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Effects of leaching method and ashing temperature of rice residues for energy production and construction materials

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Abstract

Escalating demands for infrastructure materials and energy worldwide necessitate exploration of means to efficiently utilize resources to support growing consumption. This work evaluates the potential symbiotic relationship between cultivation of an agricultural product (namely, rice), energy conversion, and utilization of bioash in the production of cement-based materials to improve the sustainability across multiple industries. Primarily, leaching methods of biomass that benefit energy conversion are evaluated as a means to simultaneously improve ash properties for use in cement-based materials. Specifically, this study considers water-leaching and H_3PO_4-leaching of rice hulls and rice straw, which were subsequently ashed at three different temperatures, 600°C, 850°C, and 1100°C. The effects of leaching on the ash characteristics, on the performance of ash-cement mortars, and on the greenhouse gas (GHG) emissions from both the mortars and energy produced are quantified. Findings showed that while acid-leaching led to higher GHG emissions for electricity generation, leaching decreased concentrations of undesirable alkali metals and chlorides in the ash. Regardless of treatment and ashing temperature, the inclusion of bioash delayed early strength development of the cement-based mortars. Yet, several permutations of treatment, feedstock type, and ashing temperature were found to contribute to the later age strength development of cement-based materials, while reducing related GHG emissions. Specifically, after 28 days of curing, mortars containing 15% cement replacement with unleached ash prepared at 600°C had 1-5% lower compressive strength, and after 56 days, mortars with leached rice hull ash prepared at 600°C had 5-6% lower compressive strengths. Further, the use of unleached and water-leached ashes in mortar led to reductions in GHG emissions up to 15%. Hence, this work shows pretreatment methods may contribute to desirable co-benefits for energy and materials production.

Keywords: Bioash Cement Binders, Rice Ash, Water Leaching, Acid Leaching, Environmental Impact Assessment

Introduction

Industrial symbiosis across food, energy, and materials production industries could contribute to meeting rising energy and materials demands,[1,2] while simultaneously improving the environmental sustainability of these industries. In particular, the use of residual biomass from the cultivation of rice – a prevalent food crop grown around the world – could be well suited to benefit the agricultural, energy, and construction material industries. In this work, rice straw and hulls (husks) are evaluated as a means to valorize agricultural biomass residue, generate electricity, and partially replace greenhouse gas (GHG) intensive cement in construction materials. Specifically, pre-combustion leaching methods that benefit energy production are evaluated as a means to simultaneously improve rice hull ash (RHA) and rice straw ash (RSA) properties for cement-based material applications.

The potential for benefits from synergistic bioash engineering are well exemplified when studying individual regions, like California, which is the state with the second largest production of cement in the United States.[3] The most popular supplementary cementitious material (SCM) in California is fly ash (FA) from coal-fired power plants. Currently, California uses approximately one million tons of FA annually[4] (equivalent to approximately 15% of the mass of Portland cement produced in the state[5]). However, as California does not combust coal as a primary energy source, this FA is imported from other regions. The nearest import sources of FA for the state have either recently been decommissioned or are currently facing issues of economic and environmental viability. Conversely, alternative energy supplies have been gaining prominence: 86 waste-to-energy power plants (including 32 biomass-to-energy plants) comprised approximately 3% of instate energy production in 2019,[6] and this energy is largely considered carbon neutral.[7] By 2050, it is projected that the demand for cement in California will increase by 65% beyond 2015 levels[8,9] and, with it, the demand for SCMs is expected to rise. At the same time, the state had the second highest annual electricity demand in the United States in 2018 at approximately 1 EJ.[10] As an agriculture-intensive state, California has a large amount of residual biomass, with an estimated potential availability of RHA and RSA of approximately 400,000 tons annually.[11–13] This availability, coupled with the demand for both energy resources and SCMs, is a strong motivator for improving our understanding of co-benefits achievable in methods to support energy generation and the use of rice-based ashes in concrete. This example is pertinent to many other areas around the world. Regions in India and China are struggling with managing rice residues.[14,15] These countries also are currently the largest producers of cement in the world and could similarly benefit from a combined avenue for residue management: the production of energy and an SCM source.[16–19]

In this work, ashes produced from rice hulls and straw are evaluated as a SCM for cement-based building materials. The use of SCMs is a common practice for improving performance-aspects of concrete and reducing environmental impacts. While RHA could be a substitute for more common SCMs and improve concrete performance,[20] these improvements are not always consistent.[21] Previous studies have shown combustion conditions have a strong effect on the production of reactive RHA.[12,22,23] Achieving high amorphous silicate content in the RHA through low temperature combustion has been favored for the production as SCMs. While lower temperatures are not commonly desirable for energy generation, gasification methods could be implemented to gain reasonable energy returns at these lower temperatures;[24] however, any resulting char may require additional processing to remove carbon and make it suitable for use in cement-based materials.[25]

Pioneering work on the combustion of rice hulls to produce a silicate material for cement replacement was performed by Mehta in the 1970’s, [20,26] which sparked significant subsequent investigation. Recent studies on the use of RHA as an SCM have found ash produced under controlled combustion conditions can replaced 5-30% of cement and yield higher strength materials.[21,27–32] For example, Vigneshwari *et al.* examined RHA as a replacement for silica fume, a highly reactive SCM, in concrete mixtures.[28] The authors found that at low combustion temperatures, namely 500-700°C, an ash with predominately amorphous silica is formed, and that ash can increase concrete compressive strength by up to 28% when it is used as a 30% replacement of the cement. Similar findings have been noted elsewhere. Sandhu and Siddique reviewed RHA use in self-consolidating concretes and found that RHA replacement of cement up to 15% provided higher strength.[29] Work done by He *et al.* and Thomas suggested a maximum strength is achieved at 20% replacement;[27,30] however, Thomas noted that greater than 10% replacement of cement with RHA can lead to workability issues.[27] Gursel *et al.* evaluated RHA-FA-limestone cement blends and found RHA improved later age strength development as well as durability properties, while significantly reducing emissions from material production.[33] Despite robust literature on RHA in concrete, RSA is not as commonly considered as an SCM, owing in part to its chemical composition, which includes higher potassium levels. The potential increased alkali metal concentrations could lead to undesirable concrete properties, such as deleterious effects on durability.

It is possible that pre-combustion leaching treatments, developed originally to benefit energy production, could have a co-benefit for cement-based materials production by removing less-desirable compounds in rice ash. Specifically, treatments prior to combustion, such as leaching, can reduce the presence of chlorides and alkali metals in addition to reducing agglomeration because of melting and fouling during combustion.[34–39] Industrial-scale leaching may be accomplished under controlled, commercial operations; though, treatment of leachate adds additional costs for operators.[38] More affordable in-field water leaching has proven feasible for treating rice straw and allows for direct recovery of nutrients back into the field; however, it is more variable in final quality and is weather dependent with higher concomitant economic risks.[36] However, systematic examination of the influence of leaching pretreatments on the viability of RHA and on RSA for use in cement-based materials has not been performed to the best of our knowledge.

To determine avenues for industrial symbiosis in which biomass leaching is used to benefit both energy conversion and materials production, further research is needed. This study investigates the use of select biomass pretreatment methods for processing rice-based residues for bioenergy and cement-based materials production, while providing an initial assessment of environmental sustainability factors for both industries. Based on experimental and analytical techniques: (1) the effects of leaching protocols and ashing temperature on ash properties are identified, (2) the mechanical properties of mortar mixtures formed with rice ashes from direct combustion methods are established, and (3) changes in environmental impacts for energy and material production from leached and unleached biomass are quantified. In doing so, this work provides both a systematic analysis from multiple engineering perspectives and a critical initial step into the consideration of agricultural resources to support varied applications. Research in this area has a strong potential to contribute to advancement of the circular economy, in which maximum value is extracted from resources and they are maintained in use for as long as possible.

