. The characterization study is compulsory for predicting the behavior of a fuel in thermal treatment. A special instrumentation is required for ultimate analysis of an experiment. But beside this the proximate analysis [60] needs only simple apparatus but a large time is required for it.

The methodology applied in this study is based on the curve de-convolution, thermo gravimetric analysis [61] and empirical correlation [62]. The study was focused to determine the content moisture, high heating value, fixed carbon, volatile matter, ash, oxygen, hydrogen, and lignin characteristics of agro industrial waste. The standard technique also gives the same result. This means that the proposed method by these researcher is also accurate and trustworthy and this can also be used for different applications. These methods save the time and help to determine all the parameters for industrial use. The pruning residue form urban and forest municipalities are fuel. This fuel is having great potential for producing energy. These are seasonally sources dispersed over huge areas. These sources of energy are often distributed over infinite areas and depends upon season to season [62, 63]. A study to investigate the gasification behaviour of biomasses residues was conducted by S. Nilson [64] and his team. Their experimental setup is shown in Figure 2.8. This study was performed on 6 different types of biomasses.

These biomass residues consisted of four forest species. These species were white popular Eucalyptus, Pinyon pine and Pinus pinaster as well as two garden pruning type were also included. Pilot fluidized gasifier was used in this experiment. The main intentions of experiments were to quantify (a) the resulting pyrolytic gas by particles of the fuel when oxygen is absent; (b) the impact of oxygen on yielded gas (c) importance of secondary reaction. The air temperature during the experiment was 900^o C, 850^o C and 800^o C.

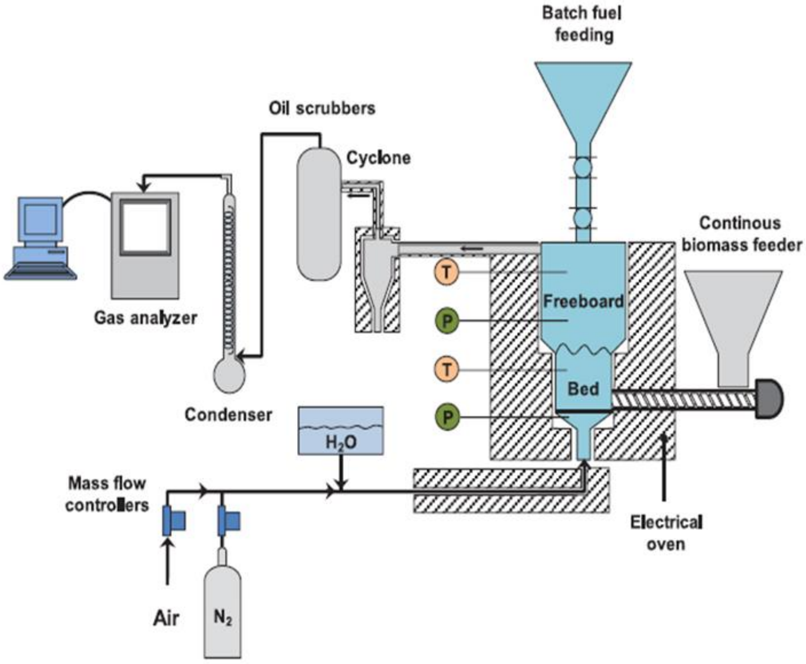

Figure 2.8 Experimental arrangement for checking behavior of gases [64]

After the experiment, it was observed that for a different fuel, a noticeable quantitative difference was found in yield of gas. Same was observed for gas heating value and char conversion. Out of all sample materials, P. pinaster was found giving the best result. Its efficiencies for cold gas were found to be almost 70% at 900^{o}C. On the other hand, garden pruning and white popular gave the worse results. The effect of throughput was considerably significant for white popular and small for garden pruning and P. pinaster.

2.5 Enhancement of Fusion Temperature

Pollution is a big problem now days. So many countries are trying to invent or develop new ways to tackle this problem. In this regard, gasification technology is gaining fame in many countries. These gasification techniques can be used to tackle global warming, air pollution acid rain and many other environmental problems. These all have severe effects on our ecosystem [65, 66]. Fenghai Li and his team worked on low rank coal to study their fusibility characteristics [67]. With the help of fusion temperature determination, the researchers inspected the melting properties of mixture of cornstalk and three other low rank coals. SEM (Scanning Electron Microscopy), X-ray diffractometry and X-ray Fluorescence Spectrometry [68] techniques were also used in this analysis. It was observed in the analysis that, if we keep the mass ratio same, the addition of different types of coal does not gives the same trend of increasing cornstalk ash fusion. The reason behind this trend is that there is a difference between components of the coal and ash contents.

It was also observed that the mineral composition is responsible for variation in melting behaviour of ash. When temperature was high, as we increase the coal mass ratio, it was observed that the Ca^{2+} ions replace the K^+ in cornstalk ash and this phenomenon forms the higher melting point anorthits. Ash fusion temperature also increases due to this phenomenon. While using renewable sources, a lot of problems and difficulties related to environmental issues occur and these problems have drawn a lot of consideration of researcher [69, 70]. If we talk about the problems faced while using renewable sources then we may count some of the major ones as difficulty in storage, transportation of material and bearing its cost. These difficulties often create puzzle in extension of technology for biomass combustion [71, 72].

Many researchers tried to reduce these problems. Qian Wang and his team is one of them [73] who tried to solve the issue which are ash related. The team investigated the problems of biomass ash during combustion, the process of combustion, ash melting temperature of cultivated biomass briquettes and fixation of potassium. Lab scale densification system was used to perform briquettes process. It was observed in results that briquette ash of maize straw showed agglomeration at 900^{o}C [74]. It was fully converted into melted form at 1000^{o}C. The melted product was found to be adhered to porcelain boat and its shape was somewhat like dark solid glaze. It was also observed that the fixed ratios of potassium were enhanced by additives. The rate of change potassium of $NH_4H_2PO_4$ was found to be in between 52.87% to 64.89%. On the other hand, rate of change for $Ca(H_2PO_4)_2$ was 39.90% to 41.74%. The effect of $Ca(H_2PO_4)_2$ on potassium ability was less as compared to that of $NH_4H_2PO_4$. The addition of XRD additives produced the high fusion point of calcium potassium phosphate.

It was also seen that melting temperature of biomass briquettes is improved by both $Ca(H_2PO_4)_2$ and $NH_4H_2PO_4$. There are a few things associated with biomass which annoys sometime like most of the biomass materials have different forms of silica and alkali earth metals as their part [75, 76]. Due to their existence, the biomass ash is considered as volatile and it melts very easily [77, 78]. A research study was conducted by Shenglei Du and his team [79] to study the transformation and fusion properties of the in organic components of the ash obtained by combustion of biomass. In boilers or gasifiers melting of ash temperature is considered to be most substantial parameter for efficient and continuous operation. The team investigated the transformation properties and Fusion characteristics of inorganic components of biomass ash by ash [80] melting point, thermal gravimetric analyzer, X-ray diffraction ,X-ray fluorescence and phase diagrams. By varying temperature, X-ray fluorescence and thermal gravimetric analyzer show the change of elemental composition, ash content and performance. It was found that at high temperature, huge quantity of eutectic composites were generated by internal reaction occurring in biomass ash [81]. Due to this there was a noticeable decrease in its melting point. Binary diagram [78] gave ash composition to fusion and phase diagram helped in assessing the melting properties of biomass ash which is rich in silica. Some of the results are shown in Figures 2.9 and Figure 2.10 below.

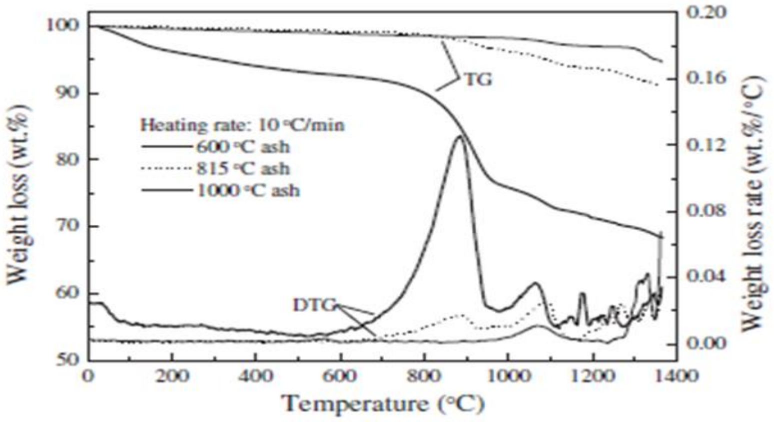

Figure 2.9 TG–DTG of wheat straw ash attained at different temperatures [79]

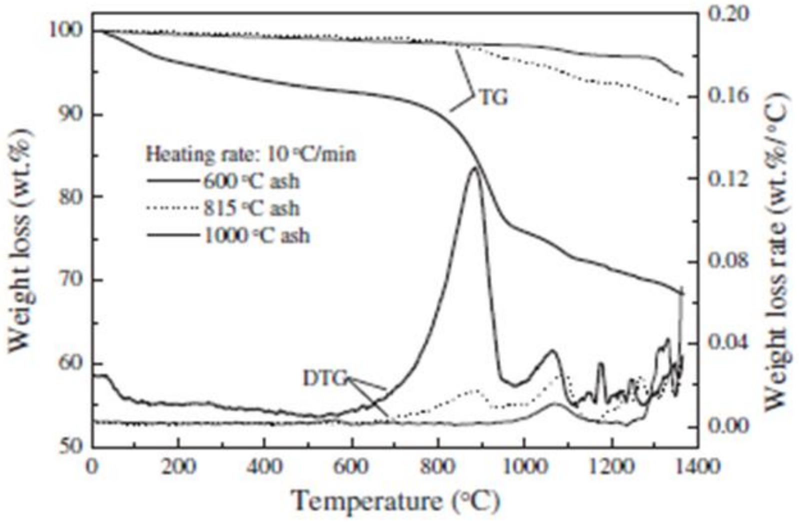

Figure 2.10 TG–DTG of poplar ash attained at different temperatures [79]

2.6 Utilization of BFA in different applications

There are several suitable applications in which the BFA can be used to enhance the characteristics, chemical and physical properties, surface texture etc. Figure 2.11 shows some applications of BFA.

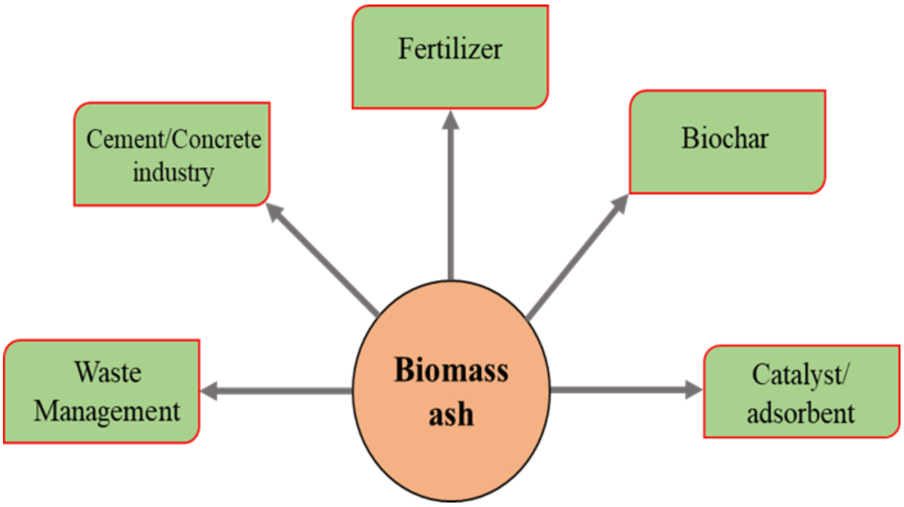

Figure 2.11 Various applications of BFA

2.6.1 Soil alteration and fertilization

Biomass ash offers a huge potential in soil applications. Stream of plant-rising, nutrient and vital elements are existing in majority (Ca, K, H, C, O, occasionally N), while in minor (Na, Mg, S, Cl, P) and trace elements (Zn, Fe, Mo, Cu, Mn) founded in biomass for refining regular balance in soil [41, 82, 83] and biomass ash also provides alkaline atmosphere (e.g. liming effect) and several benefits that supports [83-85] :

- Base cations, higher pH, mineral weathering (illuviation, dissolution of alumina-silicates and clay dispersion), salinity and acid neutralizing potential.
- Reduces acidic behaviour of risky components from soil which results in less mobilization and bioavailability.
- Lowers Mn, Fe and Al toxicity in acidic soil by shrinking their replaceable matter of ions.
- Increasing biotic actions thus providing healthier environment to microbes.
- Refines surface, airing and water volume.

Separately fly ash is used or in addition with organic matter like farm yard manure, sewage sludge or microbial culture in agriculture to optimize the growth, yield and fulfilling the nutrient requirement for cereals, pulses, oil seeds, sugarcane, vegetables and other crops [86].

