Use of non-wood biomass combustion ash in development of alkali-activated concrete

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Abstract: The work reported herein focuses on demonstrating the value of non-wood biomass combustion ash in production of alkali-activated concrete. The growing use of biomass as fuel leaves significant quantities of solid residue (ash) with qualities that are different from those of coal combustion ash. The composition of biomass ash suits development of alternative cement chemistries with significantly reduced carbon footprint and energy content when compared with Portland cement. Sustainable cement chemistries relying upon alkali aluminosilicate hydrate as the primary binder are receiving growing attention. Combustion ashes of wheat straw, switch grass, corn cob, alfalfa stem, corn stalk, cotton gin and rice hull were evaluated in this investigation. Characterization of the chemical composition, mineralogy, degree of crystallinity, solubility, pH in solution, loss on ignition, morphology and particle size distribution of non-wood biomass ashes, and the strength and moisture stability of the resulting concrete provided a basis for assessment of the merits of non-wood biomass ash as reactive raw materials in production of alkali-activated concrete.

Key words: non-wood biomass combustion ash; alkali aluminosilicate hydrate; cementitious binder; concrete; sustainability

1. Introduction

Non-wood biofuels (e.g., agricultural wastes) are among alternative fuels that are carbon neutral. Extraction of value from biomass in biorefineries is a growing practice [1]. Combustion ashes are the by-products of biomass combustion in power plants and biorefineries [1]. The relatively high silica and alkali contents of non-wood biomass ash are of value towards production of alkali aluminosilicate hydrate-based binders for high-performance and sustainable concrete materials. Table 1 compares examples of ash contents and compositions in combustion of wood, wheat straw, and algae. Combustion ashes of wheat straw and algae (examples of non-wood biomass) are distinguished from wood combustion ash by significantly reduced CaO contents, substantially increased SiO_2 and alkali ($\text{Na}_2\text{O}+\text{K}_2\text{O}$) contents, greater Cl contents (washing can lower the Cl content of ash[2]), and reduced heavy metal concentrations.

<Table 1>

Coal fly ash is now used in massive quantities as a partial replacement for cement in concrete [3]. Major research investigations have thus focused on the potential value of biomass combustion ash as a supplementary cementitious material in conventional concrete [4-7]. While some promising results have been produced with wood combustion fly ash as replacement for ~10 wt.% of cement, the relatively high alkali content of wood waste ash is a drawback for the concrete industry which is highly concerned with deleterious alkali-silica reactions. In the case of wood waste ash with moderately high alkali content, the relatively low C/S ratio of the C-S-H generated by the pozzolanic reaction of the biomass ash enables binding of relatively high quantities of alkalis within the C-S-H structure [5]. This phenomenon controls the potential for deleterious alkali-silica reactions in concrete incorporating wood combustion ash as partial replacement for cement [5]. The high alkali contents of non-wood combustion ashes, however, seriously challenge the potential for their use as supplementary cementitious materials in concrete. An alternative approach for value-added use of non-wood biomass combustion ash, pursued in this study,

1 takes advantage of the high alkali content of biomass ash towards producing structural grade binders
2 based on alkali aluminosilicate hydrates. This activation process involves reactions between non-wood
3 biomass ash, which can be classified (either inherently or after augmentation) as an aluminosilicate (AS_y),
4 and an alkali silicate solution [$RS_z(aq.)$] (typically blended with alkali hydroxide) in water (H): $AS_y +$
5 $RS_z(aq.) + nH \rightarrow RAS_{(y+z)}H_n$. This is a polycondensation reaction in which the dissolved alkali silicate
6 cross-links with the reactive aluminosilicate to form high-performance solid structures with significant
7 binding attributes.[3] The alkalis in biomass ash feasibly take part in this reaction. The resulting hydrates
8 incorporate relatively low chemically bound water contents when compared with the hydration products
9 of Portland cement.

10 Binders based on alkali aluminosilicate hydrates offer the potential to yield lower carbon footprint and
11 energy content when compared with Portland cement [8-10]. Unlike the 1D structure of calcium silicate
12 hydrate, the primary binder among ordinary cement hydrates, which relies upon weak secondary bonds to
13 form a 3D structure, alkali-activated aluminosilicates form an extended 3D structure with primary bonds
14 via polycondensation [11, 12].

15 Alkali-activated aluminosilicate binders are formed by through-solution chemical reactions between the
16 dissolved constituents of various aluminosilicate precursors with alkaline earth and alkali metal cations
17 that are present in an alkaline solution [13]. These reactions yield predominantly alkali and calcium
18 aluminosilicate hydrates [14], and tend to occur at higher rates than hydration of ordinary Portland
19 cement. The extended 2D/3D structure of calcium/alkali aluminosilicate hydrates, and their relatively low
20 content of chemically bound water, distinct molecular-scale porous morphology and robust chemistry
21 explain their advantages over the hydration products of ordinary Portland cement (primarily calcium
22 silicate hydrate). Some key performance advantages of alkali-activated aluminosilicates are: (i) stability
23 under weathering and chemical attack; (ii) impermeability; (iii) encapsulation of hazardous materials; (iv)
24 fire resistance; (v) abrasion/erosion resistance; (vi) dimensional stability; (vii) rate of strength gain and
25 ultimate strength; and (viii) adhesion and binding qualities [15-19]. The potential for reducing carbon

1 footprint and energy content are also among the advantages of alkali-activated aluminosilicate binders
2 versus ordinary Portland cement hydrates [8, 9]. Continued hydration of ordinary Portland cement
3 requires input of moisture to retain close to 100% relative humidity, which challenges practical
4 achievement of advanced hydration states in field conditions. The alkali-activated aluminosilicate binder
5 structure, on the other hand, continues to develop in ambient condition without the need for external input
6 of moisture; this is because water is consumed and then regenerated in alkali-activation of
7 aluminosilicates [11].

