BENEFICIAL UTILIZATION OF BIOMASS WASTE IN CONSTRUCTION MATERIAL

Research Monograph

by

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Scheme for Promotion of Academic and Research Collaboration

Department of Civil Engineering
Indian Institute of Technology Madras, Chennai, India
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EXECUTIVE SUMMARY

Bioenergy is one of the key sources of renewable energy production in India. The strength of India's biomass sources rests primarily on its agricultural sector. An enormous quantity of crop residues is being generated on seasonal basis in India. The gross and surplus biomass residues available in India per annum is estimated to be ∼750 million tonnes (MT) and ∼230 million tonnes (MT), respectively. The surplus crop residues are the sustainable feedstock for the production of bioenergy. In India, cereal crops (rice, wheat, etc.,) and sugarcane are found to have a significant potential to generate crop residues, i.e., 70% of surplus crop residues (∼ 160 MT). The geographical variation in the production of crop residues is quite prominent among the states and is due to the variability in crop acreage and crop productivity. Uttar Pradesh generates the highest estimate of gross (∼ 184 MT) and surplus crop residue (∼ 60 MT), respectively. The estimated production of surplus crop residue in the states like Punjab, Gujarat, Maharashtra, Madhya Pradesh, Karnataka, Tamil Nadu, and Andhra Pradesh is in the range of 10 – 38 MT, and for other states, it is less than 10 MT. As per a recent MNRE report, surplus crop residues generated in India can produce around 28 GW of power per annum. Further, bagasse cogeneration units in India are responsible for the additional generation of around 14 GW of power per annum.

The most prominent industries that use cogeneration systems for bioenergy collection in India are the sugar, rice, and paper industries. The highest number of Indian sugar industries are located in Uttar Pradesh (124 nos.) and Maharashtra (211 nos.). West Bengal, Uttar Pradesh, Punjab, Odisha, Andhra Pradesh, Telangana, Tamil Nadu, Chhattisgarh, Bihar, and Haryana are the major rice producing states of India. Maharashtra, Andhra Pradesh, Gujarat, and Uttar Pradesh hold ∼50% of India's paper manufacturing capacity. Combustion of waste biomass residues in the cogeneration power plants of these industries is responsible for the production of enormous quantities of biomass ash. According to 2020 – 2021 estimates, biomass residues from sugar (i.e., bagasse), rice (i.e., rice husk), and paper (predominantly rice husk and bagasse) industries in India generate around 3.5 MT, 5 MT, and 10 MT of ashes per annum, respectively.

In the current scenario, most of biomass ashes generated from industries are landfilled, leading to significant disposal and environmental issues. Hence, valorisation of enormous amount of biomass ash is the need of the hour. Furthermore, biomass ash can be used in developing construction materials due to the presence of amorphous silica. However, its widespread application in concrete is limited due to compositional variability and lack of source mapping of biomass ash. This monograph provides a comprehensive database of sugarcane bagasse ash (SBA), rice husk ash (RHA), and paper mill ash (PMA) availability in the 10 major states producing sugar, rice and paper, and their geographic distributions. An inclusive review of biomass and biomass ash characteristics followed by incorporation of biomass ashes in portland cement and non-portland cement-based binders is discussed. Lastly, a case study demonstrating the feasibility of utilizing Indian biomass ash in the development of low carbon alkali-activated binder is presented.

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LIST OF ABREVIATION

A	Ash content
ACI	American Concrete Institute
ASTM	American Society for Testing Materials
BA	Biomass ash
BW	Brick waste
CCA	Corn cob ash
CEA	Central Electricity Authority
C-A-S-H	Calcium aluminum silicate hydrate
C-S-H	Calcium silicate hydrate
FC	Fixed carbon
FTIR	Fourier transform infrared spectroscopy
GCV	Gross calorific value
GGBS	Ground granulated blast furnace slag
GR	Gross crop residue
HL	Hydrated lime
IPMA	Indian Paper Mill Association
IS	Indian standard
ITZ	Interfacial transition zone
K/Na-A-S-H	Potassium/Sodium aluminum silicate hydrate
KOH	Potassium hydroxide
LOI	Loss of ignition
L/S	Liquid to solid ratio
MC	Moisture content
MNRE	Ministry of New Renewable Energy
MT	Million metric tones
MW	Mega watt
NaOH	Sodium hydroxide
NOx	Nitrogen oxides
Na_2SiO_3	Sodium silicate
OPC	Ordinary portland cement
PMA	Paper mill ash
POFA	Palm oil fuel ash
QXRD	Quantitative X-ray diffraction
RPM	Rotation per minute
RHA	Rice husk ash
SAI	Strength Activity Index
SBA	Sugarcane bagasse ash
SCMs	Supplementary cementitious materials
SCC	Self-compacting concrete
SEM-EDS	Scanning electron microscopic analysis- Energy dispersive spectroscopy
SOx	Sulphur oxides
SR	Surplus crop residue
STAI	Sugar Technologists Association of India
TGA	Thermogravimetric analysis
VM	Volatile matter
VMA	Viscosity modifying agent
WA	Wood ash
WSA	Wheat straw ash
XRD	X-ray diffraction

1. INTRODUCTION

Global economic and industrial growth has increased the level of energy consumption, especially fossil fuels. India is the third largest energy consuming country in the world next to the United States and China [1]. According to ministry of power, per capita electricity consumption of India for the year 2021-2022 was 1255 kWh, which is around one-third of total per capita electricity consumption over the globe [2]. Currently, 60-70% of the energy demand is being met by coal, oil, and natural gas. These sources are being criticized for their greenhouse gas emissions, limited availability, and economic viability. Therefore, it is crucial to focus on renewable energy sources both globally and in India. Global energy technologies include renewable energy sources such as bioenergy, solar, wind, hydro, tidal, and geothermal as alternative sources for energy production. The percentage distribution of India's various energy sources is shown in Fig. 1[3-4].

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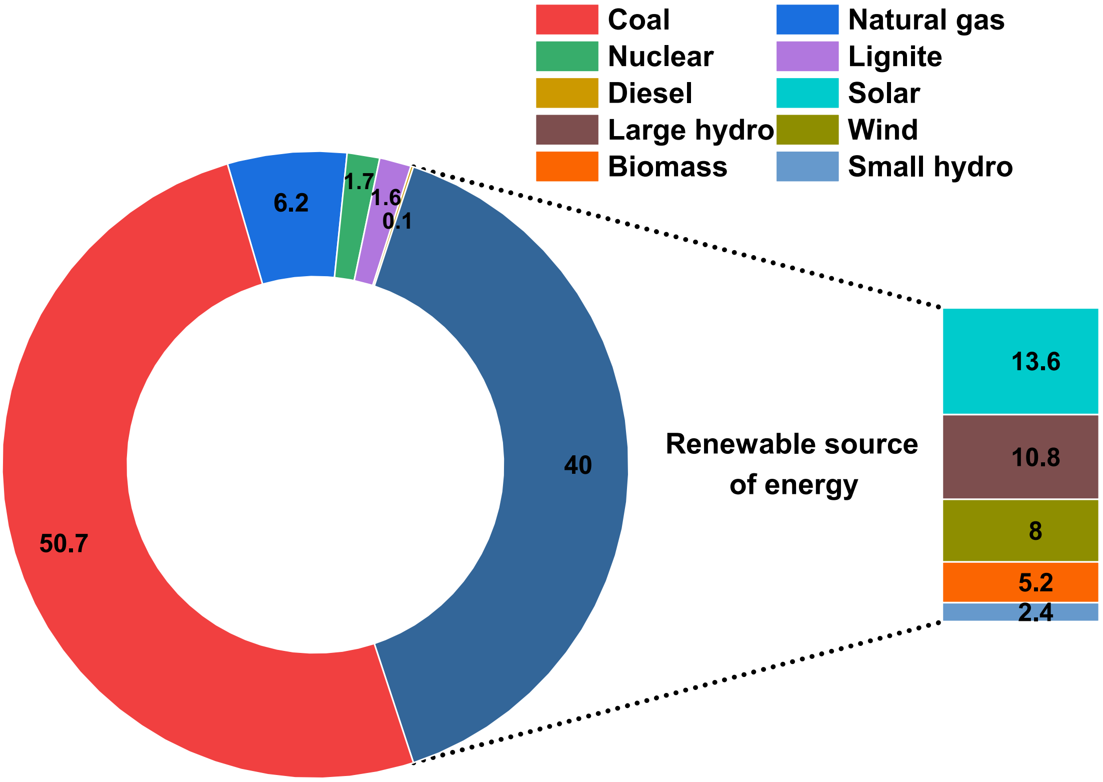

Fig. 1: Percentage segment of India's different energy sources

As of June 2022, according to the Central Electricity Authority (CEA) and the Ministry of New Renewable Energy (MNRE), conventional power sources generated 242 GW of power (i.e., 60% of the total installed capacity) [3-4]. The segment enclosed electricity produced from thermal sources such as coal (50.68%), natural gas (6.17%), nuclear (1.68%), lignite (1.64%), and diesel (0.13%). Coal-based electricity generation is gradually reducing (~50% by 2022) owing to its limited existence, high CO_2 emission, and high cost [3]. Therefore, many countries including India have taken steps towards the use of renewable sources of energy. According to the GSR 2022, India ranks fourth in the world for installed renewable energy capacity (including large hydro, wind, and solar power), and sixth for installed bioenergy capacity [5]. With a total installed renewable energy capacity of roughly 160 GW (or 40% of the installed electric capacity), India has met its nationally determined contribution (NDC) target of 2022. The nation has set a lofty goal to generate 500 GW of renewable energy by 2030 [6].

Biomass derived energy is one of the renewable energy sources that can deliver reliable grid-quality power. Unlike solar power and wind power, biomass-derived power is more reliable and fluctuation-free. Biomass is derived from the residues of vegetation, forest, by-products from crops, and agriculture industries [7]. In India, approximately 46% and 23% of the land is covered by crop cultivation and forest, respectively [8]. Due to the large dependency of country on agriculture with a high potential of biomass availability, in Indian scenarios, biomass energy conversion is quite worthwhile.

Currently, it is estimated that 750 million metric tons of biomass are produced annually in India. As of October 2022, biomass power and cogeneration sector have installed a total capacity of 10205 MW, and by 2032, it is anticipated that 73,000 MW of energy will be produced using biomass and bagasse cogeneration [3]. Figure 2 shows the grid-interactive biomass power installed capacity state-wise [3]. Leading biomass power supply states of India are Maharashtra, Karnataka, Uttar Pradesh, Tamil Nadu, and Andhra Pradesh with a total installed capacity of 2551 MW, 1837 MW, 1837 MW, 1327 MW, and 816 MW, respectively, in the year 2020. Deployment of biomass derived energy projects in India gradually rose from 1081 MW in 2011 to 10205 MW in 2022 [3-4].

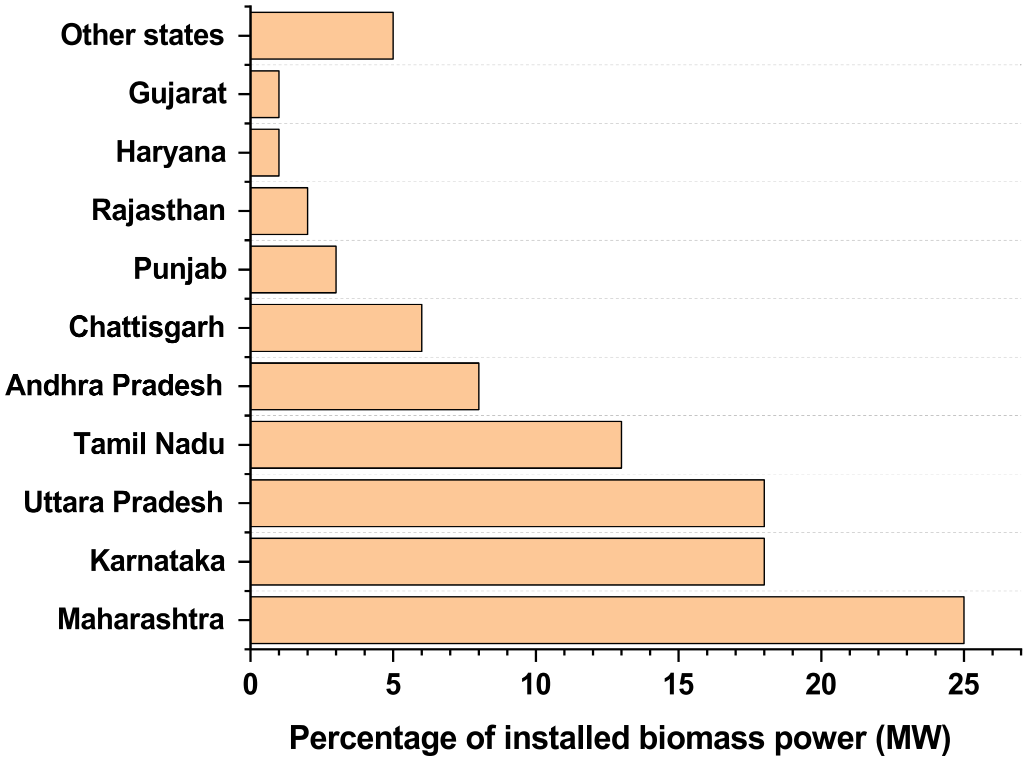

Fig. 2: State-wise installed capacity of biomass power

Thermo-chemical process (combustion, gasification, pyrolysis), mostly combustion technique, is being adopted for the generation of bioenergy [9]. The key downside associated with the combustion process in extracting bioenergy is the leftover huge quantity of ash. It is reported that the combustion of agricultural residues results in 1.5-20% of biomass ash, and again, it differs with the source of biomass [10]. The amount of biomass ash generation is anticipated to increase with the increase in bioenergy utilization. Improper management of biomass ash could result in major environmental threat and disposal issues. Considering the issues with biomass ash disposal, depleting natural resources, and the growing cost of raw materials, valorisation of biomass ash has received attention for its use in ceramic products, construction materials, soil amendments, biofertilization, catalysts, absorbents, synthesis of silica-based products, etc. [11]. Some of the applications are still in the early stages of development.

In view of physico-chemical properties of biomass ashes and their availability over the country, one of the promising ways to use these ashes sustainably could be as an alternative binding material in the development of construction materials [12-13]. In this manner, clinker manufacturing and risk of landfill can be reduced to a larger extent, hence minimizing the environmental impact. However, it is to be highlighted that, lack of scientific investigation and inadequate information about biomass ash among its wide range of availability may lead to incorrect and misinterpreted data about biomass ash. This is because, unlike fly ash, most biomass ashes have varied oxide compositions of Si, Ca, Cl, K, N, S, P, and trace elements such as As, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Pb, Sb, and Zn [14, 15]. Therefore, in-depth understanding and methodical research on biomass ash are necessary to maximize its potential usage out of less cost and energy.

Ash with a SiO_2 content of more than 50% can be utilized as a pozzolan, and this is a subject of extensive research [16]. Rice husk ash, bagasse ash, grass ash, and wheat/corn straw ash are utilized as a cement substitute or as an alkali-activated binder in the production of construction material [15]. Utilization of these ashes as a partial replacement for cement may contribute to enhancing the engineering properties of cementitious composites. Since silica particles with large surface areas are commonly employed in the construction and ceramic industries, the extraction of SiO_2 from biomass ash has also been studied [17]. Some studies were carried out using mesoporous silica-based materials, such as wheat straw ash and rice husk ash, in CO_2 capture with the support of alkali or alkali earth metal oxide [14]. Understanding the material properties of biomass ash and how they affect reactivity, engineering properties, and long-term performance for their use as a construction material was shown to have enormous potential. Any pozzolan's potential for utilization mostly hinges on its accessibility. Recent statistic data states that India is the greatest producer of rice and sugarcane accounting for 24 % and 20% of global production, respectively, resulting in a huge quantity of biomass (rice husk, bagasse) [18]. These biomass types are being employed as a source for biomass derived power and cogeneration in industrial sectors such as rice mills, sugar mills, paper mills etc.

In the last few decades, there has been a lot of interest in using biomass ash from agricultural sector as an alternative binding material. The sustainable use of biomass and biomass ashes is a concern for both developed and developing nations. Fly ash availability is decreasing due to the gradual push to reduce reliance on coal. Hence, biomass ash can be an appropriate replacement for fly ash in cement and concrete. The most predominant sources of biomass ash in India, which can be used as a supplementary cementitious material (SCM) as per the present scenario, are rice, sugar, and paper industries [11-13,15].

The present study is divided into six distinct chapters:

The first Chapter provides an introduction focusing on the growth in renewable sources of energy such as solar, hydro, wind, and biomass power, followed by the need for bioenergy, leading to the generation of biomass ash.

In the second Chapter, the availability of biomass sources in India (as per 2020-21), quantified gross and surplus biomass residues in various states of India, and geographical distribution followed by the estimated quantity of generated ashes from three major biomass ash sources (rice, sugar, and paper industries) is demonstrated.

The third Chapter provides information regarding the characteristics of biomass and biomass ash.

The fourth Chapter discusses the most current advancements in research on the performance of biomass ash in terms of reactivity, mechanical, and durability when used as a partial replacement for portland cement and as an alkali-activated binder.

In the fifth Chapter, a case study illustrating the effectiveness of an alkali-activated biomass ash binder is illustrated. This study examined the impact of three different biomass ashes—rice husk ash (RHA), sugarcane bagasse ash (SBA), and paper mill ash (PMA, primarily composed of rice husk and sugarcane bagasse) —with various oxide and phase compositions on compressive strength, bulk density, water absorption, and microstructural characteristics.

Lastly, opportunities, challenges, and future recommendations are discussed in the sixth Chapter.

* * *

2. BIOMASS AVAILABILITY IN INDIA

2.1 Geographical distribution of biomass availability in India

India is known as a tropical country on account of its hot summers, humid & rainy season, and mild winters, thus offering an ideal condition for agricultural production. The net area covered by agricultural land in India was ~ 180 million hectares in 2021 [8]. The vast cultivation of crops leads to the production of enormous quantities of biomass residues. The Ministry of New Renewable Energy's report (MNRE-2021) estimates that India has a total annual biomass availability of around 750 million metric tons [19]. Figure 3 illustrates various biomass types available in India [19].

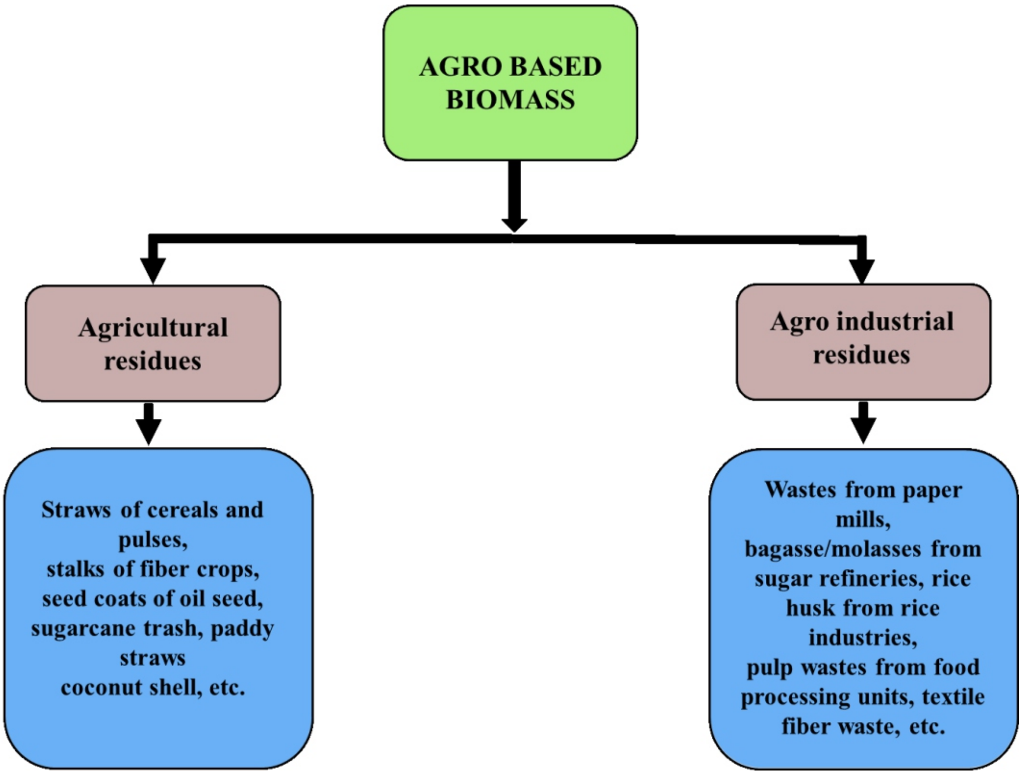

Fig.3: Classification of available agro-based biomass resources in India

Agriculture-based biomass residues are the organic material obtained from the processing and harvesting of agricultural crops [20-21]. Agricultural residues produced in the field during the time of yield, such as straw/stalk of cereals, sugar cane tops, etc. are called primary residues and these residues are more commonly used as animal feed, fertilizers, etc. Hence, their availability as bioenergy resource is low [22]. Whereas secondary agricultural residues produced during processing such as rice husk and bagasse can be utilized for energy applications [23]. Agricultural residues are sustainable feedstock for the production of bioenergy, and India holds the seventh rank among bioenergy producing countries [24]. Cereal crops (rice, wheat, etc.,) and sugarcane are found to have a significant crop residue-generating potential, contributing over 70% of surplus crop residues [22].

The waste or by-product originating from a crop production system is termed residue. The total residue produced from a crop is identified as gross crop residue (GR) and the residue left after beneficial uses, such as cattle feed, animal bedding, heating and cooking fuel, organic fertilizer, etc., is called surplus crop residue (SR) [25]. The surplus residue can be a source for the generation of bioenergy. The surplus biomass residue capable of supplementing the coal in the production of bioenergy is valued at 230 million metric tons, which corresponds to an energy potential of 10170 MW in the year 2021 [8]. Based on the survey [26-28], a list of agricultural crops, crop production capacity, residue, and the number of residues produced in India for the generation of bioenergy are compiled and presented in Table 1.

Table 1: Indian renewable biomass residues available for the generation of bioenergy

Crop	Crop production (million tons/year)	Residue	Residue produced (million tons/ year)	
			Gross	Surplus
Paddy	121.46	Straw, husk, Stalks	156.89	46.91
Wheat	108.75	Stalks, panicle	149.05	32.79
Other cereals	49.66	Straw, husk, Stalks, cobs	84.06	16.21
Pulses	25.58	Stalks, husk	15	5.7
Oilseeds	36.57	Shell, stalks	52.5	12.6
Sugarcane	399.25	Bagasse	127.5	63.75
Fibre crop	41.34	Fronds, husk, pith, shell	33.75	13.5
Other crops	50.24	Residue	130.8	38.64
Total	832.88	-	749.55	230.1

Amounts of gross and surplus residue produced in different states of India can be estimated using following expressions given in [21, 25],

$$GR(y)=\sum_{x=1}^{n} A(x,y) \times Y(x,y) \times RF(x,y) \qquad (1)$$

$$SR(y)=\sum_{x=1}^{n} GR(x,y) \times SF(x,y) \qquad (2)$$

where GR(y) and SR(y) are the gross and surplus crop residue produced in yth state from "n" number of crops, respectively. A(x,y) and Y(x,y) represent the crop area (in hectares) and crop yield (in kilogram/hectares) of the xth crop at yth state, respectively. RF is the residue to crop fraction and SF is the surplus residue fraction for xth crop in yth state. The crop-specific information such as RF and SF is obtained from elsewhere [25, 26-27]. It is to be noted that crop area and yield values are obtained from crop statistics data provided by Ministry of Agriculture and Farmers' Welfare: 3rd advance estimates of principal crops for 2020-21 [28]. Following literature and scientific reports, the total gross cultivated area of India was ~ 180 million ha. [8] and the cultivated area for the five crop categories (listed in Table 1) was estimated as ~ 155 million hectares, i.e., about 80% of the total gross area under cultivation [28]. Therefore, total of five categories of the crop, i.e., approximately 20 different crops, were used to estimate the gross and surplus crop residue biomass potential [26]. Figures 4 and 5 show the estimated geographical distribution of gross and surplus crop residue biomass potential in India for the year 2020-2021.

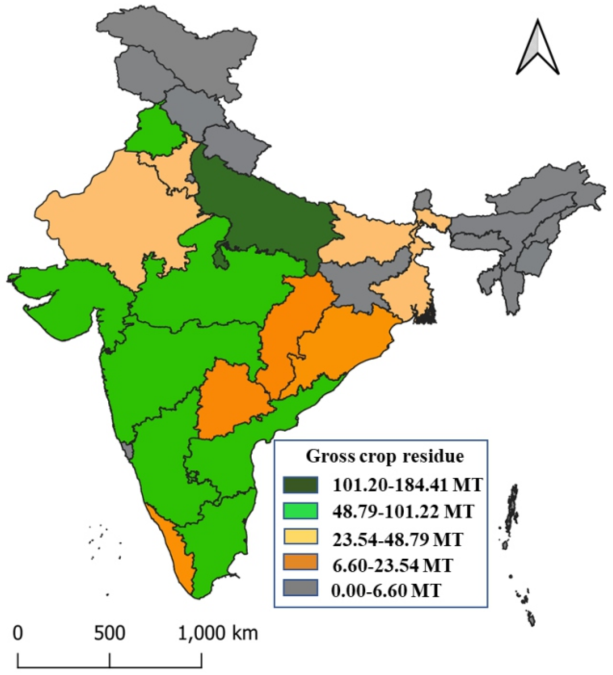

Fig. 4: Geographical distribution of gross crop residue biomass potential (in million tons) in India

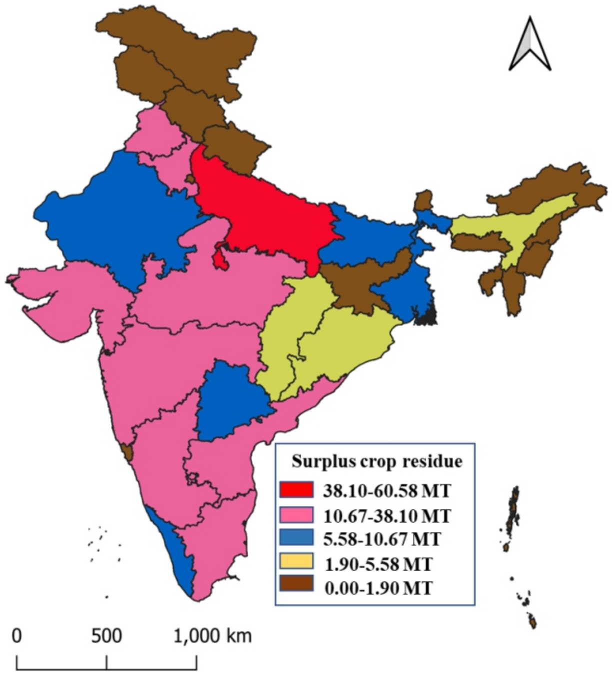

Fig. 5: Geographical distribution of surplus crop residue biomass potential in India

It can be perceived from Figs. 4 and 5 that the geographical variation in the production of crop residue is quite prominent among the states. The geographical analysis of crop residues reveals the highest estimate of gross and surplus crop residue potential for the state of Uttar Pradesh as 184.41 MT and 60.58 MT, respectively. Gross and surplus crop residue potential estimated for the states Punjab, Gujarat, Maharashtra, Madhya Pradesh, Karnataka, Tamil Nadu, and Andhra Pradesh is in the range of 48.79-101.22 MT (Gross) and 10.67-38.10 MT (Surplus). The estimated generation of gross and surplus crop residue for other states is less than 10.67 MT.