Materials and Methods

Materials

To produce treated and untreated ashes for analysis and mortar production, rice hulls and rice straw samples were acquired in August, 2019 from Northern California suppliers. Rice hulls were provided by Farmer's Rice Cooperative in Sacramento, California which, after processing, stores hulls in covered bins at ambient conditions.[40] Rice straw was acquired from Windmill Feed in Woodland, California and was stored in unprotected outdoor conditions prior to acquisition, which likely subject the feedstock to precipitation during the winter season. Both feedstocks were from the 2018 harvest. To examine the effects of using the rice-based ashes on cement-based materials, mortars were produced using natural quartz-sand from Esparto, California (with a 99.95% passing rate through a #4 sieve) and ASTM Type II/V Portland Cement (PC), from Lehigh Southwest Cement Company in Stockton, California.

Biomass Pretreatment

Prior to ashing, rice straw was milled and portions of the hull and straw biomass were leached to simulate pretreatment leaching for energy production. The rice-straw was milled to facilitate handling and lab-scale leaching. For the straw, a hammermill with 1-1/4" (32 mm) diameter round-hole screen was used to reduce the majority of the straw to lengths less than 25 mm prior to leaching and ashing. As hulls are relatively small in size, no milling was performed. The size gradations of the straw and hulls were measured prior to leaching via a sieve analysis resulting in over 59.5% of rice straw passing through a 3/8" (9.5 mm) mesh sieve and 95.3% passing a 1" (25.4 mm) mesh. For rice hulls, 99.8% passed through a #4 mesh (4.76 mm) and 32.9% passed through a #8 mesh (2.38 mm) (size distribution give in Supporting Information, Table S1).

The effects of leaching were examined through the use of two solutions: (i) tap water; (ii) 0.5 M phosphoric acid (H_3PO_4) solution (made from 85 wt.% phosphoric acid, ACS reagent grade). These solutions were selected for their reported ability to remove alkali metals from rice-based feedstock.[37,41] Comparisons were drawn to biomass that was combusted without leaching pretreatment, i.e. unleached. Bulk leaching was performed in low-density polyethylene containers using 15 L of leaching solution per kg of biomass (air-dry basis, moisture content given in Supporting Information, Table S3) to simulate a potential industrial leaching.[42] This ratio is reported to be the smallest ratio that minimized the volume of leaching solution while maintaining agitatable biomass.[43] Biomass was leached for a period of 5.5 hours and agitated every 30 minutes by manually stirring. Afterwards, the biomass solids were dewatered through manual compression between two mesh strainers over the leaching vessel and then oven dried for 2 days at 100°C.

For unleached and leached feedstock, moisture, ash, volatile matter, and fixed carbon contents were assessed. For leached biomass, moisture content was determined after dewatering by oven drying at 103±2°C for 24 hours following ASTM E871.[44] Volatile content was determined using ASTM E872 on oven-dried samples in covered crucibles in a Fisher Model 750-58 air-muffle furnace at 950°C.[45] Ash content was determined using ASTM E1755 in the furnace at 575ºC for 8 hours.[46] Fixed carbon content was determined by subtracting the percentages of volatile matter and ash from 100% dry basis.

Biomass Ashing

To produce ash, biomass was oxidized in air under controlled temperatures at for 600°C, 850°C and 1100°C in a Fisher Model 750-58 air-muffle furnace. Ashing at 600°C was selected to approximate temperatures found in literature that led to performance improvements for ash in concrete [26,28]. The 1100°C condition was chosen to approximate temperatures at which the literature suggests that ash should be less-reactive [47] and the 850°C condition was selected as the midpoint between the two to test for non-linear effects. These temperatures are also in the range of many commercial furnace exit or reactor temperatures for biomass boilers and thermal gasifiers.

For RSA, a two-stage procedure started with straw torrefaction at 250°C for 40 minutes to remove most of the volatiles and prevent ignition. After torrefaction, straw was oxidized, without ignition, at each of three final temperatures but for different lengths of time to complete the oxidation, namely at 600°C for 8 hours, 850°C for 4 hours, or 1100°C for 1 hour. To produce RHA, a modified procedure was used to mitigate carbonaceous ash production. For 600°C RHA, hulls were ashed at 600°C for 8 hours, this was the only stage for production of 600°C RHA. For the remaining two temperature conditions, a first stage heating to 600°C for 8 hours was used. After the initial 600°C, the ashes were oxidized at either 850°C for 4 hours or 1100°C for 1 hour. The ash identifications were assigned based on feedstock treatment method and oxidation temperature where “S” or “H” represent straw or hulls; “U”, “W”, or “A” signify untreated (unleached), water-leached, or H_3PO_4-solution (acid)-leached; and “600”, “850”, or “1100” is the final oxidation temperature in degrees Celsius. For example, S-U-850 represents untreated straw oxidized at 850°C.

Mixture Proportions and Mortar Batching

Bioash-cement mortars were made to determine the impact of treatment on the performance of cement-based materials. Control mortars were designed to contain 100% PC as the cementitious binder. Bioash-cement mortars were proportioned using the control mixtures, but with ashes replacing 15% of the PC. Bioashes were used in their original form without any additional treatment (e.g., leaching, milling of ash). For all mixtures, the sand-to-binder ratio, where the binder is the combined mass of PC and ash, was set at 2.50 and water-to-binder ratio fixed at 0.59. Specimens were cured at 25°C and ≧ 95% relative humidity.

Leachate Chemical Analysis

The composition of the leachates after the leaching process were measured to quantify the amount of soluble salts and micronutrients removed from the feedstock. Measurements were adjusted for background concentrations in the leaching water and acid. While amorphous silicates, sodium, and calcium can also contribute to desirable gels in cements,[7,21] the presence of other compounds, such as high levels of potassium, chlorides, or carbon can lead to undesirable performance. Soluble salts and micronutrient concentrations, K, Ca, Mg, Na, Zn, Cu, Mn, and Fe, were measured following EPA Method 200.7 using inductively coupled plasma atomic emission spectrometry.[48,49]

Ash Analysis

The elemental composition of each ash was analyzed and the oxide compositions were estimated to determine the effects of leaching condition and ashing temperature. The specific gravity of each ash was quantified by pycnometer method using an AccyPyc II 1345 Pycnometer (Micromeritics Corp., Norcross, GA). Chemical analysis for major elements and selected trace elements, together with the loss on ignition, were performed for PC and all ashes. The materials were assessed using fusion inductively coupled plasma optical emission spectroscopy (Fusion ICP-OES) to estimate oxide composition

(Agilent Model 700 Series ICP-OES, Agilent, Santa Clara, CA).[50] Both methods were carried out by Activation Labs, Ancaster, Ontario, Canada.

Concrete Compressive Strength of Mortars

Compression strength was tested on 50 mm diameter x 100 mm long (2 inch x 4 inch) cylinder mortar specimens after 7, 28, and 56 days of curing. Compression tests were conducted on a Soiltest CT-950 (Soiltest, Evanston, IL) load frame following an adaptation of ASTM C39 testing procedures,[51] where cylinder specimens were capped both ends with neoprene-padded aluminum caps and then loaded under force control. The average maximum load before failure of five replicate specimens of each mixture, tested at each age, was used to determine the compressive strength.

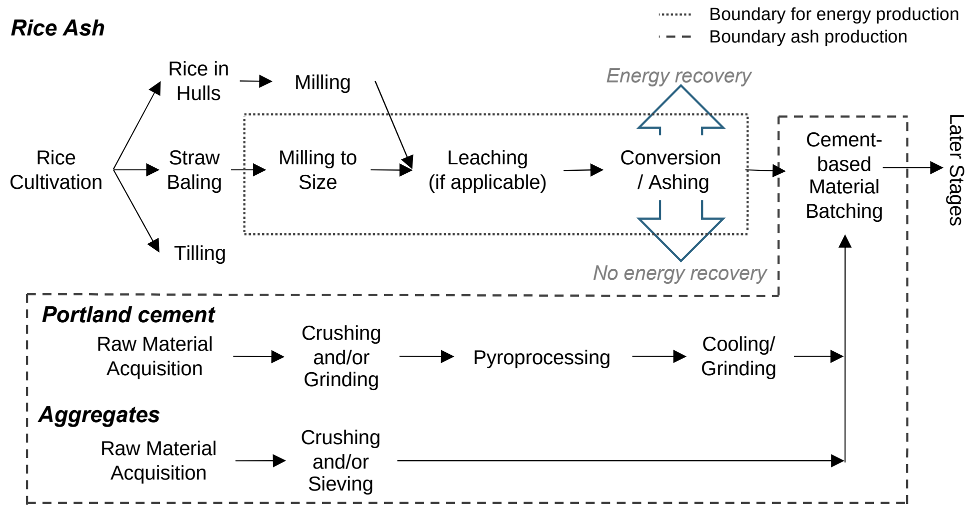
Environmental Impact Assessment

Goal and Scope of Assessment

Environmental impact assessments were performed to quantify the potential environmental benefits of using rice-biomass to produce energy and cement-based materials relative to conventional resources. The literature suggests there could be environmental benefits from the production of electricity from rice straw and hulls.[15,52] Similarly, rice-based ashes may reduce several environmental impacts from cement-based materials production.[33] In this research, two environmental impacts were examined: greenhouse gas (GHG) emissions and embodied energy. GHG emissions were weighted using the IPCC 100a scheme from 2013.[53] Embodied energy was compared using the cumulative energy demand method of calculation published by Simapro.[54] The role of treatment methods for the rice biomass, as well as impacts of rice ash relative to other constituents in mortar, were assessed to inform targeted improvements in reducing environmental burdens for the energy and materials systems.