8 The work reported herein has developed alkali-activated aluminosilicate binders for concrete production
9 which by making value-added use of the combustion ashes of non-wood biomass which are rich in silica,
10 alkalis, and (to a lesser extent) alumina. Non-wood biomass ash is formulated with supplementary
11 materials in order to achieve a desired chemical balance and particle size distribution for production of
12 high-performance, low-cost, sustainable and environmentally safe alkali-activated biomass ash-based
13 concrete.

15 **2. Value of non-wood biomass ash in production of alkali-activated aluminosilicate binders**

16 Alkali-activated materials encompass binder systems derived by reaction of an alkaline salt with a solid
17 silicate powder. The alkaline salts used in the process are essentially any soluble substance which can
18 raise the pH of the reaction mixture and accelerate dissolution of the solid precursor. When compared
19 with ordinary Portland cement, alkali-activated binders have a high degree of silicate connectivity, and a
20 higher ratio of $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ to $(\text{CaO} + \text{Na}_2\text{O})$. While alkali-activated binders tend to have lower calcium
21 contents than Portland cement binders, the presence of calcium is important to the stability and long-term
22 performance of alkali-activated binders [20, 21]. These binders assume a high degree of moisture
23 resistance and chemical stability as far as they can produce a highly coordinated (overwhelmingly Q^4)
24 ‘geopolymeric’ structure. Alkali-activated materials with relatively high aluminum contents can assume

1 this 'geopolymeric' structure. Figure 1 shows the calcium and aluminum contents of geopolymer versus
2 those of other binders including alkali activated materials and Portland cements.

3 <Figure 1>

4
5 While aluminosilicate-based binders offer distinct qualities for solidification/stabilization of heavy
6 metals, the concentration of heavy metals would still be a consideration in selection of biomass ashes as
7 aluminosilicate precursors. Another important issue is the effect of the contaminants present in biomass
8 ash, that could add reaction pathways which affect the fresh mix rheology, set time, shrinkage, strength
9 and other engineering properties of aluminosilicate-based binders [15]. Abundance, environmental impact
10 and alternative applications are also important considerations in selection of non-wood biomass ashes for
11 use as aluminosilicate precursors. The non-wood biomass type as well the combustion conditions
12 determine the properties of the combustion ash. The residues formed during biomass combustion can be
13 divided into bottom and fly ashes. The fly ash fraction typically consists of coarse and fine types. The
14 coarse fly ash particles (larger than few μm) form simply by entrainment of ash from the fuel bed.
15 Formation pathways of the fine fly ash (aerosols with $<1\ \mu\text{m}$ particle size) involve release of volatile ash-
16 forming compounds (K, Na, S, Cl) and easily volatile heavy metals (Zn and Cd, etc.) from the fuel into
17 the gas phase, and their subsequent gas phase reactions and particle formation via nucleation or
18 condensation of vapors on existing surfaces. Nucleation and condensation are competing processes;
19 nucleation can be partly or even totally suppressed if there are adequate surfaces available for
20 condensation. Otherwise, very small (few nm) aerosol particles form. Upon formation, these particles
21 start to coagulate with other aerosols and with coarser fly ashes [22].

22 This investigation will consider various types of ash resulting from combustion of abundant non-wood
23 biomasses. Typical compositions of combustion ashes of these biomasses (and coal) are given in Table 2.
24 The alumina, silica, alkali and calcium oxide contents of non-wood biomass combustion ashes are of
25 particular interest in their evaluation as precursors for production of binders based on alkali/calcium
26 aluminosilicate hydrates. The high silica content of non-wood biomass ashes stands out in Table 2.

<Table 2>

3. Materials and methods

3.1 Materials

Seven non-wood biomasses were obtained from different sources. Wheat straw was obtained from a farm in Okemos, Michigan. Two crops of wheat straw were evaluated in order to make a preliminary assessment of the variations in the qualities of the resulting ashes. Mid-Michigan switch-grass and corn stover were obtained from mid-Michigan farms. Alfalfa stem was obtained from a farm in Williamston, Michigan. Ungrounded rice hull was obtained from Riceland Food, Stuttgart, Arkansas. Cotton stalk and cotton gin were obtained through the USDA Agricultural Research Service in Lubbock, Texas.