Agro-industrial sector is one of the major contributors of biomass ash in India. Agro-based industries utilize agricultural-derived raw material to produce agro-based products that include sugar, rice, paper, vegetable oil, textile, leather, and food processing industries. A significant quantity of lignocellulose waste by-products generated by various agro-based industries can be used as a low-cost, renewable resource for the generation of bioenergy in the form of heat and power. In many agro-based industries, the development of cogeneration plants has become a crucial system due to the rising energy demand. Instantaneous production of electricity and thermal energy from cogeneration plants could save up to 30% of non-renewable fuel consumption [29]. Sugar, paper, rice, chemicals, fertilizers etc., are the industries for which significant expenses have been made for power and heat [30]. The most prominent industries that use cogeneration system for bioenergy collection in India are the sugar, rice, and paper industries.

Sugarcane and rice (paddy) crops contribute almost 60% of the total crop production in India, which is responsible for generating ~ 45-50% of the surplus crop residues [21, 28]. At the same time, India is recognized as the 15th largest paper manufacturing hub in the world with a total paper production capacity of about 15 MT per annum [31-32]. Combustion of waste biomass residues in cogeneration power plants of these industries has led to the release of an enormous quantities of ashes [33]. Biomass residues from sugar, rice, and paper industries generate around 3.5 MT, 5 MT, and 10 MT of ashes per annum, respectively. In current scenario, most of biomass ashes are being landfilled leading to significant disposal and environmental issues [34]. However, biomass ash can be an efficient construction material owing to its amorphous silica-rich phase.

Three major agro-based industries such as sugar, rice, and paper industries are considered here. Major sugar industries with large crushing capacities, rice industries, and paper industries with large production capacities as mentioned in the Sugar Technologists Association of India (STAI) handbook [35], Rice Directory List-Commodities India [36], and Indian Paper Mill Association (IPMA) [37] were taken into account in this study. The geographical distribution of major sugar, rice, and paper industries in ten major sugar, rice, and paper producing states of India was located using Google Earth Pro by collecting the precise geographical information (latitude and longitude) of each of the industries from the aforementioned specific directories. Subsequently, the mapping of biomass source locations was performed using QGIS software. Geographical distribution, the estimated quantity of biomass, and associated ash generated at ten major sugar, rice, and paper producing states of India will be discussed in the following sections.

2.1.1. Sugar industry

India is the second largest producer of sugarcane in the world after Brazil which contributes to about ~22% of sugar production in the world. A detailed geographical distribution of sugar industries in 10 major sugarcane producing states of India and the estimated production of sugarcane bagasse and bagasse ash per annum are presented in Figs. 6-7.

The highest number of Indian sugar industries are located in the states of Uttar Pradesh (124 nos.) and Maharashtra (211 nos.) with the sugarcane production capacity of 177.67 MT/year and 101.59 MT/year, respectively. Among India's major sugar producing states, Uttar Pradesh has historically been the top producer of sugar and has held that position since its inception. The eastern side and upper Gangetic plains of Uttar Pradesh are where the majority of its industries are located. Maharashtra accounts for one-fourth of the

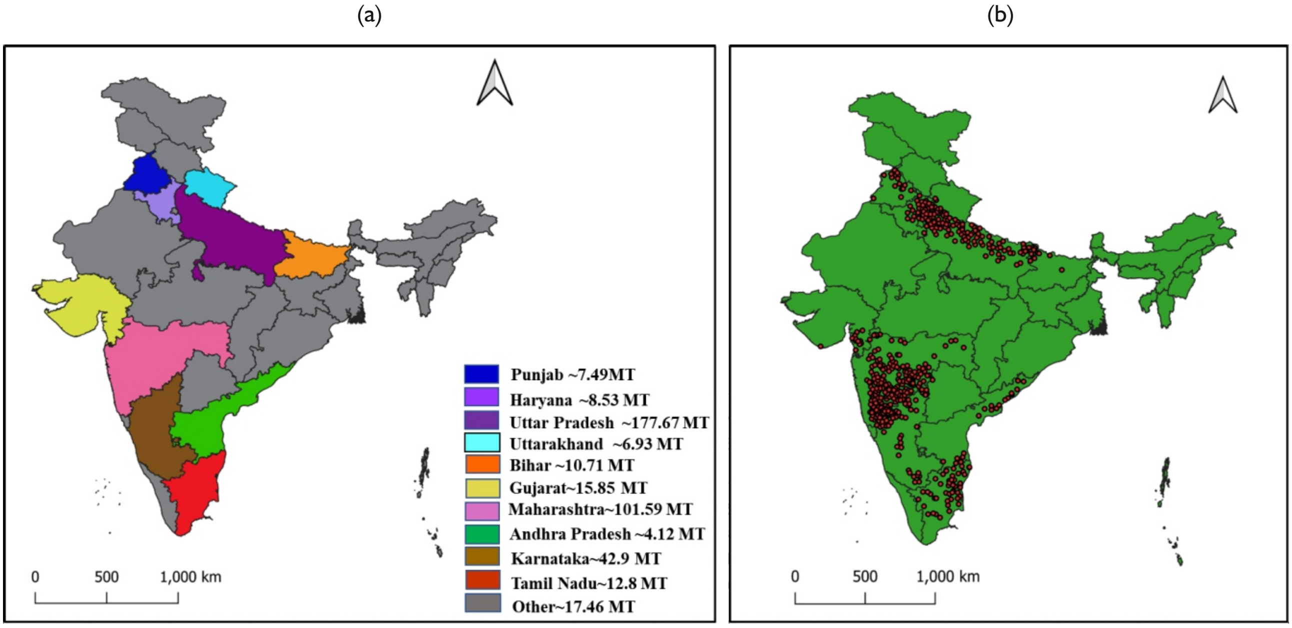

Fig. 6: a) Ten major sugarcane producing states of India, and
b) Geographical distribution of sugar industries in top ten sugarcane producing states of India

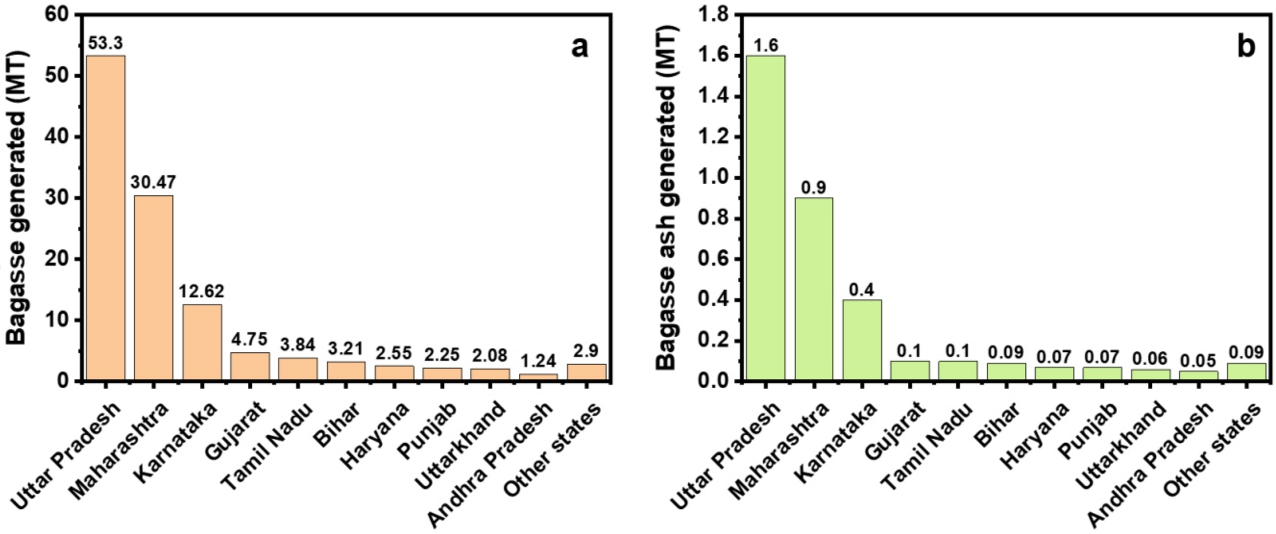

Fig. 7: State wise estimate of sugarcane a) bagasse and b) bagasse ash generated in the year of 2020-2021

nation's sugar industries, where a majority of the state's sugar mills are located in the western plateau river valleys. Uttar Pradesh and Maharashtra states alone are responsible for the generation of about 58% and 30% of total bagasse and bagasse ash per annum, respectively. Karnataka is the third top sugarcane producing state in India with a production capacity of 42.9 MT/year and the state includes around 70 sugar industries leading to the generation of 12.62 MT and 0.25 MT of sugarcane bagasse and bagasse ash per annum, respectively. The majority of sugar industries of Karnataka are located in the norther side of the state; the rest being scattered in the middle and southern part. Other major sugarcane producing states of India are Gujarat, Tamil Nadu, Bihar, Haryana, Punjab, Uttarakhand, and Andhra Pradesh with a capacity ranging from 4.12 MT/ year to 15.85 MT/year. Overall, the country produces around 400 MT of sugarcane per annum [28]. According to 2020-2021 estimates, India produced ~120 MT and ~3.5 MT of bagasse (28-30 percent of sugarcane) and bagasse ash (2-5 % of bagasse) annually.

2.1.2. Rice industry

India stands second in the production of rice over the globe, accounting for 20% of the world's rice production [38]. Figure 8 shows the geographical distribution of rice mills in the ten major rice producing states of India. The estimated production of rice husk and rice husk ash per annum for the year 2020-2021 is presented in Fig. 9.

India grows around 122 MT of paddy each year, making up 22% of the world's paddy production. India has ~45 million hectares of the total area under paddy cultivation [28]. Rice is grown throughout India; however, it is chiefly grown in northern, north-eastern plains and coastal regions of India (Fig. 8). The largest producer of rice among the regions is the Ganga-Brahmaputra valley, followed by coastal regions. Ten major rice producing states of India are West Bengal, Uttar Pradesh, Punjab, Odisha, Andhra Pradesh, Telangana, Tamil Nadu, Chhattisgarh, Bihar, and Haryana, which account for 78% of the total paddy production of the country. West Bengal is the largest rice producing state contributing ~17 MT/year. Uttar Pradesh is the second largest rice producing state (~16 MT/year) of India, which is mostly concentrated in the easter region of the state. Punjab

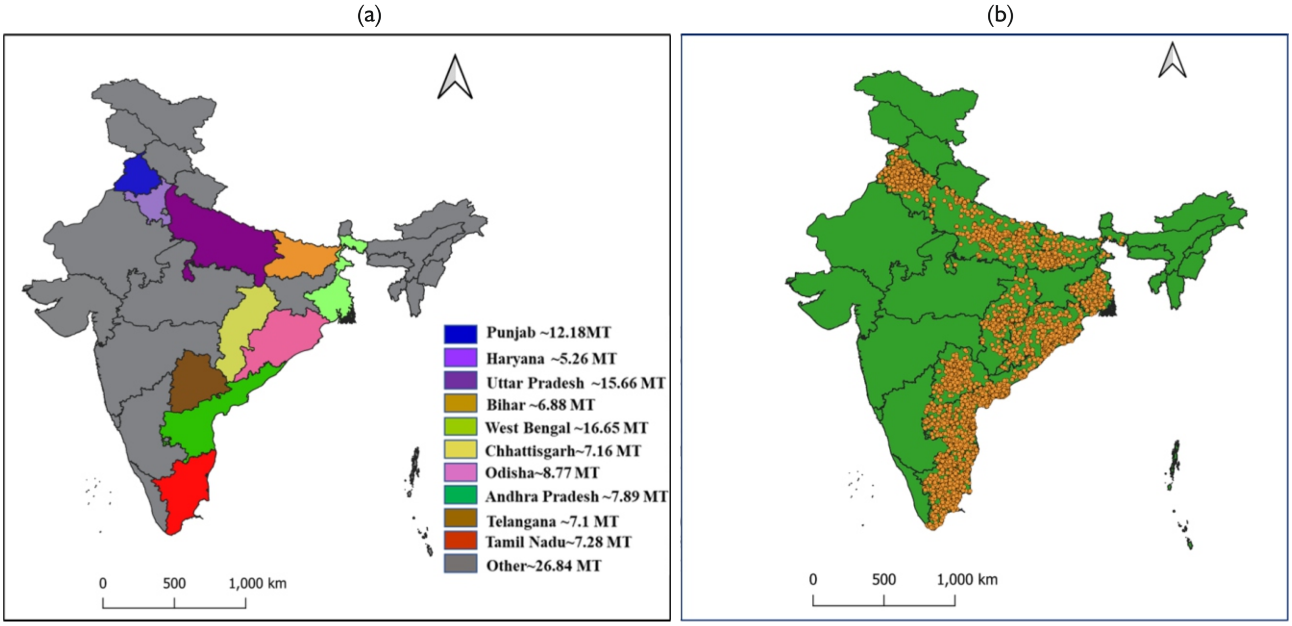
(a) (b)

Fig. 8: a) Ten major rice producing states of India, and b) Geographical distribution of rice industries in top ten sugarcane producing states of India

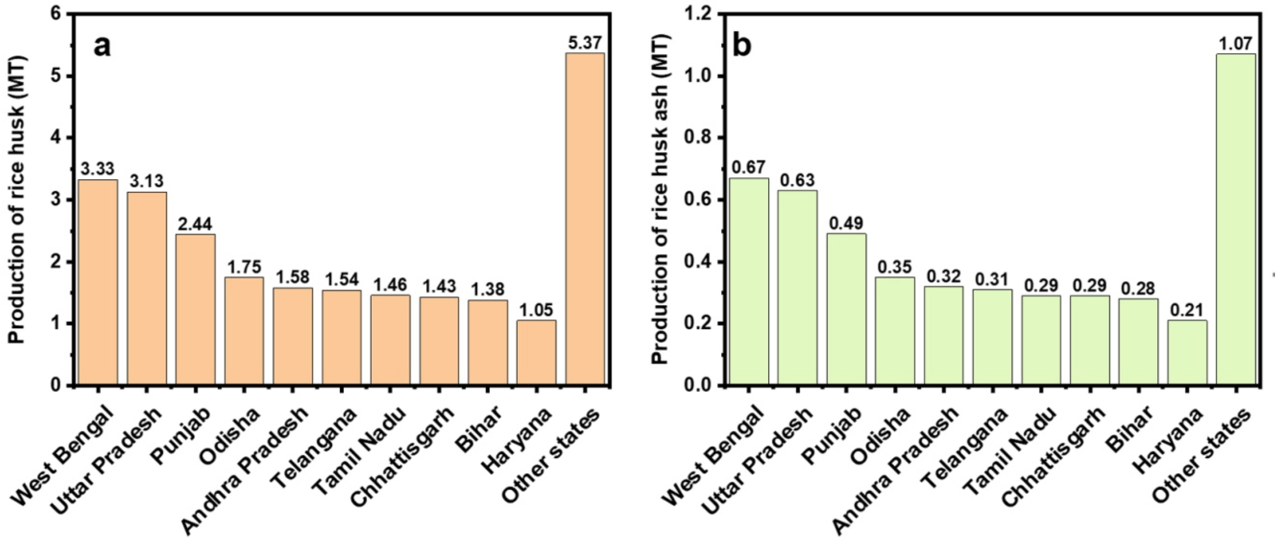

Fig. 9: State wise estimate of a) rice husk, and b) rice husk ash generated in the year of 2020-2021

occupies the third position in rice cultivation that accounts for ~6.4% of the total cultivated area, contributing to ~12 MT/year. Amongst various states of India, there exists a regional imbalance in terms of average yield between the various Indian states. Except for West Bengal, the yield levels in India's eastern states are generally not only subpar but have been stagnant for several years. This is because 70% of the land used for the cultivation of rice is rainfed and subjected to the pattern of rainfall.

India produced around ~25 MT and ~5 MT of rice husk (20% of paddy) and rice husk ash (20% of rice husk) per annum, respectively in the year 2020-2021. West Bengal, Uttar Pradesh, and Punjab alone cover approximately 15 million hectares of land for paddy cultivation with an overall paddy production capacity of 44.5 MT/year [28]. These states are responsible for the generation of ~8.9 MT and ~1.8 MT of rice husk and rice husk ash every year, respectively.

2.1.3. Paper industry

Indian paper industry contributes to approximately 3.7% of the world's paper [37]. As per CPPRI data (2019-2020), the total number of operational paper mill units in India are 526 with an installed capacity of ~27 MT [31]. The geographical distribution of paper industries in ten major paper producing states of India is presented in Fig. 10. Estimated production of paper and paper mill ash for the year 2020 in these states is shown in Fig. 11.

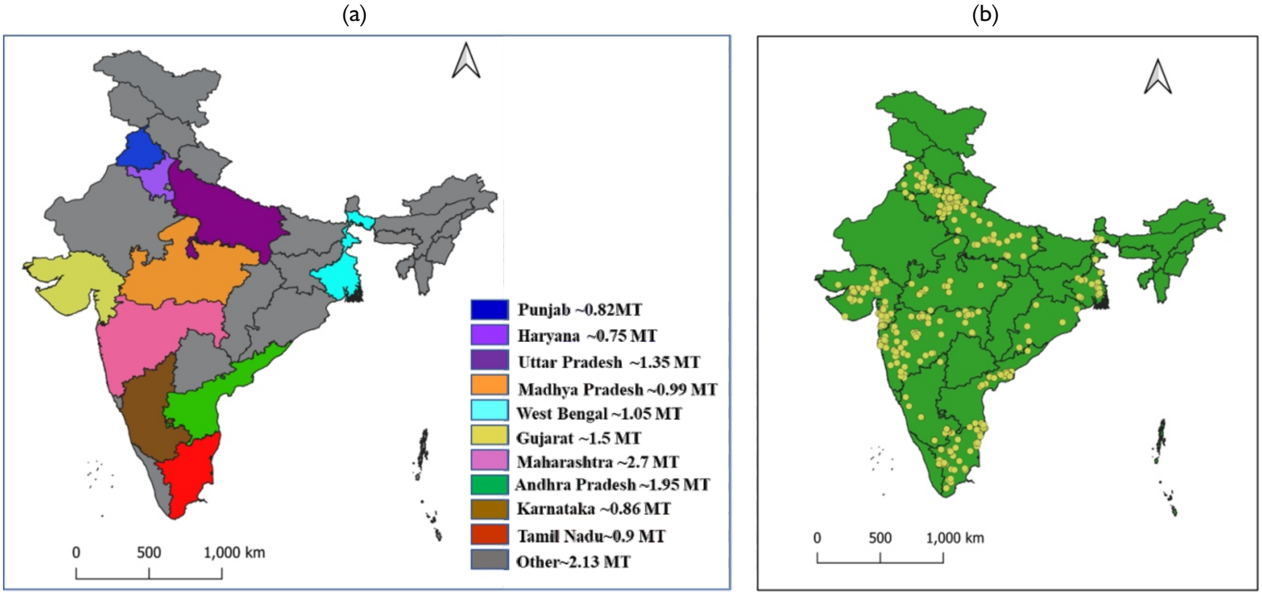

Fig. 10: a) Ten major paper producing states of India, and
b) Geographical distribution of paper industries in top ten paper producing states of India

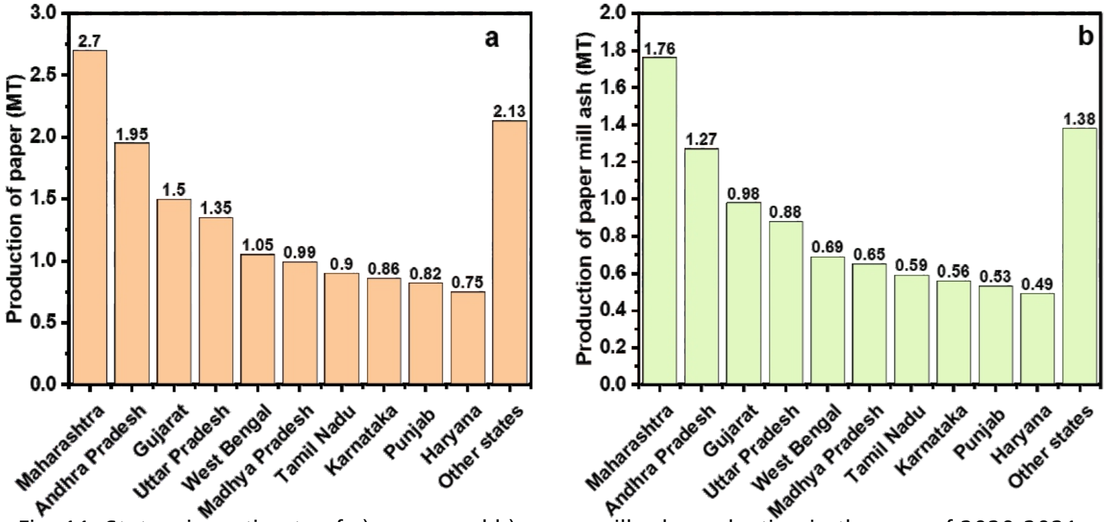

Fig. 11: State wise estimate of a) paper and b) paper mill ash production in the year of 2020-2021

Indian states that produce the most paper include Maharashtra, Andhra Pradesh, Gujarat, Uttar Pradesh, West Bengal, Madhya Pradesh, Tamil Nadu, Karnataka, Punjab, and Haryana (Fig. 10). Maharashtra, Andhra Pradesh, Gujarat, Uttar Pradesh hold ~50% of India's paper manufacturing capacity, which is estimated to generate ~50% of paper mill ashes. These paper mill ashes are produced by the combustion of mixed feedstocks such as rice husk, sugarcane bagasse, woodchips, sawdust, etc. With 63 paper industries, Maharashtra accounts for 18% of India's paper production and has 16.52% of the country's installed capacity. In turn, state is accountable for the generation of ~1.76 MT of ash (boiler and fly ash).

Andhra Pradesh, Gujarat, and Uttar Pradesh correspond to 13%, 10%, and 9% of the country's total paper production capacity, and the states are responsible for the generation of ~3.12 MT of ash per annum. Major paper industry centers of i) Andhra Pradesh are: Rajahmundry, Sirpur (Kagaznagar), Tirupati, Kurnool, Khammam, Srikakulam, Pallancheru, Nellore Bhadrachalam, Kakinada, Apidik, and Bodhan, ii) Gujarat are: Rajkot, Vadodara, Surat, Barjod, Bilmoria, Navsari, Songarh, Ahmedabad, Vapi, Bharuch, Dijandranagar, Limbdi, Gondal, Udvada and Bavla, and iii) Uttar Pradesh are: Saharanpur, Lalkuan, Meerut, Modinagar, Ghaziabad, Lucknow, Gorakhpur, Pipraich, Muzaffarnagar, Allahabad (Naini), Varanasi, Kalpi, Budaun, and Mainpuri. Subsequently, 4-7% of India's installed capacity, which has potential to produce ~ 3.5 MT of ash, is held by other states such as West Bengal, Madhya Pradesh, Tamil Nadu, Karnataka, Punjab, and Haryana. Annual paper production of India in the year 2020 was ~15 MT (as per CPPRI), which was accountable for the generation of ~10 MT (every tonne of paper production leads to the generation of 650 kg of ash, [32]) of ashes per annum. IPMA estimates that the Indian paper industry would produce around 27 MT of paper by the year 2030 [37].

2.2. Summary

A thorough examination of biomass resources offers enormous potential to investigate biomass availability in India for energy conversion. India has a total annual biomass availability of around 750 MT per year. The potential to produce crop residues in a variety of agricultural crops is found to be greatest in cereal and sugarcane crops. Of the total gross crop residue, cereal and sugar cane crops account for about 50% (390 MT annually). The significant variation in gross crop residue generation between the states can be attributed to the geography of the crops, the climate, and the biophysical environment.