Two primary products from the rice biomass were considered in this work: electricity and an SCM. To investigate the biomass as an energy resource, the GHG emissions per MJ of electricity produced from rice-based feedstocks were compared to several fossil fuel resources. For the SCM, three units of comparison were employed: (1) GHG emissions of rice-based ashes were compared directly to PC on a per kg basis; (2) the use of rice-based ashes in mortars was explored based on the production of one cubic meter of mortar (comparisons drawn for GHG emissions and embodied energy); (3) the use of rice-based ashes in mortars was examined by weighting GHG emissions per cubic meter of mortar as a ratio of compressive strength achieved by the mixture at 28 days.

The scope of this analysis is outlined in Figure 1. Impacts associated with transportation, treatment methods for the biomass prior to ashing, energy generation, and the production of mortar (including impacts from other constituents) were assessed. In this analysis, both rice straw and rice hulls were considered to be agricultural residues and no impacts from cultivation were considered. Impacts from biomass were allocated to the electricity generation. Impacts were attributed to the ash only after electricity generation, namely, only impacts from transportation impacts. Stages after mortar production and impacts generated from the treatment or conversion of waste, e.g. disposal or recovery of leachates, as well as potential offsets from using the biomass for energy production were not considered in this assessment.



Transportation, electricity, thermal energy, and material-derived air emissions accounted for where appropriate

Figure 1. Process flow diagram depicting the boundary of the assessment

Inventory Models

Relevant inventory quantities for the environmental impact assessment were based on treatment methods and mortar outlined in the Materials and Methods section. These quantities include those for leaching water, acid solution, ashing, and mortar mixture proportions. Additionally, the quantity of feedstock biomass needed to produce the ash for each mortar mixture was determined by using measured ash yields and properties (Supporting Information, Table S3). Water for leachate and for mortar batching was modeled as requiring no necessary energy input. These quantities were supplemented with values from the literature. An inventory of the materials, energy demand, quantities, and models used are stipulated in Table 1.

Table 1. Inventory model assumptions and values

Biomass treatment, electricity generation and ash production			
Input	Quantity	Reference for Quantity	Impact Model
Biomass feedstock yields and properties	Multiple values, varies by ash type	This study, see SI[*] Table S4	Not considered
H_3PO_4	15.35 kg H3PO4 : 1 kg biomass for acid leachate	This study	No impacts for water; phosphoric acid from ecoinvent[55]
Water leachate to biomass ratio	15 kg water : 1 kg biomass	This study, Yu,[43] and Yu, et al.[42]	No impacts for water
Energy to mill rice straw	0.244 MJ / kg biomass	Gursel et al.[33]	2017 2017 California average electricity grid mix[56]
Emissions from bioenergy production	Material input based on 17.209 MJ / kg (LHV[*]) and 25% efficiency	Argonne National Laboratory;[57] Biomass Energy Resource Center[58]	Biomass combustion emissions, from NRE[59, *]
1 MJ of electricity from bituminous coal, diesel, and natural gas (for comparisons)	-	-	NREL[59, *]
Mortar constituent production (for inputs for ash production, see above)			
Input	Production Method	Reference for Method	Impact Model
Cement production	Preheater-precalciner kiln, US average kiln fuel mix	Miller and Myers[60]	UCB Green Concrete Tool;[32,*] 2017 California average electricity grid mix[56]
Fine aggregate production	Quarried, crushed and/or ground	UCB Green Concrete Tool[32,*]	
Mortar batching per cubic meter	-		
Transportation			
Input	Distance	Reference for Distance	Impact Model
Biomass (field to production site)	30 km	Bakker and Jenkins[36]	Truck (transportation) emissions from NREL[59, *]
Cement raw materials to kiln	25 km	Marceau et al.[61]	
Cement / bioash to batching site	130 km	Marceau et al.[62]	
Aggregates to concrete batching site	88 km	Marceau et al.[62]	

[*] NREL = National Renewable Energy Laboratory; UCB = UC Berkeley; LHV = lower heating value; SI = Data provided in Supporting Information

Results and Discussion

Leachate and Biomass Properties

To determine how leaching can facilitate the removal of compounds that are potentially detrimental to energy production and cement-based materials, the soluble cations in the water and acid leachate were tested (Supporting Information, Table S2). Compared to the water leachate, examination of the acid leachate showed a 49% increase in potassium leached from hulls, but a 45% decrease in potassium removal from straw. This difference in leaching can be attributed to the variability in the solubility of inorganic compounds from various biomass source in different solvents coupled with the likely exposure of straw to precipitation during storage over the winter season. For example, the concentration of water-soluble potassium varied from 58-86% in rice straws examined by Baxter et al., with as little as 2-8% of the potassium being acid-soluable.[63] While water leaching removed more potassium from the straw than the acid solution, the use of acid leaching improved removal of most other soluble elements examined. However, the changes in Ca, Mg, Na, Zn, Cu, Mn, and Fe were small and unlikely to affect the ash behavior in concrete mixtures.

As anticipated, the leaching techniques applied in this work affected the ash content, volatile matter, and fixed carbon of the biomass (Supporting Information, Table S3). The differences between water-leached and unleached biomass were small. For rice straw and hulls, water leaching led to approximately 4 and 5% decrease in ash content, 3 and 4% increase in volatile matter, and 5 and 8% decrease in fixed carbon compared to unleached biomass, respectively. Phosphoric acid was selected for leaching, because past studies indicated that high alkali-removal could be achieved while maintaining high ash content,[37] which is consistent with the results of this work. Acid leaching reduced volatile matter in rice hulls by 13% and in the rice straw by 29%, but increased fixed carbon 26% and 50%, respectively. Compared to water leaching, increased amounts of ash from acid leaching could lead to a larger supply for replacing cement; however, the potential losses in recoverable energy will impact the feasibility of using the leached biomass for both energy production and cement replacement.

Ash Properties

Properties of the ash were evaluated to provide insights into how leaching affects the chemical composition, which can influence the performance of bioash-cement materials. Both different leaching solutions and different ashing temperatures altered the composition of the ashes produced. Notably, acid leaching led to high amounts of phosphorus remaining in the feedstock: 43-46% and 12-13% P_2O_5 for straw and hull ash, respectively. This increase in P_2O_5 is important to consider when evaluating the bioash-cement mortars performance and theashing behavior of the biomass. However, in order to compare ash to ash, the composition has been scaled by setting the P_2O_5 fraction of the acid-leached biomass ash to the average P_2O_5 percentage of the unleached biomass ash and then scaling a total of 100% (Table 2).