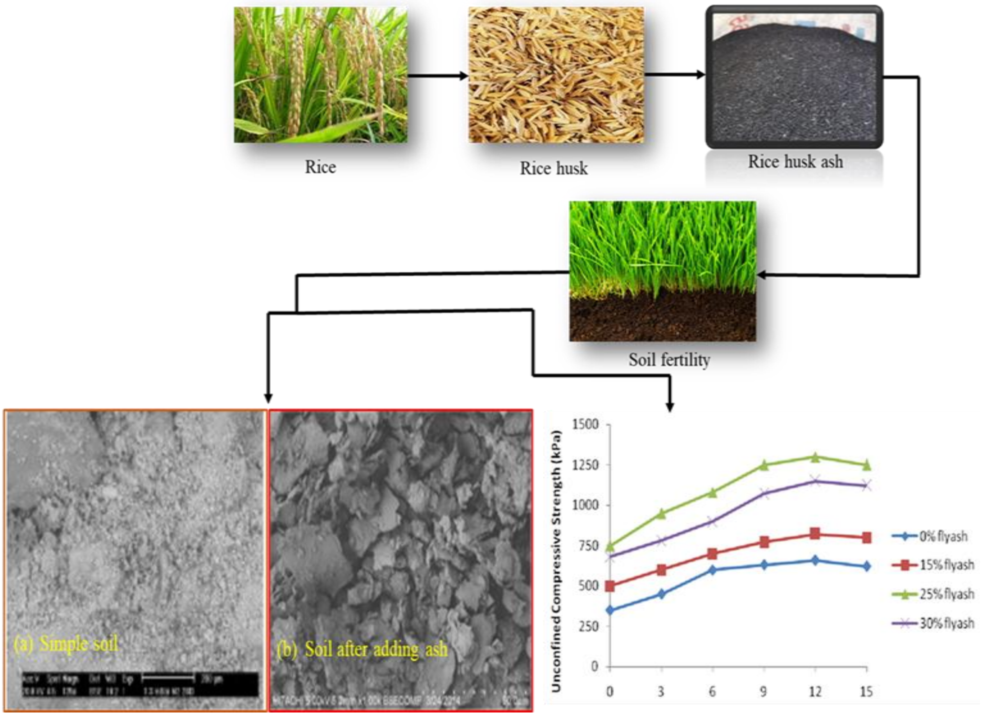

Figure 2.12 Synthesis of rice husk ash for soil stabilization [87]

Figure 2.12 generally, due to addition of ash the configuration of mixture is improved as well as strength is also improved. Moreover, the structure has become denser and uniform after addition of ash. As it is evident that fly ash is rich in nutrients, it is however deficient in Nitrogen, which is also an important nutrient for plants. After fixing the Nitrogen content by beneficial microorganisms, it can be used to increase the availability of Nitrogen too for the plants. With the addition of ash, the durability and mechanical strength is amended [87]. As fly ash enhances the availability of soil nutrients to plants, there is an increase in the value of chlorophyll and carotenoid pigments that are utilized in the photosynthesis process, it is used to enhance the attributes such as increase the number and size of fruits and flowers of the plant [86].

A study was conducted across various agro-climatic conditions in India and it was found out that adding fly ash in various crops and soil results while increasing the yield in edible part of plants [86]. Another study suggested that fly ash amendment added up to 50 mg per hectare was found to be suitable for the yield of wheat, rice, red gram, maize, mustard, banana, sugarcane, potato, and onion [88, 89]. Organic matter such as cow dung manure, press mud, sugar mill waste and farm yard waste can be used in fly ash as amendment to rise the plant growth [90]. Biomass ash furthermore can be utilized to produce vermicomposting for nutrient uptake of plants [86].

2.6.2 Application in Construction Industry

The reference studies highlight that biomass fly ash currently has huge potential in the manufacturing of construction material mainly concrete and cement. BFA is deepened in diverse constituents as each element or mineral in BFA has individual effect:

- Active (anhydrite, alumino-silicates).
- Semi-active (glass, carbonates, iron oxides and gypsum).
- Pozzolanic
- Sluggish behaviour during hydroxylation/dihydroxylation, hydration or dehydration in processes of BFA.

From mineralogical point diversity in structure and ores in BFA usually depend on assets. Due to structure of minerals and phases of active and semi-active in BFA form, reactive material in water which may result in binding effect and also hardening in system throughout evaporation process. These type of effects are consequence of new and moderately firm carbonates, hydrates, alumino silicates, oxyhydroxides, silicates and sulphates which contain water molecules. The new amorphous and crystalline products are formed that fixes the inert phases comparatively rapidly in multicomponent system. In construction industry, ash is being used in brick kilns for the manufacture of bricks, in cement industry, road construction and mine filling [86].

The in-detail usage of ash in these applications shall be discussed later. For construction of highways, soil should possess the following properties: (i) stability (ii) incompressibility (iii) good drainage (iv) ease of compaction (v) minimum volume change (vi) permanency of strength [91]. Typically, expansive soils are unwanted in highway construction in which during summer season the moisture evaporates quickly causing cracks and wide shrinkages leading to huge swelling and disruption of the pavement. This poor soil is replaced by crushed rock typically which increases the cost, this is where fly ash comes in to play as an amendment to the soft sub-grade soil. Fly ash is an economical alternate to crushed rock in the construction of highways to reduce the swelling of the embankments [91].

The diversity in structure and minerals in BFA is usually based on assets from mineralogical point of view. Figure 2.13 shows the various steps for manufacturing of cement mortars using biomass ash. In the figure given below the olives are used as feedstock for boiler to produce steam for rotating turbine. The remaining residue obtained from the boiler is collected and is treated through various processes. Firstly, due to more moisture content it is oven dried and sieved due to particle size less than 0.2 mm is required. Studies suggests that ash can be used in replacement of cement in cement constructed mortars, to keep an acceptable automated strength up to 20% fly ash could be used. If greater amount of fly ash is added, strength declines very sharply.

Another study concludes that usage of bottom ash in mortar, concrete or cement is possible but the products need to be mechanically stable while keeping the potential hazardous substances below the specified environmental quality standard limits.

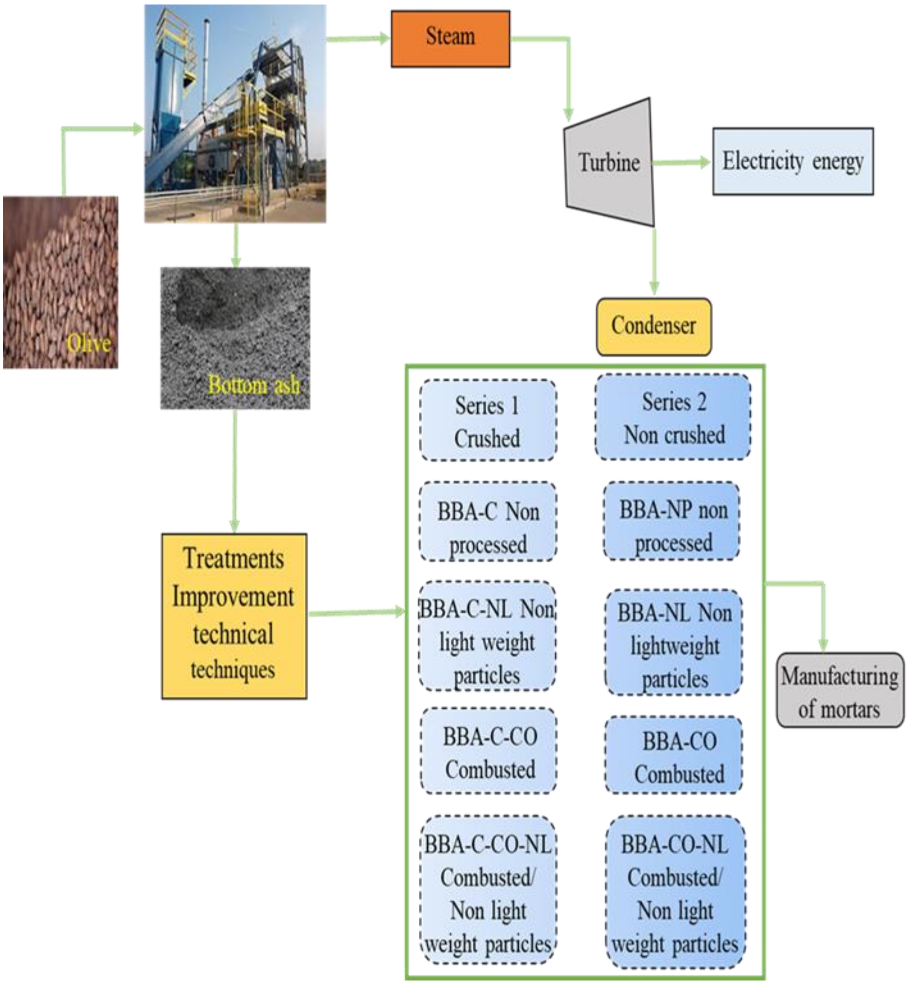

Figure 2.13 Methodology for manufacturing cement mortars using biomass ash [92]

After that the ash is crushed which is than further used for manufacturing of mortars. In addition to being used as soil amendment and used in construction, ash may be used in concrete instead of cement, for road base, as essential filler in tar and its derivate goods, light weight blocks and mock aggregates [93]. While fly ash from traditional circular fluidized bed boilers (traditionally run on coal) is used for the construction in industry (i) with cement in replacement with gypsum (ii) as a pozzolanic material for production of high strength cement and (iii) in replacement of cement in concrete [94].

To reach the desired mechanical strength, the carbon, chloride and sulphates content of biomass ash should be controlled, when used as replacement in cement [95]. In the study, bottom and fly ash derived from biomass was tested for substitution with natural combinations in concrete or mortars, its properties such as rheological performance, demand of water, mechanical power, air absorptivity, opposition to carbonation while in hardened and fresh forms were assessed and the results were promising [96].

2.6.3 Support Material for Industrial Catalysis and Reforming Applications

As previously discussed, mineralogical and chemical configuration of biomass, the ash consists of numerous metallic oxides which makes ash to be used as catalyst in different reactions [97, 98]. Number of studies states that BFA shows good characteristics when used as catalyst in hydrocracking, deSO$_X$, hydrocarbon oxidation, H_2 and deNO$_X$ [98-100]. This wide range of uses are due to chemical configuration of ash especially because of presence of AL_2O_3 and SiO_2 which increases thermal stability [101]. Between several kinds of ash, the ash acquired from rice husk can be used as catalyst and support for catalyst in various reactions. Various studies show Ni/ Cu supported rice husk ash as catalyst in hydrogenation [102]. Balakrishnan et al [101] tells the use of ash acquired from rice husk in large volume for catalysis and for synthesis of catalyst. It increases the surface area in thermal treatment. Ash supported with CaO has been used in condensation reactions, in process of transesterification [103]. But still the biomass ash catalysis delivers cost effective and friend environment approach for recycling of fly ash [98].

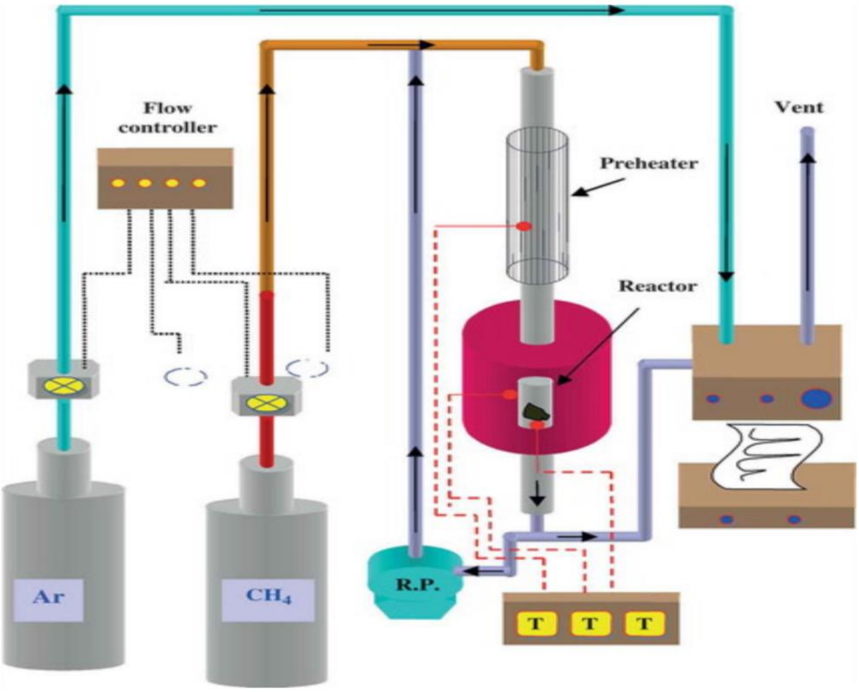

Figure 2.14 (a) Experimental setup for methane decomposition [103]

In Figure 2.14 (a) the experimental setup of methane decomposition when biomass used as catalyst. At different flow methane gas is supplied to check the conversion and hydrogen production.

