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S Supporting Information

ABSTRACT: The distribution of ash-forming elements in dried vinasse was characterized by sequentially leaching it in H_2O, NH_4Ac, and HCl. In addition, the release of inorganics during combustion and CO_2 gasification of the vinasse at 900 °C in a single particle reactor was determined. Furthermore, the vinasse was ashed at 500 °C, and the melting behavior of the ash as a function of temperature was first predicted using FactSage thermodynamic calculations and then validated using differential scanning calorimetry (DSC)−thermogravimetric analysis (TGA) measurements. The fuel fractionation results revealed that almost all of the ash-forming elements, except Si, Al, and Fe, in the vinasse were completely water-soluble. Moreover, unlike other solid fuels, significant portions of Si, Al, and Fe in the vinasse were water-soluble, owing to its origin, juice from water-extracted cane stalks, and acidic nature. Analysis results of the ashes from the combustion and gasification experiments showed that none of the water- and acetate-soluble Si, Al, Fe, and P in the vinasse was released during combustion and gasification. However, significant levels of the water- and acetate-soluble K, Na, Ca, Mg, S, and Cl were released during the vinasse thermal conversion in both gas conditions, with the release levels being higher in CO_2 than in O_2. The thermodynamic calculation and DSC−TGA measurement results showed that the initial melting temperature of the vinasse ash was 640−645 °C, and the temperatures corresponding to 15 and 70% melt fractions were 650 and 670−690 °C, respectively. The low-temperature-melting ash and the release of significant amounts of water- and acetate-soluble alkali and alkali chlorides during thermal conversion suggest that vinasse is a challenging fuel for combustion and gasification in conventional boilers and gasifiers.

1. INTRODUCTION

Vinasse is a byproduct from an ethanol distillery, which is mostly built integrated with a sugar mill, and it is known by various names, including stillage, still bottoms, spent wash, mosto, slops, vinhaca, vinhoto, or dunder.[1] Vinasse contains about 90−95 wt % water, with the balance being solids.[2] A total of 60−70 wt % of the vinasse solids are organics, while the rest are inorganics. Vinasse is one of the few fuels that share fuel properties in common with black liquor from the Kraft process. These properties include swelling during pyrolysis,[3] having a heating value of 10−15 MJ/kg on a dry basis,[1,4,5] and containing a substantial ash fraction. However, vinasse is acidic,[1] and its ash is mainly composed of potassium salts, whereas black liquor is alkaline, with sodium salts being predominant. On average, vinasse is being generated at a rate of 10−15 L (on a wet basis) per liter of ethanol produced.[2,6] During the 2012/2013 ethanol production season in Brazil, nearly 370 billion liters[7] of vinasse were generated. Such an amount of vinasse would supply approximately 125 TWh thermal energy per year. Nowadays, the main utilization of vinasse is in fertirrigation, fertilizing the soil and, at the same time, providing water for the cane plants.[8] However, the use of vinasse in fertirrigation may have adverse environmental impacts, such as greenhouse gas (GHG) emission[9] and soil and groundwater pollution.[8] Moreover, fertirrigation is insufficient to handle the total volume of vinasse being

generated. This is due to the cost of transporting the vinasse to agricultural lands farther from the sugar mill for fertirrigation. Therefore, there is a need for alternative utilization options.

Thermochemical conversion processes, i.e., pyrolysis, combustion, and gasification, in addition to effectively addressing the environmental risks posed by vinasse, can convert the organics in the vinasse into energy and chemicals.[10] Moreover, the ash from these processes can be recovered and recycled back to the soil for fertilizer.[10] Patel[3] studied gasification of vinasse concentrated to 70−75 wt % solids in a lab-scale setup under sub-stoichiometric air conditions. His report shows that 95−96% carbon conversion was achieved, and the gaseous product was composed of CO_2, CO, H_2, H_2O, CH_4, and H_2S. Our previous investigation of vinasse CO_2 gasification[11] has shown that, in addition to gasification of vinasse chars by CO_2, the char weight losses in differential scanning calorimetry (DSC)−thermogravimetric analysis (TGA) were dominated by the release of ash-forming matter. Although vinasse combustion[2,12] has not yet been successfully carried out industrially, boiler suppliers[13] have

recently embarked on the design and development of special boilers for burning concentrated vinasse.

An important parameter for the development of a thermochemical conversion process for a biomass is the behavior of ash and ash-forming elements (inorganics) in the biomass. More specifically, high levels of alkalis, in addition to a high ash content, in biomasses are the main cause for ash-related problems, corrosion, ash deposition, sintering, slagging, and agglomeration, in boilers[14] and gasifiers.[15] Therefore, development of proper control measures for the ash-related problems requires characterizing the biomass fuels for their ash and ash-forming elements.