Table 2. Ash composition, by percent, of rice-based ashes, Type II/V PC, and average compositions reported in the literature scaled so total sums to 100%. (n=1)

Ash ID		SiO_2	Al_2O_3	Fe_2O_3(T)	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
Type II/V Cement		22.40	3.86	3.61	0.046	2.32	66.78	0.05	0.57	0.187	0.17
S-U-600		84.14	0.25	0.53	1.047	1.33	1.62	0.52	9.82	0.015	0.72
S-U-850		86.70	0.19	0.54	0.918	1.30	1.39	0.47	7.80	0.011	0.67
S-U-1100		87.74	0.17	0.43	0.933	1.31	1.72	0.45	6.65	0.011	0.58
S-W-600		94.01	0.15	0.44	0.141	0.54	0.54	0.02	2.93	0.007	1.22
S-W-850		90.02	0.19	0.49	0.985	1.15	1.71	0.34	4.60	0.011	0.49
S-W-1100		90.37	0.16	0.18	0.970	1.11	1.72	0.45	4.61	0.010	0.41
S-A-600[d]		94.04	0.74	0.27	0.339	0.45	0.74	0.18	2.59	0.016	0.64*
S-A-850[d]		90.95	0.65	3.89	0.394	0.40	0.63	0.13	2.29	0.012	0.64*
H-U-600		93.40	0.17	0.35	0.138	0.61	0.56	0.06	3.29	0.009	1.40
H-U-850		94.90	0.07	0.15	0.175	0.46	0.60	0.05	2.55	0.005	1.04
H-U-1100		94.17	0.08	0.15	0.178	0.46	0.59	0.08	3.15	0.005	1.13
H-W-600		96.76	0.06	0.11	0.141	0.39	0.60	0.05	1.39	0.004	0.48
H-W-850		95.85	0.07	0.21	0.159	0.52	0.67	0.06	1.60	0.004	0.85
H-W-1100		95.55	0.13	0.15	0.148	0.36	0.53	0.03	2.52	0.008	0.58
H-A-600[d]		97.82	0.43	0.08	0.036	0.08	0.13	0.00	0.24	0.005	1.17*
H-A-850[d]		97.06	0.80	0.50	0.048	0.09	0.11	0.00	0.22	0.003	1.17*
Lit Hull Ash [a, b]	Max	95.60	2.00	0.14	-	0.20	3.21	0.21	3.71	0.02	0.46
	Min	91.42	0.78	0.03	-	0.01	0.20	0.10	1.20	0.02	0.42
Lit Straw Ash [a, c]	Max	95.60	2.00	0.88	-	2.50	3.21	0.96	16.60	0.09	8.87
	Min	72.20	0.10	0.03	-	0.01	0.20	0.10	1.20	0.01	0.43

[a] “-“ refers to values not commonly reported in the literature, [b] range of values based on 3 hull ash composition reported in Phyllis 2 [64], [c] range of values based on 14 straw ash composition reported in Phyllis 2 [64], [d] “*” indicates P_2O_5 percentage assumed based on the average for straw or hull of the unleached ash for recalculating oxides composition

Both leaching methods increased the percentage of SiO_2 for both feedstock types. Compared to unleached samples, water leaching led to increases in silica of 3-10% in RSA and 1-3% in RHA as SiO_2 is not removed by water to the same extent as other constituents (dilution effect). For acid-leached samples, silica increased 4-10% in RSA and 3-4% in RHA. The SiO_2 percentage in unleached RHA and RSA and leached RSA are within the range reported by the *Phyllis 2* database[64] and in the literature.[21,43] The leached RHA SiO_2 concentrations were, at most, 2% higher than the maximum reported by *Phyllis 2*.[64] The increase in SiO_2 fraction for both acid and water leached RHA and RSA could be beneficial to an ash for use in cement-based materials if it is reactive. Both leaching methods also decreased the K_2O fraction of the ashes, with the acid leaching being more effective at reducing the K_2O fraction: up to 74% for RSA and 93% for RHA, both ashed at 600°C. For unleached RHA and RSA, ashes prepared at a higher temperature had lower K_2O fractions. The K_2O percentage for RSA is on the lower end of the range reported by *Phyllis 2*.[64]

The untreated feedstock compositions of rice hulls and rice straw differ, which informs composition of their respective ashes. Hulls typically have an overall higher ash content than straw, and the SiO_2 content in RHA often exceeding 90-95% of the ash, which is consistent with the findings in this work. RSA typically contains greater amounts (15%) of potassium with SiO_2 concentrations of around 75%. These concentrations vary depending on geographic location, soil type, and agronomic practice (e.g., fertilization and other inputs). The higher starting concentrations of SiO_2 and lower concentrations of K_2O in the ash of the untreated straw used here, compared with typical concentrations for California rice production, suggest that some pre-leaching occurred due to precipitation either prior to harvest or during uncovered storage over the winter season prior to acquisition for these experiments.[36,39,42] Such factors influencing variability may also be present among materials reported in the *Phyllis 2* database.

In addition to composition, the ashes were evaluated for trace elements, loss on ignition, and relative density. Chlorides and the trace elements Ba, Sr, Zr, and V were detected in some ashes (Supporting

Information, Table S4). Elements Sc and Be were not detected (detection limit 1 ppm for both) in the ashes, but they were detected in the PC. Yttrium was only detected in the PC and the acid leached RSA ashed at 850°C with the concentration in ash at the detection limit of 1 ppm, which is lower than the 11 ppm of Y detected in the PC. For all trace elements detected in the ash, the concentrations are lower than those detected in the PC and thus unlikely to lead to a degraded performance compared to typical cement-based materials.

The results indicate that higher temperatures and leaching decrease the amount of chlorides present in the ash, which agrees with other reports in the literature.[42,65,66] For the ashes tested, the Cl values are low regardless of treatment or ashing temperature and thus are unlikely to impact concrete in most applications. The highest value was 1.52% Cl for S-U-600, which, if used to replace 15% of cement as done in this study, would lead to a Cl content of 0.22% for the binder. This level is below the maximum concentration recommended in ACI 318-14 for normal concretes with moderate exposure conditions.[67] For all other ashes, with measured values of 0.14% and lower, the binder Cl concentration would likely be below maximum for high-exposure conditions.

Compressive Strength of Mortars

Despite the potential performance benefits in cement-based materials from increasing the silica fraction and reducing potassium in ash, the average compressive strengths (5 replicates) indicate that the leaching methods used resulted in a loss of compressive strength at early ages (Table 3). Mortars made with S-U-600 had nearly the same (1% lower) average strength as the control at 7 days; however, S-W-600 exhibited a 17% loss in strength and S-A-600 exhibited a 45% loss in strength at that same age. Similarly, at 7-days, H-U-600 resulted in only a moderate loss of strength (5% lower), while H-W-600 and H-A-600 resulted in reductions of approximately 27% and 21%. The largest reduction in compressive strength at 7 days was observed in RSA-mortars produced with acid-leached biomass.

While milling of ash and assessing the effect of particle size on the reactivity of the leached and unleached biomass ash was outside the scope of this work, milling RHA[12,68] or inter-grinding RHA and cement[20] is shown in the literature to improve the consistency of bioash or bioash-cement blends and improve hydration.[69] Milling of RHA has also been suggested as a means to improve the reactivity of ashes produced at higher temperatures[70] and may be a topic for future study to examine if leached ash can be tailored to improve performance in cement-based materials at early ages.

Table 3. Average compressive strengths (MPa) of mortars at 7, 28, and 56 days by ash feedstock, leaching condition, and ashing temperature and strength of the control mixture (n=5)

Ashing Temperature		600°C			850°C			1100°C		
Age (Days)		7	28	56	7	28	56	7	28	56
Straw	Unleached	27.9 (2.5)	37.1 (2.5)	39.5 (3.4)	22.4 (2.1)	29.6 (1.9)	32.9 (1.9)	23.7 (1.3)	31.6 (1.9)	31.4 (1.8)
	Water Leached	23.3 (1.4)	28.3 (5.7)	34.0 (2.0)	20.8 (0.8)	27.0 (1.7)	27.7 (2.1)	17.6 (0.8)	25.9 (1.3)	31.4 (1.0)
	H_3PO_4 leached	15.6 (0.5)	22.2 (0.5)	27.4 (1.1)	20.8 (0.8)	31.4 (1.3)	34.7 (1.8)	-	-	-
Hulls	Unleached	26.8 (1.8)	34.2 (2.4)	38.8 (1.3)	21.1 (1.2)	27.2 (0.9)	29.0 (1.9)	19.8 (1.3)	29.2 (1.7)	32.7 (3.6)
	Water Leached	20.6 (0.9)	31.4 (1.8)	39.7 (1.4)	19.8 (0.8)	27.7 (2.1)	31.4 (1.8)	16.7 (0.5)	23.5 (1.3)	28.1 (1.0)
	H_3PO_4 Leached	22.2 (0.5)	34.5 (1.3)	40.2 (1.0)	19.3 (1.3)	27.7 (0.9)	32.3 (2.5)	-	-	-
Control Mortars		28.1 (1.0)	38.2 (3.4)	42.1 (3.3)						