Crop residues that are left after being put to their intended uses are considered to be surplus residues (~30% of gross crop residue). About 70% of the surplus crop residues (~160 MT/year) are made up of cereals and sugarcane. Variation in the geographical distribution of surplus residue among the states depends on crop acreage and crop yield. A huge amount of surplus residue in India is generated from Uttar Pradesh and is estimated to be 60.58 MT/year (about 20%). Other states such as Punjab, Haryana, Gujarat, Maharashtra, Madhya Pradesh, Karnataka, Andhra Pradesh, and Tamil Nadu are accountable for the generation of 10.67-38.10 MT (i.e., about 13%) of surplus residue per year. Lignocellulosic crop residues have enormous potential to produce bioenergy. This indicates a propensity to shift towards alternative energy sources, such as bioenergy. The utilization of renewable biomass for the production of bioenergy can reduce the consumption of fossil fuels. This would have a positive impact on the environment, economy, and the availability of jobs for farmers. In India, some of the agriculture-based industries, predominantly sugar followed by rice and paper, are putting this into practice and reporting benefits from turning various types of waste biomass into energy. Sugar industries are distributed in two major areas: 1) Uttar Pradesh, Bihar, Haryana, and Punjab in the North, and 2) Maharashtra, Gujarat, Karnataka, Tamil Nadu, and Andhra Pradesh in the South. Sugar industries are located in sugarcane cultivating zone and the country is accountable for the production of approximately 400 MT of sugarcane per year. Rice industries are located in major rice-growing states of the country that stretches from northwest to northeast to the southern part of India. Approximately 122 MT of rice is cropped each year in India. West Bengal stands top followed by Uttar Pradesh, Punjab, Odisha, Andhra Pradesh, Telangana, Tamil Nadu, Chhattisgarh, Bihar, and Haryana. The paper industry is one of the major agro-based industries. Paper manufacturing industries are reliant on eucalyptus and other suitable trees used as raw materials in the production of paper. Maharashtra, Andhra Pradesh, Gujarat, and Uttar Pradesh are the leading paper producing states of India. These states nearly account for 50% of overall paper manufacturing capacity. West Bengal, Madhya Pradesh, Tamil Nadu, Karnataka, Punjab, and Haryana are other producers.

These industries' cogeneration power plants release massive quantities of ashes as a result of the combustion of waste biomass residues. Sugar and rice industries predominantly use bagasse (residue from the processing of sugar cane) and rice husk (residue from rice processing) as a source for generating heat and power. While modern paper industries utilize multiple feedstocks for generating heat and power, primary sources are rice husk and bagasse including a small portion of pet coke, coal etc. As estimated in India, biomass residues from sugar, rice, and paper industries are responsible for generating $\sim$ 3.5 MT, 5 MT, and 10 MT of ash per annum, respectively. Often, biomass ashes are being dumped in landfills, creating serious disposal and environmental issues. At this juncture, it is understood that biomass ash can be an efficient construction material if designed and activated appropriately owing to its inherent amorphous silica composition.

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3. CHARACTERISTICS OF BIOMASS AND BIOMASS ASH

3.1. Biomass

Biomass is defined as an organic material that is produced through the photosynthesis process, whether directly or indirectly [39]. The heterogeneity of biomass, its origin, and its use are some of the factors that affect the definition of biomass. Biomass, in general, refers to biological material that can take on many different forms, including wood, sugarcane bagasse, rice husk, rice straw, corn cob, paper waste, municipal solid waste, animal manure, sewage, algae, etc. [40]. A broad classification of biomass is shown in Table 2 [14].

Table 2: Broad classification of biomass

Biomass classification	Types
Woody	Stems, branches, bark, chips, bamboo, etc.
Non-woody	Grasses, flowers, straws, other residues
Processed waste	Cereal husks, corncob, bagasse, shells, municipal waste, sawmill waste, etc.
Processed fuel	Charcoal, briquette, methanol, biogas, etc.

Due to the sizeable annual volumes and significant economic potential, the use of biomass resources is becoming more and more important. The production of biofuel is one application where biomass has the potential to replace conventional fuels. Biochemical and thermo-chemical are the two major processes through which biomass can be converted into energy. The biochemical process involves conversation of biomass into gaseous or liquid fuels using bacteria, enzymes/ micro-organisms. Whereas in the thermo-chemical process, biomass structure is disrupted using heat to produce energy, biofuel and biochar [41]. A thorough understanding of biomass characteristics is necessary to use it as an efficient fuel.

Biomass types have intricate structures and are made up of a variety of components. The chemical and physical characteristics of biomass species vary greatly, and it is dependent on the type of species and environmental factors such as temperature, soil, humidity, etc. [42]. Lignin, cellulose, and hemicellulose are the major constituents of biomass, which exists in different proportions and structures [39]. The inherent qualities of biomass that can be used as a source of energy include its moisture content, energy density, bulk density, size, and shape. The type of solid biofuel used, as well as its physical (particle size, shape, bulk density, temperature, and moisture content) and chemical characteristics, affect the entire thermal process of solid biomass material [43]. The main determinant of biomass quality is its calorific value, which is the quantity of energy released per unit mass upon complete combustion of biomass. The calorific value of biomass varies with the type of biomass as its organic composition such as lignin, cellulose, hemicellulose, proteins, starch, and fat [44]. The calorific value of biomass is also affected by external factors such as climate, soil, and temperature. Table 3 lists the proximate analysis, ultimate analysis, and calorific value of various agriculture-based biomass feedstocks [44-46].

Table 3: Proximate analysis, ultimate analysis, and calorific value of various agriculture-based biomass feedstocks [44-46]

Biomass type	Proximate analysis				Ultimate analysis					GCV kcal/kg
	MC	VM	A	FC	C	H	N	O	S	
	%				%					
Sugarcane bagasse	4.5	77.1	2.4	16	49.8	6	0.2	43.9	0.06	4547
Rice husk	7.2	58.2	20	14.6	49.3	6	0.8	43.7	0.08	3729
Coconut husk	13.4	56.7	2.4	27.5	45.4	4.9	1.1	48.3	0.35	3800
Ground nutshell	10.1	68	2.8	19.1	50.9	7.5	1.2	40.4	0.02	4008
Saw dust	13.8	72.9	0.6	12.7	49.8	6	0.5	43.7	0.02	4028
Corn cob	4.87	71.9	5.9	17.3	48.7	6.4	0.7	44.1	0.08	4238
Elephant grass	11.5	63.4	5.4	19.7	48.7	6.1	0.6	44.5	0.13	3601
Bamboo leaves	7.7	68.7	12.3	11.3	52	5.1	0.4	42.5	0.04	3756
Castor stalk	20.5	63.5	2.1	13.9	48.8	5.6	1	44.5	0.13	3496

* MC: moisture content; VM: volatile matter; A: ash content; FC: fixed carbon; C: carbon;
H: hydrogen, N: nitrogen; O: oxygen; S: sulphur; GCV; gross calorific value

The proximate analysis provides the weight percentage of moisture, ash, and volatile matter present in the biomass fuel (Table 3). Moisture in biomass feedstocks absorbs the heat released during combustion. Due to this, there is less net useful heat from the fuel and there is more heat loss from the stack [46]. Higher levels of moisture cause problems with fuel sizing, conveying, feeding, fuel efficiency, etc. According to Table 2, the moisture content of biomass ranges from 4 to 30%, and for raw wood species, it can range between 60 and 80%. Moisture in biomass is basically in a mineralized aqueous solution containing Al, Ca, Fe, K, Mg, Na, Ti (cations), and Br, Cl, CO_3, F, SO_4 etc., (anions) [47]. Due to the high-water content of living cells, dissolved solid matter, and varied chemical compositions (predominant anions, cations, and their ratios), this moisture content is crucial for the composition of biomass. As a result, moisture evaporation after biomass harvesting and during biomass drying leads to intense mineral precipitation (phosphates, carbonates, sulfates, chlorides, and nitrates) from a saturated solution [14].

The heating of biomass fuels liberates volatile matter such as flammable gas and smoke. Light hydrocarbons, CO, CO_2, H2, moisture, and tars are among the volatile materials that biomass typically yields [48]. In the presence of enough air, high enough temperature, and turbulence, volatile matter ignites as a flame. For the efficient combustion of excessive volatile matter, biomass fuel needs to be supplied with a lot of secondary air at a high pressure. Complete combustion of volatile matter results in dark smoke, heat loss, pollution, and soot build-up on boiler surfaces [49]. Volatile matter of agriculture-based biomass sources is found to be in the range of 50-80%. Sugarcane bagasse, saw dust, and corn cob are some of the biomasses that show high value of volatile matter [45].

Incombustible inorganic solid material after complete combustion (at 500-700 °C) of biomass fuel is known as ash. Inorganic crystalline, semi-crystalline, and amorphous is the inorganic solid phases present in the ash. Si, Al, Fe, Ca, Mg, Ti oxides, and other oxides are the major composition of ash [45]. The yield of ash varies from 0.6 to 20% (Table 2) and that may extend up to 60% for woody biomass sources. Ash fuses and forms clinker by entrapping combustible material at high biomass combustion temperatures, reducing the efficiency of combustion [49]. The yield of ash is highly dependent on species type, and combustion temperature and is also affected by soil conditions, irrigation, fertilizer, and weather. High ash yield indicates the amount of contamination added from soil, rain, wind, harvesting etc., and mineral/metallic contaminants due to manufacturing processes [14]. Agricultural biomass has higher ash residues compared to forest-based biomass as a result of high nutrient intake during the cultivation process. Commonly, metal cations (Ca, Fe, K, Mg, Mn, and Na), non-metal anions (P, S, and Cl), or non-charged species (Si) are the ash forming elements that are absorbed by biomass during its growth [14, 50]. On the other hand, fixed carbon content (solid combustible residue) in biomass varies approximately from 15-30% (Table 2). All of the carbon in biomass is organic because it is created by the photosynthetic fixation of CO_2. The amount of char formation during the thermochemical conversion process is indicated by the fixed carbon content [14]. The yield of char produced during the thermochemical conversion process increases as fixed carbon concentration increases. The amount of fixed carbon produced during the combustion of biomass depends on the lignin content of that biomass; higher fixed carbon is correlated with biomass that contains more lignin [51].

The ultimate analysis provides the percentage concentration of major elements of biomass such as carbon, hydrogen, nitrogen, oxygen, and sulfur (Table 2). Carbon, hydrogen, nitrogen, oxygen, and sulfur content in agriculture-based biomass varies between 40-55%, 5-8%, 0.2-1.5%, 40-50%, and $<0.4\%$, respectively. Higher oxygen ($>50\%$) content in biomass indicates the comparatively lower requirement of stoichiometric air for combustion [14, 45]. Nitrogen and sulfur content is found to be negligible in most agriculture-based biomass sources. Nitrogen oxides (NO_x) and sulfur oxides (SO_x), which are toxic and undesirable combustion products, are often produced when there is a high concentration of nitrogen and sulfur. Additionally, it has been claimed that the presence of sulfur causes combustion equipment to corrode because it generates the acidic sulfur dioxide and sulfur trioxide [52].

The efficiency of biomass is chiefly related to its calorific value, higher the calorific value higher the fuel efficiency [39]. The gross calorific value of agriculture-based biomass is seen to be in the range of 3500-4500 kcal/kg [44]. The percentage of moisture content has a significant impact on the quality of biomass fuel; higher moisture content has a detrimental effect on fuel quality [46]. The calorific value of biomass decreases with the increase in ash content. Higher volatile composition and fixed carbon also result in poor fuel quality. More smoke is produced when the volatile matter is present in higher concentrations [14, 45]. The presence of a higher proportion of lignin and oil content in biomass possesses higher energy than cellulose/hemicellulose and starch [53]

In comparison to coal, biomass has a very different composition. It is also being discovered that the chemical composition of biomass is highly variable compared to coal [54]. The higher variability is related to the high variations in moisture, bulk ash yield, and various genetic types of inorganic matter in biomass [14, 50]. It is necessary to characterize samples of biomass from various sources for its proximate and ultimate analysis to understand the quality of biomass fuel and combustion products generated during the process of energy generation.

3.2. Biomass ash

Solid biomass ash remained after the burning process of biomass is a complex material. The yield of biomass ash is dependent on the type of biomass, which varies in the range of 1 to 60 wt% [55]. The physical and chemical properties of the residual biomass ash serve as the primary determinants of the quality of various biomass ash-based cementitious binders. The type and origin of the biomass, the combustion method, and the operating conditions, as well as the treatment and storage of the ash, are some of the most important variables affecting the characteristics of the ashes [14]. Due to significant heterogeneity, a vast amount of information on the composition of biomass ash has been reported in the literature [55]. Predominant elemental composition of biomass ashes found in literature includes O, Ca, K, Si, Mg, Al, Cl, P, Fe, Na, S, Mn, and Ti (listed in descending order) [55-57]. Solubility of elements and pH are the additional significant factors that influence the applicability of biomass ash. The solubility rate of elements such as Cl, S, Na, K, Mn etc., in water is much higher in biomass ash compared to fly ash [57]. The leaching behaviour of ashes is highly reliant on their pH (lower the pH higher is the release of elements in ash) [16]. It is reported that burning temperature and ash storage time are the main factors that affect the pH of biomass ash [55-56].

Specific gravity, specific surface area, particle size distribution, and bulk density are the important physical characteristics of biomass ashes for their utilization. Specific gravity, surface area, and ash content of biomass ashes are shown in Table 4 [15-16, 58-60].

Table 4: Specific gravity, surface area and ash content of biomass ashes [15-16, 58-60]

Biomass ash type	Specific gravity	Surface area (m^2/g)	Ash content (%) from respective biomass
Sugar cane bagasse ash	1.9-2.3	25-52	1.8-5
Rice husk ash	2.0-2.2	50-60	20-25
Corn cob ash	1.2-2	15-20	8-10
Palm oil fuel ash	2.1-2.5	30-40	1-3
Wheat straw ash	1.9-2.2	-	1.6-20
Paper mill ash	1.2-2.1	20-35	10-50

The specific gravity of biomass ash varies from 1.8 to 3 (lower than the specific gravity of portland cement, i.e., 3.15) [15], which shows a significant influence on the workability of a concrete mix. The lower specific gravity of biomass ash is attributed to its porous nature which can be improved to a certain extent by adopting suitable processing techniques [61]. It is to be noted that lower specific gravity of biomass ash leads to the increased binder volume and demand for water when used at a higher replacement level to OPC (in portland cement concrete) or fly ash/GGBFS (in alkali-activated binders), affecting the flowability [62]. Presence of unburnt light weight carbon also influences the specific gravity of biomass ashes [13]. The specific surface area of biomass ash is another important factor that has a direct influence on the reactivity extent (specific surface area is directly proportional to reactivity). The higher specific surface area of biomass ash is due to the highly porous nature and high concentration of fibrous unburnt carbon [13]. Similar to specific gravity, the specific surface area of biomass ash can also be increased by increasing the level of grinding [63]. Hence, processing of residual biomass ash is highly recommended to achieve the required relative density and fineness.

The reactivity of ash is significantly affected by its oxide composition that varies based on the biomass feedstock composition. Weight percentage of major oxide compounds such as SiO_2, Al_2O_3, Fe_2O_3, CaO, and loss on ignition (LOI) of ashes are shown in Table 5 [13, 15, 58-59, 64].

Table 5: Oxide composition and LOI of various biomass ashes [13, 15, 58-59]

Biomass ashes	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	P2O5	MgO	SO_3	Na_2O	LOI
	%									
SBA	55-75	1.5-10	0.1-11	0.2-13	0.5-3	0.2-1	<2	-	0-0.5	3-22
RHA	80-97	0.1-2	0.1-4	0-0.2	0.5-2.5	4-10	1.5-2.3	-	0-0.5	2-13
CCA	40-65	6.5-8	1-9	0.2-14	0-5	-	0.5-5	<0.01	0-5	7-14
POFA	45-65	2-6	0.2-7	4-12	<0.5	<1	1-3.2	1-3	<0.5	2-12
WSA	52-75	2-7	0-5	3-17	3.5-8.5	<0.2	1.5-2	-	0-3	5-16
PMA	26-62	1.2-28	0.3-4	1-30	0.4-10	0.6-3	0.3-9	1.2-3	0-0.5	20-40

*SBA: sugarcane bagasse ash; RHA: rice husk ash; CCA: corn cob ash; POFA: palm oil fuel ash; WSA: wheat straw ash; PMA: paper mill ash

Chemical composition of biomass ashes changes significantly with respect to the processing technique. Combustion of biomass ashes at ideal temperature conditions (600-800 °C) results in increased amounts of silica (SiO_2) and alumina (Al_2O_3) compositions with lower LOI [65-66]. Burning biomass at higher temperatures (>700-800 °C) can result in the formation of crystalline phases. For the production of binders, biomass ashes with crystalline phases of silica such as cristobalite and tridymite with low specific surface area and reactivity are not beneficial [12]. The consumption of portlandite in cement concrete to produce calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H) is facilitated by highly reactive aluminosilicate phase of biomass ash [13]. Biomass ashes rich in reactive silica and alumina content can be used as a precursor material in the development of alkali-activated binders [13, 32]. The presence of high alumina concentration in biomass ashes promotes the development of a stronger mixture due to the formation of C-A-S-H phase during the reaction process [61]. For natural SCMs to claim as pozzolanic material, the composition of $SiO_2+Al_2O_3+Fe_2O_3$ should be greater than 70% as per ASTM C618 [68]. Most of the biomass ashes meet the requirement of ASTM standards. However, oxide compositions of a few ashes having $SiO_2+Al_2O_3+Fe_2O_3$ content below the desirable limit can be improved by adopting suitable processing techniques. Some of the natural pozzolans, for instance paper mill ash, contain SiO_2+CaO content >50%, which indicates the hydraulic property of the material [60, 69]. Further, soil type, fertilizers, and pest control agrochemicals used for harvesting biomass crops all contribute to a high alkali content of biomass ashes. The alkali content in the biomass feedstock can affect the formation of certain mineralogical phases during the combustion process [70].

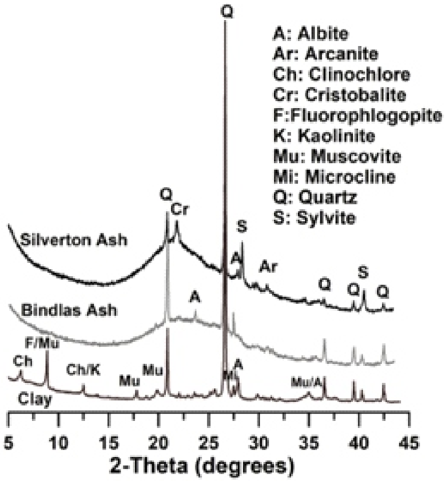
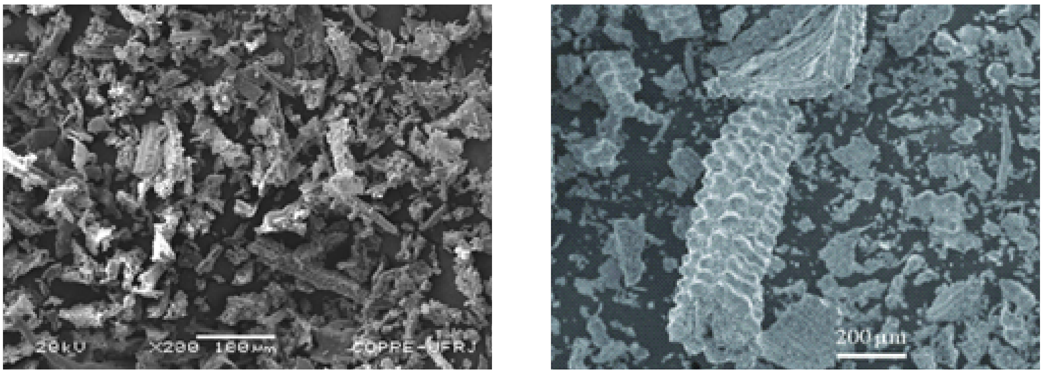
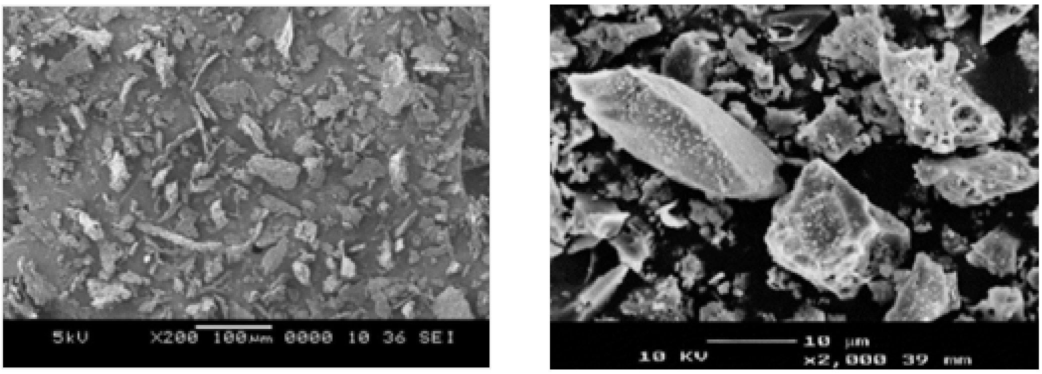


Fig. 12: XRD pattern of biomass ash showing amorphous hump between 20–30° (2-Theta) [13]

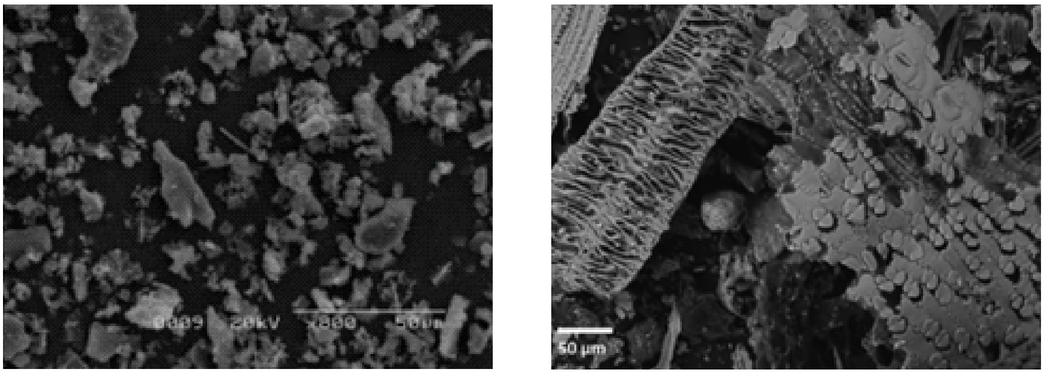
The performance of a biomass-based binder system, particularly its fresh, strength, and durability properties, can be significantly influenced by the morphology of ashes. Understanding the morphologies of different biomass ashes enable one to predict how the ashes will behave when used as a binder ingredient. The micrographs of some of the biomass ashes are displayed in Fig. 13 [13, 71-76].



a) SBA b) RHA



c) CCA d) POFA



e) WSA f) PMA

Fig. 13: Micrographs of various biomass ashes [13, 71-76]

Mineralogical composition of biomass ash depends on the combustion conditions, such as incineration temperature and residual time. In the majority of cases, an amorphous hump at the 2 value of 20–30° in XRD plots indicates the presence of amorphous phase in biomass ash (Fig. 12) [13]. However, the amorphous hump in the XRD pattern may also be caused by the presence of unburned carbon [13]. LOI provides the indirect assessment of amount of unburnt carbon present in biomass ash. The black colour of biomass ash signifies a higher value of LOI [13, 64]. Raw biomass ash has a significant amount of LOI as a result of uncontrolled burning conditions [13, 15, 60, 64]. Unburnt carbon quantity depends on the type of biomass, the type of incinerator, efficiency of incineration, and the air flow. Thermal analysis of biomass shows mass loss between 30-150 °C due to loss of adsorbed water, 150-600 °C due to loss of organic matter (cellulose and lignin), and 600-800 °C due to loss of carbonates and small carbon particles [70]. The presence of high LOI in biomass ash leads to a decrease in specific gravity, increase in water absorption, and decrease in reactivity, causing an adverse effect on the performance of the binding material. Therefore, low LOI is required for it to be used as an

SCM in blended portland cement or a precursor in alkali-activated binder systems. ASTM C618 recommends the permissible value of LOI for natural pozzolans as 10% and 5-6% for coal fly ash [68]. Unburnt fibrous particles of biomass left due to uncontrolled burning increase the LOI content. This can be reduced by burning ashes to its optimal temperature or through other processing techniques such as sieving, floatation, calcination, and classification method [13]. To achieve the required reactivity, apart from energy-consuming processing techniques, straightforward sieving process that uses less energy is sufficient [13]. Even though the reactivity of ashes is increased due to processing, ashes from various sources may not be beneficiated using the same processing technique. As a result, industries are discouraged from investing in biomass ash utilization due to the variability in ash properties and its lack of reactivity as a result of improper firing conditions.

Biomass ash from various biomass sources has different morphologies. Different spherical, fibrous, prismatic, dumbbell-shaped, and irregular particles with a high silica content are visible in the SEM micrograph of SBA (Fig. 13a). Carbon-intense fibrous particles (>75% carbon) are responsible for workability issues [71, 76]. It is therefore advised to completely remove these particles before using the material as a pozzolan and precursor in alkali-activated binder [12, 77]. Spherical particles of SBA are reported to have Si, O, and alkali components. According to Batra et al. (2008) silica is also found in prismatic and dumbbell-shaped particles. Fig. 13b illustrates the irregular, cellular, and porous structure of RHA [78]. Its reactivity is attributed to its cellular structure with a high surface area, which is mostly amorphous silica. The cellular structure of the as-collected raw RHA can be destroyed on grinding, which lowers the associated water demand and water absorption capacity of ash [72]. Corn cob ash (CCA) particles are larger and more angular (Fig. 13c). It is reported that CCA has macro and micro-sized pores, which are responsible for high water demand [73]. As can be seen in Fig. 13d, palm oil fuel ash (POFA) has irregular particles with a porous cellular surface and pedospheres that are similar to those of FA [74]. Wheat straw ash (WSA) particles were found to be largely asymmetrical, and only a small number were found to be elongated (Fig. 13e). Similar to SBA, spherical particles of WSA are made up of Si and O alone, while prismatic particles are consisting of Si and O plus a few other mineral compounds [75]. The micrograph of PMA also shows the porous morphology with intense carbon composition (Fig. 13f) [13]. In general, the majority of biomass ashes are found to be highly porous, which can be broken down on griding thereby improving the specific gravity as well as its fineness property of ashes [15].

3.3. Summary

Biomass is as distinctive as the species from which it is derived and the environment in which it grows. However, the main organic components of biomass (cellulose, hemicellulose, and lignin) have a significant influence on its properties. These components differ depending on the source of the biomass, the species, the climatic conditions, etc. In biomass, lignin makes up 15–30% of the material, and 70%–85% of cellulose and hemicellulose. The application potential of biomass, in particular its ability to produce energy, is determined by its proximate and ultimate analysis. The heating value of biomass is also considered when it is used as a feedstock in thermochemical conversion processes. In the thermochemical process, heat is used to disorganize the structure of biomass into energy, biofuel and biochar. Physical and chemical properties of biomass have an impact on the thermal process efficiency of solid biofuel.