In order to produce a desired chemical balance for formation of alkali aluminosilicate hydrates with desired binding qualities and moisture resistance, coal fly ash was used together with non-wood biomass ash, targeting viable silica-to-alumina ratios. Wheat straw ash was used in the formulation primarily as a source of silica and alkalis. The binder was synthesized by activating the blend of biomass ash and coal fly ash with using an alkaline solution comprising sodium hydroxide and sodium silicate dissolved in water. The coal fly ash used in this study was obtained from a local ready-mixed concrete plant in Lansing, Michigan. Metakaolin was used together with non-wood biomass (wheat straw) ash in order to produce a desired silica-to-alumina ratio. The metakaolin used in this study was dry Metamax® powder supplied by BASF with mean particle size of 1.3 μm . Table 3 shows chemical compositions of the coal fly ash and metakaolin used in this study. Silicon and aluminum oxides, which are critical to geopolymerization, constitute more than 96% of metakaolin; the silicon oxide-to-aluminum oxide weight ratio of this metakaolin is close to 1. In the case of coal fly ash, the silicon and aluminum oxides constitute about 75% of the total mass, and the ratio of silicon oxide-to-aluminum oxide is about 2. With

a calcium oxide content of 14.3%, this coal ash may be classified as ASTM C618 Class F, but it is at the borderline of Class F and Class C coal fly ashes.

<Table 3>

Limestone with ASTM C33 #8 particle size distribution was used as coarse aggregate, and natural sand as fine aggregate. The fineness modulus of combined aggregates was 5.0. The particle size distributions of the coarse and fine aggregates are presented in Table 4.

<Table 4>

The alkaline solution used was a combination of sodium silicate solution and sodium hydroxide solution. The sodium silicate solution used in this study was acquired from PQ Corporation (28.7 wt.% SiO₂, 8.9 wt.% Na₂O, 62.4 wt.% H₂O) with density of 1.39 g/cm³ and pH of 11.30. The sodium hydroxide (NaOH) was purchased from Sigma Aldrich in pellet form with 97%-98% purity. The NaOH solid pellets were dissolved in water to make the solutions of 6M, 10M, 14M and 18M concentrations. [23] In order to improve the workability of fresh concrete, sodium tetraborate-based (borax) was added to the mixture at low concentration.

3.2 Methods

A 20 Quart planetary mixer (Hobart A-200) was used to prepare concrete mixtures. The blended powders were first mixed for about 1 minute at medium speed. The sodium hydroxide solution was then added to the dry powder blend, and the mixing was continued for 30 seconds. The sodium silicate solution was then added, and mixed for another 30 seconds. Fine and coarse aggregates were added subsequently, and mixing was continued for about 3 minutes to produce a homogeneous mixture. The fresh concrete was cast into molds immediately after mixing, and vibrated for 2 minutes at medium speed. The fresh mix

workability was measured using the flow table test per ASTM C1473 procedures. The initial and final set times were measure following ASTM C403 procedures. Compression tests were performed per ASTM C109.

Laboratory-scale combustion of biomass was implemented with the objective of simulating large-volume combustion of biomass in power plants. The first step in the process involved combustion of a small volume of biomass in a burner with natural air flow. Biomass was ignited with flame, and allowed to burn by itself with ample air supply at a temperature of about 350°C. This combustion temperature is below that used in industrial power plants, and the resulting ash has a relatively high LOI. In order to approach the ash quality obtained in an industrial power plant, the ash obtained in the first step was subjected to 550°C for four hours in a box furnace (Model S1200C-161622 manufactured by Sentro Tech Corp.). The resulting non-wood biomass combustion ash was milled in order to produce the micro-scale particle size distribution which benefits hydration reactions. Non-wood biomass ashes were milled for four hours in a 5.6 liter ceramic jar, using steel balls with 5-10 mm diameter; the ash-to-steel ball mass ratio was 1: 10. While industrial-scale combustion of biomass generates fly ash with desired particle size distribution for direct use in hydration and geopolymerization reactions, the laboratory-scale combustion employed here produced ash particles that benefited from size reduction via ball-milling.

Scanning electron microscope observations of non-wood biomass ash were performed using a JEOL JSM-6610LV scanning electron microscope (JEOL Ltd., Tokyo, Japan). For the purpose of scanning electron microscopy, the non-wood biomass ash specimens were coated with a 20-nm thick platinum layer in an Emscope Sputter Coater model Sc 500 (Ashford, Kent, England) purged with Argon gas.

The mineralogy of ash samples was assessed via x-ray diffraction (XRD) using a Bruker D8 daVinci diffractometer equipped with Cu x-ray radiation operating at 40 kV and 40 mA. Peak intensities were obtained by counting with the Lynxeye detector every 0.05 ° 2 θ /min. Powder XRD was carried out at a reflection angle range of 2 θ =10 – 80°. Qualitative analysis of the XRD patterns yielded the mineral phases present in ash samples. The degree of crystallinity was determined using the EVA software. It is

1 calculated as the ratio of the area under all peaks to the total area under the curve (i.e., the area under
2 peaks plus the area under the amorphous peak).

3 Dissolution experiments were conducted in order to make a preliminary assessment of how readily
4 aluminosilicates become available for the through-solution condensation reactions. For this purpose, 5 g
5 of ash was dissolved in 100 ml of 10M NaOH solution, and the solution was stirred for different time
6 intervals. After stirring, the non-dissolved ash was filtered using 0.2 μm filter paper [24].