Values in parenthesis are the standard deviations for the mortar samples tested, "-" indicates no mortars produced for these conditions

At later ages, both leaching methods led to improved strength for mortars with RHA produced at 600°C or 850°C, with most strengths being higher or comparable to mortars with ash from unleached biomass at 28- and 56-days. After 28 days of curing, mortars containing unleached ash prepared at 600°C lowered compressive strength by 1-5% compared to the control, and after 56 days, mortars with leached rice hull ash prepared at 600°C had 5-6% lower compressive strengths compared to the control. The high strength from the acid leached hulls, with increased P_2O_5 content, is notable as the literature suggests that P_2O_5 should lead to reduced compressive strengths at these levels.[71] It is possible that the acid-leaching increased the fraction of amorphous silicates, which would improve reactivity and could have compensated for the increase in P_2O_5. If the additional P_2O_5 could be removed, potentially through improved leaching protocols or treatments to the ash, the acid-leached biomass may lead to additional gains in compressive strength at later ages.

Siliceous SCMs, like RHA and RSA, frequently create a delayed contribution to strength gain.[12] For mixtures containing RHA, both small increases and decreases in 7-day compressive strength have been reported in the literature [28,68] with low early-strengths attributed to slower hydration of RHA-cement mixtures,[28] possibly due to RHA absorbing free water.[69] Most of the mortars studied herein exhibited the greatest increase in strength between 7 and 28 days (ranging from 18% to 35% increase in strength), consistent with continued pozzolanic reactions after the initial cement hydration.[68,72] Lower gain in strength was observed from 28 to 56 days (ranging from a negligible change to 21% increase in strength). While many milled-ashes have been reported to improve cement-based materials at later ages,[20,27,28,31] non-milled ashes have exhibited lower strengths (approximately 20%) in literature compared to cement-only materials.[68] Notably, as mentioned earlier, the ash produced from water and acid leached biomass exhibited large gains in strength at later ages, suggesting a possible effect on the pozzolanic nature of these ashes.

Two-way ANOVA analyses for unleached ash at 7, 28, and 56 day ages reveal that, for 7-day compressive strength, both ashing temperature ($f(3.4) = 32.7$, $p = 1.4 \times 10^{-7}$) and feedstock type ($f(4.3) = 10.6$, $p = 3.3 \times 10^{-3}$) are significant variables. For 28- and 56-day compression strengths, the temperature remains a significant variable ($f(3.4) = 28.8$, $p = 4.2 \times 10^{-7}$ and $f(3.4) = 19.9$, $p = 7.9 \times 10^{-6}$, respectively). However, for 28- and 56-day ages we cannot reject the null hypothesis for feedstock type ($f(4.25) = 2.31$, $p = 0.14$ and $f(4.25) = 0.17$, $p = 0.68$, respectively), suggesting that feedstock type has a diminished impact on compressive strength at later ages. The ashing temperature dependence of compression strength corresponds to expectations from the literature that higher ashing temperatures lead to greater quantities of less reactive crystalline silica and thus lower strengths.[21]

Environmental Impact Assessment

Environmental impact comparisons were made for two products: (i) use of rice-biomass as an electricity resource; and (ii) rice-ashes as a partial PC alternative (Figure 2a and b). Results suggest that treatment methods could play a significant role in the viability of rice-biomass as a low environmental impact energy resource. Compared to the fossil fuel electricity resources examined, rice-based electricity could lead to 90-95% reductions in GHG emissions. However, the acid-leached biomass would result in net GHG emissions greater than from fossil-based resources due to the emissions associated with producing acid for the leaching solution. While not in the scope of this analysis, if the leaching solution could be recycled for multiple leaching cycles or recovered in another way, larger reductions in GHG emissions could be achieved for energy generated from acid-leached biomass. As pre-combustion impacts are assigned to electricity production, all ashes have significantly lower GHG emissions than PC, suggesting they may be promising alternatives from an environmental impact perspective.

To further examine the implications of using rice-based ashes as an SCM, environmental impacts of mortar mixtures were assessed. Figure 2c and d shows a breakdown of the contributions to the net GHG emissions and total energy demand for the mortar mixtures examined in this work. The production of PC is the largest contributor to both GHG emissions and embodied energy in these mortars. The GHG emissions attributed to RHA in cement-materials reported here are lower than in other work,[33] as the ashes studied did not undergo additional treatment (e.g. milling), thus the environmental impacts of the ash simply reflect their necessary transportation. As such, use of rice-ash to offset high-impact PC drives the GHG emissions and reductions are in the range of 10 to 15%, reflecting the mass of cement replaced. If ashes were used to replace other concrete constituents, the change in GHG emissions would differ dependent on the material the rice-based ash replaces and the quantity of the replacement rate in the mixture being studied.

Noting that each biomass type, leaching method, and ashing temperature led to different compressive strengths, comparisons were also drawn using a ratio of GHG emissions per cubic meter of mortar divided by the 28-day compressive strength of said mixture (Figure 3). These comparisons allow one to weigh tradeoffs of environmental impact and performance. In the mixtures evaluated, a lower ratio indicates a higher compressive strength and/or a lower impact relative to the other mixtures, both of which are desirable. Since the impacts prior to ashing are assigned to energy production, the resulting bioash-cement mortars all have approximately the same impact. Thus, the value in Figure 3 for bioash-cement mortars are hyperbolic in the compressive strength (y = 469.8/x) due to the constant GHG emissions per cubic meters assumed.

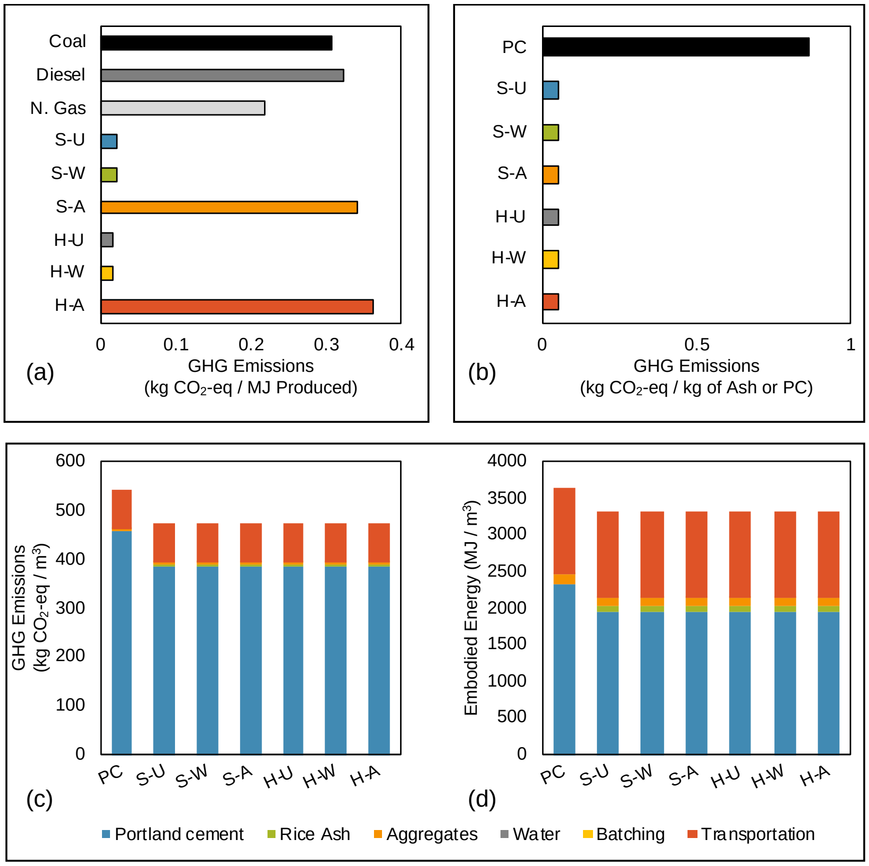


Figure 2. Comparison of greenhouse gas (GHG) emissions for (a) rice-based energy relative to fossil-fuel energy where "N. Gas" is natural gas, (b) cement relative to rice-ash, and impacts per m^3 of mortars by ash leaching condition by (c) GHG and (d) embodied energy

While this study shows that mortars made with PC and ash would result in lower GHG emissions relative to the PC mortar, only three alternatives led to a better combination of GHG emissions and compressive strength than the control PC mortar: (i) unleached rice straw ash produced at 600°C; (ii) unleached rice hull ash produced at 600°C; and (iii) acid-leached rice hull ash produced at 600°C. These findings suggest that even with loss in mechanical strength, there is a potential for the rice-based ash mortars tested in this work to contribute to a desirable combination of properties to mitigate environmental burdens if performance constraints can be met.