The proximate analysis calculates the physical characteristics of the biomass (moisture, volatile matter, ash content, fixed carbon), which directly affect how well the biomass burns. Whereas the ultimate analysis offers a qualitative and quantitative estimation of chemical properties in terms of the weight fractions of elemental components (like C, H, and O). Calorific value is the main determinant of biomass quality. Higher moisture content, volatile matter, fixed carbon, and ash yield in biomass negatively impact the calorific value. Agricultural biomass has higher volatile (50-80%) and ash residues (0.6-20%) compared to forest-based biomass as a result of high nutrient intake during the cultivation process. Fixed carbon content (solid combustible residue) in biomass varies in the range of 15-30%, which depends on the lignin content of biomass.

The physical and chemical properties of the residual biomass ashes serve as the primary determinants of the quality of various biomass ash-based concrete. The kind and origin of the biomass, the combustion method, and operating circumstances, as well as the treatment and storage of the ash, are some of the most important variables affecting the characteristics of the ashes. Predominant elemental composition of biomass ashes found in literature includes O, Ca, K, Si, Mg, Al, Cl, P, Fe, Na, S, Mn, and Ti. In comparison to portland cement, biomass ash has a lower specific gravity (1.8 to 3) and is porous by nature. Biomass ashes have a higher specific surface area because of their large fibrous unburned carbon content. The formation of crystal phases from the burning of biomass at higher temperatures (>700–800 °C) can make the ash less reactive. Morphological characteristics of biomass ash are also an important parameter that influences the reactivity, and engineering properties of biomass ash binders. Different biomass sources produce different morphologies of ash with porous, spherical, fibrous, prismatic, dumbbell, and irregularly shaped particles. To achieve the required relative density, fineness, and reactivity processing of residual biomass ashes is strongly recommended.

Biomass and biomass ash have a very distinct and highly variable composition when compared to coal and coal-driven fly ash. To comprehend the quality of biomass fuel and combustion products during the process of energy generation, it is necessary to characterize samples of biomass from various sources for both its immediate and long-term analysis.

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4. BIOMASS ASH FOR ALTERNATIVE BINDERS

Production of ordinary portland cement (OPC) consumes a significant amount of non-renewable energy and resources [79]. Utilization of waste as an alternative binder to ordinary portland cement (OPC) can minimize the environmental burden and CO_2 footprint of construction industry. To achieve sustainable goals in the construction and building sector, demand for supplementary cementitious materials (SCMs) produced from various industries is increasing gradually [80]. Industrial by-products such as fly ash (FA), ground granulated blast furnace slag (GGBFS), and silica fume (SF) are well established in the production of low-carbon green binders [80-81]. Accessibility of often-used SCMs such as FA and GGBFS is getting limited; consequently, exploration of non-traditional SCMs has become a crucial need. In recent years, biomass ashes from ago-based industries such as sugarcane bagasse ash (SBA), rice husk ash (RHA), and paper mill ash (PMA) are finding prominence in the development of an ecological binding material owing to their physicochemical property and abundant availability in an agricultural country such as India [12-13, 16, 82]. In this context, relevant literature emphasizing the incorporation of biomass ashes in OPC and non-OPC-based binders are discussed in the following section.

4.1. Biomass ash blended OPC system

4.1.1. Early age properties of biomass ash blended cementitious system

4.1.1.1. Workability

One of the vital physical characteristics of fresh concrete that influences the hardened properties of concrete such as strength and durability is its workability. Water-to-binder ratio, physico-chemical properties of the binder, shape-size of raw materials, environmental factors, and type of compaction are some of the significant factors that affect the workability of concrete [83]. The presence of biomass ash in OPC concrete can alter the workability of mortar/concrete. The workability of biomass ash-based concrete is chiefly affected by its two important factors: 1) fineness and 2) carbon content [15]. Literature reports that the addition of biomass ash (e.g., RHA, SBA, PMA, etc.) in concrete significantly reduces the workability as a function of its high-water demand [84]. This fact was noted for both unprocessed and processed biomass ashes [59]. Fig. 14 depicts the range of reduction in slump (%) concerning the control mixture [15, 59, 83-84].

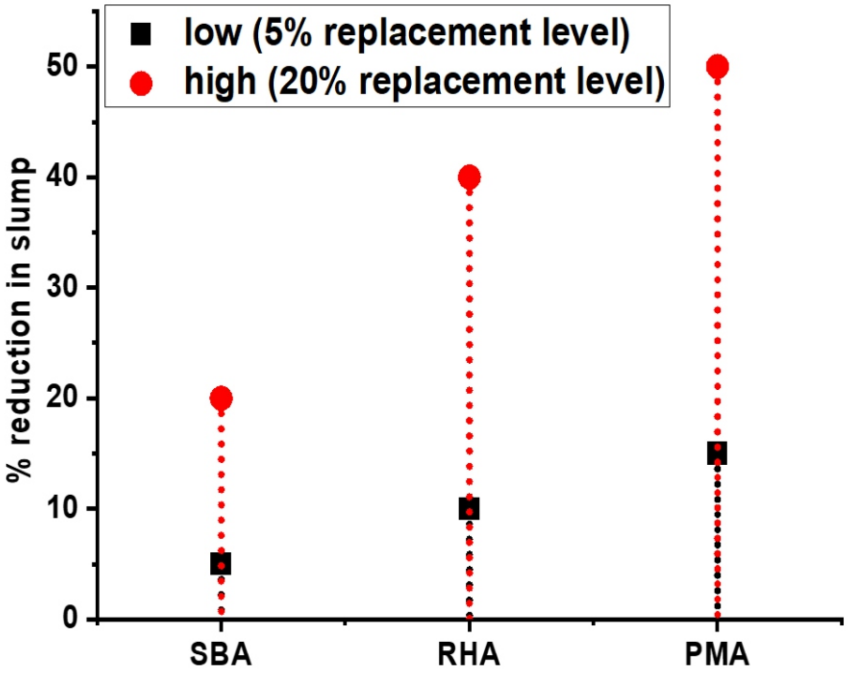


Fig. 14: Reduction in slump of biomass ash blended OPC mixes [15, 59, 83-84]

For instance, Thomas et al. [58] reported that the incorporation of 10, 20, and 30% SBA accelerated the requirement of superplasticizer dosage from 3.15 to 7.35 kg/m3 to maintain the constant slump value. Similar observations were made by the researchers on other biomass ash (RHA, PMA, etc.) based concrete [76, 85-86]. The major reasons associated with the reduction in workability and increased water demand of biomass ash-based concrete are the shape or structure of ash [60], high specific surface area [58, 62], hydrophilic property of ashes owing to their porous nature [64], and high content of unburnt carbon [83]. The reduction in workability can be prevailed by eliminating unburnt carbon content through simple processing techniques such as sieving. Investigation from Akram et al. [87] illustrates the possibility of utilization of SBA as a source of viscosity modifying agent (VMA) in developing a self-compacting concrete (SCC). It has also been stated that the cost of materials used for SCC was ~35% of control concrete.

Some of the biomass ashes such as palm oil fuel ash (POFA) when used as an alternative binder in concrete increased the workability. This is attributed to the greater availability of binder paste volume to adhere to the aggregate surface and to provide easy movement of aggregate during the process of mixing [40]. Besides, the drop in workability for POFA, baboo leaf ash (BLA), groundnut husk ash (GHA) etc., except SBA, RHA, PMA, and wood ash (WA), was reported to be less than 30 mm till the replacement level of 10-20% to OPC. It is reported that this can be compensated through a suitable mix proportion [15].

4.1.1.2. Reactivity of biomass ash in cementitious system

The reactivity of biomass ashes in OPC system is directly linked to its chemical composition. Biomass ashes mostly comprise oxides of Si, Al, Ca, Fe, Mg, and K, which are commonly found in OPC and traditional SCMs [13, 76, 85]. Fig. 15 shows the ternary diagram of biomass ash oxide composition [13, 76, 85].

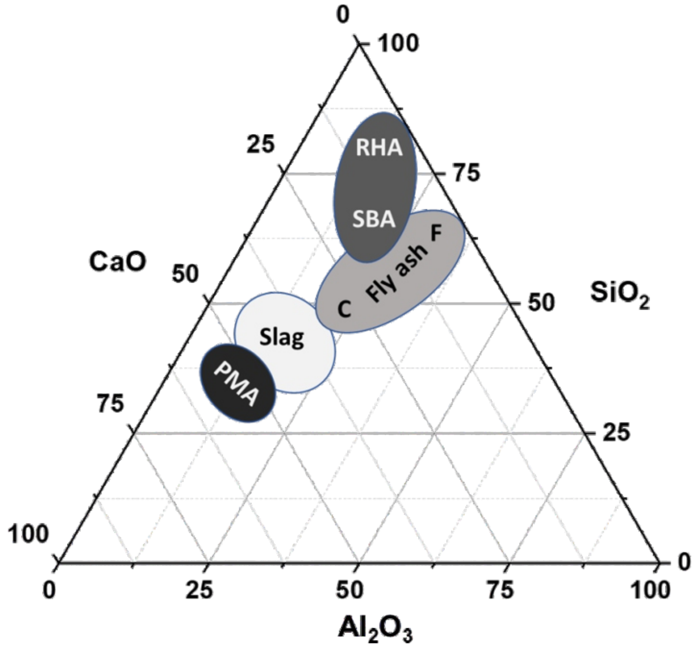


Fig. 15: Ternary plot of oxide composition of biomass ashes: SBA, RHA, PMA [13, 76, 85]

European (EN 450-1) and American (ASTM C618) standards specify that, to classify any ash as Pozzolan, it should contain minimum primary oxide composition (SiO_2+Al_2O_3+Fe_2O_3) of 70% [71, 79]. The majority of biomass ashes (varies in the range of 71-98%) meet the requirement except for PMA (varies from 20-50%) consisting of mixed ashes from different feedstocks (predominantly rice husk and bagasse) [43]. The pozzolanic reactivity of biomass ash mainly relies on its silicious and aluminous components. However, PMA contains >50% of CaO + SiO_2 composition and can be classified as a hydraulic material (EN 450-1) [41, 36]. Seifi et al. (2019) [89] noted that high free lime content in PMA-incorporated cementitious composite caused swelling-related issues, which restrict the amount of PMA that can be added. Fineness, amorphous content, and unburnt carbon are a few other characteristics of ashes that affect the reactivity of biomass ash. Figure 16 presents a range of LOI (%) and mean particle size (μm) of biomass ashes, as reported in various studies [60, 63, 84, 85 87, 89].

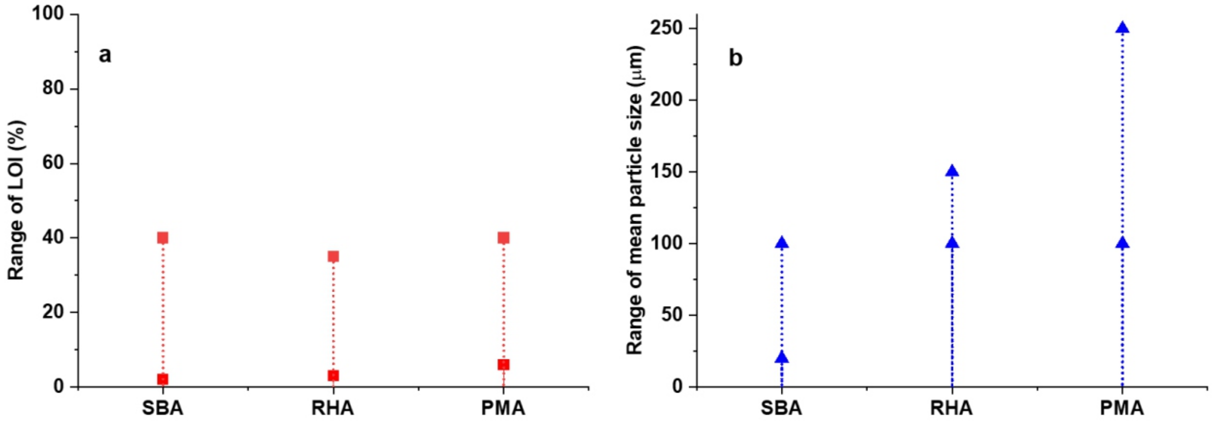


Fig. 16: Upper and lower bounds of a) LOI (%), and b) mean particle size (μm) for biomass ashes [60, 63, 84, 85 87, 89]

Biomass ashes possess a higher LOI percentage mostly $>$ 10%, significantly higher than conventional SCMs. The mean particle size of SBA, RHA, and PMA are $>$50 μm and goes up to 100-250 μm. The lignocellulose content and burning conditions are responsible for the greater variation in LOI and mean particle size. Similar to traditional SCMs, biomass ashes also tend to accelerate the cement hydration due to the filler effect [85]. The rate of reaction can be accelerated by using ashes that are glassy or amorphous and smaller in size. It is well reported that the reactivity of ash can be increased by increasing the specific surface area on grinding or other processing techniques and combustion parameters [61]. Several researchers have noticed an increase in the setting time of concrete when biomass ash is added to the OPC system [62, 65, 88]. According to Choi et al. [65], addition of fine ash to mortar slowed the retardation. The early pozzolanic reaction is governed by the specific surface area of ashes, whereas later pozzolanic reaction is controlled by the concentration of active glassy silica and alumina in the concrete's pore solution [90].

The properties of a biomass ash greatly depend on the growing condition, burning temperature, pressure, and humidity. According to one study, adding RHA which was burned in controlled conditions to an OPC system caused the setting time to be delayed compared to RHA burned in uncontrolled conditions [63]. The residual carbon content that remains in biomass ash made from the original biomass slows down the reactivity process by absorbing moisture and raising the need for water [13, 59]. Some researchers have calcined the ashes (at 600-800 °C) to remove the unburnt carbon and increase its reactivity [66]. Further, the reactivity of ash is altered in the presence of alkali salt. Alkali salts are said to increase the dissolution of amorphous phases in pore solution, which may speed up reactivity [60]. Shi and Day [91] claimed that the presence of chloride salts in ashes accelerates the hydration of C_3S, resulting in the formation of C-S-H gel and reducing the setting time.

PMA admixed cementitious composite showed accelerated hydration kinetics, taking less time to reach the second hydration peak that indicates the early setting of the sample (Fig. 17). The attributed cause for the accelerated early reaction of PMA was increased nucleation sites, the filler effect, and the presence of alkalis. However, the degree of hydration reaction was less pronounced at later ages [60].

Strength Activity Index (SAI), Chapelle, Frattini, and other tests are some of the common reactivity tests for SCMs. ASTM C311 states that a blended cement system that achieves a SAI value of greater than 75% indicates the pozzolanic reactivity of SCMs. The SAI test and Frattini test measure reactivity based on the pozzolanic reaction between reactive silica and reactive alumina from the SCMs and calcium hydroxide ($Ca(OH)_2$) from

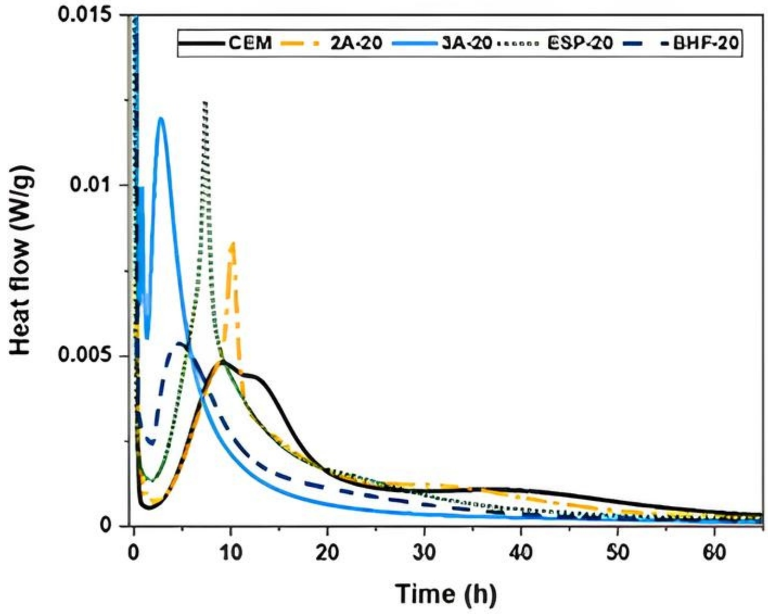


Fig. 17: Isothermal calorimetry results for blended cement [60]

portland cement hydration [92]. Since the Frattini and Chapelle tests both quantify $Ca(OH)_2$ consumption, they were not designed to evaluate the reactivity of Ca-rich SCMs. The RILEM Technical Committee 267 advises using isothermal calorimetry to measure the bound water and calcium hydroxide consumption from the binder used for the heat of hydration study at 40 °C for seven days [93]. In this reactivity test method (i.e., R3 method), KOH, K_2SO_4, and calcite in addition to SCM and portlandite are used. The high pH in the portland cement system is replicated by the presence of alkali hydroxide and alkali sulfate. Sulfates and carbonates, in particular, will affect the alkali-activated system's hydration mechanism and the reaction products. Therefore, R3 mix design might not be appropriate for determining the reactivity of binders that have undergone chemical activation [92].

In this regard, the modified R3 method eliminates the additional sulfates and carbonates is recommended to measure the reactivity of SCMs, and the test is performed at 50 °C for 10 days to facilitate a maximum degree of reaction even from the slow-reacting SCMs. Similar to the R3 method, the heat of hydration study is used to measure the bound water and calcium hydroxide consumption for the binder [92]. To categorize the reactivity of the pozzolanic material as inert, pozzolanic-less reactive, pozzolanic-more reactive, latent hydraulic-less reactive, and latent hydraulic-more reactive, the $Ca(OH)_2$ consumption is plotted against cumulative heat release after 10 days. Further, the impact of SCM composition on the reactivity assessment is also presented in Fig. 18 [94].

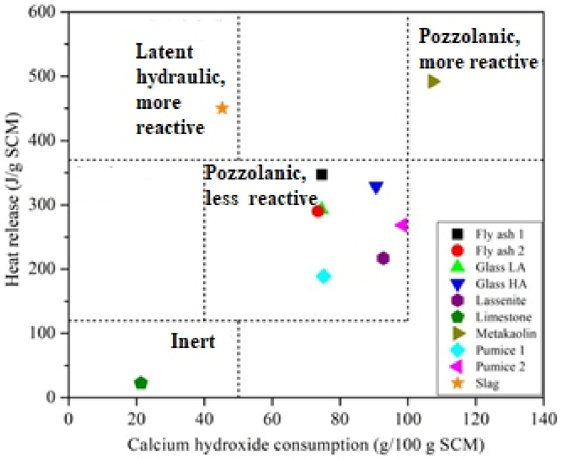


Fig. 18: Classification of pozzolanic reactivity of various SCMs [94]

The research demonstrates a clear difference in reactivity between high calcium, high alumina, and high silica content materials (Fig. 19). In high silica SCMs, an increase in temperature (40 °C to 50 °C) has a greater impact on the cumulative heat release than carbonates and sulfates. SCMs with moderate to high levels of calcium and alumina are more affected by the addition of sulfates and carbonates due to the formation of reaction phases with sulfates and carbonates [92].

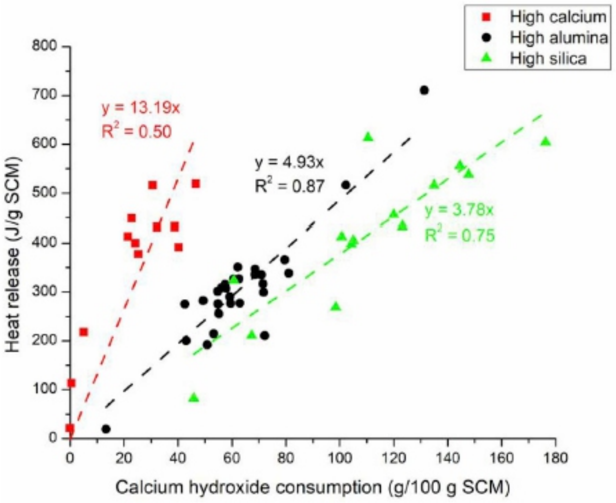


Fig. 19: Difference in reactivity between high calcium, high alumina, and high silica content materials [92]

The majority of agricultural ashes are silicious, they may need a high temperature (50 °C) for a better reaction even at early ages. Therefore, the reactivity of the silicious ashes for chemical activation can be determined using modified R3 test methods.

4.1.2. Mechanical properties of biomass ash blended cementitious system

4.1.2.1. Compressive strength

The utilization of biomass ash as a partial replacement for OPC showed an increase in compressive strength [76, 60, 95]. However, the compressive strength of biomass ash concrete tends to decline beyond its optimum level of replacement [15, 85, 96]. Among various biomass ashes studied SBA, RHA, and PMA were found to have better compressive strength at the optimum replacement level of 10-20% [60, 90]. Beyond the point of optimal replacement, compressive strength starts to decline. This decline is linked to the dilution effect and a less compact microstructure. [96]. It is noted that concrete made from biomass ash had lower early age strength (i.e., at the age of 3-14 days), which progressively increases at the later age [85]. However, a few studies have reported that RHA addition boosts strength at the early age of 1-3 days of maturing [63, 95]. Similar to conventional SCMs, biomass ash also serves as a filler material at first, aiding-in packing followed by nucleation. Additionally, when there is a high silica content, it serves as a pozzolanic material, favouring the mechanical properties.

According to the literature, adding RHA to blended cement reduces the tendency of concrete to bleed in its fresh state, creates a solid ITZ, and reduces the permeability of concrete at is the hardened state [61, 63]. Similar findings were reported by Nuruddin and Menon [97], who found that the presence of 15% SBA densified microstructure and improved pore refinement. When SBA (up to 50%) and fly ash were combined to make a ternary blended OPC system, masonry blocks produced were found to comply with IS standards bearing a compressive strength in the range of 4 to 7 MPa. [98]. An experimental investigation conducted by Moukannaa et al. (2022) on the viable use of four PMAs collected at different incineration stages from the same source at a substitution rate of 5-30 wt% of OPC showed great variation in compressive strength values [60]. PMA collected from 3rd pass hooper and electrostatic precipitator showed comparable strength to the reference mix (70 MPa at 28 days) at the optimal dosage of 10%. Whereas PMA from 2nd pass hopper and bag house filter considerably reduced the strength by 40-50% as a result of slow pozzolanic reaction and higher water demand. The degree of reactivity and packing capacity of the ashes in the concrete directly relates to the final hardened property of biomass ash concrete. The variability in compressive strength development and optimal usage of biomass ash in concrete relies on the type of cement used, water-to-binder ratio, and physico-chemical characteristics of ash such as chemical composition, particle size distribution, and concentration of amorphous silica and alumina content [15].

Compressive strength of biomass ash concrete is highly influenced by incineration conditions, and pre-and post-incineration treatment practiced in the production of ashes [85]. Burning of biomass at controlled temperature conditions enhances the reactivity of ashes, in addition, the temperature (typically in the range of 500–700 °C range) at which amorphous silicate-rich ashes formed provides optimistic compressive strength development [99]. Pre-incineration treatment such as acid leaching and post-incineration treatment such as sieving, grinding, and calcination of ash at stipulated conditions can enhance the compressive strength of concrete [31].

4.1.2.2. Flexural and splitting tensile strength

Flexural strength test and split tensile test are the indirect way of quantifying the tensile strength of concrete. Flexural and splitting tensile strength of concrete prepared using biomass ash as a partial replacement to OPC depends on similar parameters and follows a similar trend as were offered for compressive strength [15]. Variation in maximum 28 days flexural and splitting tensile strength of SBA, RHA, and PMA blended concrete at its optimum level is shown in Fig. 13. According to published research, adding biomass ash to the OPC binder system significantly alters the flexural and splitting tensile strength of concrete [58-59,76, 85]. Depending on the type and source of ash, the flexural and tensile strength of concrete may marginally increase or decrease with an increase in the dosage of biomass ash [15].

Flexural and split tensile strengths of concrete were reduced when unprocessed SBA (10–40%) was used [100]. However, some authors claimed that by incorporating processed SBA, flexural and splitting tensile strengths of concrete could be increased up to a 20% SBA replacement level [76]. Rice husk ash produced from the controlled incineration process led to an increase in tensile strength than the ash produced from uncontrolled incineration process [63]. Venkatanarayanan and Rangaraju (2015) reported that using both ground and unground incinerated RHA as a partial replacement for OPC increased the tensile strength of the concrete [59]. However, ground RHA had performance characteristics similar to silica fume. For PMA-based mortar samples, there was a noticeable increase in tensile strength up to a replacement level of 5–10%. It was also documented that the percentage of PMA can be increased when blended with GGBFS [101]. Further, the incorporation of fibres has been shown to augment the tensile properties of biomass ash-based concrete [102]

4.1.2.3. Thermal conductivity

Thermal conductivity of concrete/mortar material made up of biomass ash is affected by the particle size and composition of the ash. The incorporation of biomass ash in concrete reduces the thermal conductivity in proportional to the ash percentage. For instance, the resulted in thermal conductivity values for concrete comprising 0%, 20%, 40 % and 60% by mass of bagasse ash were 2.31, 1.91, 1.76, and 1.49 W/mK, respectively. A drop of 17-35 % in thermal conductivity with the increase in bagasse ash from 20%-60% can be attributed to the reduced unit weight of concrete [103].

Thermal conductivity is reliant on the following variables such as density, materials, pressure, temperature, and moisture. Concrete incorporated with amorphous RHA showed lower thermal conductivity [104]. According to Pathak and Madvgane [105] recycled paper mill waste ash has the potential to function as a low-temperature hot insulator due to its low thermal conductivity capacity. The addition of industrial by-products such as fly ash, silica fume, wood waste, saw dust, rice husk ash, bagasse ash, paper sludge ash, etc., have significance in reducing the thermal conductivity of cement-based composite material [103-105]. It is reported that 20% paper sludge ash in cement mortar instigated 23% downfall in thermal conductivity compared to control mortar. The reduction in thermal conductivity is attributed to a substantial decrease in bulk density of cement mortar due to the presence of intrinsic porous property [106]. In general, fly ash and biomass ash possess much lower thermal conductivity than silica fume [107]. However, only few studies have looked at the thermal conductivity of concrete made from biomass ash.