An advanced method for characterization of ash-forming elements in solid fuels is fuel or chemical fractionation. The method was first developed by Benson and Holm[16] for coal, and later Baxter et al.[14] applied a modified version of the method to seven biomass fuels. Zevenhoven-Onderwater[17] has made further refinements in the method for biomass characterization. The method can be used to determine the type of association of ash-forming elements in the fuel, whether the inorganics in the fuel are present as minerals or organically bound species. Knowledge of the association of ash-forming elements in biomass fuels enables the determination of the volatility of the ash-forming elements during a thermochemical conversion process as well as their water washability prior to a thermochemical conversion. According to Zevenhoven-Onderwater et al.,[18] the H_2O- and NH_4Ac-soluble ash-forming elements are assumed to represent the more "reactive"/ "volatile" species. These "reactive" species are assumed to be released during thermochemical conversion of biomass and may condense on superheater tubes and heat exchangers of a boiler/gasifier, causing the ash-related problems. Moreover, according to Zevenhoven-Onderwater et al., the HCl-soluble ash-forming elements and those remaining in the fraction after leaching with HCl are assumed to represent the "less-reactive" species. In contrast to the "reactive" ash-forming elements, the latter species may not cause any ash-related problems and they largely form the coarse ash particles that can be removed from the boiler/gasifier as bottom ash. However, literature data on the levels of the "reactive" inorganic species released during biomass combustion or gasification are scarce. The only available data in the literature, to the best knowledge of the authors, is the study by Frandsen et al.[19] for spruce (bark and wood chips), waste wood, and straw. Moreover, although about 40% of the ash and 55% of potassium and chloride in the sugarcane supplied to the integrated sugar−ethanol process end up in vinasse,[20] the distribution of ash-forming elements in the vinasse has not been characterized.

Another important ash property, which is useful for the design and operation of biomass thermochemical conversion processes,[21] is its melting behavior. The characteristic ash-melting temperatures are the initial or first melting, sticky, flow, and complete melting temperatures denoted as T_0, T_{15}, T_{70}, and T_{100}, respectively.[5,22,23] T_0 is the temperature at which the ash first begins to melt and below which there is no liquid phase, whereas T_{100} is the temperature above which the ash is completely molten. T_{15} and T_{70}, also known as the radical ash deformation temperature,[23] are the temperatures at which 15−20 and 70% of the ash are in the molten phase, respectively. These temperatures determine the propensity of ash deposit formation and buildup, bed agglomeration, and corrosion in boilers and gasifiers. According to Zevenhoven-Onderwater,[17] biomass ashes can be qualitatively ranked based on their T_{15}

from "bad" (T_{15} < 700 °C) to "good" (T_{15} > 900 °C). This means that ashes with T_{15} < 700 °C are problematic for combustion and gasification because they may form sticky ash deposits in boilers and gasifiers. However, ashes whose 15% melt occurs above 900 °C are not considered problematic for the thermal conversions. Vinasse ash-melting behavior has not been well-studied. In our previous work,[11] the ash-melting characteristics for vinasse chars produced at 800 °C in a N_2 gas atmosphere were calculated using FactSage thermodynamic software. The calculations showed that the vinasse ash T_0 was about 620 °C and the alkalis in the chars appeared to be fully molten at about 660 °C. However, because significant levels of K, S, and Cl were released during the char production stage, the actual values of vinasse ash-melting temperatures may deviate considerably.

A critical factor that should be considered for the implementation of the vinasse thermochemical conversion process is the considerable amount of energy needed for concentrating the vinasse to a high solids content. However, this is outside the scope of the present work. Nonetheless, there are some promising options that could alleviate the problem: heat and material integration in the integrated sugar−ethanol process[24,25] and improving the energy efficiency of the integrated process through technology upgrading.[26]

The objectives of the present study are (1) to characterize the distribution of ash-forming elements in dried vinasse, (2) to quantify the levels of the "reactive" inorganic species released during combustion and gasification of the vinasse, and (3) to determine vinasse ash-melting characteristics as a function of the temperature. In this paper, the term "reactive" refers to the sum of H_2O- and NH_4Ac-soluble fractions of an ash-forming element, while "less-reactive" represents the portions of the element leached by acid and insoluble in any of the three solvents. Chemical fractionation of the vinasse was performed by sequentially leaching it in H_2O, NH_4Ac, and HCl. The levels of the "reactive" inorganic species released during combustion/gasification were determined by combusting/gasifying the vinasse in a quartz-glass reactor, also known as a single-particle reactor (SPR), and analyzing the ashes from the combustion/gasification experiments for their inorganics using inductively coupled plasma optical emission spectroscopy (ICP−OES). To assess the melting characteristics of vinasse ash as a function of the temperature, a portion of the dried vinasse was first ashed at a low temperature, 500 °C. Then, the melting behavior of the ash as a function of temperature was calculated using FactSage thermodynamic calculations, and the calculated results were validated using DSC−TGA measurements.

2. EXPERIMENTAL SECTION

2.1. Chemical Fractionation. Chemical fractionation of dried and ground vinasse was carried out by sequentially leaching the vinasse sample in distilled H_2O, 1 M NH_4Ac, and 1 M HCl. Detailed experimental procedures for the chemical fractionation are available from Zevenhoven-Onderwater[17] and Zevenhoven et al.[27] The water-, acetate-, and acid-soluble leachates as well as the "rest fraction", the final residue from the chemical fractionation, were analyzed for their ash-forming elements, except Cl, with the ICP−OES described in section 2.4. The Cl contents of the water- and acetate-soluble fractions from the chemical fractionation were analyzed by ion chromatography (IC) described in section 2.4. The parent fuel was analyzed and reported previously.[11,20] Prior to ashing, the vinasse sample was dried and ground as described in our previous report.[11]