7 Loss On Ignition (LOI) was measured for ashes obtained with nine different combustion conditions of
8 non-wood biomass in order to identify the preferred method of combustion. Following ASTM D7348, a
9 single-step procedure was used for measurement of LOI. Three specimens were tested for each
10 combustion condition, and the average value and 95% confidence interval were obtained.

11 The Particle size distribution of biomass ashes was evaluated using a laser particle size analyzer (Malvern
12 Mastersizer 2000E laser particle size analyzer). About 2 grams of ash was dispersed in a water-based
13 solution of sodium hexametaphosphate ($(\text{NaPO}_3)_6 \cdot \text{Na}_2\text{O}$) within a glass vial by gently shaking the vial
14 for 2 hours.

15 The pH of ash in solutions was evaluated by adding ash to deionized water at 2% and 5% concentrations
16 by mass in a vial, and placing the solution on shaking table for 2 hours. A pH meter (Extech pH 110) was
17 used to determine the pH of the solutions.

18 Elemental analysis of ash was performed using the x-ray fluorescence (XRF) technique.

19 The mix design of wheat straw ash-based concrete is presented in Table 5. Concrete specimens were
20 molded, sealed, and retained at room temperature for 24 hours. This period allows for partial dissolution
21 of precursors prior to the curing step. The specimens were then demolded and subjected to 48 hours steam
22 curing at 80°C in order to advance and accelerate the hydration reactions. The specimens were then stored
23 at 50% relative humidity and room temperature in order to stabilize their moisture content prior to testing
24 at 7 days of age.

1 Cubic specimens (50-mm dimensions) were used for compression tests following ASTM C109
2 procedures, and also for determining void content, water absorption capacity and density per ASTM
3 C642. This test involves immersion of specimens in water of equal weight for 48 hours [25].
4

5 <Table 5>
6

7 The hydration process involves dissolution of aluminosilicate precursors and other chemical compounds
8 into the alkaline solution, and their reactions together with the alkali activator constituents to yield the
9 aluminosilicate-based binder. Solubility of the precursor constituents is thus an important consideration
10 which, besides the chemical composition of the precursor (e.g., wheat straw ash), influences the hydration
11 process. This implies that theoretical balancing of the chemistry of precursors without accounting for their
12 solubility may not be adequate in formulation of aluminosilicate-based binder systems. Therefore, an
13 empirical optimization program was designed and implemented in order to devise an example optimum
14 formulation of wheat straw ash-based binder. The optimization program considered three variables: solid
15 activator-to-ash ratio, solid sodium silicate-to-sodium hydroxide ratio, and water-to-total solid ratio. Table
16 6 presents the three levels of these variables considered in the optimization experimental program, which
17 produce viable chemical balances for hydration.[15, 26-28] The ratio of wheat straw ash-to-coal fly ash in
18 this optimization program was kept constant at 1:1, with coal fly ash used primarily to supplement the
19 low alumina content of wheat straw ash. The optimization experimental program was designed using the
20 Box-Bhenken design procedure in the SYSTAT© statistical software.
21

<Table 6>

The focus of the optimization experimental program was on maximizing the compressive strength of the wheat straw ash-based concrete. In addition, the fresh mix flow, set time, and the hardened material void content, water absorption capacity and density were determined.

4. Experimental results: non-wood biomass ash characteristics

Representative samples of the selected non-wood biomass combustion ashes were characterized in laboratory. The physical and chemical characteristics of these ashes, which determine their potential value in binders based on alkali aluminosilicate hydrate, were evaluated as described in the following.

The loss-on-ignition (LOI) of biomass ashes after combustion ranged from 6.8 to 18%. The LOI values after exposure to elevated temperature 550°C for 4 hours in furnace were less than 5%.

Figure 2 shows SEM images of non-wood biomass ashes after similar combustion and size reduction processes. The ash particles are of irregular shape with curved or angular morphologies. Finer particles seem to have adhered to coarser particles, which could have resulted from condensation on coarser particles during the process of ash formation; this observation could also be caused partly by the size reduction process.

<Figure 2>

The particle size distributions for different non-wood biomass ashes are presented in Figure 3, and the values of mean particle size (D_{50}) are presented in Table 7. The values of mean particle size vary from 9.6 to 85 μm , which occur within the range of micrometer-scale cementitious materials. The larger mean particle size of 85 μm , however, could produce slow rates of hydration reactions.

<Figure 3>

<Table 7>

The measured values of pH are presented in Table 8 for different non-wood biomass ashes. The pH test results of Table 8 indicate that the high alkali metal content of the non-wood biomass ash yields highly alkaline solutions. This was a primary consideration in selection of the specific (alkali aluminosilicate hydrate) binder chemistry considered in this development effort, which can make beneficial use of the high alkali content of non-wood biomass ash. The test results presented in Table 8 further indicate that the alkalinity of non-wood biomass ash is dependent upon the biomass species; the lowest pH is obtained with rice hull ash (10.11 at 2 wt.% and 10.50 at 5 wt.%), and the highest with corn cob ash (12.42 at 2 wt.% and 12.60 at 5 wt.%). It should be emphasized that the high alkalinity of solutions containing non-wood biomass ash favors their value-added use in alkali aluminosilicate hydrate binder. The range of alkalinity covered by biomass ash also implies that the binder composition should be tailored towards the type of biomass ash.