4.1.3. Durability properties of biomass ash blended cementitious system

The service life of concrete chiefly depends on the durability properties of concrete. Therefore, the assessment of the durability properties of concrete is considered to be a significant parameter for the long-term performance of concrete. Similar to cement concrete and conventional blended concrete, the durability of biomass ash blended concrete is also reliant on its permeability and aggressive exposure conditions. The durability properties of cement concrete blended with biomass ash are discussed in the following sections.

4.1.3.1. Water absorption

Ingress of water into concrete is primarily related to the interconnected pores, which is the key parameter that effects the durability properties of concrete [108-109]. The addition of biomass ash in concrete increases the water absorption of concrete, especially at the curing age of 28 days. The increase in water absorption of biomass ash-blended concrete is associated with the hygroscopic nature of biomass ash [76, 96]. Nevertheless, a gradual reduction in water absorption values was noted for concrete blended with 20% SBA or 10 % RHA at the curing age of 90 days. This can be attributed to the blocking of interconnected pores by the formation of supplementary C-S-H gel [76, 109]. Somna et al. (2012) observed that the addition of 35% of ground SBA in recycled aggregate concrete enhanced the resistance to water permeability [110]. Similarly, the utilization of RHA ground to an appropriate level also lowered the water absorption up to 7.5% replacement level as a result of reduced porosity [59]. This can be ascribed to both the pozzolanic reaction and the packing effect of finer particles. Further, beneficial reduction in water absorption was noticed when NaOH treated RHA was added to concrete [111]. De Sensale and Viacava [63] found that the use of RHA derived from both controlled and uncontrolled incineration decreased the permeability of concrete but, at higher water-to-cement ratios, RHA from controlled incineration alone resulted in decreased permeability of concrete.

The rate of water absorption was seen to increase for PMA-based concrete with an increase in PMA content from 5-20% [112]. In contrary, Mavroulidou et al. (2013) observed a decrease in water absorption with an increase in the replacement level of PMA [113]. Existing studies on water absorption and durability properties of PMA blended concrete are minimal which necessitates additional experimental research.

4.1.3.2. Drying shrinkage

Drying shrinkage of concrete impacts, the durability of a structure. Concrete can crack as a result of shrinkage stresses caused by the loss of capillary water. Drying shrinkage values for 20% SBA blended concrete were found to be lower than control specimens at all ages [15, 113]. Whereas Al-Khalaf and Yousif [114] observed higher drying shrinkage for 10% RHA blended concrete compared to that of control specimen. But, after 21 days, RHA reduced drying shrinkage through pore refinement. On the contrary, a reduction in drying shrinkage with the incorporation of 10% RHA has also been [115]. There are limited studies on the drying shrinkage performance of biomass ash-blended concrete.

4.1.3.3. Resistance to aggressive ions

A cementitious system has an alkaline medium and ingress of aggressive ions impacts the durability of concrete [116]. Acid, sulfate, and chloride attack are the most important facets that affect the durability of concrete.

Acid attack results in mass and strength loss in concrete [117]. Sulfate attack is a major cause of the deterioration of cementitious materials, especially in the marine environments [118]. Interaction of sulfate ions with calcium aluminate and calcium hydroxide phases results in the formation of ettringite and gypsum, causing expansive cracking and softening of concrete [118]. Similar to acid and sulfate attacks, diffusion of chloride ions into a cementitious system also impacts the durability of concrete structures. The interaction of chloride ions with aluminate compounds (C_3A, C_4AF) leads to the formation of chloro-complex Friedel's salt and its analogues [119]. Several researchers have observed the reduced degree of deterioration with the inclusion of various biomass ashes into concrete [59, 60, 76]

Arif et al. [120] reported increased resistance to sulfuric acid (1%) solution for cementitious mortar blended with 20% SBA compared to that of control specimens. Improved resistance to the sulfuric acid attack in the presence of SBA could be attributed to pore refinement. Furthermore, the expansion caused by exposure to sulphuric acid in SBA mortar was below the limit specified in ASTM C1260 [121]. Adding 20% SBA in concrete reduced the strength loss in 5% hydrochloric acid exposure [122-123]. When exposed to 5% sulphuric acid, the compressive strength of concrete incorporating 10% RHA decreased by only 6%, whereas the strength of the control concrete was 23%. This was attributed to reduced permeability resulting from the additional formation of C-S-H [124]. Mitikie and Waldtsadik (2022) reported a minimum loss in compressive strength and mass of the concrete mixture blended with 15% paper pulp ash on exposure to 2% sulfuric acid [125]. The primary reason associated with the increased resistance of paper pulp ash concrete was reduction in calcium hydroxide content and the production of secondary C-S-H with a lower Ca/Si ratio. The available literature demonstrates that concrete blended with SBA, RHA, and paper pulp ash exhibits enhanced performance against acid attack [116-125].

Joshaghani et al. (2016) found 17% reduction in compressive strength loss for 15% SBA blended concrete compared to that of control concrete when exposed to 5% magnesium sulfate solution [126]. This was attributed to the additional formation of C-S-H as apart of pozzolanic reaction by the use of SCBA [126]. Optimum fraction of RHA in concrete i.e., 15% showed positive influence on durability properties by enhancing the resistance to sodium sulphate attack and hydro chloric acid attack [127]. Further, it is reported that RHA reduced decalcification of the C-S-H phase, which therefore minimized the permeability of the concrete and therefore decreases the expansion of concrete caused to sulfate attack [127-128]. Nevertheless, the performance of biomass ash concrete against sulfate attack should be further investigated in detail.

The incorporation of biomass ash into concrete at its optimum level improved the resistance against chloride ingress [96]. SBA-blended concrete enhanced the resistance to chloride attack with minimal aggressive effect [76, 103]. Ground RHA incorporation reduced the rate of chloride ion penetration in concrete [59]. A similar study on RHA blended concrete states that the inclusion of nano-RHA tends to have much superior resistance to chloride ingress compared to that of fly ash-blended concrete [129]. Additionally, untreated RHA with a high water-to-binder ratio reportedly performed worse than OPC concrete with respect to resistance against chloride attack [109].

4.2. Alkali-activated biomass ash binder

Over the past few decades, alkali-activated binders developed without the use of carbon-intensive portland cement have drawn a lot of attention. This type of binder promotes a low carbon footprint by utilizing industrial byproducts such as fly ash and slag [15]. The two components of the alkali-activated binder system are the precursors (aluminosilicate materials) and the activators (alkaline solutions), where the activator enables the precursor to form a network of aluminosilicate gel [131].

Even though fly ash and slag are known to be the ideal raw materials for the creation of alkali-activated binders, their sources are remote from recovery sites [132]. In this regard, biomass ashes generated by local agricultural industries are considered to be the focus of interest for their suitable application in alkali-activated binders. The morphology and mineralogical composition of biomass ash plays an important role in process of alkali-activation [13, 16]. The design and development of a biomass ash-based alkali-activated binders are not specified in any of the standards. The mechanical and durability properties of alkali-activated binders, as well as the potential for polymerization of biomass ash, are still being studied. The impact of biomass ash on the performance of alkali-activated binder is discussed in the sections that follow based on the existing literature.

4.2.1. Reaction mechanism of biomass ash-based alkali-activated binder system

The reaction mechanism of alkali-activated binders is complex. The alkali-activation reaction involves three main steps: dissolution, polycondensation, and polymerization [77-78, 131]. The dissolution phase includes the breakdown of Si-O-Si and Al-O-Si bonds from precursors at high pH (provided by an alkaline solution). Dissolution plays a more important role in the formation of reaction products at later ages [133]. The polycondensation and polymerization processes involve the formation of a condensed ordered structure of aluminosilicate gel and calcium alumina silicate hydrate gel (C-A-S-H) or sodium/potassium aluminate silicate [N/K–A–S–(H)] gel [134]. The C–S–H is a linear "dreierketten" structure with interlayered CaO constituents and bound water molecules in interlayers (Fig. 20a). At high Al/Si concentration, Al-induced C-S-H structure (i.e., C-A-S-H) is formed (Fig. 20b). N-A-S-(H) structure has a random 3-D structure of sodium binding to silicon and alumina tetrahedra with short-range ordering (Fig. 20c) [135].

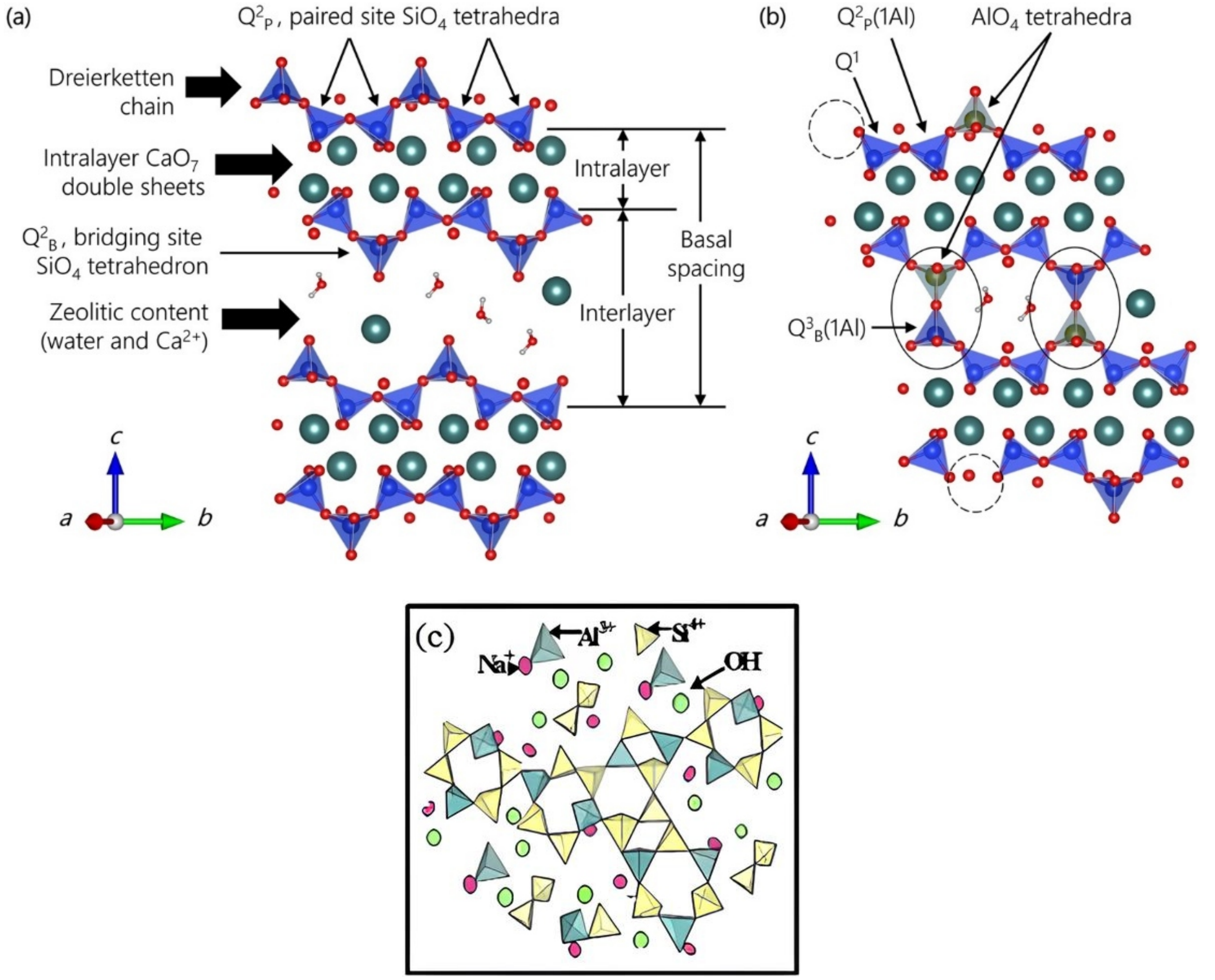


Fig. 20: Structure of (a) C–S–H (b) C-A-S-H [134] and (c) N–A–S–(H) gel [135]

In general, extent of alkali activation depends on the physico-chemical properties of the precursor, the molar concentration and the type of alkaline activator used [77-78]. Therefore, understanding of the chemical composition of the precursor material is vital to know its performance in alkali-activated binders. Figure 21 depicts the chemical composition of three different ashes, fly ash, and slag as reported in the literature [13,136-137].

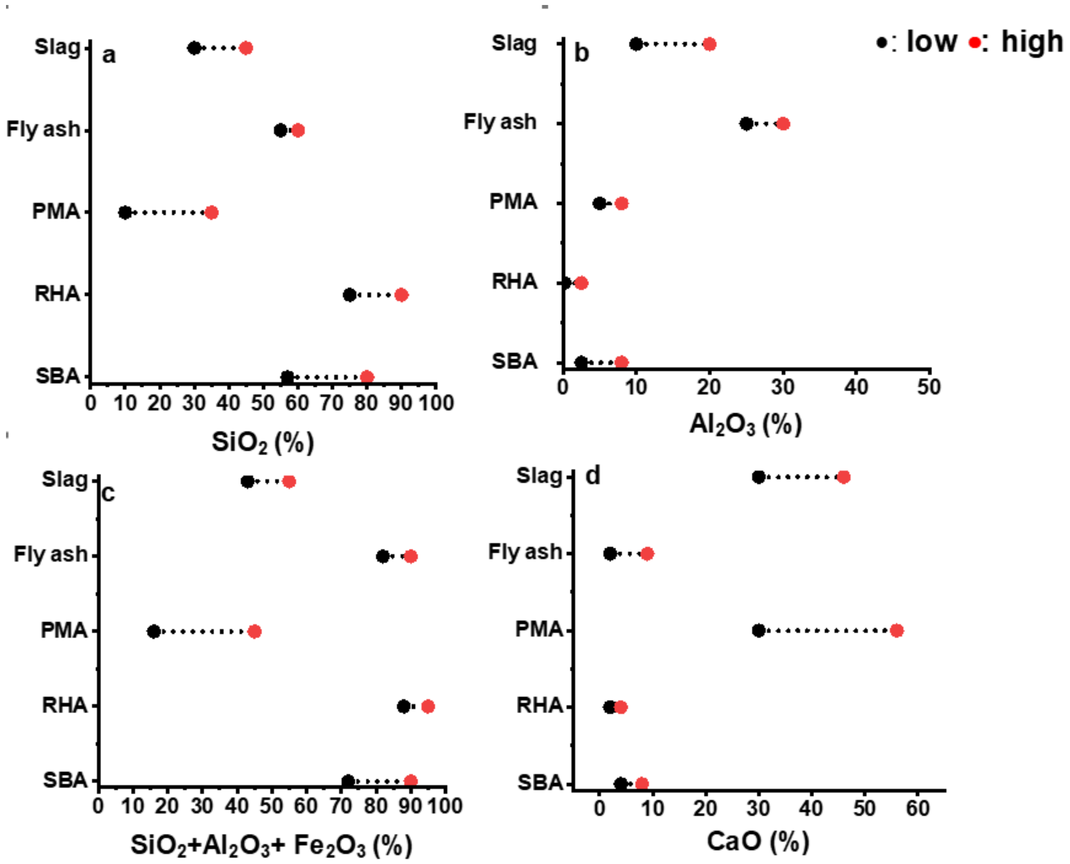


Fig. 21: Oxide composition of three different ashes, fly ash, and slag [13, 136-137]

Based on oxide composition biomass ash precursors are classified into two categories: 1) aluminosilicate precursors (with low calcium composition), and 2) high calcium precursors. The SiO_2 and Al_2O_3 rich precursor materials act as a primary source for the growth of final products such as inorganic polymer network and hydration products [13]. In addition, the presence of CaO composition increases the alkalinity as well as precursor's dissolution, thereby resulting in a strong and dense microstructure due to the formation of C-S-H phase along with the aluminosilicate network [134, 136]. Figure depicts that RHA holds the uppermost silica content in the range of 80-90% followed by SBA, comprising 55-80% of silica content. The least concentration of silica was observed for PMA (10-35%) followed by slag (30-45%). Biomass ashes (RHA, SBA, PMA) possess less alumina content (<10%) compared to that fly ash (22-30%) and slag (10-25%). The combined percentage of SiO_2+ Al_2O_3+Fe_2O_3 was seen to be the highest for RHA, subsequently for fly ash and SBA. PMA similar to slag is found to have the highest concentration of CaO composition (~50%) compared to other ashes. It is to be noted that the Fe_2O_3 concentration in biomass ashes is in the same range as that in fly ash and slag. However, alkali concertation is quite high in biomass ashes compared to that in fly ash and slag. When silicate and aluminosilicate precursors such as RHA, BA, and fly ash come in contact with alkaline medium, the main reaction product formed would be sodium-alumino-silicate hydrate [K/N-A-S-(H)] gel [137]. Whereas high calcium precursors lead to the formation of calcium silicate hydrate or calcium aluminosilicate hydrate (C-S-H/C-(A)-S-H) gel. As a source of aluminosilicate composition, biomass ash has the potential to be used in the production of clinker-free binders. Among various biomass ashes, SBA and RHA with high SiO_2 content (60-

90%) are gaining considerable attention as a precursor in alkali-activated system [13, 137].

The morphology of biomass ashes (Fig. 13) also influences its reactivity. SBA showed spherical, fibrous, dumbbell, prismatic, and irregular shaped morphology. Spherical, prismatic, dumbbell, and irregular shaped particles are composed of silica, while fibrous particles are rich in carbon composition [76]. LOI (indicative of unburnt carbon content) of SBA is 10-30%, higher than fly ash and slag [134]. The presence of unburnt carbon causes a negative impact on the reactivity [130]. Hence, low LOI ashes are considered as an ideal precursor material for reactivity. To have better reactivity of SBA in alkali-activated binder, complete removal of fibrous unburnt carbon particles is suggested [77, 109]. RHA has a cellular, irregular, and porous structure, consisting mostly of amorphous silica contributing to the reactivity. Grinding of RHA could break the porous cellular structure which is responsible for increased water absorption and amplifies the reaction capacity [138]. Calcination of ash at 600-800 ºC has been suggested for enhancing its reactivity [76]. Similarly, other biomass ashes such as PMA also showed porous morphology with high specific surface area indicating the presence of high amount of unburnt carbon (Fig. 16). It is reported that mechanical sieving of biomass ash can minimize the unburnt carbon to a certain extent [13].

Dissolution of [Si] and [Al] increases with the increase in temperature and molar concentration of the activators (Fig. 22) [139]. The [Si] dissolution is more influenced by temperature rather than molar concentration [139]. It is also to be noted that in addition to molar concentration and temperature, the dissolution of [Si] is also affected by the presence of reactive alumina.

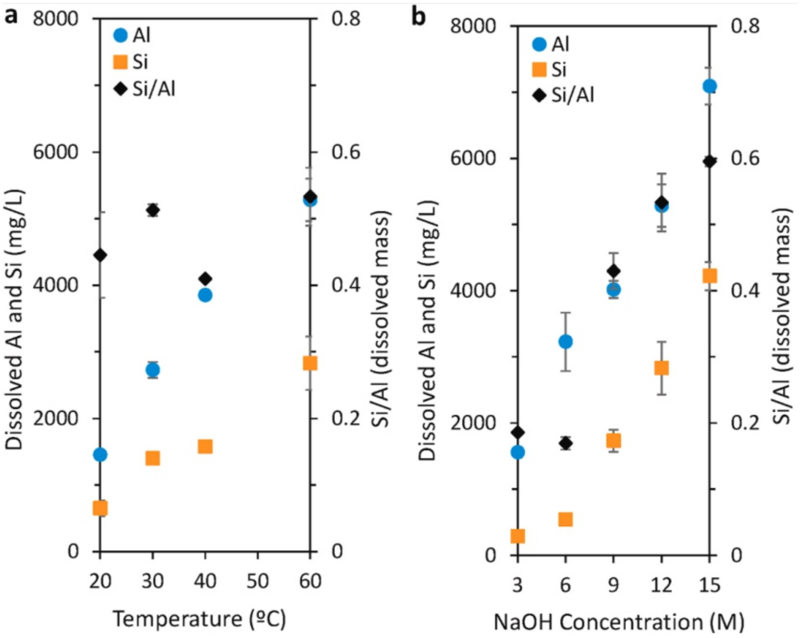


Fig. 22: Influence of (a) temperature, and (b) molar concentration on the dissolution of biomass ash [139]

Agro-based silicious biomass ash has been studied for its ability to dissolve in a low molar (0–1M NaOH) alkaline medium with and without the addition of hydrated lime [16]. The formation of C-S-H and the dissolution of Si are greatly reduced by the addition of hydrated lime. A study conducted by Chaunsali et al. [13] on two different Indian paper mill ash-derived alkali-activated binders emphasized the influence of amorphous content on the reactivity of ash. The authors noticed a direct relationship between amorphous content and the dissolution rate of [Si] and [Al] as shown in Fig. 23 [13]. It was found that the higher the amorphous content higher the dissolution rate of [Si] and [Al] into the solution. The formation of aluminium substituted C-S-H network as a product in the presence of [Ca] was also observed [13]. To fully comprehend how alumina affects the kinetics of the dissolution of [Si] species, more research is required on the dissolution of silicious ashes with added alumina in low molar activators. Compared to Ca-bearing crystalline phases such as wollastonite, hornblende, tremolite, or prehnite, the dissolution of Ca-bearing amorphous phases (in slag) is higher in an alkaline medium [140]. Furthermore, the reactivity and dissolution of [Si] and [Al] of biomass ashes may be impacted by the presence of P_2O_5 and TiO_2 [141].

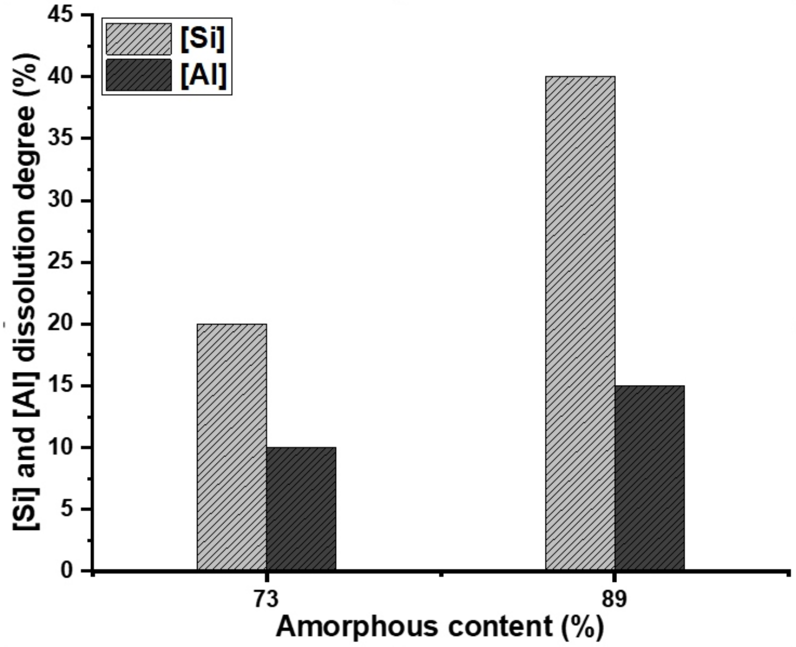


Fig. 23: Relationship between amorphous content and dissolution degree of [Si] and [Al] [13]

The dissolution rate is influenced by the type and concentration of alkaline activator. For the chemical activation of aluminosilicates, sodium hydroxide (NaOH) or potassium hydroxide (KOH), along with sodium or potassium silicates, are used as alkali activators. Since NaOH dissolves [Si] and [Al] species more quickly than KOH, it is preferred over the latter [133]. The sodium ions are thought to stabilize the dissolved silicates more effectively than the potassium ions due to their smaller size. Also, Na-based activators are most effective in breaking down the amorphous structure of the ashes and have better strength development than K-based activators [82, 133]. Use of NaOH solution as an activator create alkaline conditions that encourage the development of reactive intermediates like silanol groups, which can subsequently take part in the polycondensation process. While the presence of sodium silicate in conjunction with NaOH solution proliferates the process of polycondensation and leads to the formation of stable, three-dimensional silicate networks [130, 134]. It is reported that activation of slag using activators with higher silica modulus and Na_2O content results in a higher degree of reaction [142]. The inclusion of RHA has a significant effect on the microstructure of slag-based alkali-activated binder due to the coexistence of C-(A)-S-H and N-A-S-H phases. Furthermore, it is claimed that enriched silica content inhibits further polymerization beyond the RHA replacement level of 15% [143]. A similar observation was made when RHA was used in combination with fly ash [142].

It is important to note that biomass ashes derived from various sources possess dissimilar physical and chemical properties. Therefore, every biomass ash precursor has a different reaction mechanism when used in an alkali-activated system [144]. Production of alkali-activated binder using biomass ash is still not very popular owing to its coarse granularity [130]. However, the reactivity of biomass ash precursor can be increased by griding, sieving, and blending with active aluminosilicate materials [136].

4.2.2. Mechanical properties of biomass ash-based alkali-activated binder

4.2.2.1. Compressive strength

Compressive strength of biomass ash-based alkali-activated binder is influenced by several factors that include the properties of biomass ash, the alkaline activator, the molar concentration of alkaline activator, and curing regime [145]. Alkali activators play a key role in the development of compressive strength as it promotes the process of the polymerization reaction. Several activators are being used in the alkali-activation process, most common in this regard are NaOH and Na_2SiO_3 [131]. The compressive strength of slag-activated binder was found to be higher upon using Na_2SiO_3 solution, possibly due to the development of a more consistent microstructure compared to NaOH solution. Unlike slag-activated binder, fly ash offered greater strength properties when activated through a combined activator solution of NaOH + Na_2SiO_3 [134]. A similar kind of performance was observed when slag was replaced with 25% of BA in alkali-activated binder, maximum compressive strength was exhibited at 9M NaOH combined with Na_2SiO_3 solution [146]. Literature states that the combined use of NaOH and Na_2SiO_3 as an activator result in superior compressive strength when the precursor material is either fly ash or slag or biomass ash [77]. Tippayasam et al. (2014) observed 11 MPa increase in compressive strength after 91 days of curing for SBA-based alkali-activated binder when blended with kaolin content [147]. Compressive strength of slag-SBA blended alkali-activated binder was found to be enhanced at ambient curing conditions compared to that of thermal curing. In contrast, for fly ash-based alkali-activated binder, the compressive strength performance was observed to be higher when subjected to heat curing [77].