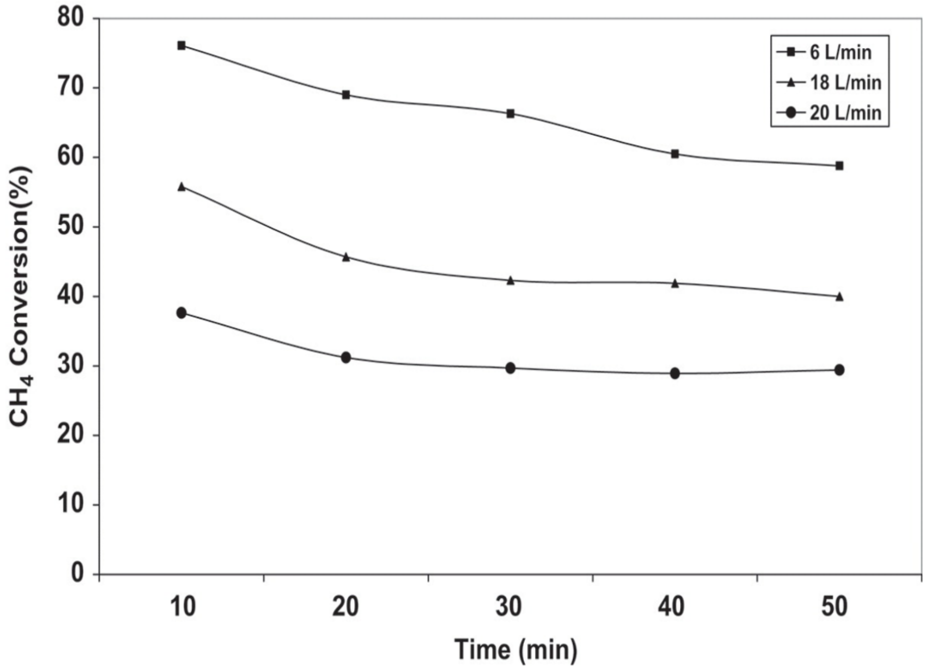

Figure 2.14 (b) Methane conversion with respect to different flow rate [103]

Figure 2.14 (b) methane conversion with different flow rates. At 6L/min the conversion of methane is more due to less flow rate as compare to other because retention time of reaction is increased.

2.7 Summary

To reduce the greenhouse emissions, the utilization of biomass is proficient path for producing power and its impact on accumulative carbon footprint. Generation of power from these sources (biomass) produces residue majorly in the form of ash. However, as demand of power production rises, the utilization of the biomass as feedstock increases resultantly the quantity of residue (ash) rise in power plants. Formation of the ash in biomass power plants nurtures number of problems exclusively handling of ash and its utilization for energy applications. The continuous rise in ash quantity will challenge ash storing facilities while increasing management, transferring and dispersal costs. Direct disposal to the landsides may have noteworthy effects on soils and reprocessing of soil nutrient. This review investigates the basic challenges in biomass ash production, environmental concerns, and handling issues.

Furthermore, the review explores the various opportunities in the biomass ash utilization in conventional application such as agriculture, construction, and cement industry. Moreover, the status and prospects of ash utilization in nanotechnology specially in the industrial catalysis has been elucidated. The recommendations were also made to pave the path for efficient utilization of biomass ash to improve the overall economy of the biomass-based power pants.

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Chapter 3

Methodology

3.1 Preparation of samples of biomass ash for ash fusion determinator

The samples of biomass fly ash (BFA) and biomass bottom ash (BBA) were taken from local Packaging company having biomass power plant in Kasur, Punjab and as standard coal fly ash (CFA) was delivered by CKIC, China. The blend of biomass ash comprises of corn stalk, wooden packaging, rice straw, wheat straw and black liquor obtained from paper industry. Before experimentation, to remove moisture content all samples CFA, BBA and BFA were kept in oven 120 ˚C for 5 hrs. Preparation of samples for ash fusion determination is shown in Fig 3.1. For grinding the sample Hard grove Grindability Index Tester (USA, ASTM D 409-08) was used to make the samples suitable for ash fusion experiment as displayed in Figure 3.1 (a). After grinding the required size for ash fusion determinator was less than (0.2 mm) for that the samples of ash were strained in Sieving WS Tyler RX-29-10 (USA). Samples of ash were added in beaker where solution of binder and deionized water was prepared. Paste of samples were prepared by making cones in mould which was 20 mm in height and 6 mm bottom.

3.2 Ash fusion analysis

Ash Fusion determination5E-AF4000 (CKIC, China) was used for the experiment via using standard GB/T 219-2008, ISO540-1995(E). Camera with high resolution was fitted and software 5E-AF4000 was used to capture pictures of cones sample with different temperature (HT, ST, DT, OT and FT) as shown in Figure 3.1 (b). Oxidizing environment was created for the experiment. The cup made of ceramic was placed on alundum tube located in furnace compartment and heated at rate of 25 ˚C min-1 from 200 ˚C to 850 ˚C and after achieving 850 ℃, the heating rate was automatically decreased up to 5 ˚C min-1.

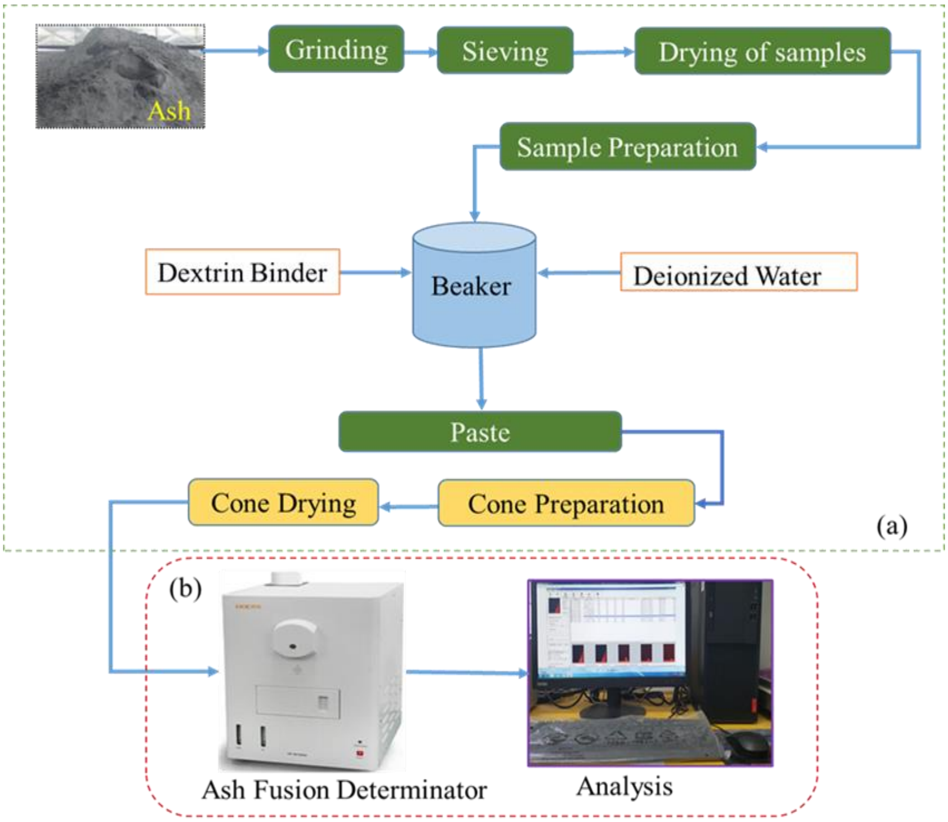

Figure 3.1 (a) Diagram for preparing ash samples (b) Experimental system for ash fusion determinator

At each 15˚C rise the images were captured through digital probe which was fitted in furnace. Five type of temperatures were obtained from determinator like spherical temperature (ST), flow temperature (FT) hemispherical temperature (HT), deformation temperature (DT) and original temperature (OT).

3.3 Characterization of ash samples

3.3.1 CHN Analyzer

To view the percentage of carbon, hydrogen and nitrogen in ash samples CHN Analyzer (5E-CHN2200, CKIC, China) was used. The required particle size of ash was less than 0.2 mm for CHN analysis. 80 mg of each sample CFA, BBA and BFA was used for analysis. The gases required for that was O_2, N and He were used in CHN analysis.

Figure 3.2 CHN Analyzer

3.3.2 Sulphur Analyzer

For determining the percentage of sulphur in the CFA, BFA and BBA Sulphur Analyzer 5E-IRS II (CKIC, China) was used. 1350℃ was the required temperature of furnace while 50℃ was required for oven and flowrate of O_2 was 20 mL min-1.

Figure 3.3 Sulphur Analyzer

3.3.3 X-Ray Diffraction

To determine physicochemical properties, X-ray diffraction was conceded using D8 Advance (Bruker Advanced, Germany) provided with Bragg-Brentano pattern and scintillation sensor with radioactivity wavelength of 1.5328 Å was used to inspect the phase identification. From 5° to 90° and step size 0.05° per 5 s the samples were scanned. Software used for determining the phase identification was DIFFRAC Plus EVA Version 5.0. Moreover, SEMJEOL JSM-6490A (Japan), morphology of CFA, BBA and BFA was examined.

Figure 3.4 X-Ray Diffraction

3.3.4 Thermogravimetric analysis

Thermal strength of samples CFA, BFA and BBA was analyzed via using TGA 5500 (TA Instruments, USA). For purging, N_2 gas was supplied at flow rate of 40 mL min-1 for 45 minutes before the analysis started starting analysis. For TGA 10 mg of sample was used. The maximum temperature at which sample was heated at 900℃ with flow of nitrogen gas 40 mL min-1 with 5℃ min-1 heating rate.

Figure 3.5 Thermogravimetric Analyzer

3.3.5 Fourier Transform Infrared Spectroscopy

To see the functional groups in CFA, BFA and BBA FTIR was performed using Cary 630 (Agilent Technologies, USA). Resolution of 2 cm-1 with absorption range of infrared spectra was 4000 to 650 cm-1 was scanned.

Figure 3.6 Fourier Transform Infrared Spectroscopy

3.3.6 X-Ray Fluorescence

To view the elemental composition of CFA, BFA and BBA Elemental Analyzer JSX 3202 M (JEOL, Japan) was used for that. The pallets with circular shape were formed for the analysis. 5 g of sample was isostatic pressed at 45 MPa in the vacuum environment. Nitrogen in liquid from was used for that analysis at flowrate of 25 mL min^{-1}.

Figure 3.7 X-Ray Fluorescence

3.4 Amendment of biomass ash samples

Using hydrothermal method CeO_2 particles were prepared. To make solution of 0.1 M $Ce(NO_3)_3$ was added in desired quantity. Dropwise the NaOH solution of 0.3 M was added to nitrate solution with continuous stirring for 4 h at room temperature.

After obtaining solution in slurry form it was put into Teflon autoclave and kept for 160°C in oven for 24 h. Through centrifugation process the obtained precipitates were separated at 9000 rpm for 30 min. The attained sample was oven dried at 120 ℃ and calcined at 800 °C. By using CeO_2 as nano particles the two samples BFA and BBA were altered by introducing in beaker via adding 60 mL of deionized water with continuous stirring at 70 °C. CeO_2 particles were added in the solution after 15 min, with stirring for 4 hours at 120 ℃ for removing the water and oven dried for overnight at 120 °C. Three different loading of CeO_2 nanoparticles (5, 7, 9 %) were loaded.

3.5 Characterization and preparation of Co/BFA catalyst

Via wet impregnation process Co loaded BFA was prepared. To make the solution of 0.1 M nitrate specific quantity of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) was added to deionized water. After continuous stirring for 15 min at 65°C, 1 g of BFA was added to precursor solution. The obtained solution was stirred for 4 h at 120 °C and after stirring it was oven dried overnight and for 5 h calcined in furnace at 800 ℃. To determine physicochemical properties and characteristics and check suitability for methane decomposition the obtained sample was characterized via using TGA, SEM and XRD.

3.6 Experimental setup for methane decomposition and calculations

Experimental setup for methane decomposition is shown in Figure 3.8**.** Mass flow controller with model (MF4603-n1-1-bv-a, Servoflo Corporation, USA) was used for feed gas, CH_4. The reactor comprises of cylindrical SS steel (SS-316) tube with dimension14 mm outer diameter, 40 cm in length and having 12 mm inner diameter. Catalyst was loaded in mid of reactor tube which was gripped by quartz wool. For measuring the temperature of reactor thermocouple was positioned near catalyst bed. The product and feed gases were introduced into Gas Chromatograph (GC-2010 Pro, SHIMADZU Japan) equipped with TCD column (RT-MS5A, 30 m x 0.32 mm ID, 30 µm) used to detect H_2, CO_2, CH_4, and CO.