<Table 8>

Table 9 compares the degrees of dissolution of different non-wood biomass ashes as well as that of coal fly ash after different periods of immersion in 10M NaOH solution. The degrees of dissolution of non-wood biomass ashes are generally higher than that of coal fly ash, except for switch-grass ash (5.98% after 60 min compared to 7.78% for coal ash). Cotton cob ash produced the highest degree of dissolution after 60 min (24.76%). The data presented in Table 9 indicates that ashes from various non-wood biomass species exhibit different degrees of dissolution in alkaline solution, which could impact the rate (and the extent) of strength development in upon hydration.

<Table 9>

Elemental analysis was performed on the non-wood biomass ashes (Table 10). Some important features of the wheat straw ash that are relevant to its use in geopolymerization include relatively high SiO_2 and K_2O contents, and relatively low calcium and aluminum contents. Alfalfa, cotton stalk and cotton gin show low SiO_2 and Al_2O_3 with highly K_2O content. The rice hull ash shows high SiO_2 content (more than 90%) with small percentage of K_2O . This characteristic chemical composition suits alkali activation and geopolymerization as far as the non-wood biomass ash is blended with alumina-rich constituents (e.g., coal fly ash, slag, metakaolin). The high alkali content of non-wood biomass ash plays the favorable activation role in the course of geopolymerization.

<Table 10>

Figure 4 shows the XRD patterns of non-wood biomass ashes. These patterns were evaluated in order to identify the mineral phases present in the ash samples. The XRD patterns of the ash samples exhibit similar peaks. Rice hull ash exhibits an amorphous structure with a broad peak around silica, which points at the prevalence of amorphous silica in the rice hull ash structure. Wheat straw ash exhibits a generally amorphous structure marked by a broad peak around calcite and quartz peaks, and also exhibits sharp peaks associated with crystalline sylvite. Cotton cob and cotton gin ashes exhibit more crystalline structures with peaks corresponding to quartz, calcite, calcium silicate, sylvite and sodium aluminum oxide. Cotton stalk ash exhibits a crystalline structure with peaks associated with quartz, calcite, sylvite and sodium aluminum oxide. Among the three cotton residues, cotton cob ash exhibits some amorphous patterns with a broad peak around calcite, sylvite and quartz peaks. Alfalfa ash exhibits a crystalline structure with peaks corresponding to quartz, calcite, sylvite and calcium silicate. Finally, the switchgrass ash exhibits an amorphous structure marked by a broad peak around calcite and quartz peaks, with few crystalline species among which only sodium aluminum oxide could be identified.

Analysis of the XRD data (Figure 4) yielded the degrees of crystallinity of different non-wood biomass ashes. Table 11 presents the degrees of crystallinity of different biomass ashes as well as that of a coal fly ash. The results confirm the findings of Figure 4, indicating that alfalfa, cotton stalk and cotton gin ashes have relatively high degrees of crystallinity, and wheat straw and rice hull ashes provide relatively low degrees of crystallinity. The coal fly ash considered here provides a relatively low degree of crystallinity. The above analysis of XRD patterns points at the differences between the degrees of crystallinity and the mineral composition of different biomass ashes. There is, however, no clear correlation between the degree of crystallinity and the extent of dissolution of biomass ash in alkaline solution or their pH in solution. Consideration of particle size of different non-wood biomass ashes also does not help with establishing such correlations. The concentration of defects in crystalline structures and the relative solubility of various minerals could explain the lack of such correlations.

<Figure 4>

<Table 11>

5. Experimental results: wheat straw ash-based geopolymer concrete materials

The effect of NaOH concentration on the compressive strength of concrete incorporating wheat straw ash is presented in Figure 5. There is some gain in compressive strength with increasing concentration of NaOH in solution. Compressive strengths range from 50 to 60 MPa, which are higher than those provided by normal-strength Portland cement concrete.

<Figure 5>

The test data generated in the optimization experimental program is presented in Table 12. Figure 6 shows some trends reflecting the effects of design variables on the compressive strength test results in the optimization experimental program. Compressive strength is found to be most sensitive to water-to-solid ratio, which could be explained by the rise in porosity and probably the drop in pH with increasing water content. There is a relatively small effect of (solid) activator-to-ash ratio on compressive strength, indicating that compressive strength peaks at a medium activator-to-ash ratio of 0.27. Compressive strength seems to be insensitive to the variations in (solid) sodium silicate-to-sodium hydroxide ratio within the range considered in the optimization experimental program. This could be due to the relatively high available silica content of non-wood biomass ash. The response surfaces developed using the compressive strength test data are presented in Figure 7. Response surface (Ridge) analysis of the compressive strength test data yielded the following optimum levels (at 95% confidence) of design variables for the geopolymer concrete material incorporating wheat straw ash:

Solid activator-to-ash ratio:	0.273
Solid sodium silicate-to-sodium hydroxide ratio:	1.326
Water-to-solid ratio	0.272