Compressive strength of RHA-blended alkali-activated fly ash concrete increased with the increase in NaOH concentration from 8M to 10M. Maximum compressive strength was recorded for 10M NaOH concentration with 35% RHA. This was due to the fact of greater dissolution of Si and Al in an alkali solution with a higher concentration. However, strength was noticed to be reducing beyond 10M NaOH concentration. The associated reason for this was the hindered dissolution of aluminosilicates as a result of the higher viscosity of the activator solution. Furthermore, higher NaOH concentration led to an early precipitation of aluminosilicate gel [138]. Incorporation of 5-15% RHA in alkali-activated slag binders yielded higher compressive strength compared to that of fly ash blended alkali-activated system [142]. Compressive strength of compacted (at 10MPa) alkali-activated binder formulated using mixed ash in combination with clay and hydrated lime at 2M NaOH concentration showed the compressive strength of 12 MPa at the age of 7 days [13]. The majority of studies indicate that biomass ash-based alkali-activated binder can reach its maximum compressive strength at 7 days of age [136]. Nevertheless, the compressive strength of alkali-activated binder varies greatly with respect to the dissolution rate of precursor material in the chosen alkaline medium as well as the curing condition [77, 131].

4.2.2.2. Flexural and splitting tensile strength

Similar to compressive strength, the flexural and tensile strength of alkali-activated biomass ash-based binder tends to increase with curing period. Most studies used alkali activator solution based on $NaOH/Na_2SiO_3$ to activate biomass ash precursors. The inclusion of a smaller percentage of RHA (10%) as a replacement to slag in alkali-activated binder exhibited 2.6% increase in tensile strength compared to 100% slag-based alkali-activated binder. This can be attributed to the filler effect of smaller particles of RHA [148]. Further increase in RHA percentage led to reduction in the tensile and flexural strength of alkali-activated binders because of the difference in solubility that affects the polymerization reaction due to an increase in SiO_2/Na_2O ratio [149].

4.2.3. Durability properties of biomass ash-based alkali-activated binder

Alkali-activated concrete is also prone to deterioration brought about by the migration of externally aggressive agents, just as OPC concrete. Water absorption, acid attack, sulfate attack, chloride attack, leaching, etc., are some of the most deteriorating mechanisms that affect the longevity of concrete structures. The durability performance of biomass ash blended alkali-activated binders against the aforementioned aspects are discussed in the subsequent sections.

4.2.3.1. Water absorption

Slag and fly ash-based alkali-activated binders were found to have lower water absorption than OPC concrete.

Pore filling effect of finer particles and the formation of C-A-S-H/N-A-S-H gel are the associated reason for the curtailment of water absorption [143]. In contrast, the utilization of biomass ash such as RHA, and palm oil fuel ash (POFA) in combination with slag as a ternary blended alkali activated system increased the tendency to absorb water compared to OPC concrete. Similarly, the combination of fly ash + slag + RHA in alkali-activated binder also amplified the rate of water absorption. This is because of the use of sole activator NaOH. Whereas, in the case of fly ash/slag-based alkali-activated binder, NaOH solution was used in combination with Na_2SiO_3 solution [150]. This is in line with the discussion in the section above, where it was stated that the use of NaOH and Na_2SiO_3 solution in combination promotes the development of dense microstructure. Pereira et al. [146] noticed that the use of a high molar NaOH solution (8M) in alkali-activated slag binder comprising 25% SBA could improve the resistance to water absorption. This can be attributed to the increased dissolution, polymerization, and subsequently the microstructure of the binder. The porous and fibrous morphology of untreated biomass ashes accounts for the reported increase in water absorption for alkali-activated biomass ash binder. This can be reduced by processing biomass ash mechanically or thermally [78].

4.2.3.2. Drying shrinkage

Drying shrinkage of alkali-activated slag binder was found to be reduced significantly when blended with RHA. It is reported that the drying shrinkage of RHA-blended alkali-activated slag binder is lower compared to that of OPC binder. This is because of minimal amount of water in the alkali-activated binder medium, reducing the mesopores in the system [151]. There is very limited information available in relation to the drying shrinkage of alkali-activated biomass ash-based binder.

4.2.3.3. Resistance to aggressive ions

Alkali activated binder concrete exposed to aggressive acid media leads to the dissolution and leaching of concrete medium [148]. Sulfuric acid, hydrochloric acid and nitric acid are reported to be as highly deleterious acids for concrete structures [146]. The damage caused by an acid attack is generally measured in terms of compressive strength loss, mass loss and depth of corrosion. Deterioration of OPC concrete exposed to hydrochloric acid for 200 days is much higher than alkali-activated slag concrete. While SBA-blended alkali-activated slag concrete showed comparable results to that of OPC concrete. The polymerization process in alkali-activated binder provides a film of silica gel, providing a barrier effect for further attack [146].

Ingress of sulfate ions into alkali-activated binder concrete undergoes expansion followed by strength loss, disintegration, and cracking as OPC concrete. Magnesium, sodium, and potassium sulfates are the most common chemicals responsible for the sulfate attack of concrete [130]. Alkali-activated slag binder exposed to $MgSO_4$ solution showed a similar level of deterioration to that of OPC concrete. However, the loss in compressive strength of specimens exposed to Na_2SO_4 solution was observed to be lesser than the previous. The performance of alkali-activated slag binder against sulfate attack was seen to be better with the inclusion of RHA compared to that of SBA [146].

Alkali-activated binders possess relatively higher resistance to chloride ingression compared to OPC concrete. This is due to the development of dense microstructure and reduced permeability [152]. Inclusion of 10% RHA improved the microstructure of alkali-activated slag binder, and hence assisted in lowering the permeability of chloride ions [148].

Very few studies illustrate the performance of alkali-activated biomass ash binder against aggressive media. On the potential use of biomass ash blended alkali-activated binder in concrete structures exposed to hostile environments, the available data offered conflicting information. It is still unknown how effectively biomass ash-based alkali-activated binders can withstand chemical assaults. Hence, a thorough investigation is required in this area.

4.2.3.4. Leaching effect of biomass ash binder

The leaching process is driven by the pH difference between the alkaline pore solution of the binder and the leaching solution. Understanding leaching characteristics is crucial for comprehending the toxicity or environmental impact, disposal problems, and potential applications of biomass ash [153]. Heavy metals are frequently considered an important contaminant for environmental reasons, but the assessment of durability may also require a focus on structural species and major ionic constituents (Ca, K, and Na). According to a previous study, heavy metals leaching in the case of biomass ashes has remained extremely low [154]. However, the leaching of Ca, Si, Na, and K ions affects the chemical stability of the reaction product found in the biomass ash-based binder system.

Numerous earlier studies [155-157] have investigated the alkali binding of calcium silicate hydrates. The majority concentrated on calculating the alkali binding potential of synthetic C–S–H gels in alkaline solutions with known concentrations. A higher percentage of acidic silanol (Si-OH) surface species have been observed in C-S-H at low Ca/Si ratios; these species are easily deprotonated and can have their charges balanced by nearby alkali species [157-158]. The desorption behaviour of alkalis from synthetic C-S-H gels, which were initially used for sorption experiments, was also studied by Hong and Glasser [157] and the extent of alkali desorption ranged from 55–70%. The rapid leaching behaviour of C-S H gels low Ca/Si ratio (0.2–0.6) studied by Swanton et al. (2016) reports that leaching of C-S-H gels having Ca/Si > 0.29 change and shift towards a compatible point with Ca/Si ratio closer to 0.84. While C-S-H gels with Ca/Si < 0.29 led to silica-rich leaching [159].

The leached ions from biomass ash binder mainly involve Na/K, Ca, and Si, as these elements are found in higher concentrations in the pore solution. A leaching study conducted by Chaunsali et al. [155] on biomass ash binder against neutral (deionized water, pH $\sim$1.2) and acidic media (0.1M HNO_3, pH $\sim$7.3) reported the extent of Na, Ca, and Si elemental leaching. Leaching was more intense when there was a greater pH gradient between the leaching solution and the sample pore solution. The authors also noticed exacerbated leaching of alkalis at higher solution-to-sample ratio [155]. The loosely bound alkalis in the C-S-H phase or the residual salts that remain after sample drying are responsible for significant alkali leaching [157]. On the other hand, geopolymer binders are primarily made up of sodium aluminosilicate phase with strongly bound sodium in its network-like structure [160]. Calcium leaching is minimal in neutral and two orders of magnitude higher in acidic condition. This indicates that structurally bound Ca in C-S-H phase is more stable in neutral conditions than in an acidic environment. The leaching of silica in both neutral and acidic environment are insignificant [155, 161]. Decalcification, silica leaching, and formation of alkali-silica gel from freely available alkalis lead to the degradation of structure [25]. A field study conducted on biomass ash bricks indicated C-S-H phase would maintain stability at near-neutral pH environment (Fig. 24) [155].

Fig. 24: Biomass ash brick wall subjected to outside environment [155]

The leaching properties of binders are affected by the size of the specimen. Due to its high specific surface area, it was discovered that finely ground powder samples (< 45 micrometre) had an upper bound on desorption. Additionally, it is stated that small samples with thicknesses of 15 to 2 mm demonstrated a greater degree of alkali desorption than large cube samples with dimensions of 50 x 50 x 50 mm (Fig. 25). This is brought on by the slower diffusion through the dense microstructure [162].

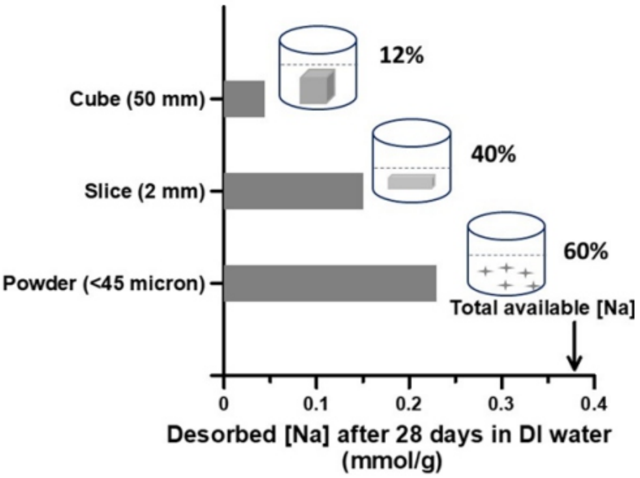


Fig. 25: Influence of sample size on alkali leaching from biomass ash binder [162]

4.2.4. Life cycle analysis (LCA)

Life cycle assessment (LCA) is defined as "the collection and assessment of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle" by ISO 14040:2006 [163]. This is one of the most important factors for the sustainability performance of alkali-activated biomass ash binders. The particular outcomes and conclusions of LCA for an alkali-activated biomass ash binder rely on a number of variables including materials, production processes, energy sources, and transportation type [164]. LCA consists of four basic steps: (i) scope and aim, (ii) inventory of the life cycle processes, (iii) characterization and measurement of the life cycle impact, and (iv) result interpretation [165].

Alkali-activated biomass ash binder is regarded as a sustainable material due to its exceptional durability and significantly fewer carbon dioxide emissions than OPC. Studies show that these binders have approximately 8 – 80% lower CO_2 intensity than that of OPC [166]. The greenhouse gas (GHG) emission profile of alkali-activated biomass ash binder systems varies conspicuously depending on the source of precursors, treatment, and transport of raw materials, alkaline activators, fabrication, and curing process [164]. However, in contrast to the

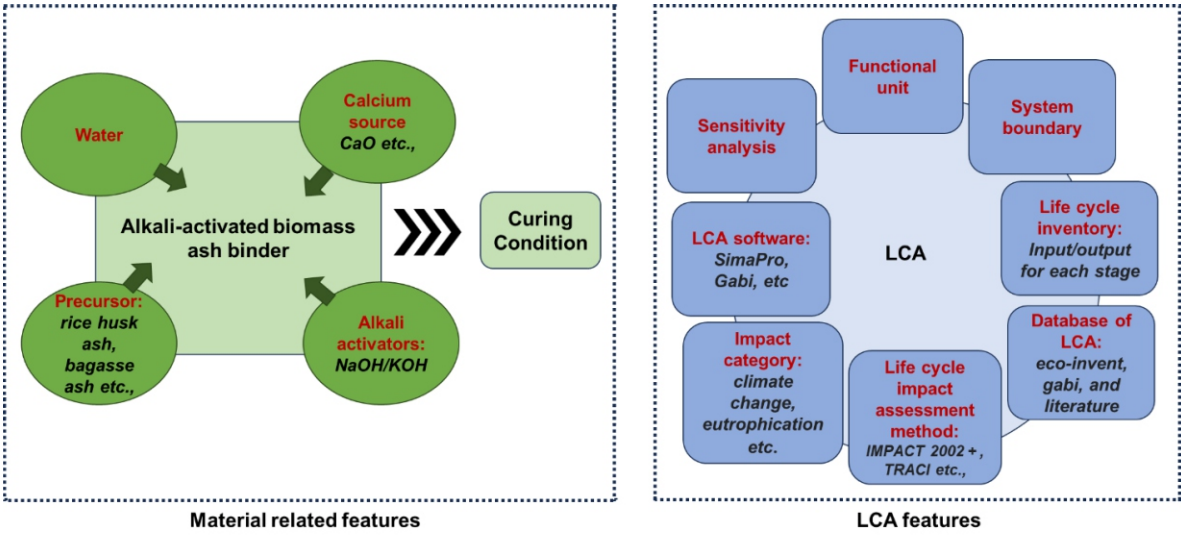


Fig. 26: Two key features considered in the LCA of alkali-activated biomass ash binder [165]

LCA of cementitious systems which has undergone years of functional investigations, the LCA of the alkali-activated binder system is still in its infancy and needs extensive research [165]. The two key characteristics considered in the life cycle assessment of alkali-activated biomass ash binder [165] are shown in Fig. 26.

4.2.4.1. Components of alkali-activated biomass ash binder system considered for LCA

Alkali-activated biomass ash binder systems possess intricate mixture designs; hence, several factors should be taken into account when determining the life cycle analysis of such binders. Alkali-activated biomass ash binder systems are produced by the reaction of aluminosilicate raw materials (precursor) with an alkaline solution (alkaline activator).

a) Precursor

Fly ash (FA), ground granulated blast furnace slag (GGBFS), and metakaolin (MK) are the most preferred precursors in the production of alkali activated binder [134,136]. But from the standpoint of environmental protection, it is unclear whether these precursors are accessible in sufficient quantities to meet the demand and fulfil their envisioned purpose in the future. For instance, coal-fired power stations were shut down as a result of growing awareness of global warming and the adoption of environmental protection regulations in many developed nations, making lower availability of fly ash [167-168]. Many research efforts highlighted the LCA of numerous new alternative precursors for alkali-activated binder and demonstrated their potential [169]. In this regard, environmental silica rich materials such as rice husk ash, sugar cane bagasse ash, and palm oil fuel ash which are abundantly available resources in many countries were chosen to prove the suitability as precursors for alkali-activated binder system [169].

b) Alkaline activator

Silicates or sodium or potassium hydroxides are the most widely employed alkaline activators for the synthesis of AAMs [170]. Most alkali hydroxides are made by electrolyzing concentrated salt solutions, and they are often purchased as pellets or imitations. An alkaline hydroxide solution, which is the main outcome of electrolysis, is dried to produce pellets or flakes [171]. These pellets are then dissolved in water for small-scale application to get the necessary solution concentration. However, using the alkaline hydroxide solution produced by electrolysis in large-scale applications could lower the cost and environmental impact [171]. Fusion, hydrothermal, and thermochemical techniques are methods used to prepare alternate activators [165].

One of the strategies for producing alkali activated binders with the least amount of environmental impact is to reduce the amount of alkaline activator in the mixture [165]. Other methods include using other native sources to produce reactive silicate and hydroxide ions. In this perspective, rice husk ash, bagasse ash, maize cob ash, or other biomass ashes are being studied as potential silica source for producing alkali-activated binder [172].

4.2.4.2. Features of LCA

a) Functional unit

Functional unit (FU) is one of the most important pillars of LCA, representing a product's capability to carry out a specific function. The function of the compared alternatives must be represented by FU at all stages and is considered as a reference to which all inputs and outputs are referred. For concrete and mortar, "1 m^3" was the most frequently used FU in the literature. When the focus of the investigation is on the alkali-activated binder (or paste) system and bricks/blocks, "1 kg" or "1 ton" and "1 number" or "1 m^2" are most commonly used FU, respectively [165]. For instance, Petrillo et al. [173] compared residential concrete paving blocks manufactured with OPC and AAMs using the 10000 SBE (Standard Brick Equivalent). Poinot et al. [64] compared the environmental and economic analyses of alkali-activated bricks and the fired clay equivalent considering the functional unit of brick as 1 unit of size 9″ × 4″ × 2.5″ and the densities of the bricks compared in the analysis were the same (1.36 g/cm^3). A common and equitable FU is required to provide comparability amongst the alternatives studied when the LCA is used to compare the environmental effect of various alkali-activated binders and conventional cementitious binders.

b) System boundary

The results of LCA are strongly influenced by the definition of system boundaries which determine the unit processes involved in measuring environmental impacts. The boundaries of a system should be clearly illustrated in a representation that gives an overview of the included or omitted processes because a wide variety of materials are used in alkali-activated binders [174]. Production (A1-A3), construction (A4-A5), use (B1-B5), end-of-life (C1-C4), and possible use/recovery/recycling potential (D) are the general activities that make up the lifespan use of alkali-activated binders in building construction as per EN 15804 [175] (Fig. 27).

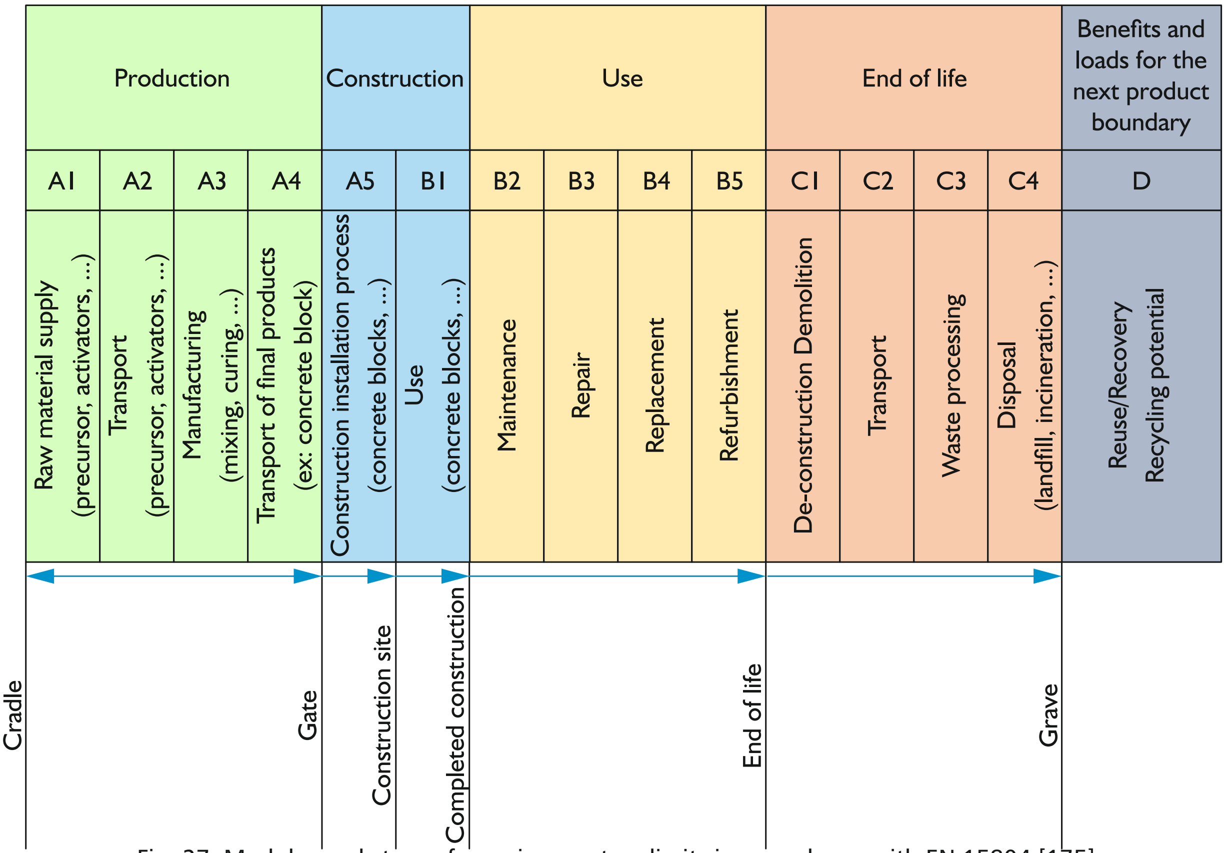


Fig. 27: Modules and stages for various system limits in accordance with EN 15804 [175]

For LCA analysis of alkali-activated binders, it is vital to take into account the materials supplied for precursor and activators (A1) including raw material extraction, processing, grinding (if required), heating (if applicable), and waste treatment. Another important stage is the manufacturing of products and by-products (A3), particularly mixing and curing AAM mixes [176]. More than 65% of the examined products used room-temperature curing without being affected by the environment. But, in some instances, thermal curing is considered and is reported to have approximately 40 kg CO_2-eq/m^3 emission during the process of steam curing (85 °C/24 h) [166]. The transportation of raw materials (A2) has been cited as one of the most significant variables affecting the carbon emissions connected with the manufacturing of alkali-activated binder. Poinot et al. [64] considered only resources and processes involved in brick manufacturing as system boundary. The primary reason for excluding environmental impact related to use and disposal was lack of data. In a study [177], prefabricated geopolymer facade cladding panels consisting primarily of recycled construction and demolition debris were examined for benefits and loads beyond the system boundary over the course of a whole life stage (A1–D). They concluded that majority of the environmental footprint emanates from production stage (modules A1–A3). However, other life cycle phases are less often evaluated and should be considered in future investigation.

c) Life cycle inventory (LCI) and database

Another major step in LCA is life cycle inventory, which often gathers specific data relating to chosen FU inside a boundary system [64, 165]. Unfortunately, there is no standard for gathering LCI data for cement-based or alkali-activated binder-based products. The initial information might be obtained from the laboratory, official reports, or environmental product declarations (EPDs) from the building industries and additional information required could be obtained from reputable environmental databases and scholarly literature. Secondary data, such as the Ecoinvent database, GaBi database, literature study, and expert opinion, were used to fill in any gaps left by missing, insufficient, or inaccessible primary data [174]. Majority of LCA studies used the Ecoinvent database as a resource owing to its transparency and comprehensiveness [165].

The production of sodium hydroxide was reported to have minimum, maximum, and average Ecoinvent values of 0.633, 1.915, and 1.274 kg CO_2-eq/kg, respectively. Similarly for sodium silicate production, these values were reported to be as 0.425 (minimum), 1.5632 (maximum), 0.9941 (average), kg CO_2-eq/kg, respectively. According to Fawer et al., sodium silicate powder has stronger effects on climate change (+48%), photochemical ozone formation (+71%), fossil fuel depletion (+63%), and reduction in the category of acidification (-15%). Font et al. considered rice husk ash (RHA) and olive stone biomass ash (OBA) to be waste, taking into account CO_2 emissions from necessary pre-treatment processes such milling but ignoring the impact of extraction [178]. Similarly, the European Standard EN-15804 for sustainable construction does not consider the emissions for fly ash, furnace bottom ash, or slag-tap granulate in modules A1–A3 [175]. Therefore, demand for these waste streams is also anticipated to increase with the advancement of the alkali-activation technology, necessitating more investigation into the allocation processes.

d) Life cycle impact assessment (LCIA) method and Software

The life cycle impact assessment (LCIA) phase translates data from the life cycle inventory on primary flows into environmental impact scores. The growth of LCI data and impact assessment approaches increases the complexity of product systems and necessitates the usage of LCA software [174]. The numerous LCA techniques developed to evaluate the environmental impact include CML, ReCiPe (Midpoint), IMPACT 2002+, TRACI, and Ecoindicator. The purpose and extent of the LCA project determine the appropriate method to use. SimaPro is one of the most popular LCA programs (PRe-Consultants, 2008). Open LCA and GaBi are the other important LCA software [165]. Selection of appropriate methodology and software relies on the goal and scope of an LCA project.

e) Interpretation of results

Final step of LCA is analysing and interpreting the results. Alkali-activated binders were found to have fewer

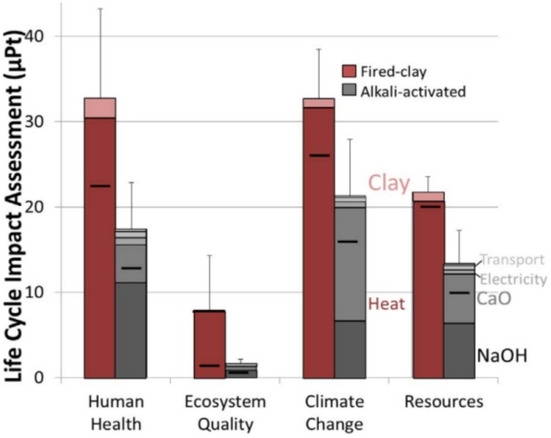


Fig. 28: A comparison of alkali-activated vs. burnt clay bricks using the life cycle impact assessment (LCIA) method [64]

environmental effects than OPC in the categories of eutrophication, acidification, and climate change, but higher environmental effects than OPC in the category of dust emissions [64, 165, 180]. According to one LCIA interpretation of the brick system, which compares fired-clay brick with alkali-activated boiler ash brick, the alkali-activated brick has a lesser environmental impact than the fired clay brick (Fig. 28) [64]. Resources, climate change, ecosystem quality, and human health were the four damage assessment categories wherein alkali-activated brick outperformed the fired-clay brick [64].