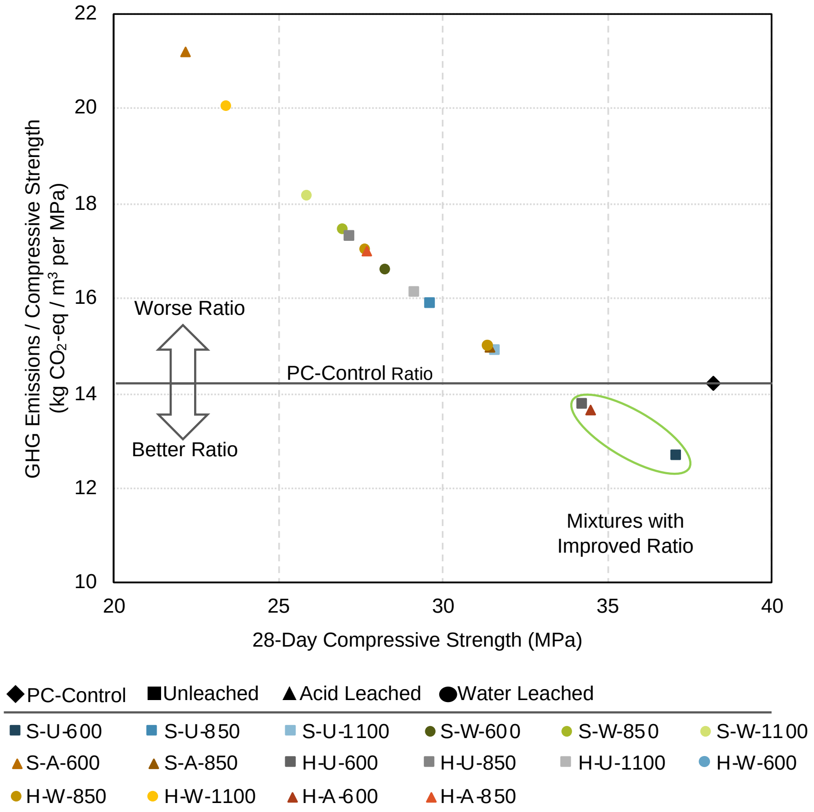


Figure 3. Greenhouse gas emissions relative to 28-day compressive strength for each of the mortars tested.

Conclusions

With growing energy and material resource demands worldwide, pathways to improved environmental sustainability through industrial symbiosis could be a critical means to improving the circular economy. In this work, we examine the effects of rice-biomass pretreatment and ashing temperature on energy conversion and the use of ash in cement-based materials to support a critical step in understanding a potential symbiotic relationship. Through a combination of experimental and analytical techniques, this research provides context for the influence of such treatments on ash properties, on strength development in cement mortars containing rice ash, and on potential shifts in environmental impacts. Some key findings from this work include:

- Feedstock leaching was shown to remove more than 90% of chloride and up to 93% of potassium, while increasing silica concentration by 1-10% in ash.
- While leaching methods did not benefit early-age strength of cement-based mortars, higher rates of strength development were noted for ashes produced from leached biomass, leading to mortars with comparable strength to the control mixture at 56 days.
- Despite more limited investigation on RSA in the literature, this work showed RSA-cement mortars from unleached and leached biomass achieved similar or better compressive strengths than the corresponding RHA-cement mortars at all ashing temperatures – a significant finding considering the larger quantities of straw biomass available.
- Agreeing with the literature, this work further supports the dependency of rice ash reactivity on ashing temperature, where more reactive ashes were noted at 600°C.
- Environmental impact assessment results showed the use of refined chemicals in leaching, such as the acids explored in this work, could drive net GHG emissions in rice-based energy production.
- When considering ash as a residue from energy generation, reductions in emissions for cement-based mortar production were shown to be approximately equal to the cement replacement rate (~10-15% lower emissions in this study).
- When impacts are considered in tandem with the compressive strength of the mortars, untreated hulls produced at 600°C, untreated straw produced at 600°C, and acid leached straw produced at 600°C all provided reduced impacts.

While this research provides a valuable initial step in understanding potential industrial symbiosis for rice energy generation and infrastructure materials production, further research is needed. Such future studies should identify the effects of ash treatment requirements for ash produced from different combustion equipment as well as the stage at which treatment is performed (e.g., leaching of ash in addition to or in place of biomass leaching) to improve to ash properties and consistency. Future consideration of co-products, such as nutrient reclamation from leachates or recycling leachates for reuse, could improve the extent to which these products may mitigate costs and decrease environmental impacts. Future study should also consider additional conversion or ashing methods, such as gasification or biochemical conversion of rice-based biomass, to simultaneously benefit energy and materials production. Additionally, the ability of alternative pretreatment methods, such as an alkali [73] or acid digestion and enzymatic hydrolysis[74] to valorize feedstock for energy and cement-based material production should be considered, and the influences of all these processes evaluated for potential economic consequences.

Supporting Information: The Supporting Information is available free of charge.

- Hull and straw feedstock size-gradations (Table S1); leachate chemical analysis (Table S2); post-leaching and unleached (untreated) feedstock moisture, ash, volatile matter, and fixed carbon content (Table S3); ash and Portland cement trace elements content, LOI, and specific gravity (Table S4) (PDF)

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References:

(1) IEA. Data and Statistics https://www.iea.org/data-and-statistics?country=WORLD&fuel=Electricityandheat&indicator=Electricitygenerationbysource (accessed Oct 17, 2020).
(2) IEA. Technology Roadmap: Low-Carbon Transition in the Cement Industry. **2018**.
(3) van Oss, H. G.; Survey, U. S. G. *Minerals Yearbook: Cement*; Bureau of Mines, 2012.
(4) Caltrans. *Fly Ash: Current and Future Supply. A Joint Effort Between Concrete Task Group of the Caltrans Rock Products Committee and Industry*; 2016.
(5) van Oss, H. G.; Survey, U. S. G. *Mineral Commodity Summaries: Cement*; US Geological

Survey, 2016.

(6) California Energy Commission. California Biomass and Waste-To-Energy Statistics and Data https://ww2.energy.ca.gov/almanac/renewables_data/biomass/index_cms.php (accessed Jun 15, 2020).

(7) Kumar, N.; Kupwade-Patil, K.; Higuchi, R.; Ferrell, D. P.; Luttrull, V. A.; Lynam, J. G. Use of Biomass Ash for Development of Engineered Cementitious Binders. *ACS Sustain. Chem. Eng.* **2018**, *6* (10), 13122–13130. https://doi.org/10.1021/acssuschemeng.8b02657.

(8) A, I. E.; Agency, I. E. *Energy Technology Transitions for Industry*; International Energy Agency: Paris, 2009. https://doi.org/10.1787/9789264068612-en.

(9) State of California Department of Finance. Projections: Population Projections (Baseline 2016).

(10) California Energy Commission. Electricity Consumption by County http://www.ecdms.energy.ca.gov/elecbycounty.aspx (accessed Jun 25, 2020).

(11) USDA. *National Agriculture Statistics Service, 16 July 2012.US Department of Agriculture*; United States Department of Agriculture, 2012; Vol. 2018.

(12) Mehta, P. K.; Monteiro, P. J. M. *Concrete : Microstructure, Properties, and Materials*, 3rd ed.; McGraw-Hill: New York, 2006.