<Table 12>

<Figure 6>

<Figure 7>

Effects of the mix design variables in the optimization test program on the (initial) set time and fresh mix flow of geopolymer concrete are presented in Figures 8 and 9, respectively. The set time test results indicate that increasing the (solid) activator-to-ash ratio consistently increases the set time of geopolymer

concrete incorporating wheat straw ash. The set time of geopolymer concrete tends to be higher at an intermediate level of solid sodium silicate-to-sodium hydroxide ratio. The increase in water-to-solid ratio first decreases and then increases the initial set time of geopolymer concrete incorporating wheat straw ash. The solid activator-to-ash ratio plays a significant role in controlling the initial set time of the geopolymer mixture. The increase in set time with increasing solid activator-to-ash ratio might be due to the consequent rise in SiO_2 content (and thus the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio). It has been found that the set time of low-calcium geopolymer systems is controlled by the Al_2O_3 content, with set time increasing at higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios [29]. The fresh mix flow of geopolymer concrete increases consistently with increasing (solid) sodium silicate-to-sodium hydroxide ratio. Unlike Portland cement concrete, the fresh mix flow of geopolymer concrete seems to be insensitive to water-to-solid ratio within the range considered in the optimization experimental program. Flow is also observed to peak at an intermediate level of solid activator-to-ash ratio. The sodium silicate-to-sodium hydroxide ratio seems to be a key factor influencing the workability of fresh non-wood biomass ash-based geopolymer concrete. The improved workability obtained at higher sodium silicate-to-sodium hydroxide ratios could be explained by the consequent drop in Na_2O concentration which lowers the fresh viscosity and increases the flow diameter [30]. Also, the addition of sodium silicate makes extra soluble silicates available, raising the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio towards and optimum level which yields improvements in both the fresh mix workability and the hardened material density and strength [31].

<Figure 8>

<Figure 9>

5.1 Moisture stability of alkali-activated non-wood biomass ash-based concrete

It was noticed that alkali-activated non-wood biomass ash concrete exhibits signs of cracking and deteriorations after immersion in boiling (100°C) water (Figure 10). Compression tests indicated that 75-

80% of compressive strength is lost after immersion in boiling water. As shown in Figure 11, unlike the geopolymer concrete based on biomass ash, that based on coal fly ash experienced a rise in compressive strength after immersion in boiling water. Moisture resistance is a key feature of concrete; an extensive effort was undertaken in order to refine the biomass ash-based concrete chemistry for realizing the high levels of moisture resistance required for its successful transition to construction markets.

<Figure 10>

<Figure 11>

The geopolymerization process involves dissolution of aluminosilicate precursors in an alkaline solution, which are then condensed and further polycondensed to form an extended 3D structure which exhibits high levels of moisture resistance and durability. Intermediate condensation steps can yield solids consisting of relatively small aluminosilicate and sodium silicate molecules with high compressive strength. These solids, however, lack adequate resistance against deterioration in moist environments. High levels of moisture resistance can be realized if the chemistry of solution in fresh mix favors advancement of the geopolymerization process through the polycondensation step which yields stable 3D networked structures.

The steps involved in the geopolymerization process comprise three main stages of dissolution, condensation and polycondensation. The chemistry of solution, including the balance of Al, Si and Na (or K) in dissolved compounds, determine if the process concludes with polycondensation of 3D alkali aluminosilicate species which are moisture-resistant, or stops at the condensation step, yielding relatively small molecules which are susceptible to moisture attack due to the dissolution of the alkali cations exposed on their exterior. The mineralogy of mix ingredients (including biomass ash) determines the composition of dissolved species in fresh mixture, and the potential for proceeding through initial

condensation to conclude the polycondensation step which is required for realizing high levels of moisture resistance.

The non-wood biomass (wheat straw) ash is used primarily as a source of siliceous and alkali constituents for production of geopolymer concrete. This composition is supplemented with other waste constituents (e.g., coal fly ash) to introduce adequate aluminous compounds. However, one cannot ensure achievement of a desired chemical balance in solution by simply balancing the solid chemistry. The solubility of minerals present in solid compounds determines if a desired chemical balance in solids would translate into a desired solution chemistry. Moisture-sensitivity of the early generation of alkali-activated biomass ash-based concrete indicates that a desired chemical balance in solution was not realized, and the process stopped at the initial condensation stage which yields a high level of compressive strength but inadequate moisture resistance. An extensive trial-and-adjustment approach was undertaken in order to refine the chemistry of solution to enable progress through the polycondensation step to yield a moisture-resistant 3D networked structure.

The original binder composition comprised 50% biomass ash and 50% coal fly ash. After several trials, it was found that a binder comprising 50% biomass ash, 25% metakaolin and 25% coal fly ash enables progress of the geopolymerization reactions through the polycondensation step. This could be due to the desired aluminosilicate chemistry formed in the solution. Furthermore, it was found that addition of a relatively low percentage of calcium sulfate hemi-hydrate (gypsum) to the mix benefits formation of a moisture-resistant geopolymer structure. Past experience [32] has indicated that exterior ions raise the leaching of alumina from the source materials to form additional aluminosilicates, and to increase the concentration of calcium to form additional calcium silicate hydrate. The addition of gypsum could also reduce the total porosity of end products; the greatest drop in total porosity was realized with the addition of gypsum at 5% by weight of total ash (Figure 12).

<Figure 12 >

6 Conclusions

The value of diverse categories of non-wood biomass combustion ash as raw materials for production of an alternative cementitious binder for concrete production was evaluated. The key findings of the project are summarized below.