The findings of the comparison study performed by Zahmak et al. [179] on evaluating the life cycle assessment (LCA) of various alkali-activated binders (AAB) made with industrial waste materials such as fly ash (FA) and ground granulated blast-furnace slag (GGBFS) as precursors for ground improvement and cement-based binder at field scale are shown in Fig. 29.

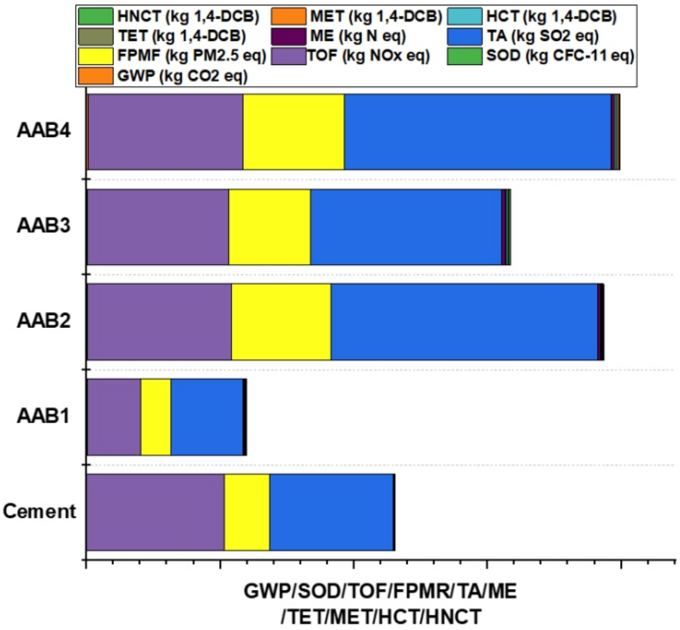


Fig. 29: Life cycle assessment results of various alkali-activated binder mixes and cement-based binder at field scale [179]

A total of four alkali-activated binders such as AAB1 (100% FA with 0% Na_2SiO_3)/NaOH, AAB2 (100% FA with 50% Na_2SiO_3)/NaOH, AAB3 (50% FA + 50% GGBFS with 0% Na_2SiO_3)/NaOH), AAB4 (with 50% Na_2SiO_3)/NaOH as well as one cement-based binder have been taken into consideration [179]. Several impact factors such as Global Warming Potential (GWP), stratospheric ozone depletion (SOD), tropospheric ozone formation (TOF), fine particulate matter formation (FPMF), terrestrial acidification (TA), Marine eutrophication (ME), terrestrial ecotoxicity (TET), Marine Ecotoxicity (MET), human carcinogenic toxicity (HCT), human non-carcinogenic toxicity (HNCT) were evaluated from cradle-to-construction. In general, it has been shown that the alkali activators NaOH and Na_2SiO_3 are the main cause of the adverse effects of AAB, with Na_2SiO_3 being the most significant, especially in the categories of terrestrial and human impacts. This was evident in the AAB mix (AAB1), which had the fewest alkali activators and no Na_2SiO_3 and had the least effect on GWP, TOF, FPMF, and TA. It was concluded that the manufacturing of alkaline activators had a significant environmental impact in terms of GWP, which mostly resulted from high electricity consumption in alkaline activators' production processes. On the other hand, the cement-based binder showed superior performance to all other binders in terms of SOD, ME, TET, MET, HCT, and HNCT.

When AAM components are transported over short distances and heat treatment is not necessary, AAMs have a lower carbon footprint than OPC. Numerous studies rely heavily on the current literature or databases, which may not accurately reflect local facts and cause significant uncertainty in the findings. Uncertainty and sensitivity analyses are therefore necessary for LCA investigations, particularly those that compare AAMs and

OPC-based materials.

4.3. Summary

Biomass ashes (RHA and SBA) that are rich in silica composition and have primary oxide composition ($SiO_2+Al_2O_3+Fe_2O_3$) of $>70\%$ make the material ideal for usage as pozzolanic material (as per ASTM C618). Whereas biomass ashes (e.g., PMA) having CaO + SiO_2 composition $>50\%$ can be classified as hydraulic material (EN 450-1). Most of the biomass ashes witnessed porous morphology with high amorphous content and unburnt carbon having LOI $>10\%$. The LOI value of biomass ashes can be minimized through thermo-mechanical processing techniques. The addition of biomass ash in the cementitious mix increases the water demand and thereby reduces the workability of the mix. Optimum replacement of biomass ash (10-20%) in cement and concrete could improve the mechanical and durability properties of concrete. Furthermore, biomass ash-blended concrete performs as an insulating material for construction.

Even though, it is obvious to use biomass ash as an appropriate alternative cementitious material. The selection of certain biomass ash as an SCM must consider factors such as workability and strength of the corresponding blended concrete. Therefore, in-depth studies on framing standards are required to offer guidance in the categorization of biomass ashes for the specific application. The detailed study on durability characteristics of biomass ash-blended concrete is needed to assess its long-term performance. More studies related to processing methods, reactivity, microstructure, and mineralogical properties of biomass ash in blended cementitious concrete are required for a thorough understanding of its performance.

Available literature reports that alkali-activated binder system performs better at high molar ratios and high temperatures. However, the application of alkali-activated binder is constrained by a similar formulation. The dissolution of aluminosilicates in an alkaline medium is accelerated by high temperature and strong activator; in addition, the presence of high reactive alumina also influences the dissolution rate of Si. Further, the processing of ash increases the dissolution rate. The addition of calcium enhances the bond strength of C/N–A–S–(H) binder. The microstructure analysis of C/N–A–S–(H) binder shows better bond strength upon Ca addition.

The development of alkali-activated binders using biomass ash is not widely reported. Hence, there is a need for detailed investigations on various biomass ashes to understand their effect on the performance of alkali-activated biomass ash-based binders. Understanding the reaction kinetics of biomass ash in alkali-activated system similar to fly ash and slag is vital. More research is needed on the impact of processing and the role of low molar alkaline activator on the degree dissolution of [Si] and [Al] species. Mechanical and durability performance of high-volume biomass ash-based binders as a function of precursor and activator chemistry, curing conditions, and type of reaction products requires further investigation.

Other major obstructions in the development of alkali-activated binders are the high cost of alkaline activators, long transport distance and high emissions involved during manufacturing process. Therefore, to reduce the emission and cost, the feedstock for alkali-activated binders should be sourced from nearby locations and the efforts should be directed towards using low-molarity activators. Lastly, more research is needed to understand the influence of source variability of biomass ash on its performance on alternative cementitious systems.

5. A CASE STUDY ON ALKALI-ACTIVATED BIOMASS ASH BINDER

Problem: Enormous amounts of biomass ashes generated from the co-generation plants of various agro-based industries are mostly being landfilled. Valorization of biomass ashes produced by bioenergy processing is essential to address the problems with the environment and the economy.

Solution: One potential solution to the environmental issues brought on by these waste products is to use biomass ash as a building material. From this perspective, this case study focusses on the feasibility of utilizing Indian biomass ash from three major industries such as paper, sugar, and rice mills in the development of carbon neutral alkali-activated binder.

5.1. Materials

Indian biomass ashes (BA) from three major industries such as paper (paper mill ash, PMA), sugar (sugarcane bagasse ash, SBA), and rice (rice husk ash, RHA) industries were used in this study. It is to be noted that paper mill ash was sourced from Silverton paper mills in Muzaffarnagar, Uttar Pradesh composed of approximately 85 % rice husk and 15% bagasse. In addition, ground brick waste (BW) from locally accessible bricks, hydrated lime (HL), and sodium hydroxide (NaOH) solution were used as a filler, calcium source, and alkaline activator, respectively for the development of alkali-activated biomass ash binder. The oxide composition of PMA, SBA, RHA, and BW determined using X-ray fluorescence (XRF) is shown in the Table 6. XRD patterns and phase compositions of raw materials derived from quantitative X-ray diffraction (QXRD) analysis are shown in Fig. 30 and Table 7.

Table 6: Oxide composition of biomass ashes and brick waste

Oxide composition (wt.%)	BA1 (PMA)	BA2 (SBA)	BA3 (RHA)	BW
SiO_2	73.07	66.64	90.75	62.22
Al_2O_3	0.97	4.13	0.71	17.65
Fe_2O_3	1.28	1.99	0.52	9.22
SO_3	-	-	-	0.17
CaO	2.08	4.55	0.86	3.51
Na_2O	0.20	0.51	0.55	0.56
MgO	0.85	3.35	0.66	0.73
K_2O	3.78	11.6	1.23	3.59
P_2O_5	1.31	3.12	0.68	0.19
TiO_2	-	-	-	1.24
MnO	-	-	-	0.16
CuO	-	-	-	0.03
SrO	-	-	-	0.09
LOI	13.3	3.1	3.64	3.05

Table 7: Phase composition of biomass ashes and brick waste

Phase composition (wt.%)	PMA	SBA	RHA	BW
Quartz	4.8	11.1	6.3	45.5
Cristobalite	0.7	10.7	6.4	-
Sylvite	0.1	0.7	0.3	-
Feldspar	0.5	2.1	0.8	-
Calcite	0.6	0.2	-	-
Muscovite	-	-	-	8.2
Microcline	-	-	-	14.32
Sanidine	-	-	-	17.5
Kaolinite	-	-	-	0.2
Amorphous	93.3	75.1	86.16	14.28

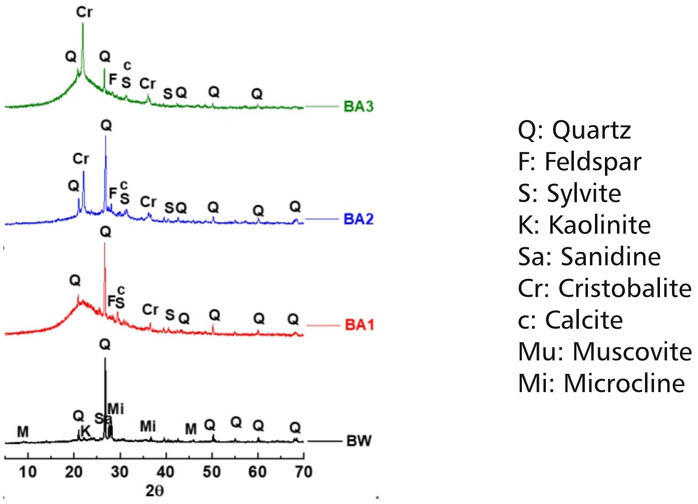


Fig. 30: XRD pattern of biomass ashes and brick waste

5.2. Methods

5.2.1. Sample preparation

Samples were prepared with the intention of using biomass ash as efficiently as possible. Both biomass ash (BA) and ground brick waste (BW) were processed by sieving through 300 μm and 600 μm sieve, respectively. Next, the samples were put in an oven set at 105 °C degrees to expel the inherent moisture content. Hydrated lime (HL) was also sieved to get rid of the large clumped-together particles. Alkaline activator solution of 1M NaOH was prepared by liquifying 97% pure sodium hydroxide pellets in de-ionised water. It should be noted that the prepared solution was left out for 24 hours to reach room temperature.

Based on maximum compressive strength attainment, all biomass ash-based binders were formulated using biomass ash, brick waste, and hydrated lime at the ratio of 50:40:10 (by wt. %). Formulation and mix designation of all biomass ash-based alkali-activated binders is presented in Table 8.

Table 8: Formulation and mix designation biomass ash-based alkali-activated binders

Mix formulation (BA: BW: HL)	Mix designation	PMA	SBA	RHA	BW	HL	L/S ratio
		(% by wt.)					
50:40:10	BA1	50	-	-	40	10	0.42
	BA2	-	50	-			
	BA3	-	-	50			

*L/S: Liquid to Solid ratio

At first, biomass ash, brick waste, and hydrated lime were dry mixed in a Hobart mixer for 5 minutes (at low speed of 62 RPM). Then, 1M NaOH solution was added at a liquid-to-solid ratio of 0.42 and wet mixed for 20 minutes at high speed of 285 rpm. Two cubical moulds of inner dimension 50 mm were placed one above the other; samples were then hydraulically pressed and compacted using a hydraulic compression testing machine of 250 kN capacity to a final pressure of 15 MPa (37.5 kN) at the loading rate of 1000 N/sec. The top mould was later removed by sliding, and the final specimen dimension was recorded as 50 mm × 50 mm for the base and 50 ± 3 mm for the height. Following that, samples were wrapped in plastic sheet and kept in an oven that was set to 40 °C until the day of testing. Three specimens of each mixture we tested at two distinct curing ages. Fig. 31 demonstrates the setup of the mould used to make the cube specimens of biomass ash-based binder.

After achieving appropriate curing age of 7 days, crushed samples were subjected to solvent exchange technique using isopropyl alcohol to stop the hydration process [13]. The samples were then filtered, vacuum dried, ground, and sieved using a 75 μm sieve in preparation for characterization methods like X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). In addition, chunk from the core of the samples was taken for scanning electron microscopic analysis (SEM).

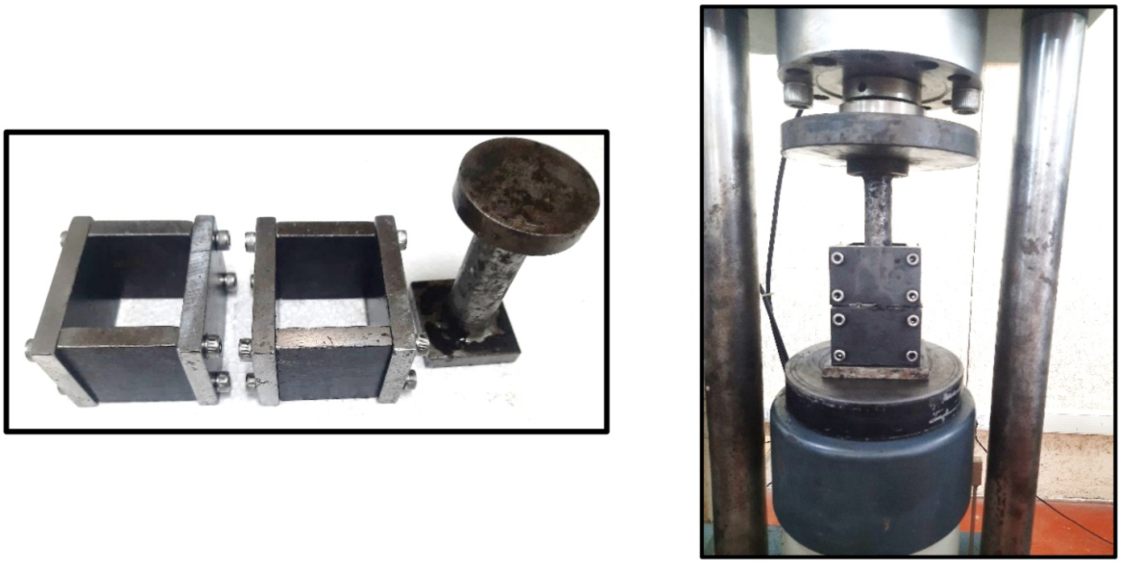


Fig. 31: Setup of the mould used to make biomass ash-based binder cubes

5.2.2. Compression strength

The compressive strength of hydraulically pressed biomass ash-based binder specimens (50 mm × 50 mm × 50 mm size) was determined at the ages of 7 and 28 days. Specimens were tested using hydraulic compression testing machine of 250 kN capacity at a loading rate of 250 N/sec.

5.2.3. Water absorption and bulk density

The water absorption test was conducted as per IS:3495 (part II) [180] using 50 mm × 50 mm × 50 mm size specimens. Bulk density was measured as the ratio of the weight of specimens (at its saturated surface dry condition) to the volume of the specimen (size: 50 mm × 50 mm × 50 mm).

5.2.4. X-ray diffraction (XRD)

X-ray diffraction was used to characterize the mineralogical composition of reaction products. XRD pattern of fine powdered samples (passing through 75 μm sieve) was obtained through MiniFlex Rigaku powder X-ray diffraction instrument operated with Cu Kα radiation (40 kV/40 mA). The scanning speed, step size, and deflection angle (2θ) were all kept constant at 2°/min, 0.01° and 10° to 70°, respectively. Quantitative analysis of XRD data was performed using X'Pert High Score Plus software allied with Rietveld analysis.

5.2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out for powdered samples passing through 75 μm sieve using FEI-Quanta FEG 200F. Samples were heated to a temperature of 35-900 °C (heating rate: 10 °C/ min) in a nitrogen purge environment (flow rate: 20 ml/min). To calculate the bound water content of reaction products, TGA was done on samples that had been cured for 7 days.

5.2.6. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to identify the change in the functional group of alkali-activated biomass ash binder. The FTIR spectroscopy was performed on powdered samples that had passed through a 75 μm sieve. FTIR spectra were obtained from Bruker (Alpha II) FTIR equipment at the wavenumber range of 1650 to 600 cm−1 with the resolution of 2 cm−1 and at 32 scans. Attenuated total reflection (ATR) sampling mode was used to run the samples.

5.2.7. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS)

Chunk samples collected from the core of the crushed sample was vacuum dried and gold-sputtered were used for performing microstructural analysis. A JEOL, JSM-638OLA, scanning electron microscope (SEM) equipped with energy dispersive X-Ray spectroscopy (EDS) was used for characterizing the morphological and elemental composition of hydrated samples.

5.3. Results and Discussion

5.3.1. Compressive strength

Figure 32 shows the compressive strength results for cubic specimens made with three biomass ashes (PMA-BA1, SBA-BA2, and RHA-BA3) over 7 and 28 days of curing time (at 40 °C).

The alkaline-activated biomass ash-based binder made from PMA (BA1) achieved the compressive strength of 14.5 MPa after 7 days of curing. Whereas SBA (BA2) and RHA (BA3) binder specimens reached the compressive strength of 7.8 MPa and 10.2 MPa, respectively. The evolution of early-age strength by these specimens was quite high; BA1, BA2, and BA3 binders reached 90%, 82%, and 80% of 28-day strength at 7 days. The highest compressive strength exceeding 15 MPa was observed at 28 days for alkali-activated PMA binder (BA1). This could be attributed to the higher effective amorphous content (amorphous content – LOI) of PMA compared to that of other ashes used in the study as illustrated in Fig. 33.

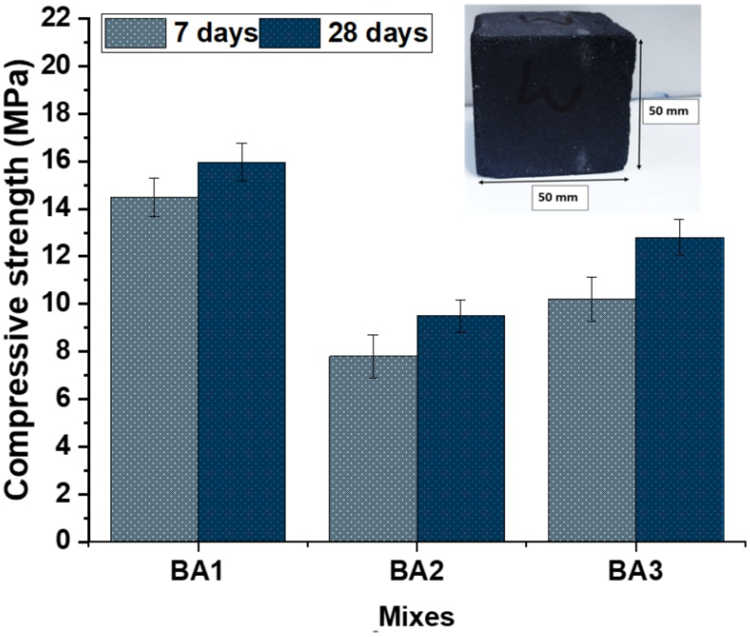


Fig. 32: Compressive strength results of alkali-activated biomass ash binders

The compressive strength achieved for BA2 (bagasse ash) and BA3 (rice husk ash) binders at 28-day curing period was found to be 9.5 MPa and 12.8 MPa, respectively, which is relatively lower than that of BA1 binder specimens. However, all the binder specimens met the minimum compressive strength requirement of 3.5 MPa as per Indian standard code (IS 3495 (Part 1): 1992). Though SBA and RHA possess low LOI (<5%) compared to that of PMA (i.e., 13.1), the effective amorphous content was found to be lower for these ashes (Fig.18). The use of brick waste powder (filler) and hydrated lime (calcium source) made it possible to obtain a desirable compressive strength for all biomass ash specimens. Produced alkali-activated biomass ash binder cubes are black in colour without any efflorescence (within the boundary of Fig. 32).

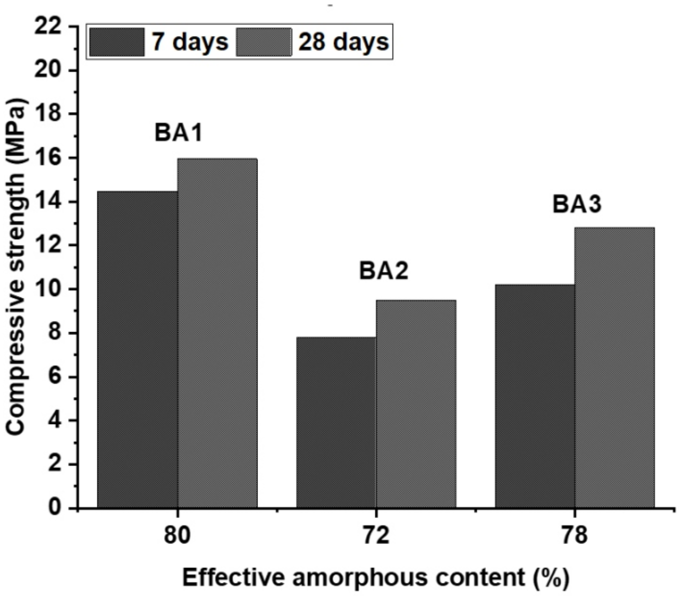
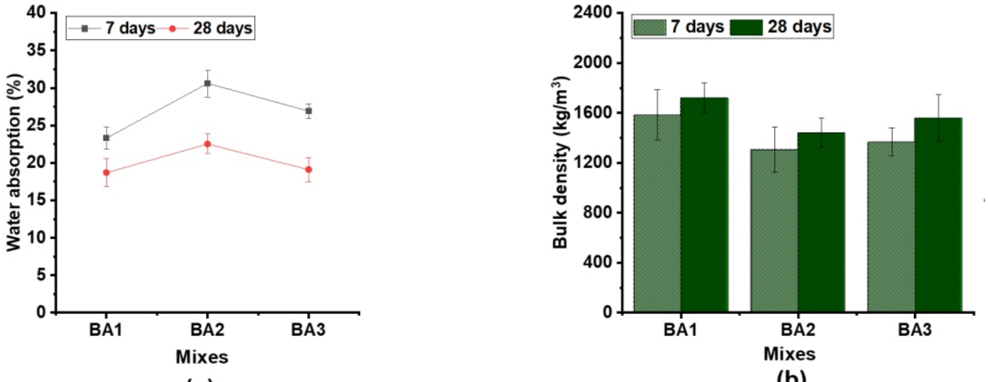


Fig. 33: Compressive strength of biomass ash binder v/s effective amorphous content of biomass ashes

5.3.2. Water absorption and bulk density

The effect of biomass ash on water absorption and bulk density of alkali-activated binder was studied and the results are shown in Fig. 34. It is evident that with the increase in curing time water absorption values of all biomass ash binders decreased, while bulk density increased as a result of the greater formation of hydration products, irrespective of binder type. The highest water absorption (31% at 7 days of curing and 23% at 28 days) was observed for BA2 binder, which possesses lower bulk density as well as compressive strength. BA1 and BA3 exhibited lower water absorption values (< 20%) than BA2 at both the duration of curing. At the same time, bulk density was also found to be higher (>1500 kg/m^3) in these mixes. As per IS: 3495 (Part II) code, water absorption value cannot be greater than 20% (by weight) up to 12.5 class bricks [181]. Even though water absorption values cannot meet the requirement of higher-class bricks i.e., >15, among three different biomass ash binders, BA1 and BA3 binders fall within the specified standard limit of <20%. Higher water absorption in biomass ash binders can be attributed to the hygroscopic nature of ashes due to the presence of porous structures and unburnt fibrous particles in biomass ashes.