(13) Jenkins, B. M.; Baxter, L. L.; Miles, T. R.; Miles, T. R. Combustion Properties of Biomass. *Fuel Process. Technol.* **1998**, *54* (1–3), 17–46. https://doi.org/10.1016/S0378-3820(97)00059-3.

(14) Singh, J.; Singhal, N.; Singhal, S.; Sharma, M.; Agarwal, S.; Arora, S. Environmental Implications of Rice and Wheat Stubble Burning in North-Western States of India. In *Advances in Health and Environment Safety*; Siddiqui, N. A., Tauseef, S. M., Bansal, K., Eds.; Springer Singapore: Singapore, 2018; pp 47–55. https://doi.org/10.1007/978-981-10-7122-5_6.

(15) Wang, G.; Shen, L.; Sheng, C. Characterization of Biomass Ashes from Power Plants Firing Agricultural Residues. *Energy and Fuels* **2012**, *26* (1), 102–111. https://doi.org/10.1021/ef201134m.

(16) van Oss, H. G.; Mines, B. of. *Minerals Yearbook: Cement 2012*; United States Geological Survey, 2015.

(17) Oss, V.; G.H. *Minerals Yearbook: Cement 2015*; United States Geological Survey, 2018.

(18) World Bank. Energy use (kg of oil equivalent per capita) http://data.worldbank.org/.

(19) U.S. Geological Survey. *Mineral Commodity Summaries 2020*; 2020.

(20) Mehta, P. K. PROPERTIES OF BLENDED CEMENTS MADE FROM RICE HUSK ASH. *J Am Concr Inst* **1977**, *74* (9), 440–442. https://doi.org/10.14359/11022.

(21) Miller, S. A.; Cunningham, P. R.; Harvey, J. T. Rice-Based Ash in Concrete: A Review of Past Work and Potential Environmental Sustainability. *Resour. Conserv. Recycl.* **2019**, *146*, 416–430. https://doi.org/10.1016/j.resconrec.2019.03.041.

(22) Rajamma, R.; Ball, R. J.; Tarelho, L. A. C.; Allen, G. C.; Labrincha, J. A.; Ferreira, V. M. Characterisation and Use of Biomass Fly Ash in Cement-Based Materials. *J. Hazard. Mater.* **2009**, *172* (2–3), 1049–1060. https://doi.org/10.1016/j.jhazmat.2009.07.109.

(23) Chao-Lung, H.; Anh-Tuan, B. Le; Chun-Tsun, C. Effect of Rice Husk Ash on the Strength and Durability Characteristics of Concrete. *Constr. Build. Mater.* **2011**, *25* (9), 3768–3772. https://doi.org/10.1016/j.conbuildmat.2011.04.009.

(24) Parvez, A. M.; Mujtaba, I. M.; Wu, T. Energy, Exergy and Environmental Analyses of Conventional, Steam and CO2-Enhanced Rice Straw Gasification. *Energy* **2016**, *94*, 579–588. https://doi.org/10.1016/j.energy.2015.11.022.

(25) Klinghoffer, N. B.; Castaldi, M. J.; Nzihou, A. Influence of Char Composition and Inorganics on Catalytic Activity of Char from Biomass Gasification. *Fuel* **2015**, *157*, 37–47. https://doi.org/10.1016/j.fuel.2015.04.036.

(26) Mehta, P. K. Elastomeric and Plastomeric Materials Containing Amorphous Carbonaceous Silica.

U.S. Patent No. 3,951,907, 1976.

(27) Thomas, B. S. Green Concrete Partially Comprised of Rice Husk Ash as a Supplementary Cementitious Material – A Comprehensive Review. *Renew. Sustain. Energy Rev.* **2018**, *82* (July 2016), 3913–3923. https://doi.org/10.1016/j.rser.2017.10.081.

(28) Vigneshwari, M.; Arunachalam, K.; Angayarkanni, A. Replacement of Silica Fume with Thermally Treated Rice Husk Ash in Reactive Powder Concrete. *J. Clean. Prod.* **2018**, *188*, 264–277. https://doi.org/10.1016/j.jclepro.2018.04.008.

(29) Sandhu, R. K.; Siddique, R. Influence of Rice Husk Ash (RHA) on the Properties of Self-Compacting Concrete: A Review. *Constr. Build. Mater.* **2017**, *153*, 751–764. https://doi.org/10.1016/j.conbuildmat.2017.07.165.

(30) He, Z. hai; Li, L. yuan; Du, S. gui. Creep Analysis of Concrete Containing Rice Husk Ash. *Cem. Concr. Compos.* **2017**, *80*, 190–199. https://doi.org/10.1016/j.cemconcomp.2017.03.014.

(31) Fapohunda, C.; Akinbile, B.; Shittu, A. Structure and Properties of Mortar and Concrete with Rice Husk Ash as Partial Replacement of Ordinary Portland Cement – A Review. *Int. J. Sustain. Built Environ.* **2017**, *6* (2), 675–692. https://doi.org/10.1016/j.ijsbe.2017.07.004.

(32) Gursel, A. P.; Horvath, A. GreenConcrete LCA Webtool http://greenconcrete.berkeley.edu/concretewebtool.html (accessed Nov 13, 2014).

(33) Gursel, A. P.; Maryman, H.; Ostertag, C. A Life-Cycle Approach to Environmental, Mechanical, and Durability Properties of "Green" Concrete Mixes with Rice Husk Ash. *J. Clean. Prod.* **2016**, *112*, 823–836. https://doi.org/10.1016/j.jclepro.2015.06.029.

(34) Chaivatamaset, P.; Sricharoon, P.; Tia, S.; Bilitewski, B. The Characteristics of Bed Agglomeration/Defluidization in Fluidized Bed Firing Palm Fruit Bunch and Rice Straw. *Appl. Therm. Eng.* **2014**, *70* (1), 737–747. https://doi.org/10.1016/j.applthermaleng.2014.05.061.

(35) Thy, P.; Jenkins, B. M.; Lesher, C. E.; Grundvig, S. Compositional Constraints on Slag Formation and Potassium Volatilization from Rice Straw Blended Wood Fuel. *Fuel Process. Technol.* **2006**, *87* (5), 383–408. https://doi.org/10.1016/j.fuproc.2005.08.015.

(36) Bakker, R. R.; Jenkins, B. M. Feasibility of Collecting Naturally Leached Rice Straw for Thermal Conversion. *Biomass and Bioenergy* **2003**, *25* (6), 597–614. https://doi.org/10.1016/S0961-9534(03)00053-9.

(37) Liu, H.; Zhang, L.; Han, Z.; Xie, B.; Wu, S. The Effects of Leaching Methods on the Combustion Characteristics of Rice Straw. *Biomass and Bioenergy* **2013**, *49*, 22–27. https://doi.org/10.1016/j.biombioe.2012.12.024.

(38) Jenkins, B. M.; Mannapperuma, J. D.; Bakker, R. R. Biomass Leachate Treatment by Reverse Osmosis. *Fuel Process. Technol.* **2003**, *81* (3), 223–246. https://doi.org/10.1016/S0378-3820(03)00010-9.

(39) Jenkins, B. M.; Bakker, R. R.; Wei, J. B. On the Properties of Washed Straw. *Biomass and Bioenergy* **1996**, *10* (4), 177–200. https://doi.org/10.1016/0961-9534(95)00058-5.

(40) Reynolds, K. Personal Communication. Farmer's Rice Cooperative 2020.

(41) Thy, P.; Yu, C.; Jenkins, B. M.; Lesher, C. E. Inorganic Composition and Environmental Impact of Biomass Feedstock. *Energy and Fuels* **2013**, *27* (7), 3969–3987. https://doi.org/10.1021/ef400660u.

(42) Yu, C.; Thy, P.; Wang, L.; Anderson, S. N.; Vandergheynst, J. S.; Upadhyaya, S. K.; Jenkins, B. M. Influence of Leaching Pretreatment on Fuel Properties of Biomass. *Fuel Process. Technol.* **2014**, *128*, 43–53. https://doi.org/10.1016/j.fuproc.2014.06.030.

(43) Yu, C. W. Leaching Pretreatments for Improving Biomass Quality : Feedstocks, Solvents, and Extraction Modeling (Dissertation), University of California, Davis, 2012.