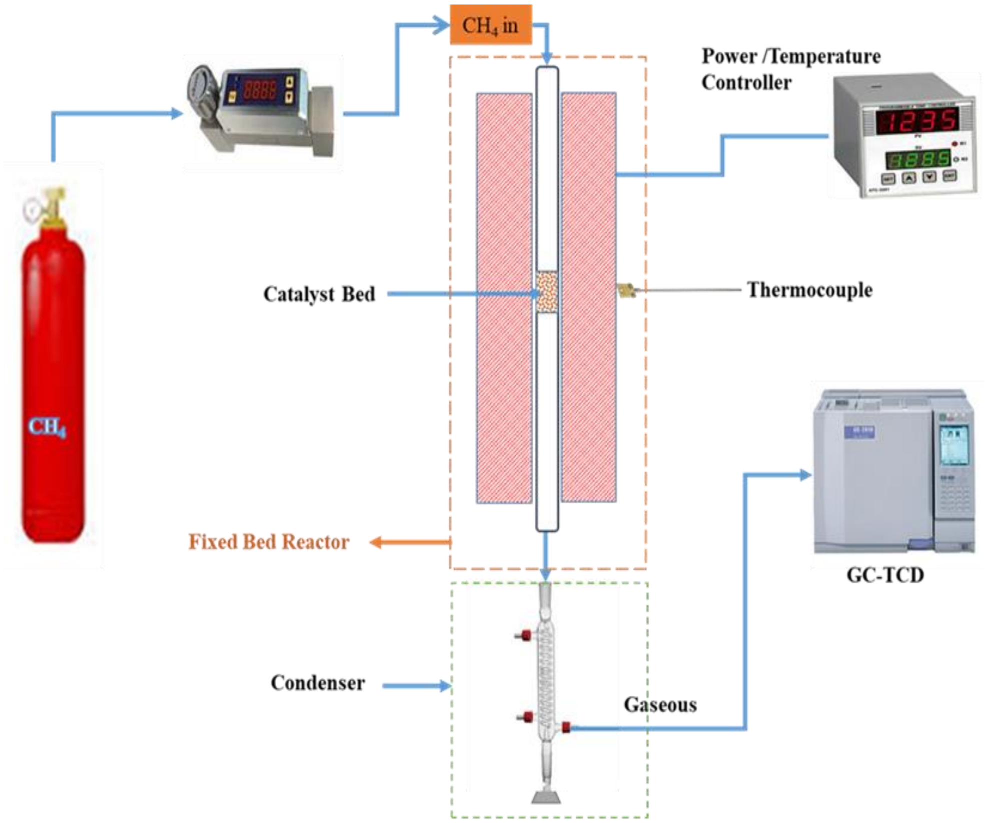

Figure 3.8 Schematic of methane decomposition experimental setup

The performance of fixed bed reactor in methane decomposition was analysed based on CH_4 conversion (Eq. 2) and H_2 selectivity (Eq. 3) and H_2 yield (Eq. 4). Every experiment was repeated thrice, and average values were reported in each parameter to reduce the experimental errors.

$$CH_4\,\text{conversion}\left(X_{CH_4}\right)\% = \left[\frac{(\,nCH_4)_{\text{converted}}}{(nCH_4\,)_{\text{in}}}\times 100\right] \tag{2}$$

$$H_2\ \text{selectivity}\left(S_{H_2}\right)\% = \left[\frac{(nH_2\,)_{\text{produced}}}{(2\times nCH_4)_{\text{converted}}}\times 100\right] \tag{3}$$

$$H_2\ \text{Yield}\left(Y_{H_2}\right)\% = \left[\frac{(nH_2\,)_{\text{produced}}}{(2\times nCH_4)_{\text{in}}}\times 100\right] \tag{4}$$

Chapter 4

Results and Discussion

4.1 Biomass ash characterization

Ultimate analysis was performed to determine the percentage of carbon, hydrogen, nitrogen and sulphur content in ash samples. Figure 4.1(a) shows the sulphur analysis in CFA, BFA and BBA. The maximum amount of sulphur (6.3%) is present in CFA as compared to BFA (4.4 %) and BBA (0.9%). This is due to sedimentary environment of coal seams whereas in biomass, origin and growing conditions affect the sulphur contents. However, Figure 4.1(b) shows carbon content in ash samples. The analysis verifies that BBA had highest percentage of carbon (17.8%) due to unburnt organic matter and the desired fusion temperature had not achieved while in CFA it was (1.2%) due to partly complete combustion. However, in Figure 4.1(c) hydrogen percentage was found to be negligible in analysis. There was zero nitrogen detected in the analysis.

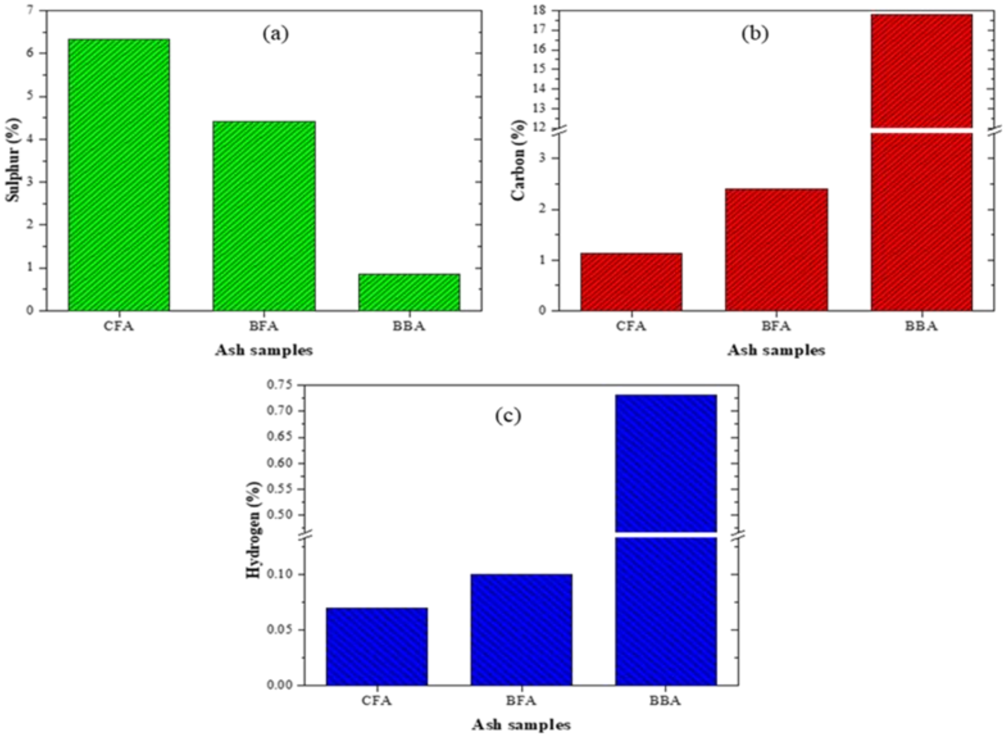

Figure 4.1 CHN-S (a) sulphur analysis (b) carbon analysis (c) hydrogen analysis of ash samples analysis

Figure 4.2 presented the acquired XRD peak patterns of the biomass ash and modified ash samples along with CFA as standard case. The samples show both amorphous and crystalline phases. Table 4.1 and Figure 4.2 displayed all recognize phases associated with XRD pattern. Firstly, in CFA the major peak represents $CaSO_4$ (PDF# 37-1496) at 2θ=25.5◦ with main plane (020) [1]. SiC (PDF # 29-1129) was detected at 2θ=35.5◦ with main peak (111) [2]. The $CuFe_2O_4$ (PDF# 25-0283) was found the main peak at 2θ=35.6◦ having hkl (311) [3]. While the $CaCO_3$ having PDF# 47-1743, was detected at 2θ= 29.4◦ with plane (104) [4]. As represented in Figure 4.2 simple BFA shows various peaks in crystalline phase. Ca (PDF#10-0348) was detected at 28.3° with main phase (101) [5]. SiO_2 (PDF# 46-1045) was scanned at angle 26.5° with phase (101) representing crystalline form [6].

Also, K_2O with pdf# 23-0493 was presented at angle 39.5° the main phase (220) and Fe_2O_3 (PDF# 16-0653) was found at angle 32.8◦ [7], and Al_2O_3 (PDF# 46-1131) was present at angle 30.3°, hkl (020) as major peaks [8]. Presence of higher content of SiO_2 generates low melting composite [9]. Furthermore, XRD of BBA showed several materials in various forms. The SiO_2 (PDF# 46-1045) was detected at 2θ=26.6◦, with main phase (101). The $CaCO_3$ (PDF# 47-1743) was identified at angle 29.4° (104).

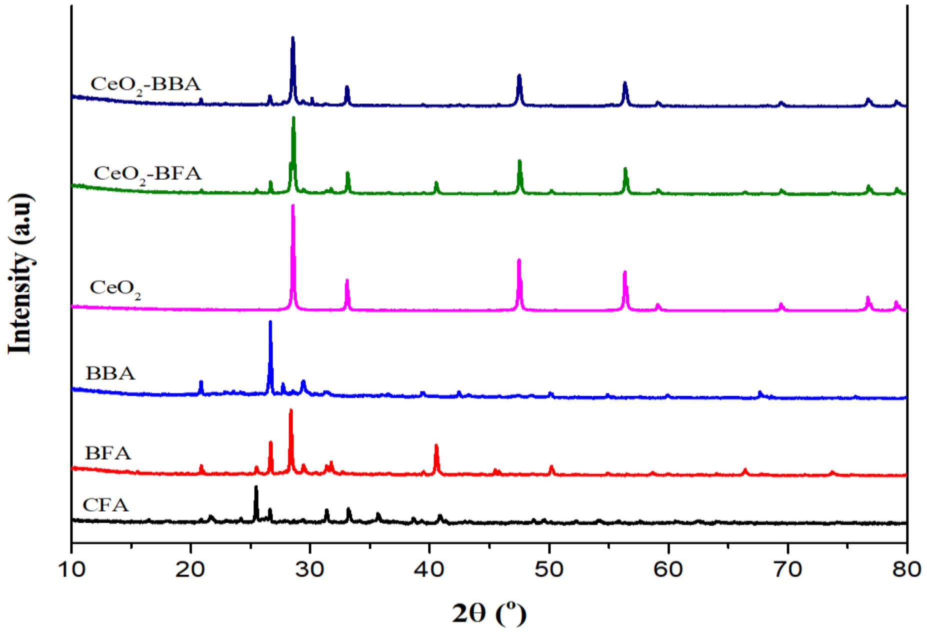

Figure 4.2 XRD analysis of the samples

And Fe_2O_3 with (PDF# 16-6653) identified at angle of 32.8◦, hkl (420). was also presented in BBA. In XRD pattern of CeO_2 modified BFA was presented in Figure 4.2.

Table 4.1 XRD analysis

Samples	Compound	PDF #	2θ (°)	Phase *(hkl)*
CFA	$CuFe_2O_4$	25-0283	35.6	*(311)*
	SiC	29-1129	35.5	*(111)*
	$CaSO_4$	37-1496	25.4	*(020)*
	$CaCO_3$	47-1743	29.4	*(104)*
BFA	$CaSO_4$	37-1496	25.4	*(020)*
	$CaCO_3$	47-1743	29.4	*(104)*
	Ca	10-0348	28.3	*(110)*
	SiO_2	46-1045	26.5	*(101)*
	K_2O	23-0493	39.47	*(220)*
	Fe_2O_3	16-0653	32.8	*(420)*
	Al_2O_3	46-1131	30.3	*(020)*
BBA	SiO_2	46-1045	26.6	*(101)*
	Fe_2O_3	16-0653	32.8	*(420)*
	$CaCO_3$	47-1743	29.4	*(104)*
CeO_2	CeO_2	43-1002	28.5	*(111)*
CeO_2-BFA	Ca_2SiO_4	23-1042	33.0	*(110)*
CeO_2-BBA	SiO_2	47-1300	28.6	*(211)*

CeO_2 showed significant crystalline phase (PDF # 43-1002), $2\theta=28.5^\circ$, hkl=111 displays sharp diffraction pattern but remaining compounds were same as in XRD of BFA. The CeO_2-BBA, CeO_2 (PDF # 43-1002) was presented and SiO_2 (PDF# 47-1300) angle of 28.6° (211) is detected however, the rest of the peaks were showing same as in simple BBA sample. All in all, the biomass ash samples showed the metal oxides such as Fe_2O_3, Al_2O_3 and SiO_2 a suitable support for catalyst synthesis and zeolite formation.

The morphology of the ash samples was analysed using SEM presented in Figure 4.3**.** Figure 4.3 (a) shows in micrograph of BFA that depicts the amorphous structure in the form of agglomerated particles with irregular shapes while Figure 4.3 (b) depicting BBA showed the micro flake like structure. Flake structures were usually considered as more suitable for catalytic application while incorporating the other metal and metal oxide.