2.2. Release of the "Reactive" Fractions of the Vinasse Ash-Forming Elements during Combustion and Gasification. To determine the levels of the "reactive" fractions of the vinasse ash-forming elements released during combustion and gasification, the vinasse was first combusted/gasified in the SPR at 900 °C. Then, the amounts of the inorganics released were calculated on the basis of elemental analyses and ash yield results of the ashes from the combustion and gasification experiments. The methods for the elemental analyses of the ashes are described in section 2.4. The inorganics released during combustion and gasification were assumed to be the H_2O- and NH_4Ac-soluble portions of the vinasse ash-forming elements. The assumption was adopted from Zevenhoven-Onderwater.[17]

The SPR is supplied with synthetic air as well as CO_2 and N_2 gases. Both CO_2 and N_2 gases were 99.99% pure. The gas conditions used in the SPR were 10 vol % O_2/90 vol % N_2 and 50 vol % CO_2/50 vol % N_2 for the combustion and gasification experiments, respectively. Detailed descriptions of the SPR can be found elsewhere.[28,29] The experimental procedures with the SPR were reported previously,[10] except the following additional conditions used in the present work: (1) About 200 mg of the dried and ground vinasse sample was used. (2) The experiments were repeated at least 10 times in each gas atmosphere. (3) The ashes from the combustion and gasification experiments were recovered, ground to a fine powder, and stored in an airtight container for further analyses. (4) The empty sample holders were weighed before and after each experiment, but no significant change in the weight of the sample holders was observed. During the combustion experiments, flames were formed, indicating that the actual combustion temperature could exceed 900 °C. It took approximately 3 min for the vinasse combustion to complete, whereas the time required for complete gasification was about 10 min. The ash from the combustion experiments appears porous and pale yellow, while that produced in CO_2 was stiff and light gray in color.

2.3. Ash-Melting Behavior. To assess the melting characteristics of vinasse ash with temperature, the dried and ground vinasse was first ashed at 500 °C in a muffle furnace (model L51/SR, Naber, Germany). Then, the melting behavior of the ash was calculated using FactSage, version 7.2,[30] and the results were validated using DSC−TGA measurements. The low temperature used for the ashing was to minimize loss of inorganics. The ashing experiments were carried out as per the CEN/TS 14775 standard apart from the final 500 °C temperature and the holding times used. It took almost 3 days for the ashing to complete, i.e., to burn off the organic fraction of the vinasse completely. Complete combustion of the organic material was verified using a DSC−TGA test. About 8 mg of the ash sample was placed in a DSC−TGA and heated to 500 °C in synthetic air, i.e., 20 vol % O_2/80 vol % N_2. Then, the system was kept isothermal at 500 °C for about 50 min. No significant change in the weight of the ash sample was observed during the isothermal period, indicating that complete removal of the organic carbon was achieved in the muffle furnace. Further details of the procedures for the ashing experiments are available in our previous work.[20] The vinasse cannot be put in DSC−TGA directly because it swells during pyrolysis. The ashing experiments were performed in triplicates; the ashes from the three experiments were mixed and ground to a fine powder and stored in an airtight container.

The FactSage calculations were made using three different inputs: the original fuel composition, the ash composition determined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM−EDX), and the ash composition determined by ICP−OES and IC. In the latter case, the C and O analysis results of the ash from SEM−EDX were used. For the FactSage calculations, the databases used were the FTpulp for the alkali salt phases, the FToxid for the molten slag phase and solid oxide/silicate phases, and the FactSage pure substance database for the gas components and other solid compounds. In addition, thermodynamic data not available in the commercial FactSage databases were used for the interaction of alkali salts with calcium and magnesium compounds in the molten salt phase. These data have been published by Lindberg and Chartrand[31] and described in the review paper by Lindberg et al.[32]

The DSC−TGA experiments were performed using an SDT Q600 (TA Instruments, New Castle, DE, U.S.A.). The DSC−TGA is supplied with CO_2 and N_2 gases. Both CO_2 and N_2 gases were 99.99% pure. The gas conditions used in the DSC−TGA were 100 vol % N_2 and 90 vol % CO_2/10 vol % N_2. The CO_2 gas atmosphere was used to suppress ash weight loss as a result of carbonate decomposition. About 10 mg of the ash sample was weighed into a pan made of Al_2O_3 and placed in the DSC−TGA furnace, which was being purged with 100 mL/min N_2 or 90 mL/min CO_2 and 10 mL/min N_2. The temperature of the system was first raised from room temperature to 900 °C at 10 °C/min. Then, the system was cooled from 900 to 200 °C at a rate of 10 °C/min. During heating, the formation of the first melt was seen as an endothermic peak in the DSC curve. During cooling, the solidification of the final melt resulted in an exothermic peak. Mass loss during heating was observed from the TGA curve. Universal Analysis software, version 4.5A, was used to evaluate the DSC−TGA data. The DSC−TGA experiments were repeated 2 times in each gas atmosphere, and the average values were reported.