(44) E871-82, A. Standard Test Method for Moisture Analysis of Particulate Wood Fuels 1. *Annu. B. ASTM Stand.* **2014**, *82* (Reapproved 2013), 2. https://doi.org/10.1520/E0871-82R13.2.

(45) ASTM. Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels E872 - 82. *ASTM Int.* **2011**, *82* (Reapproved 2006), 14–16. https://doi.org/10.1520/E0872-82R06.2.
(46) ASTM. Standard Test Method for Ash in Biomass E1755 - 01. **2015**, No. Reapproved 2015. https://doi.org/10.1520/E1755-01R07.2.
(47) Nair, D. G.; Fraaij, A.; Klaassen, A. A. K.; Kentgens, A. P. M. A Structural Investigation Relating to the Pozzolanic Activity of Rice Husk Ashes. *Cem. Concr. Res.* **2008**, *38* (6), 861–869. https://doi.org/10.1016/j.cemconres.2007.10.004.
(48) Environmental Protection Agency. METHOD 200.7 - Determination of Elements and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emmission Spectropemtry. *US Environ. Prot. Agency* **1991**, *EPA/600/4-*, 31–82.
(49) UC Davis Analytical Laboratory. SOP 835.03: Solubles: Al, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Zn https://anlab.ucdavis.edu/analysis/Water/835 (accessed Jul 27, 2020).
(50) Diamantopoulos, J. Personal Communication. *Activation Laboratories Ltd.* 2020.
(51) ASTM. ASTM C39 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens 1. *ASTM Int.* **2008**, *i*, 1–7.
(52) Shafie, S. M.; T.M.I.Mahlia; Masjuki, H. H.; Rismanchi, B. Life Cycle Assessment (LCA) of Electricity Generation from Rice Husk in Malaysia. *Energy Procedia* **2012**, *14*, 499–504. https://doi.org/https://doi.org/10.1016/j.egypro.2011.12.965.
(53) Intergovernmental Panel on Climate Change. *IPCC Fifth Assessment Report. The Physical Science Basis*; 2013.
(54) PRé, various authors. *SimaPro Database Manual: Methods Library*; Amersfoort, Netherlands, 2019.
(55) Althaus, H.; Chudacoff, M.; Hischier, R.; Jungbluth, N.; Osses, M.; Primas, A.; Hellweg, S. *Life Cycle Inventories of Chemicals. Final Report Ecoinvent Data v2.0 No 8.*; 2007.
(56) Comission, C. E. Total System Electric Generation https://ww2.energy.ca.gov/almanac/electricity_data/total_system_power.html.
(57) GREET; Laboratory, A. N. *The Greenhouse Gases, Regulated Emissions, and Energy Use In Transportation Model, GREET 1.8d.1*; Argonne, IL, 2010.
(58) Biomass Energy Resource Center (BERC). Biomass Energy: Efficiency, Scale, and Sustainability. Montpelier, Vermont 2009.
(59) National Renewable Energy Laboratory. U.S. Life Cycle Inventory Database https://www.lcacommons.gov/nrel/search%0A%0A.
(60) Miller, S. A.; Myers, R. J. Environmental Impacts of Alternative Cement Binders. *Environ. Sci. Technol.* **2020**, *54* (2), 677–686. https://doi.org/10.1021/acs.est.9b05550.
(61) Marceau, M. L.; Nisbet, M. A.; VanGeem, M. G.; Portland Cement Association. *Life Cycle Inventory of Portland Cement Manufacture*; Portland Cement Association: Skokie, Illinois, 2006.
(62) Marceau, M. L.; Nisbet, M. A.; VanGeem, M. G.; Portland Cement Association. *Life Cycle Inventory of Portland Cement Concrete*; Portland Cement Association: Skokie, Illinois, 2007.
(63) Baxter, L. L.; Miles, T. R.; Miles Jr, T. R.; Jenkins, B. M.; Dayton, D. C.; Milne, T. A.; Bryers, R. W.; Oden, L. L. *Alkali Deposits Found in Biomass Power Plants Volume II: The Behavior of Inorganic Material in Biomass-Fired Power Boilers—Field and Laboratory Experiences*; 1996; Vol. II.
(64) ECN.TNO. Phyllis2, database for (treated) biomass, algae, feedstocks for biogas production and biochar https://phyllis.nl/.
(65) Thy, P.; Yu, C.; Blunk, S. L.; Jenkins, B. M. Inorganic Composition of Saline-Irrigated Biomass. *Water. Air. Soil Pollut.* **2013**, *224* (7), 1–17. https://doi.org/10.1007/s11270-013-1617-y.
(66) Thy, P.; Jenkins, B. M.; Grundvig, S.; Shiraki, R.; Lesher, C. E. High Temperature Elemental Losses and Mineralogical Changes in Common Biomass Ashes. *Fuel* **2006**, *85* (5–6), 783–795.

https://doi.org/10.1016/j.fuel.2005.08.020.

(67) ACI 318-14. *ACI 318-14 - Building Code Requirements for Structural Concrete*; 2014.

(68) Alex, J.; Dhanalakshmi, J.; Ambedkar, B. Experimental Investigation on Rice Husk Ash as Cement Replacement on Concrete Production. *Constr. Build. Mater.* **2016**, *127*, 353–362. https://doi.org/10.1016/j.conbuildmat.2016.09.150.

(69) Park, K.; Kwon, S.; Wang, X. Analysis of the Effects of Rice Husk Ash on the Hydration of Cementitious Materials. *Constr. Build. Mater.* **2016**, *105*, 196–205. https://doi.org/10.1016/j.conbuildmat.2015.12.086.

(70) Zain, M. F. M.; Islam, M. N.; Mahmud, F.; Jamil, M. Production of Rice Husk Ash for Use in Concrete as a Supplementary Cementitious Material. *Constr. Build. Mater.* **2011**, *25* (2), 798–805. https://doi.org/10.1016/j.conbuildmat.2010.07.003.

(71) Nurse, R. W. The Effect of Phosphate on the Constitution and Hardening of Portland Cement. *J. Appl. Chem.* **2007**, *2* (12), 708–716. https://doi.org/10.1002/jctb.5010021208.

(72) Celik, K.; Meral, C.; Petek Gursel, A.; Mehta, P. K.; Horvath, A.; Monteiro, P. J. M. Mechanical Properties, Durability, and Life-Cycle Assessment of Self-Consolidating Concrete Mixtures Made with Blended Portland Cements Containing Fly Ash and Limestone Powder. *Cem. Concr. Compos.* **2015**, *56*, 59–72. https://doi.org/10.1016/j.cemconcomp.2014.11.003.

(73) Cheng, Y. S.; Zheng, Y.; Yu, C. W.; Dooley, T. M.; Jenkins, B. M.; Vandergheynst, J. S. Evaluation of High Solids Alkaline Pretreatment of Rice Straw. *Appl. Biochem. Biotechnol.* **2010**, *162* (6), 1768–1784. https://doi.org/10.1007/s12010-010-8958-4.

(74) Lau, B. B. Y.; Yeung, T.; Patterson, R. J.; Aldous, L. A Cation Study on Rice Husk Biomass Pretreatment with Aqueous Hydroxides: Cellulose Solubility Does Not Correlate with Improved Enzymatic Hydrolysis. *ACS Sustain. Chem. Eng.* **2017**, *5* (6), 5320–5329. https://doi.org/10.1021/acssuschemeng.7b00647.

TOC/Abstract Graphic

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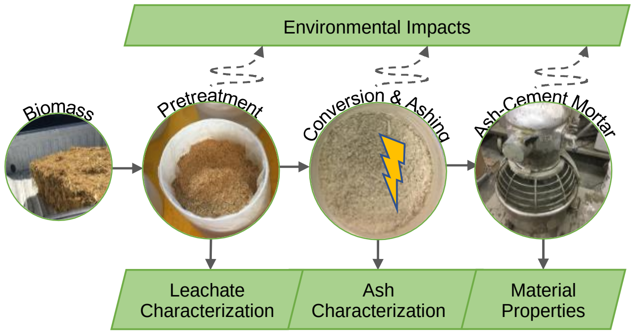

Synopsis

Ash composition, material properties, and environmental impacts were examined to identify synergies among residual rice-crop biomass diversion, energy conversion, and building material production.