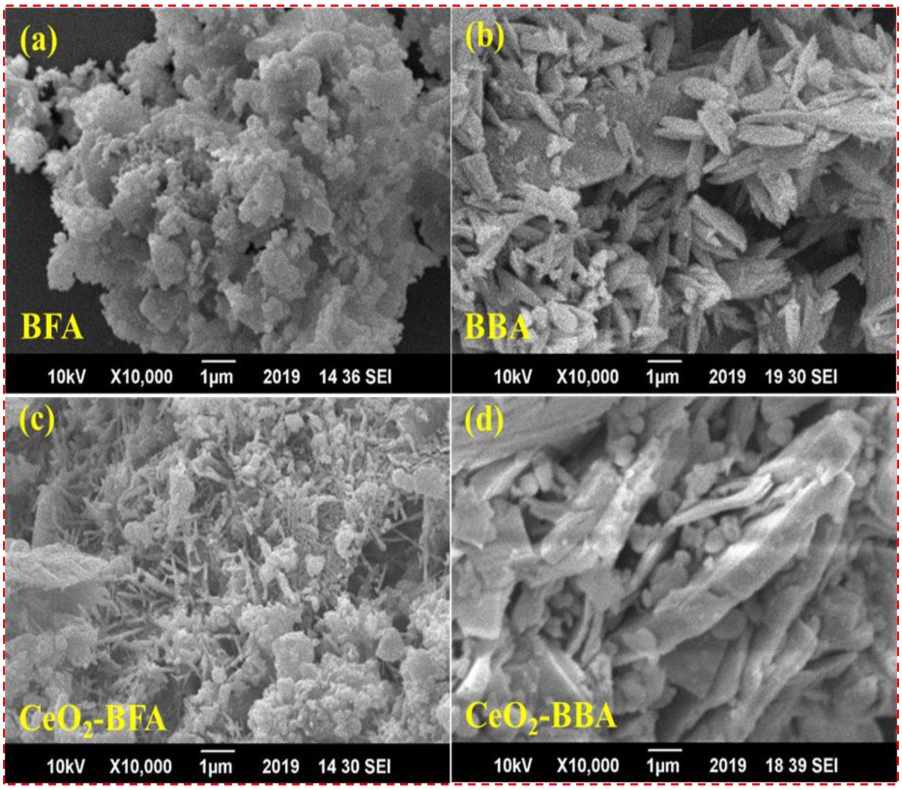

Figure 4.3 SEM micrographs biomass ash and modified biomass ash samples (a) BFA (b) BBA (c) CeO_2-BFA (d) CeO_2-BBA

While modifying the ash samples with the addition of CeO_2 leads to evolution of structure in the organic and as well as inorganic constituents. In Figure 4.3 (c) the nano wire like structure was formed after the addition of CeO_2 to BFA. CeO_2 had reduced the silicates and aluminates ratio and properly fused into the structure. The addition of CeO_2 into BBA Figure 4.3 (d) formed a complete micro flake structure with the dispersion of CeO_2.

The thermal stability and weight loss of the ash samples were analysed by TGA presented in Figure 4.4**.** Several inorganic matter which including Si, Al, Fe, Ca etc. evaporates at high temperature. The obtained TGA curves were divided into three phases. First phase was usually described for moisture removal which was observed at less than 200 ℃. In second phase significant amount of weight loss was observed in between (200- 600) ℃ which described the oxidation of organic matter while the last phase was from temperature ranging from (600 - 900) ℃ mostly describes the transferring and reactions of inorganic matter (Valencia et al., 2012). In Figure 4.4 (a), the significant weight loss was recorded between 300 ℃ to 900 ℃ which describes the oxidation of organic matter and transferring into another phase like Si, Fe, Ca etc. The total weight loss in the sample was about 14%. Figure 4.4 (b) showed the weight loss of the ash sample BBA. The moisture content was removed under 200 °C while the weight loss between 200 ℃ to 600 ℃ showed the oxidation of unburnt particles in bottom ash. Presence of bulk number of unburnt particles is the reason of weight loss that has been observed between 200 ℃ to 600 ℃. The total weight loss was about 38 % in BBA sample.

However, for the CeO_2 modified ash samples, the weight loss with respect to temperature was reduced. In case of CeO_2-BFA Figure 4.4 (c), the mass reduction was almost (7%). Ash sample become more stable and maximum weight loss can be seen from temperature ranging 600 ℃ to 900 ℃. Ratio of base to acid was changed by addition of CeO_2 which stabilized thermally. Moreover, Figure 4.4 (d) shows the total weight loss of 21 %. By the addition of CeO_2, the weight loss was approximately reduced from 38% to 21% which showed that the addition of CeO_2 changed the morphology and composition of samples and enhanced the thermal stability. Figure 4.4 (e) shows the TGA curve of CeO_2 with maximum weight loss was about 5 % mostly associated with the removal of moisture content.

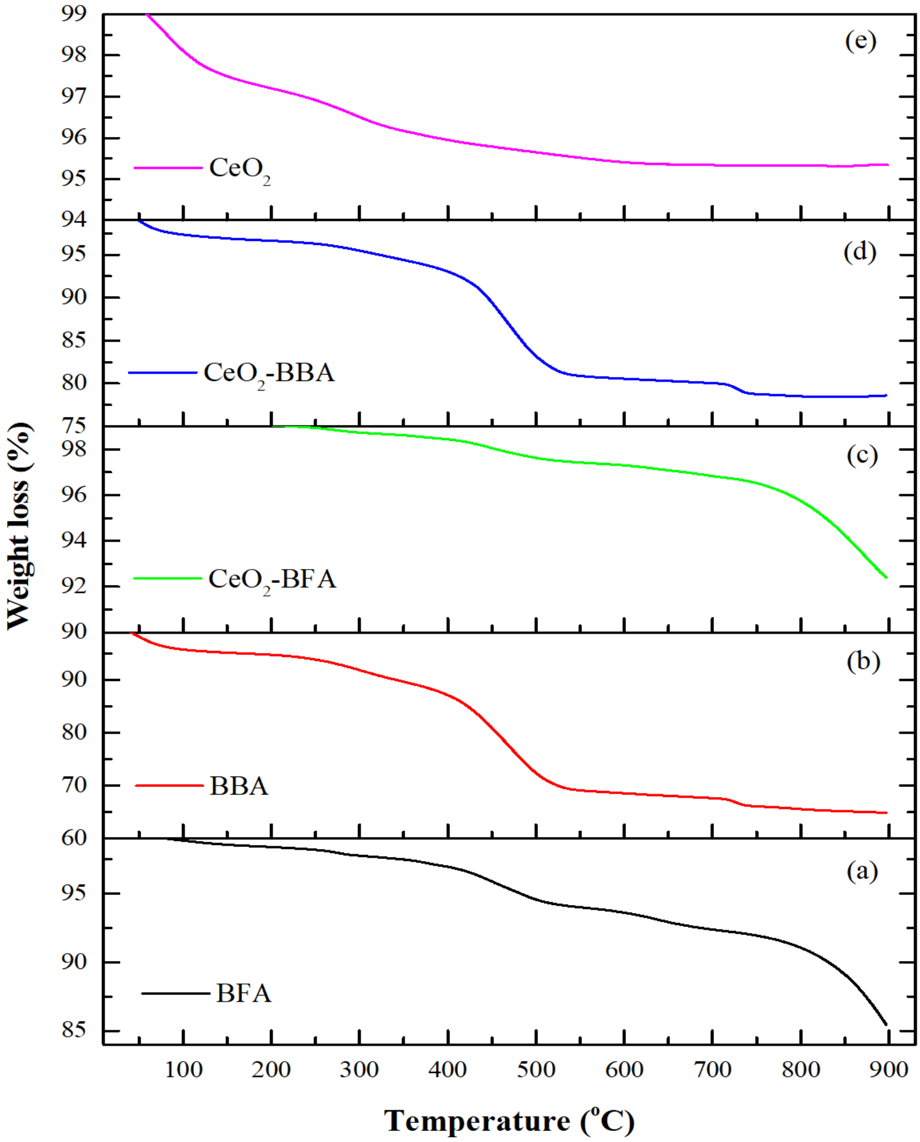

Figure 4.4 TGA profiles for the samples

Figure 4.5 shows the FTIR analysis of the ash samples. This reveals the typical appearance for BFA, BBA and CFA. bands relevant to vibrations. In CFA, BFA and CeO_2-BFA, the major peak with wavenumber (1110 cm-1) represents the stretching vibrations of Si-O. Furthermore, in BBA, CeO_2-BBA, CFA, BFA and CeO_2-BFA, the spectral band throughout at (1420 cm-1, 880 cm-1) was distinct of asymmetric tensile vibrations C=O which proposes the appearance of carbonate compounds in the ash samples. Peak of band associated with existence of calcium sulphates in form of anhydrite can be noticed at 678 cm-1 in CFA. In sample of BBA and CeO_2-BBA the peak having wavenumber (975 cm-1) represents Si-O. The OH functional group does not exist indicating the absence of moisture and which shows the suitability for the catalytic applications

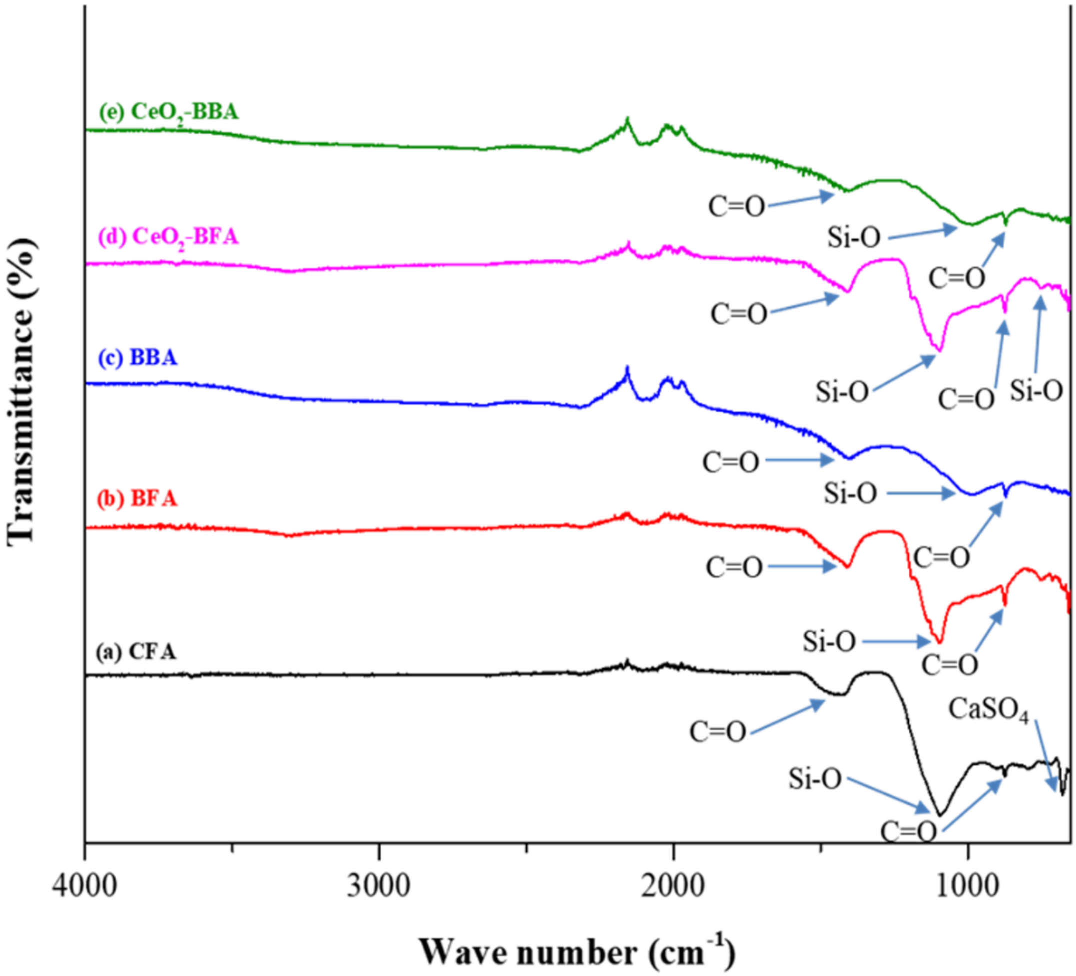

Figure 4.5 FTIR analysis of the ash Samples

The composition of the ash samples is analyzed by XRF presented in Table 4.2. The percentage of main elements are varying owing to contrasting origin. Main constituents in ash are SiO_2, Fe_2O_3, SrO and CaO etc. in the configuration of oxides, carbonates and silicates which may be responsible for formation deposits on heat transfer surfaces during the power generation application in a biomass fed boiler.

In case of BFA and BBA samples, the combined percentage of SiO_2 and Fe_2O_3 was 76% and 81.8% respectively. After modification of ash samples, concentration of sulphates and calcites had been changed by varying ratio of other elements. Percentage of SiO_2 and Fe_2O_3 in BFA has been reduced to 42.6% to 18.8% and in case of Fe_2O_3 it reduced from 33.4% to 22.6%. However, in case of modification of BBA, formation of magnesium oxide had been observed and the percentage of Fe_2O_3 has been changed from 42.1 to 24.4%. Hence, the achieved results of XRF has established that cerium oxide (CeO_2) had distinguished the major elements present in ash by decreasing the percentage of calcites and sulphates which cause fouling and slagging in boiler. Generally, existence of CaO and Fe_2O_3 decrease ash fusion temperature. As the result showed that different oxides were present in as a sample which expressed the suitability to utilize in catalytic applications.