2.4. Elemental Analyses and Chemical Compositions of the Vinasse Ashes. The ash-forming elements, except Cl, of the vinasse ashes described in sections 2.2 and 2.3 were analyzed using ICP−OES (model Optima 5300 DV) from PerkinElmer, Waltham, MA, U.S.A. The Cl contents of the ashes were analyzed by IC (Metrohm, Switzerland). The procedures for the analyses of the ash-forming elements by ICP−OES and IC (for Cl) are available from Dirbeba et al.[11] In addition to the analysis with ICP−OES and IC, the elemental composition of the vinasse ash produced at 500 °C was analyzed using SEM−EDX (model 1530 Gemini) from LEO, Germany. Prior to analysis with SEM−EDX, about 0.2 g of the vinasse ash sample was pressed into a 10 mm diameter pellet. The SEM−EDX experiments were performed in triplicates, and the average values were reported. Moreover, the major inorganic compounds present in the vinasse ashes were identified using an Empyrean X-ray diffractometer (XRD, PANalytical, Netherlands) equipped with a PIXcel[3D] detector (PANalytical, Netherlands). The XRD operating parameters used were as follows: voltage, 45 kV; current, 40 mA; temperature, 25 °C; Cu Kα X-ray radiation wavelength (θ), 1.540 60 Å; step size (2θ), 0.0130°; 2θ range, 10−100°; and scan step time, 18.87 s. Data from the XRD were analyzed using X'pert HighScore software (PANalytical, Netherlands), and the database used for the inorganic materials was PDF-4+ from the International Center for Diffraction Data (ICDD, Newtown Square, PA, U.S.A.).

3. RESULTS AND DISCUSSION

3.1. Chemical Fractionation. Figure 1 shows the vinasse chemical fractionation results on a weight percent dry vinasse basis (db). The results in milligrams per kilogram (db) are
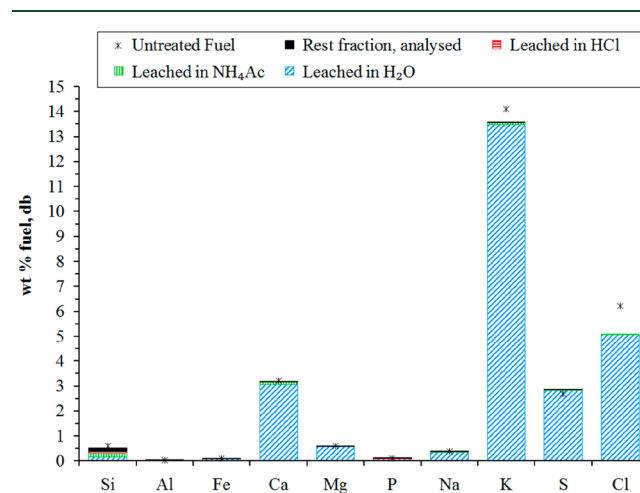

Figure 1. Fuel fractionation results for dried and ground sugarcane vinasse.

given in Table S1 of the Supporting Information. As seen in the figure, the mass balance closure for the ash-forming elements, except for Si and Cl, is in the range of 90−100%. The balance closures for Si and Cl are 85 and 82%, respectively. The relatively lower balance closure for Si is probably due to incomplete digestion of silica with HF prior to analysis with ICP−OES, whereas missing Cl is likely unanalyzed Cl in the HCl-soluble and "rest fraction".

As observed from Figure 1, almost all analyzed Na, K, S, and Cl were H_2O-soluble. Approximately 95% of Ca and Mg were leached in H_2O, with the balance being mainly NH_4Ac-soluble. The H_2O-soluble percentages for Si, Al, and Fe were about 25, 30, and 70%, respectively, while the corresponding NH_4Ac-soluble percentages were 25, 20, and 3%. About 10, 35, and 15% of Si, Al, and Fe, respectively, in the vinasse were leached by HCl, whereas about 25, 15, and 10% of Si, Al, and Fe, respectively, were insoluble in any of the solvents. The H_2O-, NH_4Ac-, and HCl-soluble portions of P were 83, 2, and 5%, respectively, whereas about 5% of P in the vinasse was found in the "rest fraction".

Unlike with other solid fuels,[27,33] whose Si, Al, and Fe are mostly insoluble in the three solvents, significant portions of these elements were water-soluble in the vinasse. There are two main possible reasons that could explain such an anomaly. First, the vinasse originates from sugarcane juice, which is obtained by extraction of pulverized sugarcane stalks with water. Most of the ash-forming elements, including H_2O-soluble Si, Al, and Fe, in the vinasse were, therefore, those fractions leached by water from the sugarcane stalks during the juice extraction process. Second, the acidic,[1] pH 4−5, nature of vinasse might have enhanced the dissolution of these ash-forming elements from the vinasse that otherwise should have been present in the insoluble form.

3.2. Yields, Elemental Analyses, and Chemical Compositions of the Vinasse Ashes. Table 1 lists yield and elemental analysis results of the vinasse ashes produced at both 500 and 900 °C. The ash yield results are given on a weight percent original dry fuel basis, while the results for the elemental analyses are on a weight percent ash basis.

The vinasse ash yield at 500 °C is slightly higher than the 34.1 wt % vinasse (db) result reported in our earlier study.[11] This is likely because, in this study, the vinasse was ashed at 500 °C, as opposed to 540 °C in the previous work. As seen from the table, the ash yield results obtained from the vinasse combustion and gasification experiments in the SPR are lower than that obtained from the vinasse ashing in the muffle furnace. This was mainly due to the higher temperature used in the SPR than in the muffle furnace. The ash yield result obtained in CO_2 from the SPR at 900 °C is lower than the result obtained in O_2 at the same temperature by about 2 wt %. The variation in the ash yield results may be attributed to differences in the levels of inorganics released in both gas atmospheres, as discussed in section 3.3.