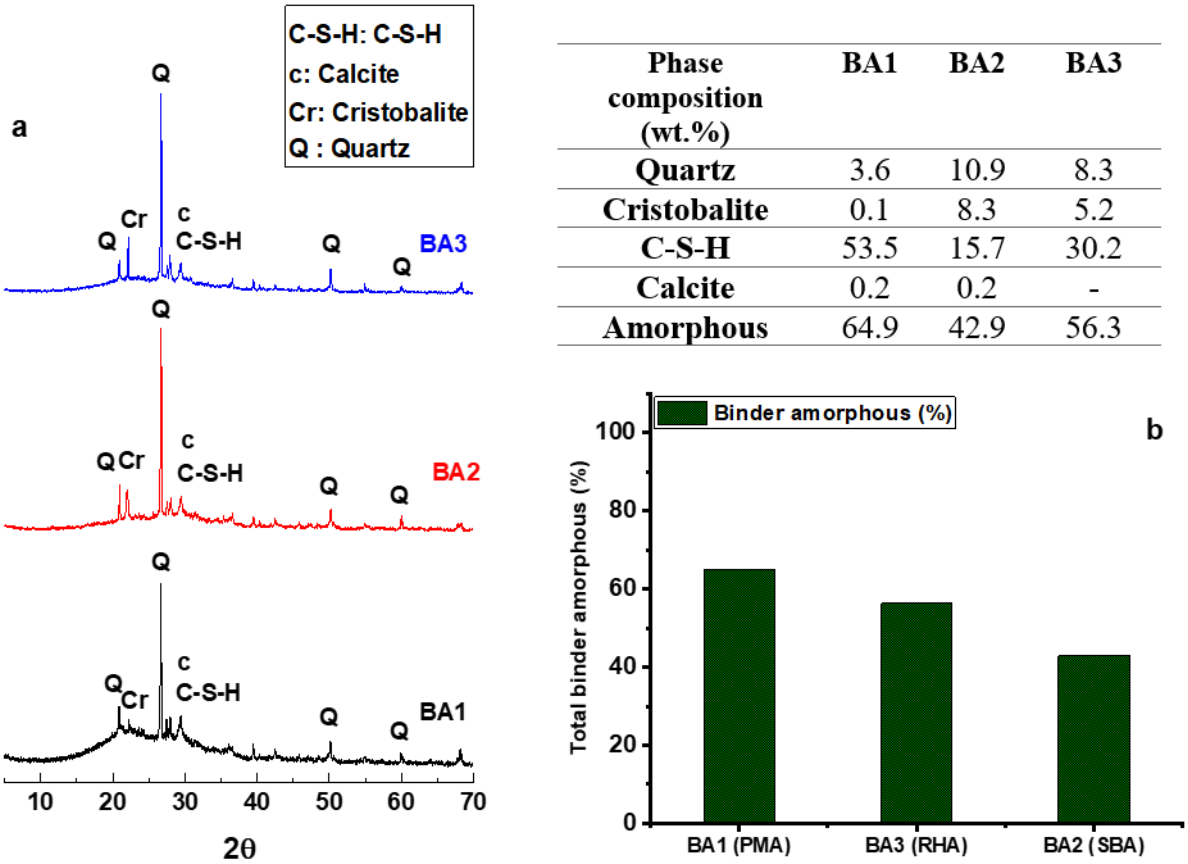
(a) (b)

Fig. 34: a) Water absorption and b) bulk density of alkali-activated biomass ash binder at 7 and 28 days

The bulk density of biomass ash binders was observed to be at a lower end compared to that of the standard bulk density of fired clay brick (~1900 kg/m^3). This could be attributed to the lesser specific gravity of biomass ashes (2-2.1) used in this study than that of fired clay (2.4-2.9), leading to an increase in ash amount amid other constituents in a unit volume of the specimen. The highest bulk density for BA1 (1720 kg/m^3) could be due to the formation of more binding gels with varied ratios of Ca/Si and Al/Si, possibly related to the high amorphous content in ash. However, further research is required to fully understand this occurrence.

5.3.3. Phase composition, bound water content of reaction products, and functional groups of biomass ash-binder

Section 3.1 signifies that more than 80% of 28 days compressive strength was achieved in 7 days. In this perspective, phase composition, bound water content, and functional groups of reaction products for biomass ash-binders were determined for 7 days of samples and presented in Figs. 35-37, respectively.

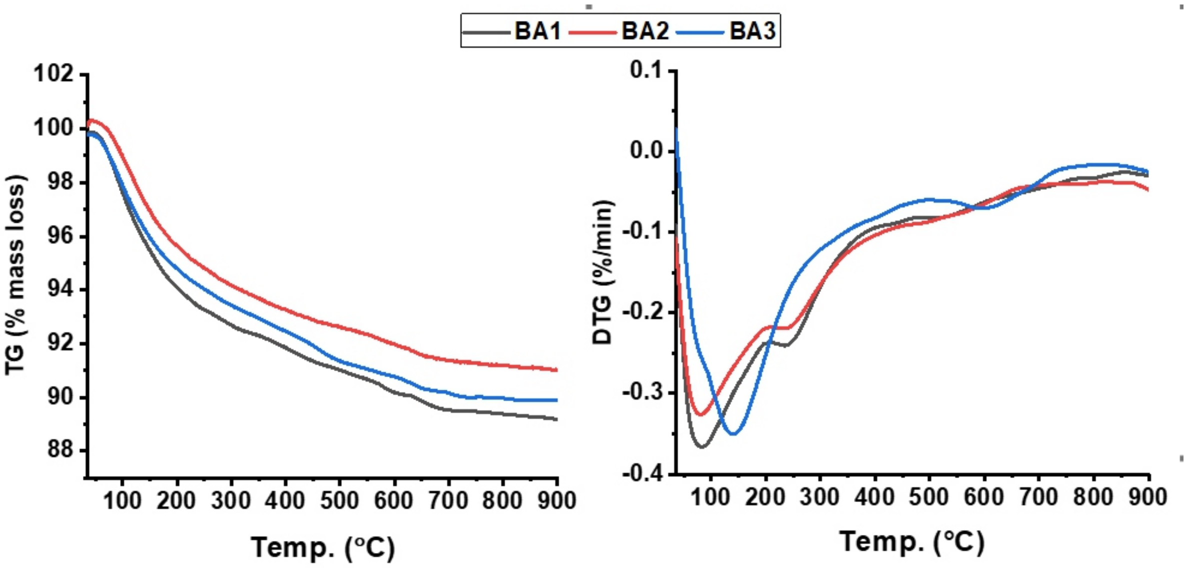


Phase composition (wt.%)	BA1	BA2	BA3
Quartz	3.6	10.9	8.3
Cristobalite	0.1	8.3	5.2
C-S-H	53.5	15.7	30.2
Calcite	0.2	0.2	-
Amorphous	64.9	42.9	56.3

Fig. 35: (a) XRD pattern and phase composition of biomass ash binders- at 7 days and (b) total amorphous content in the binder

To evaluate the hydration growth and phases formed in alkali-activated biomass ash binders, quantitative X-ray diffraction (QXRD) analysis was carried out for 7 days of samples (Fig. 35). In the case of all biomass ash binders, most of the peaks (quartz, cristobalite, calcite) from raw ash are seen along with an additional peak of calcium-silicate-hydrate (C-S-H) at the diffraction angle (2θ) of 29.2°. Similar to alkali-activated slag/fly ash system, biomass ash binders also offered C-S-H as a main hydration product at lower alumina constitution. It is reported that Ca/Si ratio present in C-S-H phase of biomass ash binder is lower compared to the portland cement system due to low calcium content [13].

Fig. 35b demonstrates the total amorphous content of the biomass ash binder. PMA based biomass ash binder (BA1) exhibited higher amorphous content of 65%. The total amorphous content in SBA and RHA based binders (BA2 and BA3) was found to be lower by 18.5% and 13%, respectively at 7 days. The possible reason for higher total amorphous content in BA1 binder compared to BA2 and BA3 are 1) higher amorphous content in raw PMA (93.3%) and 2) lower percentage of quartz and cristobalite phases. Higher amorphous content in raw PMA and a lower percentage of quartz and cristobalite phases are two possible reasons associated for the higher total amorphous content in BA1 binder compared to BA2 and BA3. The higher compressive strength of BA1 binder can probably be attributed to this fact. Bound water content of the reaction product was quantified through thermogravimetric analysis and the same is presented in Fig. 36.



Mixes	Δmass loss (%)	
	50-300 °C	50-600 °C
BA1	7.25	9.98
BA2	5.82	8.02
BA3	6.12	9.01

Fig. 36: TG-DTG results of biomass ash binder at 7 days

C-S-H phase shows the structural water loss from interlayers at the temperature boundary of 50-600 °C. At temperatures between 50-600 °C, biomass ash binders showed a mass loss of 9 to 10%. Approximately 97% of total mass loss from 50-900 °C was seen between 50-600 °C. However, most of the bound water from C-S-H phase is lost between the temperature range of 50 and 300 °C (~70-73% of mass loss between 50 and 600 °C). Further, mass loss allied to calcite phase at a temperature boundary of 700-800 °C is negligible (<1.5%). The majority of TG mass loss in biomass ash binders is instigated from C-S-H phase with small portion of calcite and hydrated ash decomposition.TG-DTG results exhibited the highest mass loss at 50-600 °C for BA1 (~10%) specifying the higher C-S-H formation (Fig. 36). While, for BA2 and BA3 it was quantified to be 8% and 9%, respectively relatively lower to BA1. The TGA and QXRD results agree reasonably well.

The functional groups of biomass ash-binders were assessed using FTIR spectra (Fig. 37) to verify the development of major reaction products. All types of binders exhibited a broad band in a range of 1200-900 cm-1, which could be attributed to the stretching vibrations of Si-O [109]. The band observed at 976 cm-1 (BA1), 963 cm-1 (BA2), and 967 cm-1 (BA3) corresponds to the Si-O-T (T= Si or Al) stretching vibrations. The shift detected in that band toward higher or lower frequencies indicated the prevalence of one or more reaction products [182]. At lower aluminium content in correspondence to silica in binder samples (refer Fig. 22d), it can be assumed that this band registered in the region 963-976 cm^{-1} characterizes the Si-O-Si

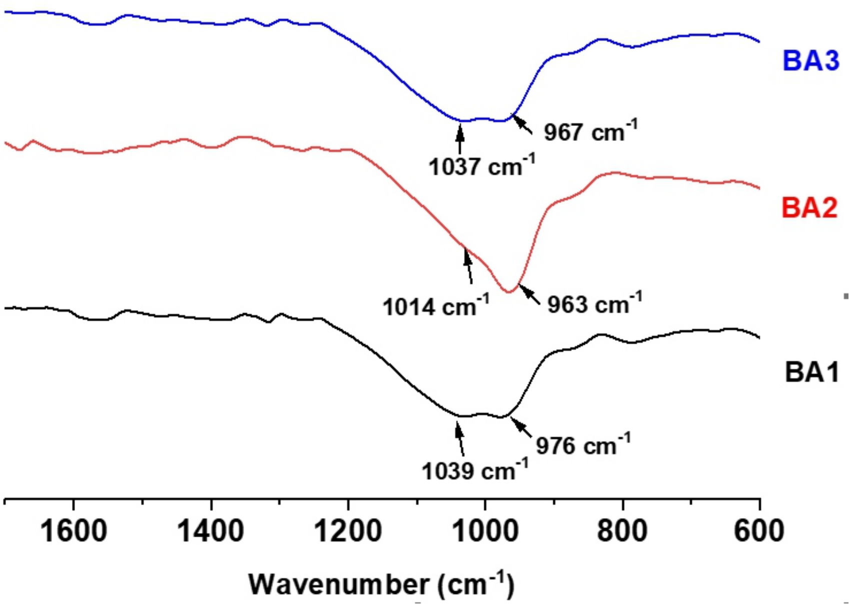


Fig. 37: FTIR spectra of biomass ash-binders at the curing time of 7-day

stretching. It can be deduced from this that C-S-H gel was the main reaction product.

5.3.4. Microstructure characterization

Scanning electron microscopy (SEM) in secondary electron mode was used to observe the morphology of 7-day biomass ash binders and the same is presented in Fig. 38.

The microstructure of all the binders (BA1, BA2, and BA3) used in this study was dissimilar. For BA1 binder, a relatively dense, homogenous microstructure composed of mostly C-S-H gel is seen along with fewer

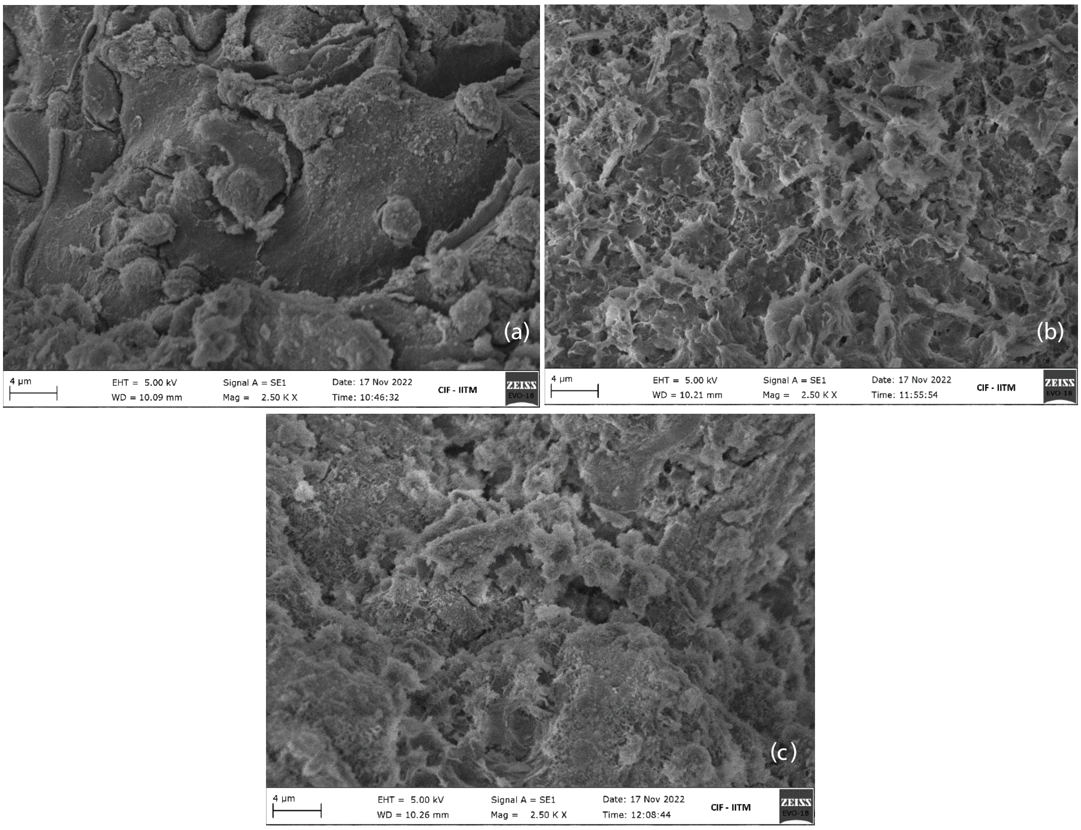


Fig. 38: Scanning electron micrographs of biomass ash binders at 7 days, a) BA1 b) BA2, and c) BA3

unreacted particles. Some porous unreacted particles entrenched in the gel matrix are visible throughout BA2 and BA3 samples (Fig. 38b and 38c). Micrographs showed a honeycomb like C-S-H structure. In BA2 binders, pores, voids, and unreacted particles are more prevalent (Fig. 38b). The development of the agglutinating phase with gel network is said to be influenced by the presence of crystalline quartz in the system [182]. Hence, it is reasonable to assume that the filling effect is caused by crystalline quartz particles.

5.4. Summary

Substituting conventional supplementary cementitious materials (fly ash and slag) by biomass ash (such as bagasse ash and rice husk ash) is recommended owing to their availability and accessibility. Sugarcane bagasse ash and rice husk ash is determined to be a potential mineral admixture for use in India due to its availability, cost, quality, and accessibility. Paper industry is also identified as one of the major sources for the production of huge quantity of biomass ashes from its cogeneration system in India. From this viewpoint, the present case study examined the viability of using Indian biomass ash from three major industries such as paper, sugar, and rice mills in the development of an alkali-activated binder. The study can be summarized as follows.

- Biomass ash is a suitable material for alternative / composite cements in India owing to its wide availability, accessibility, and high content of amorphous SiO_2.
- Thermo-mechanical processing of biomass ash significantly improves its reactivity.
- Compressive strength of hydraulically pressed biomass ash-based binder formulated from biomass ash, brick waste and hydrated lime (i.e., 50:40:10) using 1M NaOH solution (L/S ratio of 0.42) met the requirement of Indian standard code (IS 3495 (Part 1): 1992) limit of 3.5 MPa.
- Among three different sourced biomass ashes, paper mill ash-based binder system with higher amorphous content resulted in highest strength and lowest water absorption. Almost 80% of 28-day strength was achieved at 7 days for all biomass ash binders.
- Biomass ash binders presented C-S-H as a primary hydration product at lower alumina constitution, similar to the alkali activated slag/fly ash system. Higher C-S-H phase and denser microstructure was found for paper mill ash-based binder.

6 : OPPORTUNITIES, CHALLENGES AND FUTURE RECOMMENDATIONS

6.1. Opportunities for using biomass ash in construction industry

Compared to coal, biomass produces higher amount of ash. The total amount of ash produced is also anticipated to increase as more biomass is burned to meet the rising demand [183]. The construction sector can benefit from the potential use of biomass ash. According to the cited studies, biomass ash currently has enormous potential in the production of construction materials, primarily cement and concrete. Biomass ash is enriched with various constituents that may affect the reaction differently. Structure and mineral diversity in biomass ash are typically based both on soil and soil harvesting impurities added. Fig. 39 shows the steps involved in the application of biomass ash.

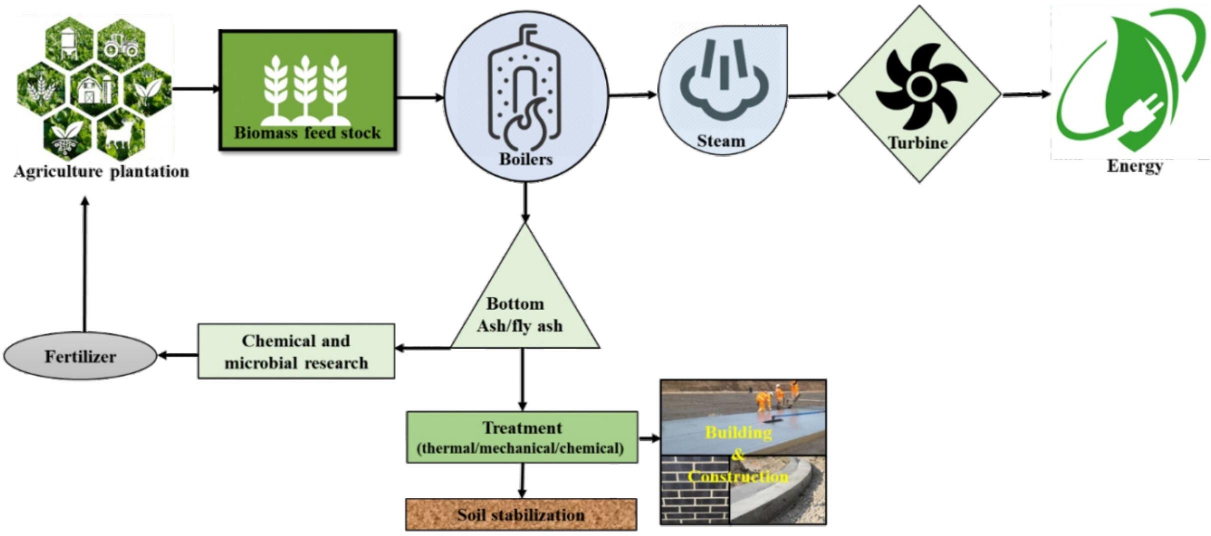


Fig. 39: Steps involved in the application of biomass ash

Ash is used in the construction industry and can be used for a variety of purposes that includes the production of bricks, making cement, building roads, and mine-filling. Biomass ash, rich in SiO_2, Al_2O_3, and Fe_2O_3 content, is useful for a variety of applications in construction. Biomass ash can be used in the construction sector as a cement-based retardant (instead of gypsum), a raw material for the production of pozzolanic cement, a substitute for cement in portland cement concrete, and a precursor in the development of alkali-activated binders. Due to the pozzolanic properties of ash, several studies have described the useful uses of biomass ash in cement. When 10–20% of biomass ash is substituted in cement, it exhibits favourable properties. Similar to fly ash, pozzolanic properties of biomass ash contribute to the mechanical and durability performance of concrete. Consequently, it is preferable to use biomass ash in cementitious material rather than a landfill because it is a more practical and environmentally friendly method. Further, after crushing and blending with biomass ash, the second-life cement product can be used again in road applications. Current research is focusing on the development of aluminate silicate alkalis-based binders that have good performance and are long-lasting for use in concrete owing to the high concentration of alkalis and silica in biomass ash.

In addition, to being used in cement and concrete, it is also being used in soil amendments and as a pavement base. For road construction, the soil should have stable, incompressible, good drainage, strength, and less volume change properties. Poor soil with expansive nature leads to swelling, cracking, and huge disturbance in pavements. Therefore, in a typical scenario, these soils are replaced with crushed rocks there by increasing the cost of road construction. In this perspective, biomass ash with the potential to reduce embankment swelling was proposed to be an inexpensive substitute for crushed rock. Some other opportunities to apply biomass ash in construction technology are to use it as a filler in tar, as light weigh aggregate, and as the production of light weight building blocks [184]. For the production of clay bricks, an appropriate amount of organic material, sand, and clay was used. The desired porosity in the bricks was accomplished by using fly ash. Biomass ash can therefore be used in the production of bricks [13].

6.2. Challenges in using biomass ash as a binding material

When attempting to use biomass ash as an alternative source of binding material, the following issues must be taken into account:

- Even though several studies in literature are available on the utilization of biomass ash (most popular in this regard are rice husk ash and bagasse ash) as a binding ingredient, there are a lot of uncertainties with respect to the physico-chemical properties of ash derived from biomass sources. Depending on the source and organic makeup of the biomass, physico-chemical characteristics vary greatly among different biomass ashes.
- Biomass ashes comprise the hazardous elements due to the absorption and deposition of mineral ions through soil or by the use of chemical fertilizers during the growth phase of vegetation. Therefore, it is crucial to comprehend how these ions affect the creation of binders and to keep the amount of potentially hazardous minerals below the established limit under environmental quality standards.
- Unlike coal fly ashes, biomass ashes need processing to reach the desired strength at higher dosages. Carbon, sulfate, and chloride content present in biomass ashes need to be controlled when used as a replacement material for cement.
- It is essential to choose a specific type of biomass ash as a cement substitute based on factors like the workability and strength of the corresponding blended concrete. It is challenging to group biomass ashes according to the required application from the pool of biomass ashes.
- The selection of an appropriate alkaline activator, its dosage, and other associated parameters for biomass ash varies individually depending on its chemical composition in the development of alkali-activated biomass ash binder.
- Unlike conventional pozzolanic material, the majority of the biomass ashes do not meet ASTM C618 standards. Due to the lack of knowledge regarding the engineering properties of non-coal driven materials, the American Society for Testing Materials (ASTM) and American Concrete Institute (ACI) standards currently do not recommend the use of biomass ashes in concrete.
- Acceptance from the cement and concrete industries represents one of the biggest potential obstacles to the use of biomass ashes as SCMs in concrete. When there is a perception that there is a lack of knowledge about a material's performance, especially in terms of its new properties and durability properties, industries are reluctant to adopt new materials.
- The availability and accessibility of biomass ashes are both highly ambiguous that depend on the biomass sources. The geographical distribution of biomass sources varies depending on the temperature, climate, and agricultural land. Construction industries consume a lot of materials, so it is necessary to have a consistent supply of high-quality ash in sufficient quantities with few variations in its properties.
- Numerous studies already conducted on LCA of alkali activated binders rely heavily on current literature or databases, which may not accurately reflect local facts and cause significant uncertainty in the findings.

All these facts limit the practical application of biomass ashes in construction industries.

6.3. Recommendations and future scope for study

It is sustainable to repurpose biomass ashes as alternative cementitious materials or alkali-activated binders because it lessens the environmental impact of carbon-intensive processes such as cement clinker production and open-field burning of biomass. However, biomass ashes are not widely used in practice. The primary reason for the delay in implementing biomass ashes-based concrete or alkali-activated binder on an industrial scale is the absence of a thorough performance evaluation. The effectiveness of concrete can therefore be affected by various biomass ashes, and further research is necessary to understand this effect. Material properties, supply,

and costs are the broad areas that require more research in the development of biomass ash-based building materials.
To enable better utilization of biomass ash in the construction industry, the following studies are recommended for additional research:

- A comprehensive database that provides details on the accessibility and availability of various biomass ashes is lacking. Therefore, it is essential to conduct additional research studies to create a systematic database that provides information on the availability of different biomass ash.
- Numerous studies have been performed on the use of rice husk ash and sugarcane bagasse ash as additional cementitious materials. However, other available biomass ashes derived from agriculture waste such as paper mill ash, corn cob ash, ground nutshell ash, wheat husk ash, rice straw ash, etc., are less explored. There is a huge need to understand the properties of these biomass ashes for its application in cement and concrete.
- The performance of concrete over the long term is greatly influenced by durability. Very limited studies are available related to the durability of biomass ash-based concrete. It is necessary to conduct more research on how biomass ash affects the durability characteristics of concrete.
- Even though several studies are reported on the physico-chemical and microstructural properties of ashes, the role of these ashes on strength and durability can be better understood through microstructural and mineralogical analyses of the blended cementitious system. Therefore, in addition to studies on the ashes, more research should be done on the microstructural and mineralogical analysis of blended cement paste.
- Ash properties are impacted by pre-combustion treatments, post-combustion treatments, and combustion methods, which affects the reactivity of ashes. Hence, for the effective use of ashes, it is crucial to comprehend the impact of these parameters.
- The literature extensively reports on the fresh properties such as slump and slump flow of biomass ash blended cementitious mixtures. However, the rheological properties of biomass ash blends have received little in-depth research. The selection and compatibility of superplasticizers as well as the dosage optimization about various biomass should therefore be encouraged in future research on rheological properties.
- The majority of studies are concentrated on using biomass ash as a partial replacement for OPC. The research on the sole use of biomass ash as a binder in an alkali-activated system is uncommon.
- The high cost of alkaline activators is a major barrier to the production of alkali-activated biomass ash binders. Therefore, approaches for obtaining inexpensive alkaline activators from biomass sources rich in silica are advised.
- The reaction kinetics of biomass ashes in alkali-activated binder is unclear. To comprehend their performance, research studies focusing on the reaction mechanism of biomass ashes must be conducted.
- Although biomass ash blended concrete has been found to perform satisfactorily, applications of biomass ash in other building materials like hollow blocks, tiles, alkali-activated concrete, and paver blocks are minimal. The effects of these biomass ashes on other construction products must therefore be understood through further research.
- Identification or development of codes for biomass ashes is very much essential to benefit the acceptance of biomass ashes for civil engineering applications as a supplementary cementitious material. These research directions would help in comprehending the potential advantages of biomass ashes in the concrete materials sectors.
- Uncertainty and sensitivity analyses are necessary for LCA investigations, particularly those that compare alkali activated binder and OPC-based binders.

These research directions would help us to know the potential advantages of using biomass ash in concrete materials industries.

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Scheme for Promotion of Academic and Research Collaboration

Department of Civil Engineering

Indian Institute of Technology Madras, Chennai, India