Table 4.2 XRF analysis of ash BFA, BBA and CeO_2-BFA/BBA

Constituents	**BFA (%)**	**BBA (%)**	**CeO_2+BFA (%)**	**CeO_2+BBA (%)**
SiO_2	42.6	39.7	18.8	13.2
K_2O	4.1	1.4	1.34	0.6
CaO	7.4	7.1	2.8	2.4
Fe_2O_3	33.4	42.1	22.6	24.4
ZnO	0.7	0.4	-	-
Br	1.7	-	-	-
SrO	10.3	7.1	3.7	2.6
PbO	0.6	-	-	-
TiO_2	-	0.10	-	-
MnO	-	1.3	-	-
CeO_2	-	-	10.7	9.5
MgO	-	-	-	7.3

4.2 Ash Fusion Analysis

To investigate the fusion temperature of ash samples, variation in height of cone with respect to temperature was obtained. Figure 4.6 illustrates the four key ash fusion temperatures throughout contrasting steps in fusion of ash and modified ash samples. It was observed that CFA has high ash fusion temperature as compared to

BFA and BBA fusion temperature. This is actually due to difference in ratio of SiO_2/Al_2O_3 in CFA and biomass ash. Whereas in case of BFA and BBA, the breakdown of structure occurred at high temperature which further leads to the oxidation of unburnt organic material and produces holes and wide pores in sample. Original temperature (OT) is almost the same for all samples, because there is no effect on composition of minerals and structure is well-known.

Prominent mass reduction starts after 930 °C, as the temperature increases, the reduction in mass starts and the elements start to vaporize in the moderate heating rate which was 5°C min-1. However, in the case of CFA the initial DT was 1298 °C. The fusion of aluminates and silicates phases increased the fusion temperature due to heating process, loss of potassium and chlorine rise. When the DT is achieved and temperature reached about 1300°C, the carbonates start to melt until all the carbonates were evaporated, subsequently the ST (base of ash cone is equal to its height) appears at 1312 °C and after that the remaining high melting oxides were evaporated until HT (base of ash cone becomes twice to its height) (1321°C) was achieved. The ash becomes liquid at the end of FT (1327 °C) because high melting point elements are completely oxidized.

The ST is detected as the key temperature in boiler operations, because approximately all active metal like nickel potassium etc started to evaporate with lower heating rate. Eutectic compounds exist in BFA and BBA due to the alkaline nature of the biomass. The composition of biomass based ash consisted of metal oxides and silicates which resulted in low fusion temperature. In biomass ash samples, it was observed that the difference in all temperatures was low. Variation in the melting temperature was observed in obtained ash samples. OT represents that there was no effect of heat on minerals which is 928 °C in case of BFA and BBA as presented in Figure 4.6. The DT for BFA was achieved at 1172 °C while DT for BBA was recorded on 1162 °C. DT of BBA was less as compared to BFA was due to presence of K_2O The biomass ash samples were shrunk when the DT achieved due to decrement in area.

The high content of SiO_2 generates low melting composite while reacting with alkali oxides which was further confirmed during XRD and XRF analysis. Due to small temperature difference, biomass ash condenses rapidly and directly starts to deposit on heating surfaces. Presence of Al_2O_3 in BFA increases the DT which was confirmed later in XRD. In ST (1187 °C) and HT (1192 °C). Figure 4.6, morphology of samples was changed due to the vaporization of carbonates. The FT of BFA was (1195°C), upon which the area of the cone ash sample has been increased. While in BBA the ST was (1196 °C) it was higher than simple BFA which was due to presence of MnO. The HT of BBA is 1207 °C, due to melting properties which affects from the eutectic compounds and carbonates vaporize. while the FT of BBA was 1211 °C, in which the area of cone ash was increased.

Figure 4.6 and all fusing mineral oxidized. However, after modification of BFA and BBA using CeO_2 nanoparticles, there were significant changes in ash fusion temperature as demonstrated in Figure 4.6, DT of CeO_2-BFA was reduced to 1063 °C. These changes had been observed due to the difference in decreasing base to acid ratio but there was bulk change in ST of CeO_2-BFA (1318 °C). As the melting temperature increases, the morphological variations occur which further disintegrated to the pore formation and surface of the modified CeO_2-BFA. HT of CeO_2-BFA was recorded 1357 °C. The percentage of Cl and potassium was directly interlinked with the fusion temperature. The increasing H was observed due to the decreased amount of K by increasing temperature which was also confirmed by XRF. Furthermore, the FT of CeO_2-BFA has been increased up to 1369 °C. It was examined in morphological studies that the structure of cone ash sample has been changed. The pores in sample was decreased and as well as diameter was also affected, comparatively it was increased

In modified CeO_2-BBA, the DT decreased to 974 °C due to formation of smaller holes in the structure and frequent removal of low melting point elements such as Zn. XRF confirmed formation of smaller amount of MgO. The ST of modified CeO_2-BBA was 1317 °C Figure 4.6. Diameter of pore structure was directly proportional to the fusion temperature. Hence the diameter of pore structure of ash cone sample increases as the temperature increases. Obviously, it will also affect morphology of cone ash sample. While the HT of CeO_2-BBA was 1343 °C Figure 4.6, the addition of CeO_2 increased the thermal stability of ash sample and improved surface functionality to absorb all organic compounds. At FT (1347 °C), all solid changed into liquid. Melting temperature of biomass ash is greatly influenced by characteristics of CeO_2 whereas physical and chemical properties of ash tends to effect scaling and fouling.

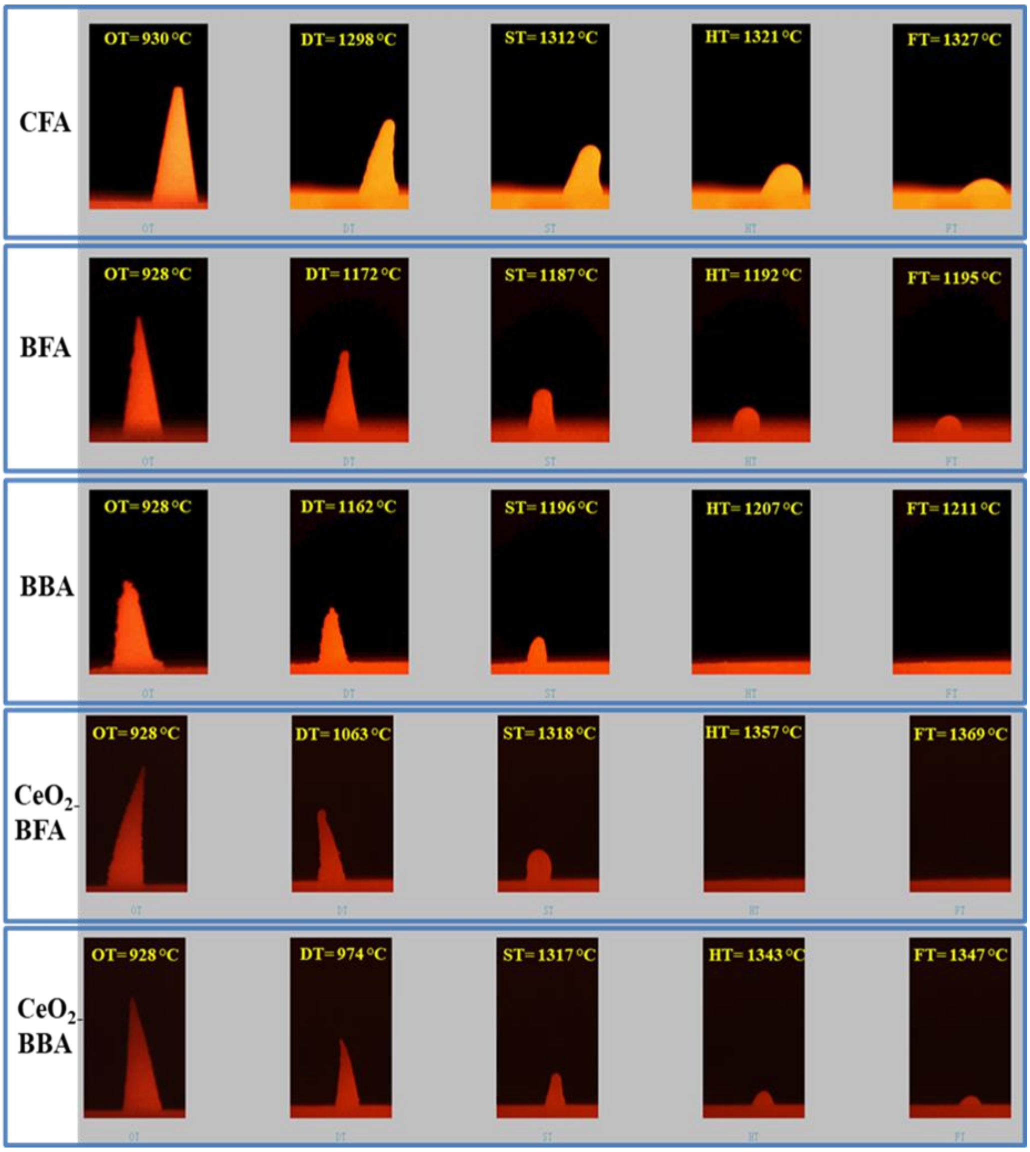

Figure 4.6 Ash fusion analysis of simple and modified biomass ash samples

4.3 Ash Prospects for industrial applications

The biomass ash characterization reveals that the carbonates, SiO_2, Fe_2O_3 and SrO were prominent elements in the ash. These elements find their application in various industrial processes like excessive amount of Ca in fly ash assist to enhance pH value. BFA used in soil encouraged yield and plant growth due to presence of elements such as Fe, K, Mg etc. So BFA can be utilized in acidic soil. SOx and NOx plays vital role in harmful emissions. In scrutinizing biomass-based ash samples, sulphur content was minimum and nitrogen less hence ash samples are fine for climatic change. Moreover, biomass ash can be used to eliminate H_2S from biogas plants. Utilization of ash can be used for cleaning flue gases by removal of harmful gases because of adsorption phenomena and production of ceramics by increasing strength. BFA consists of less content of unburnt carbon and bulk percentage of silicates, so synthesis of zeolite was possible under these properties.

For various applications like treatment of water and adsorption of gas, zeolites have been made from ash. BFA from different sources shows same pozzolanic properties when mix in concrete to increase performance. More importantly, the biomass ash can be used as a support system for catalyst synthesis for various reforming processes. Apart from economic suitability, fly ash impacts favourably on resulting concrete used in cement. Such effect involves reducing water demand, cement to water ratio, decrease in heat evolution and provides solid support to steel structure. Additionally, BBA increases the material porosity and decreases thermal conductivity, hence it is good for building blocks. Somewhat BBA displays such properties which are good for using as filler in road construction and furthermore can be utilized in concrete.

Presence of unburnt carbon in BBA permits ash usage as a fuel. Use of this unburnt carbon enhances residence time and material agitation in boiler. Contrarily to this biomass ash, leaching from water-soluble can be employed for recovery of components, combination of various minerals and manufacturing of materials. Although constituents of water-soluble in biomass ash can capture and depot atmospheric CO_2. Additionally, ash can be exploited for manufacturing of geopolymers. Their composition depends upon the base material present in ash. In order to utilize the biomass ash, the performed detail analysis of ash sample showed good characteristics and properties which are feasible to use as a catalyst support for catalysis. The cobalt impregnated BFA sample was tested for cracking of methane to validate the BFA suitability for catalysis application. Various characterizations were performed before and after cracking of methane to check the stability.

4.4 Biomass ash as catalyst for Methane Cracking

4.4.1 Characterization of fresh Co/BFA catalyst

The XRD of fresh Co/BFA was presented in Figure 4.7 (a). The co loaded BFA showed the metallic form Co at 2θ = 44.2° with hkl (111) PDF#15-0806 with d-spacing of 0.204. The oxide (Co_3O_4) form was also detected at 2θ = 36.8° with hkl (311), space group fd3m(227) with d-spacing of 0.24. Figure 4.7 (b) illustrates the TGA of Co/BFA catalyst. TGA identified the thermal effects that ensure due to chemical and physical properties. There was no significant weightless until 600℃. The 4% weightless was observed above 600°C. Oxidation of organic matter was second zone ranging from (200 – 600) ℃ and the last zone was transferring and reactions of inorganic matter till 900 ℃.