As observed from Table 1, the main cationic inorganic elements in the vinasse ashes are potassium and calcium, while chloride and sulfur are the dominant anionic components. It can be observed from the table that, when converted to a weight percent original dry fuel basis using the ash yields, the Si results for the ashes produced in the SPR are high compared to that of the parent fuel. This is probably due to contamination of the ashes with Si from the quartz-glass sample holder. For the ash produced at 500 °C, the Cl result from the IC is significantly higher than the value obtained from

Table 1. Yield and Elemental Analysis Results of Vinasse Ashes[a]

gas condition	ash yield (wt % fuel, db)	analysis method	C	O	K	Na	Ca	Mg	Si	Fe	Al	P	S	Cl
									elemental composition (wt % ash)					
standard ashing at 500 °C	34.8 ± 0.05	ICP–OES	7.2 ± 0.4[b]	38.8 ± 0.4[b]	27.2 ± 0.2	1.1 ± 0.01	9.1 ± 0.1	1.4 ± 0.01	1.6 ± 0.01	0.2 ± 0.001	0.2 ± 0.002	0.3 ± 0.1	4.8 ± 0.04	14.1 ± 0.3[c]
		SEM–EDX	7.2 ± 0.4	38.8 ± 0.4	25.8 ± 0.1	1.5 ± 0.1	10.6 ± 0.1	2.2 ± 0.04	1.9 ± 0.02	0.3 ± 0.02	0.2 ± 0.01	0.3 ± 0.01	3.9 ± 0.03	7.3 ± 0.04
combustion (10% O_2/90% N_2) at 900 °C	28.3 ± 1.0	ICP–OES	NA[d]	NA	45.1 ± 0.3	1.1 ± 0.01	11.0 ± 0.1	1.8 ± 0.01	2.5 ± 0.1	0.5 ± 0.3	0.1 ± 0.001	0.3 ± 0.004	7.2 ± 0.3	12.5 ± 0.2[c]
gasification (50% CO_2/50% N_2) at 900 °C	26.5 ± 1.0	ICP–OES	NA	NA	32.6 ± 0.3	0.9 ± 0.01	10.0 ± 0.1	1.6 ± 0.01	4.0 ± 0.1	0.4 ± 0.3	0.1 ± 0.001	0.3 ± 0.003	5.3 ± 0.4	11.4 ± 0.1[c]

[a]Relative errors were based on three determinations (for elemental compositions) or experiments repeated at least 3 times (for char yields). [b]Values are from SEM–EDX. [c]Results are from IC. [d]NA = analysis was not performed.

SEM−EDX. Moreover, carbon obtained from SEM−EDX is most likely from carbonates present in the ash. The existence of carbonates in the ash was confirmed from the XRD analysis, as discussed below.

The major ash-forming matter detected by the XRD for the ash produced at 500 °C was KCl, $K_2(SO_4)$, $Na_2(CO_3)$, $Ca_3(PO_4)_2$, $K_2Ca(CO_3)_2$, MgO, and SiO_2. Iron silicide (FeSi) was also proposed as a stable phase, but it is not likely to form at these conditions. For the ashes produced in the SPR at 900 °C in both O_2 and CO_2 gas conditions, the main ash-forming compounds identified by the XRD were KCl, CaO, K_2SO_4, K_2CO_3, MgO, $Ca_3(PO_4)_2$, Ca_2SiO_4, and Ca_2SiO_4·$0.05Ca_3(PO_4)_2$. However, the reduced forms of ash-forming compounds, such as CaS and K_2S_3, were detected only in the ash produced at 900 °C in CO_2. The XRD spectra for the three vinasse ashes are provided in Figure S1 of the Supporting Information. Most of the inorganic elements forming these compounds originated from the sugarcane stalks used for sugar and/or ethanol production. For example, we reported in the study by Dirbeba et al.[20] that about 55% of potassium and chloride in sugarcane stalks eventually culminate in the vinasse. Carbonates, phosphates, and sulfates arise, in part, from the addition of chemicals, such as sulfur, lime, diammonium phosphate, and sulfuric acid, to the integrated sugar−ethanol production process at different production stages. Lime as $Ca(OH)_2$ and sulfur as SO_2 are added at the cane juice treatment stage to remove impurities from the juice prior to sugar and/or ethanol production. Sulfuric acid is added to molasses, the final residue from sugar production, for treatment for fermentation. Diammonium phosphate is usually used as a nutrient for the microbial mass, yeast, which is responsible for the fermentation process.