1. Cementitious binders based on alkali aluminosilicate hydrates can make value-added use of two major constituents of non-wood biomass combustion ash: silica and alkali metal (potassium) cations.
2. Thorough characterization of seven different non-wood biomass ashes, covering their chemical composition, mineralogy, degree of crystallinity, solubility, alkalinity, morphology and particle size distribution, indicated that they all offer viable attributes for use as raw materials in production of binders based on alkali aluminosilicate hydrates for concrete production.
3. Non-wood biomass ash-based binder compositions supplemented with alumina-rich constituents (e.g., coal fly ash) can be formulated to yield a desired chemical balance for production of high-quality binders in concrete production. The relatively low calcium content of the formulations considered here imply that alkali aluminosilicate hydrates could have been formed probably in combination with secondary binders comprising calcium silicate hydrates. A systematic approach was developed and verified for formulation of inorganic binders which make value-added and large-volume use of non-wood biomass ash.
4. Non-wood biomass combustion ash can be formulated into cementitious binders for production of concrete materials with a desired balance of strength and moisture resistance. Care should be taken to formulate binders with a desired chemical balance in the dissolved matter at early age, which advance the hydration process through the critical polycondensation step. The result is a networked alkali aluminosilicate hydrate structure which exhibits a high degree of stability under hydrothermal effects.

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Table 1. Characteristics of typical wood, agricultural waste and algae combustion ashes [2, 3].

Biomass	Ash, wt.% of fuel	Ash composition (wt.% of ash)										
		CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	Fe ₂ O ₃	MgO	Cl	SO ₃	P ₂ O ₅	GCV ^(a)
Wood	0.4	30	7	1	1	8	1	6	2	10	5	21
Wheat straw	6	7	52	3	2	23	1	2	6	9	3	19
Ulva lactuca (algae)	35	8	24	0	8	11	2	12	9	19	4	13

^(a) Gross calorific value, MJ/kg

Table 2. Chemical compositions of ashes produced by combustion of some agricultural residues, algae, cattle manure and coal at the specified temperatures and durations [2, 9, 20-25].

Residue	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO%	MgO%	Na ₂ O%	K ₂ O%	LOI	Combustion Temp., °C	Combustion Time, hr
Corn cob	66.4	7.5	4.4	11.6	2.1	0.4	4.9	1.4	650	8
Wheat straw	54.2	4.6	1.1	12.5	2.4	NA	NA	7.2	670	5
Vetiver grass	57.5	3.7	1.7	5.5	1.2	0.1	15.5	12	900	9
Rice husk	93.2	0.4	0.1	1.1	0.1	0.1	1.3	3.7	650	NA
Oil palm shell	63.6	1.6	1.4	7.6	3.9	0.1	6.9	9.6	NA	NA
Cotton stalk	51.1	9.4	3.8	12.3	3.7	2.4	11.7	NA	NA	NA
Green macroalgae	23.5	0	1.5	8.3	12.4	7.8	10.4	NA	NA	NA
Cattle manure	52	7.8	3.2	15.4	2.9	0.7	4.9	2.5	NA	NA
Coal fly ash	55.2	19	5.2	3.6	1.7	0.5	1.3	1	NA	NA

NA = Not available in the reference reporting the chemical composition

Table 3. Chemical composition of the coal fly ash and metakaolin, weight%.

	SiO ₂	CaO	Al ₂ O ₃	K ₂ O	Na ₂ O	LOI
Coal fly ash	43.1	14.3	23.3	1.7	0.9	1.7
Metakaolin	52.5	0.04	44.4	0.15	0.25	0.6

Table 4. Particle size distributions of the coarse and fine aggregates.

Size, mm	% Passing	
	Coarse aggregate	Fine aggregate
0.15	0.00	1.56
0.30	0.00	6.77
0.60	0.00	36.93
1.18	1.01	64.54
2.36	6.13	92.10
4.75	21.67	100.00
9.50	99.48	100.00
12.50	100.00	100.00

Table 5. Mix proportions of wheat straw ash-based concrete.

Material	Quantity, Kg/m ³
Coal fly ash	247
Biomass ash	247
Fine aggregate	691
Coarse aggregate	858
Sodium silicate solution	123.5
NaOH solution	123.5
Activator solution/Ash	0.6

Table 6. The variables and their levels considered in the optimization experimental program.

	Variable	Level -1	Level 0	Level 1
A	Solid activator-to-ash ratio	0.23	0.27	0.31
B	Solid Na_2SiO_3 -to- NaOH ratio	1.00	1.50	2.00
C	Water-to-solid ratio*	0.27	0.3	0.33

*Total Solid includes solid Na_2SiO_3 , solid NaOH , and ash.

Table 7. Mean particle sizes of different non-wood biomass ashes.

Non-wood biomass ash	Mean particle size, μm (D_{50})
Wheat straw ash	9.6
Switch-grass ash	21.4
Alfalfa ash	15.6
Corn cob ash	19.5
Rice hull ash	9.35
Cotton stalk ash	24.5
Cotton gin ash	85.0

Table 8. Measured values of pH for biomass ashes at different concentrations in deionized water.