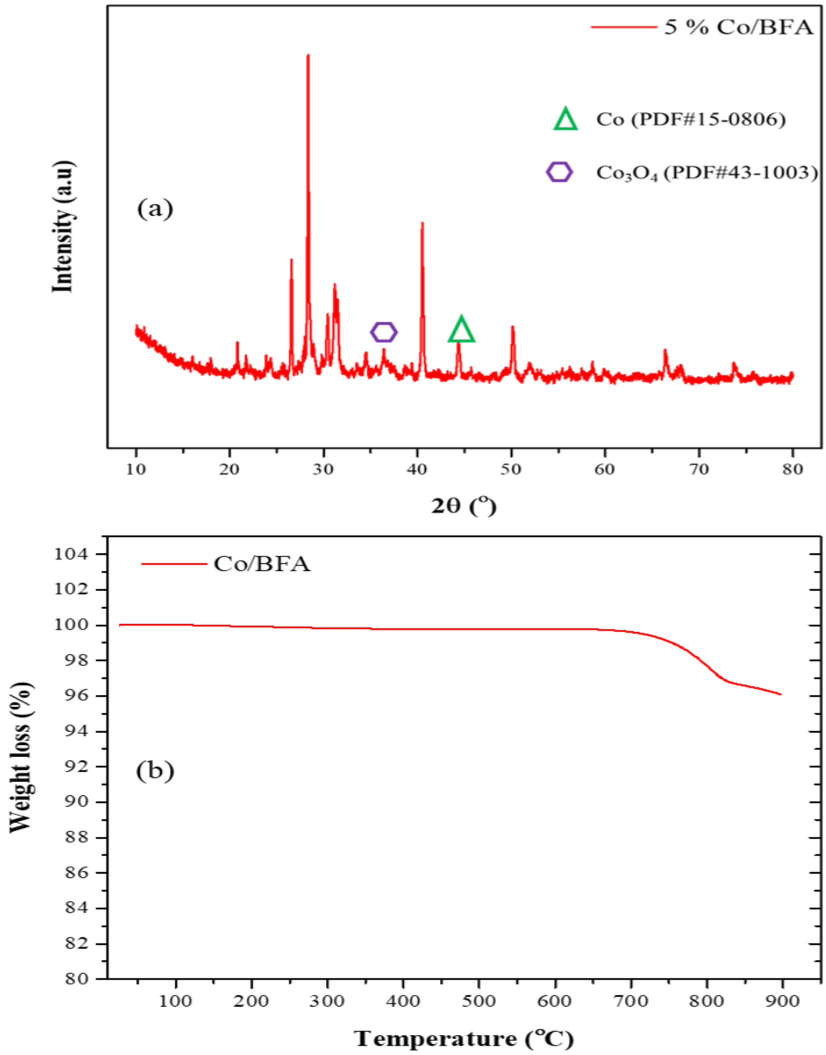

Figure 4.7 (a) XRD of fresh 5% Co/BFA (b) TGA profile of fresh 5% Co/BFA catalyst

The Figure 4.8 showed the SEM images of fresh Co/BFA catalyst with two different magnifications. The irregular structure in form of bits was presented in SEM image presented in Figure 4.8 (a). The impregnated Co can be seen in fresh catalyst sample which is further confirmed in XRD. After the fusion of Co into BFA, the agglomerated sample structure was transformed into crystalline structure. However, in

Figure 4.8 (b) at higher magnification gravestone type structure was observed. Co was intermixing with BFA and non-uniform particles were obtained.

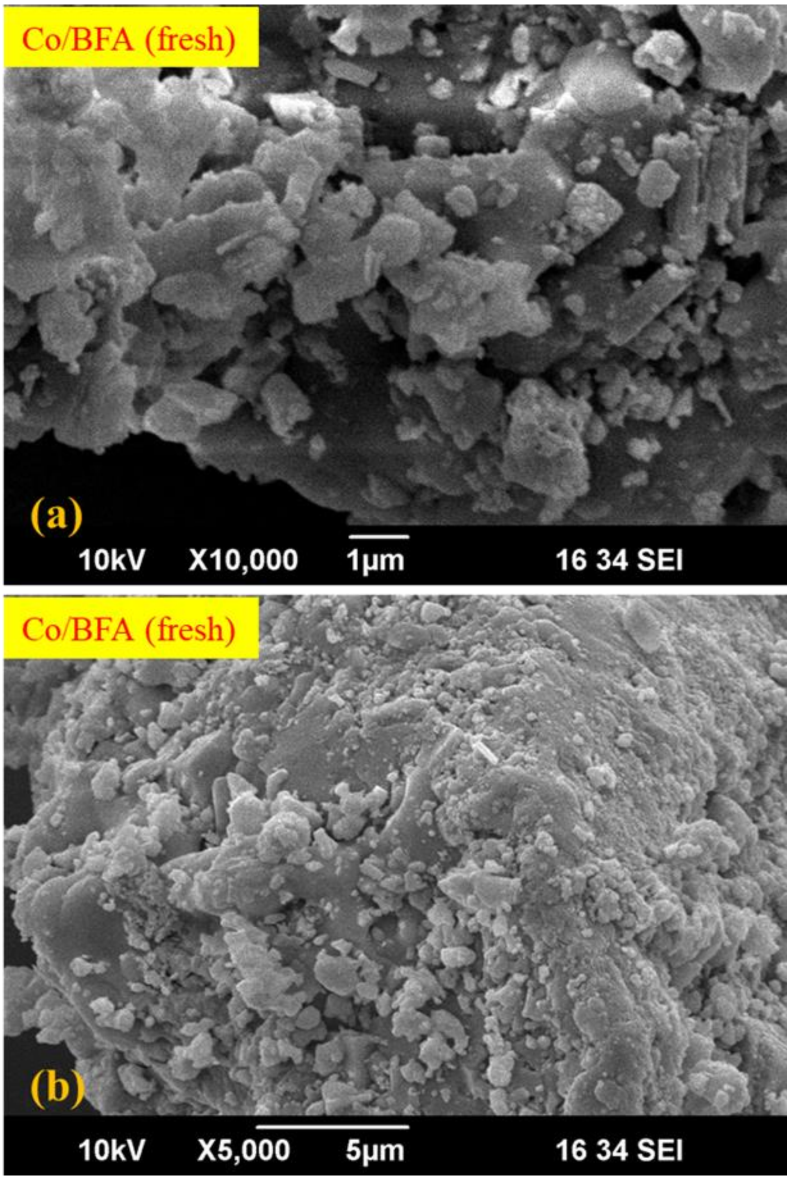

Figure 4.8 SEM micrographs of Co/BFA catalyst (a) 1 µm (b) 5 µm

4.4.2 Catalytic activity on methane decomposition

Figure 4.9 (a) illustrates the CH_4 conversion over different Co loadings on BFA. The increasing trend in conversion of CH_4 (X_{CH4}) with experimental conditions; reaction temperature =800 °C and flow rate =20 mL min-1. Various Co loading such as 2.5%, 5%, 7.5% and 10% and its effect on the CH_4 conversion. As the Co loading increases, the conversion of CH_4 increased. While using BFA, the CH_4 conversion was approximately 31%. While addition of Co increased in the conversion. The 2.5% Co/BFA depicts 33 % the CH_4 conversion. However, in 10% Co/BFA the conversion was up to 46%. Figure 4.9 (b) showed the selectivity of hydrogen production. There was not much variation in selectivity. When simple fly ash was used as catalyst, the selectivity was 39%. When 2.5% Co/BFA was used as catalyst the selectivity increased to 45%. Maximum selectivity was achieved to 50% for 10% Co/BFA due to thermal stabilization. Similarly, Figure 4.9 (c) displays the graph for yield Y_{H_2} (%) of hydrogen production. In case of simple fly ash, the Y_{H_2} (%) was round about 12%. As the percentage of Co increases in fly ash, the yield increases. In other words, percentage of Co is directly proportional to BFA which can also be seen in Figure 4.9 (c). By addition of 2.5% Co in 2 gram of fly ash the yield has been increase from 10% to 15% while in case of 10% Co addition, the Y_{H_2} (%) is 23%.

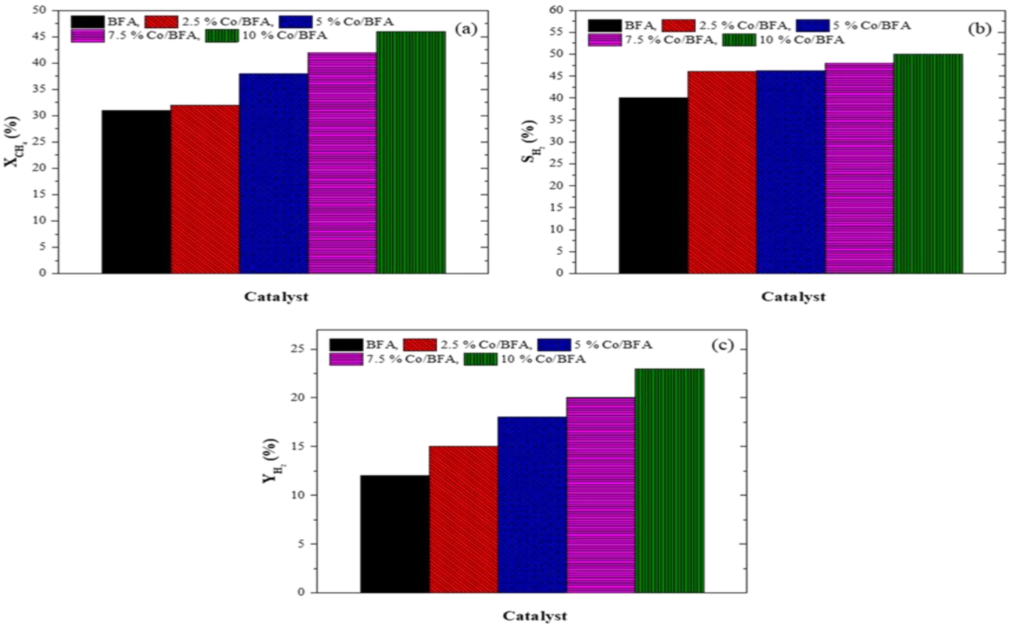

Figure 4.9 Effect of the Co loading over BFA (a) CH_4 conversion (b) H_2 selectivity (c) H_2 yield: catalyst loading = 0.2 g, reaction temperature = 800 °C, feed flow rate = 20 ml min^{-1}

Now the effect of the 5% Co/BFA time on stream (TOS) on CH_4 conversion, H_2 selectivity and H_2 yield with catalyst loading 0.2 g, reaction temperature was 800 °C, feed flow rate of 20 ml min-1 is shown in Figure 4.10. The support formation and surface properties also influenced the CH_4 conversion, H_2 selectivity and H_2 yield. The methane conversion was found increased for first 3 hrs after that it was gradually increased. Approximately after 5.5 h, the catalyst was fully deactivated. Round about 0.6 g was accumulated on 0.2 g of Co/BFA catalyst sample. Life of catalyst and catalytic activity mainly depends upon the pore structure of catalyst. It may also affect the morphology of deposited carbon and exhaust gas composition. Moreover, with slight decrement in selectivity after 1 hr is starts increasing throughout the time. Similarly, the YH_2 was increasing from the starting to end.

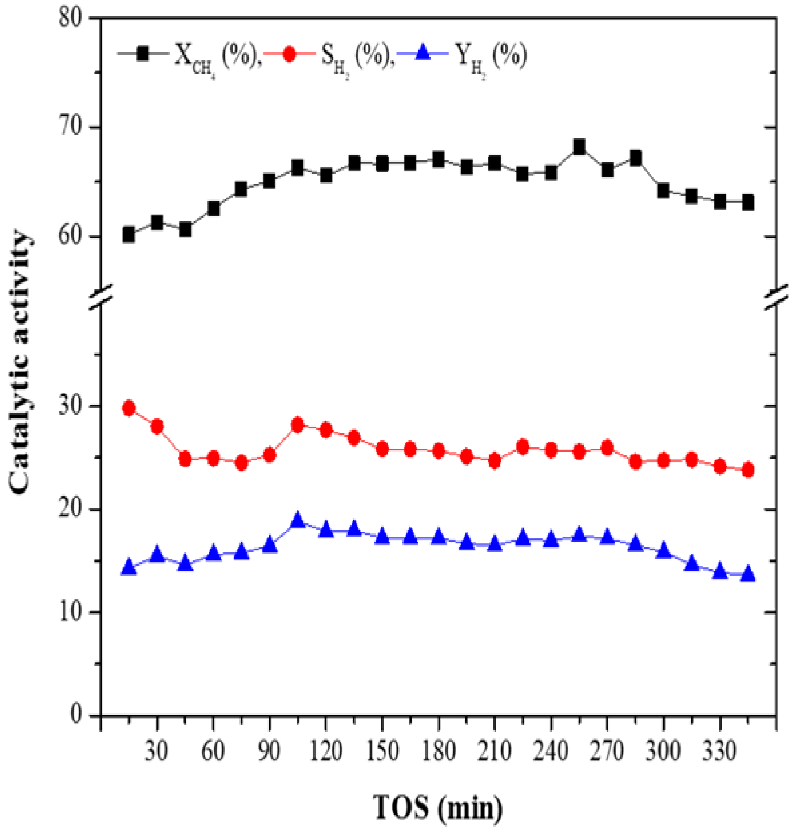

Figure 4.10 Effect of the 5% Co/BFA time on stream (TOS) on CH_4 conversion, H_2 selectivity and H_2yield: catalyst loading = 0.2 g, reaction temperature = 800 °C, feed flow rate = 20 mL min^{-1}

4.4.3 Characterization of Spent Co/BFA

Figure 4.11 (a) presented the XRD pattern of spent catalyst of Co/FA. The carbon peak in the spent catalyst was identified 2θ = 26.6° with hkl (006) PDF#26-1076 with d-spacing of 0.334. The other peak of C70 was detected at 2θ = 13.28° with hkl (002), with d-spacing of 0.665 with PDF# 50-1364. Figure 4.11(b) shows the TGA of Co/BFA spent catalyst. Moisture content in respective spent catalyst was less as compared to fresh Co/BFA. Weight loss in TGA curve has been observed after 650°C. The total weight loss was about (4%). However, after using Co/BFA as a catalyst, mass reduction with respect to temperature was reduced. Catalyst became more stable whereas the structure and composition were changed, surface area had been increased and the curve showed higher thermal stability and catalytic activity.