3.3. Release of the "Reactive" Fractions of the Vinasse Ash-Forming Elements. Figure 2 shows the total
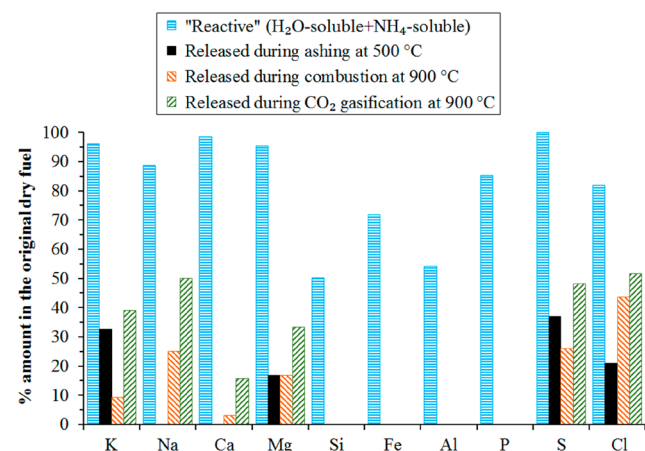

Figure 2. Total "reactive" fraction of vinasse ash-forming elements and the inorganics released during ashing, combustion, and gasification.

amounts of the "reactive" fraction of the ash-forming elements in the vinasse and the levels of the ash-forming elements released during the ashing, combustion, and gasification experiments. The values are given as percentages of the original ash-forming elements in the dry vinasse. The total amount for a "reactive" ash-forming element was obtained by adding the H_2O- and NH_4Ac-soluble amounts from the fuel fractionation (see section 3.1). The release levels for the ash-

forming elements were calculated as follows: First, the vinasse ash elemental analysis results given in Table 1 of section 3.2 were converted to a weight percent dry vinasse basis using the ash yield results given in the table. Then, the amount of an ash-forming element released on a weight percent dry vinasse basis was obtained by subtracting the amount of the element in the ash from its amount in the parent fuel given in section 3.1.

Figure 2 shows that almost all Ca and S, 95% of K and Mg, and 90% of Na in the vinasse were "reactive", while "reactive" Si and Al were about 50 and 55%, respectively. The "reactive" portions of Fe, P, and Cl in the vinasse were about 72, 85, and 82%, respectively.

Results of the inorganics released given in Figure 2 can be summarized as follows: (1) Although considerable levels of Si, Fe, Al, and P in the vinasse were "reactive", none of these ash-forming elements were released during ashing, combustion, and gasification. (2) About 33, 17, 37, and 21% of K, Mg, S, and Cl, respectively, in the fuel were released during the vinasse ashing at 500 °C. However, no Na and Ca were released. The release of K, Mg, and Cl may be due to evaporation of KCl and $MgCl_2$ as a result of the prolonged ashing time used. In addition, studies have shown that, during pyrolysis and combustion of a biomass, about 25−70%[34,35] of Cl and 30−55%[34,35] of S in the fuel are released at temperatures of ≤500 °C. (3) Normally, the release of inorganics during thermochemical conversion of biomass increases with increasing temperature.[19,34] However, the levels of K and S released during the vinasse ashing at 500 °C are higher than the corresponding levels released during combustion at 900 °C. The high K release level at 500 °C is most likely due to evaporation of KCl, owing to the extended ashing time used. It has been shown that holding times strongly influence the release of ash-forming elements, especially alkalis, during biomass thermochemical conversion.[36] The lower S release at 900 °C under combustion conditions than at 500 °C during the ashing might be due to sulfur capture[37] by K and Ca in the vinasse at 900 °C. (4) About 9, 25, 3, 17, 26, and 44% of K, Na, Ca, Mg, S, and Cl, respectively, in the fuel were released during the vinasse combustion at 900 °C. The corresponding release numbers for the ash-forming elements during the vinasse gasification at 900 °C were 39, 50, 16, 33, 48, and 52%. The levels of these inorganics released under combustion conditions are higher than the corresponding values under gasification conditions at the same temperature. There are two main reasons that may explain the higher release levels of the ash-forming elements under gasification conditions. First, the relatively reducing gas condition under gasification compared to combustion might have enhanced the release. We observed in our previous work[11] that more ash-forming matter was released from vinasse chars under reducing conditions than oxidizing, owing to successive reduction of alkali carbonates on carbon and ultimately vaporization of the alkali metals. The reduced forms of ash-forming compounds were detected by the XRD only in the ash produced in CO_2 (see section 3.2). Second, the longer time needed for gasification to complete than for combustion might have played a role here too.