Non-wood Biomass Ash	pH 2 wt. %	pH 5 wt. %
Wheat straw ash	10.98	11.10
Switch grass ash	12.07	12.15
Alfalfa ash	11.93	11.98
Corn cob ash	12.42	12.60
Rice hull ash	10.11	10.50
Cotton stalk ash	12.08	12.33
Cotton gin ash	11.91	12.11

Table 9. Extents of dissolution of coal fly ash versus biomass ashes.

Ash Type	15 min	30 min	60 min
Coal fly ash	5.28%	5.98%	7.78%
Wheat straw ash	2.91%	6.01%	11.95%
Switch grass ash	3.34%	5.45%	5.98%
Alfalfa ash	8.53%	13.46%	19.20%
Corn cob ash	8.20%	10.22%	24.76%
Rice hull ash	Not Available	Not Available	Not Available
Cotton stalk ash	8.81%	14.28%	22.09%
Cotton gin ash	11.33%	16.12%	24.49%

Table 10. Chemical compositions obtained via XRF analysis and LOI values of the biomass ashes(wt.%).

	SiO ₂	CaO	Al ₂ O ₃	K ₂ O	MgO	P ₂ O ₅	Fe ₂ O ₃	SO ₃	LOI
Wheat straw	52.60	4.27	0.10	20.10	3.07	4.25	0.25	2.43	3.30
Alfalfa ash	2.78	15.11	0.15	59.02	-	6.05	0.73	4.14	3.50
Corn cob	13.69	18.35	0.74	47.82	5.40	4.22	4.71	2.51	3.30
Rice hull	92.02	0.00	0.00	3.97	-	-	-	2.21	4.6
Cotton stalk	3.66	-	0.80	31.37	7.40	-	2.20	5.42	9.80
Cotton gin	4.47	23.15	0.57	47.63	4.20	4.00	1.75	7.21	7.25

Table 11. The degrees of crystallinity for different biomass ashes and coal fly ash.

Ash	% of Crystallinity
Coal fly ash	32.9
Wheat straw ash	34.9
Switch grass ash	38.5
Alfalfa ash	65.9
Corn cob ash	49.2
Rice hull ash	28.5
Cotton stalk ash	63.8
Cotton gin ash	72.7

Table 12. Experimental results generated in the optimization test program.

Mix no.	Set time (Min)		Flow	Compressive strength (7- day)	Specific gravity	Absorption	Voids
	Initial	Final					
				MPa		%	%
1	32	144	60	56.00	2.25	4.96	11.27
2	62	>360	66	51.00	2.21	5.50	8.14
3	26	55	82	67.40	2.23	5.98	11.22
4	59	125	86	54.91	2.22	5.93	11.65
5	35	95	65	64.00	2.25	5.23	10.35
6	85	>300	52	73.75	2.23	4.99	10.70
7	43	130	91	54.82	2.19	6.23	14.96
8	72	240	81	56.40	2.20	5.58	11.45
9	58	360	56	86.42	2.20	0.14	14.85
10	53	62	135	61.40	2.25	4.97	10.37
11	75	>330	84	58.35	2.19	5.92	11.88
12	35	~75	84	56.45	2.18	5.87	13.59
13	50	158	70	61.30	2.21	5.62	12.39
14	50	155	67	59.45	2.19	6.30	14.18
15	48	150	70	64.00	2.23	5.32	10.68

Figure 1. Classification of different subsets of alkali-activated materials, with comparisons to ordinary Portland cement and calcium sulfoaluminate binder chemistry (darker shading corresponds to higher concentrations of Na and/or K) [19].

(a) Wheat straw ash

(b) Alfalfa ash

(c) Rice hull ash

(d) Switch-grass ash

(e) Corn cob ash

(f) Cotton stalk ash

(g) Cotton gin ash

Figure 2. SEM images of different non-wood biomass ashes after size reduction.

Figure 3. Particle size distributions of milled non-wood biomass ashes.

Figure 4. X-ray diffraction results for different non-wood biomass ashes.

Q: SiO_2 (Quartz), C: CaCO_3 (Calcite), Ca: Calcium silicates, N: sodium aluminum oxide, and S: KCl (Sylvite)

Figure 5. Effect of NaOH concentration on the seven-day compressive strength of geopolymer concrete (mean values and 95% confidence intervals).

Figure 6. Effects of the optimization mix design variables on the compressive strength of geopolymer concrete materials incorporating non-wood biomass ash.

Figure 7. Response surfaces of the compressive strength test data generated in the optimization experimental program for the geopolymer concrete incorporating non-wood biomass ash.

Figure 8. Effects of the optimization mix design variables on the initial set time of geopolymer concrete materials incorporating non-wood biomass ash.

Figure 9. Effects of the optimization mix design variables on the fresh mix flow of geopolymer concrete materials incorporating non-wood biomass ash.

Figure 10. Alkali-activated non-wood biomass ash-based concrete after immersion in boiling water.

Figure 11. Residual compressive strength, after immersion in boiling water, of alkali-activated concrete materials based on non-wood biomass ash and coal fly ash.

Figure 12. Residual strength (after immersion in boiling water) of alkali-activated concrete materials comprising biomass ash: coal fly ash: metakaolin at 50: 25: 25 weight ratios without (Mix-1) and with (Mix-2) addition of gypsum at 5% by total weight of ash.