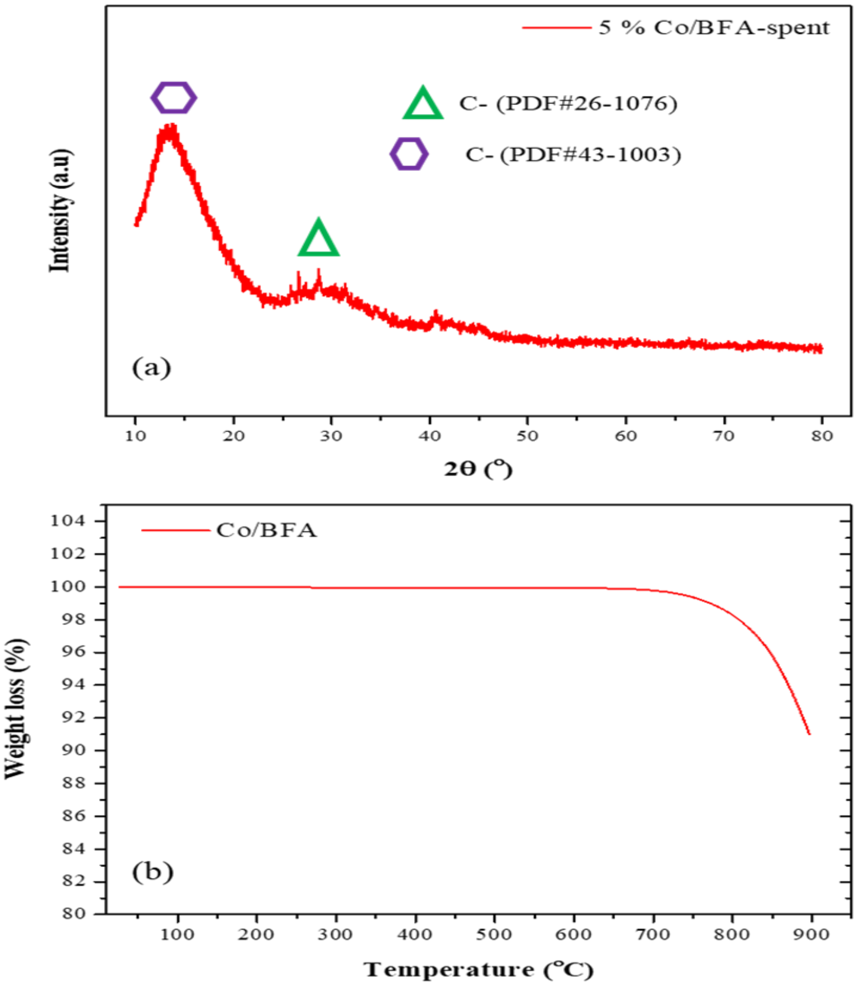

Figure 4.11 (a) XRD profile of Spent Co/BFA (b) TGA profile of spent Co/BFA catalyst

It was observed that the morphology was totally changed of spent Co/BFA. After using as a catalyst in cracking of methane the particles were separated and gravestone type particles with irregular shape and size were formed. Figure 4.12 (a) and (b) with two different magnifications, it was clearly observed that surface area and volume of Co/BFA had been decrease. The BFA particles were fused into Co. Furthermore, the results show that the typical pore thickness in spent catalyst was increased after methane cracking reaction, denoting that micro-pore might be blocked by deposits of carbon formed. Surface of Co/BFA covered by carbon deposits, which had reduced the catalytic activity.

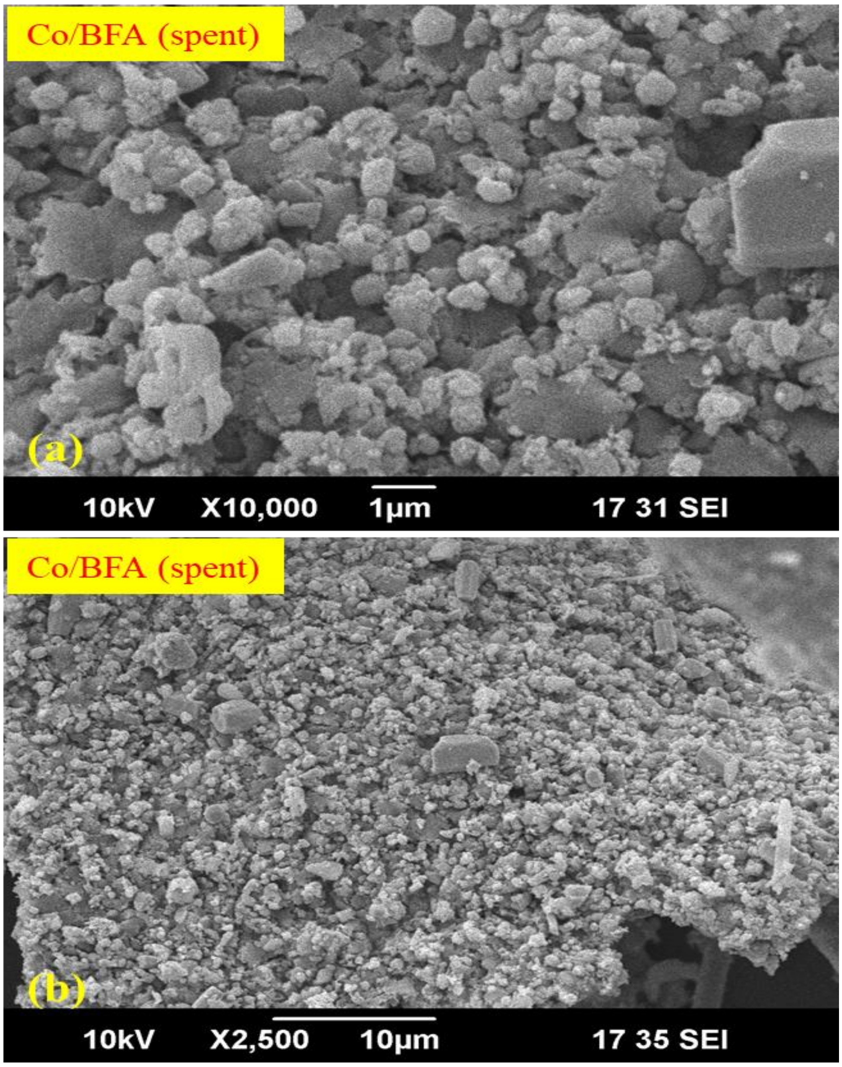

Figure 4.12 SEM micrographs of spent Co/BFA catalyst (a) 1 µm (b) 10 µm

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Chapter 5

Conclusions and Recommendation

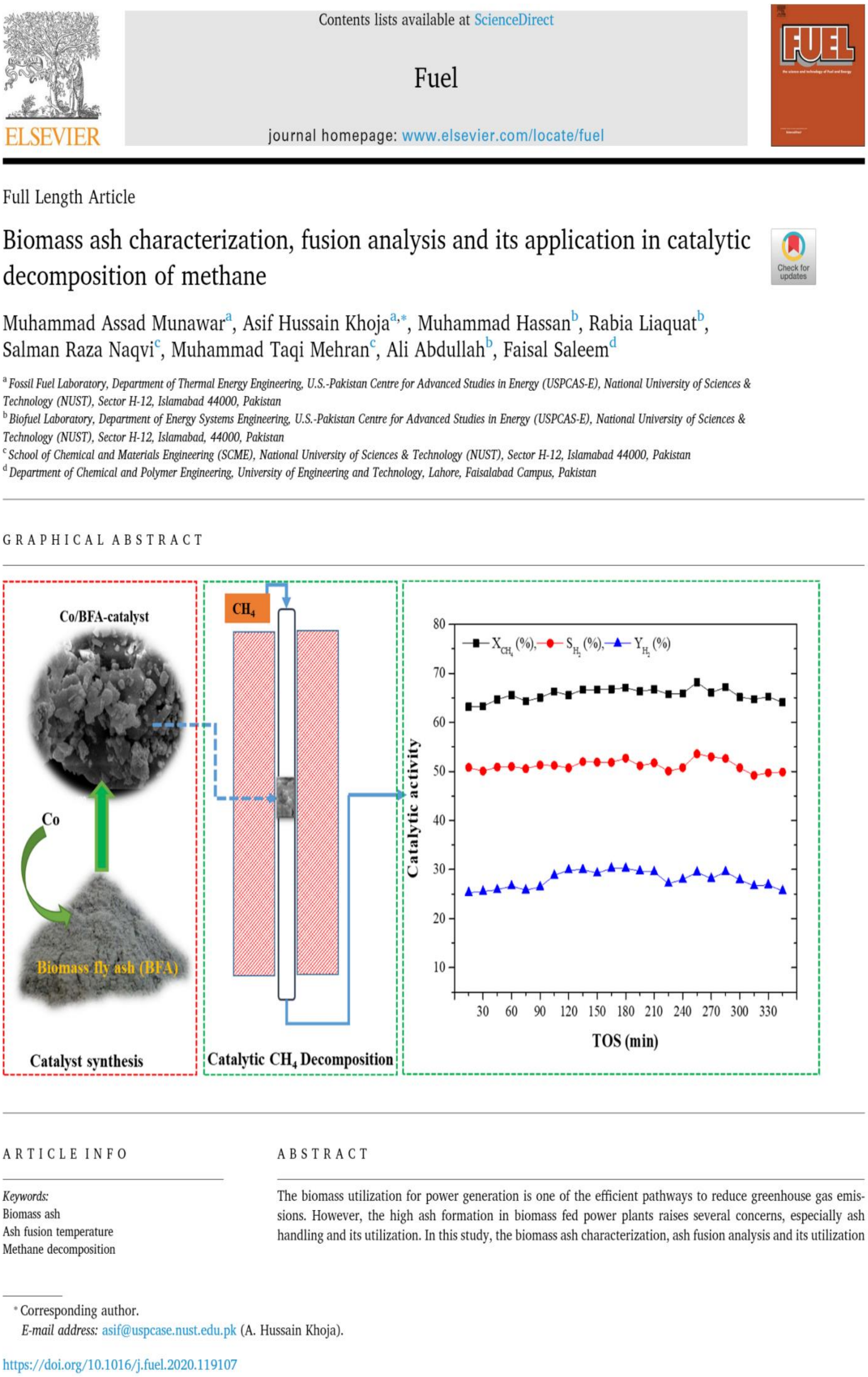
5.1 Conclusions

Biomass ash was investigated for ash fusion analysis and characterization to check its suitability for the CH_4 decomposition. The modified BFA and BBA using CeO_2 nanoparticles increased the ash fusion temperature while reducing the alkaline nature of BFA/BBA and change the morphology. Regarding morphology, proper flakes were formed and CeO_2 was properly infused into ash by forming wires type structure. In. TGA, a drastic change was observed in mass reduction, but thermal stability has been observed while modifying using CeO_2. The detail characterization reveals its suitability for various applications especially, as a support material for methane decomposition. The Co loaded BFA was tested for methane decomposition to produce hydrogen. The 63% CH_4 conversion with greater than 30% H_2 yield has been observed for Co/BFA at 700℃ for more than 330 min on TOS. Further investigation may lead to various fuel processing applications via direct employment of BFA in catalysis.

5.2 Recommendations

- Using nanoparticles in biomass based boilers which produces ash in more quantity, is most promising technique to reduce ash production.
- Through this technique the ash fusion temperature of biomass will be increased.
- Losses in the boiler will be decreased via enhancing efficiency of boiler and as well as of power plant.
- Moreover, using more thermally stable nanoparticle than cerium oxide further improvement can be observed.
- Furthermore, it will prove even better as direct support when used as catalyst.

Appendix A: Research Paper



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Full Length Article

Biomass ash characterization, fusion analysis and its application in catalytic decomposition of methane

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GRAPHICAL ABSTRACT

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ABSTRACT

The biomass utilization for power generation is one of the efficient pathways to reduce greenhouse gas emissions. However, the high ash formation in biomass fed power plants raises several concerns, especially ash handling and its utilization. In this study, the biomass ash characterization, ash fusion analysis and its utilization

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