In general, not all of the "reactive" fractions of the vinasse ash-forming elements were released during combustion and gasification under the present experimental conditions. For other biomasses, Frandsen et al.[19] reported that there is no direct correlation between the release levels of ash-forming elements during combustion and the "reactive" fractions of the
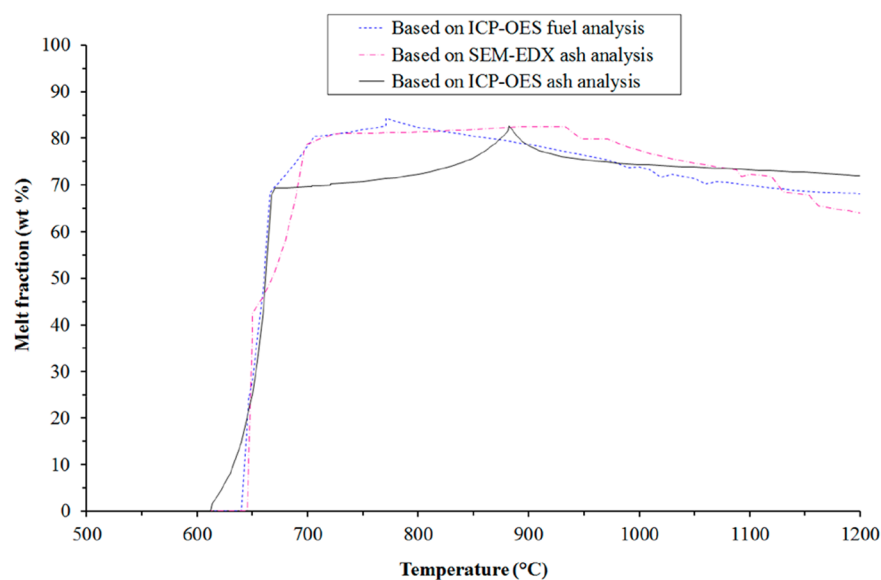
Figure 3. Results of melt fraction (wt %) versus temperature (°C) from the FactSage calculations for vinasse and vinasse ash produced at 500 °C.
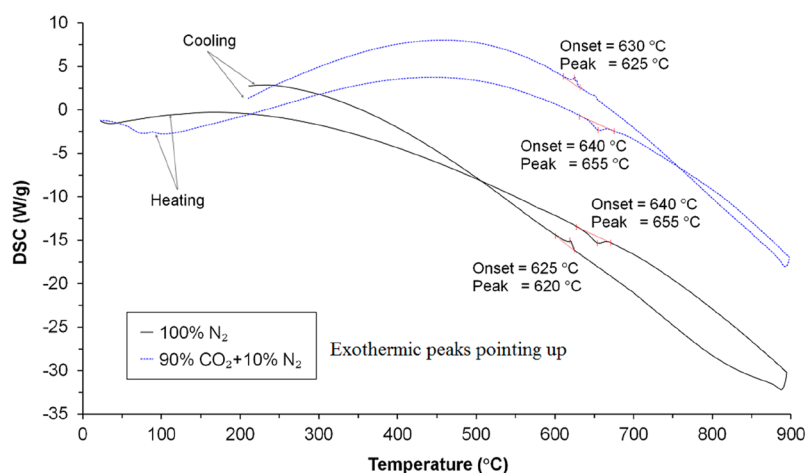

Figure 4. Results of DSC (W/g) measurements in 100% N_2 and 90% CO_2/10% N_2 versus temperature (°C) for vinasse ash produced at 500 °C.
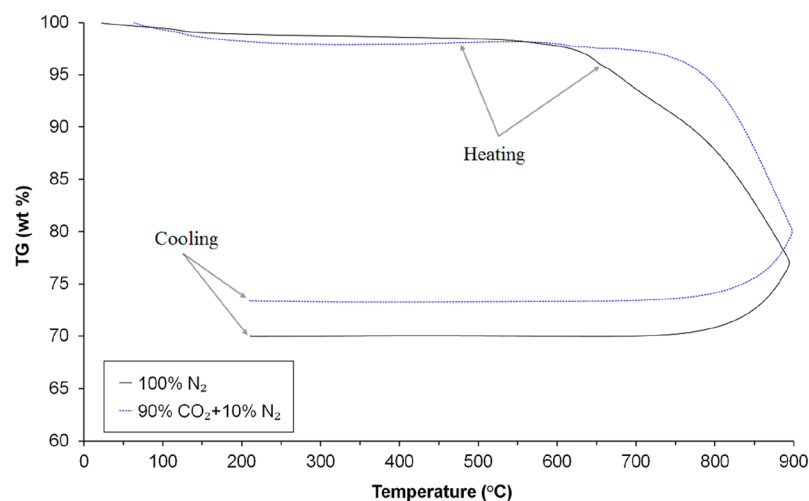

Figure 5. Results of TG (wt %) measurements in 100% N_2 and 90% CO_2/10% N_2 versus temperature (°C) for vinasse ash produced at 500 °C.

ash-forming elements from the chemical fractionation. One possible reason mentioned by Frandsen et al. for the deviations is the interaction between the released inorganic elements and those remaining in the ash, where the two fractions may react,

forming a non-released species. For example, according to Johansen et al.,[34] Si in biomass fuels plays a significant role in the retention of alkalis in the ash as silicates during pyrolysis and combustion of the biomass. Probably Si in the vinasse might have played a similar role. The presence of silicates in the ashes produced at 900 °C was confirmed from the XRD analysis, as discussed in section 3.2. Nevertheless, the release of significant portions of "reactive" potassium and chloride in the vinasse indicates that vinasse may be a problematic fuel for combustion and gasification using conventional boilers and gasifiers.

3.4. Ash-Melting Behavior. Figure 3 shows the results of the vinasse ash melt fraction versus temperature from the FactSage software when the fuel and ash elemental analysis results were used as inputs to the software. Figures 4 and 5 are the DSC and thermogravimetry (TG) measurement results, respectively, versus the temperature for the vinasse ash produced at 500 °C.

In general, as seen from Figure 3, the vinasse ash-melting curves are very similar whether the fuel or ash elemental analysis results were used as input data for the FactSage thermodynamic calculations. The calculations show that the initial melting temperature, T_0, for the vinasse ash is in the range of 640−645 °C. The calculated results agree with the DSC measured value, 640 °C in both N_2 and CO_2 gases, during heating the ash sample to 900 °C (see Figure 4). However, a lower T_0 value, about 612 °C, was obtained from the FactSage calculations when the ash elemental analysis results from ICP−OES were used as input data for the FactSage software. This is may be due to the higher Cl result obtained from IC for the ash. Moreover, it can be observed from Figure 4 that the onset of crystallization temperatures, 625 °C in N_2 and 630 °C in CO_2, of the molten ash are lower than the corresponding T_0 values. These shifts from the T_0 values can be attributed to changes in the composition of the molten ash because of ash weight losses in DSC−TGA (see Figure 5). The losses are most likely due to evaporation of alkali chlorides and decomposition of carbonates present in the ash (see paragraph 4 of section 3.2). It can be seen from Figure 5 that about 30% of ash weight was lost in the N_2 gas atmosphere. However, the loss in CO_2 was less by about 3%, probably as a result of the CO_2 suppressing decomposition of carbonates, such as $MgCO_3$, Na_2CO_3, and $CaCO_3$. Nevertheless, it is interesting to see that the onset of crystallization temperatures given in Figure 4 are close to the 620 °C[11] T_0 value that we obtained earlier for vinasse char produced at 800 °C in the N_2 gas atmosphere.

Moreover, it can be seen from Figure 3 that the vinasse ash T_{15}, sticky temperature, is about 650 °C, and the ash appears to be 70% molten in the temperature range of 670−690 °C, the ash flow temperature. The TG measurement results, given in Figure 5, show that there is only about 3−5% ash weight loss in the sticky and flow temperature range. However, it can be noticed from Figure 3 that the melt fraction does not reach 100% because there are high-temperature-melting oxide phases, and it starts decreasing at temperatures above 850 °C as a result of the evaporation of alkali chlorides. The high-temperature-melting oxide phases obtained from the FactSage thermodynamic calculations were mainly $CaO(s)$, $MgO(s)$, $Ca_3Al_2O_6(s)$, $Ca_2SiO_4(s)$, and $Ca_2Fe_2O_5(s)$.

The melting of 70% of the vinasse ash in a narrow temperature range, i.e., 640−690 °C, has an important implication on the inorganic compound present in the vinasse

ash: a low-temperature-melting species, probably KCl, is dominant in the ash. The existence of KCl in the vinasse ash was confirmed from the XRD analysis, as discussed in section 3.2. Here too, the low-temperature-melting ash suggests that vinasse is a problematic fuel for combustion and gasification in conventional boilers and gasifiers.

The predicted major solid phases based on the predictions below the melting temperature (about 500−700 °C) are $(K,Na)Cl$, i.e., KCl-rich solid solution, $(K,Na)_2Ca(CO_3)_2$, i.e., $K_2Ca(CO_3)_2$-rich solid solution, and alkali sulfate carbonate solid solutions, i.e., K-rich sulfate and carbonate, similar to the XRD results given in section 3.2. A significant fraction of calcite, $CaCO_3$, is also predicted to be stable. Various Ca−Mg silicates are also predicted to form, whereas the XRD showed MgO and SiO_2 to be stable, indicating slow reactions between the solid oxides and silicates.

4. CONCLUSIONS

In this work, the distribution of ash-forming elements in dried vinasse and the release of "reactive", H_2O- and NH_4Ac-soluble, inorganics at 900 °C under combustion and gasification conditions were studied using chemical fractionation and a single particle reactor, respectively. Moreover, the vinasse was ashed at 500 °C, and the ash-melting behavior as a function of temperature was first calculated using FactSage thermodynamic calculations and then validated using DSC−TGA measurements. The following conclusions can be drawn: (1) The chemical fractionation results revealed that almost all of the ash-forming elements, except Si, Al, and Fe, of the vinasse were completely water-soluble. Moreover, unlike other solid fuels, significant portions of Si, Al, and Fe in the vinasse were leached by water. (2) Results of analyses of the ashes from the vinasse combustion and CO_2 gasification experiments showed that not all of the "reactive" fractions of the vinasse ash-forming elements were released. In fact, none of "reactive" Si, Al, Fe, and P in the vinasse was released during both combustion and gasification. However, significant amounts of "reactive" K, Na, Ca, Mg, S, and Cl in the vinasse were released during the vinasse thermal conversions at 900 °C. The release levels of these latter "reactive" ash-forming elements were higher during gasification than combustion. This is probably due to the enhanced release of the inorganics in the case of gasification because of the relatively reducing gas atmosphere and the extended reaction time used. (3) The FactSage-calculated and DSC−TGA-measured initial melting temperature for the vinasse ash produced at 500 °C was 640−645 °C, and the ash appeared to be 15 and 70% molten at 650 and 670−690 °C, respectively. The melting of most of the vinasse ash in a narrow temperature range indicates that a low-temperature-melting ash-forming matter, probably KCl, dominates the vinasse ash. (4) The release of significant levels of "reactive" potassium and chloride in the vinasse during combustion and gasification and the low-temperature-melting vinasse ash indicate that vinasse is a problematic fuel for combustion and gasification in conventional boilers and gasifiers.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energy-fuels.8b04177.

Fuel fractionation results for dried sugarcane vinasse (mg/kg, db) (Table S1) and XRD spectra for the vinasse ashes from the ashing, combustion, and gasification experiments (Figure S1) (PDF)

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Notes
The authors declare no competing financial interest.

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